PHOTOISOMERISATION OF SOME CHLORO-NITROSO TERPENES

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ALEXANDER J. N. HOPE, B.Sc., A.R.I.C.

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INDEX

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INTRODUCTION

(i) Light Absorption and Photo-processes

The classical electromagnetic theory of radiation, originally due to Clerk-Maxwell (1873), though capable of accounting for many optical phenomena with a high degree of precision, was inadequate in interpreting discrete absorption and emission of light by matter. Description of such processes later became possible on introduction of the quantum theory by Plank (1900), in which it was considered that energy transference occurs only in small units or quanta (E), directly proportional to the frequency of radiation.

$$E = h\tilde{\nu} \qquad \ldots\ldots (1)$$

The two approaches are not entirely independent, however, and an understanding of the fundamental processes associated with the interaction of light and matter is possible only on the basis of their joint consideration.

The most successful treatment of atomic structure is derived from the application of quantum-mechanical principles, resulting in the concept of the wave-nature of the electron, and extention of the approach to molecules is obtained by approximating these to polynuclear systems, surrounded by the electrons whose energy and distribution is to be determined. Unfortunately, the method is strictly limited by the considerable mathematical difficulty attending its application to complex structures. A pictorial representation is provided, however, by the 'molecular orbital' approach (reviewed Coulson, 1947) applied by Bowen (1943, 1950) to explain the mechanism of interaction of a light-wave with a molecule.

In this treatment, a series of wave-patterns or 'orbitals' is considered to exist round the nucleus of the atom, the charge distribution of the electron being represented by the square of the wave-amplitude. 'Permitted', or quantised energy levels on Plank's theory then correspond to the electron occupying the appropriate orbital. Since this resembles a wave-pattern of vibrations about a point, resonance is set up when the electron oscillation frequency co-incides with the electric vector of the incident wave and energy transference takes place by increase in amplitude of electronic oscillation, so that the electrom is carried over to a stable excited state (orbital transition). In such circumstances the total energy of the wave is taken up by interaction, and the light is said to be absorbed. Radiation of any other frequency merely induces 'forced' electron oscillations resulting in an unstable (non-quantised) transition which rapidly reverts to the original state. In this case, the light-wave suffers a reduction in velocity but no loss of energy and the process is accompanied by the usual characteristics of transmitted light (refraction, dispersion, etc.).

For absorption in the visible and ultra-violet regions of the spectrum, the frequency corresponds to the energy required for excitation of the outermost (valency) electrons. Equation (1) gives such changes as 50-100 K cal/mole, which is the energy difference of the two molecular orbitals between which transfer takes place. This is of the same order of magnitude as that required for many chemical reactions and accounts for the photo-sensitivity of such processes.

Since electronic transitions in molecules are accompanied by subsidiary vibration and rotation changes of structural units the absorption is spread over a range of frequencies. In solution this vibrational-rotational fine structure is generally masked by solute-solvent interaction, and continuous absorption results, appearing in the extinction curve as a 'band envelope' which has the following characteristics.

(i) The position in the spectrum, given by the location of the head of the band. This is the frequency of greatest probability of transition (Frank-Condon principle) and is characteristic of the chromophoric group or conjugated system present.

(ii) The shape and width of the band. The former is determined solely by the vibration-energy curve of the excited state, while the latter is dependent on the relative internuclear distances of ground and excited levels.

(iii) The absorption intensity, determined by the 'oscillator strength', i.e. the number of oscillating units per molecule, and proportional to the integrated band area.

The importance of (i) is shown by its dependence on the energy of orbital transition. Although this is fundamentally characteristic of the chromophoric system, vicinal forces which act in such a way as to diminish energy differences between ground and excited levels will cause the light absorption to be moved towards the red end of the spectrum (bathochromic displacement), and those which cause increase in energy differences will result in absorption shift towards the blue (hypsochromic displacement).

The second feature further illustrates the dependence of factors influencing the various energy states of the molecule, e.g. substituants, but the matter does not lend itself to other than purely empirical treatment.

The third characteristic is of greater importance, and from this can be derived the mean life, τ , of the excited state, usually of the order of 10^{-7} sec. (Lewis and Kasha, 1945)

$$\frac{1}{\tau} = 2.88 \times 10^{-9} \tilde{\nu}^{2} \int \epsilon \, d\tilde{\nu} \qquad \text{.....(2)}$$

where $\tilde{\nu}$ is the frequency (cm.$^{-1}$) of the centre of the band. Strong bands therefore correspond to small τ values and to transitions which are 'permitted', i.e. accompanied by a change in dipole moment of the system. Conversely, 'forbidden' transitions which occur only on distortion of the symmetry of atomic levels by vicinal forces, intense fields, etc., require large τ values and weak absorption bands result; e.g. it has been suggested by Lewis and Kasha (loc. cit.) that the red band of nitroso-compounds may be attributed to such a 'forbidden' singlet → triplet transition.

The close relationship between structure and electronic spectra is particularly well illustrated by the recent work of Braude (1945, 1950) who has shown that for a 'permitted' transition in a given chromophore, both absorption intensity and transition probability can be derived from simple geometrical considerations of molecular structure.

In contrast to the detailed physical concepts by which absorption processes may be interpreted, however, the exact mechanism of most resultant photochemical reactions is but vaguely understood. Remarkably little information is available from which a clear picture of the method of change in the activated transition state may be formed. In general, it may be said that electronic excitation gives rise to a change in amplitude of oscillation with a corresponding weakening of bonding forces and results in a highly unstable state which may lose the excess energy by one of the three following routes.

(i) Return of the molecule to its original state by the emission of one or more light quanta. This is known as fluorescence.

(ii) Collisions with neighbouring molecules giving rise to an increase in kinetic energy, apparent as a heat change in the system.

(iii) Chemical reaction. This may be rupture or rearrangement of the original molecule, or reaction with another molecule.

When the third condition is satisfied, the resultant process may be described as a photochemical reaction.

The following of such a photo-change is invariably attended by considerable difficulty because of the limitations imposed on methods of measurement by the small magnitude of the chemical transformation. Optical methods are most suitable, where applicable, and the concentration of a particular molecular species can often be derived spectrophotometrically from a consideration of the decrease in height of a characteristic band in its absorption spectrum. For this purpose it is necessary to be able to determine the property as a molecular parameter.

The intensity of absorption of a parallel beam of monochromatic light in an isotropic medium is related to the thickness of the absorbing layer (ℓ) and the concentration of absorbent (c) by the Beer-Lambert law, which states that the fraction of incident light absorbed is proportional to the number of absorbent molecules (n) in the light path,

$$\text{hence} \quad \frac{I}{Io} = e^{-kn}$$

$$\text{or } \log \frac{Io}{I} = 0.4343 \text{ kn.}$$

where I_0 is the intensity, of incident light, I the intensity of transmitted light, log I_0/I is termed 'extinction' and k is a constant known as the extinction coefficient. At constant temperature 'n' is proportional to 'c' (c in gm-mols./L.), so that

$$\log \frac{I_0}{I} = 0.4343\, \epsilon' c\, \ell$$

$$\text{or } \log \frac{I_0}{I} = \epsilon c\, \ell \qquad \ldots\ldots (3)$$

where ϵ is called the molecular extinction coefficient, conveniently used to plot the intensity of absorption against wavelength, giving rise to the characteristic absorption spectrum.

The actual amount of chemical change produced in such a system depends on the relation between molecules 'photo-activated' by absorbing a light quantum and final chemical changes ensuing. The quantum efficiency is given by the ratio

$$\gamma = \frac{\text{number of molecules chemically changed}}{\text{number of quanta absorbed}}$$

the importance of which was first emphasised by Einstein (1912). Subsequently, Warburg (1924) made the pertinent observation that equation of the ratio to unity was essentially axiomatic, and that divergence of observed results from this value was attributable to the large number of secondary reactions invariably attending the initial process.

Chemical transformation resulting from absorption of radiation is far from a simple matter. In photochemical reactions accompanied by a gain in free energy, the light acts against the chemical forces of the system, the absorbed energy is converted, partially, into chemical free energy and there will, therefore, be a tendency for the resultants of the process to revert spontaneously to the reactants. If the latter (dark) reaction is sufficiently rapid, an equilibrium will eventually result. Such a 'photostationary state' is attained where illumination produces a final composition of the system which is appreciably different from that of the thermodynamic equilibrium. As long as the photochemical conditions are not changed, the composition will remain unaltered, but on removal of the light source, the system will tend to change in the direction of the thermal equilibrium. A theoretical treatment of photostationary states has been made by Olson (1931).

Coehn and Stuckart (1916) have distinguished three types of photochemical equilibrium.

(i) Only the forward reaction is light sensitive. This is the simplest case in which equilibrium is attained when the velocity of the photo-process becomes equal to that of the reverse dark reaction. As a corollary to this, when the velocity of this dark reaction is inappreciable, the photochemical process goes practically to completion.

(ii) Both direct and reverse reactions are sensitive to light of the same wave-length. In this case the reaction proceeds simultaneously in both directions at rates determined by experimental conditions.

(iii) Both reactions are light-sensitive, but to different wave-lengths. This essentially reduces to (i) under the usual conditions of monochromatic radiation.

Since most photochemical processes have small temperature coefficients, the final equilibrium is dependent almost entirely on the above conditions. Of these, the first finds by far the greatest application in practice and many examples of resulting photostationary states are to be found in the literature.

(ii) Optical Methods in Stereochemistry

Classical methods of stereochemistry have proved invaluable in the elucidation of structural problems, but are largely empirical in nature. With the application of wave-mechanical techniques, however, an understanding of the relation between atomic structure and valency configuration has been made possible. This may be considered as forming a modern theoretical basis of stereochemistry since it provides an insight into the origin of directed bonding. The subject has been discussed qualitatively from a molecular orbital standpoint by Coulson (1947, 1952) and by Mills (1942).

It is known that the wave-aspects of the outermost electrons supply the mechanism through which chemical combination is effected, and these have been shown to possess a marked directional character in space (Pauling, 1931). The concept of bonding by linear compounding of these atomic orbitals, developed initially by Lennard-Jones (1929) was subsequently applied by Slater (1931) and Pauling (loc. cit.) who showed that the energy of such a molecular orbital is lowest (i.e. binding energy is greatest) when the component atomic orbitals overlap one another as much as possible.

In the case of the carbon atom, the normal (ground) state is one in which there are two unpaired electrons ($2p^2$) corresponding to bivalency. Preparation for the formation of a saturated molecule, requires promotion of an inner (2s) electron to an empty ($2p_z$) orbital necessitating an increase in energy of about 65 K cal/mole, and giving a total of four valency electrons (sp^3 state). In order that equivalent bonds may result, the four 'pure' orbitals must be mixed yielding 'hybridised' orbitals, when calculation shows (van Vleck, 1933) that the most stable structure results when these four wave-functions are directed symmetrically in space, forming an angle of 109° 28' with one another. The fundamental reason for the tetrahedrally directed valence around a carbon atom is thus disclosed and provides the key to the problem of stereochemistry in organic compounds.

An important consequence of the tetrahedral nature of carbon lies in the potential configurational asymmetry of this unit, long recognised as the source of optical rotatory power in isotropic media (Pasteur, 1848). In contrast, however, to the simplicity of the structural conditions leading to such optical activity, the mechanism of the interaction of a light wave with a molecule causing rotation of the plane of polarisation has resisted complete interpretation.

The first attempt to develop a theory of optical rotatory power was due to Drude (1902). This was based on the classical theory of dispersion and required the existence of electric charges vibrating in helicoidal paths, a view untenable on the modern basis of molecular structure.

A more satisfactory formulation is the classical coupled-oscillator approach of Born (1915) and Oseen (1915), extended to a more precise form by Kuhn (1929, 1930). In the simplest case, the dissymmetric molecule is considered as composed of a number of non-parallel harmonic oscillating units of known mass and charge. Resonance by interaction gives rise to coupling of the vibrations and it is shown that the energy transferred is different for the incident right- and left-handed circularly polarised light, resulting in small differences of refraction of the two and so in optical rotation.

Paralleling this theory, another similar in principle, has been developed by Gray (1916), de Mallemann (1927) and Boys (1934), referred to as the 'polarizability theory' of optical activity since it expresses the rotatory power of a molecule in terms of the configuration and polarizabilities of the constituent groups. By introducing a number of approximations, Kirkwood (1937) has been successful in reducing the calculations to a tractable form and has shown it to be successful in determining the absolute configurations and specific rotations of simple molecular structures.

A more modern approach to the interpretation of optical activity has been made on a wave-mechanical basis by Condon, Alter and Eyring (1937). Detailed reviews are available by Condon (1937) and by Kauzmann, Walter and Eyring (1940). It is satisfactory to note that the close relationship between absorption and optical activity is clearly recognised by this theory, for electronic transitions must be the central feature of any model which is to give an adequate treatment of rotatory power. The problem is considered as a one-electron transition within the given chromophoric group, following the procedure successfully employed in the interpretation of absorption spectra. Quantum mechanical calculations are based on the theories of Rosenfeld (1928) on the electric and magnetic moments induced in a molecule by a perturbing electromagnetic field, the perturbations of the initial and final electronic states by neighbouring radicals leading to alteration of these states and giving transitions which are optically active, provided the system as a whole has no plane or centre of symmetry.

It is in such a treatment that an adequate theory of rotatory power, free from the defects of the artificial oscillator model must be sought. This method is capable of accounting for the observed order of magnitudes of optical rotations, but a rigorous application to give strictly quantitative results is not yet possible. In general, it may be said that the older classical theory is attended by the same limitations, the greatest advantage of the wave-mechanical approach being the new and broader concept of vicinal action in molecular structure affecting optical rotation.

Although Drude's 'charged particle' theory proved of little value in providing a theoretical treatment of rotatory power, it resulted in the first satisfactory study of rotatory dispersion and led him to deduce a general equation which represented a simple relationship between optical rotation and wave-length.

This proved valid for many substances in regions of transparency, but was quite inadequate in predicting their rotations in the neighbourhood of optically active absorption bands, evident from Cotton's work (1896) on the active coloured tartrates. In these cases the rotation was found to reach a maximum on one side of the band, falling through zero at the head of the band, to a minimum value of opposite sense on the other side. Such anomalous rotatory dispersion in the region of absorption subsequently became known as the 'Cotton effect'.

The band in this region is usually assignable to a particular chromophore linked to the asymmetric carbon atom, and it is a peculiar feature of such a system that structural inversion results in reversal of the associated Cotton effect. In this way, a method of assigning relative configurations to stereoisomers differing in spacial distribution of groups about an active centre is possible; further, the velocity of isomeric transformation during a reaction is readily determinable from the rate of inversion of the Cotton effect.

Rotatory power, therefore, serves in the investigation of certain stereochemical problems but it is strictly limited in scope. Other methods, while lacking such precision of interpretation possess the advantage of wider fields of application. Among these may be mentioned infra-red and Raman spectroscopic techniques which have developed rapidly as methods of determining structure, while the application of electronic absorption spectra to questions of configuration provides an outstanding contribution of optical methods to the development of stereochemistry. Apart from the fact that they are independent of conditions of asymmetry, electronic spectra are a much more sensitive index of differing steric configurations than rotatory power. The existence of detectable optical isomers with appreciable life times requires energy barriers of about 15 K cal/mole or more, to prevent spontaneous racemisation by thermal excitation, whereas the smallest significant wave-length displacements ($\sim 50 A^{o}$) correspond to energy increments of only 1 or 2 K cal/mole in the near ultra-violet region of the spectrum.

Purely empirical use of absorption properties, e.g. for the distinction of geometrical isomers was made as long ago as 1910 by Hantzsch, but it is only comparatively recently that such correlations have been put on at least a qualitative theoretical basis by Gillam (1936) and Zechmeister (1944). More precise formulations of the relationship between the geometry of absorbing systems and their electronic spectra have been given by Mulliken (1939). 'Saturated' bonds do not normally give rise to electronic absorption, but multivalent linkages, whether in conjugated systems or chromophores, are characterised by definite bands in the spectrum. In an idealised model the unsaturation electrons are regarded as moving in the electrical field due to the constituent atoms. Absorption promotes electronic motion along the axis of the system, and wave-length and intensity are governed by the number 'n' of mobile electrons and by the effective path length 'ℓ' of the electronic oscillation. The following relationships have been derived for small values of 'n' (Mulliken, loc. cit.)

$$\lambda \propto \sqrt{\ell} \quad \text{and} \quad \epsilon \propto \ell^2$$

so that λ is a very much less sensitive function of ℓ than is ϵ. Increase of absorption intensity with increasing conjugation is explained on this basis. The observed differences in λ between cis-trans isomers must, therefore, be due to factors other than 'ℓ', e.g. a change in the submerged vibrational structure of the electronic band which may give rise to displacements of the order of 50A^{o} in the highest point of the band envelope, in a direction difficult to predict. The small differences in λ max. between the stereoisomeric azobenzenes and their derivatives may well be due to this effect. In highly conjugated systems such as the stilbenes (Lewis, 1937, 1940) uniplaner arrangement of double bonds and phenyl rings providing a large number of mobile electrons and increasing the path length, is the most important factor in determining the various energy levels of the different forms. Steric influences give rise to the same type of effect in saturated systems, and a rise in potential energy of the ground state over that of the excited state, in the thermodynamically less stable isomer will result in a lower energy of transition for this epimer with a corresponding bathochromic displacement of λ max.

The application of electronic absorption spectroscopy to problems of structural organic chemistry are many and the subject has received much attention in recent reviews, e.g. Braude (1945), Klotz (1945), Zechmeister (1944), Lewis and Calvin (1939) and others. Clearly, the method is particularly suited to the investigation of photochemical processes resulting in molecular rearrangement. When photoisomerisation occurs by virtue of transformation at an asymmetric centre, the reaction is accompanied by a change in rotatory power and the process may more accurately be described as 'photomutarotation'. In such cases the elucidation of configuration differences from a study of electronic spectra is supplemented by a consideration of rotatory dispersion. The two conjugate methods have proved of outstanding value in the present studies.

PART I

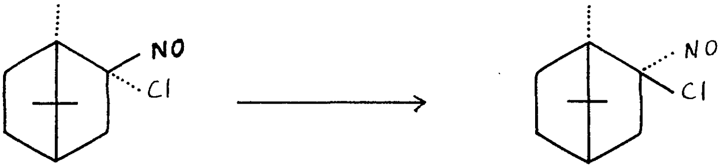
PHOTOMUTAROTATION

of

(-)-2-chloro-2-nitrosocamphane

(i) General Considerations

It has been reported by Mitchell, Watson and Dunlop (1950), that the results observed on irradiation of (-)-2-chloro-2-nitrosocamphane with red light are due to the simultaneous occurrence of the two processes - (1) fairly rapid mutarotation and (2) slow photolysis. The second of these is normal for such chloro-nitroso compounds, but the first was the introduction of a new type of photochemical reaction, and was attributed to the interconversion of the two possible stereoisomeric forms.



This pertinent deduction has since proved to be fundamentally correct, but the simple experiments first carried out did not permit these authors to make precise measurements of the processes involved.

In the present study, a photoelectric estimation of concentration has been developed, permitting the calculation of specific rotations at time intervals during the irradiation. These values show the true course of mutarotation, unaccompanied by photolysis as previously reported. A similar estimation has been used by Carlin in studying the kinetics of rearrangement of benzidine (1951) and o-hydrazotoluene (1954) spectrophotometrically, and it has been pointed out that a number of fundamental requirements must be met before such a method can be successfully employed. In the present instance, the absorption curves of the two forms are identical in shape but displaced some 60A° from one another so that they overlap (Graph II). The only point at which measurements may be made is dictated by equality of molecular extinction coefficients of the two isomeric forms, so that the value at this wave-length remains unchanged throughout the reaction. At shorter wave-lengths the observed absorption will appear to decrease, and at longer wave-lengths to increase. The experimental realisation of such an isosbestic point may in itself be considered sufficient evidence for the existence of two stereoisomers in equilibrium (Weigert, 1916), and gives the only wave-length at which a photoelectric estimation of these will be valid.

Specific rotations may be calculated from the usual formula

$$[\alpha] = \frac{100\,\alpha}{l.c} \qquad \text{......} \quad (3)$$

where the concentration (c), after a time interval is given in terms of the extinctions at the pre-determined wave-length ($k = \log I_0/I$)

$$c = c_o \frac{k}{k_o}$$

The rotation, so calculated, is the true value for the total blue, chloro-nitroso compound present and is independent of accompanying decomposition only if it may be assumed that the products of photolysis have but negligible contributions to the optical rotatory power or absorption in the given region. Irradiation of a sample to complete decomposition and examination of the resultant optical properties has shown this to be the case for the material being studied.

Experimental Procedure

All photochemical experiments in the present work have been carried out on the optical system illustrated in Figure 1.

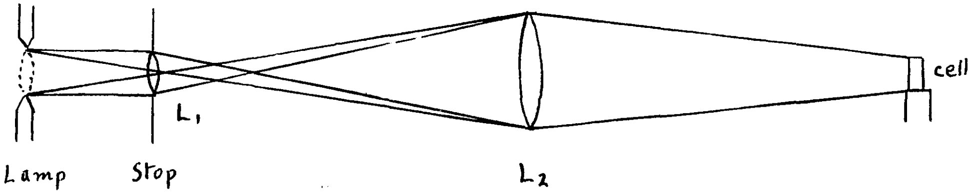


Fig. 1

A high-pressure mercury discharge lamp acted as source, the light traversing the condensing lens L_1, surrounded by a circular stop which was imaged on the cell-carrier by L_2. A yellow Ilford filter, inserted immediately behind L_1 ensured that only the mercury yellow doublet ($\lambda = 5770, 5790$) was transmitted. This is the most suitable and readily available source of 'monochromatic' light lying within the nitroso absorption band since ϵ_{5780} lies within the range 2.5 - 8 for all of the materials studied.

In the ultra-violet photochemical experiments, irradiation was carried out directly with a low-pressure mercury Kromayer lamp, cooled by circulating water. No attempt was made to render this source monochromatic because of the large number of mercury lines in this region of the spectrum (see Bowen, 1953), but the introduction of a Chance OX 7 filter eliminated all visible light.

The concentration of the solutions used in these experiments was determined by the limitations of the methods used in estimating the optical properties. For polarimetric work, the concentration should be as high as possible within the limit permitting visual reading, so that the observed rotation will be correspondingly large, while for spectrophotometric determinations a maximum value is imposed by the absorption of the material at the given wave-length. The concentration must then be chosen so that the transmission reading falls within the scale limits of the instrument. The optimum value was found to be of the order of 1.5% for all the materials studied, giving maximum readings for log I_o/I 0.8 and rotations of the order of 1°. Solutions were contained in a sealed 1 cm. Vitreosil cell with strain-free end pieces, and a special carrier enabled it to be fitted directly into the spectrophotometer, so that both polarimetric and absorption measurements could be made rapidly during the course of irradiation. Because of the ease with which these compounds undergo photo-oxidation, the alcohol used as solvent in all cases, was freed from dissolved oxygen by previous distillation in an atmosphere of nitrogen.

Rotation measurements were taken with a Hilger triple-field polarimeter, reading to 0.01°, and with a constant half-shadow angle of 5°. A 12-v projection lamp served as source, the light being rendered monochromatic by transmission through a Winkel-Zeiss monochromator.

Absorption measurements were made with a Unicam S.P. 500 spectrophotometer using slit-widths of 0.04 mm. Since the spectral distribution in the red region is given as 43 $m\mu$/mm. of slit width, accuracy is obtained to 1.7 $m\mu$, and readings may accordingly be quoted to the minimum scale calibration (2 $m\mu$ here).

(ii) (-)-2-Chloro-2-nitrosocamphane

The structure of 2-chloro-2-nitrosocamphane requires that any chemical reaction giving rise to this material shall yield a product consisting of a mixture of the possible isomers, when the equilibrium attained will depend on the sum of all stereo-directing influences, both structural and environmental, operative in the reacting state. The first of these has been fully illustrated by the study of a number of chloro-nitroso derivatives obtained by systematic substitution of the 10- position by a series of chromophoric groups of varying steric size and influence (Veitch, 1953), while the second has been investigated by the preparation of the material under various chemical conditions (Watson, 1950) which may be briefly summarised.

Mitchell, et al. (1950) have shown that production of 2-chloro-2-nitrosocamphane by the usual method (Mitchell and Dawson, 1944) - chlorination of d - camphor oxime in dry ether, gave a material with optical rotations which varied in different preparations. By using the oxime hydrochloride instead of the oxime, a product with greatly enhanced optical properties was obtained. A similar directional influence of hydrogen chloride in the interconversion of isomeric oximes has been reported by Taylor and Roberts (1933), and is attributed by them to a decrease in the torsional rigidity of the carbon-nitrogen double bond by the electric fields of the ion-pair, so that stereoisomeric change takes place under conditions where the less stable form would normally exist in the absence of a catalyst. It is conceivable that a similar influence is exerted by the acid in the above preparation, so that one of the isomeric forms is preferentially produced. Such treatment yields a product showing a Cotton effect with $[\alpha]_{\text{max.}} \simeq +700^\circ$, $\epsilon_{\text{max.}} = 13.8$. However, this is not a stereochemical individual since treatment on activated alumina raises the rotation further. Although chromatography on a number of adsorbents is successful in effecting chemical purification, only special alumina (Light and Co.) appears to have this remarkable effect of greatly increasing the optical rotation.

In a typical case, a specimen of the blue material with the above properties was dissolved in the minimum volume of light petroleum and passed down a column (30 cm. x 1 cm.) of alumina which had been acid-washed till neutral as described by Prins and Shoppee (1946), then activated at 200° for 4 hr. Elution of the blue band with the same solvent yielded a product having $[\alpha]_{\text{max.}} = +803^\circ$, $\epsilon_{\text{max.}} = 13.7$. Repetition of this treatment raised $[\alpha]_{\text{max.}}$ to $+964^\circ$ while $\epsilon_{\text{max.}}$ remained unaltered, illustrating that this is not merely a purification but involves a change in the relative proportion of the two stereoisomers.

It was initially suggested by Hope and Mitchell (1953) that such a process is the result of isomerisation to the form of lower free energy (higher rotation) during adsorption on this polar phase. However, it seems more likely that the configuration differences influence the relative adsorption affinities of the existing isomers, with partial separation of the blue bands during development of the chromatogram, and preferential destruction (oxidation) of the more strongly adsorbed form which has the lower rotation. Such differences in adsorbabilities are well established for a large number of simple pairs of the closely related type of cis-trans isomers, e.g. maleic - fumaric acid (Freundlich and Schikorr, 1926) and mesaconic - citraconic acid (Schilow and Nekrassow, 1927), the stilbenes (Zechmeister and McNeely, 1942) and the isomeric azobenzenes (Cook and Jones, 1939). This contention is further supported by the following facts.

(i) A number of such treatments are necessary before the maximum value of rotation can be attained, and the overall yield is always low, $< 50\%$, so that extensive decomposition accompanies the optical purification.

(ii) Fractionation of the eluent in a typical instance yielded materials with the following rotations:-

Fraction 1, $[\alpha]_{\max.} = +893^\circ$
Fraction 2, $[\alpha]_{\max.} = +739^\circ$
Fraction 3, $[\alpha]_{\max.} = +621^\circ$

while $\epsilon_{\text{max.}}$ remained constant at 13.7 illustrating complete chemical purity in each case.

The second of these, in itself, renders untenable the original theory which would require the later fractions to give products of higher optical rotation.

The purest material which can consistently be produced by the above methods has the following properties:-

$[\alpha]_{\text{max.}} = +964^\circ$ at $\lambda = 6000A^\circ$
$\epsilon_{\text{max.}} = 13.8$ at $\lambda = 6600A^\circ$
m.p. 145 - 146° (d)

Since these cannot be induced to undergo further change, it must be concluded that complete separation of one isomeric form has been attained. This (-)-2-chloro-2-nitrosocamphane serves as starting material for the photochemical work later described.

The rotatory dispersion is recorded in Table 1, Graph I(i). It will be seen that a typical Cotton effect is obtained with the following characteristics

$[\alpha]_{\text{max.}} = +964^\circ$ at $6000A^\circ$ Reversal $6700A^\circ$ $[\alpha]_{\text{min.}}$ -964° at $7100A^\circ$

the indentation at the positive maximum originating from a second component, obvious as a 'shoulder' on the absorption band in the same spectral region. The remarkably high value of maximum rotation for this compound has greatly facilitated the

TABLE 1

Rotatory Dispersion of (-)-2-Chloro-2-nitrosocamphane

c = 0.280%　　Solvent : alcohol (oxygen free)

l = 1 dm.　　t = 18°

$10^{-1}\lambda$ (A°)	α°	$[\alpha]^\circ$	$10^{-1}\lambda$ (A°)	α°	$[\alpha]^\circ$
500	+1.32	+471	630	+2.65	+946
520	+1.44	+514	640	+2.60	+929
540	+1.60	+571	650	+2.15	+768
550	+1.80	+643	660	+0.95	+339
560	+1.92	+686	670	0	0
570	+2.16	+771	680	-1.75	-625
580	+2.45	+875	690	-2.25	-804
590	+2.65	+946	700	-2.55	-911
600	+2.70	+964	710	-2.65	-946
610	+2.65	+946	720	-2.45	-875
620	+2.60	+929			

GRAPH I

Rotatory Dispersions of
(a) (−)-2-Chloro-2-nitrosocamphane
(b) (+)-2-Chloro-2-nitrosocamphane

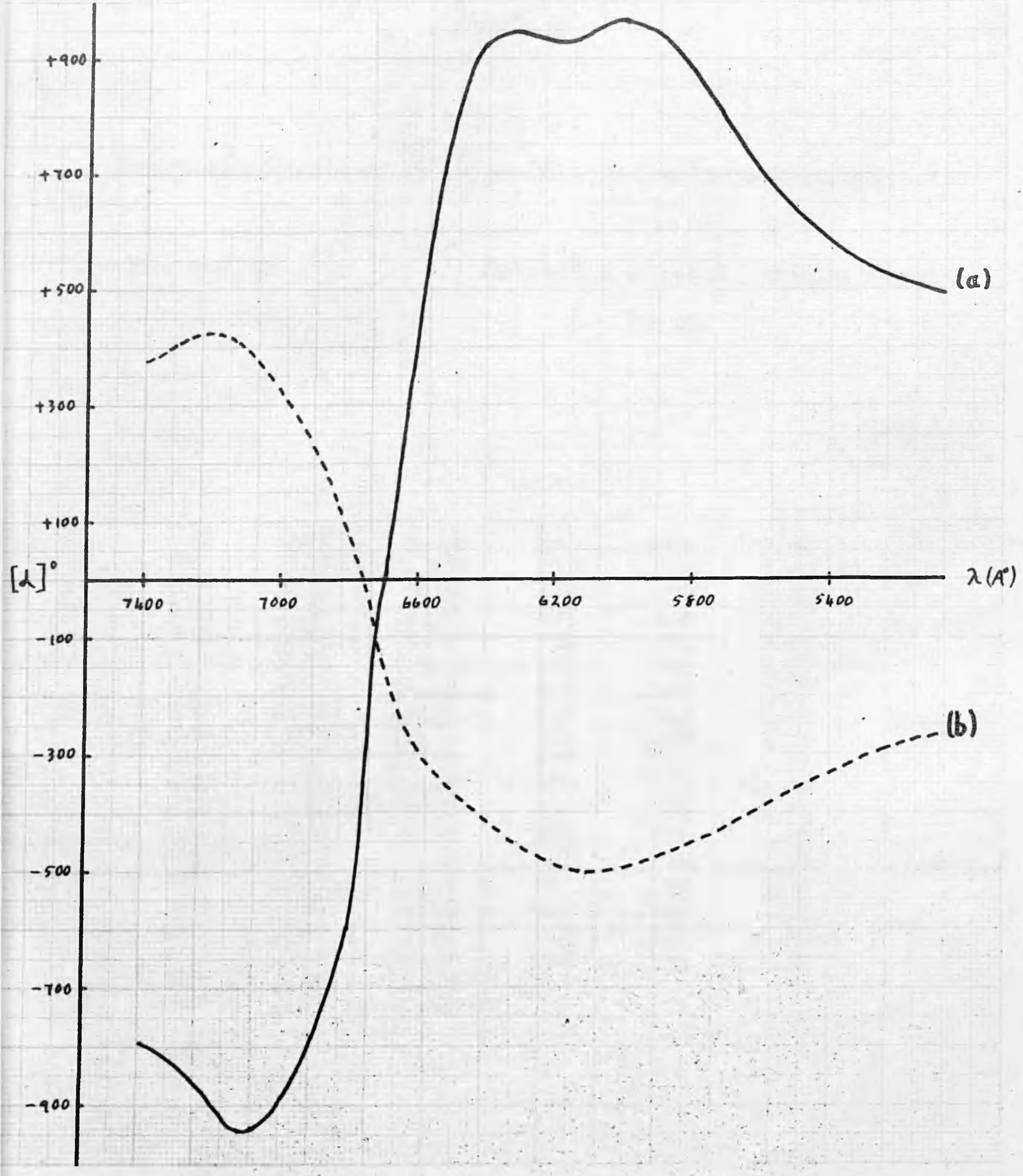


TABLE 2

Absorption Spectrum of (-)-2-Chloro-2-nitrosocamphane

c = 1.400% Solvent : alcohol (oxygen free)

= 0.0694M ℓ = 10 mm.

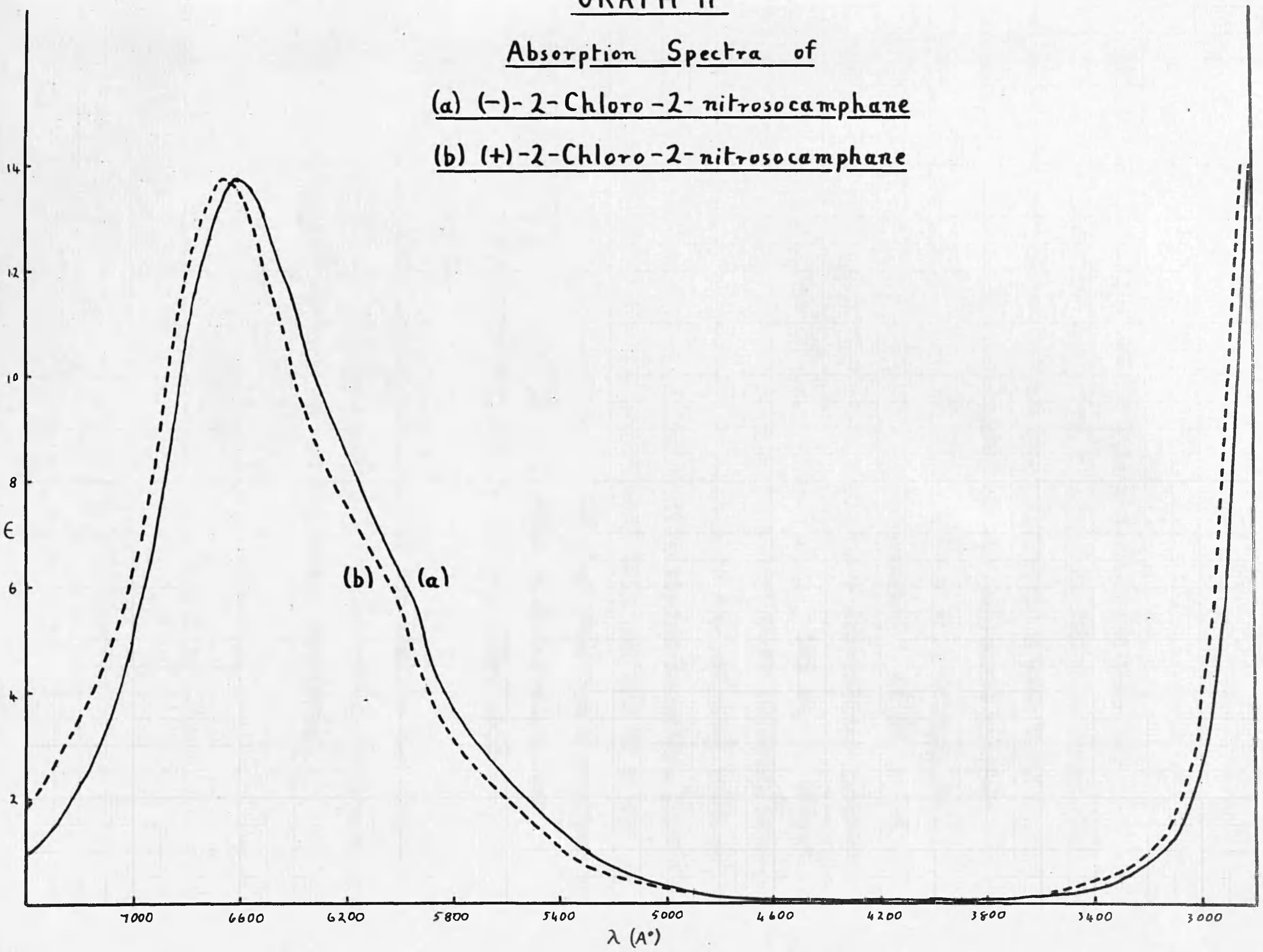
$10^{-1}\lambda$ (A°)	$\log \frac{I_0}{I}$	ϵ	$10^{-1}\lambda$ (A°)	$\log \frac{I_0}{I}$	ϵ
740	.068	0.98	530	.065	0.95
730	.103	1.48	510	.034	0.49
720	.159	2.29	490	.017	0.24
710	.235	3.39	470	.005	0.07
700	.352	5.07	450	.005	0.07
690	.520	7.49	430	.005	0.07
680	.730	10.52	410	.007	0.10
670	.875	12.61	390	.007	0.10
660	.955	13.76	370	.008	0.11
650	.900	12.97	350	.013	0.21
640	.797	11.48	330	.033	0.47
630	.685	9.87	320	.053	0.74
620	.592	8.53	310	.085	1.22
610	.512	7.38	305	.130	1.87
600	.434	6.25	300	.189	2.27
590	.337	4.86	295	.300	4.32
580	.257	3.70	290	.430	6.20
570	.204	2.94	285	.711	10.22
560	.165	2.38			
550	.127	1.38			

GRAPH II

Absorption Spectra of

(a) (−)-2-Chloro-2-nitrosocamphane

(b) (+)-2-Chloro-2-nitrosocamphane



polarimetric estimation of the photochemical process.

The absorption spectrum is given in Table 2, Graph II(a), where two selective regions are apparent; a weak band in the visible which is characteristic of all monomeric nitroso compounds and gives rise to their normal blue colour, and another in the ultra-violet due to halogen. It is worthy of note that reviews of the literature have erroneously recorded a band in this latter region with $\epsilon_{max.} \simeq 100$ at $\lambda = 3000A^{\circ}$ as a characteristic of the nitroso chromophore (Braude, 1945a, Gillam and Stern, 1954). Reference to the original work of Baly and Desch (1908) on tert-nitrosoisopropylacetone, however, shows that these authors appreciated this was due to a bimolecular form of the material, and they observed a progressive decrease in the strength of this band with corresponding increase in intensity of the blue colour, under conditions of depolymerisation.

The effect of light lying within the visible and ultra-violet regions of absorption of (-)-2-chloro-2-nitrosocamphane is separately considered in the following Sections.

(iii)(a) Behaviour on Irradiation with Monochromatic Light lying within the Region of Visible Absorption

Irradiation of a solution of (-)-2-chloro-2-nitrosocamphane in oxygen-free alcohol was carried out according to the experimental procedure described in Section (i). Table 3 contains the relevant optical data after a number of time-intervals to completion of the reaction.

Inspection of the results shows that the process is accompanied by a change in rotation from $[\alpha]_{6025} = +947^0$ to $[\alpha]_{6025} = -290^0$. However, a corresponding fall in the absorption from $\epsilon_{6625} = 13.80$ to $\epsilon_{6625} = 7.79$ occurs in the same time, so that extensive photolysis accompanies the primary process which gives rise to a product of negative rotatory power at this wave-length.

Application of the photoelectric estimation of concentration previously described has proved invaluable in permitting determination of specific rotations at each time-interval, and the true course of the reaction is indicated by these. Such estimations have been carried out at $\lambda = 6625A^0$, a wave-length which has been dictated from considerations set out later in this Section

The calculated specific rotation falls from $[\alpha]_{6025} = +947$,

TABLE 3

Irradiation of (-)-2-Chloro-2-nitrosocamphane
with
Mercury Yellow Light (λ = 5770, 5790A°)

c = 1.206% Solvent : alcohol (oxygen free)

= 0.0598M ℓ = 10 mm. (sealed cell)

Absorption Measurements at λ = 6625A°

Rotation Measurements at λ = 6025A°

Time (hr.)	α°	$[\alpha]^\circ_{obs.}$	$[\alpha]^\circ_{calc.}$	$\log \frac{I_0}{I}$	ϵ	$\log \epsilon$
0	+1.14	+947	+947	.825	13.80	1.140
0.25	+0.94	+779	+804	.800	13.38	1.127
0.50	+0.75	+622	+652	.785	13.13	1.118
1.00	+0.42	+349	+374	.770	12.87	1.110
2.00	+0.02	+17	+18	.760	12.71	1.104
3.00	-0.21	-175	-192	.752	12.57	1.099
4.00	-0.37	-307	-341	.743	12.40	1.093
6.00	-0.49	-406	-455	.735	12.30	1.090
15.00	-0.45	-374	-508	.608	10.17	1.007
20.00	-0.41	-340	-510	.550	9.20	0.964
27.00	-0.35	-290	-513	.466	7.79	0.892

rapidly at first, and then more slowly, to a limiting value of $[\alpha]_{6025} = -508^{\circ}$ which resists further change on continued irradiation, although the corresponding absorption values tend to zero. From these results it may be conclusively asserted that mutarotation does, in fact, occur, and evidence is presented later (p 118) in support of the contention that the final value is that of a stereochemically uniform material resulting from the reaction and not that of an equilibrium mixture which would be derived from a photostationary state.

The gradual inversion of the Cotton effect during irradiation has already been described qualitatively (Mitchell et al., 1950). By employing the method developed in the present work, it has been possible to determine the form of the rotatory dispersion curve of the irradiated material precisely. For this purpose, the solution resulting from the previous experiment was used. This has the properties recorded in the final values of Table 3, so that the concentration is given by

$$c = c_0 \frac{k}{k_0} = 1.206 \frac{0.466}{0.825} = 0.681\%.$$

For convenience of polarimetric readings, the solution was transferred to a 0.5 dm. cell. The rotatory dispersion is recorded in Table 4 and illustrated in Graph I, showing a Cotton effect with the following characteristics

TABLE 4

Rotatory Dispersion of 2-Chloro-2-nitrosocamphane
after Irradiation with
Mercury Yellow Light ($\lambda = 5770, 5790 A^\circ$)
(calculated)

c = 0.681% Solvent : alcohol (oxygen free)

l = 0.5 dm. t = 18°

$10^{-1}\lambda(A^\circ)$	α°	$[\alpha]^\circ$	$10^{-1}\lambda(A^\circ)$	α°	$[\alpha]^\circ$
500	−0.89	−261	640	−1.40	−412
520	−0.98	−287	650	−1.22	−358
540	−1.14	−335	660	−1.00	−295
550	−1.23	−361	670	−0.45	−131
560	−1.33	−392	680	+0.25	+74
570	−1.45	−426	690	+0.76	+224
580	−1.54	−452	700	+1.11	+327
590	−1.62	−477	710	+1.34	+395
600	−1.68	−494	720	+1.45	+426
610	−1.72	−506	730	+1.39	+409
620	−1.64	−483	740	+1.28	+378
630	−1.54	−452			

$[\alpha]_{max.} = -508°$ at 6060A° Reversal 6760A° $[\alpha]_{min.} = +430°$ at 7160A°

This is an inverted form of the original with smaller maxima values and showing a displacement of some 60A° to longer wavelengths, evident from the points of reversal of the curves. This shift is of importance when considered with the accompanying changes in absorption, which will now be discussed.

The material resulting from the irradiation shows an absorption spectrum which is recorded in Table 5 and plotted in Graph II(b), the calculated values of molecular extinction coefficient being based on the final concentration already derived for the rotatory dispersion. This gives an absorption curve of exactly the same form as the original, but displaced some 60A° to longer wave-lengths with remarkable regularity in both the visible and ultra-violet regions.

A more detailed investigation of the intermediate stages of the reaction has shown that the absorption spectra, determined at various time-intervals, show a gradual displacement from the original to the final as the reaction proceeds, in the same way as for the rotatory dispersion. Such a series of curves is found to pass through a common point of $\epsilon = 13.8$, $\lambda = 6625$A° giving rise to the isosbestic required for the photoelectric estimation of concentration and determining the only wave-length suitable for this.

From these changes observed during irradiation, a number

TABLE 5

Absorption Spectra of 2-Chloro-2-nitrosocamphane after Irradiation with Mercury Yellow Light ($\lambda = 5770, 5790 A^\circ$) (observed and calculated)

c = 1.206% (calc. 0.681%) Solvent : alcohol (oxygen free)
= 0.0598M(calc. 0.0337M) ℓ = 10 mm.

$10^{-1}\lambda(A^\circ)$	$\log \frac{I_0}{I}$	ϵ (obs.)	ϵ (calc.)	$10^{-1}\lambda(A^\circ)$	$\log \frac{I_0}{I}$	ϵ (obs.)	ϵ (calc.)
740	.060	1.00	1.78	530	.023	0.38	0.69
730	.086	1.44	2.56	510	.014	0.23	0.40
720	.117	1.95	3.48	490	.005	0.08	0.14
710	.159	2.65	4.73	470	.002	0.03	0.07
700	.213	3.56	6.32	450	.002	0.03	0.07
690	.295	4.93	8.77	430	.002	0.03	0.07
680	.399	6.67	11.82	410	.002	0.03	0.07
670	.453	7.57	13.42	390	.002	0.03	0.07
660	.454	7.59	13.54	370	.004	0.07	0.12
650	.403	6.73	11.96	350	.017	0.28	0.32
640	.338	5.65	10.03	330	.020	0.33	0.60
630	.289	4.83	8.59	320	.030	0.50	0.90
620	.256	4.28	7.59	310	.053	0.89	1.60
610	.224	3.74	6.65	305	.085	1.43	2.53
600	.186	3.11	5.53	300	.119	1.98	3.54
590	.139	2.32	4.13	295	.186	3.11	5.52
580	.105	1.75	3.12	290	.303	5.07	9.02
570	.083	1.39	2.46	285	.419	7.00	12.46
560	.067	1.12	1.98				
550	.051	0.85	1.50				

of conclusions can be drawn concerning the relationship between the materials existing before and after the reaction.

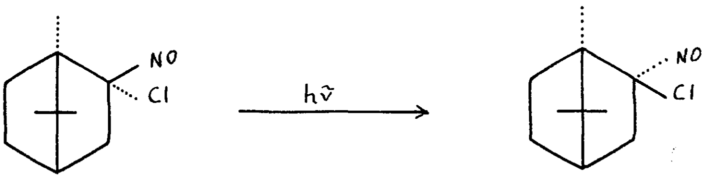
(i) Non-identity of the rotatory dispersion and absorption curves show that these are not one and the same compound.

(ii) The remarkable similarity of absorption spectra necessitates closely related structures, and both show the selective absorption characteristic of monomeric nitroso compounds.

(iii) Inversion of the Cotton effect requires inversion of the asymmetric centre giving rise to the optical activity in this spectral region, i.e. inversion of the NO - Cl centre, C_2.

(iv) Analysis of the final material proves it to be isomeric with the original (Section (iv)).

Such considerations permit of but one interpretation of this reaction; photomutarotation of (-)-2-chloro-2-nitrosocamphane, which may be represented



(-)-2-chloro-2-nitrosocamphane (+)-2-chloro-2-nitrosocamphane

The configurations have been derived from further considerations and are discussed at the conclusion of the following Section.

It is interesting to note that when 2-chloro-2-nitroso-camphane, prepared from (±) camphor was exposed to light, no observable rotation developed at any stage in the reaction, but the absorption curve of the final material was found to be displaced 50 - 60A° to longer wave-lengths, showing that both enantiomorphic forms had mutarotated, but in opposite directions and at exactly the same rate.

(iii)(b) Behaviour on Irradiation with Polychromatic Light lying within the Region of Ultra-violet Absorption

The preceeding work has shown that absorption of light in the region of the visible band gives rise to a photo-excited state which undergoes spontaneous rearrangement by inversion of the chlorine and nitroso groups on C_2. Since such energy transference is directed to excitation of the nitroso group, it seemed likely that a similar effect might be obtained by absorption through the other functional group, i.e. chlorine, which gives rise to the ultra-violet region shown in Graph II. The mercury arc emits a number of strong lines at λ = 2970, 2650 and 2480A°, well within the required spectral region. In the following work those of longer wave-lengths have been carefully filtered out, so that the results may be unambiguously attributed to absorption through the required chromophore. The experimental procedure has been described (p 21).

As a preliminary test of this hypothesis, it was decided to use the displacement of absorption as a diagnostic test for stereomutation. The experiment was continued until spectrophotometric measurement showed that about 50% decomposition had taken place. The spectrum was redetermined at this time, and with the aid of the usual estimation of concentration, the true absorption was calculated (Table 6). This is compared with the original in Graph III (i)(a and b), where it is evident that the shift characteristic of photomutarotation has again taken place.

The displacement after this arbitrary time of 100 min. is about $30A^{\circ}$, in comparison with the full value of $60A^{\circ}$ previously observed, so that the rearrangement is only about half complete under these conditions. This is in agreement with evidence supplied from rotation data, the value of $[\alpha]_{6025} = +310^{\circ}$ attained here, lying approximately mid-way between the original of $[\alpha]_{6025} = +949^{\circ}$ and the final limiting value of $[\alpha]_{6025} = -508^{\circ}$ (Table 3).

Having shown qualitatively that photomutarotation occurs under the influence of ultra-violet light, it became desirable to investigate the process in greater detail by the usual polarimetric and spectrophotometric methods. The appropriate optical data for a number of times during a typical irradiation are set out in Table 7. Termination of the reaction was necessitated after 210 min. when 75% of the material had undergone photolysis so that further absorption readings became too small to permit accurate measurement. During this period, the calculated specific rotations fall from $[\alpha]_{6025} = +953^{\circ}$ to $[\alpha]_{6025} = +231^{\circ}$, but do not attain a constant value as in the irradiation with light in the visible region. Comparison of the time required for this fall in rotation with the corresponding values

TABLE 6

Absorption Spectrum of 2-Chloro-2-nitrosocamphane after Irradiation with Ultra-violet Light

c = 1.564% (calc. = 0.740%)   Solvent : alcohol (oxygen free)

= 0.0775M (calc. = 0.0366M) ℓ = 10 mm.

	Initial		Final		
$10^{-1}\lambda$(A°)	$\log \frac{I_0}{I}$	ϵ	$\log \frac{I_0}{I}$	ϵ	ϵ (calc.)
750	.045	0.59	.029	0.37	0.79
730	.109	1.40	.065	0.84	1.78
710	.252	3.25	.141	1.81	3.85
700	.376	4.85	.198	2.55	5.41
690	.563	7.26	.290	3.74	7.93
680	.800	10.32	.400	5.16	10.93
670	.960	12.38	.475	6.13	13.00
660	1.060	13.67	.497	6.41	13.59
650	1.010	13.03	.470	6.06	12.84
640	.890	11.48	.408	5.26	11.15
630	.775	10.00	.350	4.51	9.57
620	.660	8.58	.310	3.97	8.40
610	.573	7.39	.272	3.51	7.43
600	.487	6.28	.227	2.92	6.21
590	.374	4.82	.185	2.39	5.06
580	.290	3.74	.133	1.72	3.63
570	.223	2.87	.106	1.36	2.90
560	.190	2.45	.086	1.11	2.35
550	.145	1.87	.068	0.88	1.86
540	.104	1.34	.048	0.62	1.31

GRAPH III

(i)

Absorption Spectra of

(a) (−)-2-Chloro-2-nitrosocamphane before Irradiation

(b) (±)-2-Chloro-2-nitrosocamphane after u-v Irradiation

(ii)

Absorption Spectra of

(a) Bornyl Chloride

(b) isoBornyl Chloride

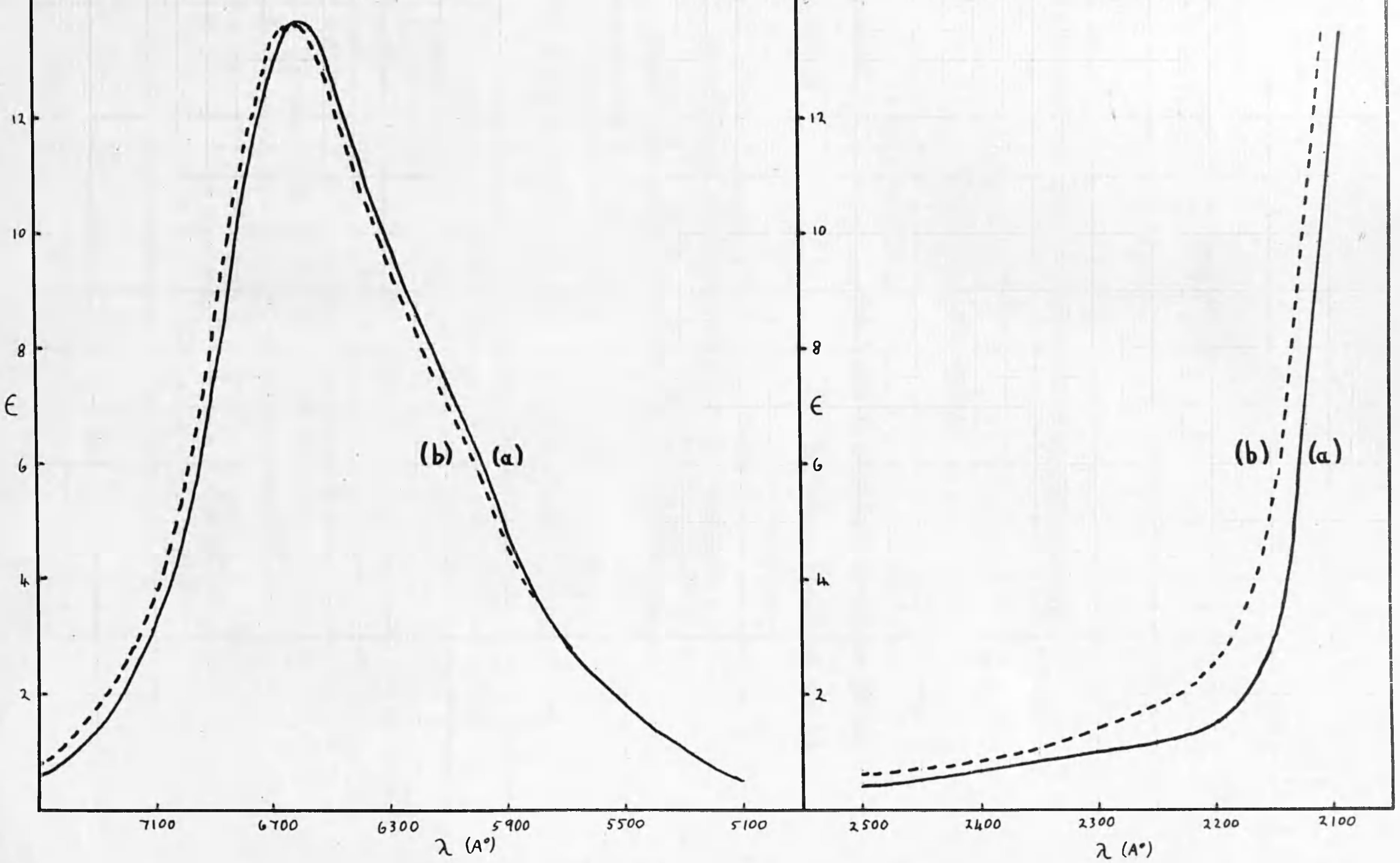


TABLE 7

Irradiation of (-)-2-Chloro-2-nitrosocamphane
with
Ultra-violet Light

c = 1.888% Solvent : alcohol (oxygen free)

= 0.0936M ℓ = 10 mm. (sealed cell)

Absorption measurements at λ = 6625A°

Rotation measurements at λ = 6025A°

Time (min.)	α°	$[\alpha]^{\circ}_{obs.}$	$[\alpha]^{\circ}_{calc.}$	$\log \frac{I_0}{I}$	ϵ	$\log \epsilon$
0	+1.80	+953	+953	1.27	13.55	1.132
5	+1.68	+889	+926	1.22	13.03	1.115
15	+1.51	+800	+876	1.16	12.40	1.093
30	+1.25	+662	+801	1.05	11.10	1.045
45	+1.04	+551	+736	0.95	10.21	1.009
60	+0.85	+450	+665	0.86	9.18	0.963
90	+0.56	+298	+531	0.71	7.58	0.880
135	+0.33	+175	+411	0.54	5.77	0.761
180	+0.17	+90	+286	0.40	4.28	0.631
210	+0.11	+50	+231	0.32	3.42	0.534

during the irradiation with mercury yellow light (Table 3), shows that the rate of photomutarotation has been almost halved in the present case, while the fall in absorption values indicates an increase, by a factor of about twenty, in the rate of photolysis. Accordingly, it is conceivable that under these conditions, total rearrangement is never attained before complete destruction of the material. The failure of the specific rotation to reach a constant figure is attributed to this. The particular value reached has no precise significance and is not characteristic of the wave-length of radiation.

To confirm this, it would be necessary to start with material which had already undergone extensive rearrangement and subsequent purification. Exposure of such an isomeric mixture to light would obviously permit stereoisomerisation to proceed further before complete decomposition. Fortunately, the required material may be obtained without the laborious processes of irradiation and purification since this is essentially the product resulting from incomplete transformation by light in the visible region. Accordingly, a solution of (-)-2-chloro-2-nitroso-camphane was exposed to the mercury arc, on the usual optical system, until $[\alpha]_{6025}$ had fallen from +947° to a calculated value of +484° ($\epsilon_{6625} = 11.76$). This solution was then submitted to ultra-violet radiation, and the specific rotations calculated at various time-intervals. The results are set out in Table 8

TABLE 8

Irradiation of (±)-2-Chloro-2-nitrosocamphane with Ultra-violet Light

c = 2.656%
= 0.1318M

Solvent : alcohol (oxygen free)
ℓ = 10 mm. (sealed cell)

Absorption Measurements at λ = 6625A°
Rotation Measurements at λ = 6025A°

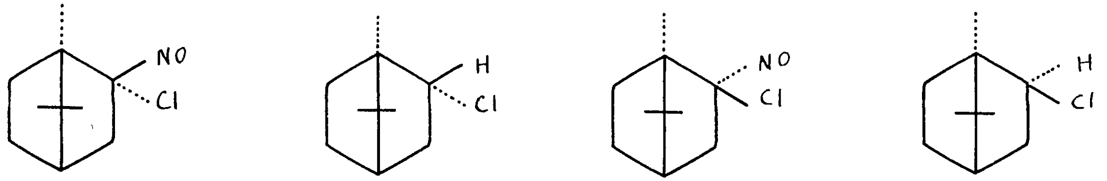
Time (min.)	α°	$[\alpha]^{\circ}_{obs}$	$[\alpha]^{\circ}_{calc.}$	$\log \frac{I_0}{I}$	ϵ
0	+1.09	+410	+484	1.55	11.76
30	+0.78	+294	+400	1.33	10.10
60	+0.59	+222	+349	1.16	8.80
90	+0.43	+162	+300	0.98	7.43
120	+0.30	+113	+242	0.85	6.46
150	+0.19	+72	+176	0.74	5.62
180	+0.09	+34	+95	0.64	4.87
210	+0.03	+11	+37	0.55	4.18
240	−0.01	−4	−14	0.48	3.65
270	−0.06	−23	−100	0.41	3.12
300	−0.08	−30	−157	0.35	2.70

showing that the rotation continues to decrease further from $[\alpha]_{6025} = +231^\circ$ previously observed, to a negative value of -157°, at which time photolysis has again become so extensive as to prevent further measurements.

It may, therefore, be concluded that the reaction follows the same course under the influence of both visible and ultra-violet light, the only factor preventing attainment of complete stereoisomerisation in the latter case, being the relative rates of photomutarotation and photolysis.

CONFIGURATIONS

Having shown that (-)-2-chloro-2-nitrosocamphane isomerises under the influence of light, it remained to assign configurations to the isomeric forms. The compounds of established structure most closely related to them are bornyl and isobornyl chlorides, whose absorption curves show a close analogy to the materials under investigation. Surprisingly these spectra are not available in the literature, and so have been determined here. For the present work, the compounds were required in a high state of purity. Bornyl chloride was obtainable from commercial 'pinene hydrochloride' while isobornyl chloride was prepared by rearrangement of camphene hydrochloride, under carefully controlled conditions according to Meermein and van Emster (1922). The absorption spectra were examined as far as the lower limit of the instrument, n-hexane being used as solvent to preclude the possibility of differences arising from dissociation. The data are recorded in Table 9 and illustrated in Graph III (ii) where it is seen that a close parallelism exists between the spectra of these two materials and those of the isomers under investigation (Graph II). Accordingly, it is suggested that the following pairs have similar configurations.

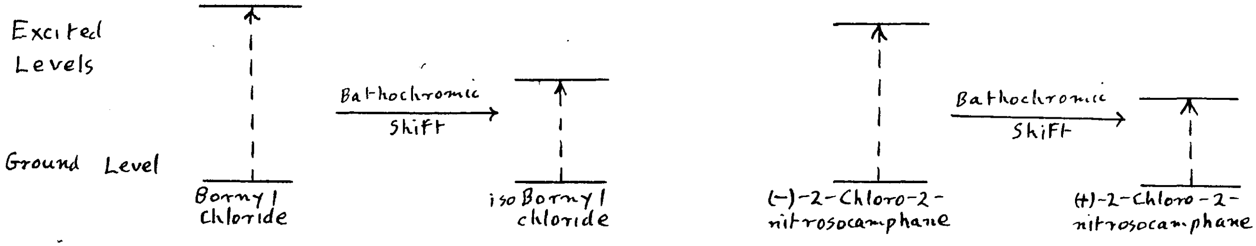


(−)-2-chloro-2-nitrosocamphane | Bornyl chloride | (+)-2-chloro-2-nitrosocamphane | isoBornyl chloride

$\underbrace{\text{(−)-2-chloro-2-nitrosocamphane} \quad \text{Bornyl chloride}}_{\text{endo}} \quad \underbrace{\text{(+)-2-chloro-2-nitrosocamphane} \quad \text{isoBornyl chloride}}_{\text{exo}}$

It may be pointed out that this is only a comparison and not a rigorous treatment, since a bathochromic displacement of absorption indicates only a lower energy of electronic transition, i.e. a smaller difference between the ground and excited levels.

Fig. 2



Energies of Transition

TABLE 9

Absorption Spectra
of
Bornyl and isoBornyl Chlorides

Bornyl Chloride c = 0.723% = 0.0419M Solvent : n-hexane l = 10 mm.			**isoBornyl Chloride** c = 0.802% = 0.0464M Solvent : n-hexane l = 10 mm.		
$10^{-1}\lambda(A^{\circ})$	$\log \frac{I_o}{I}$	ϵ	$10^{-1}\lambda(A^{\circ})$	$\log \frac{I_o}{I}$	ϵ
250	.020	0.48	250	.033	0.71
245	.021	0.50	245	.033	0.71
240	.028	0.67	240	.039	0.84
235	.036	0.86	235	.050	1.08
230	.044	1.00	230	.066	1.43
225	.050	1.20	225	.085	1.83
223	.053	1.27	223	.093	2.00
221	.058	1.38	221	.108	2.32
219	.067	1.60	219	.134	2.88
217	.087	2.08	217	.174	3.74
215	.125	2.98	215	.251	5.40
213	.217	5.18	213	.376	8.10
212	.280	6.69	212	.490	10.55
211	.380	9.87	211	.590	12.70
210	.460	10.98			

However, since the trans-chloro compound (bornyl chloride) in one pair of stereoisomers has the higher energy of transition, it is reasonable to suppose that this will also be the case in the other pair of similarly substituted camphane structures.

It is satisfactory to note that confirmatory evidence is supplied from a study of the related 3-halogeno-camphors as recently reported by Cookson (1954).

Compound	$\lambda_{max.}$ (A°)	Endo → Exo Shift
3α - chlorocamphor	3050	10A°
3β - chlorocamphor	3060	Bathochromic
3α - bromocamphor	3100	20A°
3β - bromocamphor	3120	Bathochromic

Here again, the more stable trans-halogeno isomers absorb at shorter wave-lengths, i.e. have higher energies of transition. In view of such conformity in the series, the original comparison may be considered valid.

(iv) (+)-2-Chloro-2-nitrosocamphane

To complete the evidence for the structural changes postulated during the photomutarotation of (-)-2-chloro-2-nitrosocamphane, it remained only to isolate the second isomeric form of the compound and compare its properties with those of the material derived from the irradiation.

Two separate approaches to this problem were available.

(i) Isolation of the required isomer by chemical or physical methods from the stereoisomeric mixture.

(ii) Complete photochemical rearrangement to the less stable form, with subsequent purification from the products of photolysis.

For the first of these an extention of the theory of the stereo-directing influence of hydrogen chloride in the preparation was called for. This has been mentioned in Section (ii). It was argued that if the reaction could be carried out under conditions in which the free hydrochloric acid would be removed as quickly as it was produced, the resulting material should show an increase in the proportion of the less stable form. Accordingly, chlorination of the oxime in pyridine was attempted at low temperature and yielded a product with $[\alpha]_{\mathrm{max.}} \simeq +250^{\circ}$, in confirmation of the above considerations. Repeated preparations, under a variety of conditions, however, did not appreciably decrease the specific rotation further from this intermediate value, so that the required stereochemical individual cannot be obtained by this procedure. Although the method is unsuitable for the present work, it is worthy of note that the equilibrium attained requires approximately equimolecular amounts of the two forms.

It has already been pointed out that chromatography on alumina is effective for the required purpose, but that almost complete destruction of the more strongly adsorbed isomer occurs before separation is finally achieved (p 26) while the high solubility in all organic solvents precludes the possibility of separation by fractional crystallisation. It was considered that differences in physical properties were more likely to yield successful results and fractional sublimation under high vacuum was attempted but this too, failed to achieve separation of the stereoisomers. The first approach was abandoned in view of such negative results, and attention turned to the remaining method.

Initially this proved equally unsuccessful since continued irradiation of alcoholic solutions of the compound resulted in such extensive photolysis that an intractable gum invariably resulted on removal of the solvent. It was found that photomutarotation occurs equally well when a thin film of the solid is exposed to a strong light source and this has formed the basis of the following method.

A cylindrical 200 ml. cell containing 0.25 gm. (−)-2-chloro-2-nitrosocamphane was placed vertically on one end and evacuated to 0.1 mm. The bottom surface was kept at 30-40°C on a warm plate and the upper end cooled to −180° by contact with a brass vessel containing liquid air. The material sublimed on the cold upper surface in the course of 30 min., forming a thin uniform film. The end of the cell was then irradiated with light from a carbon arc, the condensing beam first passing through a circulating water filter and an infra-red filter (Chance ON 20). Exposure was continued for 30 min., during which time the cell was reversed frequently. Thereafter, the vacuum was released and the solution of the material in light petroleum chromatographed on sugar charcoal (25 x 1 cm.). The product had $[\alpha]_{6060} = -438°$; $\epsilon = 13.7$ (for $\lambda = 6650A°$); m.p. 140-141° (d). This procedure was repeated several times and the products were combined and used as starting material for the second stage which consisted of irradiation and purification as before. This gave a product with the following properties.

$[\alpha]_{\text{min.}} = -508°$ at $\lambda = 6060A°$
$\epsilon_{\text{max.}} = 13.8°$ at $\lambda = 6650A°$
m.p. 140-141° (d)

Continued processing by these methods did not change the rotation further, so that it must be concluded that complete separation of the required stereoisomeric (+)-2-chloro-2-nitrosocamphane has been attained. Analysis has confirmed that this product is isomeric with the starting material.

Found: C, 59.8; H, 7.6; N, 6.7%
$C_{10}H_{16}ONCl$ requires C, 59.7; H, 7.9; N, 6.9%

Later, a modification of the above technique was developed which facilitated preparation of the material in larger quantities. This consisted of irradiating a strong solution of (-)-2-chloro-2-nitrosocamphane in light petroleum in the beam of the carbon arc as before. The solvent was permitted to reflux under nitrogen to minimise photo-oxidation and the temperature of the reaction was limited by the low boiling point. This method had the outstanding advantage that the transformation could be followed by removing a sample of solution at various time-intervals, diluting and determining the concentration spectrophotometrically. The specific rotation was then calculated from the observed result, and completion of the reaction indicated by attainment of the limiting value of this property. Purification of the resulting solution, after concentration, was carried out by chromatography on sugar charcoal as before when the resulting material had the properties described above.

The rotatory dispersion and absorption spectrum of

(+)-2-chloro-2-nitrosocamphane were determined and found to be identical in all respects with the results calculated for the final products of irradiation of the (-) isomer by mercury yellow light and recorded in Table 4 - Graph I(b) and Table 5 - Graph II(b) respectively, so that they need not be repeated here.

In conclusion, it may be asserted that the photomutarotation of (-)-2-chloro-2-nitrosocamphane by light lying within the spectral regions of selective absorption, has been established as occurring by conversion of this material to the stereoisomeric (+)-2-chloro-2-nitrosocamphane, which differs from the original, only in configuration of the asymmetric centre C_2.

(v) Kinetic Studies

Although a thorough kinetic study of the photochemical reactions occurring on irradiation of (-)-2-chloro-2-nitrosocamphane is clearly necessary to an understanding of these component processes, this has been made possible only with the development of the polarimetric and spectrophotometric methods derived in the preceding Sections. In this way an understanding of the relative importance of the primary and secondary processes has been obtained and their velocities determined. Comparison of the work in the visible and ultra-violet regions has shown that the course of the overall reaction is directly dependent on the relationship between these two rates.

Theoretical Considerations

Two sets of factors influence the velocity of a photochemical reaction.

(i) Those concerned with the radiation, e.g. the wave-length and distribution of intensity of the radiation penetrating into the reaction mixture, the area illuminated and the nature of the optical path.

(ii) The remaining variable factors which exert an influence in the same way as in thermal reactions, e.g. temperature, pressure, concentration of reactant, catalysts and solvent.

It is the purpose of the present work to offer comparative rather than absolute values of the reaction velocities and since all experiments were carried out under circumstances in which the above conditions were identical (except the difference in radiation for the two spectral regions concerned) comparison of the results may reasonably be made.

Simple kinetic behaviour has been observed in a surprisingly large number of photochemical reactions, i.e. direct proportionality between absorbed energy and reaction velocity. Kinetic equations have been derived for such behaviour by Wegscheider (1923) in the case of an irreversible homogeneous photochemical reaction which proceeds only on illumination and in which the absorbing substance is transformed. The illumination is effected by a parallel beam of monochromatic light, entering the system at right angles to the cell face and emerging from a parallel wall. Assuming concentration differences are eliminated and the vessel is completely illuminated, it can be shown, that after time 't' the concentration is expressed by the general equation

$$k \alpha I_0 t = \alpha S x + \ln \frac{1 - e^{-\alpha S a}}{1 - e^{-\alpha S(a-x)}} \qquad \text{...... (4)}$$

where k = velocity constant
α = molecular absorption coefficient
q = cross-sectional area of beam
S = length of beam in reacting system
I_0 = incident light intensity

a = initial concentration of absorbing (and reacting) species

$(a - x) = c$ = concentration at time t

Two limiting cases of equation (4) are of importance.

(i) Strong Absorption of the Light i.e. $\alpha S a$ large

Under these circumstances, the second term on the right-hand side of equation (4) may be neglected since it approaches the value of ln 1. The equation reduces to

$$x = \frac{k I_0 t}{S} \qquad \ldots\ldots \text{(5)}$$

The amount of material is thus proportional to the time, i.e. the reaction velocity is constant throughout the experiment.

(ii) Weak Absorption of the Light i.e. $\alpha S a$ small

Under these conditions, the term $\alpha S a$ of equation (4) may be neglected and the exponentials of the numerator and denominator of the logarithmic term expanded into the series.

$$e^{-x} = 1 - x + \frac{x^2}{2} \ldots\ldots$$

Approximating to the first two terms, equation (4) becomes,

$$k \alpha I_0 = \frac{1}{t} \ln \frac{a}{a - x} \qquad \ldots\ldots \text{(6)}$$

i.e. the reaction velocity is proportional to the concentration of unchanged reactant, which is the characteristic of a unimolecular reaction. Since the present studies have been carried out under conditions of very weak absorption ($c \simeq 1.5\%$), this second condition is of particular interest, and the kinetics of unimolecular processes may be considered further.

In a First Order reaction, the rate is directly proportional to the concentration. This may be expressed by

$$-\frac{da}{dt} = ka \qquad \text{......} \quad (7)$$

where 'a' is the concentration of reactant and 'k' is a proportionality constant. If the decrease in concentration after time 't' is represented by 'x', the following may be simply derived

$$\ln \frac{a}{a-x} = kt \qquad \text{......} \quad (8)$$

This is the general equation which all First Order reactions must satisfy, and is seen to resemble equation (6) in form. Rearrangement gives

$$\frac{k}{2 \cdot 303} t + \log (a-x) - \log a = 0 \qquad \text{......} \quad (9)$$

so that the plot of log (a - x) against time will give a straight line of gradient

$$g = -\frac{k}{2 \cdot 303} \qquad \text{......} \quad (10)$$

offering a convenient method for calculation of velocity constants from the slope of the line.

In order to compare the kinetic values derived for the component reactions of photomutarotation and photolysis in the present work, the results must be calculated on the basis of the same units. The two processes may be considered.

(i) <u>Photomutarotation</u>

In this case, the concentration is expressed in terms of the initial, intermediate and final specific rotations, $[\alpha]_i$, $[\alpha]$ and $[\alpha]_\infty$ respectively, but in order to bring this into conformity with the following process of photolysis, the decrease in concentration due to photomutarotation must be represented as a fall in molecular extinction coefficients.

Let a $= \{[\alpha]_i - [\alpha]_\infty\} = \epsilon_{max.}$

hence (a-x) $= \{([\alpha]_i - [\alpha]_\infty) - ([\alpha]_i - [\alpha])\}$

$= \{[\alpha] - [\alpha]_\infty\}$

now since $\{[\alpha]_i - [\alpha]_\infty\} = \epsilon_{max.}$

therefore $\{[\alpha] - [\alpha]_\infty\} = \epsilon_{max.} \dfrac{[\alpha] - [\alpha]_\infty}{[\alpha]_i - [\alpha]_\infty}$

so that equation (9) may now be written

$$\frac{k_1}{2.303} t + \log\left\{\epsilon_{max.} \frac{[\alpha] - [\alpha]_\infty}{[\alpha]_i - [\alpha]_\infty}\right\} - \log \epsilon_{max.} = 0 \quad \text{......} \ (11)$$

in which case the plot of $\epsilon_{max.} \frac{[\alpha] - [\alpha]_\infty}{[\alpha]_i - [\alpha]_\infty}$ against time will give a straight line with gradient given by equation (10).

(ii) Photolysis

The measurement of photolysis is given by the decrease in intensity of the blue colour of the solution. This is determined from the spectrophotometric measurements at the isosbestic wave-length. If the observed molecular extinction coefficients are calculated on the basis of the original concentration, then

$$a = \epsilon_{max.}$$
$$(a-x) = \epsilon$$

so that, for this purpose equation (9) becomes

$$\frac{k_2}{2.303}t + \log\epsilon - \log\epsilon_{max.} = 0 \qquad \ldots\ldots (12)$$

and the plot of ϵ against time will give a straight line with gradient as before.

A further characteristic constant of such unimolecular reactions is the half-life period which, since independent of initial concentration, is convenient for comparison of velocities

$$t_{\frac{1}{2}} = \frac{2.303\log 2}{k} = \frac{0.693}{k} \qquad \ldots\ldots (13)$$

Since all photochemical reactions consist of a number of stages, the kinetics of the overall reaction can be derived satisfactorily only on the basis of the consecutive component reactions. The following will occur in the present case

$$\begin{array}{llllll} A \longrightarrow A^* & \cdots\cdots & k_5 & B \longrightarrow B^* & \cdots\cdots & k_4 \\ A^* \longrightarrow B & \cdots\cdots & k_1 & B^* \longrightarrow C & \cdots\cdots & k_2 \\ A^* \longrightarrow C & \cdots\cdots & k_3 & & & \end{array}$$

where A represents the original molecular species

B represents the molecular species resulting from photomutarotation of A

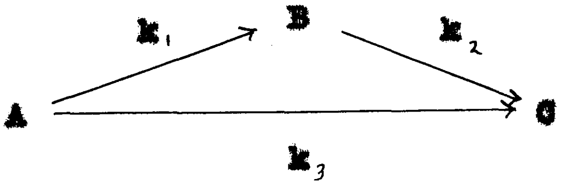
C represents the molecular species resulting from photolysis of either A or B

the starred members indicating the photo-excited states.

The rate of a total reaction is determined by the velocities of the slower component processes so that the very rapid photo-excitation may be considered as non-rate-determining in the present case, i.e.

$$k_1,\ k_2 \text{ and } k_3 \ll k_4 \text{ and } k_5$$

This permits simplification of the process to



where the conversion of A to C may proceed by either of the two competing routes. It will be shown that under certain conditions, the first of these is preferred and the second may be neglected, so that the mechanism further reduces to

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Such a two-stage process is of particular importance and may be considered further.

In general, the precise mathematical treatment of consecutive reactions is extremely difficult. However, the simplest case outlined above may be treated by the following considerations.

Let 'a' be the initial concentration of A, 'x' the amount of it changed in time 't' and 'y' the concentration of 'c' formed at the same instant. Then at time 't'

$$C_A = (a - x), \quad C_c = y, \quad C_B = (x - y)$$

The rate of disappearance of 'A' is given by

$$\frac{dx}{dt} = k_1(a - x) \qquad \ldots\ldots \quad (14)$$

while the rate of decomposition of 'B', which is the same as the rate of formation of 'C' is

$$\frac{dy}{dt} = k_2(x - y) \qquad \ldots\ldots \quad (15)$$

Solution of these rate equations give the dependence of concentration of 'A', 'B' and 'C' on time. Integration of equation (14), substitution of the value of 'x' so obtained, in equation (15) and integration of the latter yields the following expressions.

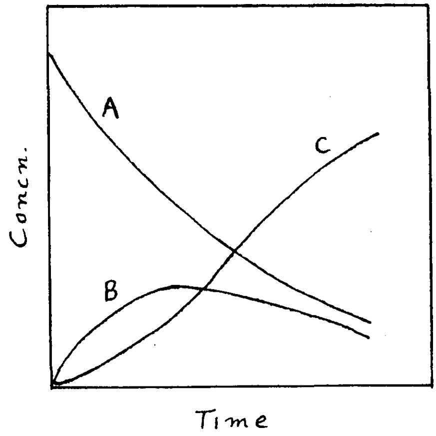
$$C_A = a e^{-k_1 t} \qquad \text{......} \quad (16)$$

$$C_B = \frac{k_1 a}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t} \right) \qquad \text{......} \quad (17)$$

$$C_C = \frac{a}{k_2 - k_1}\left[\left(k_2 - k_2 e^{-k_1 t} \right) - \left(k_1 - k_1 e^{-k_2 t} \right) \right] \qquad \text{......} \quad (18)$$

Figure 3 shows the typical variation of C_A, C_B and C_C with time for consecutive reactions with $k_1 < k_2$.

Fig. 3



It is seen that the concentration of the intermediate product, 'B', rises to a maximum and then falls with time. This is characteristic of consecutive reactions with comparable values of velocity constants and has been used to identify such a mechanism in the present work.

Kinetics of the Photochemical Processes occurring on Irradiation with Monochromatic Light lying within the Region of Visible Absorption

An attempt may now be made to apply the kinetic methods formulated to the reactions occurring on irradiation of (−)-2-chloro-2-nitrosocamphane with mercury yellow light. The experiment has already been described (p 29) and the observed data recorded in Table 3. From these, the required values have been calculated and are set out in Table 10. The course of photomutarotation of species 'A' is shown in terms of molecular extinction coefficients in Graph IV (i) and is seen to be exponential in form. The plot of the logarithms of the ordinates against time gives a straight line which is shown on the same graph. It is evident that the process of photomutarotation does, in fact, conform to kinetics of the First Order. The characteristic constants may therefore be calculated.

$$\tan\theta = 0.243$$

Now $$g = \tan(180 - \theta) = -\tan\theta$$

from equation (10) $$k_1 = -2.303g = \underline{0.56\ \text{hr.}^{-1}}$$

equation (13) gives $$(t_1)_{\frac{1}{2}} = \frac{0.693}{k_1} = \underline{1.24\ \text{hr.}}$$

The photolysis observed during this irradiation does not

TABLE 10

Kinetics of the Photomutarotation of (-)-2-Chloro-2-nitrosocamphane on Irradiation with Mercury Yellow Light ($\lambda = 5770, 5790A^o$)

(Data derived from TABLE 3)

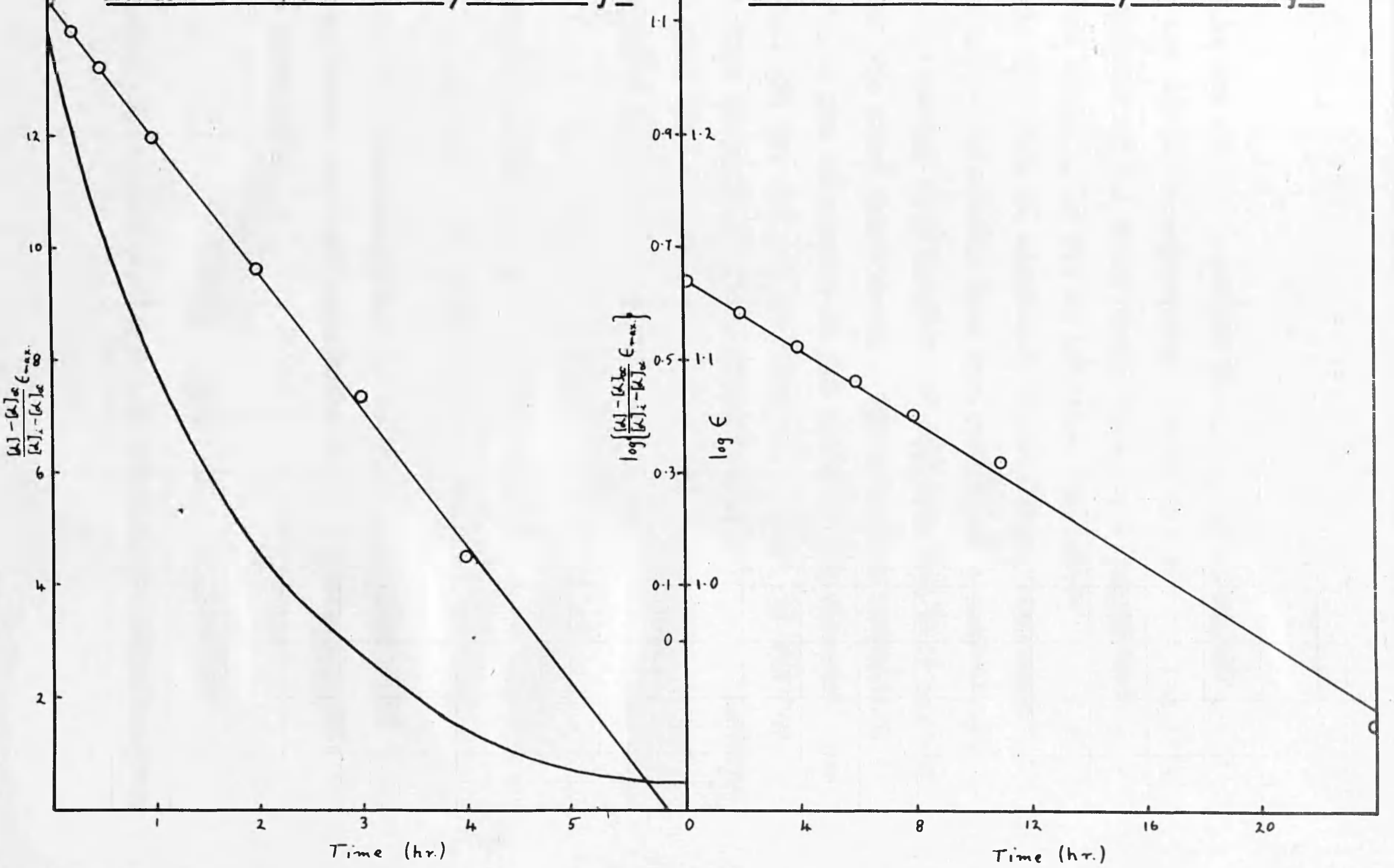
$[\alpha]_i = +947^0$; $[\alpha]_\infty = -508^0$

$\{[\alpha] - [\alpha]_\infty\} = x$; $\{[\alpha]_i - [\alpha]_\infty\} = y$

$\epsilon_{max.} = 13.80$ at $\lambda = 6625A^0$

Time (hr.)	x^0	$\frac{x}{y}\epsilon_{max.}$	$\log\{\frac{x}{y}\epsilon_{max}\}$	ϵ	$\epsilon - \frac{x}{y}\epsilon_{max}$	$\epsilon_{max.} - \epsilon$
0	1455	13.80	1.140	13.80	0	0
0.25	1312	12.07	1.082	13.38	1.31	0.42
0.50	1160	10.48	1.020	13.13	2.65	0.67
1.00	882	7.85	0.895	12.87	5.02	0.93
2.00	526	4.58	0.661	12.71	8.13	1.09
3.00	316	2.72	0.435	12.57	9.85	1.23
4.00	167	1.42	0.152	12.40	10.98	1.40
6.00	53	0.44	-0.357	12.30	11.86	1.50
15.00	0	-	-	10.17	10.17	3.63
20.00	-	-	-	9.20	9.20	4.60
27.00	-	-	-	7.79	7.79	6.01

GRAPH IV



(i)

Kinetics of the Photomutarotation of (−)-2-Chloro-2-nitrosocamphane on Irradiation with Mercury Yellow Light

(ii)

Kinetics of the Photolysis of (+)-2-Chloro-2-nitrosocamphane on Irradiation with Mercury Yellow Light constitute the second component reaction, since the observed results are due to decomposition of both species 'A' and 'B'. The photolysis of 'A' under these conditions is, no doubt, small, but there is as yet no evidence from which it may be concluded that this is completely negligible. The required information is obtainable from irradiation of (+)-2-chloro-2-nitrosocamphane, i.e. species 'B' and this has been carried out under the usual conditions. The molecular extinction coefficients are calculated on the basis of the original concentration and are set out in Table 11. Log ϵ is plotted against time in Graph IV (ii), illustrating a linear relationship so that this reaction also obeys the First Order law. The constants are derived in the usual way.

$$\tan\theta = 0.0087$$

$$\text{from equation (10) } k_2 = 2.303 \times 0.0087 = \underline{0.02 \text{ hr.}^{-1}}$$

$$\text{equation (13) gives } (t_2)_{\frac{1}{2}} = \frac{0.693}{k_2} = \underline{34.3 \text{ hr.}}$$

It is seen that photomutarotation is very much more rapid than photolysis under the same experimental conditions, the relative rate is given by

$$\frac{k_1}{k_2} = \frac{0.56}{0.02} = \underline{28.0}$$

Having shown that photolysis of species 'B' obeys kinetics

TABLE 11

Kinetics of the Photolysis of (+)-2-Chloro-2-nitrosocamphane on Irradiation with Mercury Yellow Light (λ = 5770, 5790A°)

c = 1.150%
= 0.0571M

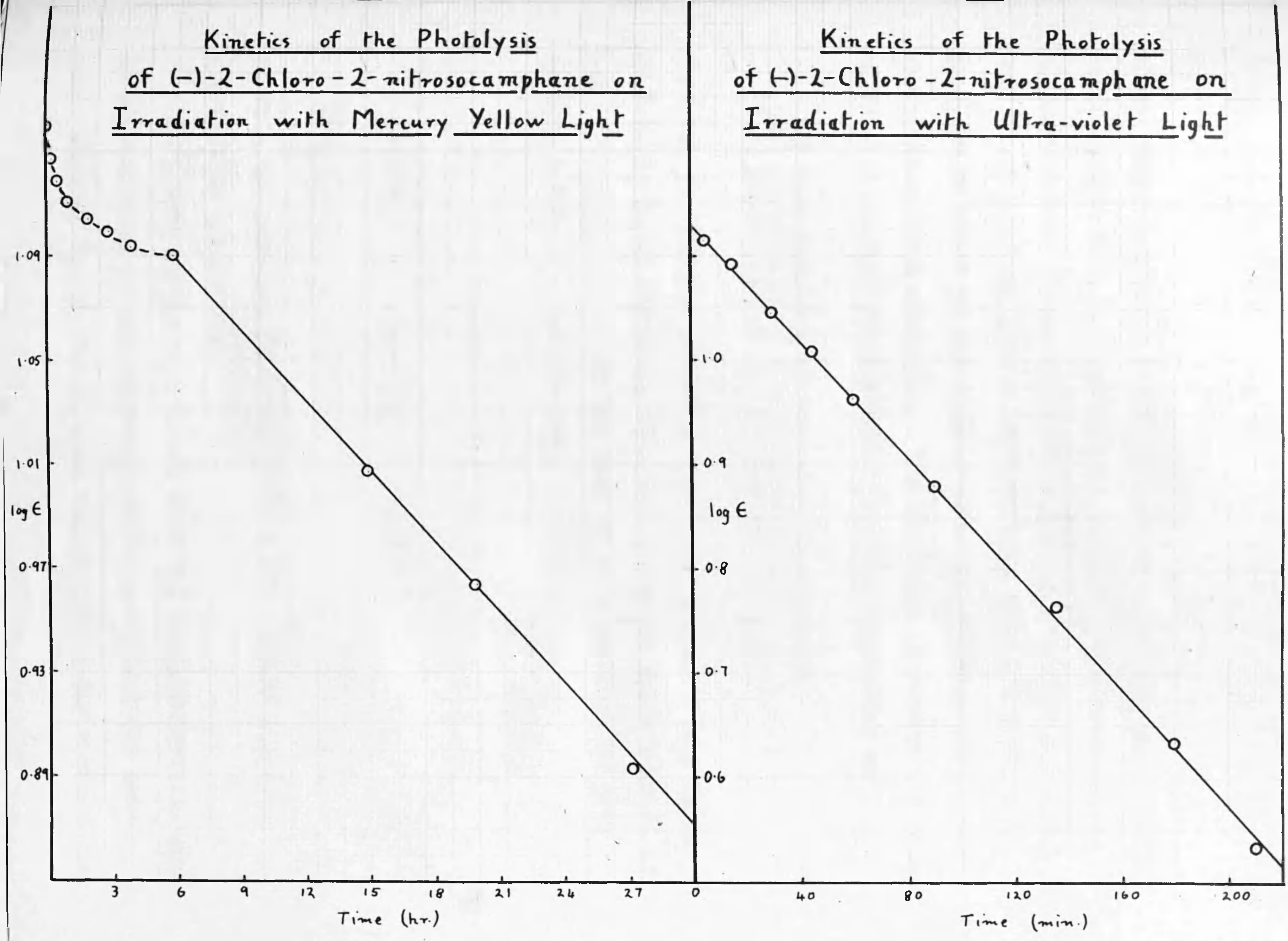
Solvent : alcohol (oxygen free)
l = 10 mm. (sealed cell)

$[\alpha]_i - [\alpha]_\infty$ = -508° at λ = 6025A°

Absorption Measurements at λ = 6625A°

Time (hr.)	$\log \frac{I_0}{I}$	ϵ	$\log \epsilon$
0	0.783	13.72	1.137
2	0.752	13.18	1.120
4	0.728	12.76	1.106
6	0.702	12.30	1.090
8	0.678	11.89	1.075
11	0.645	11.30	1.053
24.5	0.495	8.67	0.938

GRAPH V



(i) Kinetics of the Photolysis of (−)-2-Chloro-2-nitrosocamphane on Irradiation with Mercury Yellow Light

(ii) Kinetics of the Photolysis of (−)-2-Chloro-2-nitrosocamphane on Irradiation with Ultra-violet Light of the First Order, it is of interest to note that the plot of log ϵ against time during the irradiation of (-)-2-chloro-2-nitrosocamphane (Table 3) initially gives a complex curve but this later resolves into a straight line (Graph V (i)), the gradient of which is the same as that representing photolysis of the rearranged molecule. The inflexion indicates the time at which a complex photochemical reaction consisting of

(i) rearrangement of the original molecule,
(ii) photolysis of the original molecule,
(iii) photolysis of the rearranged molecule

resolves to a simple process, viz. (iii) alone. This value of 6.3 hr. is in agreement with that given by the intersect of $\log\left\{\frac{[\alpha] - [\alpha]_\infty}{[\alpha]_i - [\alpha]_\infty}\,\epsilon_{max.}\right\}$ on the axis of time in Graph IV (i). At this point, t = 6.0 hr. and

$$\log\left\{\frac{[\alpha] - [\alpha]_\infty}{[\alpha]_i - [\alpha]_\infty}\,\epsilon_{max.}\right\} = 0$$

giving $$\frac{[\alpha] - [\alpha]_\infty}{[\alpha]_i - [\alpha]_\infty} = 1$$

now $$\epsilon_i - \epsilon_\infty = 13{\cdot}80$$

so that the reaction is $\frac{(13.80 - 1)}{13.80} \times 100 = 92.8\%$ complete under these conditions.

As a test of the hypothesis that the overall reaction may be approximated to two rate-determining processes the concentration of C_A, C_B and C_C were calculated at the various times in terms of molecular extinction coefficients (Table 10). Consideration shows that these are given by

$$C_A = \frac{[\alpha] - [\alpha]_\infty}{[\alpha]_i - [\alpha]_\infty} \epsilon_{max.}$$

$$C_B = \epsilon - \frac{[\alpha] - [\alpha]_\infty}{[\alpha]_i - [\alpha]_\infty} \epsilon_{max.}$$

$$C_C = \epsilon_{max.} - \epsilon$$

The values have been plotted in Graph VI which exhibits the general form illustrated in Figure 3 for consecutive reactions, i.e. the concentration of 'A' falls continuously, that of 'C' increases continuously, but the concentration of 'B' first rises to a maximum and then falls with time. The fact that the curves of 'A' and 'B' intersect in this case is a consequence of the appreciably different rate constants for the two processes.

More precise confirmation is given in Table 12 (a), where the observed values of C_A, C_B and C_C at a number of arbitrary times are compared with those calculated from equations (16), (17) and (18) using the values of k_1 and k_2 previously obtained. All of these are in remarkably good agreement in view of the number of approximations introduced, substantiating the general validity of the mechanism postulated for the total photochemical reaction.

GRAPH VI

Consecutive Reaction Kinetics on Irradiation of (–)-2-Chloro-2-nitrosocamphane with Mercury Yellow Light

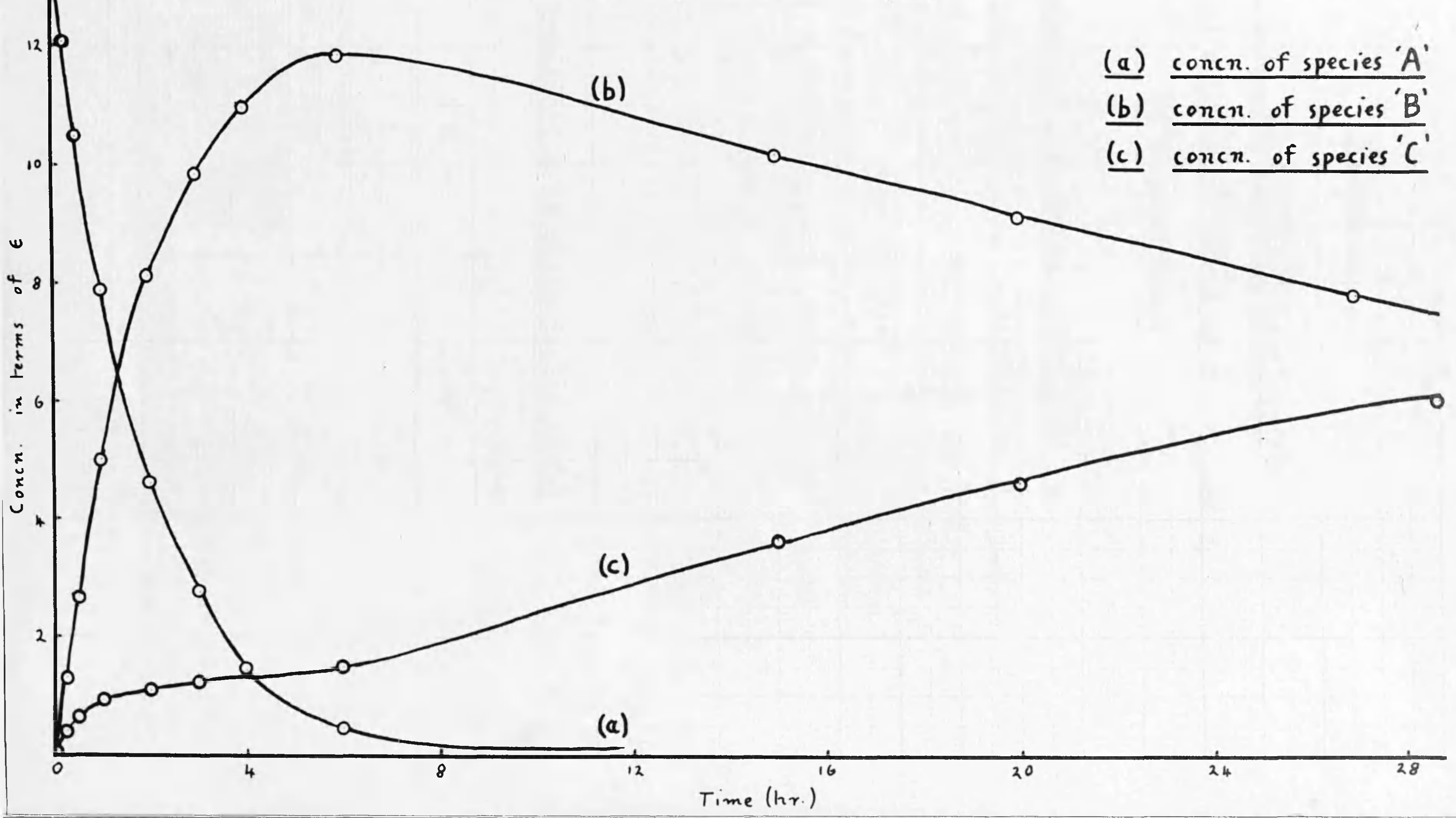


TABLE 12

Consecutive Reaction Kinetics
Observed and Calculated Values of C_A, C_B and C_C
at various Times

(a) Irradiation by Mercury Yellow Light

	C_A		C_B		C_C	
Time (hr.)	obs.	calc.	obs.	calc.	obs.	calc
2	4.58	4.51	8.13	9.05	1.23	1.28
3	-	-	-	-	-	-
4	1.42	1.47	10.98	11.65	-	-
6	0.33	0.44	-	-	-	-
10	-	-	11.20	11.64	2.35	2.08
15	-	-	-	-	3.63	3.18

(b) Irradiation by Ultra-violet Light

	C_A		C_C	
Time (min.)	obs.	calc.	obs.	calc.
45	-	-	3.34	0.50
60	10.90	11.20	-	-
90	-	-	5.97	1.56
135	8.56	8.75	-	-
180	7.38	7.60	-	-
210	-	-	10.13	4.83

Kinetics of the Photochemical Processes occurring on Irradiation with Ultra-violet Light

Irradiation of (-)-2-chloro-2-nitrosocamphane with ultra-violet light gives results which differ from those obtained with visible light in that photomutarotation is never complete and photolysis occurs much more rapidly. It is of interest, therefore, to extend the kinetic methods to this process to discover if any information can be gained concerning the mechanism operative under these conditions.

The photomutarotation of species 'A' to 'B' has been calculated from the experimental data recorded in Table 7. This is expressed in Table 13 in terms of molecular extinction coefficients as before. The logarithm of this quantity against time is plotted in Graph VII (i) illustrating a linear relationship from the slope of which the characteristic constants may be derived.

$$\tan\theta = 0.084$$

from equation (10) $k_1 = 2.303 \times 0.084 = \underline{0.19\ \text{hr.}^{-1}}$

equation (13) gives $(t_1)_{\frac{1}{2}} = \frac{0.693}{k_1} = \underline{3.59\ \text{hr.}}$

Irradiation of (+)-2-chloro-2-nitrosocamphane under conditions identical with the above gives the rate of photolysis

TABLE 13

Kinetics of the Photomutarotation of (-)-2-Chloro-2-nitrosocamphane on Irradiation with Ultra-violet Light

(Data derived from TABLE 7)

$[\alpha]_i = +953^\circ$; $[\alpha]_\infty = -508^\circ$ (assumed)

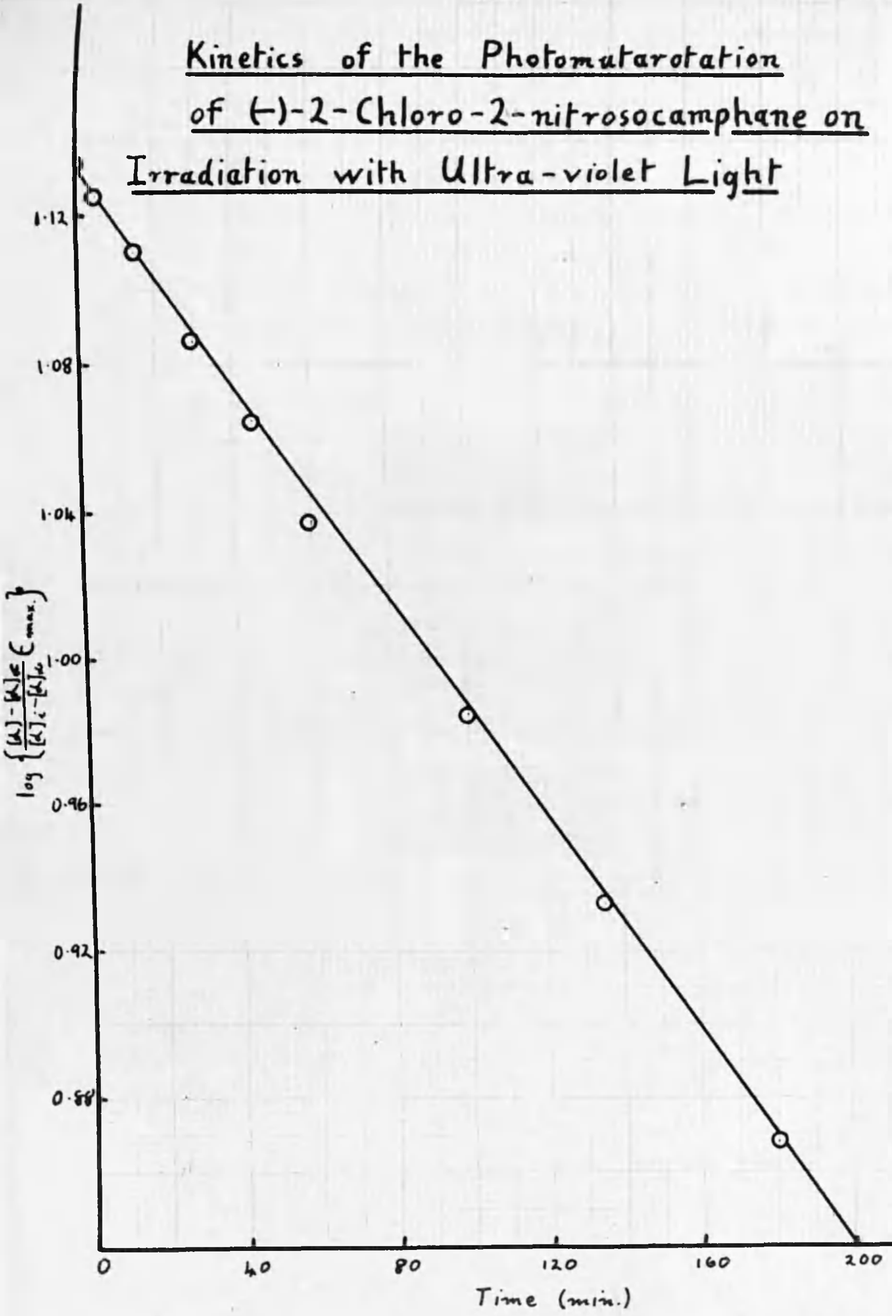
$[\alpha] - [\alpha]_\infty = x$; $[\alpha]_i - [\alpha]_\infty = y$

$\epsilon_{max.} = 13.55$ at $\lambda = 6625 A^\circ$

Time (min.)	x°	$\frac{x}{y}\epsilon_{max.}$	$\log\left\{\frac{x}{y}\epsilon_{max.}\right\}$	$\epsilon_{max.} - \epsilon$
0	1461	13.55	1.134	0
5	1434	13.34	1.125	0.52
15	1385	12.89	1.110	1.15
30	1309	12.18	1.086	2.45
45	1244	11.60	1.065	3.34
60	1173	10.90	1.037	4.37
90	1039	9.65	0.985	5.97
135	918	8.56	0.933	7.78
180	793	7.38	0.868	9.27
210	739	6.88	0.838	10.13

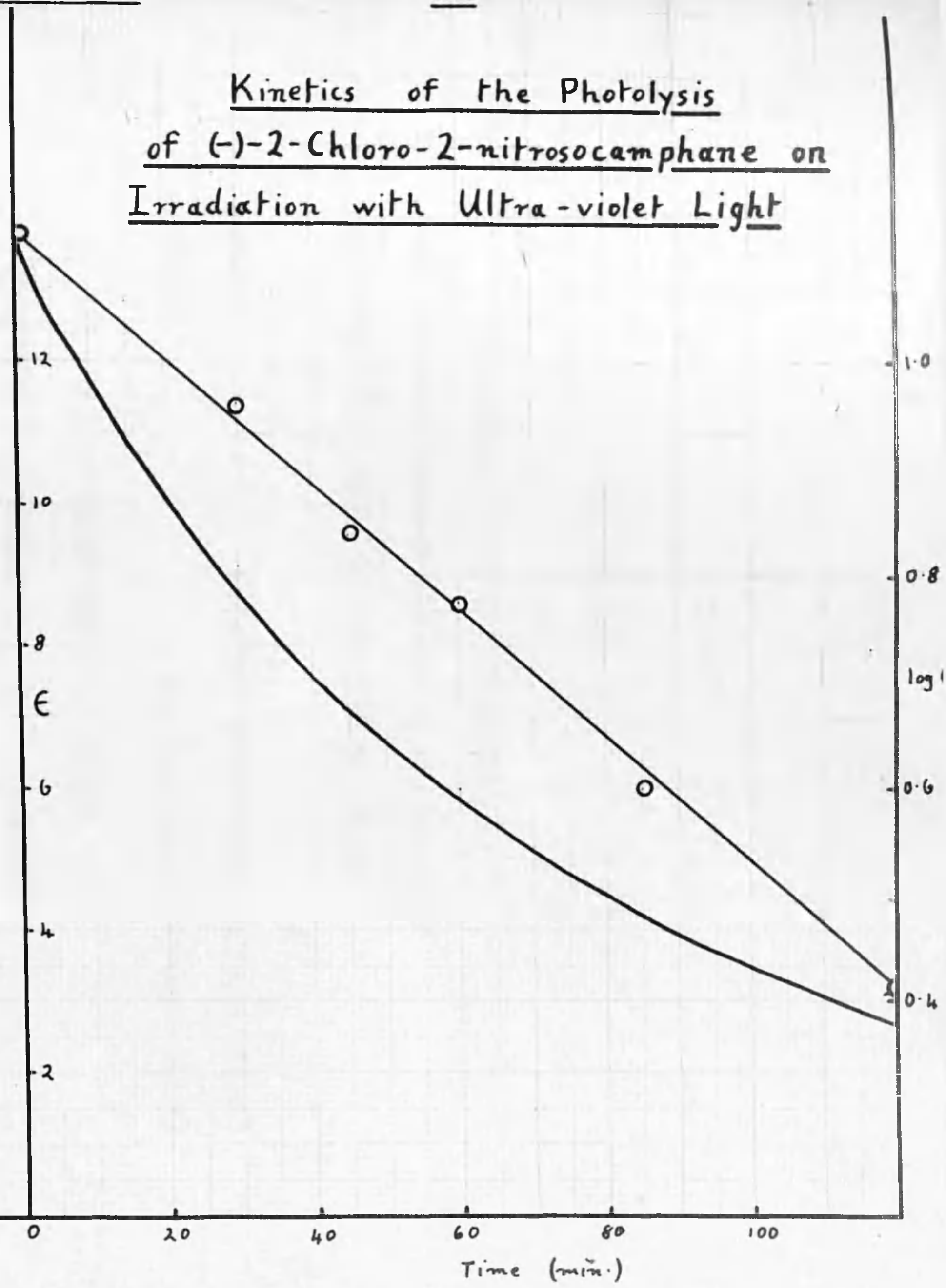
GRAPH VII

(i)



Kinetics of the Photomutarotation of (−)-2-Chloro-2-nitrosocamphane on Irradiation with Ultra-violet Light

(ii)



Kinetics of the Photolysis of (−)-2-Chloro-2-nitrosocamphane on Irradiation with Ultra-violet Light

TABLE 14

Kinetics of the Photolysis of (+)-2-Chloro-2-nitrosocamphane on Irradiation with Ultra-violet Light

c = 1.241% Solvent : alcohol (oxygen free)

= 0.0617M ℓ = 10 mm. (sealed cell)

$[\alpha]_i = [\alpha]_\infty = -508^\circ$ at λ = 6025A°

Absorption Measurements at λ = 6625A°

Time (min.)	$\log \frac{I_0}{I}$	ϵ	$\log \epsilon$
0	0.847	13.75	1.138
30	0.562	9.12	0.960
45	0.432	6.86	0.836
60	0.370	6.01	0.779
90	0.243	3.95	0.597
120	0.163	2.64	0.421
150	0.106	1.72	0.236

of the rearranged product. The data from such an experiment are recorded in Table 14 and illustrated in Graph VII (ii). Again, the plot of log ϵ against time is a straight line indicating First Order kinetics so that the usual constants may be calculated

$$\tan\theta = 0.360$$

from equation (10) $k_2 = 2.303 \times 0.360 = \underline{0.83\ \text{hr.}^{-1}}$

equation (13) gives $(t_2)_{\frac{1}{2}} = \dfrac{0.693}{k_2} = \underline{0.84\ \text{hr.}}$

The rate of photomutarotation relative to photolysis is given by the ratio

$$\frac{k_1}{k_2} = \frac{0.19}{0.83} = \underline{0.23}$$

which is very much smaller than that observed in the visible irradiation. This results in a different mechanism for the overall reaction in the present case, which is made evident from the following considerations.

It was argued that if the processes occurring on ultra-violet irradiation of (-)-2-chloro-2-nitrosocamphane were essentially photomutarotation followed by photolysis of the rearranged product, the plot of log ϵ against time should yield a curve of the same form as that obtained from the visible irradiation, i.e. complex initially and later resolving into a straight line. The results from Table 7 are shown in Graph

V (ii) where it is evident that a linear relationship exists between these quantities at all times. This is attributed to the relatively minor role played by component (i) (p 56) so that the overall reaction appears to be photolysis of both species, and simple kinetics result.

Further, in attempting to apply the calculations of consecutive reactions to the foregoing data, it was observed that although C_A and C_c could be derived at various times in the usual way (Table 7), attempts to obtain C_B as the difference

$$C_B = C_{(A+B)} - C_A = \left\{ \epsilon - \frac{[\alpha] - [\alpha]_\infty}{[\alpha]_i - [\alpha]_\infty} \epsilon_{max.} \right\}$$

led to negative and therefore meaningless values for this quantity. Table 12 (b) compares observed values of C_A and C_c with those calculated from equations (16) and (17) using the velocity constants of the reactions previously determined. It is worthy of note that the values of C_A compare reasonably well. This follows from the dependence of equation (16) on k_1 alone confirming that the method used in deriving this rate constant is strictly accurate, while the calculated values of C_c, dependent on both k_1 and k_2 are in no way comparable with the observed data.

It must be concluded that the results for the reaction sequence,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

obtained from independent experimental studies of the two part-processes are not in agreement with the results observed during the irradiation of (-)-2-chloro-2-nitrosocamphane with ultra-violet light. The third component reaction cannot therefore be neglected, and the total process

$$\begin{tikzcd} & B \arrow[dr, "k_2"] & \\ A \arrow[ur, "k_1"] \arrow[rr, "k_3"'] & & C \end{tikzcd}$$

must be considered.

The investigation has been successful in illustrating the complexity of the reaction mechanism under these conditions, although a precise analysis has not been possible in this case since there is no available method by which k_3 may be evaluated.

PART II

PHOTOISOMERISATION

of

(i) (+)-2-Chloro-2-nitrosopinane

(ii) (-)-2-Chloro-2-nitrosocarane

(iii) (+)-2-Chloro-2-nitroso-p-menthane

(iv) (-)-3-Chloro-3-nitroso-p-menthane

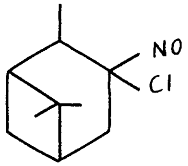
(v) ± -2-Chloro-2-nitroso-1-methylcyclohexane

(i) PHOTOISOMERISATION OF (+)-2-CHLORO-2-NITROSOPINANE

General Considerations

Attribution of the photoisomerisation of (-)-2-chloronitrosocamphane to inversion of the asymmetric chloro-nitroso centre, C_2, requires a difference in environmental influence of the remainder of the molecular structure on the normal and photo-excited states of the chromophores. The effect is no doubt due to the proximity of either the 10-methyl group or the 1:4 gem-dimethyl bridge since these give rise to the only influences near enough to affect the stereochemistry of the centre concerned.

An obvious extention of the investigation was therefore the study of a series of derivatives in which the molecular skeleton had suffered varying degrees of modification, so that the effect on the photochemical processes might be determined. The present work is concerned with the first member.

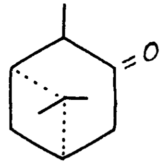


2-chloro-2-nitrosopinane

In this case the bridge has been moved to link C_4 and C_6, so that although the gem-dimethyl groups occupy essentially the same position in space with relation to the functional groups, the locking effect has been removed from the stereochemistry of C_1.

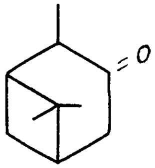
(+)-2-Chloro-2-nitrosopinane

It was at first considered an unfortunate complication that the structure of pinocamphone requires the existence of two isomeric forms



pinocamphone

$\alpha_D = +23^\circ\ 57'$



isopinocamphone

$\alpha_D = +11^\circ\ 0'$

so that no interpretation of the results would be possible unless the ketone were initially isolated as a stereochemically uniform material; a requirement which has been met in the present case.

It has been reported that pinocamphone and isopinocamphone may be prepared by oxidation of the corresponding pinocampheols, but isolation of the isomeric forms of the alcohol (of which there are four) is in itself a very laborious procedure (Schmidt, 1944). Although l-isopinocampheol occurs in oil of Hyssop, the fraction is too minute to provide a profitable source of starting material. A more satisfactory procedure has been found in application of the method used by Aschan (1933) for the separation of the closely related α and β santenones, i.e. fractional crystallisation of the semicarbazones and subsequent hydrolysis to yield the isomeric ketones.

The crude pinocamphone was obtained by fractionation of Hyssop oil in which it occurs to about 50% and the semicarbazone of this submitted to crystallisation from methanol to constant m.p. 228 - 230°, corresponding to that of the normal form (Aschan, loc. cit.). Mild hydrolysis by steam distillation with oxalic acid yielded the required material which gave an oxime but no oxime hydrochloride under the usual conditions. The blue oil resulting from chlorination of this oxime distilled only under high vacuum to give (+)-2-chloro-2-nitrosopinane with the properties

$[\alpha]_{max.} = +390^{\circ}$ at $\lambda = 6600A$

$\epsilon_{max} = 19.12$ at $\lambda = 6350A$

b.p. 47° at 0.4 mm.

Found: Cl, 17.5%; C H NOCl requires Cl, 17.6%

The rotatory dispersion is set out in Table 15 and shown in Graph VIII (i)(a) where it is seen that the Cotton effect typical of these blue compounds results. This has the characteristics

$[\alpha]_{max.} = +390^{\circ}$ at 6600A Reversal 6700A $[\alpha]_{min} = -390^{\circ}$ at 5700A°

TABLE 15

Rotatory Dispersion of (+)-2-Chloro-2-nitrosopinane

$c = 1.00\%$ Solvent : alcohol (oxygen free)

$l = 10$ mm. $t = 18^\circ$

$10^{-1}\lambda$ (A°)	α°	$[\alpha]^\circ$	$10^{-1}\lambda$ (A°)	α°	$[\alpha]^\circ$
540	−0.13	−310	620	−0.17	−170
550	−0.33	−330	630	−0.02	−20
560	−0.36	−360	640	+0.19	+190
570	−0.39	−390	650	+0.36	+360
580	−0.39	−390	660	+0.39	+390
590	−0.37	−370	670	+0.37	+370
600	−0.33	−330	680	+0.32	+320
610	−0.28	−280	690	+0.25	+250
			700	+0.21	+210

TABLE 16

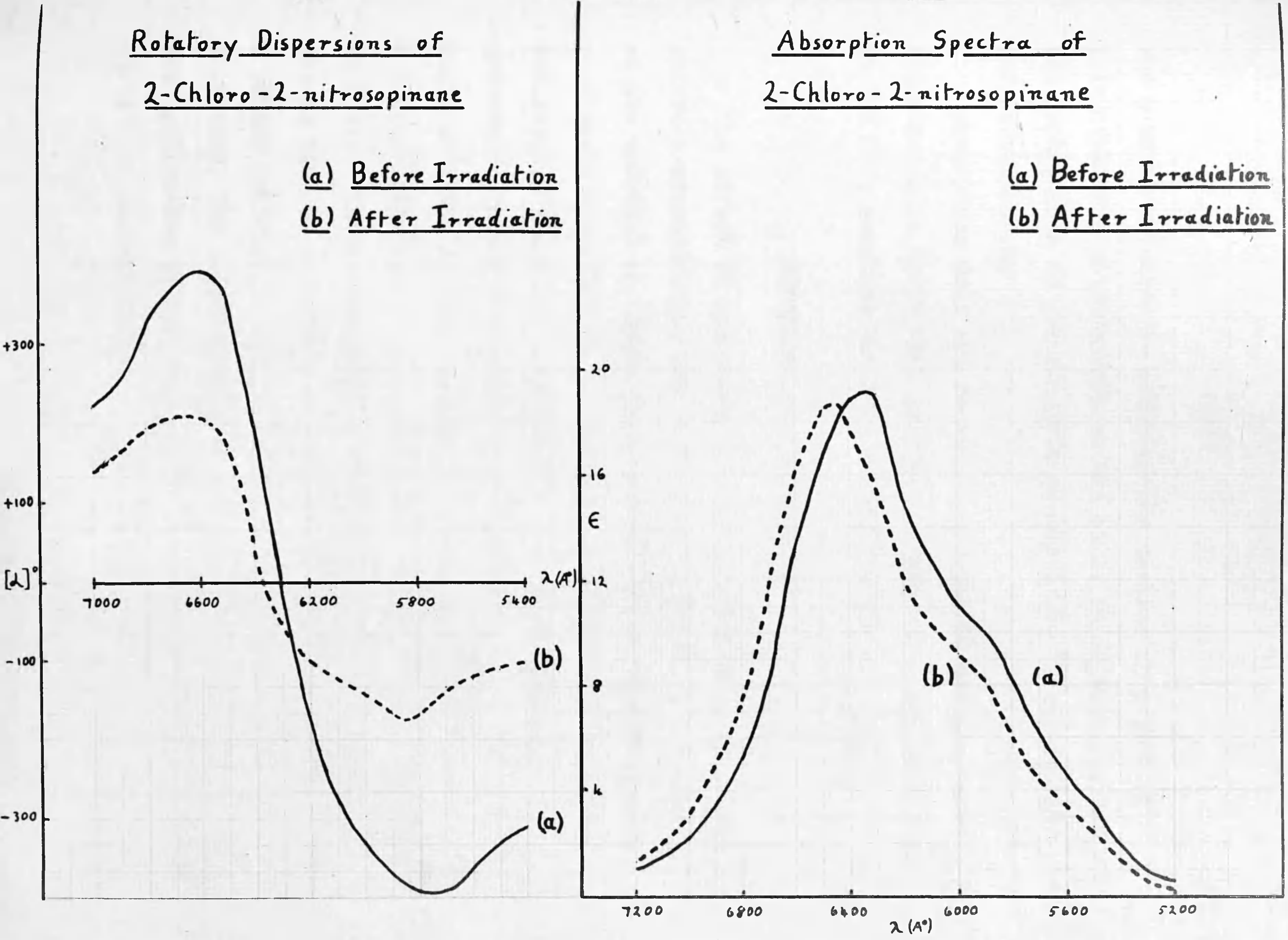
Absorption Spectrum of (+)-2-Chloro-2-nitrosopinane

c = 1.00% Solvent : alcohol (oxygen free)

= 0.0496M ℓ = 10 mm.

$10^{-1}\lambda$ (A°)	$\log \frac{I_0}{I}$	ϵ	$10^{-1}\lambda$ (A°)	$\log \frac{I_0}{I}$	ϵ
720	.052	1.05	620	.736	14.84
710	.074	1.49	610	.637	12.84
700	.112	2.25	600	.549	11.06
690	.174	3.50	590	.498	10.04
680	.265	5.34	580	.412	8.30
670	.404	8.11	570	.307	6.18
660	.648	13.06	560	.226	4.55
650	.826	16.65	550	.175	3.52
640	.934	18.83	530	.096	1.94
630	.945	19.03	510	.049	0.98

GRAPH VIII



(i) Rotatory Dispersions of 2-Chloro-2-nitrosopinane

(a) Before Irradiation
(b) After Irradiation

(ii) Absorption Spectra of 2-Chloro-2-nitrosopinane

(a) Before Irradiation
(b) After Irradiation

The maximum rotation is considerably smaller than that of (-)-2-chloro-2-nitrosocamphane but still quite suitable for the application of polarimetric measurements to be used in the present work.

Absorption data are recorded in Table 16 and the curve illustrated in Graph VIII (ii)(a). This shows the same form as the blue camphane but with a higher value of ϵ_{max}.

Behaviour on Irradiation

The effect of monochromatic visible radiation on (+)-2-chloro-2-nitrosopinane was determined by exposing a solution of the material in oxygen free alcohol on the optical system previously described (p 21) and the process of the reaction followed by the usual polarimetric and spectrophotometric methods. Data for a number of time-intervals are set out in Table 17 where it will be seen that the calculated specific rotation falls from $[\alpha]_{5800} = -390^{\circ}$ to a limiting value of -167° in 7 hr. The primary fall in rotation is again evident, giving rise to a product with the same sign of rotation as the original material. The rotatory dispersion was determined at this time, the concentration of blue compound being given by the application of the usual formula to the appropriate values at 't' = 7 in Table 17.

TABLE 17

Irradiation of (+)-2-Chloro-2-nitrosopinane
with
Mercury Yellow Light ($\lambda = 5770, 5790A^{o}$)

c = 1.00% Solvent : alcohol (oxygen free)

= 0.0496M ℓ = 10 mm. (sealed cell)

Absorption Measurements at $\lambda = 6400A^{o}$

Rotation Measurements at $\lambda = 5800A^{o}$

$$-\{[\alpha] - [\alpha]_{\infty}\} = x$$

Time (hr.)	α°	$[\alpha]^{\circ}_{obs.}$	$[\alpha]^{\circ}_{calc.}$	x	$\log x$	$\log \frac{I_0}{I}$	ϵ	$\log \epsilon$
0	-0.39	-390	-390	225	2.352	.912	18.41	1.265
0.5	-0.32	-320	-320	155	2.190	.912	18.41	1.265
1.0	-0.28	-280	-281	116	2.065	.910	18.37	1.264
2.0	-0.22	-220	-221	56	1.748	.908	18.32	1.263
4.0	-0.18	-180	-182	17	1.230	.902	18.20	1.260
7.0	-0.16	-160	-165	0	-	.885	17.87	1.252
17.5	-0.16	-160	-167	-	-	.845	17.04	1.231
29.0	-0.15	-150	-169	-	-	.795	16.03	1.205
44.0	-0.14	-140	-167	-	-	.740	14.92	1.174

$$c = c_o \frac{k}{k_o} = 1.00 \frac{0.885}{0.912} = 0.970\%$$

This has been used to calculate specific rotations which are given in Table 18 and illustrated in Graph VIII (i)(b) showing a Cotton effect with

$[\alpha]_{max.} = +206^\circ$ at 6700A° Reversal 6400A° $[\alpha]_{min.} = -180^\circ$ at 5550A°

A bathochromic displacement at almost 100A° has taken place from the original curve and this has determined the wave-length chosen for polarimetric readings as the mean of the two minima, i.e. $\lambda = 5800$A°.

The absorption spectrum was examined at the same time and the results, based on the original concentration, recorded in Table 19. Very little photolysis has occurred during this period: ϵ_{6400} has fallen from 18.41 to 17.87, so that it is hardly necessary to calculate the true values from the estimated concentration in order to compare this curve with the original. The two are shown in Graph VIII (ii) where it is apparent that a shift of about 100A° to longer wave-lengths has again resulted, thus fixing the isosbestic wave-length for spectrophotometric measurements at $\lambda = 6400$A°. The shift is of considerably greater magnitude than that observed for 2-chloro-2-nitrosocamphane but no particular significance is attributed to this as the energy changes corresponding to such displacements in this spectral

TABLE 18

Rotatory Dispersion of 2-Chloro-2-nitrosopinane
after Irradiation with
Mercury Yellow Light (λ = 5770, 5790A°)
(calculated)

c = 0.970%
Solvent : alcohol (oxygen free)

l = 10 mm.
t = 18.5°

$10^{-1}\lambda(A^{\circ})$	α°	$[\alpha]^{\circ}$	$10^{-1}\lambda(A^{\circ})$	α°	$[\alpha]^{\circ}$
550	-0.11	-114	620	-0.10	-103
560	-0.12	-124	630	-0.05	-52
570	-0.13	-134	640	+0.05	+52
580	-0.16	-167	650	+0.16	+167
590	-0.16	-167	660	+0.20	+206
600	-0.14	-144	670	+0.20	+206
610	-0.12	-124	680	+0.19	+195
			690	+0.16	+167

TABLE 19

Absorption Spectrum of 2-Chloro-2-nitrosopinane
after Irradiation with
Mercury Yellow Light ($\lambda = 5770, 5790A^{o}$)
(observed)

c = 1.00%　　　　Solvent : alcohol (oxygen free)

= 0.0496M　　　　l = 10 mm.

$10^{-1}\lambda\ (A^{\circ})$	$\log \frac{I_o}{I}$	ϵ	$10^{-1}\lambda\ (A^{\circ})$	$\log \frac{I_o}{I}$	ϵ
720	.066	1.33	620	.576	11.61
710	.100	2.01	610	.507	10.22
700	.149	3.00	600	.454	9.15
690	.239	4.81	590	.402	8.10
680	.379	7.64	580	.297	5.98
670	.581	11.71	570	.215	4.33
660	.803	16.18	560	.166	3.34
650	.914	18.42	550	.131	2.64
640	.873	17.60	530	.065	1.31
630	.763	15.38	510	.028	0.56

region are of the order of only a few K cal/mole.

Further determination of both rotatory dispersion and absorption curves were made after completion of the irradiation at 44 hr. However, the calculated values showed no further change from those previously observed, so that the reaction must have attained completion within the initial period of 7 hr.

Kinetic Studies

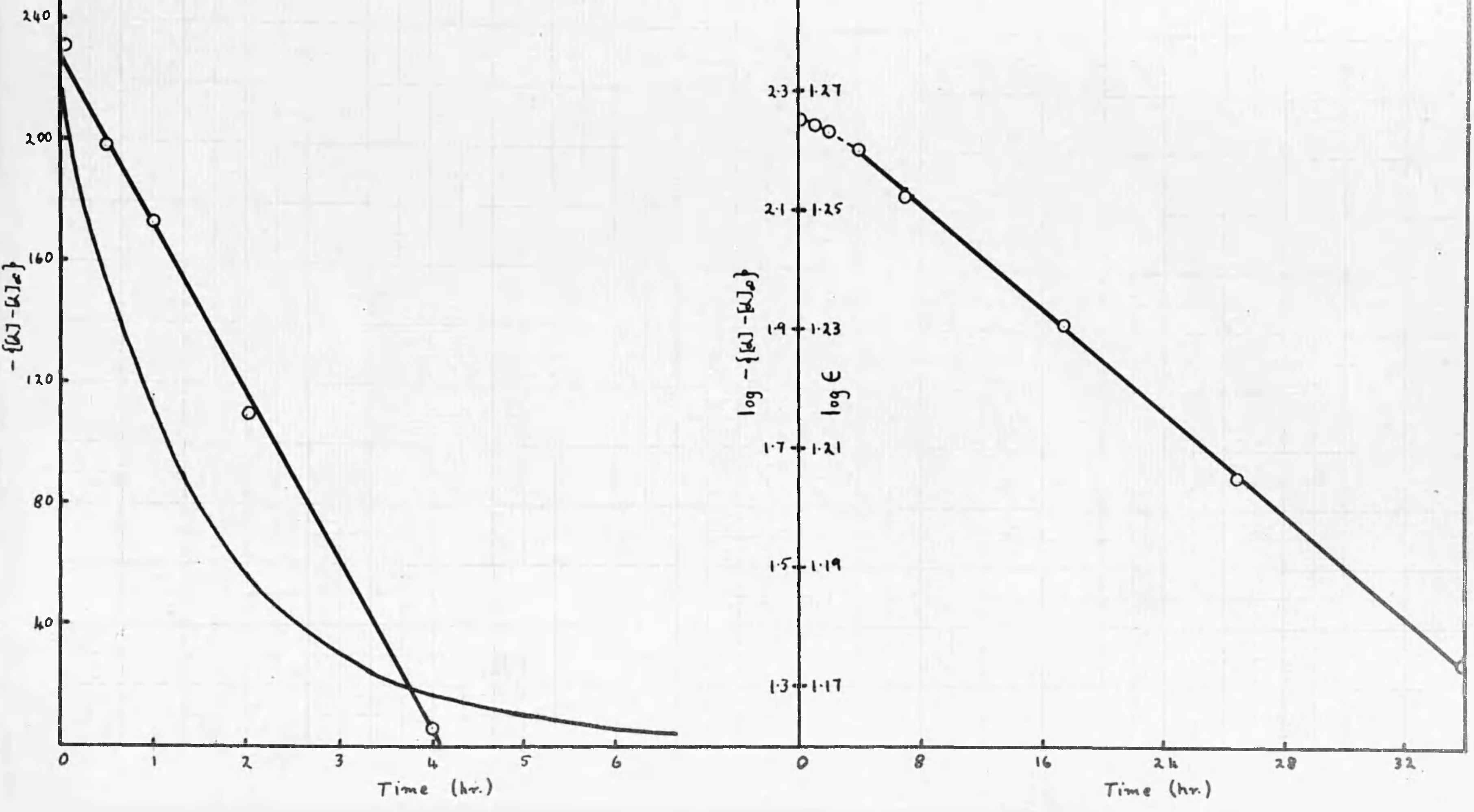
It is of interest to apply the kinetic methods previously used to the present investigation. In this way a comparison of the rates of the component processes and their relative importance in determining the overall reaction mechanism may be studied.

The primary fall in rotation has been followed polarimetrically and the reaction velocity may be determined simply from the change in specific rotation. When $[\alpha]_i$, $[\alpha]$ and $[\alpha]_\infty$ have the usual significance, equation (9) may be written

$$\frac{k}{2\cdot 303} t + \log\left\{[\alpha] - [\alpha]_\infty\right\} - \log\left\{[\alpha]_i - [\alpha]_\infty\right\} = 0 \quad \ldots\ldots \text{(19)}$$

The appropriate data have been calculated and are included in Table 17, and since negative rotations have been used in the estimations, it is necessary to represent the decrease in this property as $-\left\{[\alpha] - [\alpha]_\infty\right\}$ to obtain a positive difference. The plot of the quantity and its logarithm against time are shown in Graph IX (i), where the latter is seen to be a linear

GRAPH IX



(i)

Kinetics of the Photoisomerisation of 2-Chloro-2-nitrosopinane

(ii)

Kinetics of the Photolysis of 2-Chloro-2-nitrosopinane relationship confirming kinetics of the First Order. The constants are calculated from the slope of the line

$$\tan\theta = 0.288$$

from equation (10) $k_1 = 2.303 \times 0.288 = \underline{0.66\ \text{hr.}^{-1}}$

equation (13) gives $(t_1)_{\frac{1}{2}} = \dfrac{0.693}{k_1} = \underline{1.05\ \text{hr.}}$

The kinetics of photolysis of both original and rearranged species is indicated by the fall in concentration of blue material during the reaction. This may conveniently be measured as the change in ϵ_{6400} recorded in Table 17. Log ϵ_{6400} is plotted against time in Graph IX (ii). Initially complex, this resolves to a straight line as the reaction proceeds, indicating simple kinetics for the photolysis of species 'B' after completion of the primary process. It is satisfactory to note that the inflexion of this curve occurs after about four hours, in excellent agreement with the time of 4.0 hr. given by the intersect of log $-\{[\alpha] - [\alpha]_\infty\}$ on the 't' axis. At this point

$$\log -\{[\alpha] - [\alpha]_\infty\} = 0$$

giving $$-\{[\alpha] - [\alpha]_\infty\} = 1$$

Now since $$-\{[\alpha]_i - [\alpha]_\infty\} = -\{-390^\circ + 167^\circ\} = 223^\circ$$

the reaction is $\dfrac{223 - 1}{223} \times 100 = 99.6\%$ complete at this time.

Kinetics of the photolysis of species 'B' are determined as First Order from the linear relationship of the latter part of Graph IX (ii). The usual constants may be derived from this

$$\tan\theta = 0.0021$$

from equation (10) $k_2 = 2.303 \times 0.0021 = \underline{0.005\ \text{hr.}^{-1}}$

equation (13) gives $(t_2)_{\frac{1}{2}} = \frac{0.693}{k_2} = \underline{144.6\ \text{hr.}}$

The rate of fall in rotation relative to photolysis is given by

$$\frac{k_1}{k_2} = \frac{0.66}{0.005} = 132.0$$

this unusually high value arising from the exceptional photochemical stability of the material and not from a rapid primary process. The velocity of fall in rotation is only slightly greater than that of (-)-2-chloro-2-nitrosocamphane under identical experimental conditions. This is given by the ratio of the appropriate velocity constants

$$\frac{0.66}{0.56} = 1.18$$

From the foregoing results it may be concluded that the mechanism of the total reaction

$$\begin{tikzcd}
 & B \arrow[dr, "k_2"] & \\
A \arrow[ur, "k_1"] \arrow[rr, "k_3"'] & & C
\end{tikzcd}$$

can be approximated to the first two stages in this case without introduction of appreciable error.

Conclusions

The results derived in the preceeding Sections bear a close analogy to those observed for (-)-2-chloro-2-nitrosocamphane under the same conditions. These may be enumerated.

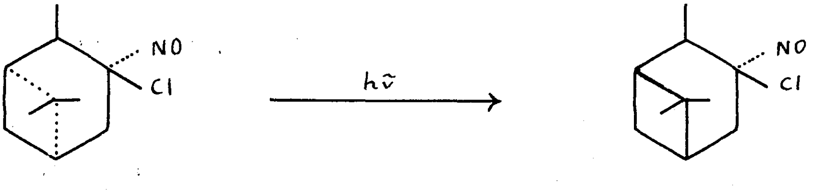
(i) Fall of specific rotation to a limiting value

(ii) Bathochromic displacement of the curves of both rotatory dispersion and absorption.

(iii) Consecutive component reactions obeying simple kinetics with similar overall mechanisms and comparable rates for the primary processes.

There is, however, a very important consideration in which they differ: non-inversion of the Cotton effect in the present case. It might be argued that this is attributable to incompletion of the initial process, i.e. attainment of a photo-stationary state, but the available evidence does not support this contention. There is no dark reaction of the material either before or after irradiation; a necessary criterion for such a state (p 7). Further, the value of $[\alpha]_{\infty} = -167^{\circ}$ yields simple results for the kinetic calculations which would not be expected if this were not at least very close to the final value. It seems reasonable to conclude that the primary reaction is either complete, or very nearly so, under these conditions.

Since non-inversion of the Cotton effect precludes inversion of the chloro-nitroso centre, an alternative reaction must be considered which will yield a product with optical properties very closely related to those of the original material. An isomerisation of the pinocamphone → isopinocamphone type presents itself as the obvious interpretation,



normal iso

i.e. rearrangement of the molecular skeleton to accommodate the excited chromophore endo to the bridge, which has been described by Shoppee (1952) and Barton (1953) as the more stable position. This offers the same relative result as inversion of the NO - Cl centre in the camphane skeleton where the position of the gem-dimethyl bridge is fixed. Since the former is expected to be a change of lower energy, it will be preferred in structures where this is possible.

It is worthy of mention that the parent ketones of this series show a similar relationship of optically rotatory power (p 63).

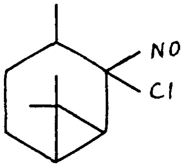
The above considerations, together with the sign of the original ketone, and that of the Cotton effect which gives the spacial arrangement of the groups on C_2, have enabled the configurations indicated to be attributed to the isomeric forms.

In accordance with the definitions for such photo-processes already given (p 17), it may be concluded that (+)-2-chloro-2-nitrosopinane undergoes photoisomerisation on irradiation with light lying within the region of visible absorption.

(ii) PHOTOISOMERISATION OF (-)-2-CHLORO-2-NITROSOCARANE

General Considerations

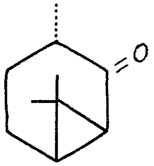
Investigation of the photo-processes occurring on irradiation of (+)-2-chloro-2-nitrosopinane introduced a new type of intramolecular rearrangement which proved to be a logical consequence of imposing conditions of photomutarotation on such a potentially labile structure. Continuing the skeletal modifications, the next member of the series necessitated a molecule in which the secondary ring system had been further condensed, leading to the obvious choice of 2-chloro-2-nitrosocarane.



In this, the mutual influence of the asymmetric centre C_2 and the gem-dimethyl bridge is but little changed from the previous case. It remained to discover if photoisomerisation by cis-trans skeletal rearrangement was general to such structures on exposure to light of suitable wave-length, and to determine, if possible, whether this change took place through displacement of the C_1 methyl group or of the cyclopropane ring, by the photoexcited chromophore.

(-)-2-Chloro-2-nitrosocarane

As only one form of carone is known to exist, the absence of cis-trans modifications greatly simplified preparation of this chloro-nitroso compound making it unnecessary to develop a technique for the separation of isomers.

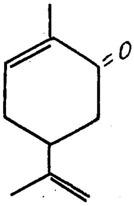


d-carone

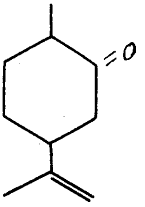
$\alpha_D = +145.6^{\circ}$

High optical rotatory power is characteristic of the structure, evident from the oxime which has $[\alpha]_D = +283^{\circ}$; six times the magnitude of the rotation of the oxime camphor. It appears, therefore, that the choice of the basic ring system was particularly suitable for the present study. An unusually high rotation may be predicted for the 'blue compound' leading to greater precision in the determination of the course of the reaction from measurements of optical rotation.

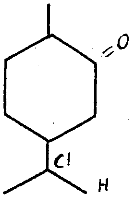
Carone itself has not been found to occur in nature but is obtained by ring closure of the readily available dihydrocarvone hydrochloride on boiling with alcoholic alkali. Commercial 'carvol' (d-carvone, 1) served as starting material, and reduction of the double bond conjugated with the carbonyl group was effected on careful treatment with zinc dust in alcoholic alkali according to the method of Wallach (1894) yielding dihydrocarvone (II). This readily adds hydrogen chloride to give the required intermediate (III).



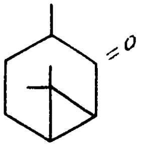
I



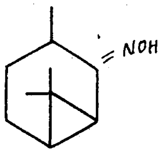
II



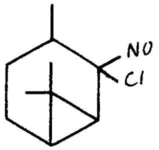
III



IV



V



VI

The ketone (IV) boils at 210° with partial isomerisation to carvenone (Baeyer, 1894) but distills under reduced pressure to give a colourless, mobile oil yielding an oxime but no oxime hydrochloride under the usual conditions. Chlorination in dry ether gives (-)-2-chloro-2-nitrosocarane as a viscous blue oil which distills under high vacuum.

$$[\alpha]_{max.} = +1800^{\circ} \text{ at } \lambda = 5900A^{\circ}$$

$$\epsilon_{max.} = 16.42 \text{ at } \lambda = 6675A^{\circ}$$

b.p. 56-57° at 0.25 mm.

Found Cl, 17.7%; $C_{10}H_{16}NOCl$ requires Cl, 17.6%

The maximum rotation, as anticipated, is remarkably high, almost double that of the previously unsurpassed (-)-2-chloro-2-nitrosocamphane. The complete rotatory dispersion is recorded

TABLE 20

Rotatory Dispersion of (-)-2-Chloro-2-nitrosocarane

$c = 0.676\%$ Solvent : alcohol (oxygen free)

$l = 10$ mm. $t = 18^\circ$

$10^{-1}\lambda$ (A°)	α°	$[\alpha]^\circ$	$10^{-1}\lambda$ (A°)	α°	$[\alpha]^\circ$
550	+0.92	+1361	640	+1.13	+1671
560	+0.96	+1420	650	+0.88	+1302
570	+1.01	+1494	660	+0.18	+266
580	+1.14	+1686	670	-0.60	-888
590	+1.21	+1790	680	-1.05	-1553
600	+1.19	+1760	690	-1.08	-1598
610	+1.10	+1627	700	-1.00	-1479
620	+1.05	+1553	710	-0.93	-1375
630	+1.14	+1686	720	-0.89	-1317

TABLE 21

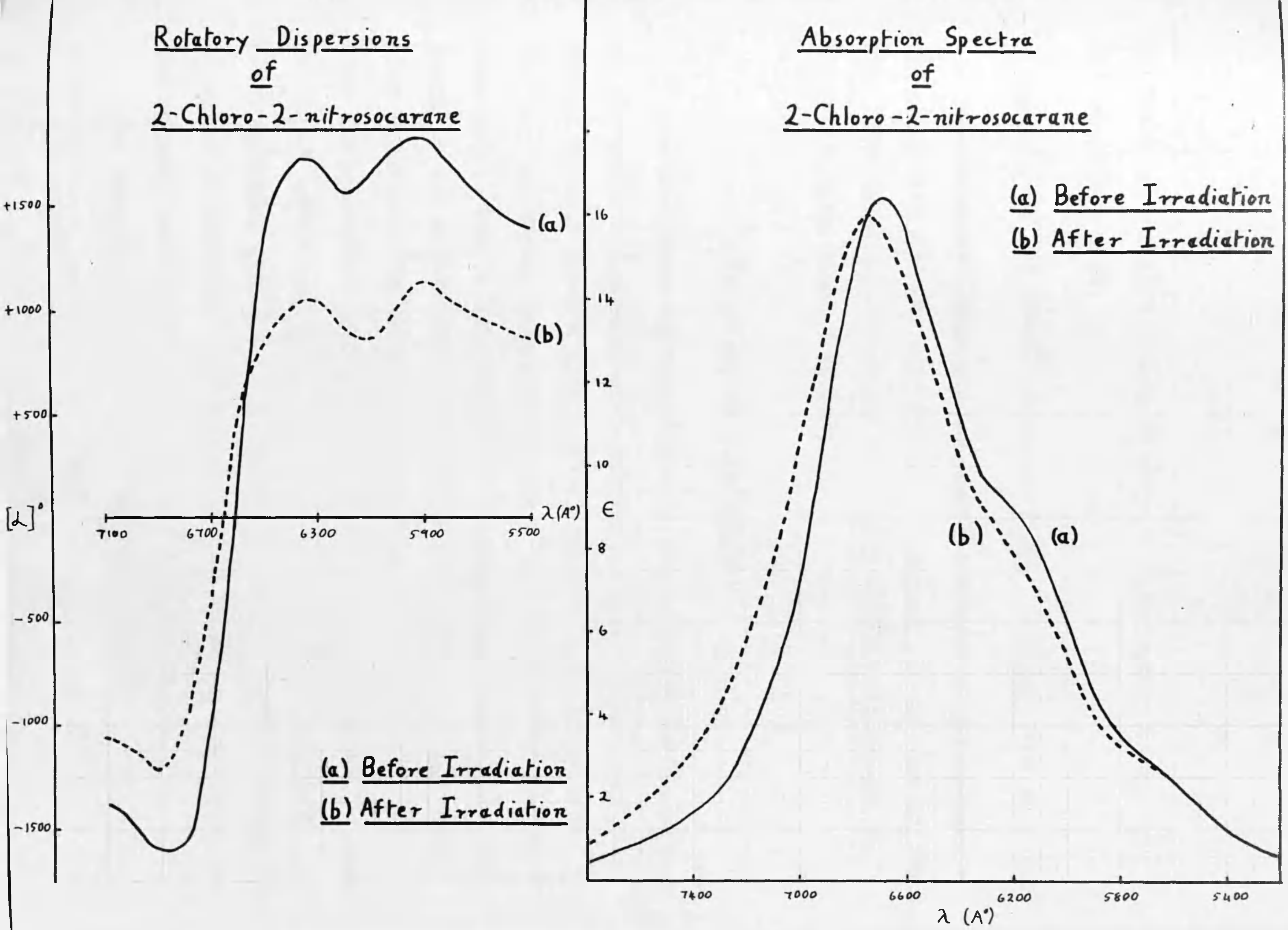
Absorption Spectrum of (-)-2-Chloro-2-nitrosocarane

c = 0.676%　　　**Solvent : alcohol (oxygen free)**

= 0.0335M　　　l = 10 mm.

$10^{-1}\lambda$ (A°)	log $\frac{I_o}{I}$	ϵ	$10^{-1}\lambda$ (A°)	log $\frac{I_o}{I}$	ϵ
780	.016	0.45	650	.448	13.37
770	.022	0.66	640	.368	10.99
760	.031	0.93	630	.320	9.55
750	.042	1.25	620	.297	8.86
740	.056	1.67	610	.260	7.76
730	.084	2.51	600	.204	6.09
720	.116	3.46	590	.148	4.42
710	.171	5.10	580	.112	3.34
700	.240	7.16	570	.095	2.84
690	.358	10.69	560	.080	2.39
680	.484	14.45	550	.058	1.73
670	.550	16.42	540	.040	1.19
660	.520	15.52			

GRAPH X



(i) Rotatory Dispersions of 2-Chloro-2-nitrosocarane

(a) Before Irradiation

(b) After Irradiation

(ii) Absorption Spectra of 2-Chloro-2-nitrosocarane

(a) Before Irradiation

(b) After Irradiation

in Table 20 and illustrated in Graph X (i)(a) showing the usual Cotton effect with

$[\alpha]_{max.} = +1800A^{o}$ at $5900A^{o}$ Reversal $6620A^{o}$ $[\alpha]_{min.} = -1600^{\circ}$ at $6850A^{o}$

Absorption studies form an important part of the present investigation and the data for this compound are set out in Table 21. The curve characteristic of chloro-nitroso compounds is illustrated in Graph X (ii)(a).

Behaviour on Irradiation

For photochemical investigation the material was irradiated in alcoholic solution by mercury yellow light in precisely the manner already described for the preceeding 'blue compounds' (p 21). As usual, rotation and absorption measurements were employed to follow the course of the reaction, there values being based on the concentration estimated photoelectrically at each time interval. Data are given in Table 22 where it is seen that the specific rotation falls from +1790° to a limiting value of +1249° after 1.25 hr. As in the case of (+)-2-chloro-2-nitrosopinane, this value remains unchanged on further irradiation in spite of continued photolysis, thus indicating completion of the primary reaction responsible for the fall in rotation.

The rotatory dispersion was determined after 1.5 hr. and the

TABLE 22

Irradiation of (-)-2-Chloro-2-nitrosocarane
with
Mercury Yellow Light ($\lambda = 5770, 5790 A^\circ$)

c = 0.676% Solvent : alcohol (oxygen free)

= 0.0335M l = 10 mm.

Absorption Measurements at $\lambda = 6710 A^\circ$

Rotation Measurements at $\lambda = 5940 A^\circ$

$$[\alpha] - [\alpha]_{\infty} = x$$

Time (hr.)	α°	$[\alpha]^\circ_{obs}$	$[\alpha]^\circ_{calc.}$	x	$\log x$	$\log \frac{I_0}{I}$	ϵ	$\log \epsilon$
0	+1.21	+1790	+1790	537	2.730	.550	16.41	1.215
0.25	+0.77	+1139	+1452	199	2.299	.430	12.82	1.108
0.50	+0.60	+888	+1338	85	1.929	.362	10.80	1.033
1.00	+0.40	+591	+1271	18	1.255	.255	7.62	0.882
1.25	+0.33	+488	+1249	-	-	.215	6.42	0.808
1.50	+0.28	+414	+1253	-	-	.182	5.43	0.735

TABLE 23

Retatory Dispersion of 2-Chloro-2-nitrosocarane
after Irradiation with
Mercury Yellow Light (λ = 5770, 5790A$^\circ$)
(calculated)

c = 0.231%
Solvent : alcohol (oxygen free)

l = 10 mm.
t = 18.5°

$10^{-1}\lambda(A^\circ)$	α°	$[\alpha]^\circ$	$10^{-1}\lambda(A^\circ)$	α°	$[\alpha]^\circ$
550	+0.20	+837	640	+0.23	+994
560	+0.21	+909	650	+0.19	+821
570	+0.22	+953	660	+0.11	+477
580	+0.24	+1038	670	-0.08	-345
590	+0.26	+1126	680	-0.21	-909
600	+0.23	+994	690	-0.28	-1210
610	+0.20	+865	700	-0.26	-1126
620	+0.21	+909	710	-0.25	-1081
630	+0.24	+1038	720	-0.24	-1040

calculated values based on the concentration estimated at this time. These are given in Table 23 and the curve superimposed on that of the original material in Graph X (i)(b). This gives a Cotton effect with

$[\alpha]_{\text{max.}} = +1126^{\circ}$ at 5975A° Reversal 6680A° $[\alpha]_{\text{min.}} = -1265$ at 6925A°

The result compares well with that for the 2-chloro-2-nitrosopinane. Once more the product of irradiation shows a curve of rotatory dispersion similar to the original but of smaller magnitude without change of sign. Further, the points of reversal show a bathochromic displacement of about 75A°. Accordingly, the wave-length chosen for polarimetric readings during the reaction was the mean of these two minima, giving values which were practically unaffected by the gradual displacement.

Determination of the absorption spectrum at this time showed that extensive photolysis had accompanied the fall in rotation. Transmissions at the maxima are proportional to concentrations

Final $(\log I_0/I)_{\text{max.}} = 0.188$ at $\lambda = 6750$A°
Initial $(\log I_0/I)_{\text{max.}} = 0.550$ at $\lambda = 6675$A°

so that only $\frac{0.188}{0.550} \times 100 = 34.2\%$ of total 'blue compound' remains after this time. The concentration, therefore, is given by

TABLE 24

Absorption Spectrum of 2-Chloro-2-nitrosocarane after Irradiation with Mercury Yellow Light (λ = 5770, 5790A°) (observed and calculated)

c = 0.676% (calc. = 0.231%) Solvent : alcohol (oxygen free)

= 0.0335M(calc. = 0.0115M) l = 10 mm.

$10^{-1}\lambda$ (A°)	$\log \frac{I_0}{I}$	$\epsilon_{obs.}$	$\epsilon_{calc.}$	$10^{-1}\lambda$ (A°)	$\log \frac{I_0}{I}$	$\epsilon_{obs.}$	$\epsilon_{calc.}$
780	.010	0.30	0.87	650	.140	4.18	12.22
770	.015	0.45	1.31	640	.117	3.49	10.21
760	.021	0.63	1.83	630	.102	3.04	8.91
750	.028	0.84	2.45	620	.090	2.69	7.86
740	.036	1.07	3.14	610	.078	2.33	6.81
730	.050	1.50	4.37	600	.062	1.85	5.41
720	.069	2.06	6.02	590	.045	1.34	3.93
710	.095	2.84	8.30	580	.037	1.10	3.23
700	.126	3.76	11.00	570	.032	0.96	2.79
690	.156	4.66	13.62	560	.028	0.84	2.45
680	.176	5.25	15.37	550	.020	0.60	1.75
670	.180	5.37	15.72	540	.018	0.54	1.57
660	.136	4.86	14.23				

$$c = c_0 \frac{k}{k_0} = 0.676 \frac{0.188}{0.550} = 0.231\% = 0.0115M$$

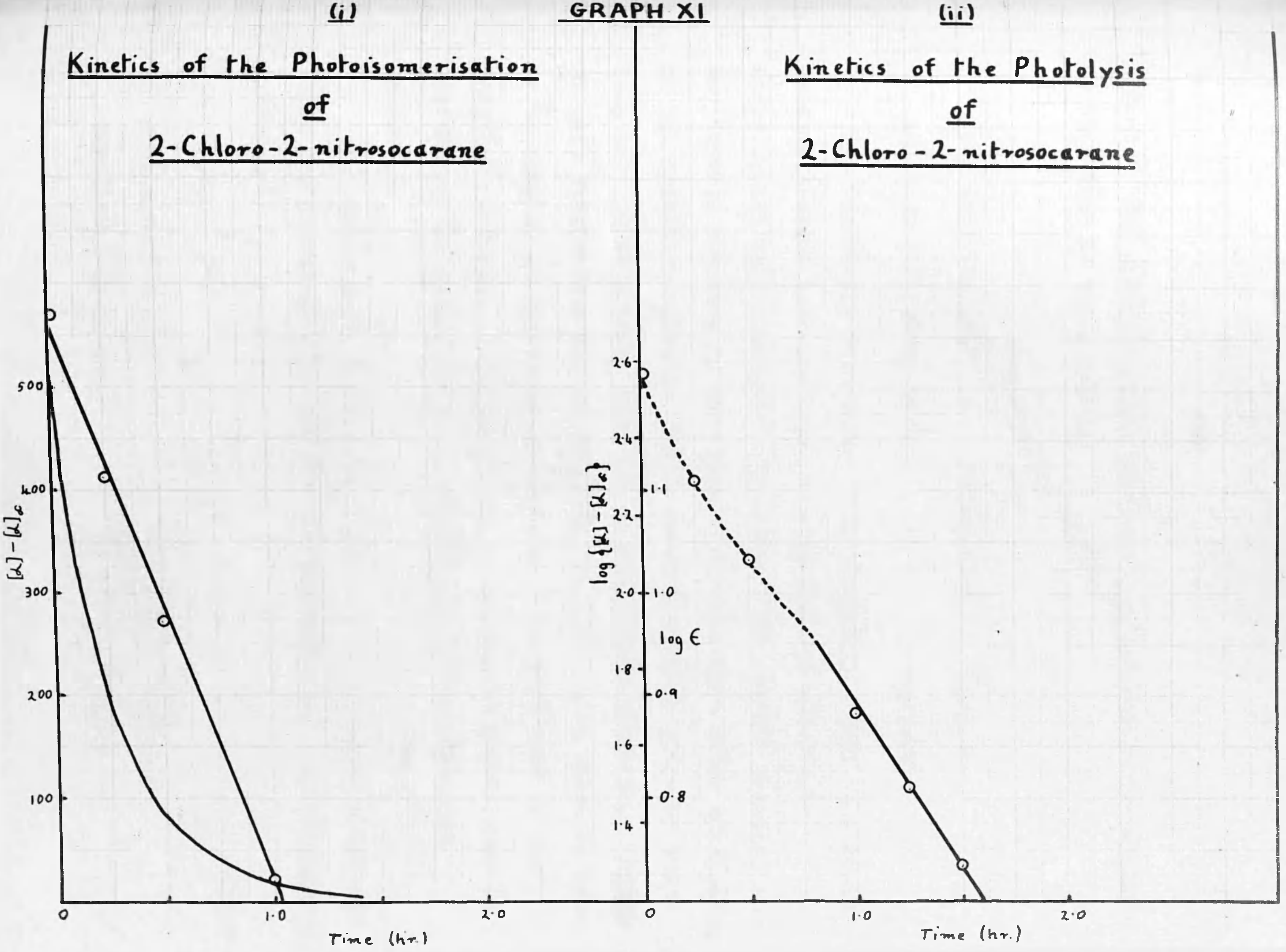
and this is the value which has been used in determining the final curves of rotation and absorption. The latter is shown in Graph X (ii)(b) (Table 24) together with that of the starting material. Again, the product shows the characteristic bathochromic displacement from the original, about 75A°, giving the isosbestic wave-length used for intermediate measurements as 6710A°.

Kinetic Studies

In previous examples of photoisomerisation a clearer view of the inner mechanism of the photochemical reaction has emerged from the application of kinetic methods. It is instructive to extend these to the present study and compare the results with those derived in other cases.

Polarimetric investigation has shown that the primary reaction is again one which causes a fall in optical rotatory power of the material. This property has been employed to measure the changes, and values of $[\alpha] - [\alpha]_\infty$ are included in Table 22 at each time interval. For First Order kinetics, equation (19) should be satisfied, as is indeed found to be the case. The relationship of $[\alpha] - [\alpha]_\infty$ and the logarithm of this quantity with time are shown in Graph XI (i), the latter being clearly

GRAPH XI



(i)

Kinetics of the Photoisomerisation of 2-Chloro-2-nitrosocarane

(ii)

Kinetics of the Photolysis of 2-Chloro-2-nitrosocarane linear. The characteristic constants are derived from the slope of this line in the usual way

$$\tan \theta = 1.490$$

from equation (10) $k_1 = 2.303 \times 1.490 = \underline{3.43\ \text{hr.}^{-1}}$

equation (13) gives $(t_1)_{\frac{1}{2}} = \dfrac{0.693}{k_1} = \underline{0.20\ \text{hr.}}$

The remarkably high value of k_1 indicates a much more rapid primary process than has been observed for the previously investigated chloro-nitroso compounds. The overall reaction is comparable, however, in that photolysis continues after completion of the initial reaction. Total decomposition is given by the fall in ϵ_{6710} with time, and this is recorded in Table 22. Graph XI (ii) illustrates the relationship of log ϵ_{6710} /t which is seen to be complex at first, simplifying to a straight line as the reaction proceeds. The inflexion, as before, is significant in indicating the transfer from a compound to a simple kinetic mechanism.

The linear part of this curve provides the necessary information for calculation of the kinetic constants for the secondary process.

$$\tan \theta = 0.323$$

from equation (10) $k_2 = 2.303 \times 0.0323 = \underline{0.744\ \text{hr.}^{-1}}$

equation (13) gives $(t_2)_{\frac{1}{2}} = \dfrac{0.693}{k_2} = \underline{0.933\ \text{hr.}}$

Comparison of the rates of primary to secondary reaction is given by the ratio

$$\underline{\frac{k_1}{k_2}} = \frac{3.43}{0.744} = \underline{\underline{4.61}}$$

and from this value it may be concluded that the composite mechanism

$$\begin{tikzcd} & B \arrow[dr, "k_2"] & \\ A \arrow[ur, "k_1"] \arrow[rr, "k_3"'] & & C \end{tikzcd}$$

may, to a first approximation, be reduced to the first two stages.

It is of interest to compare the velocity of the initial photochemical reaction with that of (+)-2-chloro-2-nitrosopinane. The ratio of the primary rate constants is

$$\frac{3.44}{0.66} = \underline{\underline{5.22}}$$

This shows a considerable increase in velocity in the present case and would appear to be a consequence of the lower stability of the excited state induced by the more highly strained structure.

Conclusions

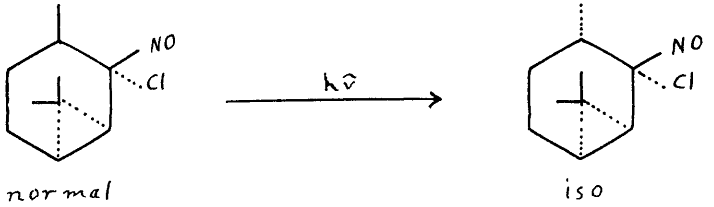
The suitability of the structure of (-)-2-chloro-2-nitrosocarane for the present work has been clearly illustrated. Some doubt remained, however, concerning the stability of the cyclopropane ring in the presence of free hydrochloric acid produced during photo-decomposition. Baeyer (1894) has shown that with hydrogen bromide and acetic acid, carone undergoes ring fission with addition of HBr to dihydrocarone hydrobromide.

Attempts to prepare the 'blue compound' of the intermediate dihydrocarvone hydrochloride were repeatedly unsuccessful and led to the formation of a green resinous material under the most carefully controlled conditions. It must be concluded that this dihalageno compound is highly unstable and accordingly may be excluded as an end product of the photochemical reaction. The observed results can, therefore, be interpreted in the usual way.

Comparison may conveniently be made with the case of 2-chloro-2-nitrosopinane. The relevant results have already been enumerated (p 70). To these may be added

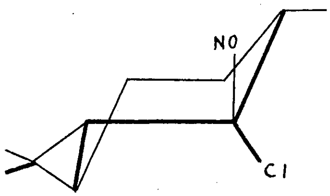
(iv) Non-inversion of the Cotton effect on completion of the primary reaction.

The interpretation of these observations has already been given and the change may be considered to be of the same type in the present instance,

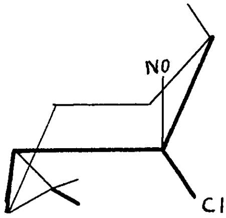


indicating skeletal rearrangement in such a way that the excited chromophore finally occupies the more stable endo position; in this case, with respect to the C_1 methyl group.

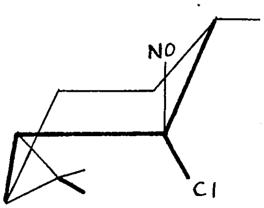
A two-dimensional representation of such a molecule is misleading, however, and the distribution of the various groups in space is better indicated as follows



VII



VIII



IX

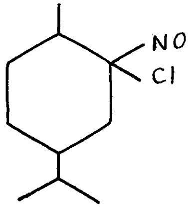
The configuration of C_2 is derived from the sign of the Cotton effect, and the skeletal structure is assumed to be trans (normal) so that the original material must be represented by either VII or VIII. Of these, it is clearly illustrated in VII that all neighbouring groups are as far removed from the sphere of influence of the absorbing chromophore as possible, accordingly no change could be accounted for on the basis of this structure. The alternative VIII, however, shows the C_1 methyl group suitably oriented to necessitate transformation to IX on nitroso excitation. This is the change which is postulated, occurring through inversion of C_1 and not of the secondary ring system as in the previous case.

In conclusion, (-)-2-chloro-2-nitrosocarane may be cited as a further example of a compound which undergoes photoisomerisation on absorption of radiation in the visible region.

(iii) PHOTOISOMERISATION OF (+)-2-CHLORO-2-NITROSO-p-MENTHANE

General Considerations

The phenomenon of photo-rearrangement of chloro-nitroso derivatives of bicyclic terpene structures has been well illustrated by the cases of 2-chloro-2-nitrosocamphane (6,5 - membered ring system), 2-chloro-2-nitrosopinane (6,4 - membered ring system), and 2-chloro-2-nitrosocarane (6,3 - membered ring system). The question next arose of whether such a process were limited to strained polycyclic structures, or if it were of more general character. Elucidation of this point necessitated investigation of a similar derivative in which the secondary ring had been completely removed, the molecule still retaining the possibility of existing in syn and anti forms. Such considerations led to the choice of 2-chloro-2-nitroso-p-menthane as the material most closely related to those previously studied and satisfying the above conditions.

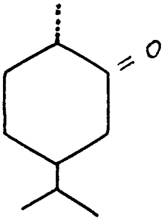


2-chloro-2-nitroso-p-menthane

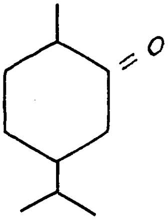
The continuity of the series has been carefully maintained and the gem-dimethyl group is now situated on C_8, outside the sphere of influence of the chromophoric centre. It is interesting to note, therefore, that if photoisomerisation is shown to occur in this structure, it must inevitably proceed by inversion of the C_1 methyl and not of the isopropyl group.

(+)-2-Chloro-2-nitroso-p-menthane

Carvomenthone, like pinocamphone, is known to exist in stereoisomeric forms



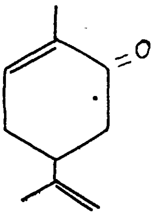
carvomenthone



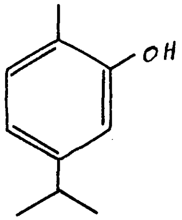
isocarvomenthone

the above configurations being derived from their relationship with the established structures of the corresponding menthones (Read and Johnston 1934, 1935). Of each modification, the syn and anti forms of the oxime have been prepared (Hückell and Doll, 1936) so that the task of obtaining a stereochemically homogeneous intermediate for the present work appeared formidable.

Fortunately, for the first stage, it has been possible to obtain a high degree of epimeric purity in the ketone by choosing as starting material the naturally occurring carvone. Carvomenthone itself is found to occur in small quantities in the oil Blumea Malcomii (Read et al., 1934) and has been prepared independently by Baeyer (1893) and Wallach (1893) by oxidation of carvomenthol. Commercial 'carvol', on distillation, provided the necessary d-carvone which was hydrogenated using a palladium hydroxide-calcium carbonate catalyst according to the method described by Read and Johnston (1934). These authors have investigated the equilibrium of l-carvomenthone and l-isocarvomenthone resulting from the preparation of this material by various methods and have concluded that the above procedure yields a product in which the normal form is highly predominant. In contact with the catalyst, some isomerisation of carvone to the aromatic structure carvacrol invariably takes place, and since these are inseparable by subsequent distillation, it was found convenient to continue to the oxime stage before attempting purification.



carvone
b.p. 230°



carvacrol
b.p. 238°

The crude l-carvomenthone was oximated in the usual way and the precipitated material dried on porous plate to remove oily products consisting of unchanged carvacrol and low-melting isomeric oximes. Fractional recrystallisation from light petroleum to constant melting point finally yielded a material with

$$[\alpha]_D = -30.9^\circ$$

$$\text{m.p. } 95\text{-}97^\circ$$

Comparison of these properties with those of the four possible modifications recorded under (Hückell et al., 1936) shows conclusively that the method has been successful in isolating a stereochemically individual oxime of the normal form of the ketone.

Oximes of Carvomenthone

	l-carvomenthone		l-isocarvomenthone	
	I	II	I	II
$[\alpha]_D$	-42.3°	91.2°	-72.5°	-65.5°
m.p.	100-101°	30-32°	64-65°	30-31°

The required intermediate was, therefore, available in the desired state, and since the formation of an oxime hydrochloride does not take place under the usual conditions, the 'blue compound' was prepared by direct chlorination of the oxime in dry ether. Removal of the solvent yielded (+)-2-chloro-2-nitroso-p-menthane as a non-viscous blue liquid which distilled under high vacuum and had the properties

TABLE 25

Rotatory Dispersion of (+)-2-Chloro-2-nitroso-p-menthane

$c = 1.50\%$ Solvent : alcohol (oxygen free)

$\ell = 10$ mm. $t = 18.5^{\circ}$

$10^{-1}\lambda$ (A°)	α°	$[\alpha]^{\circ}$	$10^{-1}\lambda$ (A°)	α°	$[\alpha]^{\circ}$
550	-0.20	-133	640	-0.37	-247
560	-0.23	-153	650	-0.21	-140
570	-0.27	-180	660	+0.08	+53
580	-0.31	-207	670	+0.28	+187
590	-0.37	-247	680	+0.40	+267
600	-0.34	-222	690	+0.47	+313
610	-0.32	-213	700	+0.51	+340
620	-0.34	-227	710	+0.53	+353
630	-0.37	-247	720	+0.48	+320

TABLE 26

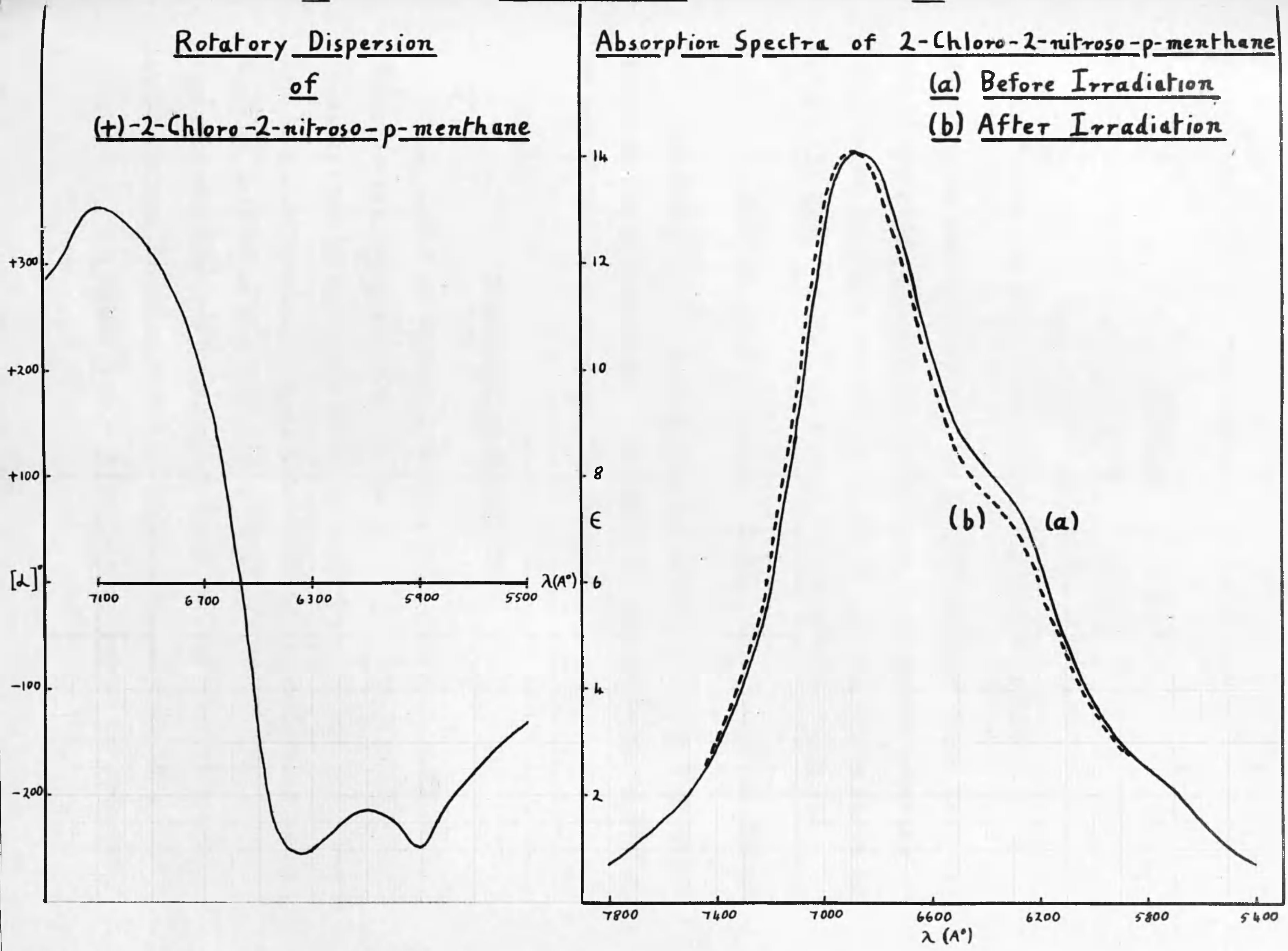
Absorption Spectrum of (+)-2-Chloro-2-nitroso-p-menthane

c = 1.204% Solvent : alcohol (oxygen free)

= 0.0593M ℓ = 10 mm.

$10^{-1}\lambda$ (A°)	$\log \frac{I_o}{I}$	ϵ	$10^{-1}\lambda$ (A°)	$\log \frac{I_o}{I}$	ϵ
780	.042	0.71	650	.525	8.85
770	.066	1.11	640	.485	8.19
760	.091	1.53	630	.450	7.59
750	.121	2.04	620	.382	6.44
740	.171	2.88	610	.290	4.90
730	.243	4.10	600	.225	3.79
720	.346	5.83	590	.177	2.98
710	.511	8.62	580	.152	2.56
700	.717	12.09	570	.125	2.11
690	.830	14.00	560	.091	1.53
680	.820	13.83	550	.060	1.01
670	.730	12.31	540	.043	0.73
660	.614	10.36			

GRAPH XII



(i) Rotatory Dispersion of (+)-2-Chloro-2-nitroso-p-menthane

(ii) Absorption Spectra of 2-Chloro-2-nitroso-p-menthane

(a) Before Irradiation

(b) After Irradiation

$[\alpha]_{max.} = +353^{\circ}$ at $\lambda = 7100A^{\circ}$

$\epsilon_{max.} = 14.08$ at $\lambda = 6870A^{\circ}$

b.p. 53.5° at 0.5 mm.

Found: Cl 17.3%; $C_{10}H_{18}NOCl$ requires Cl 17.4%

The maximum rotation is seen to be considerably lower than for the corresponding bicyclic derivatives. Complete rotatory dispersion data are set out in Table 25 and the curve shown in Graph XII (i). A typical Cotton effect results with

$[\alpha]_{max.} = +353^{\circ}$ at $7100A^{\circ}$ Reversal 6570A $[\alpha]_{min} = -247$ at $5900A^{\circ}$

Determination of absorption has shown the band characteristic of these compounds. The results are recorded in Table 26 and illustrated in Graph XII (ii)(a).

Behaviour on Irradiation

The result of exposing an alcoholic solution of (+)-2-chloro-2-nitroso-p-menthane to mercury yellow light has been investigated by the photochemical technique already described (p 21), polarimetric and spectrophotometric measurements being used to determine the progress of the reaction. The appropriate data are recorded in Table 27 and have been calculated from the concentration (estimated) at each time interval in the usual way. A surprising result is observed.

TABLE 27

Irradiation of (+)-2-Chloro-2-nitroso-p-menthane
with
Mercury Yellow Light (λ = 5770, 5790A°)

c = 0.892% Solvent : alcohol (oxygen free)
= 0.0438M l = 10 mm.

Absorption Measurements at λ = 6870A°

Rotation Measurements at λ = 5900A°

Time (hr.)	α°	$[\alpha]^\circ_{obs}$	$[\alpha]^\circ_{calc}$	$\log \frac{I_0}{I}$	ϵ	$\log \epsilon$
0	-0.22	-247	-247	.610	13.93	1.144
1.0	-0.17	-191	-257	.453	10.34	1.014
2.0	-0.14	-157	-254	.378	8.63	0.936
3.0	-0.12	-135	-256	.322	7.35	0.866
4.0	-0.11	-123	-268	.280	6.39	0.806
5.0	-0.09	-101	-247	.250	5.71	0.757
6.0	-0.08	-90	-246	.223	5.09	0.707
7.0	-0.07	-78	-236	.202	4.61	0.664
8.0	-0.07	-78	-263	.181	4.13	0.616
9.0	-0.06	-67	-250	.164	3.74	0.573
10.0	-0.06	-67	-282	.145	3.31	0.520

The corrected specific rotation is seen to remain constant, within the limits of experimental accuracy, throughout the reaction. This was at first interpreted as due to the absence of a primary change, but further consideration has shown that it is rather the inability of the method to detect such a process.

Attention was, therefore, turned to absorption data, to determine if the shift characteristic of photoisomerisation had taken place. Photolysis is seen to occur fairly rapidly and after a time of 3.5 hr. $\epsilon_{max.}$ has fallen to 6.83; rather less than half the original value, and accordingly the lower limit for which complete spectral determination can be made accurately. A fresh sample of the solution on which the previous absorption measurements had been made was used, being irradiated on the same optical system for 3.5 hr., at which time $\epsilon_{max.}$ was confirmed to be 6.83. The concentration of 'blue compound' at this time is given by the usual equation

$$c = c_0 \frac{k}{k_0} = 1.204 \frac{6.83}{14.08} = 0.0584\% = 0.0287M$$

and this value has been used in the calculation of molecular extinction coefficients which are set out in Table 28. The curve is superimposed on that of the original material in Graph XII (ii)(b) where a small bathochromic displacement,

TABLE 28

Absorption Spectrum of 2-Chloro-2-nitroso-p-menthane after Irradiation with Mercury Yellow Light ($\lambda = 5770, 5790A^{\circ}$)

(observed and calculated)

c = 1.204% (calc. = 0.584%) Solvent : alcohol (oxygen free)

= 0.0593M(calc. = 0.0287M) ℓ = 10 mm.

$10^{-1}\lambda(A^{\circ})$	$\log \frac{I_0}{I}$	ϵ obs.	ϵ calc.	$\epsilon_i - \epsilon_f$	$10^{-1}\lambda(A^{\circ})$	$\log \frac{I_0}{I}$	ϵ obs.	ϵ calc.	$\epsilon_i - \epsilon_f$
780	.018	0.30	0.62	-	650	.242	4.08	8.41	+0.44
770	.028	0.47	0.97	-	640	.220	3.71	7.65	+0.54
760	.043	0.73	1.51	-	630	.204	3.44	7.09	+0.50
750	.058	0.98	2.02	-	620	.180	3.03	6.25	+0.19
740	.085	1.43	2.95	-0.07	610	.136	2.29	4.72	+0.18
730	.122	2.06	4.24	-0.14	600	.105	1.77	3.65	+0.14
720	.174	2.93	6.04	-0.21	590	.084	1.42	2.92	+0.06
710	.258	4.35	8.96	-0.34	580	.075	1.26	2.60	-
700	.358	6.04	12.45	-0.36	570	.060	1.01	2.08	-
690	.405	6.83	14.08	-0.08	560	.044	0.74	1.53	-
680	.390	6.58	13.56	+0.27	550	.032	0.54	1.11	-
670	.342	5.77	11.90	+0.41	540	.027	0.46	0.95	-
660	.282	4.75	9.79	+0.57					

estimated at about 15A°, is indicated. This might be considered as approaching the limit of experimental accuracy, but confirmatory evidence is supplied on consideration of the data set out in the last column in Table 28, which records the difference between initial and final molecular extinction coefficients. All of these are seen to be negative at wavelengths longer than the head of the band and positive at shorter wave-lengths. Such a lack of random distribution of error cannot be attributed to any method of calculation but must be considered as due to a small but detectable bathochromic displacement. Precise determination of the isosbestic point is unnecessary in this case and the wave-length of the head of the band has been used for intermediate absorption measurements.

A rotatory dispersion curve was also constructed at this time, the specific rotations being calculated from the estimated concentration. In agreement with the data in Table 27, no difference from the original material could be found, so that the results need not be recorded further. This method has a much lower experimental accuracy than the former, however, and it may only be concluded that any changes in rotations are too small to be detected. Further determinations of both rotatory dispersion and absorption made at later times served merely to confirm the above results.

Kinetic Studies

Since it has not been possible to follow the initial process polarimetrically in this case, the application of kinetic methods is severely limited and serves merely to indicate the overall mechanism of the reaction.

Absorption measurements provide the only data available for the present investigation and give the total concentration of 'blue compound' present at each time interval during the photochemical reaction. These values are given in terms of molecular extinction coefficients in Table 27 and the logarithm of this parameter is plotted against time in Graph XIV (ii) (a). The curve is of the usual form indicating a two-component process to the point of inflection at a time of about four hours, thereafter simplifying to photolysis alone. Since this latter part of the curve is linear, First Order kinetics are indicated and the velocity constants may be calculated

$$\tan \theta = 0.0466$$

from equation (10) $k_2 = 2.303 \times 0.0466 = \underline{0.107 \text{ hr.}^{-1}}$

equation (13) gives $(t_2)_{\frac{1}{2}} = \dfrac{0.693}{k_2} = \underline{6.47 \text{ hr.}}$

The rate of photolysis is therefore intermediate between those of (+)-2-chloro-2-nitrosopinane ($k_2 = 0.005$ hr.$^{-1}$) and (-)-2-chloro-2-nitrosocarane ($k_2 = 0.744$ hr.$^{-1}$), and since the primary reaction attains completion in a relatively short period, it may be deduced that the usual mechanism applies

$$\begin{tikzcd}
& B \arrow[dr, "k_2"] & \\
A \arrow[ur, "k_1"] \arrow[rr, "k_3"'] & & C
\end{tikzcd}$$

with permissable approximation to the first two stages.

Transition from complex to simple kinetics has been shown in previous cases to represent change from a compound photochemical reaction consisting of

(a) photolysis of the original molecule
(b) rearrangement of the original molecule
and (c) photolysis of the rearranged molecule

to (c) alone. Such a state may be considered sufficient criterion for this type of mechanism and provides the third method by which photoisomerisation can be detected.

Conclusions

It is instructive to compare the results observed on irradiation of (+)-2-chloro-2-nitroso-p-menthane with those of the previously investigated materials.

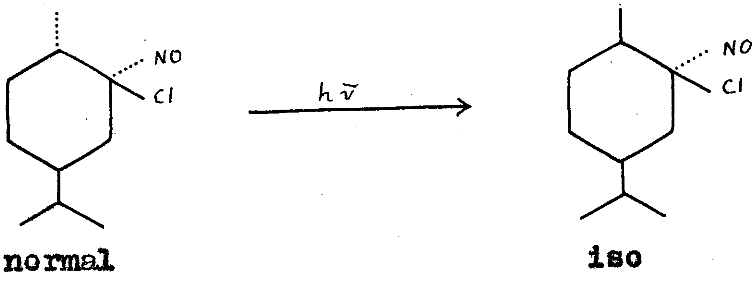
(i) There is no detectable change in optical rotatory power throughout the reaction in this case.

(ii) The usual bathochromic displacement of absorption curve is observed, of considerably smaller magnitude here.

(iii) Kinetic considerations show that the total reaction consists of consecutive component processes. The overall mechanism is similar to the previous cases.

(iv) Non-inversion of the Cotton effect precludes inversion of the asymmetric centre C_2.

This is the first instance in which the initial process cannot be detected from changes in optical rotatory power, however, the results can be satisfactorily interpreted only on the basis of the usual type of intramolecular isomerisation in which the two epimers have rotatory powers not appreciably different. Confirmatory evidence is supplied from the small but real displacement of the visible absorption band.



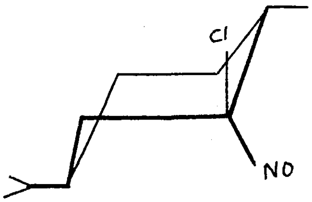
The above configurations are derived from the following considerations

(i) The precursor of the 'blue compound' has been shown to be a stereochemically homogeneous material of the normal (trans) form. It is reasonable to conclude that the skeletal structure of the resultant chloro-nitroso compound will be trans also.

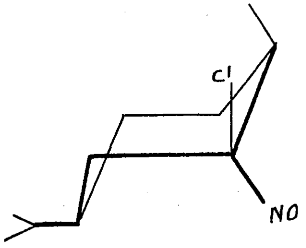
(ii) Sign of the Cotton effect gives the relative configuration of the centre C_1 with respect to the established configuration of (-)-2-chloro-2-nitrosocamphane.

(iii) Cis-configuration of the nitroso chromophore and neighbouring methyl group must exist before photo-rearrangement is possible.

The isomers are more clearly illustrated in three-dimensional representations



normal



iso

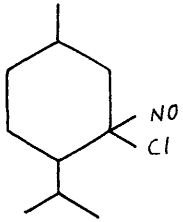
which are in agreement with the conclusions of Bose (1952). Expressed in terms of Barton's recently elaborated method of conformational analysis (1950, 1951), "carvomenthone, being the more stable epimer, should have both the methyl and isopropyl groups linked by equatorial bonds while isocarvomenthone should have the isopropyl group equatorially linked and the methyl group polar linked".

In the photochemical reaction under consideration it is evident that excitation of the nitroso chromophore causes repulsion of the vicinal methyl group to the sterically more stable endo position, resulting in inversion of the molecular structure to the iso form. The phenomenon of photoisomerisation is thus shown to extend to suitable monocyclic derivatives as in the present case.

(iv) PHOTOISOMERISATION OF (-)-3-CHLORO-3-NITROSO-P-MENTHANE

General Considerations

As an extension of the series 3-chloro-3-nitroso-p-menthane was chosen as a molecule which was expected to yield interesting information compared with the previous member.

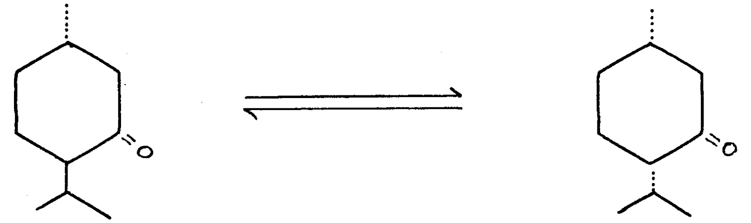


3-chloro-3-nitroso-p-menthane

Modification of the structure in this case has resulted in situation of the chromophoric centre vicinal to the isopropyl group instead of the C_1 methyl. The results may, therefore, be expected to agree qualitatively with those derived for the corresponding 2-epimer, but to be of slightly different magnitude. It was hoped that if such evidence were available it would prove valuable in substantiating the validity of the previous interpretation of the photochemical reaction, particularly in view of the absence of information from rotation data.

(-)-3-Chloro-3-nitroso-p-menthane

Since the early experiments of Beckmann (1889), the isomerisation of the menthones has been the subject of extensive study by a number of workers particularly noteworthy among whom are Read and his collaborators (J. 1925-1952, reviewed 1930).



l-menthone $[\alpha]_D = -28.46^\circ$

l-isomenthone $[\alpha]_D = -93^\circ$

The mechanism of this inversion under the influence of acids has been investigated by Bell (1938) who postulates a prototropic change, and since the asymmetry of C_4 is lost in the enolic intermediate, inversion of the isopropyl group is permitted to yield the isomeride. It is interesting to note that the kinetics of this rearrangement are found to be of the First Order. Obviously the same mechanism cannot be operative in the inversion of the chloro-nitroso derivatives, but the results serve to indicate the ease with which these structures undergo internal rearrangement.

The first synthesis of l-menthone was that of Moriya (1881) by the oxidation of l-menthol. Subsequently it has been prepared by reduction of d-pulegone, piperitone and other unsaturated ketones. Modification of the former method, however, is most suitable and results in a reaction which has been reported by Read (1926) to be completely free from accompanying inversion, so that, by this procedure, no difficulty was experienced in obtaining a stereochemically uniform starting material. After distillation the ketone had the properties

b.p. 78.5°/10 mm.

$[\alpha]_D = -24.9^\circ$

The oxime and oxime hydrochloride were prepared in the usual way, care being taken in the latter stage to introduce the minimum amount of HCl, a potentially powerful inverting agent. A salt with melting point 117-119° was obtained

l-menthone oxime hydrochloride m.p. 117-119°	l-isomenthone oxime hydrochloride m.p. 132°

showing that stereochemical homogeniety had been retained. Chlorination in dry ether gave an emerald green solution which yielded (-)-3-chloro-3-nitroso-p-menthane as a non-viscous blue liquid on removal of the solvent and distillation under high vacuum. The properties were found to be unchanged on chromatographic treatment with Light's activated alumina.

$[\alpha]_{max} = +225^\circ$ at $\lambda = 6200A^\circ$

$\epsilon_{max} = 20.62$ at $\lambda = 6750A^\circ$

b.p. 56° at 0.25 mm.

TABLE 29

Rotatory Dispersion of (-)-3-Chloro-3-nitroso-p-menthane

c = 1.069% Solvent : alcohol (oxygen free)

= 0.0525M t = 18°

10^{-1} λ(A°)	α°	[α]°	10^{-1} λ A°	α°	[α]°
550	+0.16	+150	640	+0.16	+150
560	+0.17	+159	650	0	0
570	+0.19	+178	660	-0.16	-150
580	+0.21	+196	670	-0.30	-281
590	+0.22	+206	680	-0.35	-327
600	+0.18	+168	690	-0.36	-338
610	+0.17	+159	700	-0.37	-346
620	+0.24	+225	710	-0.36	-338
630	+0.23	+215			

TABLE 30

Absorption Spectrum of (-)-3-Chloro-3-nitroso-p-menthane

c = 0.911%　　Solvent : alcohol (oxygen free)

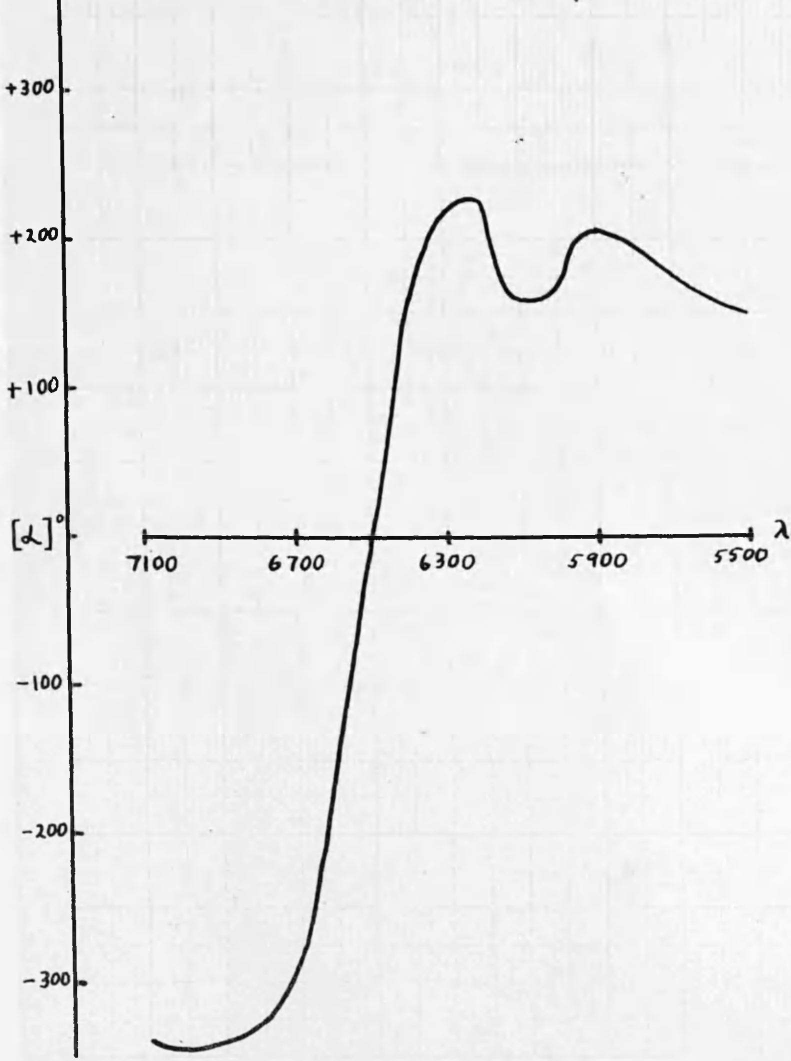
= 0.0448M　　ℓ = 10 mm.

$10^{-1}\lambda(A^\circ)$	$\log \frac{I_0}{I}$	ϵ	$10^{-1}\lambda(A^\circ)$	$\log \frac{I_0}{I}$	ϵ
780	.025	0.56	650	.610	13.62
770	.038	0.85	640	.532	11.88
760	.056	1.25	630	.500	11.16
750	.081	1.81	620	.408	9.11
740	.118	2.63	610	.332	7.41
730	.189	4.22	600	.258	5.76
720	.293	6.54	590	.196	4.38
710	.438	9.78	580	.165	3.68
700	.638	14.24	570	.135	3.01
690	.830	18.58	560	.096	2.14
680	.888	19.82	550	.064	1.43
670	.830	18.53	540	.050	1.12
660	.720	16.07			

GRAPH XIII

(i)

Rotatory Dispersion of (-)-3-Chloro-3-nitroso-p-menthane

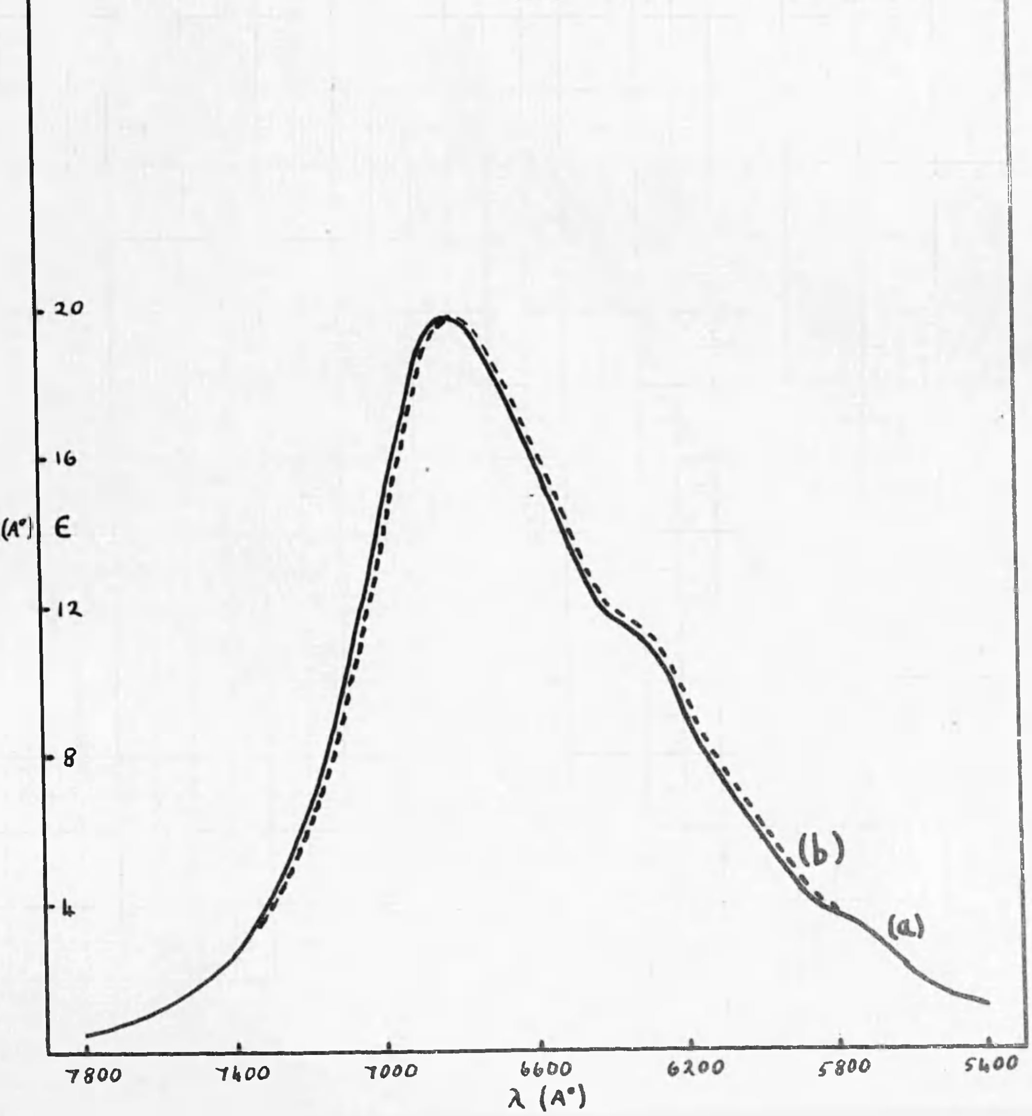


(ii)

Absorption Spectra of 3-Chloro-3-nitroso-p-menthane

(a) Before Irradiation

(b) After Irradiation



Found Cl, 17.5%; $C_{10}H_{18}NOCl$ requires Cl, 17.4%

Like the closely related (+)-2-chloro-2-nitroso-p-menthane, the maximum rotation is quite small, which appears characteristic of such strainless monocyclic structures. The rotatory dispersion is of the usual form as illustrated in Graph XIII (i) and recorded in Table 29.

$[\alpha]_{max} = +225^{\circ}$ at 6200A$^{\circ}$ Reversal 6500A$^{\circ}$ $[\alpha]_{min.} = -346^{\circ}$ at 7000A$^{\circ}$

Precise location of the visible absorption band is of fundamental importance in the present study and has been determined from the data set out in Table 30. The result is shown in Graph XIII (ii)(a) before exposure of this material to visible radiation.

Behaviour on Irradiation

The photo-processes occurring on irradiation of (-)-3-chloro-3-nitroso-p-menthane by mercury yellow light on the optical system previously described (p 21) have been investigated by the usual methods based on rotation and absorption measurements and kinetic results derived from these.

To ensure that the initial photochemical reaction, if present, was not obsecured by simultaneous photolysis, spectrophotometric estimations of concentration have been employed at each time interval and corrected values are recorded from these. Complete information is given in Table 31 which provides a most interesting result. Calculated specific rotations are seen to remain essentially constant, but the obvious interpretation of absence of the primary process here must be considered with caution and attention turned to the remaining methods before a final assessment may be made.

That photolysis of this material proceeds fairly slowly is illustrated by the data in Table 31, the value of molecular extinction coefficient requiring rather more than the 9.25 hr. given to fall to half the original value. In view of the extremely small displacement found in the case of (+)-2-chloro-2-nitroso-p-menthane it was concluded that a longer exposure was desirable in this case before attempting to determine any band displacement. Accordingly, the previous experiment was repeated and irradiation continued for 22 hr. at which time $\epsilon = 7.97$. Investigation of the absorption simultaneously with a fresh sample of the unirradiated material yielded data which are recorded in Table 32 along with the corrected values of ϵ derived from the concentration estimated at this time

$$c = co\,\frac{k}{k_o} = 0.911\,\frac{.357}{.888} = 0.227\% = 0.0179M.$$

The curve is superimposed on that of the original material in

TABLE 31

Irradiation of (-)-3-Chloro-3-nitroso-p-menthane
with
Mercury Yellow Light (λ = 5770, 5790A°)

c = 1.069% Solvent : alcohol (oxygen free)

= 0.0525M l = 10 mm. (sealed cell)

Absorption Measurements at λ = 6800A°

Rotation Measurements at λ = 5800A°

Time (hr.)	α°	$[\alpha]_{obs.}$	$[\alpha]_{calc.}$	$\log \frac{I_0}{I}$	ϵ	$\log \epsilon$
0	+0.20	+187	+187	1.060	20.19	1.305
0.25	+0.18	+178	+193	0.980	18.67	1.271
0.75	+0.18	+168	+193	0.925	17.62	1.246
1.75	+0.19	+168	+203	0.875	16.67	1.222
3.25	+0.16	+150	+198	0.800	15.24	1.183
5.25	+0.15	+140	+202	0.732	13.94	1.144
7.25	+0.13	+122	+193	0.670	12.76	1.106
9.25	+0.11	+103	+182	0.604	11.50	1.061

TABLE 32

Absorption Spectrum of 3-Chloro-3-nitroso-p-menthane
after Irradiation with
Mercury Yellow Light ($\lambda = 5770, 5790A^o$)
(observed and calculated)

c = 0.911% (calc. = 0.227%) Solvent : alcohol (oxygen free)
= 0.0448M(calc. = 0.0179M) l = 10 mm.

$10^{-1}\lambda(A^o)$	$\log \frac{I_o}{I}$	$\epsilon_{obs.}$	$\epsilon_{calc.}$	$\epsilon_i - \epsilon_f$	$10^{-1}\lambda(A^o)$	$\log \frac{I_o}{I}$	$\epsilon_{obs.}$	$\epsilon_{calc.}$	$\epsilon_i - \epsilon_f$
780	.010	0.22	0.55	-	650	.246	5.49	13.69	-0.07
770	.015	0.33	0.82	-	640	.217	4.84	12.06	-0.18
760	.022	0.49	1.22	-	630	.203	4.53	11.30	-0.14
750	.032	0.71	1.77	-	620	.172	3.84	9.58	-0.47
740	.046	1.03	2.57	+0.06	610	.134	2.99	7.46	-0.05
730	.075	1.67	4.17	+0.05	600	.108	2.41	6.01	-0.25
720	.113	2.52	6.29	+0.25	590	.079	1.76	4.39	-0.01
710	.172	3.84	9.58	+0.20	580	.067	1.49	3.72	-0.04
700	.254	5.67	14.14	+0.10	570	.055	1.23	3.07	-
690	.331	7.39	18.43	+0.10	560	.036	0.80	2.00	-
680	.357	7.97	19.87	-0.05	550	.030	0.67	1.67	-
670	.335	7.48	18.65	-0.12	540	.022	0.49	1.22	-
660	.292	6.51	16.23	-0.16					

Graph XIII (ii)(b) where a shift of about 10A° to shorter wavelengths is seen to result. Confirmation is given from the values of $\epsilon_i - \epsilon_f$ in Table 32. Again the absence of random discrepancies is perhaps more satisfactory evidence of the reality of absorption displacement than the small difference observed on graphing the results. It has been unnecessary to make a precise determination of the isosbestic point for such a small shift, and the head of the band has been used for purposes of intermediate measurements. Further investigation of rotatory dispersion at this time gave results which were in close agreement with those of the original material and so are recorded in Table 29.

Finally, it may be stressed that the methods here employed for the detection of photoisomerisation are not invalidated by the magnitude of the changes observed, since rearrangement in spacial distribution of groups cannot be correlated quantitatively with changes in optical properties of the resulting isomerides. It is satisfactory to note, in such cases, that further confirmation is available on investigation by kinetic methods.

Kinetic Studies

In the absence of rotation data kinetics are, of necessity, limited to the application of spectrophotometric measurements set out in Table 31. The fall of molecular extinction coefficient is a measure of the decrease in concentration of the total 'blue compound' as the reaction proceeds. For conformation to the First Order law, the logarithm of this quantity plotted against time should yield a straight line. The results obtained are illustrated in Graph XIV (ii)(b) which shows the relationship to be complex up to a time of about three hours and thereafter linear. The characteristic constants for this final process may be calculated

$$\tan\theta = 0.020$$

from equation (10) $k_2 = 2.303 \times 0.020 = \underline{0.046\ \text{hr.}^{-1}}$

equation (13) gives $(t_2)_{\frac{1}{2}} = \dfrac{0.693}{k_2} = \underline{15.08\ \text{hr.}}$

illustrating the greater photochemical stability of this material over the corresponding 2-epimer ($k_2 = 0.107$ hr.$^{-1}$).

That such a reaction mechanism, with velocity constants of the above order of magnitude, consists of primary, secondary and tertiary components of which the last may be neglected, has been demonstrated previously. The significance of these results will now be considered.

Conclusions

The following observations have been made during the irradiation of (-)-3-chloro-3-nitroso-p-menthane.

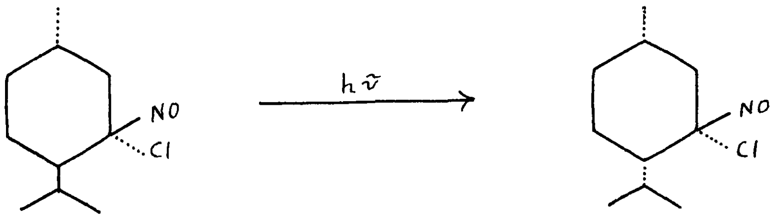
(i) No change is detectable in optical rotatory power. This precludes any possibility of inversion of the asymmetric centre C_3.

(ii) There is a small displacement of the visible absorption band to shorter wave-lengths.

(iii) Kinetic considerations show the overall reaction to be a composite one and confirm the existence of a primary process.

The available evidence is consistent with the requirements for intramolecular rearrangement as in the previous cases.

Displacement of the absorption band has already been established as a diagnostic test for isomerisation and kinetics provide evidence of completion of the initial reaction after 3 hr. The results are in no way invalidated by the lack of supporting data from rotation measurements which merely implies failure of the method to meet the required degree of precision. It has already been pointed out that the magnitude of the changes observed has no particular significance since these cannot be derived from steric considerations. The transformation may, therefore, be represented



normal iso

configurations being based on the following considerations

(i) The structure of the original ketone and subsequent intermediates suggest that it is justifiable to assume a normal, i.e. trans, configuration for the initial 'blue compound'.

(ii) It is more reasonable to consider that the sign of the Cotton effect gives the configuration of the centre C_3 with respect to the corresponding 2-derivatives, than otherwise.

(iii) Cis-orientation of the active chromophore and vicinal alkyl group are required in a structure capable of change.

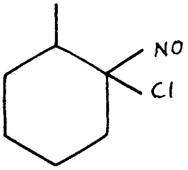
The above configurations are seen to be in agreement with these requirements, and it is evident that for the form of lowest free energy, inversion of the iso-propyl group on C_4 must follow photo-excitation of the chromophore responsible for absorption in the given spectral region.

It is a peculiar feature of this material that on irradiation the absorption should suffer a hypsochromic displacement, in contrast to all other members of the present series which have been found to be bathochromic. The example is not isolated, however, and finds comparison in the (+)-2-chloro-2-nitroso-apocamphane-1-carboxylic acid studied by Veitch (1953). Direction of displacement is of doubtful significance, however, for it has already been pointed out (p 38) that this is related only to the energy of electronic transition.

(v) PHOTOISOMERISATION OF 2-CHLORO-2-NITROSO-1-METHYLCYCLOHEXANE

General Considerations

The present investigation has been concerned with a study of the photochemical behaviour of chloro-nitroso derivatives of a series of structures in which the secondary ring system has been progressively degraded from that of the parent camphane. The results recorded in the preceeding Sections show that photoisomerisation occurs when a vicinal constraint (alkyl group or ring system) falls within the sphere of influence of the photo-excited chromophore. In all cases yet studied, two sterically effective groups (or group plus ring) have been operative, in that rearrangement proceeds by inversion of one with respect to the other. It was of interest, therefore, to consider the case in which the secondary ring system had been completely removed, leaving the undernoted structural unit, common to all members of the present series.



2-chloro-2-nitroso-1-methylcyclohexane

It remained to determine if any change were detectable on irradiation of this material, i.e. if photoisomerisation is attributable to rearrangement of the spacial distribution of groups centred on C_1 and C_2, or dependent entirely on the existence of cis-trans skeletal modifications.

1-2-Chloro-2-nitroso-1-methylcyclohexane

The preparation of this 'blue compound' was greatly facilitated by the ready availability of the starting material, o-methylcyclohexanone which, by its simplicity of structure obviated the tedious task of separation of isomerides esperienced in previous preparations. The ketone has one outstanding disadvantage, however, being available only from synthetic sources it is not optically active, though potentially so by virtue of the asymmetric centre C_1. The literature contains no reference to attempted resolution although this has been carried out for the corresponding 3-epimer. It was considered that separation of the enantiomorphs might be effected through the function of the carbonyl group by one of the following methods.

(i) Using the reagent 5(α-phenylethyl) semioxamazide developed by Leonard (1950), which has proved successful in the case of 3-methylcyclohexanone.

(ii) Through the amine-bisulphite addition complex used by Adams (1949), again with success for the 3-epimer.

(iii) By the method of Woodward (1941) using l-menthylhydrazine as in the classic resolution of camphor.

Of these, the first seemed the most profitable, and work was commenced on the attempted resolution. At about the same time, however, a repeated study of the photo-processes attending the irradiation of (+)-2-chloro-2-nitrosopinane brought to light the shift in absorption band accompanying rearrangement, and subsequent re-investigation of the other 'blue compounds' established such a spectral displacement as characteristic of photoisomerisation. The final proof of the validity of this deduction was supplied when the chloro-nitroso compound of (±) camphor was irradiated in the usual way and the expected band displacement observed, showing that the absorption shift was in the same direction for both enantiomorphs (Hope and Mitchell, 1953). This method of detecting photoisomerisation has, therefore, proved a useful tool in extending the investigation of such processes to optically inactive and racemic compounds, while kinetic data have served further to substantiate the results derived. In view of these methods of investigation, it was felt that the resolution of o-methylcyclohexanone was no longer justified, and attention turned to a study of the chloro-nitroso compound from the inactive ketone.

The oxime and oxime hydrochloride of (±)1-methylcyclohexanone were formed in the usual way and the salt chlorinated in a large volume of dry ether to give a deep green solution after several hours. Removal of the excess chlorine and solvent yielded i-2-chloro-2-nitroso-1-methylcyclohexane as a non-viscous blue liquid which distilled under vacuum.

$\epsilon_{\text{max.}} = 15.14$ at $\lambda = 6850A^{o}$

b.p. 67-68° at 14 mm.

Found Cl, 22.0%; $C_7H_{12}NOCl$ requires Cl, 22.0%

Consideration of previous 'blue compounds' illustrates the low value of rotatory power of such monocyclic chloro-nitroso structures, so that it is doubtful if the optically active material would have proved of much greater value for the present studies than the above. It is true that absence of rotation data render it impossible to verify the stereochemical homogeniety of the synthesised material, but conditions have been controlled to conform to those employed in all other cases, so that there is no reason to suppose it is other than the isomeride possessing the lowest free energy and greatest stability which is produced here. The necessary absorption data before irradiation have been recorded in Table 33 and are illustrated in Graph XIV (i).

TABLE 33

Absorption Spectrum

of

i-2-Chloro-2-nitroso-1-methylcyclohexane

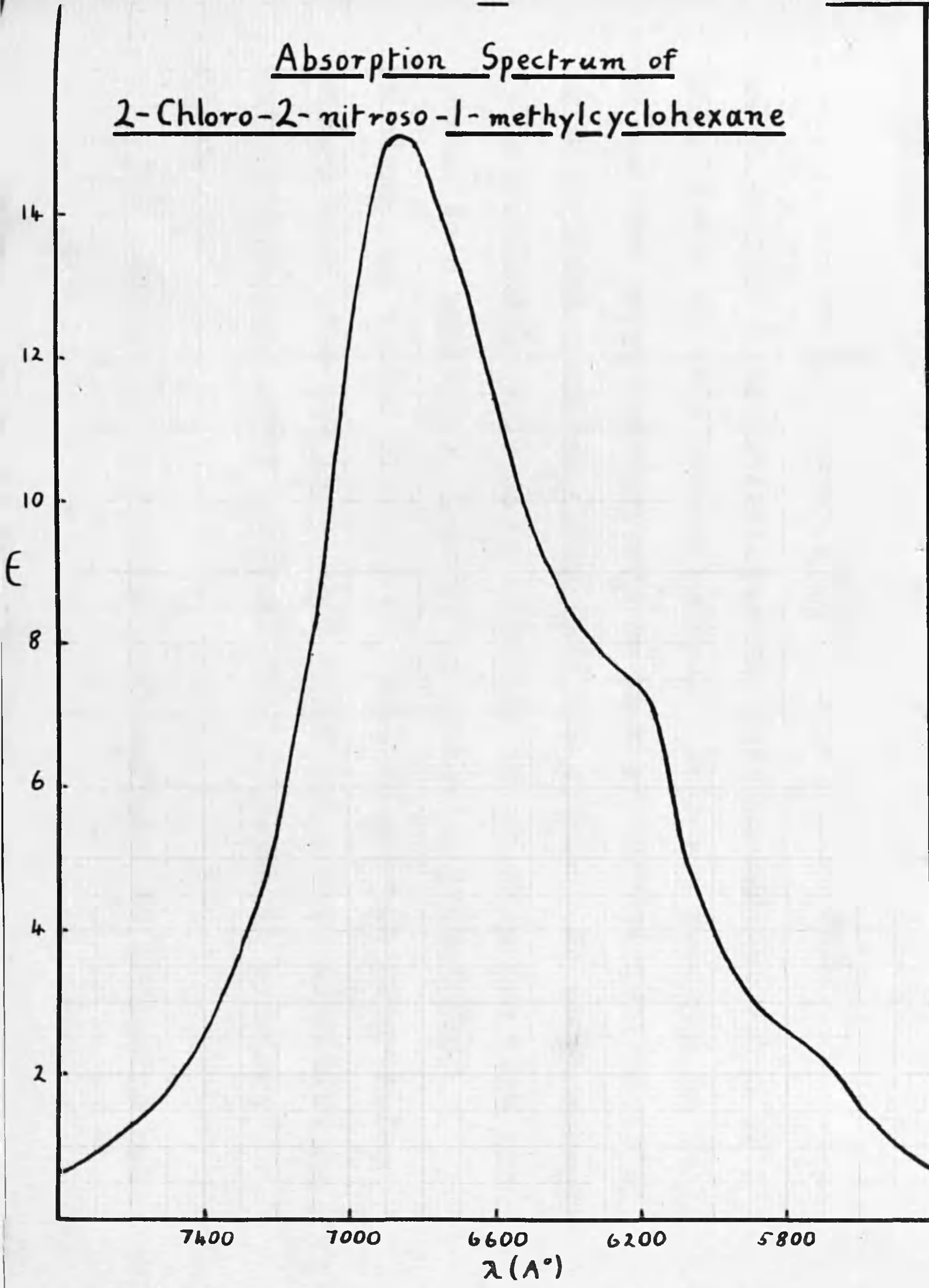
c = 1.080% Solvent : alcohol (oxygen free)

= 0.0674M ℓ = 10 mm.

$10^{-1}\lambda(A^\circ)$	$\log \frac{I_o}{I}$	ϵ	$10^{-1}\lambda(A^\circ)$	$\log \frac{I_o}{I}$	ϵ
780	.043	0.64	650	.650	9.64
770	.062	0.92	640	.574	8.51
760	.090	1.33	630	.530	7.86
750	.121	1.79	620	.500	7.42
740	.174	2.58	610	.364	5.40
730	.252	3.76	600	.264	3.92
720	.370	5.49	590	.208	3.09
710	.529	7.84	580	.174	2.58
700	.800	11.87	570	.148	2.20
690	1.000	14.84	560	.104	1.54
680	1.001	14.85	550	.068	1.01
670	.900	13.35	540	.046	0.68
660	.770	11.42			

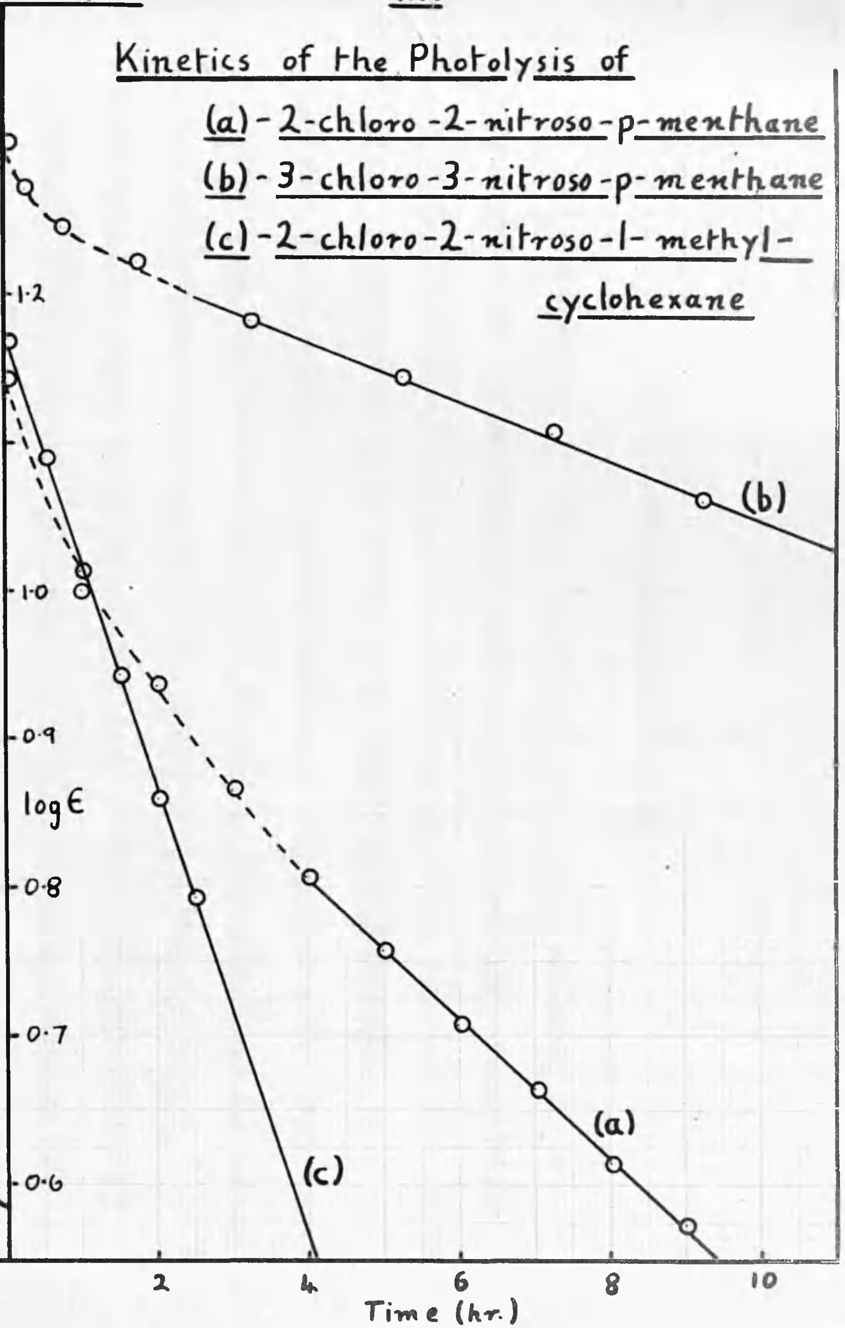
GRAPH XIV

(i)



Absorption Spectrum of 2-Chloro-2-nitroso-1-methylcyclohexane

(ii)



Kinetics of the Photolysis of

(a) - 2-chloro-2-nitroso-p-menthane

(b) - 3-chloro-3-nitroso-p-menthane

(c) - 2-chloro-2-nitroso-1-methyl-cyclohexane

Behaviour on Irradiation

Investigation of the molecular processes arising from irradiation of an alcoholic solution of i-2-chloro-2-nitroso-1-methylcyclohexane under anaerobic conditions and on the usual optical system has been limited to the interpretation of data derived from absorption measurements. These are set out at various time intervals in Table 34 where the decrease in molecular extinction coefficients is seen to be fairly rapid, falling from 14.84 to 5.25 in 2.5 hr. The concentration of material remaining at this time was estimated spectrophotometrically

$$c = c_0 \frac{k}{k_0} = 1.080 \frac{0.418}{1.00} = 0.452\% = 0.0282M$$

and a complete absorption spectrum determined, the value of ϵ being based on this concentration. Data are recorded in Table 35 and the curve superimposed on that of the original material, re-determined simultaneously with the above. No displacement is detectable in this case, although irradiation has been continued to a limitation imposed by extensive photolysis. Further, the values of $\epsilon_i - \epsilon_f$ in Table 35 show no progressive change with wave-length, a test which has proved sensitive in determining even small spectral displacements in previous cases.

The absence of an initial rearrangement is indicated but

TABLE 34

Irradiation of l-2-Chloro-2-nitroso-1-methylcyclohexane
with
Mercury Yellow Light ($\lambda = 5770, 5790 A^{\circ}$)

c = 1.080% Solvent : alcohol (oxygen free)

= 0.0674M ℓ = 10 mm. (sealed cell)

Absorption Measurements at $\lambda = 6900 A^{\circ}$

Time (hr.)	$\log \frac{I_o}{I}$	ϵ	$\log \epsilon$
0	1.000	14.84	1.171
0.5	.829	12.31	1.090
1.0	.687	10.20	1.008
1.5	.593	8.79	0.944
2.0	.488	7.25	0.860
2.5	.418	6.22	0.793

TABLE 35

Absorption Spectrum
of
l-2-Chloro-2-nitroso-1-methycyclohexane
after Irradiation with
Mercury Yellow Light (λ = 5770, 5790A°)
(observed and calculated)

c = 1.080% (calc. = 0.452%) Solvent : alcohol (oxygen free)

= 0.0674M(calc. = 0.0282M) ℓ = 10 mm.

$10^{-1}\lambda(A^\circ)$	$\log \frac{I_0}{I}$	$\epsilon_{obs.}$	$\epsilon_{calc.}$	$\epsilon_i - \epsilon_f$	$10^{-1}\lambda(A^\circ)$	$\log \frac{I_0}{I}$	$\epsilon_{obs.}$	$\epsilon_{calc.}$	$\epsilon_i - \epsilon_f$
780	.017	0.25	0.59	-	650	.288	4.27	10.13	-0.49
770	.024	0.36	0.85	-	640	.254	3.77	8.94	-0.43
760	.037	0.55	1.30	-	630	.245	3.63	8.61	+0.25
750	.050	0.74	1.75	-	620	.214	3.18	7.54	-0.12
740	.072	1.07	2.53	+0.05	610	.152	2.28	5.41	-0.01
730	.105	1.55	3.67	+0.09	600	.122	1.81	4.39	-0.47
720	.156	2.31	5.48	+0.01	590	.088	1.31	3.10	-0.01
710	.236	3.50	8.30	-0.46	580	.072	1.07	2.53	+0.05
700	.337	5.00	11.86	+0.01	570	.057	0.84	1.99	-
690	.418	6.21	14.73	+0.11	560	.042	0.63	1.49	-
680	.430	6.38	15.14	-0.30	550	.026	0.38	0.90	-
670	.386	5.72	13.57	-0.22	540	.015	0.23	0.54	-
660	.334	4.96	11.77	-0.35					

consideration must be given to kinetic studies before the results may be unambiguously interpreted.

Kinetic Studies

The change in concentration of reactant with time is conveniently represented by the value of molecular extinction coefficient at the head of the absorption band and the plot of log $\epsilon_{max.}$/t is shown in Graph XIV (ii)(c) (Table 34). It is significant that a completely linear relationship results, necessitating First Order kinetics and a simple overall mechanism with no indication of primary and secondary processes. The velocity constant may be calculated from the straight line in the usual way

$$\tan\theta = 0.156$$

from equation (10) $k_2 = 2.303 \times 0.156 = \underline{0.359\ \text{hr.}^{-1}}$

equation (13) gives $(t_2)_{\frac{1}{2}} = \frac{0.693}{k_2} = \underline{1.93\ \text{hr.}}$

The reaction is represented as destruction of the rearranged molecular species, i.e. the second component of the possible sequence

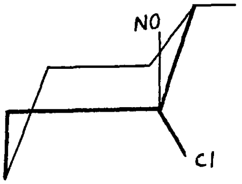
$$\begin{tikzcd} & B \arrow[dr, "k_2"] & \\ A \arrow[ur, "k_1"] \arrow[rr, "k_3"'] & & C \end{tikzcd}$$

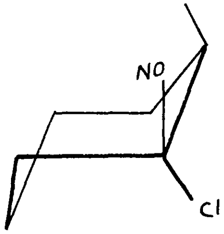
and is considerably more rapid than the photolysis of species 'B' observed for other 'blue compounds', with the exception of the highly unstable rearranged (+)-2-chloro-2-nitrosocarane.

Conclusions

Irradiation of i-2-chloro-2-nitroso-1-methylcyclohexane has given rise to results which differ fundamentally from those observed in other cases. It is unfortunate that no information is available from rotation data, but spectral displacement of absorption and compound kinetics, both characteristic of photo-isomerisation under these conditions, have not been observed.

The facts are explicable on the assumption of absence of initial rearrangement before photolysis. It is difficult, however, to reconcile this view with a consideration of the molecular processes known to occur in closely related structures and interpretation of the results must be derived with care. An alternative explanation suggests itself on consideration of the relative thermodynamic stabilities of the theoretically possible stereoisomers.





The energy barrier separating such structures would be expected to be very small, and it is conceivable that the corresponding photo-processes, if existent, would be extremely rapid and accordingly detectable only with great difficulty. Such an interpretation requires that the energy of transition of the nitroso group (band location) is unaffected by the relatively small structural differences in isomeric forms, and that rearrangement proceeds with a quantum efficiency of such magnitude as to be without influence on the kinetics of photolysis.

Whatever the true explanation, the results are significant in illustrating two points of outstanding importance in relation to the previous work.

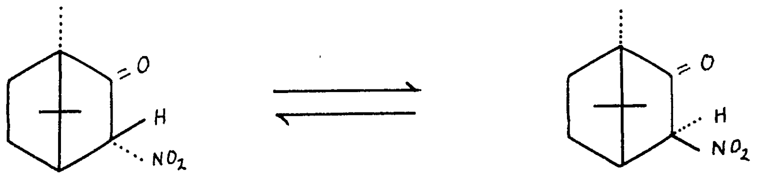
(i) In cases where primary rearrangement is absent (or undetectable) the kinetics show a linear relationship of the logarithm of concentration with time throughout the period of irradiation. Compound kinetics may, therefore, be unambiguously interpreted as representing complex photo-processes, thus substantiating the validity of the third method employed for detecting rearrangement.

(ii) Photoisomerisation, in the sense in which it has been previously observed, is not dependent merely on the relative spacial arrangement of the groups on the asymmetric and vicinal centres, but is possible only in structures theoretically capable of existing in cis-trans skeletal modifications.

In this respect, the present investigation of 1-2-chloro-2-nitroso-1-methylcyclohexane has proved invaluable in providing unusual opportunities for the study of results observable on irradiation of a structure intimately related to those of the other members of the series but rendered essentially incapable of undergoing the primary process of photoisomerisation.

DISCUSSION

It has long been known that many terpenes and their derivatives readily undergo rearrangement in the presence of both acidic and basic catalysts. What is perhaps the most prominent work in this field is due to Lowry and his collaborators (J., 1898-1915) on substituted camphors and related compounds. The mutarotation of α-nitrocamphor is particularly interesting and was erroneously considered by its investigator to be due to partial conversion of the normal into the aci-form in solution. He noted acceleration of the change on exposure to light (1900) but records no attempt to carry out the transformation by this means alone. More recently, Bell and Sherred (1940) have shown that the reaction is, in fact, due to interconversion of the two possible stereoisomers.



In less complicated terpene structures, skeletal transformation of the normal → iso type is common and has been well illustrated by the work of Read (reviewed, 1930) on such compounds as pinocamphone, carvomenthone and menthone, in which cases the equilibrium existing between the isomeric forms under a variety of conditions has been extensively studied. A close analogy, therefore, exists between the rearrangements of these materials and the photoisomerisations observed for their chloro-nitroso derivatives.

Interpretation of the changes attending the photo-processes has been based on the data summarised in the accompanying chart and derived from three separate methods of investigation, some relevant points of which may be briefly considered.

(i) Optical Rotatory Power - Only in the case of I there a reversal in sign of rotation on completion of the transformation, so that this is the only member in which inversion of the asymmetric centre need by considered. Criticism has been directed against the postulated structural change (Veitch, 1953) on the argument that the Cotton effect is not completely inverted and the final value of $[\alpha]_{max} = -508^{\circ}$ falls considerably short of the initial $[\alpha]_{max} = +964^{\circ}$. It must be pointed out, however, that the epimers described have the relation of diastereoisomers and not enantiomorphs so that there is no sound basis for supposing even approximate equality of optical rotatory powers. In all other cases, modification of the curve of rotatory dispersion suggests molecular rearrangement without direct effect on the active centre.

(ii) Electronic Absorption Spectra - Progressive displacement of $\lambda_{max.}$ in a characteristic absorption band during a reaction is usually attributable to some form of isomerisation, and

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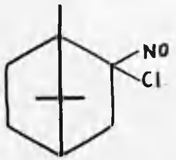
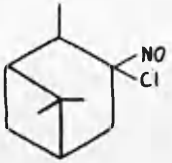
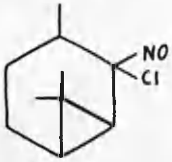
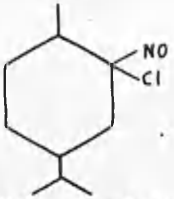
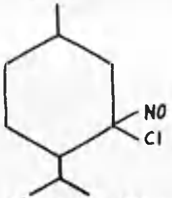
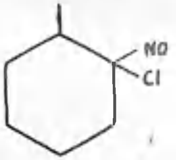
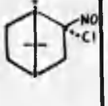
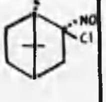
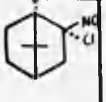
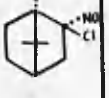
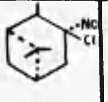
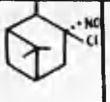
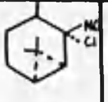
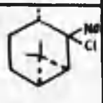
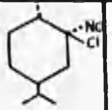
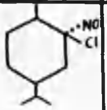
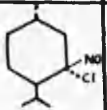
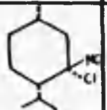
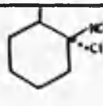
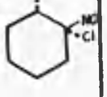
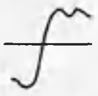
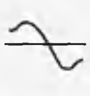
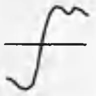
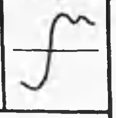
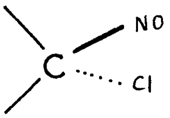
														
	2-Chloro-2-nitrosocamphane				2-Chloro-2-nitroso-pinane		2-Chloro-2-nitroso-carane		2-Chloro-2-nitroso-p-menthane		3-Chloro-3-nitroso-p-menthane		2-Chloro-2-nitroso-1-methylcyclohexane	
	Visible Irrad^{n}		U-v Irrad^{n}											
Wave Length of Radiation (A°)	5770 5790 } Hg(y)		< 3200		5770 5790 } Hg(y)		5770 5790 } Hg(y)		5770 5790 } Hg(y)		5770 5790 } Hg(y)		5770 5790 } Hg(y)	
Rearrangement	Photomutarotation		Photomutarotation		Photoisomerisation		Photoisomerisation		Photoisomerisation		Photoisomerisation		Photoisomerisation (?)	
Displacement of Absorption Band	60 A° Bathochromic		30 A° Bathochromic		100 A° Bathochromic		75 A° Bathochromic		15 A° Bathochromic		10 A° Hypsochromic		None	
k_1 (hr.$^{-1}$)	0·56		0·19		0·66		3·43		——		——		——	
k_2 (hr.$^{-1}$)	0·02		0·83		0·005		0·74		0·11		0·05		0·36	
${}_1t_{\frac{1}{2}}$ (hr.)	1·24		3·59		1·05		0·20		——		——		——	
${}_2t_{\frac{1}{2}}$ (hr.)	34·30		0·84		144·6		0·93		6·47		15·08		1·93	
Relationship of Velocity Constants	$k_1 \gg k_2$		$k_1 < k_2$		$k_1 \gg k_2$		$k_1 > k_2$		$k_1 > k_2$		$k_1 > k_2$		$k_1 > k_2$ (?)	
Structure	Before Irrad^{n}	After Irrad^{n}	Before Irrad^{n}	After Irrad^{n}	Before Irrad^{n}	After Irrad^{n}	Before Irrad^{n}	After Irrad^{n}	Before Irrad^{n}	After Irrad^{n}	Before Irrad^{n}	After Irrad^{n}	Before Irrad^{n}	After Irrad^{n}
														
Cotton Effect													Inactive	
$[\alpha]_{\max.}$ at λ	+964° 6000 A°	−508° 6060 A°	+964° 6000 A°	−157° 6025 A°	+390° 6600 A°	+206° 6700 A°	+1800° 5900 A°	+1126° 5975 A°	+353° 7100 A°		+225° 6200 A°			

numerous examples of change in spectral location due to rearrangements of the cis-trans type are to be found in the literature. The interpretation of experimental data must be derived with care, however, since a change in dielectric constant of the medium frequently results in the same effect by the differing contribution of solvation to the stabilities of ground and excited levels. It is known that irradiation of chloro-nitroso compounds invariably results in considerable photolysis to the corresponding oxime with liberation of hydrogen chloride (Mitchell, Schwarzwald and Simpson, 1941) so that these reactions are accompanied by the necessary change in the solvent. To confirm that the displacements of $\lambda_{max.}$ in the present cases were independent of these conditions, samples of hydrochloric acid, in quantities calculated to represent 100% decomposition, were introduced into solutions of the blue materials and their spectra re-determined. No change was detectable for any of the compounds studied so that the observed shifts may be unambiguously interpreted as arising from molecular transformation.

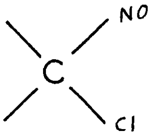
(iii) Kinetic Studies - A truly internal rearrangement must be unimolecular in character and obey First Order kinetics. This has been found to be the case for a large number of stereoisomerisations, e.g. the mutarotation of α-nitrocamphor (Bell and

Sherred, 1940) and the menthone ⟶ isomenthone interconversion (Bell and Caldin, 1938). In a photochemical reaction the further requirement of incomplete absorption of incident radiation is necessary before such simple kinetics become possible. This condition has been satisfied in the experimental procedure adopted in the previous investigations and the overall mechanism has been shown to be dependent only on the relative rates of the individual component processes. Comparison of the velocity constants for each compound is given in the chart, where k_1 is seen to be considerably greater than k_2 in all cases with the exception of the ultra-violet irradiation of I. Here $k_2 > k_1$ so that completion of the primary reaction before total decomposition of both isomeric forms is not possible. Kinetic considerations have proved of value in assessing the relative importance of individual reactions but do little to explain the exact mechanism of photochemical transition.

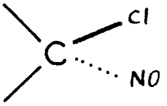
Of the tetrahedrally directed valence about the active centre to which the absorbing chromophore is attached, two bonds are employed in ring formation, the remaining two joining the functional groups to carbon in such a way that the planes of the pairs are perpendicular (a). This is the configuration of greatest thermodynamic stability and rotation of the molecule from this state will require the surmounting of a potential energy barrier in the region where the four linkages fall in a common plane (b). Beyond this point the potential energy again decreases and there will be a minimum when the planes of paired bonds are again at right angles (c). The height of the barrier above the average energy level of a given form is the energy of activation of the transition.



(a)



(b)



(c)

It is extremely improbable that a molecule absorbs enough vibrational energy from radiation for complete dissociation to occur. It is much more likely that the first stage in a photo-rearrangement is excitation to a higher electronic level. In the case of monomeric nitroso compounds, the change has been attributed by Lewis and Kasha (1945) to a low-energy singlet triplet transition which is expected to occur but rarely, i.e. with very low probability, in accordance with the observed low intensity of the absorption band. Such a state requires the uncoupling of the spins of a pair of unsaturation electrons, so that the resultant triplet state may be considered as analogous to a diradical. It is apparent that this marked weakening of bonding may well affect the configuration of the molecule, the final result being partial de-localisation of the C-N bonding orbital with subsequent transition to (b). From this state the excess energy may be lost by re-emission of radiation or in the form of kinetic energy by collision. Many activated molecules, however, will pass over the barrier to the second form (c), the relative stabilities of initial and final states being determined by the steric constraints and non-bonded interaction forces of the molecular environment. In time, the number passing over the barrier in one direction will equal the number passing in the other and a condition of equilibrium will be attained, the position of this photostationary state depending on the relative rates of the photochemical and thermal dark reactions.

In the materials studied, no detectable reverse reaction has been observed on leaving the products of irradiation in absence of light for long periods. It must be concluded that the reverse thermal reaction is very slow, so that the photoprocess may be assumed to proceed practically to completion. (-)-3-Chloro-3-nitroso-p-menthane is a possible exception to this general rule, for there is some evidence that on keeping the original material for periods of the order of one year, some change to a substance of opposite sign of rotation occurs. The resulting material has not been isolated in a pure state, however, and the observation is of doubtful significance.

Configurations of the materials resulting from photochemical transformation are included in the chart together with their original structures, both having been derived from considerations presented in the appropriate Sections. In the case of I the unusual rearrangement may be attributed to the unique bridged formation of the molecule in which the stereochemistry of centres C_1 and C_4 is locked by the gem-dimethyl bridge, so that a normal → iso change is not possible. Absorption of radiation with subsequent accommodation of the photo-excited nitroso group on the energetically favoured endo position (Shoppee, 1952; Barton, 1953) must, therefore, proceed through inversion of the asymmetric centre resulting in the observed mutarotation. In this respect the compound is the exception of the series. In other materials cis-trans rearrangement occurs more readily. This is not a surprising result considering the small energy differences between the various conformations of such ring structures, e.g. the energy barrier separating the axial and equatorial forms of methylcyclohexane has been calculated by Pitzer and Beckett (1947) as only 2 K cal/mole. A transformation of this type in the present case again results in endo positioning of the excited chromophore and sterically influencing alkyl group or ring system, which is essentially the same result as that derived in the photomutarotation of I.

The investigation has clearly illustrated the effect of neighbouring groups and secondary ring systems as structural factors influencing the course of rearrangement. The stereomutation of (-)-2-chloro-2-nitrosocamphane is not a unique example as was initially anticipated and a similar change induced by light has been found in simpler terpene structures. It may be predicted that photoisomerisation will be common to all chloro-nitroso compounds where the asymmetric centre is included in a ring system carrying sterically influencing groups in positions rendering the molecule potentially capable of existing in cis and trans forms. The phenomenon doubtless extends to a wider field of compounds where the changes are less readily detectable.

PREPARATIONS

Note All stages involving the final chloro-nitroso compounds were carried out in very diffuse light.

(-)-2-Chloro-2-nitrosocamphane

d-Camphor Oxime. - The method of Auwers (1889) proved convenient in the preparation of large quantities of the oxime which had m.p. 118°; $[\alpha]_D$ = -42.2° (1% alc.).

d-Camphor Oxime Hydrochloride. - Dry hydrogen chloride from the Tucker generator (1949) passed into a solution of the oxime in anhydrous ether at 0°, precipitated the required oxime hydrochloride as a fine, crystalline material m.p. 159°; $[\alpha]_D$ = -43.6° (1% alc.).

(-)-2-Chloro-2-nitrosocamphane. - The above camphor oxime hydrochloride in dry ether was chlorinated according to Mitchell et al. (1950), but with the following modifications. After removal of the ether, the blue solid was dissolved in the minimum volume of light petroleum, and the unchanged oxime hydrochloride filtered off. The filtrate was transferred to a column of sugar charcoal (50 x 2.5 cm.), and the blue band eluted with the same solvent. This treatment yielded a product with $[\alpha]_{max.} = +707^{\circ}$ at $\lambda = 6000A^{\circ}$; $\epsilon_{max} = 13.6$ at $6600A^{\circ}$; m.p. 145-146° (d). Passage of the material through a column (50 x 2.5 cm.) of Light's alumina (activated at 200° for 4 hr.) gave a product with $[\alpha]_{max.} = +803^{\circ}$; $\epsilon_{max.} = 13.7$; m.p. 145-146° (d). Re-adsorption on alumina raised $[\alpha]_{max.}$ to $+964^{\circ}$ while the absorption maximum and m.p. remained unchanged.

Inactive 2-Chloro-2-nitrosocamphane

The preparation and purification were similar to those for (-)-2-chloro-2-nitrosocamphane. After chromatographic treatment on sugar charcoal, the product was found to have absorption maximum and m.p. identical with the above compound.

Bornyl Chloride

Commercial 'pinene hydrochloride' (22.5 gm.) was crystallised twice from 'AnalaR' amyl alcohol (18.5 gm.). The crystals were washed with methyl alcohol (2 ml.), and trituration with this solvent removed the remaining traces of amyl alcohol. The product, dried 'in vacuo' over sodium hydroxide, had m.p. 132-133°; $[\alpha]_D = +25.9^{\circ}$ (1% alc.).

isoBornyl Chloride

This is best prepared by the rearrangement of camphene hydrochloride under carefully controlled conditions according to Meerwein and van Emster (1922). In refluxing the hydrochloride in presence of ethyl bromide at 56° for 6 days, the constant boiling point apparatus described by Tucker (1953) was found convenient with acetone as bath fluid. Subsequent purification was similar to that for bornyl chloride. The authors claim 99.6% stereochemical purity by this method. The product in this case had the satisfactory m.p. 159-160°.

(+)-2-Chloro-2-nitrosocamphane

A photochemical technique has been employed for the preparation of this material from (-)-2-chloro-2-nitrosocamphane. The procedure has been fully described in the text (pp 42-43).

(+)-2-Chloro-2-nitrosopinane

1-Pinocamphone. - Distillation of oil of hyssop gave a fraction, b.p. 212-214/741 mm. This crude pinocamphone was purified through the semicarbazone which, after recrystallisation from a large volume of methanol had m.p. 228-230°. The ketone was regenerated by steam distillation with oxalic acid, and on subsequent distillation had the properties b.p. 208-209°/745 mm.; $n_D^{17} = 1.4743$; $\alpha_D = -19.7^\circ$.

l-Pinocamphone Oxime. - The above ketone was oximated by the method of Cook and Bachmann (1936) to give a product which distilled at 83°/0.4 mm. and had $\alpha_D = -18.9^\circ$.

(+)-2-Chloro-2-nitrosopinane. - This oxime (4 gm.) was dissolved in dry ether (100 ml.), and chlorine passed in for 1.5 hr., the solution early attaining a deep emerald colour. Removal of the solvent and excess chlorine under reduced pressure left the chloro-nitroso compound as a blue oil which distilled under vacuum, b.p. 47°/0.4 mm.; $[\alpha]_{max.} = +390^\circ$ at $\lambda = 6600$A°; $\epsilon_{max.} = 19.12$ at $\lambda = 6350$A°; Found Cl, 17.5%. $C_{10}H_{16}NOCl$ requires Cl, 17.6%.

(-)-2-Chloro-2-nitrosocarane

d-Carvone. - This ketone is available in the form of commercial 'carvol' which was found satisfactory on re-distillation, b.p. 231-233°/755 mm.; $n_D^{18} = 1.4980$; $\alpha_D = +56.5^\circ$.

l-Dihydrocarvone. - Saturation of the double bond conjugated with the carbonyl group is best effected by reduction with Zn/KOH as described by Wallach (1894) and was found to proceed smoothly and in good yield. Purification of the product through the bisulphite compound, as described, gave dihydrocarvone, b.p. $88.5^\circ/11.2$ mm. $n_D^{20} = 1.4703$; $\alpha_D = -15.93^\circ$.

l-Dihydrocarvone Hydrochloride. - According to Klotz (1944), saturation of the remaining double linkage is attained on passing dry hydrogen chloride into the ketone until an increase in weight corresponding to 120% of the theoretical amount has occurred. The product of this process was found, on distillation, to contain unchanged l-dihydrocarvone, and further treatment with hydrogen chloride was necessary to give the required material which distilled at $68-70^\circ/0.25$ mm. and had $n_D^{20} = 1.4800$; $\alpha_D = -13.07^\circ$.

d-Carvone. - Ring closure of the above dihydrocarvone hydrochloride was effected in alcoholic potassium hydroxide, essentially as described by Richter, Wolff and Presting (1931), but modified according to Klotz (loc. cit.). The product had b.p. $86-87^\circ/12.2$ mm.; $n_D^{20} = 1.4781$; $\alpha_D = +131^\circ$. Removal of unsaturated impurities by washing with neutral permanganate solution raised the rotation to $+145.6^\circ$, the other properties remaining unchanged.

d-Carvone Oxime. - Oximation of the above ketone by the method of Cook et al. (loc. cit.) resulted in the required material, which, on distillation had, b.p. $123-125^\circ/14$ mm.; $\alpha_D = +283^\circ$.

(-)-2-Chloro-2-nitrosocarane. - Dry chlorine was passed into a solution of the oxime (1.2 gm.) in anhydrous ether (10 ml.) which was kept at -10° by means of a freezing mixture. The usual green colour developed after a few minutes, but chlorination for a period of not less than 1 hr. was found necessary to ensure complete reaction of the oxime. Removal of the solvent and excess chlorine under reduced pressure and without raising the temperature, gave the chloro-nitroso compound as a blue viscous oil which distilled under vacuum, but which was very sensitive to thermal decomposition at bath temperatures even slightly in excess of the boiling point, b.p. 56-57°/0.25 mm.; $[\alpha]_{max.} = +1800°$ at $\lambda = 5900$A°; $\epsilon_{max.} = 16.42$ at $\lambda = 6675°$; Found: Cl, 17.7% $C_{10}H_{16}NOCl$ requires Cl, 17.6%.

(+)-2-Chloro-2-nitroso-p-menthane

l-Carvomenthone. - d-Carvone was obtained as before on distillation of commercial 'carvol', and hydrogenated as described by Read and Johnston (1934) with a palladium hydroxide-calcium carbonate catalyst. After 3.25 hr. 97.8% of the theoretical amount of hydrogen had been absorbed. The product contained a considerable amount of carvacrol by isomerisation of the original ketone, and since this is inseparable by distillation, the above material was used in preparation of the next stage and purification effected there.

1-Carvomenthone Oxime. - The crude 1-carvomenthone was oximated by the usual pyridine method and the resulting mixture poured into ice-water. The precipitated oxime was dried on porous plate, then 'in vacuo' and on crystallisation from low-boiling petroleum had, m.p. 95-97°; $[\alpha]_D = -30.9^\circ$ (1.1% alc.).

(+)-2-Chloro-2-nitroso-p-menthane. - The oxime (2.5 gm.) in dry ether (100 ml.) was chlorinated for 0.5 hr. at 0°, the solution initially becoming a deep blue, and later green. Removal of the solvent and excess chlorine under reduced pressure left the blue non-viscous chloro-nitroso compound, b.p. 53.5°/0.5 mm.; $[\alpha]_{max} = +353^\circ$ at $\lambda = 7100A^\circ$; $\epsilon_{max.} = 14.08$ at $\lambda = 6870A^\circ$; Found Cl, 17.3% $C_{10}H_{18}NOCl$ requires Cl, 17.4%.

(-)-3-Chloro-3-nitroso-p-menthane

1-Menthone. - Chromic oxidation of 1- menthol was found to proceed satisfactorily (Org. Syn., I, 340) giving the required ketone in good yield and in a high degree of stereochemical purity. Re-distillation gave a product with the properties, b.p. 78.5°/10 mm.; $n_D^{20} = 1.4506$; $[\alpha]_D^{20} = -24.9^\circ$ (1% alc.).

1-Menthone Oxime. - Oximation of the above ketone proceeded smoothly by the usual method, yielding a product which distilled under reduced pressure, b.p. 82°/0.2 mm. and solidified to a low-melting solid on standing overnight at 0°.

l-Menthone Oxime Hydrochloride. - Dry hydrogen chloride was passed into a solution of the oxime (2 gm.) in anhydrous ether (20 ml.) for 2-3 min. after which the excess gas and about half of the solvent were removed at the pump. On allowing this solution to stand in the refrigerator, the required oxime hydrochloride was obtained as a fine crystalline material, m.p. 117-118°.

(-)-3-Chloro-3-nitroso-p-menthane. - A solution of the oxime hydrochloride (0.5 gm.) in dry ether (250 ml.) was chlorinated in the usual way for 2.5 hr., during which time the colour gradually developed to a dark green. Removal of the solvent and excess chlorine left a residual blue oil which was taken up in the minimum volume of light petroleum, and traces of oxime hydrochloride filtered off. The filtrate yielded the required chloro-nitroso compound which distilled under vacuum, b.p. 56°/0.25 mm.; $[\alpha]_{max.} = +225°$ at $\lambda = 6200A°$; $\epsilon_{max.} = 20.62$ at $\lambda = 6750A°$; Found; Cl, 17.5% $C_{10}H_{18}NOCl$ requires Cl, 17.4%.

Inactive 2-Chloro-2-nitroso-1-methylcyclohexane

The oxime of 2-methylcyclohexanone, prepared by the pyridine method had b.p. 114-115°/16 mm. and yielded an oxime hydrochloride on treatment of an ethereal solution with dry hydrogen chloride. Chlorination of this salt (0.5 gm.) in anhydrous ether (250 ml.) at 0° for 2 hr. gave an emerald green solution. Removal of the solvent and excess chlorine under reduced pressure left the required compound as a viscous blue oil, b.p. 67-68°/14 mm.; $\epsilon_{max.} = 15.14$ at $\lambda = 6850$; Found: Cl, 22.0% $C_7H_{12}NOCl$ requires Cl, 22.0%.

SUMMARY

Investigation of the photochemical reactions attending light absorption of a number of chloro-nitroso terpene derivatives has shown a simple intramolecular rearrangement in the case of the following compounds

(i) (-)-2-chloro-2-nitrosocamphane
(ii) (+)-2-chloro-2-nitrosopinane
(iii) (-)-2-chloro-2-nitrosocarane
(iv) (+)-2-chloro-2-nitroso-p-menthane
(v) (-)-3-chloro-3-nitroso-p-menthane
(vi) i -2-chloro-2-nitroso-1-methylcyclohexane.

When such photoisomerisation occurs by transformation at an asymmetric carbon atom, there is a resultant change in optical rotatory power and the process has been more accurately described as 'photomutarotation'.

The phenomenon was first observed with (-)-2-chloro-2-nitrosocamphane (Mitchell, Watson and Dunlop, J., 1950, 3440) which has formed the parent member of the above series, the others having been structurally designed to illustrate the environmental influence of the neighbouring groups and ring system of the camphane skeleton on the chromophoric centre.

Three distinct methods of investigation have been employed, studies of (a) optical rotatory power, (b) electronic absorption spectra, and (c) reaction kinetics. The first of these has found particular application in the case of (i) where spectral displacement and reversal of the Cotton effect on irradiation indicates inversion of the chlorine and nitroso groups about the active centre. The second method has shown the bathochromic displacement of absorption characteristic of this change, and kinetic measurements illustrate a complex mechanism which has been successfully analysed to consecutive First Order component processes. Final evidence of the postulated rearrangement has been provided by isolation of the isomeric (+)-2-chloro-2-nitrosocamphane form the product of irradiation of the (-) form.

In all other cases, skeletal transformation of the normal → iso type has been found to take place, and occurs more readily than inversion of the asymmetric centre. Such a change causes a decrease in specific rotation without reversal of the original Cotton effect. The usual displacement of absorption is observed and kinetic studies have shown the overall mechanism to be similar to that of (i).

Configurations have been assigned to each pair of stereoisomeric compounds from considerations of their optical properties. These are based on the structures of (+)- and (-)-2-chloro-2-nitrosocamphane which in turn have been derived from the established configurations of the closely related bornyl and isobornyl chlorides.

It is concluded that isomerism proceeds through steric interaction of the photo-excited chromophore and vicinal alkyl group or ring system, whichever is more favourably situated. Photomutarotation results only when the molecular structure is rigidly fixed. In all other cases skeletal rearrangement is preferred.

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