PHOTOCHEMICAL STUDIES
WITH
CHLORONITROSO-COMPOUNDS

THESIS

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by

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1. INTRODUCTIONS.

(i) Optical Rotatory Dispersion.

The rotation of the plane of polarisation of a beam of light by a quartz plate (cut perpendicular to the axis) was discovered by Arago (1) in 1811. Biot showed that the angle of rotation is directly proportional to the thickness of the plate and inversely proportional to the square of the wavelength of the light. Biot (2) also demonstrated "Optical Activity" in organic liquids and solutions and he introduced the term "pouvoir rotatoire moleculaire" now called "Specific Rotation" which he showed to be affected by temperature, solvent, and concentration.

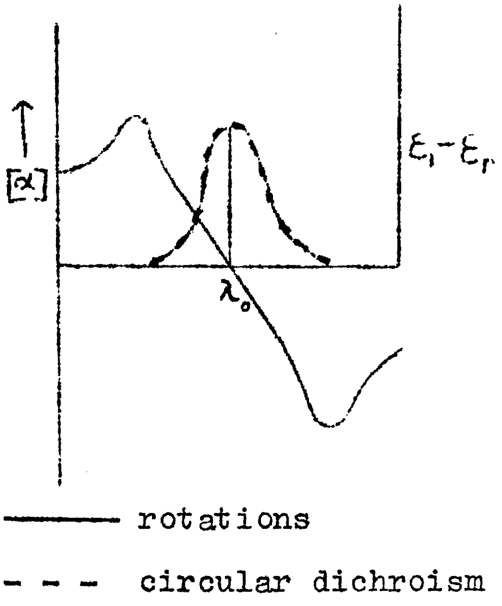
Fresnel (3) showed that when a beam of monochromatic plane polarised light enters a transparent optically active medium it is resolved into two circularly polarised beams (one right handed and the other left handed) which travel with different speeds. On emerging from the medium they recombine to give a beam of plane polarised light with its plane of polarisation rotated through an angle equal to half the phase difference developed between the two circular components,

$$\alpha = \frac{\pi l}{\lambda}(n_l - n_r)$$

where l is the length of medium (in cms.) through which the light passes and n_l, n_r are the refractive indices of the medium for left handed and right handed circularly polarised light.

Cotton (4) showed that in certain coloured optically active solutions unequal absorption of the two circularly polarised beams occurs. He called the phenomenon "Circular Dichroism".

Cotton made a detailed study of Fehling's solution and solutions of potassium chromium tartrate and found that these solutions show "Anomalous Rotatory Dispersion", that is they do not obey Biot's inverse square law, and, in the region of absorption these solutions exhibit circular dichroism.



The figure shows the type of results obtained in the neighbourhood of an absorption band (ε_{max} at λ_0).

The circular dichroism curve has much the same shape as the absorption curve with a maximum at λ_0.

Approaching the band from longer wavelengths the specific rotation increases at first, reaches a maximum near λ_o, drops to zero at λ_o, falls to a minimum on the short wave side of λ_o and then increases again. This "Cotton Effect" is quite general for optically active substances in the region of "Optically Active" absorption bands. The sign of the circular dichroism ($\varepsilon_l-\varepsilon_r$) is the same as the sign of the rotation on the long wave side of the absorption band (Natanson's rule).

Drude (5) deduced equations for circular dichroism and rotatory dispersion in the region of absorption assuming that the electrons in the optically active medium move in helical paths under the influence of the fields produced by light waves.

His equations can be given as:-

$$\varepsilon_l - \varepsilon_r = \frac{4\pi \operatorname{Log}_{10} e}{C} \times \frac{D\Gamma\lambda}{(\lambda^2-\lambda_o^2)^2+\Gamma^2\lambda^2}$$

$$n_l - n_r = \frac{D\lambda(\lambda^2-\lambda_o^2)}{(\lambda^2-\lambda_o^2)^2+\Gamma^2\lambda^2}$$

where D is a constant λ_o the wavelength of the head of the absorption band and Γ a damping factor related to the half width of the band.

Using these equations Natanson obtained good agreement between the observed and calculated data for solutions of potassium chromium tartrate.

When rotation measurements at wavelengths well removed from an absorption band are considered, Drude's equation may be simplified to

$$[\alpha] = \sum \frac{k}{\lambda^2 - \lambda_0^2}$$

where k is a constant and λ_0 a wavelength, usually in the ultra-violet region. In many cases one term is sufficient to express the rotatory dispersion and even quite complicated curves can often be represented by two terms.

Boys (6) assumed that, in simple molecules with one asymmetric carbon atom, the rotatory power depended on the polarisability of the four groups surrounding the central carbon atom. Using observed specific refractivities he was able to calculate the order of magnitude of the rotations of a few simple molecules such as secondary butyl alcohol. He also claimed to have established the absolute configurations of a few simple molecules. According to Boys when a dextro molecule is viewed, with the largest group nearest to the observer the other groups are observed to decrease in size in a clockwise direction.

Born's Theory (7) assumes the existence in an optically active molecule of at least four non-planar isotropic coupled oscillators.

In Kuhn's theory (8) two non parallel anisotropic oscillators are assumed to be present in the optically active molecule. Kuhn uses frequencies throughout, and develops an expression (similar to that of Drude) involving the oscillator strength of the band and the anisotropy factor ($g_0 = \frac{\varepsilon_l - \varepsilon_r}{\varepsilon}$) in the constant D. By using the empirical equation:-

$$\varepsilon = \varepsilon_0 e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2}$$

in the expression for the oscillator strength Kuhn finally arrives at the equation.

$$[\alpha] = \frac{57 \cdot 30}{2\sqrt{\pi}} \frac{\nu}{\nu_0} g_0 \varepsilon_0 \left[e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)} \int_0^{\frac{\nu_0 - \nu}{\theta}} e^{x^2} dx - \frac{\theta}{2(\nu_0 - \nu)} \right]$$

θ is the half-width of the band divided by 1.6651. In the more modern theories which have been developed in America (9), the coupling of two or more oscillators is considered unnecessary for the development of optical activity, since this can arise from the motion of one electron in the unsymmetrical fields present in an asymmetric molecule. The absorption by a molecule in the visible and ultra violet regions of the spectrum is due to electronic transitions. Most molecular spectra can be accounted for on the basis of one electron transitions in the chromophoric groups. First of all it is necessary to assign definite electronic states to the chromophoric group and definite transitions to each absorption band. The perturbation of these states by neighbouring atoms and groups then leads to altered states which give transitions which are optically active provided the system as a whole has no plane or centre of symmetry.

The one electron theory gives an explanation of the "induced optical activity" shown, for example, by the carbonyl group of many optically active ketones since any dispersion electron may be made optically active if Coulombic effects transmitted through space from other atoms in the molecule place it in a dissymmetric field.

Kwoh and Eyring (10) have recently calculated values for the rotatory power of benzoin using the one electron theory. Their results are of the same order of magnitude as observed experimentally.

A general quantum mechanical theory of optical activity which includes the one electron theory, the coupling theory, and additional terms involving the products of the electric moment of one group with the magnetic moment of a different group, was evolved by Kirkwood (11). Kirkwood's theory is essentially a simplification of Born's theory expressed in quantum mechanical form. In the quantum theory of rotatory power the molecular rotation, at frequency v, is given by the expression:-

$$[M]_{\nu} = \frac{288\pi^{2} N \nu^{2}}{c^{2}} \frac{(n_{\nu}^{2}+2)}{3} g_{\nu}$$

For the specific rotation using sodium light this becomes:-

$$[\alpha]_D = 4.96 \times 10^5 \frac{n^2 + 2}{3M} g$$

By a simple transformation of Born's expression for the gyration parameter (g) Kirkwood obtained the expression

$$g = g^{(o)} + g^{(1)} + \sum_{K=1}^{N} g_k$$

where $g^{(o)}$ is the sum over pairs of groups involving the magnetic moments of the electronic centres of gravity of these groups relative to the molecular centre of gravity (Kirkwood's term)

$g^{(1)}$ is a similar sum involving the magnetic moments of each group relative to its own centre of gravity

and g_k is the gyration parameter of group k relative to its own centre of gravity (Condon's one electron term)

If it is assumed that the phase of the incident light can be regarded as the same throughout each individual group then the terms $g^{(1)}$ and g_k vanish. As a first approximation, in his calculations Kirkwood put $g = g^{(o)}$ and neglected the other terms.

All workers have neglected $g^{(1)}$ which is always small, and in the one electron theory the terms g_k

are regarded as important and $g^{(o)}$ has been neglected.

Recently Kuhn (12) has reviewed the quantum mechanical approach to optical activity. He considers that the term $g^{(o)}$, which corresponds to his coupling theory, is the most important.

Although he admits that the one electron theory has made an outstanding contribution to the basic theory of optical activity, he states that the contribution of the one electron terms are only significant in exceptional cases in comparison with the coupling theory terms. He also points out that the high value of the anisotropy factor, which is observed in many weak absorption bands, had been incorrectly regarded as evidence in favour of the one electron theory. Kuhn warns his readers that although, when using the one electron theory, by choosing suitable parameters, it is possible to obtain values, for the specific rotation of an optically active substance, which are of the right order of magnitude, it is not permissible to neglect the coupling term when assigning configurations to the two enantiomorphs. The question of absolute configurations is discussed in the next section.

It is interesting to note that all the theories of optical activity, both classical and quantum, give terms for the rotatory dispersion which, in regions of transparency, reduce to simple Drude equations.

In the last few years, since the spiral structures of D.N.A. (13) and some polypeptides has been discovered coupled oscillator theories have, once more, aroused some interest. Thus it has been shown that for every transition in its individual residues, a helix has two transitions whose moments are respectively parallel and perpendicular to the screw axis. Accordingly Moffitt (14) says, "Polypeptides and D.N.A. are perhaps the only family of molecules to which one may, in the light of modern valence theory, apply the coupled oscillator theory with reasonable confidence".

More recently Murakami (14) has accounted for the observed rotatory dispersion of proteins and D.N.A. on the basis of Kirkwood's (11) coupled oscillator theory. In the case of D.N.A. it was also necessary to take account of Condon's (15) one electron effect.

Unfortunately, while the problem of optical activity is solved in a mathematical sense, it is not yet possible to compute optical rotatory powers with accuracy.

When in an asymmetric molecule, the following chromophoric groups have been shown to exhibit the Cotton effect -NO, -ONO, $-NO_2$, N_3, -CSS- and >CO.

Kuhn worked with dimethyl α-azidopropionamide in his classical researches on asymmetric photolysis.

Lowry investigated xanthates and other sulphur compounds. During the course of that work Lowry and Hudson (16) fitted their experimental data to Kuhn's equation which they expressed on a wavelength scale. When circular dichroism measurements are not available the modified equation:

$$[\alpha] = \frac{[\phi]}{m}\,\frac{\lambda_0}{\lambda}\left[e^{-\left(\frac{\lambda_0-\lambda}{\theta}\right)}\int_0^{\frac{\lambda_0-\lambda}{\theta}} e^{x^2}\,dx - \frac{\theta}{2(\lambda+\lambda_0)}\right]$$

is useful. $[\phi]$ is the maximum value of the specific rotation and m is the maximum value of the expression in the brackets.

These equations have been used in several of Mitchell's papers on nitroso and nitro compounds and they provide a useful correlation between absorption and circular dichroism on the one hand and rotatory dispersion on the other.

Recently Djerassi (17), who has studied very many optically active compounds containing the carbonyl group, has suggested a convenient classification of rotatory dispersion curves into three types:-

1. Plane curves. Curves with no maximum or minimum, called positive or negative according as they rise or

fall towards shorter wavelengths.

2. Single Cotton effect curves. Curves with one maximum and one minimum. These are positive or negative according as the wave is entered from the positive or the negative side going towards shorter wavelengths. Djerassi favours the terms peak and trough rather than maximum and minimum which can be misleading.

3. Multiple Cotton effect curves. Curves with several peaks and troughs.

(ii) Recent developments in polarisation apparatus

Advances have recently been made in the practical measurement of rotatory dispersion. Thus, in addition to his contributions to the theory of optical activity, Kuhn (18) devised an ultraviolet polarimeter which was used in conjunction with a quartz spectrograph.

The rotatory dispersion of many organic substances which absorb in the ultraviolet has been determined with modifications of this apparatus. Mitchell and co-workers (19) have studied 2:2-dinitrocamphane, santonide, and parasantonide which in cyclohexane has the highest specific rotation peak of any known solution.

The rotatory dispersion of quartz (20) and some organic substances have been measured in the infra-red region of the spectrum but interest in this field was limited, as for many years measurements were difficult and no examples of anomalous rotatory dispersion in the infra-red region had been observed. More recently, however, interest has been aroused by some workers in America and Switzerland. Gutowsky (21), using a Perkin-Elmer model 12B infra-red automatic recording spectrometer, in conjunction with two selenium film infra-red polarizers, has measured the rotatory dispersion of α-quartz from 2.2 - 9.7μ. He observed anomalous retatory dispersion in the vicinity of the absorption band at 3.7μ. Hediger and Günthard (22) describe infra-red polarizers consisting of 6 selenium foils 10μ thick which, they claim, give 94% polarization by transmission. They have studied the retations of methyl ethyl carbinol and (-)-methyl- -methcxy propionate in some of the absorption bands, and claim to have observed anomalous rotatory dispersion.

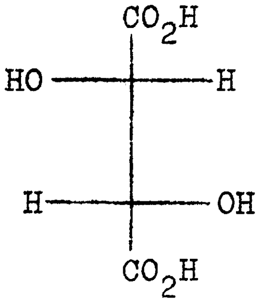
Photoelectric polarimeters are now also being used. Rudolph (23) describes a polarimeter which is available commercially in America. Quartz Rochon prisms are employed as polariser and analyser and the rotations are measured by the method of symmetrical angles, using a photomultiplier. Brand and co-workers (24) have used a zirconium arc and a Beckmann monochromator in conjunction with the Rudolph polarimeter in order to measure the rotatory dispersion, from 7500-2500Å, of some steroids, amino acids and peptides.

Mitchell (25) describes an attachment which can be fitted to a Unicam spectrophotometer in order to enable r~~e~~tation and circular dichroism measurements to be made. With it the rotatory dispersion of caryophyllene nitrosite has been measured up to 10,000 Å and I have measured the circular dichroism of several chloronitroso-compounds. There is no reason why, with a suitable photomultiplier Mitchell's apparatus should not be used for measurements in the ultraviolet.

(iii) The Problem of Absolute Configuration.

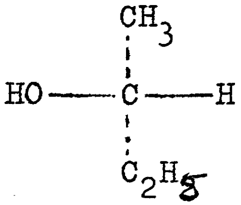
Every optically active substance can exist in two enantiomorphic forms and for many years chemists have wanted to know which form represents the dextro-and which the laevo-compound.

Relative configurations have been known for many years and Fisher (26) related his compounds to D(-)-tartaric acic which was represented by convention as shown (assuming the H and OH groups above the plane of the paper and the CO_2H groups below)



There are two approaches to the problem of absolute configuration. The theory of optical rotatory power can be applied to a given structure and the sign of the calculated rotation immediately enables the dextro-or laevo-label to be assigned to the given structure or a compound of known sign of rotation can be taken and its structure determined.

Applying their theories of optical activity to the enantiomorph of sec-butanol shown various workers arrived at conflicting results.



Boy's and Kirkwood's theories assigned the configuration shown to the dextro-form while Kuhn's theory assigned it to the laevo-form, and the one electron theory to either form depending on the assumptions made in the calculation.

More recently the absolute configurations of the tartaric acids have been investigated by Bijvoet (27) at Utrecht. He determined the structure of sodium rubidium tartrate using zirconium K_α radiation which just excites X radiation from the rubidium atom and enables the determination of the absolute configurations to be made. Fortunately, as it happens, the Fischer convention is correct. This means that the molecule shown is l-sec-butanol as Kuhn predicted.

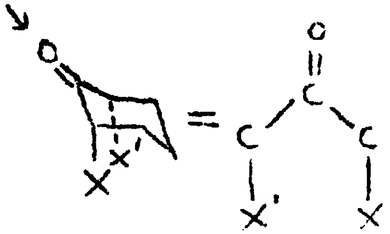
In a series of papers Djerassi (28) has recently tried to correlate the absolute configuration of some optically active ketones with the sign of the Cotton effect.

Much of his work has been concerned with steroids, which are particularly suited to this type of investigation since they contain a chain of seven contiguous asymmetric carbon atoms, and, as any carbonyl group in the ring structure cannot be more than one carbon atom removed from this chain, it is not surprising that the position of the carbonyl group affects the Cotton effect of the whole molecule. He has already measured the rotatory dispersion of more than 600 steroids and shown how the shape of rotatory dispersion curve can be related to the position of the carbonyl group and the configuration of the carbon atoms in the chain. Thus in 3-keto-steroids the form of the rotatory dispersion curve provides the simplest method of determining the cis- or trans-fusion of rings A and B.

Djerassi (29) then extended his investigations to simpler ketones. For, "Since the absolute configuration of steroids, with respect to D-glyceraldehyde, is known and since the dispersion curves of steroidal ketones are found again in their bicyclic analogues, it is concluded that it is possible to establish the absolute configuration of numerous simple molecules by comparing their rotatory dispersion curves with the curves of appropriate reference steroids".

For example in this way Djerassi claims to have shown that the configuration allotted by Klyne (30) on the basis of molecular rotation differences for the sodium D line, to the sesquiterperoid ketone eremophilone is incorrect.

Djerassi has also studied the effect of halogenation on ketones. Equatorial substitution of chlorine or bromine in the carbon atom next to the carbonyl group does not appear to affect the sign of the Cotton effect but in axial substitution the $-\overset{O}{\overset{\|}{C}}-\overset{X}{\overset{|}{C}}-$chromophore becomes dominant and controls the sign of the Cotton effect. According to Djerassi (31) in a ring ketone, looking along the O=C< bond in the direction of the arrow, if the axial chlorine or bromine atom lies to the right (i.e. X) then the Cotton effect will be positive if to the left (i.e, X^1) negative.



While the determination of absolute configurations from rotatory dispersion data, over a wide range of wavelengths, appears to be more reliable than the older methods, based on differences of molecular rotation at a given wavelength, only time will show whether too much confidence is being placed on the newer method.

It does not appear to be possible to deduce the configurations of simple optically active aldehydes from rotatory dispersion measurements since Levene and Rothen (32) have shown that 2-methyl-butanol and 3-methyl-pentanol, of like configuration have opposite Cotton effects.

Unfortunately in my researches, on chloronitrosoterpenes, I have been unable to relate the sign of the Cotton effect to the configuration of the groups about carbon atom 2, but I have tried to deduce the configuration from other consideration such as conformational analysis and liability to photomutarotation.

(iv) Asymmetric photolysis

Over sixty years ago Van't Hoff (33) suggested that circularly polarised light might be employed as an asymmetric photochemical agent.

Early attempts to obtain an asymmetric photolysis were all unsuccessful because insufficient care was taken to fulfil all the requirements.

Thus since only absorbed light can bring about decomposition asymmetric photolysis need not be expected if both enantiomorphs absorb light, of the wavelengths which bring about decomposition, to the same extent.

After Cotton had demonstrated the circular dichroism of solutions of copper d-tartrate he endeavoured to bring about the asymmetric photolysis of an alkaline solution of copper racemate by exposing two glass cells, containing the solution, to right handed and left handed circularly polarised light respectively (34). Neither of the solutions developed rotation.

The failure of Cotton's experiment was readily understood after Mitchell (35) had shown that Fehling's solution does not exhibit circular dichroism in the near ultra-violet region of the spectrum which Byk (36) had shown to be responsible for the decomposition.

In order to achieve a successful asymmetric photolysis it is necessary to use the racemic form of an optically active substance which:-

1) is decomposed by light of suitable wavelengths with the destruction of an asymmetric centre ($\gamma \ll 1$).

2) exhibits circular dichroism at the wavelengths which may bring about the decomposition.

3) is stable in the dark.

It is convenient to use a solid which is readily recovered in a pure condition from the partially photolysed mixture.

For a compound fulfilling these conditions Kuhn (37) has deduced the relationship:-

$$\alpha^1 = \alpha\frac{g}{2}\,(1-\beta)\ \mathrm{Log}\ \frac{1}{1-\beta}$$

where α^1 = rotation developed by solution containing the dl-mixture.

α = rotation for solution of pure d-compound
(conc. equal to that of dl mixture at start)

g = anisotropy factor = $\frac{\varepsilon_l - \varepsilon_r}{\varepsilon}$

β = fraction of material decomposed

The maximum rotation is developed in a solution which has been about 60% decomposed

($\alpha^1/g\alpha = 0.183$)

Kuhn (37) and his co-workers obtained two positive results.

On exposure of alcoholic solutions of ethyl α-bromopropionate to circularly polarised U.V. light ($\lambda = 2800$ Å) until 50% of the ester was decomposed and recovery of the residual ester rotations of up to 0.05° (1 dm tube) were obtained.

More conclusive results were obtained on exposure of hexane solutions of the recemic form of the dimethylamide of α-azidopropionic acid to circularly polarised light (3200 - 2800 Å). After about 40% decomposition the dimethylamide was recovered from the cells. That from the cell which had been irradiated with right handed circularly polarised light showed a rotation of $+ 0.78^{\circ}$ (1 dm., Hg yellow light) and for that which had been irradiated with left handed circularly polarised light the rotation -1.04° was found.

Substituting the values $\alpha = 340^{\circ}$, $g = 0.024$, and $\beta = 0.4$ in Kuhn's equation $\alpha^{1} = 1.25^{\circ}$ so the observed rotations are of the same order as the expected rotations.

Mitchell's asymmetric photolysis of humulene nitrosite is described in the following section dealing with with C-nitroso compounds.

(v) Nitroso Compounds and the Cotton Effect

Compounds containing a nitroso group directly attached to carbon are suitable for photochemical studies since, except when they form dimers, they are all coloured blue and give blue solutions which decompose when exposed to light of suitable wavelengths. The maximum absorption for visible light occurs between 6800 and 6200 Å and thus in many cases it is possible to measure rotations on both sides of the absorption band using a visual polarimeter.

Many of these nitroso compounds have been studied by Dr. Mitchell and his co-workers at Glasgow during the last three decades.

The earliest compounds to be studied were the nitrosites of caryophyllene and humulene (38) which are readily obtained from the hydrocarbons by treating them with nitrous acid. The first asymmetric decomposition produced by visible light was the photolysis of a solution of humulene nitrosite in ethyl butyrate but unfortunately the products have not been isolated and, as humulene cannot be obtained in an optically active state, the rotation which should be developed on irradiation with circularly polarised light cannot be calculated. If racemic caryophyllene could be prepared, its nitrosite would be a suitable substance for asymmetric photolysis.

Interesting results were obtained by Mitchell and Cormack (39) who studied the nitrosites of bornylene, phellandrene and zingiberine. Bornylene nitrosite is a white crystalline solid which dissolves in organic solvents at room temperature to give colourless solutions. At 14° a 1.6% solution shows a slight irregularity in its rotatory dispersion but when the solution is warmed a blue colour develops as the dimeric molecules dissociate and at 63° a definite peak and trough in the rotatory dispersion curve is seen.

The pseudo-nitrols are readily prepared by adding fuming nitric acid to acetic acid solutions of ketoximes and Mitchell and Gordon (40) studied them as it was thought that they might be suitable for asymmetric work since the NO group is readily oxidised to NO_2 in the presence of light.

Unfortunately, however, oxidation can occur even in the dark and work on these compounds was abandoned.

Attention was then directed to some observations of Lynn (41) who found that when a solution of nitrosyl chloride in n-heptane was exposed to sunlight a transient blue colour developed, hydrogen chloride was evolved, and an oil separated. Later the oil was shown to contain di-n-propyl ketoxime. It was concluded that the blue colour was due to the formation of secondary nitroso paraffins which in presence of light isomerised to the corresponding ketoximes thus:-

$$C_7H_{16} + NOCl \xrightarrow{-HCl} \underset{\text{(blue)}}{C_7H_{15}NO} \xrightarrow{\text{(red light)}} C_7H_{14} : NOH \text{ (oil)}$$

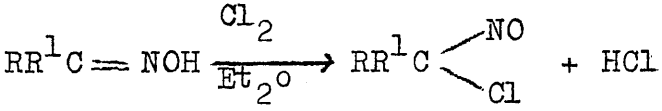
This reaction appeared to be promising for asymmetric photochemical work since if n-hexane were used instead of n-heptane secondary nitrosoparaffins with asymmetric carbon atoms would be obtained and the asymmetric centre would be destroyed on photoisomerisation. Accordingly Mitchell and Carson (42) studied the action of sunlight on a solution of nitrosyl chloride in n-hexane. They showed that the blue compounds were formed by the action of light at the blue end of the spectrum and decomposed by red light. By irradiating the solution through a filter of copper sulphate solution and fractional distillation of the blue solution formed, they obtained a blue liquid, bp = 39-42° /13m.m., which was shown to consist mainly of a mixture of $\beta\beta$ - and $\gamma\gamma$ -chloronitrosohexanes. It was shown that if the blue compounds were dissolved in alcohol and exposed to red light photolysis took place with the formation of oximes and the solution remained homogeneous.

It had previously been shown by Reinboldt and

Dewald (43) that chloronitroso compounds were converted by the action of light and air into the corresponding chloronitro compounds but they did not try photolysis in the absence of oxygen.

Reinboldt and Dewald prepared their chloronitroso compounds by the action of nitrosyl chloride on etherial solutions of the corresponding ketoximes.

Earlier Piloty (44) had prepared bromonitroso and chlorinitroso compounds from aqueous or hydrochloric acid solutions or suspensions of the ketoxime and free bromine or chlorine. Mitchell and co-workers (45) found that the chlorine treatment could conveniently be carried out using ether~~i~~al solutions of the ketoxime



$$RR^1C{=}NOH \xrightarrow[Et_2O]{Cl_2} RR^1C\begin{matrix}\diagup NO\\ \diagdown Cl\end{matrix} + HCl$$

This is the method of preparation which has usually been employed at the Glasgow School

Hammick and Lister (46) did some photochemical experiments on chloronitroso compounds and attempted to measure the quantum yields of the photolyses.

Unfortunately, however, they did not take sufficient care to exclude oxygen from their solutions and so their results were somewhat uncertain. They did not investigate the photolysis products but it is interesting to note that they believed that the primary reaction was an elimination of the radical NOH and they detected very little hydrogen chloride.

Dr. Mitchell and his co-workers (45) on the other hand found that at least about 90% of the chlorine in their chloronitroso compounds was liberated in the ionic form during photolysis.

More recently Naismith (47) has shown that, in the case of β-chloro-β-nitroso-$\gamma\gamma$-dimethylbutane both reactions take place. In benzene or carbon tetrachloride Hammick's scheme holds good and the principal products are tetramethylethylene dichloride and a gummy polymer. In much of Hammick's work benzene was used as solvent. In alcohol or methanol tertiarybutyl ketoxime, hydrochloric acid, and acetaldehyde or formaldehyde are the main products although Hammick's reaction also occurs to some extent.

In most of the photochemical work of the Glasgow School alcohol or methanol has been used as solvent as it is advantageous to handle a homogeneous reaction mixture and to avoid the additional experimental complications associated with the evolution of gaseous reaction products.

By 1940 it was known that alcoholic solutions of many of these chloronitroso compounds are photolysed by red light with a quantum yield of about unity. It was hoped that, since most of the chloronitroso compounds are asymmetric, it might be possible to bring about an asymmetric photolysis using circularly polarised light but, as no chloronitroso compounds had been prepared in optically active forms, it was not possible to measure the circular dichroism of a chloronitroso compound and predict the magnitude of the rotations which might be expected to develop on irradiation of a solution with right or left handed circulary polarised light. In 1940 Mitchell and Simpson (48) prepared l-menthyl d-β-chloro-β-nitroso-butyrate and measured its rotatory dispersion, absorption, and circular dichroism. The specific rotation rises to a peak of + 485° at 6600 Å and reaches a trough of -115° at 5660 Å. The absorption reaches a maximum ($\mathcal{E}$ = 17.20) at 6350 Å, and the circular dichroism ($\epsilon_l - \epsilon_r$) reaches a maximum of 0.650 at the same wavelength. This gives an anisotropy factor of 4%. The substance is interesting since when the partial rotations due to the NO group, calculated from Hudson's equation, are subtracted from the observed rotation the remaining curve gives the normal rotatory dispersion of the rest of the molecule.

Mitchell and Dawson (49) irradiated solutions of β-chloro-β-nitroso-αδ-diphenylbutane in methanol with right and left handed circulary polarised light until 90% of the starting material had been photolysed the rotations developed were $\alpha^{20}_{5300} = -0.10^\circ$ and $+\ 0.11^\circ$ respectively ($l = 1$, $C = 4\%$) in methanol. This corresponds to $[\alpha]^{20}_{5300} = -2.50^\circ$ and $+\ 2.75^\circ$.

Similar results were obtained by Naismith (47) working with β-chloro-β-nitroso-γγ-dimethylbutane and β-chloro-β-nitroso-n-hexane. He also succeeded in resolving γ-chloro-γ-nitroso-δ-phenylvaleric acid by recrystallization of its (+)-d-(2-hydroxy-1-naphthyl) benzylamine salt from ethyl acetate.

The rotation reaches a peak of + 372° at 5900 Å and a trough of - 394° at 6800 Å. The maximum value of the anisotropy factor is 2.3%, a disappointingly low value.

Two courses of action were considered:-

1) The introduction of a nitroso group into an optically active secondary chloro compound.

2) The production of an optically active blue compound by chlorination of the oxime of an optically active ketone.

The first course was tried by Watson (50) but later abandoned since, although in some cases it was possible to introduce a nitroso group into the molecule by irradiating a mixture of the secondary chloride and nitrosyl chloride with blue light, the reaction was complicated by additional substitution of chlorine atoms into the molecule and it was found to be impossible to obtain active material by this method.

The second approach proved more fruitful although, as it necessarily introduces at least one additional asymmetric centre into the molecules, it does sacrifice simplicity.

As several nitroso terpene derivatives had been shown to have high anisotropy factors a terpenic ketone was considered suitable and camphor was selected since it is cheap and readily obtained both in active and inactive forms.

Cap/ (–)-2-chloro-nitroso-camphane, obtained by chlorination of an etherial solution of camphoroxime or camphoroxime hydrochloride and chromatographing the product on a column of Light's alumina, surpassed all expections. The rotatory dispersion curve shows a peak $[\alpha] = +964^{\circ}$ at 6000 Å and a trough $[\alpha] = -964^{\circ}$ at 7000 Å, the molecular extinction coefficient reaches a maximum value of 13.7 at 6600 Å, and the anisotropy factor reaches the remarkable value of 15%. higher than had previously been found for any organic substance.

(-)-2-chloro-2-nitroso-camphane would appear to be the best substance available for the demonstration of the Cotton effect as its absorption band is so conveniently situated in the middle of the visible spectrum.

While (-)-2-chloro-2-nitroso-camphane was being studied a new phenomenon, photomutarotation was discovered. When a solution is irradiated with red light the rotatory dispersion curve is inverted and the absorption is displaced about 60 Å towards the red. From the point of view of asymmetric photolysis this is an unfortunate complication but the new phenomenon is of interest for its own sake and has been the subject of much of the subsequent research on chloronitroso compounds.

Watson also prepared the pyridine salt of (+)-2-chloro-2-nitroso-camphane-10-sulphonic acid, 2-chloro-2-nitroso-isocyclene, and a somewhat impure sample of (+)-2-chloro-2-nitroso-fenchane from commercial fenchone.

Veitch (51) studied some chloronitroso camphor derivatives including those derived from ketopinic acid, apocamphor-1-acetic acid, 10-bromocamphor, and 10-benzylcamphor.

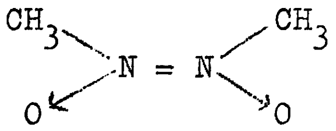
All those compounds show some photoisomerisation as well as photolysis.

Mitchell and Hope (52) studied the chloronitroso derivatives prepared from (-)-pinocamphone, (+)-carone, and (-)-carvomenthone. All these compounds undergo rearrangements as well as photolysis and skeletal rearrangements were postulated to account for the observed band shifts and changes in rotatory power. During this work Hope developed two useful methods of distinguishing between photoisomerisation accompanied by photolysis and simple photolysis. Since both methods depend only on absorption measurements they can both be used even when only inactive material is available for study. In the first method band shifts are clearly shown by exposing the solution to light and making absorption measurements at intervals and then scaling the curves up to the original height if a band shift has occurred all the points on one side of the scaled up curve will be higher and on the other side lower than at the start of the experiment. The second method makes use of the observation that a graph of $\text{Log}_{10}\epsilon$ against time of irradiation is only linear if simple photolysis is taking place.

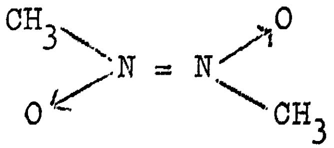
That, then, is the story of the researches of the Glasgow School on nitroso compounds up until 1954 when I started my studies.

Some work on nitroso compounds has been done, in recent years, by chemists in other Schools, although none of them has been interested in either photomutarotation or asymmetric photochemical action.

Coe and Doumani (53) investigating the photolysis of t-Butyl nitrite by U.V. Light obtained dimeric nitrosomethane and acetone. Chilton, Gowenlock and Trotman (54) showed that dimeric nitrosomethane exists in two forms to which they ascribe the structures.



and



This is of interest because two of my compounds are dimeric solids.

Banus (55) prepared trifluoronitrosomethane by the action of U.V. light on a mixture of methyl iodide and nitric oxide in the presence of mercury to absorb iodine and also by treatment of silver trifluoroacetate with nitrosyl chloride.

Lewis and Kasha (56) believed that the absorption of the nitroso group involved a singlet-triplet transition but more recently Orgel (57) considers it to be a σ — π singlet — singlet transition.

Lüttke (58) has published papers giving useful I.R. absorption data for some nitroso compounds.

Most of the papers published in recent years come from Müller's laboratories (59) in Tübingen. Müller described the formation of some chloronitroso cycloalkanes by the action of nitrosyl chloride, or a mixture of chlorine and nitric oxide, on the corresponding cycloalkanes in U.V. light. Müller, who was mainly interested in the preparation of the cyclanone oximes, then described the reduction of the chloronitroso compounds by red light, catalytic hydrogenation, and by a whole host of reducing agents including hydrazine, hydroxylamine, lithium aluminium hydride, zinc and hydrochloric acid and sodium bisulphite. In my work I have had occasion to use both catalytic hydrogenation and reduction with hydrazine hydrate.

Müller also discovered that bis-nitrosocycloalkanes could be obtained if, in the above photochemical preparation, the supply of chlorine was limited. These substances are colourless solids. On heating they melt to the blue monomer which readily isomeriees to the corresponding oxime.

Bis-nitrosocycloalkanes can also be prepared by bromine water oxidation of N-cycloalkylhydroxylamines in solution in hydrochloric acid or by the action of nitrosyl chloride on the Grignard reagent in dry ether.

Perhaps this latter method could be used to prepare 2-bromo-2-nitroso-camphane from 2:2-dibromocamphane.

OPTICAL and PHOTOCHEMICAL MEASUREMENTS.

Scope of the Research

The research had two objects. First to elucidate, if possible, the cause and mechanism of photomutarotation, a phenomenon which had previously been observed by Watson, Veitch, and Hope in some chloronitroso compounds, and secondly to use the information obtained to suggest suitable new compounds for asymmetric photochemical work.

Many of the substances studied by Hope could undergo skeletal rearrangements and moreover were mostly somewhat unstable liquids. My researches have been mainly on chloronitroso compounds in which the carbon skeleton is held rigid by a 1-4 bridge. Later, work was done on some cyclopentane derivatives, and it was discovered that photomutarotation can also occur in them.

In the 1-4 bridged series of compounds I have studied the photomutarotation and photolysis of (-)-2-chloro-2-nitroso-camphane (I), (+)-2-chloro-2-nitroso-10-bromocamphane (II) and (+)-2-chloro-2-nitrosofenchane (III) and I have studied the photolysis of 2-chloro-2-nitroso-norcamphane (IV) which does not undergo photomutarotation.

All these bridged ring compounds photolyse to give similar products, the ketoxime, hydrochloric acid, and acetaldehyde. When the solvent (EtOH) is removed, under vacuum, from the colourless solution of the photolysis products the oxime hydrochloride is obtained in the case of the chloronitroso compounds from camphor, fenchone, and norcamphor but in the case of 10-bromocamphor recrystallization of the product is necessary and the oxime is obtained.

2-chloro-2-nitroso-norcamphane was at first believed to photolyse differently as the quantum yield (0.33) is about ten times higher than that of any of the other bridged ring compounds and acetaldehyde was not detected. It has, however, since been shown that norcamphoroxime hydrochloride reacts with an alcoholic solution of acetaldehyde to yield norcamphor, acetaldoxime and hydrochloric acid. This explains the ready formation of norcamphor 2:4-dinitrophenylhydrazone when 2:4-dinitrophenylhydrazine is added to the photolysis products. Acetaldehyde can be isolated as its dimedone derivative immediately after the photolysis is completed.

In the cyclopentane series of chloronitroso compounds I have studied 1-chloro-1-nitroso-cyclopentane and its 2-phenyl and 3-methyl derivatives. These substances photolyse differently from the 1-4 bridged ring compounds as acetaldehyde cannot be detected in the photolysis products even when the solvent is taken off under vacuum immediately after the photolysis is completed. All the cyclopentane derivatives liberate their chlorine as ions, and in the case of the 3-methyl derivative the quantum yield has been measured and found to be 1.18. This value is similar to that found by Cameron (45) for 2-chloro-2-nitroso-butane and it is possible that the mechanism of decomposition is similar. 2-chloro-2-nitroso-phenylcyclopentane was found to photomutarotate when a solution in benzene or alcohol is exposed to light. A hypsochromic shift of 50 Å is readily observed in the absorption band, and when $\mathrm{Log}_{10}\rho$ is plotted against time of irradiation a curve is obtained which later simplifies to a straight line.

The decomposition, by ultraviolet light, of alcoholic solutions of 2-chloro-2-nitro- and 2-bromo-2-nitro-camphane has also been studied.

In each case the halogen atom is liberated as ion and camphoroxime and acetaldehyde are produced. The sign of the rotation, in the visible, does not change, and in the case of the chloro-nitro-compound it has been shown that the graph of $\mathrm{Log}_{10}\rho$ against time of irradiation is linear.

This shows that photomutarotation has been eliminated and only simple photolysis occurs.

It is thus possible to stop photomutarotation in two ways, either by removing the methyl groups in the vicinity of the -NO chromophore, or by oxidising the chromophore to $-NO_2$. One possible method of suppressing photomutarotation might be to replace the chlorine atom in 2-chloro-2-nitrosocamphane by a larger atom or group but when an attempt was made to prepare 2-bromo-2-nitroso-camphane by the action of bromine or N-bromosuccinimide on camphoroxime in the presence of a weak base the bromonitroso-compound could not be obtained and bromonitrocamphane was formed.

COMPOUNDS STUDIED

I. 2-chloro-2-nitrosocamphane

Experiments with (-)-2-chloro-2-nitroso-camphane.

This compound was extensively studied by Mitchell, Watson, and Dunlop (60) and by Mitchell and Hope (61). During the course of my researches, however, problems have arisen which required further investigation of the properties of this substance. The quantum yield of the photomutarotation has been determined and experiments have been made in an attempt to find a possible mechanism for this process.

The products of the photolysis of the substance in alcoholic solution have been examined and previous findings confirmed. It has been shown that gem-chloronitroso compounds are readily reduced to the corresponding oximes by hydrogenation in alcoholic solution using a Raney nickel catalyst.

Preparation of (-)-2-chloro-2-nitroso-camphane.

Camphoroxime (10gms.) was dissolved in 500 mls dry ether, chlorine was then led in until the solution was dark green in colour, the mixture was then left for a few minutes and then the excess chlorine was removed in a stream of dry air. The ether was then evaporated off in a darkened draught cupboard, the residue dissolved in low boiling pet. ether (bp $< 40^{\circ}$), washed thoroughly with water, and dried over anhydrous sodium sulphate. The blue pet. ether solution was then purified by passing it twice through a 5' x 1½" column of "H" alumina. Finally the pet. ether was evaporated off in a stream of air leaving blue crystals of the pure product.

Yield 1.6 gms mp = 145°

Determination of the molecular weight of (-)-2-chloro-2-nitrosocamphane in benzene.

Nitroso compounds often dimerise in the solid state and are sometimes associated in solution. It was felt that it was desirable to determine the molecular weight of (-)-2-chloro-2-nitrosocamphane in benzene for comparison with that found for dimeric chloronitroso compounds such as those prepared from norcamphor and 2-phenylcyclopentanone. Association, if it had occurred, would have affected the reliability of concentrations calculated from optical density measurements.

20 mls. of benzene (17.58 gms) was placed in the usual Beckmann apparatus and its freezing point determined, a pellet of (-)-2-chloro-2-nitrosocamphane (0.1437 gms) was then added and, after it had dissolved, the freezing point of the solution was determined and the molecular weight calculated from the freezing point in the usual manner.

Freezing point of benzene = 0.555°, 0.560°, 0.565°

mean = 0.560°

Freezing point of solution = 0.775°, 0.770°, 0.770°

mean = 0.772°

$$\text{Therefore } -\Delta T_f = 0.772 - 0.560^\circ$$

$$= 0.212^\circ$$

$$MW = \frac{1000 \times 5.10 \times 0.1437}{17.58 \times 0.212}$$

$$= 196.5$$

$C_{10}H_{16}NOCl$ requires M.W. = 201.7

Therefore (-)-2-chloro-2-nitrosocamphane is monomeric in benzene.

Optical Measurements

Effect of change of solvent on photomutrotation

1. Addition of water.

Solutions of (-)-2-chloro-2-nitroso-camphane were made up in absolute alcohol and in an 80% ethanol-water-mixture. Absorption measurements were made of the original solutions and then again after 45 mins. exposure to the Hg/Cd arc lamp. Rotations were measured at the start of the experiment and then at 15 minute intervals. As the figures below show the course of the photomutarotation is not affected by the presence of water in the solvent.

84.3 mg/5mls EtOH in 1cm cell. 84.3 mg/5mls 80% EtOH-H_2O in 1 cm cell.

λ	ρ_0	ρ_{45}	ρ_0	ρ_{45}
6500	1.078	1.000	1.151	1.035
6550	1.178	1.045	1.194	1.065
6600	1.155	1.079	1.175	1.084
6650	1.104	1.061	1.111	1.087
6700	1.048	1.025	1.035	1.027
6750	0.970	0.970	-	0.970

At 6000 Å		
$\alpha_0 = 1.05^\circ$		$\alpha_0 = 1.05^\circ$
$\alpha_{15} = 0.10^\circ$		$\alpha_{15} = 0.20^\circ$
$\alpha_{30} = -0.38^\circ$		$\alpha_{30} = -0.28^\circ$
$\alpha_{45} = -0.50^\circ$		$\alpha_{45} = -0.55^\circ$

2. Addition of cyclohexene.

64.5mg (-)-2-chloro-2-nitroso-camphane was dissolved in mixture of 4mls EtOH and 1ml cyclohexene. In a 1cm cell $\alpha_0 = 0.88^\circ$ after 30 mins exposure to Hg/Cg lamp $\alpha_{30} = -0.44^\circ$.

3. Irradiation in allyl alcohol.

85.9mg (-)-2-chloro-2-nitrosocamphane made up to 5mls in allyl alcohol, placed in 1cm cell, and irradiated with Cd/Hg lamp.

$\alpha_0 = 1.17^\circ$, $\alpha_{15} = 0.06^\circ$, $\alpha_{45} = -0.46^\circ$, $\alpha_{90} = -0.53^\circ$,

$\alpha_{180} = -0.51^\circ$, $\alpha_{270} = -0.44^\circ$

Photomutarotation is unaffected.

<u>Effect of low temperature</u>

A 0.85% solution of (-)-2-chloro-2-nitrosocamphane in EtOH was placed in a sealed tube and cooled in an unsilvered Dewar flask containing liquid air and exposed to the light from a Cd/Hg lamp.

Absorption measurements in 1cm cell.

λ	ρ_0	$\rho_{4\frac{1}{2}}$
6500	1.122	1.125
6550	1.155	1.155
6600	1.164	1.163
6650	1.115	1.118
6700	1.053	1.053
6750	0.980	0.980

$\alpha^{0}_{6000} = 1.10^\circ$ $\alpha^{4\frac{1}{2}}_{6000} = 1.10^\circ$

These results show that no photomutarotation or photolysis occurred after 4½ hours exposure to the light from the Cd/Hg lamp.

In order to show that the cessation of the photoreactions is not due to the absorption of light by the bluish liquid air, the solution, in a 1cm cell, was placed behind the Dewar flask and irradiated by light which had passed through it. Rotations were measured at intervals and the optical density was determined after 75 minutes irradiation.

$\alpha_0 = 1.10^\circ$ $\alpha_{15} = 0.25^\circ$ $\alpha_{30} = -0.13^\circ$ $\alpha_{75} = -0.53^\circ$

λ	ρ_0	ρ_{75}
6500	1.125	1.014
6550	1.155	1.064
6600	1.163	1.097
6650	1.118	1.101
6700	1.053	1.047
6750	0.980	0.980

Both photomutarotation and photolysis have occurred. Above experiment was repeated substituting acetone and drikold for the liquid air. After 2 hours irradiation the rotation had fallen from + 1.10° to − 0.90° and ρ_{6000} from 1.164 to 1.027. Obviously at −70-80° photomutarotation and photolysis still take place.

Photomutarotation of (-)-2-chloro-2-nitrosocamphane in the solid state

Specimen used in experiment had following properties.

62.9mg/10mls in EtOH   zero = 0.88° l = 1dm

λ	θ	α	$[\alpha]$
6000	5.43	4.55	+723
7000	355.59	-5.27	-827

l = 1cm c = 0.03125

λ	ρ	ε
6400	0.387	12.37
6450	0.405	12.95
6500	0.415	13.25
6550	0.413	13.20
6600	0.395	12.60

About 100mg of the solid material was compressed into a pellet and placed between two discs of cellophane 13mm in diameter. The pellet and discs were placed between two polarimeter tube end glasses and screwed on to one of the end pieces of a polarimeter tube. The pellet was then irradiated through the 10mm apertures of the end piece of the tube for 8 hours using a Cd/Hg lamp. After this time the pellet was removed from the tube. The irradiated portion had lost some of its transparency and undergone some photodecomposition but the outer rim which had been shielded by the brass end screw of the tube was still as transparent in appearance as it had been at the commencement of the experiment. 26.1mg of material made up to 5mls in EtOH gave the following results.

C = 0.522% zero = 0.88° l = 1dm corrected C = 0.424%

λ	θ	α	$[\alpha]$	$[\alpha]$ corrected
6000	359.40	-1.46	-278	-344
7000	2.01	+1.19	+228	+281

l = 1cm C = 0.0257M

λ	ρ	ε
6500	0.267	10.38
6550	0.277	10.78
6600	0.274	10.65
6650	0.264	10.28

Concentration corrected for photolysis = $\frac{0.522 \times 10.78}{13.27} \times 100\%$

Therefore during irradiation $\frac{13.27 - 10.78}{13.27} \times 100\% = 18.7\%$

of the original material underwent photolysis.

Originally 83.5% of the blue compound was in the (-) form

Finally 9.8%

This experiment shows conclusively that photomutarotation can occur in the solid state.

Similar results are obtained when the solid is irradiated in an evacuated tube but under these conditions photomutarotation could be taking place in the vapour phase.

Changes in Circular Dichroism during photomutarotation of (-)-2-chloro-2-nitrosocamphane

Since circular dichroism can now readily be measured on the Unican SP 500 spectrophotometer using the attachment devised by Dr. Mitchell (25), it was decided to observe the changes in the circular dichroism of a solution of (-)-2-chloro-2-nitroso-camphane during the course of its photomutarotation. Accordingly a 1.286% alcohol solution of the blue compound was prepared and measurements were made of its absorption, circular dichroism, and rotation at 6000 Å. The solution (in a 1cm cell) was exposed to the light from a Cd/Hg arc, and the optical measurements repeated after 30 minutes, 100 minutes, and 300 minutes irradiation.

Studies of photomutarotation using Circular Dichroism measurements

$C_0 = 0.0638$ $C_{30} = 0.0620$ $C_{100} = 0.0590$ $C_{300} = 0.0513$

$\alpha_{6000} = +0.94$ $\alpha_{6000} = +0.12^\circ$ $\alpha_{6000} = -0.48$ $\alpha_{6000} = -0.52$

$[\alpha]_{6000} = +731$ $[\alpha]_{6000} = +96$ $[\alpha]_{6000} = -403$ $[\alpha]_{6000} = -504$

$\varepsilon_m = 13.61$

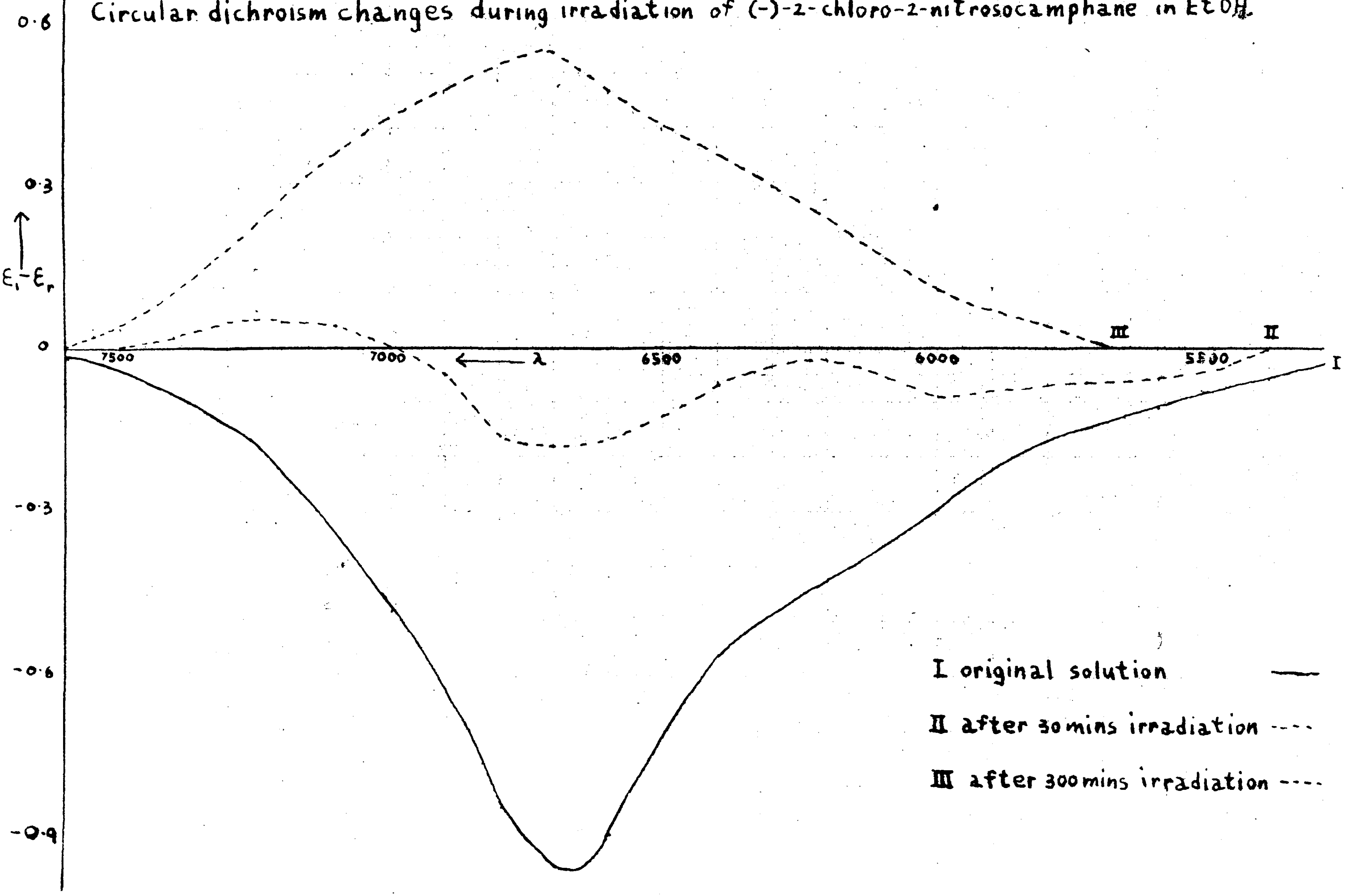
$\rho_m = 0.870$ $\rho_m = 0.845$ $\rho_m = 0.805$ $\rho_m = 0.700$

$\lambda_m = 6575$ $\lambda_m = 6600$ $\lambda_m = 6600$ $\lambda_m = 6600$

Time	0mins	30mins	100mins	300mins
λ	$\varepsilon_1-\varepsilon_r$	$\varepsilon_1-\varepsilon_r$	$\varepsilon_1-\varepsilon_r$	$\varepsilon_1-\varepsilon_r$
7750				0.008
7600	-0.026			0.016
7500	-0.138	0.000	0.049	0.033
7400		0.019	0.131	0.117
7300		0.047	0.175	0.176
7250	-0.179	0.047		
7200		0.047	0.232	0.234
7100		0.040	0.338	0.353
7000	-0.487	0.000	0.379	0.388
6900		-0.050	0.448	0.461
6800	-0.845	-0.163	0.448	0.485
6700			0.448	0.540
6650			0.448	0.493
6600	-0.893	-0.163	0.422	0.461
6550			0.415	0.428
6500			0.394	0.396
6400	-0.566	-0.063	0.337	0.364
6300			0.282	0.290
6200	-0.427	-0.021	0.232	0.234
6100			0.197	0.167
6000	-0.299	-0.092	0.132	0.101
5900			0.059	0.067
5800	-0.158	-0.071	0.029	0.042
5700				0.000
5600	-0.116	-0.063	0.000	0.000
5400	-0.061	0.000	-0.037	0.000
5200	-0.055	-0.042	-0.059	0.000
5000			-0.028	0.000

Graph I.

Circular dichroism changes during irradiation of (-)-2-chloro-2-nitrosocamphane in EtOH.



Estimation of the Quantum Efficiency of the Photomutarotation of (-)-2-chloro-2-nitroso-camphane.

The apparatus used was similar to that described by Mitchell and Schwarzwald (45). Light from a 12 volt projection lamp was rendered monochromatic by means of a Christiansen filter kept at constant temperature in a thermostat. The energy flux was measured by means of a thermopile which was calibrated by means of a Hefner candle. It was found that when the lamp was run off the departmental batteries a very steady energy flux was obtained. The photolyte was contained in a circular glass cell (1cm. thick, capacity 4.27 mls.) fitted with a ground glass stopper. Allowance was made for incomplete absorption of the light.

As the specific rotations of both forms of 2-chloro-2-nitroso-camphane are known the composition of a mixture of the two forms can be calculated from a knowledge of its rotation and absorption.

If $C =$ concentration of both forms present.

Then $Cx =$ concentration of (-) form

where $x = \dfrac{[\alpha] + 494}{1458}$

$[\alpha] =$ specific rotation of mixture at 6000 Å at which wavelength the rotations of the (-) and (+) forms are + 964 and - 494 respectively.

At first the experiments were complicated by photooxidation and attempts were made to prevent this by using alcohol distilled in a current of nitrogen as the solvent. Later I found that it was simpler to irradiate the cell for a few hours to complete the photooxidation and then continue the irradiation to observe the photomutarotation and very slow photolysis.

In an experiment the results were as follows:-

Time of irradiation				
6 hrs.	$\rho = 0.875$	$\alpha = 1.02^\circ$	$[\alpha] = 792$	$x_1 = 88.2/100$
20 hrs.		$\alpha = 0.74^\circ$	$[\alpha] = 574$	$x_2 = 73.3/100$

$C = 1.290\% = 0.0643M$

6 hrs. $\bar{C} = 0.0643 \times 88.2/100$

20 hrs. $\bar{C} = 0.0643 \times 73.3/100$

Therefore millimoles inverted $= 0.0643 \times \frac{14.9}{100} \times 4.27$

$= 0.04091$

Energy absorbed $= \pi \times 0.81 \times \frac{41.5}{47.5} \times 2.25 \times 10^{-5} \times 14 \times 3600$

$\times 0.88$ cals $=$ 2.218 cals.

Since only the energy absorbed by the (-) form is used in the photomutarotation, and average fraction of (-) form present = 0.8075

Energy used = 2.218 x 0.8075 cals.

= 1.791 cals.

$$\gamma = \frac{\text{Mols. taking part}}{\text{cals absorbed}} \times \frac{28470}{\lambda}$$

$$= \frac{4.091 \times 10^{-5}}{1.791} \times \frac{28470}{\lambda}$$

$$= 0.973$$

Products of the photolysis of (-)-2-chloro-2-nitrosocamphane in oxygen free ethanol.

Mitchell, Watson, and Dunlop (60) showed that in the presence of oxygen an alcoholic solution of 2-chloro-2-nitroscamphane is photo-oxidised to 2-chloro-2-nitrocamphane. They also showed that, in the absence of oxygen a slower photolysis takes place when the blue solution is exposed to red light but they did not fully determine the products of this reaction. The alcohol used in the following experiments was freed as far as possible from the dissolved oxygen by refluxing for about 15 minutes in a current of O_2 free nitrogen, and then allowing the alcohol to cool in a slow stream of nitrogen.

Even so some of the solids isolated from the photolysis products of chloronitroso-terpenes were found to have low melting points which were not raised appreciably by recrystallization from aqueous alcohol. I believe that this may be due to the presence of some chloronitro-compound formed by photo-oxidation, and not readily removed by recrystallization. The products were isolated as follows.

Glass tubes (about 1cm bore, capacity 10-20mls) were filled with a 6% solution of 2-chloro-2-nitrosocamphane in alcohol and sealed (leaving as small an air space as possible) and irradiated by six 100W lamps in the apparatus described by Veitch (51). After the solutions had become colourless (about 100 hours) the tubes were opened and the contents examined in the following manner.

1. Few drops of the solution added to an alcoholic solution of silver nitrate gave a white ppt., insol. in warm dilute HNO_3, but soluble in ammonia. Reprecipitated from ammoniacal solution by dilute HNO_3. This shows the presence of Cl^- ion.

2. A portion of the solution, which smelt strongly of acetaldehyde, was distilled into a saturated aqueous solution of dimedone. Colourless crystals of the derivative, mp = 140°, confirmed the presence of acetaldehyde.

3. The solvent was removed from a tubeful of photolysis products heated on the water bath under reduced pressure. The residue was treated with water, extracted with ether, and the extract dried over sodium sulphate. Evaporation of the ether extract gave an almost quantitative yield of a crystalline solid, mp = 110 - 111°. Recryst. from EtOH mp = 116° Solution of solid in ether gave a blue colour when treated with chlorine.

Mixed mp of camphoroxime (mp = 117°) and product = 117°

Therefore product is camphoroxime.

4. The solvent was removed from a tubeful of photolysis products as above. The residue was then placed in a vacuum

desiccator over $CaCl_2$ for a few hours to remove traces of alcohol. In this manner crystals were obtained which, when freed from oily impurities by washing with ethyl acetate, melted at 156 - 157°.

Mixed mp of camphoroxime hydrochloride (mp = 156 - 157°) and product = 156 - 157°

Compound gave N = 7.0% $\left.C_{10}H_{16}\overset{+}{N}HOH\right\}\ Cl^-$ requires N = 6.9%,
Cl = 17.47%

47.0mg prodt. treated with 25mls 0.0101N. $AgNO_3$ and back titrated 0.0106N. KCNS by Volhard's method.

Required 2.90mls Equiv. to 3.04 mls $AgNO_3$

$$\text{Therefore } Cl^- = \frac{22.96 \times 35.5 \times 0.0101}{47.0} \times 100\%$$

$$= 17.55\%$$

A specimen of camphoroxime HCl left in the department by Dr. Hope gave Cl^- = 17.10%

5. To show that no compound containing covalent chlorine is producted in the photolysis 35.7mg of 2-chloro-2-nitrosocamphane in 5 mls EtOH was irradiated until colourless (about 70 hours). The Cl^- formed was estimated by Volhard's method. Used 25mls 0.0101N $AgNO_3$

Required 7.50 mls 0.0106N. KCNS Equiv. 7.85mls $AgNO_3$

$$\text{Therefore } Cl^- = \frac{17.15 \times 35.5 \times 0.0101}{35.7} \times 100\%$$

= 17.30% (98.3% theory since $C_{10}H_{16}NOCl$ requires Cl = 17.58%)

Catalytic hydrogenation of 2-chloro-2-nitroso-camphane

According to Müller (59) Raney Nickel is not an effective catalyst for the reduction of gem-chloronitroso compounds to the corresponding oximes. I have found, however, that satisfactory results can be obtained using nickel prepared as described by Tucker (63) provided that plenty of catalyst is used. This reaction is of importance as it was used to investigate the photoisomerisation of 2-chloro-2-nitroso-10-bromocamphane.

The hydrogenation was conducted in the apparatus described in Tucker's paper.

2 gms Ni/10mls abs. EtOH Temp. = 18° Pressure = 758mm

Time (mins)	0	5	20	30	35
mls H_2 absorbed	0	10	16	18	19

0.7 gms of the blue compound in 15mls EtOH was added and the hydrogenation commenced (78.4mls H_2 required at NTP = 83.5 mls at 18°/758 mm)

Time (mins)	0	25	45	70	85	100	105
mls H_2 absorbed	0	48	66	74	79	83	83.5

The hydrogenation was stopped, the mixture filtered to remove the nickel, and the alcohol taken off under reduced pressure.

The pale greenish solid was then shaken up with ether and water in a separating funnel. The greenish aqueous layer contained Ni^{++} as was shown by the formation of a red precipitate with dimethylglyoxime.

The ether layer was dried over sodium sulphate and the solid residue obtained from the extract (0.2 gms mp = 106°) recrystallized three times from 60 - 80° pet. ether. The final product melted at 117-118° and the melting point was not depressed when it was mixed with d-camphoroxime.

Preparation of (+)-2-chloro-2-nitrosocamphane

1.34 gms of 2-chloro-2-nitrosocamphane was dissolved in 30 mls methanol, placed in a 10cm. glass stoppered tube, and irradiated with a Cd/Hg lamp until inversion was completed (~17 hrs.).

The bulk of the methanol was then removed under vacuum, the residue treated with water and extracted with 40-60^{0} pet. ether. The extract was dried over sodium sulphate, evaporated to a small bulk, and then chromatographed on fine mesh silica gel.
400 mg of the solid product were obtained $\varepsilon_{max} = 15.7$

Rotary dispersion

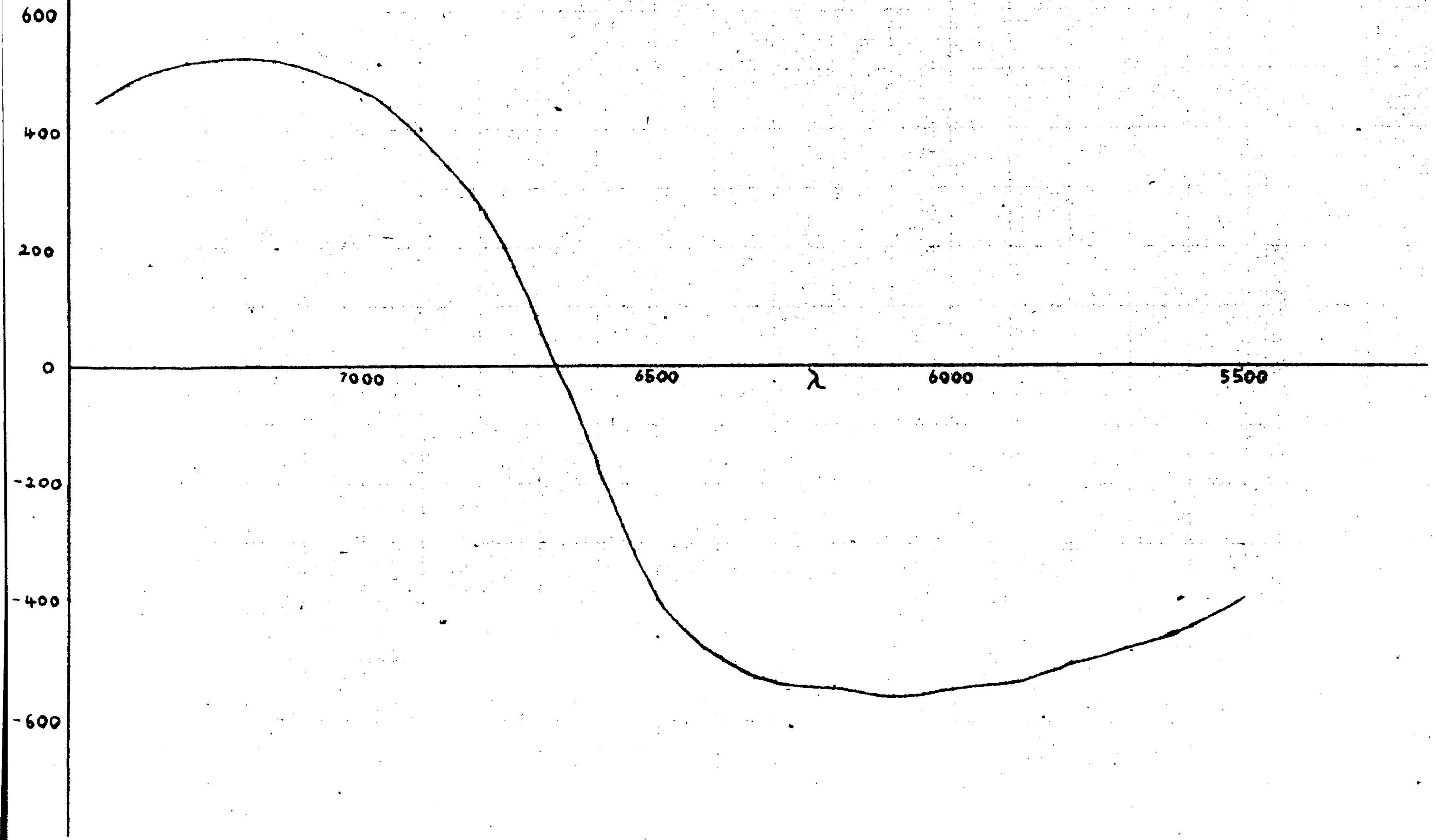
$c = 0.302\%$ $l = 1dm$

λ	α	$[\alpha]$	λ	α	$[\alpha]$
7400	1.44	+477	6400	-1.48	-490
7300	1.55	+513	6300	-1.61	-535
7200	1.57	+519	6200	-1.64	-542
7100	1.46	+483	6100	-1.69	-559
7000	1.34	+450	6000	-1.66	-548
6900	1.21	+401	5900	-1.64	-535
6800	0.84	+267	5800	-1.51	-500
6700	0.20	+ 64	5700	-1.45	-480
6600	-0.53	-109	5600	-1.32	-437
6500	-1.38	-457	5500	-1.22	-404
			5250	-0.96	-318

Graph 2

Rotatory dispersion of (+)-2-chloro-2-nitrosocamphane in EtOH

c = 0·302%



These results are shown on Graph 2.

Relative stabilities of the two isomers

Meerwein (62) has shown that an isomerisation of isobornyl chloride to bornyl chloride occurs in solution. The most suitable solvent for showing this effect was chlorobenzene containing some dissolved stannic chloride to catalyse the reaction. In order to allot configurations to the two 2-chloro-2-nitrosocamphanes it was decided to make up solutions of the two isomers in the solvent and then, by rotation measurements, find out if any isomerisation occurred in either case. Unfortunately both the chloronitroso compounds were decomposed by the stannic chloride but, the blue colour of the solution persisted much longer in the case of the (-)- form than with the (+)- form. This would appear to indicate that the (-)- form is the more stable.

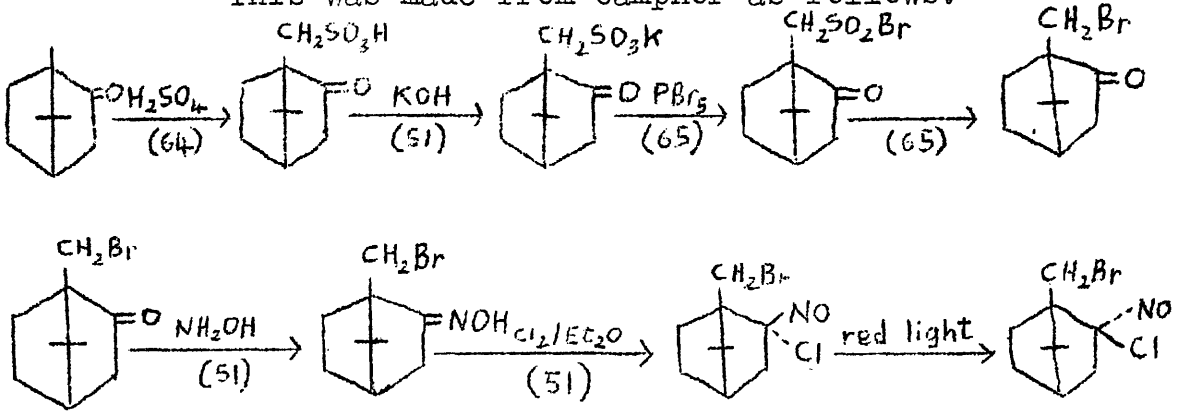
The two forms also differ in their stability to hydrochloric acid. When 30mg of the (-)- form was dissolved in 9 mls EtOH and 1 ml concentrated hydrochloric acid added. The rotation of the solution had hardly altered after six days storage in the dark. When this experiment was repeated with the (+)- form the blue colour had almost disappeared after six days. The residual solution showed a very slight positive rotation. It was treated with water and extracted with about 1½-2 mls pet. ether. The dried pet. ether extract, in a 10cm micro polarimeter tube, showed a definite negative Cotton effect. $\alpha_{6000} = + 0.38^{\circ}$, $\alpha_{7000} = - 0.31^{\circ}$

This shows the presence of some (-)-2-chloro-2-nitrosocamphane possibly formed from the (+)-2-chloro-2-nitroscamphane by the action of the acid.

II. 2-chloro-2-nitroso-10-bromocamphane

Synthesis of 2-chloro-2-nitroso-10-bromocamphane.

This was made from camphor as follows:-



Camphor sulphonic acid and its potassium salt.

Camphor was sulphonated as described by Reychler (64). 500 gms camphor gave 413 gms camphor-10-sulphonic acid mp=190°

250 gms of the acid dissolved in 250 mls alcohol was treated with 50 gms potash dissolved in 55 mls 90% alcohol. The potash was added slowly with constant stirring. The potassium salt which separated almost immediately was filtered off, washed with absolute alcohol and dried in a desiccator for two days. Yield 200 gms (70%).

10-Bromocamphor

This was prepared by treating the potassium salt with phosphorus pentabromide as described by Lowry (65) and decomposing the sulphonyl bromide by boiling in xylene solution.

64 gms salt gave 17.6 gms bromocamphor (32%) mp = 74-76°

Lit. yield 20%

2:4 -dinitrophenylhydrazone mp = 152°

10-Bromocamphoroxime.

14.4 gms 10-bromocamphor, 16 gms hydroxylamine hydrochloride and 140 mls anhydrous pyridine was refluxed for 3 hrs. The product was poured on to crushed ice, and the oxime which separated was dried on porous plate and recrystallised from alcohol.

Yield 8.4 gms oxime mp = 151°

Recryst. 8.0 gms oxime (50%) mp = 155°

Bromocamphoroxime hydrochloride.

0.63 gms of bromocamphoroxime was dissolved in 15 mls ether, cooled in a freezing mixture, and dry HCl gas led in. 0.55 gms of the hydrochloride separated. mp = 152°

130.5 mg of the hydrochloride dissolved in alcohol required 10.95 mls 0.04N.$AgNO_3$ solution. Diphenylamine was used as an adsorption indicator.

Therefore Cl = 11.9% $C_{10}H_{17}NOClBr$ requires Cl = 12.5%

When an attempt was made to recrystallize this substance from absolute alcohol all the HCl remained in solution and bromocamphoroxime was obtained. This accounts for Veitch's failure to obtain this compound.

2-chloro-2-nitroso-10-bromocamphane.

This operation was carried out in subdued light. 2 gms oxime was dissolved in 150 mls anhydrous ether and cooled in ice. Dry chlorine was passed in for 2 hrs. The ether was taken off under reduced pressure finally with gentle warming to 45°. The remaining deep blue viscous oil was dissolved in 40-60° pet. ether and chromatographed on a bentonite - kieselguhr column.

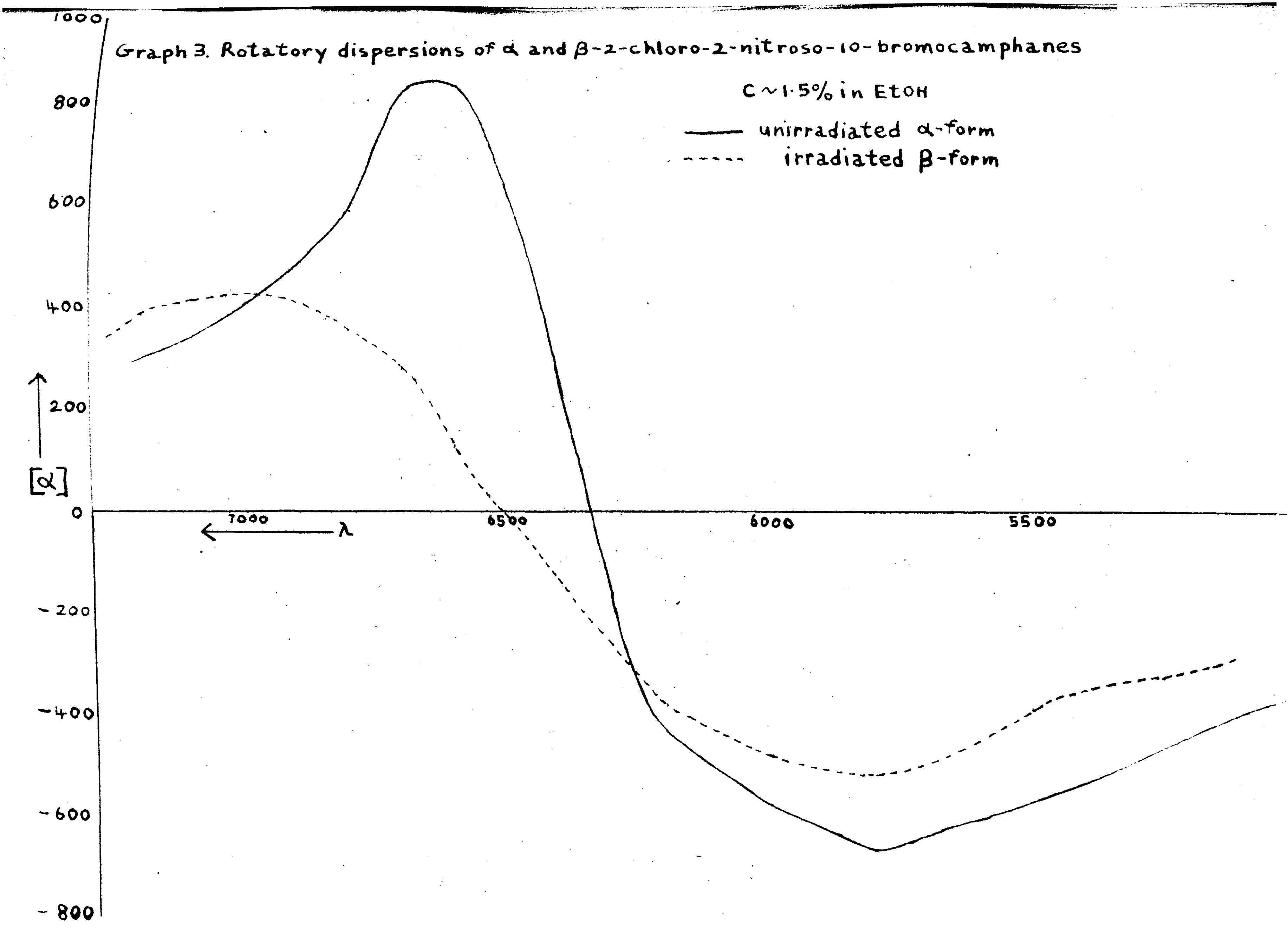
Yield 2 gms (84%) mp = 126-130° $\mathcal{E}_{6450} = 17.6$

A batch of the above was put through column of "O" alumina. Eluted with 40-60° pet. ether.

Gave solid mp = 126-129° $\mathcal{E}_{6475} = 18.7$

Rotatory dispersion C = 1.532%

λ	α	$[\alpha]$	λ	α	$[\alpha]$
7000	0.61	398	5900	-0.93	-607
6800	0.88	575	5800	-1.02	-666
6700	1.27	828	5700	-0.96	-627
6600	1.26	822	5600	-0.93	-607
6500	0.93	607	5400	-0.82	-535
6400	0.32	209	5200	-0.69	-450
6200	-0.67	-437	6650	1.28	836
6000	-0.87	-574	6375	-0.00	-0



Graph 3. Rotatory dispersions of α and β-2-chloro-2-nitroso-10-bromocamphanes

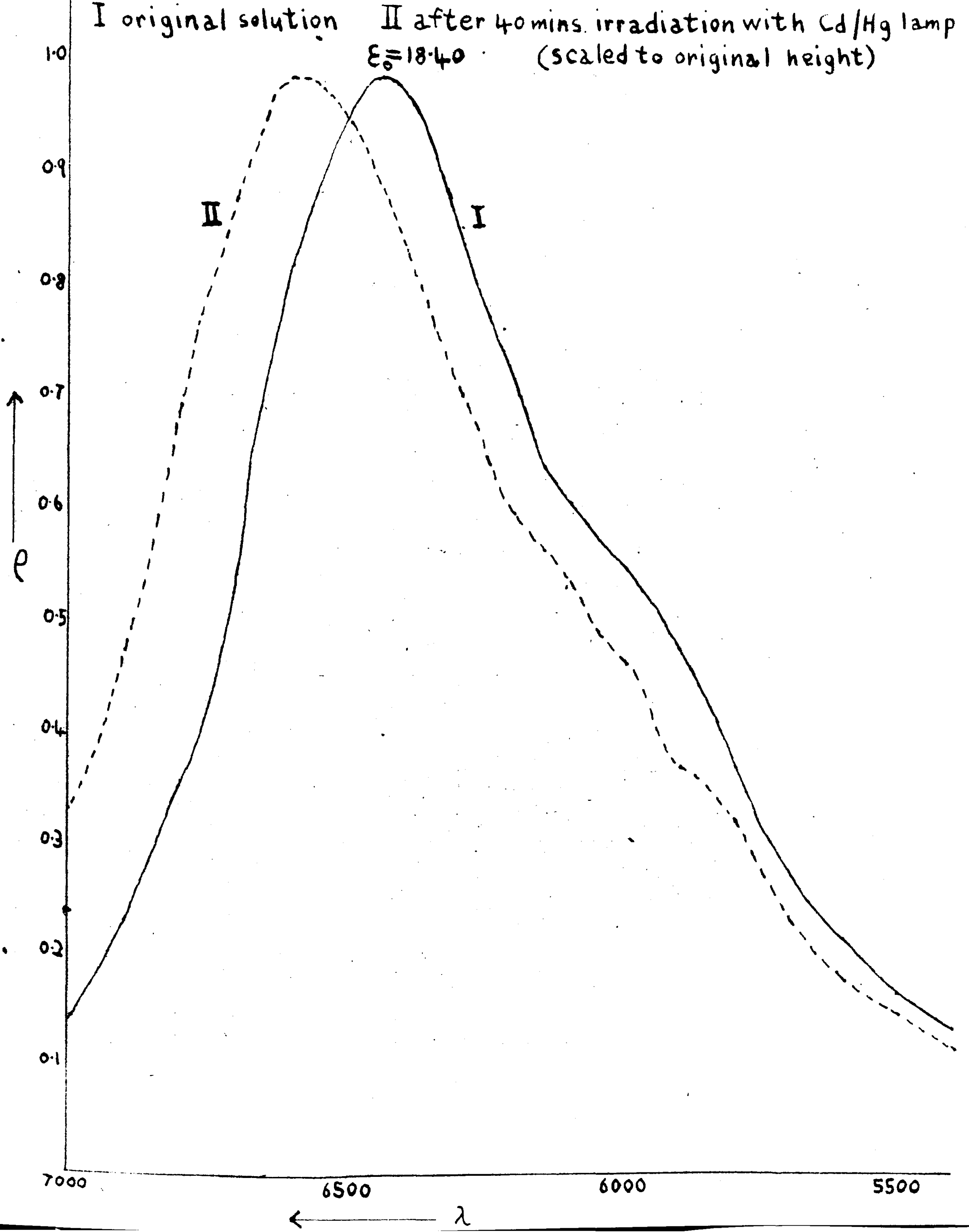
Shift of absorption band on irradiation of an alcoholic solution of 2-chloro-2-nitroso-10-bromocamphane.

A solution of 74.7 mg 2-chloro-2-nitroso-10-bromocamphane in 5 mls alcohol was placed in a stoppered 1 cm. glass cell and its absorption measured. The solution was then irradiated with the light from a Hg/Cd box type lamp and the absorption measured again after various periods of irradiation.

λ	ρ_0	ε_0	ρ_{40}	$\rho_{0,40}$	ρ_{80}
7500					0.032
7400					0.054
7300					0.080
7200					0.094
7100					0.142
7000	0.140	2.63	0.242	0.328	0.190
6900	0.229	4.30	0.347	0.471	0.227
6800	0.355	6.67	0.510	0.692	0.425
6700	0.540	10.15	0.644	0.874	0.537
6650	0.690	12.96	0.696	0.945	0.595
6600	0.815	15.32	0.722	0.980	0.610
6575			0.720	0.977	0.615
6550	0.880	16.54	0.715	0.971	0.610
6500	0.925	17.38	0.693	0.941	0.595
6450	0.980	18.42	0.655	0.889	
6400	0.965	18.13	0.609	0.827	0.524
6350	0.910	17.10	0.560	0.760	
6300	0.850	15.97	0.516	0.700	0.436
6250	0.770	14.47	0.470	0.638	
6200	0.705	13.25	0.440	0.597	0.384
6200	0.705	13.25	0.448	0.608	
6150	0.635	11.93	0.415	0.563	
6100	0.605	11.37	0.394	0.535	0.338
6050	0.572	10.75	0.361	0.490	
6000	0.547	10.28	0.340	0.462	0.297
5900	0.474	8.91	0.276	0.367	0.242
5800	0.367	6.90	0.236	0.320	0.188
5700	0.269	5.06	0.167	0.228	0.139
5600	0.213	4.00	0.129	0.175	0.117
5500	0.162	3.05	0.107	0.145	0.093
5400	0.133	2.50	0.082	0.111	

Graph 4.

Shift of the absorption band on irradiation of an alcoholic solution of 2-chloro-2-nitroso-10-bromocamphane (74·7mg/5mls EtOH)



After 140 mins ρ_{max} 0.440 at $\lambda = 6575$ Å

It is readily seen that there has been a bathochromic shift in the absorption band. This shows that a photoisomerisation is occurring in addition to the photolysis.

Isomerisation of 2-chloro-2-nitroso-lo-bromocamphane.

0.5 gms of 2-chloro-2-nitroso-10-bromocamphane dissolved in 30 mls alcohol irradiated in 10 cm. glass tube with Hg/Cd lamp.

Time	0	2h 15m	3h 55m	4h 55m	6h 55m	9h 10m	10h 35m
α_{5461}	-8.9	-6.4	-5.8	-5.5	-5.3	-5.0	-4.8

Alcohol was removed under reduced pressure on a water bath and the residue was dissolved in 40-60 pet. ether and chromatographed on a column of "O" alumina.

77.4 mg. of product dissolved in 5 mls alcohol.

λ	7300	7200	7100	7000	6900	6800	6700	6600
$[\alpha]$	315	380	405	415	395	350	275	125
λ	6400	6300	6200	6100	6000	5800	5500	5250
$[\alpha]$	-150	-345	-380	-430	-480	-512	-390	-325

$\varepsilon_{6400} = 18.40$ N = 4.78% Cl, Br = 41.03%

$C_{10}H_{15}NOClBr$ requires N = 4.99% Cl, Br = 41.12%

Hydrogenation of 2-chloro-2-nitrose-10-bromocamphane.

1. Unirradiated α-form.

0.26 gms compound in 5 mls alcohol hydrogenated, using 0.5 gms Raney Ni, until colourless (20 mls H_2 absorbed) Filtered. Alcohol taken off from filtrate under reduced pressure. Residue dissolved in ether and washed with water. Ether layer evaporated in stream of air.

Yield 131 mg solid mp = 141° Recryst. from alcohol mp = 152-153° Recryst. again mp = 155-156°.

Mixed mp with bromocamphoroxime mp = 156°. The identity of the product was confirmed by comparing its I.R. spectrum with that of bromocamphoroxime.

2. Irradiated β-form.

0.36 gms with 1gm Ni required 30 mls H_2. Treated as above gave an identical product.

Later it was found that the reduction can be accomplished more simply by adding a few drops of hydrazine hydrate to the solution of the blue compound in alcohol. The same products result.

Photolysis products.

Veitch investigated the photolysis of 2-chloro-2-nitroso-10-bromocamphane in oxygen free alcohol. He isolated 10-bromocamphoroxime and showed, by titration with standard silver nitrate solution, that 99% of the chlorine is liberated as Cl^- ions. He also stated that he smelt acetaldehyde when he opened the tubes of the photolysis products.

In order to confirm this observation 0.3 gms of 2-chloro-2-nitroso-10-bromocamphane dissolved in 10 mls alcohol was irradiated in a sealed tube until colourless. The products were distilled, collecting the first fraction of the distillate in a saturated aqueous solution of dimedone. Crystals separated overnight. mp = 139-140° Cyclised deriv. mp = 174°

Mixed mp of crystals with acetaldehyde deriv. mp = 139-140°

Circular dichroism of α-and β-2-chloro-2-nitroso-10-bromocamphane

Dr. Mitchell's apparatus (25) enables the circular dichroism of solutions to be measured rapidly and with reasonable accuracy. Circular dichroism measurements are useful in the study of the photoisomerisation of substances showing the Cotton effect because they will often show whether a solution contains a mixture of substances with opposite Cotton effects when a study of the rotatory dispersion of the solution is inconclusive.

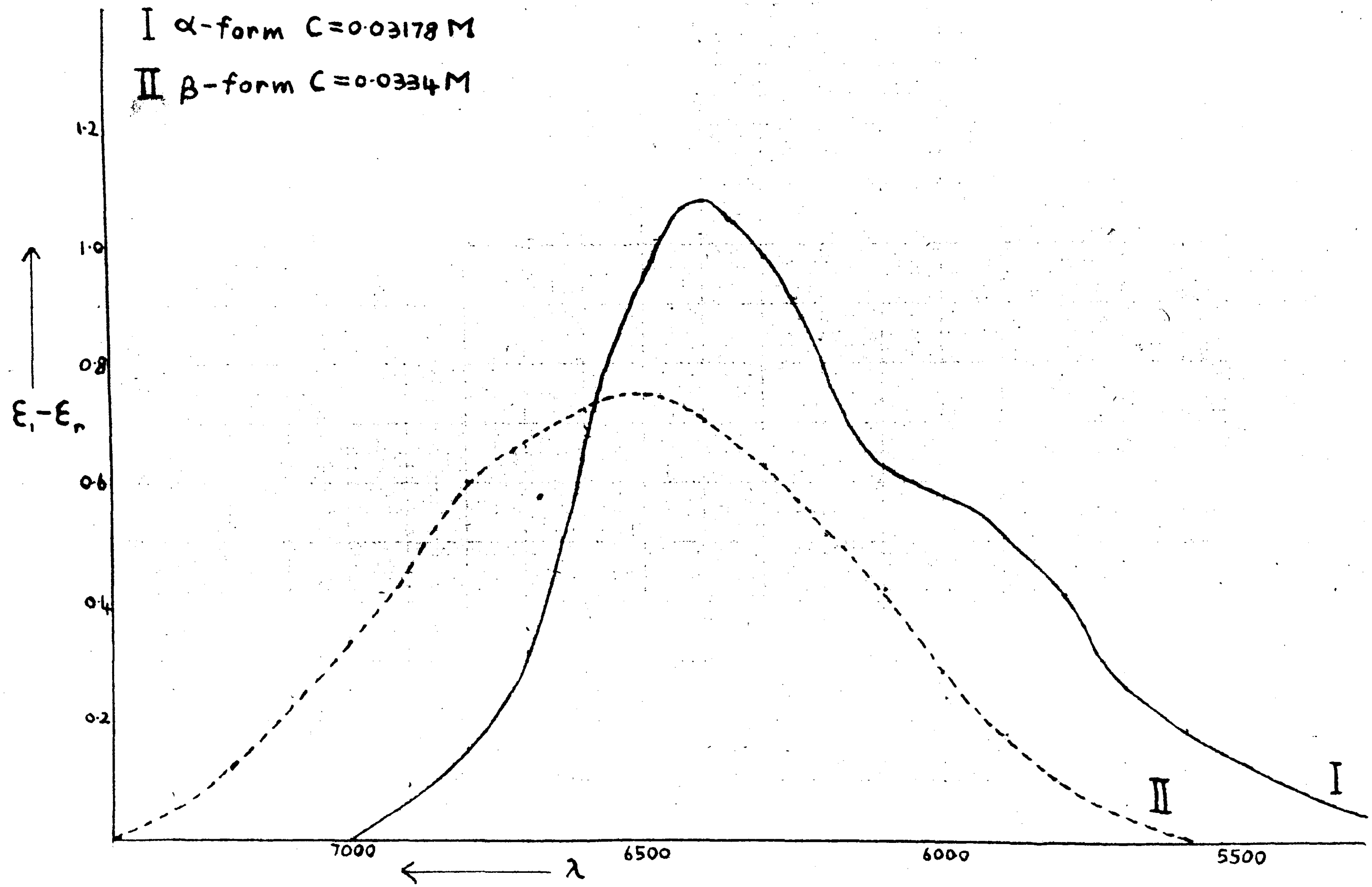
	α-form C = 0.03178M	β-form C = 0.0334M
λ	$\varepsilon_l - \varepsilon_r$	$\varepsilon_l - \varepsilon_r$
7400		0.000
7300		0.078
7200		0.120
7100		0.240
7000	0.000	0.330
6900	0.094	0.450
6800	0.126	0.600
6700	0.315	0.660
6600	0.693	0.721
6500	0.946	0.750
6400	1.072	0.705
6300	0.978	0.630
6200	0.797	0.510
6100	0.629	0.420
6000	0.577	0.240
5900	0.504	0.180
5800	0.410	0.090
5700	0.252	0.060
5600	0.189	0.000
5500	0.126	
5400	0.095	

These results are plotted out on Graph (5).

If inversion of the rotatory dispersion curve had occurred the sign of the circular dichroism would have changed. Even incomplete inversion would reduce the circular dichroism at long wavelengths but the measurements show that this is in fact increased. This can only happen if the isomerised 2-chloro-2-nitroso-10-bromocamphane has the same type of Cotton effect as the original compound - a remarkable result!

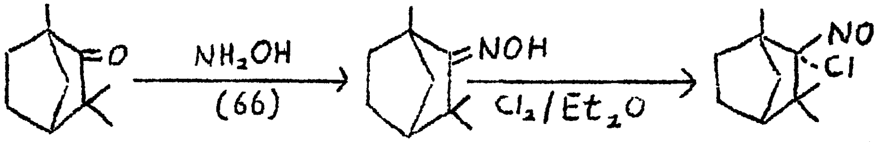
Graph 5

Circular dichroism of 2-chloro-2-nitroso-10-bromocamphane in alcohol.



III. 2-chloro-2-nitrosofenchane

Synthesis of (+)-2-chloro-2-nitroso-fenchane



Some of the earlier part of this investigation was carried out in collaboration with Mr. R.W. Hay who worked on this compound as part of his research for the degree of B.Sc.

Prep. of α-d-fenchone oxime.

This compound was readily obtained as described by Wallach (66).

Yield: Practically theoretical $[\alpha]_D$ 46.9° mp = 163-165°

Preparation of β-d-fenchone oxime.

This compound was prepared as described by Delephine (66). From 70 gms fenchone only 23 gms of oxime were obtained. On recrystallisation from alcohol this yielded 11 gms pure β-oxime (mp = 123°) and in a second crop 9 gms α-oxime (mp = 162°).

Preparation of 2-chloro-2-nitro-fenchane.

This compound was prepared in the same manner as Forster (67) describes for the corresponding compound in the camphane series 2½ gms α-fenchone oxime suspended in a solution of 5 gms KOH in 10 mls water. Added with stirring (15 mins.) to 500 mls ice cold NaOCl (prepared from

20 gms NaOH). Stood 12 hrs. Filtered, dried over $CaCl_2$ and recrystallised from alcohol until mp. was constant. mp = 200°.

$C = 55.43\%$ $H = 7.03\%$ $N = 6.79\%$ $Cl = 16.46\%$ $[\alpha]_D = 5.74^\circ$

$C_{10}H_{16}NO_2Cl$ requires $C = 55.16\%$ $H = 7.41\%$ $N = 6.43\%$ $Cl = 16.29\%$.

This compound was prepared as it was a possible impurity in the chloronitroso compounds (formed by photooxidation). However since its rotation is so low its presence would not affect the shape of the rotatory dispersion curves of the chloronitroso compounds.

Preparation of (+)-2-chloro-2-nitroso-fenchane.

About $\frac{3}{4}$ gms fenchone oxime were dissolved in about 100 mls dry ether and, after cooling in ice, treated with chlorine gas (15 mins.). Excess chlorine blown off in a current of dry air. Ether taken off in draught cupboard.

Blue solid was then dissolved in 40-60° pet. ether and chromatographed on silica gel (some batches of silica gel decompose compound) and then on sugar charcoal (finer than 60 mesh, coarser than 120 mesh) or alumina (too strongly activated alumina may cause decomposition)

$[\alpha]_{6000} = -486^\circ$ $\varepsilon_{max} = 21.85$ Yield 300 mg.

Test for dark reactions.

(+)-2-chloro-2-nitroso-fenchane is unstable unless kept in a refrigerator. A solution in alcohol became colourless after about a fortnight. The substance photomutarotates however on exposure to light and the inverted compound is much more stable.

Photolysis products.

Some (+)-2-chloro-2-nitroso-fenchane was dissolved in alcohol and placed in a hermetically sealed tube and exposed to light until colourless (about 14 days). The alcohol was then taken off under vacuum and the residue recrystallised from aqueous alcohol.

White crystalline solid mp = 160°

Mixed mp with α-d-fenchone oxime = 161°

mp of α-d-fenchone oxime = $162\text{-}163^\circ$

The identity of the substance with α-d-fenchone oxime was confirmed by comparing I.R. spectra.

Acetaldehyde was shown to be present in another batch of photolysis products by steam distilling into a solution of dimedone when white crystals of the derivative mp = 140° separated.

On addition of an alcoholic solution of silver nitrate to a few drops of the photolysis products a white precipitate, insoluble in dilute nitric acid but soluble in ammonia, was formed. Therefore chlorine ions are present.

Estimation of the chlorine ions liberated during the photolysis.

The chlorine in 33.5 mg of the compound was found by dissolving it in EtOH, reducing the blue solution with excess of hydrazine hydrate, and acidifying with dilute nitric acid.

16 mls of 0.01134N.$AgNO_3$. Back titration by Volhard's Method required 1.30 mls 0.01061 N.KCNS.

Equivalent to 1.22 mls $AgNO_3$.

$$Cl^- = \frac{(16 - 1.22) \times 35.5 \times 0.01134}{33.5} \times 100\%$$

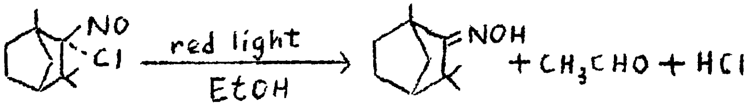
$$= 17.76\% \quad (C_{10}H_{16}NOCl \text{ requires } 17.62\%)$$

53.2 mg of the blue compound was dissolved in 5 mls O_2 free EtOH, placed in a sealed tube, and irradiated until colourless, (∼ 260 hrs.). The tube was then opened and the products treated with 25 mls 0.01134N.$AgNO_3$ Required 2.7 mls 0.007036N.KCNS. Equivalent to 1.67 mls $AgNO_3$

$$Cl^- = \frac{(25 - 1.67) \times 35.5 \times 0.01134}{53.2} \times 100\%$$

$$= 17.66\% \text{ (99.6\% Cl found in specimen)}$$

The overall reaction appears to be



This is analogous to the reactions of the compound from camphor.

Inversion to (-)-2-chloro-2-nitroso-fenchane

0.75 gms (+)-2-chloro-2-nitroso-fenchane was dissolved in 30 mls alcohol and placed in a glass stoppered decimeter cell. It was irradiated with a mercury vapour lamp. The inversion was followed by measuring the rotation for Hg green light at intervals.

t(hrs.)	α	t(hrs.)	α	t(hrs.)	α
0	-7.0°	$7\frac{3}{4}$	4.9°	$15\frac{1}{2}$	4.8°
1	-2.9°	$9\frac{3}{4}$	5.1°	$17\frac{1}{2}$	4.6°
$2\frac{3}{4}$	0.7°	11	5.1°	23	4.2°
4	2.8°	13	5.0°	25	4.1°
$5\frac{3}{4}$	4.3°				

The alcohol was then taken off under vacuum and the sticky solid left dissolved in 40-60° pet. ether and chromatographed on Light's alumina. The solvent was then removed in a stream of air when a blue solid was obtained 0.24 gms

$$[\alpha]_{6000} = 514^{\circ} \qquad \varepsilon_{max} = 21.75$$

When same was chromatographed twice more ε_{max} rose to 24.5.

OPTICAL MEASUREMENTS.

Rotations	(+)-2-chloro-2-nitroso fenchane 2.264%		(−)-2-chloro-2-nitroso fenchane 2.104%	
Wavelength Å	Rotation°	[α]	Rotation°	[α]
5400	-0.70	-309	0.69	329
5600	-0.81	-358	0.86	410
5700	-0.88	-390	0.99	472
5800	-0.96	-425	1.07	526
5900	-1.06	-468	1.13	492
6000	-1.10	-486	1.08	514
6100	-1.11	-490	1.00	476
6200	-1.07	-473	0.94	447
6300	-1.08	-477.5	1.00	476
6400	-1.04	-460	0.95	452
6500	-0.98	-433.5		
6600	-0.90	-398	-0.56	-266
6800	0.11	50	-2.24	-1067
6900	0.72	318		
7000	1.18	522	-1.66	-790
7100	1.12	495		
7200	1.07	473	-0.82	-391

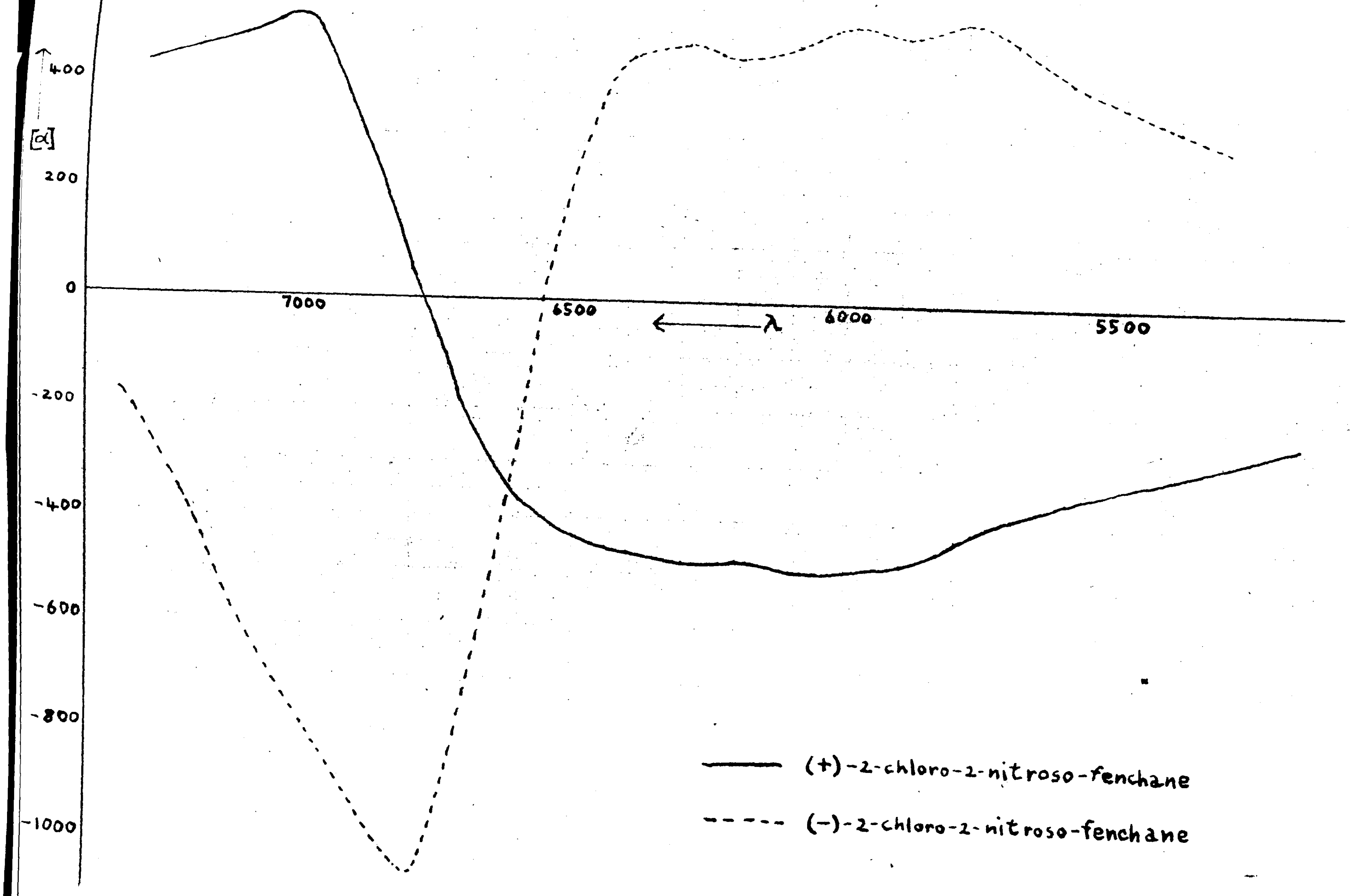
These results are shown on Graph 6.

Absorption of (+) Form $C = 0.05727$ M

λ	ρ	ε	λ	ρ	ε
5600	0.115	2.01	6600	1.06	18.5
5800	0.1925	2.36	6650	1.15	20.1
5900	0.253	4.42	6700	1.18	20.6
6000	0.355	6.2	6750	1.225	21.85
6100	0.46	8.05	6800	1.21	21.2
6200	0.57	9.95	6900	1.02	17.8
6300	0.65	11.4	7000	0.722	12.6
6400	0.73	12.8	7100	0.457	8.0
6500	0.89	15.6	7200	0.283	4.95
			7300	0.1975	3.45

Graph 6.

Rotatory dispersions of (+)- and (−)-2-chloro-2-nitroso-fenchanes



Circular Dichroism of (+) Form

λ	$\varepsilon_l-\varepsilon_r$	λ	$\varepsilon_l-\varepsilon_r$
6000	0.157	6750	0.604
6100	0.175	6800	0.604
6200	0.227	6900	0.54
6300	0.280	7000	0.41
6400	0.3425	7100	0.245
6500	0.394	7200	0.131
6600	0.51	7300	0.07
6650	0.54	7400	0.00
6700	0.595		

Absorption of (-) Form.

C = 0.05568M

λ	ρ	ε	λ	ρ	ε
5500	0.1075	1.93	6650	1.21	21.75
5600	0.149	2.68	6700	1.18	21.2
5800	0.220	3.95	6800	1.065	19.2
5900	0.299	5.38	6900	0.738	13.27
6000	0.422	7.6	7000	0.447	8.04
6100	0.557	10.0	7100	0.275	4.95
6200	0.635	11.4	7200	0.18	3.24
6300	0.708	12.7	7300	0.112	2.01
6400	0.812	14.6	7400	0.073	1.31
6500	0.970	17.4	7500	0.0445	0.8
6600	1.15	20.65	7600	0.03	0.54

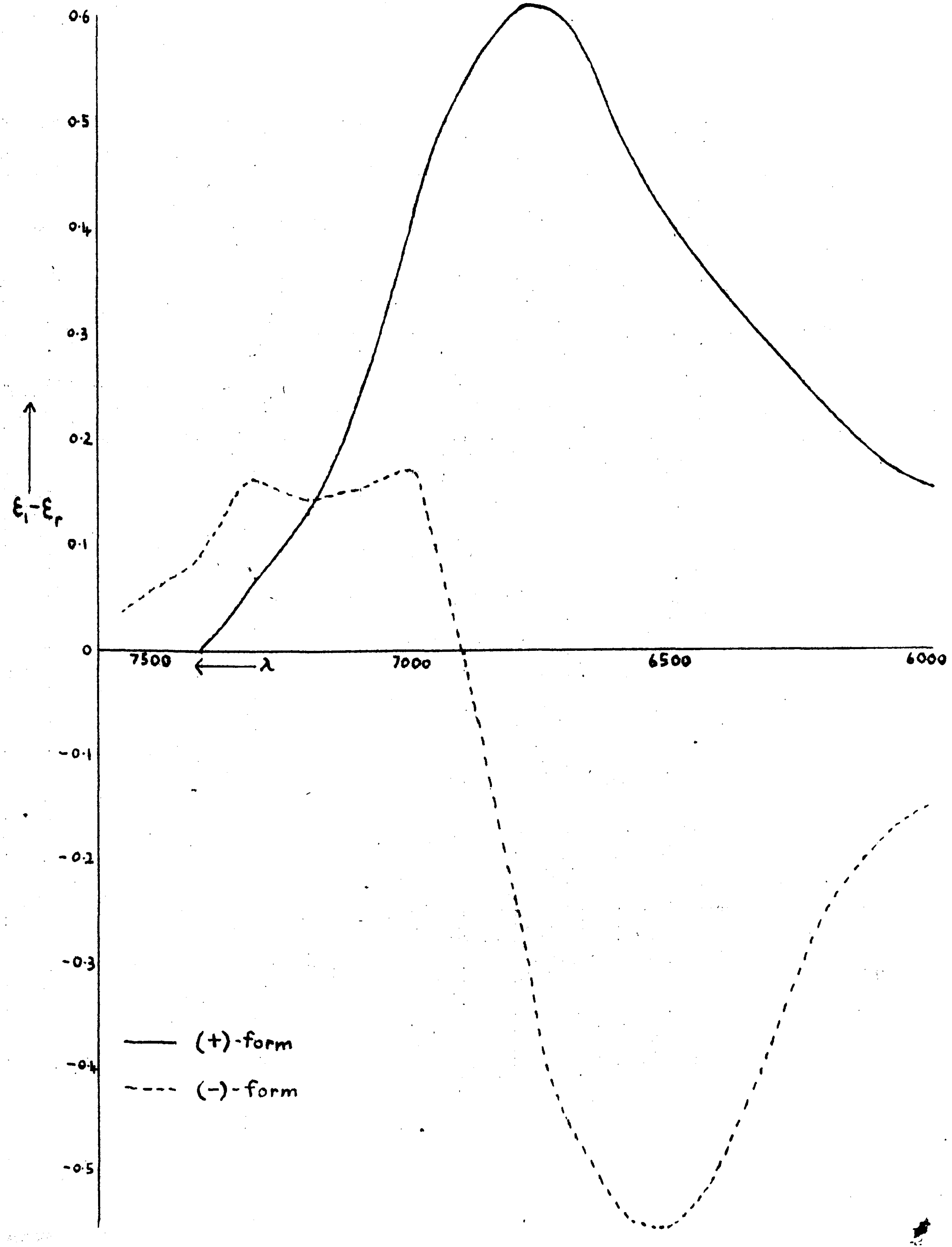
Circular dichroism of (-) Form.

λ	$\varepsilon_l-\varepsilon_r$	λ	$\varepsilon_l-\varepsilon_r$
6100	-0.153	6800	-0.234
6200	-0.1887	6900	0.000
6300	-0.225	7000	0.171
6400	-0.38	7100	0.1527
6500	-0.495	7200	0.144
6600	-0.558	7300	0.162
6650	-0.54	7400	0.09
6700	-0.45	7500	0.066

These results are shown on Graphs 7 and 8.

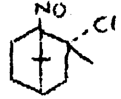
Graph 8

Circular dichroism of (+)- and (-)-2-chloro-2-nitroso-fenchanes



Circular dichroism measurements were made on the Unicam using an attachment, consisting of a nicol prism and a quarter wave plate which can be rotated through 90°, recently perfected by Dr. Mitchell.

The circular dichroism curve shows the presence of at least two components, one with negative circular dichroism and the other with positive circular dichroism.

It was thought that the positive component might be a component such as 

formed by Wagner rearrangement during the photolysis. This substance would be expected to decompose on treatment with silver nitrate. Accordingly samples of the inverted form were treated with excess alcoholic silver nitrate in the hope that the positive loop in the circular dichroism graph would disappear. Graph 9 shows that this is indeed the case.

I. Treated with excess alcoholic $AgNO_3$, stood 10 mins. filtered, excess $AgNO_3$ pptd. with alcoholic NaOH, filtered, acidified with acetic acid, neutralised with ammonia. EtOH taken off under vacuum and residue chromatographed on alumina (solvent 40-60° pet. ether)

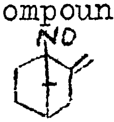
34.0 mg/5 mls $\rho_{6500} = 0.835$.

λ	$\varepsilon_1-\varepsilon_r$	λ	$\varepsilon_1-\varepsilon_r$
6000	-0.295	6800	-0.470
6100	-0.295	6900	0.000
6200	-0.355	7000	0.060
6300	-0.486	7100	0.125
6400	-0.680	7200	0.125
6500	-0.885	7300	0.125
6600	-0.975	7400	0.086
6700	-0.770	7500	0.030

II. As above but treatment continued for ½ hr.

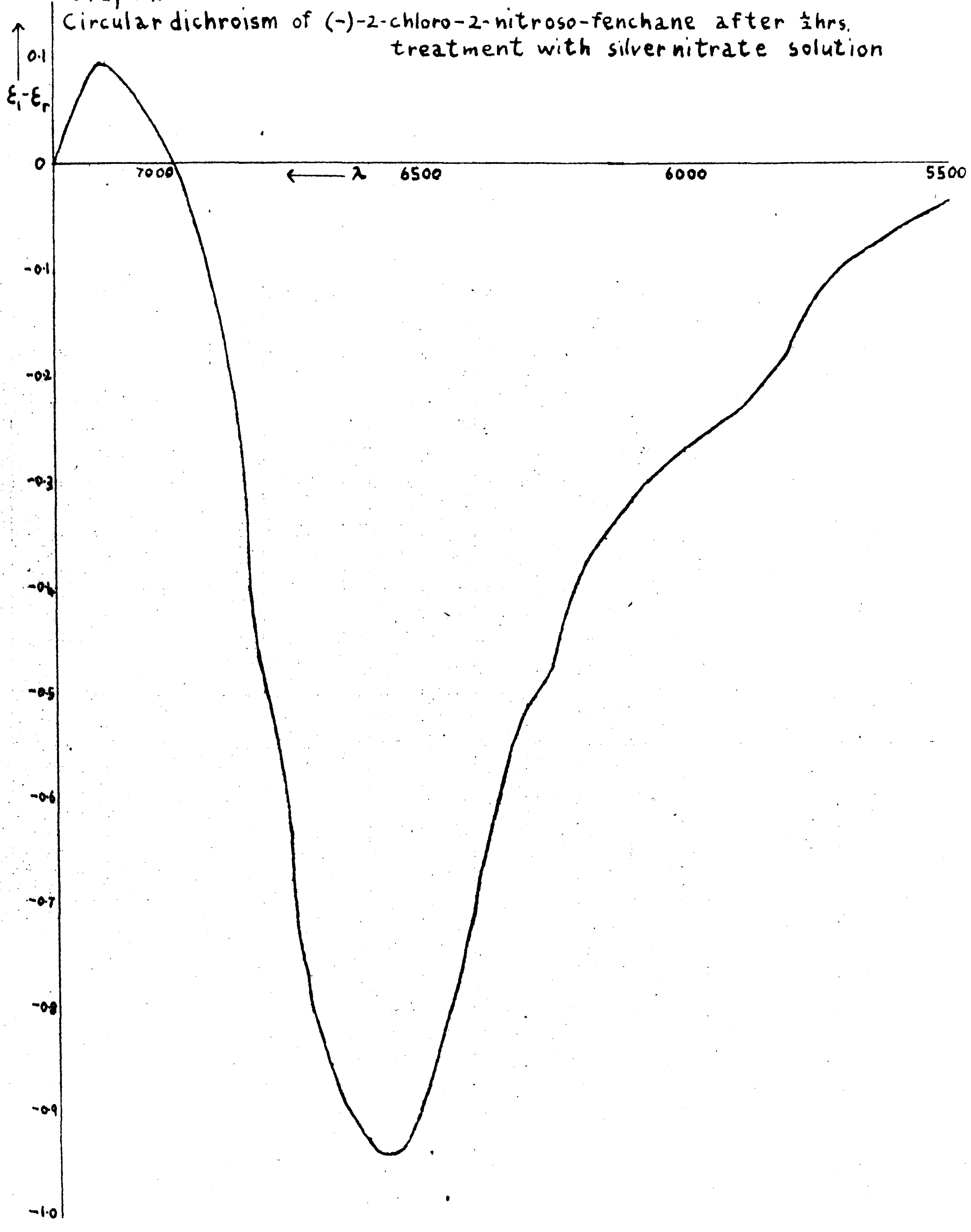
λ	$\varepsilon_1-\varepsilon_r$	λ	$\varepsilon_1-\varepsilon_r$
7200	-0.000	6400	-0.7115
7100	+0.096	6350	-0.5947
7000	0.000	6300	-0.5132
6950	0.000	6250	-0.4758
6900	-0.0463	6200	-0.3921
6850	-0.2357	6150	-0.3546
6800	-0.4846	6100	-0.3194
6750	-0.6300	6050	-0.2907
6700	-0.8084	6000	-0.2731
6650	-0.8877	5900	-0.2357
6600	-0.9207	5800	-0.1674
6550	-0.9780	5700	-0.0947
6500	-0.8877	5600	-0.0638
6450	-0.8084	5500	-0.0374

Cl = 17.39% $C_{10}H_{16}NOCl$ requires Cl = 17.58%

This result eliminates the possibility of a Wagner rearrangement since the compound which would be formed by the silver nitrate treatment  would not contain chlorine.

Graph 9.

Circular dichroism of (−)-2-chloro-2-nitroso-fenchane after ½ hrs. treatment with silver nitrate solution



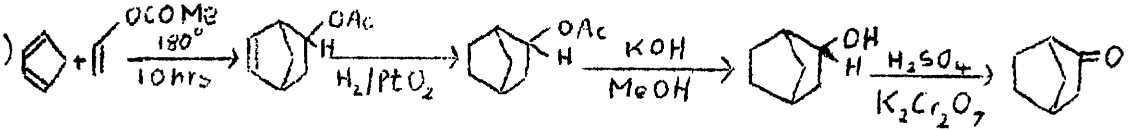
IV. 2-chloro-2-nitroso-norcamphane

Bis-(2-chloro-2-nitroso-bicyclo-[2:2:1]-heptane)

Bis-(2-Chloro-2-nitroso-bicyclo-[2:2:1]-heptane)

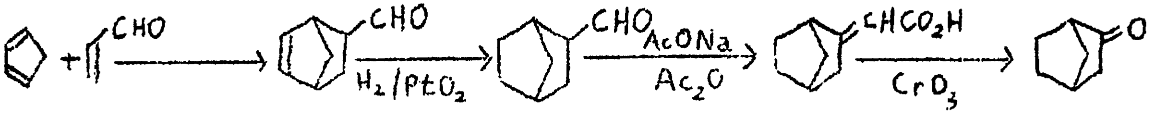
It was thought that photomutarotation might be a steric effect due to the methyl groups in camphor. Accordingly it was decided to prepare 2-chloro-2-nitroso-bicyclo-[2:2:1]-heptane from norcamphor and to examine its properties.

Several syntheses are given in the literature:-

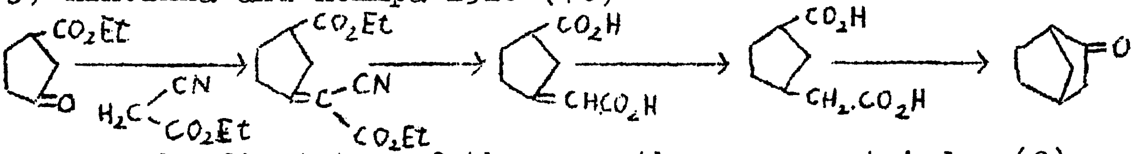
1)


Alder and Rickert 1939 (68)

2) Diels and Alder 1928 (69)



3) Hintikka and Kommpa 1918 (70)



The first two of these syntheses were tried. (2) worked successfully as far as the enol-acetate but I could not isolate any norcamphor. (1) however works much better and I was able to prepare several grams of norcamphor without much difficulty.

Preparation of Endo-dehydronorbornyl Acetate.

Cyclopentadiene was prepared, as required, by thermal cracking of dicyclopentadiene as described by Stoll (71).

540 gms of dicyclopentadiene gave a total of 493 gms of cyclopentadiene.

Batches of 100 gms cyclopentadiene + 160 gms. vinyl acetate were heated up in an autoclave to 180 -190° for 10 hrs. as described by Alder and Rickert (68). Yields of dehydronorbornyl acetate varied between 75 and 85 gms. Lit. yield 100 gms. bp = 73 - 77°/14 mm.

It was decided to increase the proportion of vinyl acetate as recommended by Winstein and Trifan (72).

Batches of 150 gms cyclopentadiene + 300 gms vinyl acetate were heated to 175 - 185° for 10 hrs.

Yields varied between 167 and 176 gms (48.5 - 51%)

Lit. yield 45%

The total quantity of dehydronorbornyl acetate prepared was 567 gms bp = 73 - 77°/14 mm. $n_D^{12} = 1.4749$

Preparation of Endo-norbornyl Acetate.

Batches of endo-dehydronorbornyl acetate were hydrogenated in acetic acid solution using Adam's platinum oxide catalyst as described in the literature (68) and (72). The apparatus used was that described by Tucker (63).

In one experiment 69 gms of dehydronorbornyl acetate was dissolved in 100 mls of glacial acetic acid and 100 mg of catalyst added. 10.8 litres of hydrogen were absorbed (100%). The resulting mixture was then filtered, diluted with water, extracted with ether, and the extract dried over sodium sulphate. On distillation 56 gms norbornyl acetate was obtained.

bp = 80 - 84°/19 mm Yield 80%

Yields varied from 70-90%

From a total of 400 gms dehydronorbornyl acetate 345 gms of norbornyl acetate was obtained.

bp = 72 - 78°/12 mm. Lit. bp = 81 - 83°/12 mm

Preparation of Norborneol.

Norbornyl acetate was hydrolysed by refluxing with excess methyl alcoholic potash. It was found necessary to use at least three times the theoretical amount of potash and to continue the hydrolysis for at least 24 hrs.

From a total of 293 gms norbornyl acetate 156 gms norborneol was obtained.

Derivs.

Norbornyl 3:5-dinitrobenzoate mp = 118°
Recryst mp = 120° Lit mp = 123°
Norbornyl acid phthalate mp = 108° Lit mp = 109-110°
Norbornyl α-naphthyl urethane mp = 108-109°
Recryst mp = 110-111°

C = 76.91% H = 7.05% N = 4.83%

$C_9H_{19}NO_2$ requires C = 76.84% H = 6.81% N = 4.98%

Preparation of Norcamphor.

Norcamphor was obtained as described by Alder (68).

10 gms norborneol added to a mixture of 10 gms

potassium dichromate and 14 gms sulphuric acid in 150 mls water. Oxidation was completed after gentle warming for ½ hr. The mixture was then made alkaline with caustic potash solution and steam distilled. Norcamphor crystals separated from distillate.

Yield 6 gms mp = 94° Lit. mp = 93-94°
Norcamphor semicarbazone mp = 194° Lit. mp = 196°
Norcamphor Semioxamazone mp = 171°
Norcamphor 2:4-dinitrophenylhydrazone
mp = 128° (from MeOH)
N = 19.5% $C_{13}H_{14}N_4O_4$ requires N = 19.3%

<u>U.V. Absorption of Norcamphor</u>

c = 30 mg/10 mls ethanol C = 0.0273M l = 1 cm

λ	ρ	ε	λ	ρ	ε
3500	0.004	0.15	2870	0.575	21.1
3400	0.007	0.24	2860	0.576	21.15?
3300	0.014	0.51	2850	0.566	20.75
3200	0.060	2.19	2840	0.564	20.70
3100	0.216	7.92	2830	0.554	20.35
3000	0.443	16.25	2820	0.545	20.0
2980	0.470	17.25	2810	0.540	19.8
2960	0.497	18.30	2800	0.535	19.6
2940	0.550	20.2	2780	0.502	18.40
2930	0.561	20.6	2760	0.475	17.45
2920	0.568	20.8	2740	0.445	16.35
2910	0.572	21.0	2720	0.415	15.25
2900	0.575	21.1	2700	0.384	14.10
2890	0.576	21.15	2600	0.249	9.14
2880	0.582	21.35	2500	0.159	5.84
2870	0.575	21.1	2400	0.121	4.42
			2300	0.108	3.96
			2200	0.119	4.36

Norcamphoroxime

This was prepared from norcamphor and hydroxylamine as described in the literature (73) bp = 80-90°/1½ mm.

Norcamphoroxime Hydrochloride.

This compound was prepared from the oxime as it was thought that the chloronitroso compound might be more easily prepared from it than from oxime. (60) It was later found that the chloronitroso compound was easily prepared from the oxime.

HCl gas was passed into a solution of 0.9 gms norcamphoroxime in dry ether at 0°C.

Yield 1.1 gms mp ~ 108°C

N = 8.63% Cl = 21.80%, 22.00% $C_7H_{12}NOCl$ requires N = 8.67%
Cl = 21.94%

Preparation of 2-chloro-2-nitro-norcamphane.

0.27 gms of norcamphoroxime was suspended in 10 mls of 15 % caustic potash. The mixture was added with shaking to an ice cold mixture of 18 mls bleach (7.35 gms available Cl_2/100 mls) and 120 mls water. The mixture was left overnight and the solid product was filtered off and washed well with water.

Gave 0.51 gms of a camphor-like solid mp = 73-74°
Recryst. from dilute alcohol mp = 74-75°

N = 7.43°, $C_7H_{10}NO_2Cl$ requires N = 7.97%

0.224% solution in EtOH gave UV absorption maximum at 2813Å
ε_{max} = 36.40

Absorption C = 0.001277M

λ	ρ	ε	λ	ρ	ε
3500	0.051	4.00	2725	0.420	32.95
3250	0.108	8.47	2700	0.403	31.60
3200	0.133	10.41	2650	0.364	28.55
3100	0.208	16.30	2600	0.339	26.60
3050	0.262	20.55	2575	0.373	29.25
3000	0.323	25.35	2550	0.469	36.80
2950	0.389	30.50	2525		
2875	0.449	35.94	2500	0.602	47.30
2812.5	0.463	36.40			
2800	0.460	36.10	2475	0.785	61.5
2775	0.453	35.60	2930	0.408	32.10
2750	0.437	34.30	2900	0.433	34.00

2-Chloro-2-nitroso-bicyclo-[2:2:1]-haptane.

1.5 gms norcamphoroxime was dissolved in 40 mls dry ether and cooled in ice. Chlorine gas was passed through the solution until the blue solution turned an emerald green colour. The ether was then evaporated off in a stream of air. The solid remaining (~1.3 gms) was washed thoroughly with 40° pet. ether to remove monomer.

Yield 600mg of white dimer.

C = 52.87% H = 5.57% N = 8.21% Cl = 21.97%

$C_7H_{10}NOCl$ requires C = 52.67% H = 6.31% N = 8.77
Cl = 22.21%

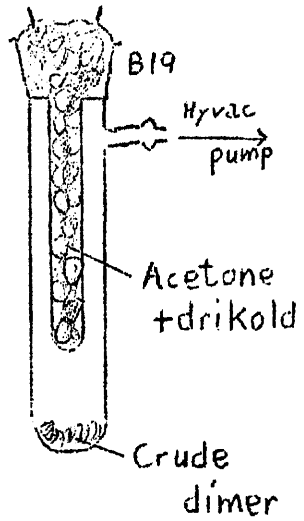
This compound is a pure white solid (mp ~44°C) which melts to give a deep blue liquid. It is very volatile. A few mg left on a watch glass will disappear overnight. The vapour is lachrymatory. It dissolves in all the common organic solvents giving deep blue solutions.

In alcohol $\varepsilon_{max} = 22.5$ $\lambda_{max} = 6500$ Å C = 0.031 M

Since the solutions of the compound are decomposed by light the compound must be prepared in a subdued light.

Purification of Bis-(2-chloro-2-nitroso-norcamphane)

A Quickfit filter tube was selected and a small amount of the crude dimer placed in it. The tube was set up for sublimation as shown.



At a pressure of 1 mm of mercury the compound sublimed readily at 40°C. The sublimate which was blue at first whitened after an hour or two. The central tube was removed and the pure dimer scraped off into a specimen tube and placed in a vacuum desiccator over P_2O_5 and paraffin wax (1 hr/2 mm).

Analysis gave C = 52.36% H = 6.48% N = 8.94% Cl = 22.13%

ε_{max} = 26.18 at 6500 Å (in alcohol C = 0.01757M)

Absorption Spectrum of 2-chloro-2-nitroso-norcamphane.

14.03 mg of resublimed dimer dissolved in 5 mls ethanol.

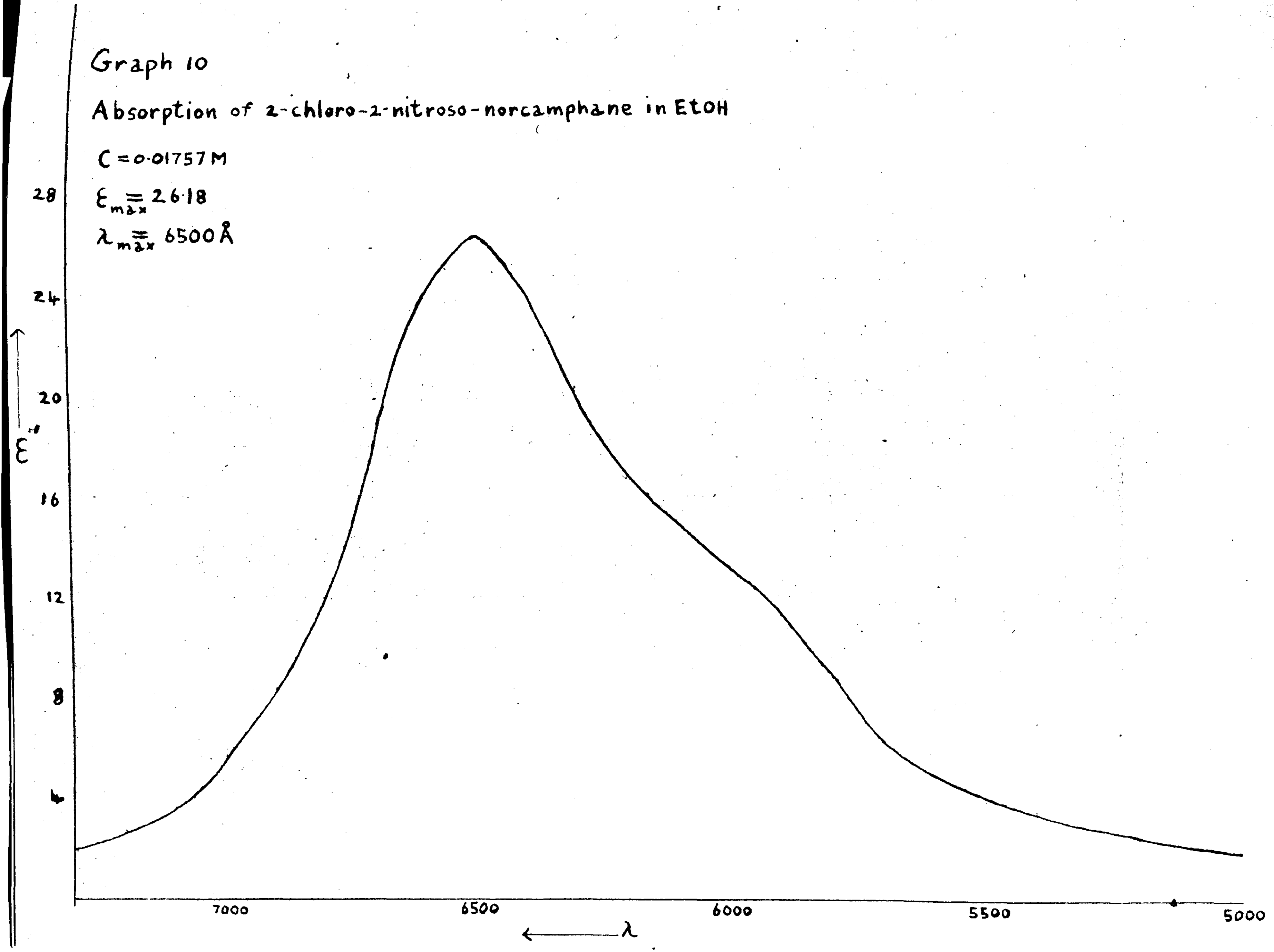
$C = 0.01757M$

λ	ρ	ε	λ	ρ	ε	λ	ρ	ε
6500	0.460	26.18	6450	0.447	25.44	5550	0.078	4.44
7500	0.023	1.31	6400	0.425	24.19	5500	0.068	3.87
7400	0.027	1.54	6350	0.390	22.20	5400	0.062	3.53
7300	0.035	1.99	6300	0.357	20.32	5200	0.052	2.96
7200	0.047	2.68	6250	0.322	18.33	5000	0.026	1.48
7100	0.063	3.59	6200	0.295	16.79	4800	0.022	1.25
7000	0.100	5.69	BC6200	0.293	16.68	4600	0.024	1.37
6950	0.116	6.60	6150	0.276	15.71	4400	0.023	1.31
6900	0.147	8.37	6100	0.264	15.03	4200	0.023	1.31
6850	0.170	9.68	6050	0.245	13.94	4000	0.020	1.14
6800	0.210	11.95	6000	0.231	13.15	3800	0.028	1.59
6750	0.257	14.63	5950	0.217	12.35	3600	0.038	2.16
6700	0.320	18.21	5900	0.198	11.27	HL3600	0.038	2.16
6650	0.382	21.74	5850	0.175	9.96	3400	0.078	4.44
6600	0.420	23.90	5800	0.156	8.88	3200	0.138	7.85
6550	0.439	24.99	5750	0.132	7.51	3100	0.157	8.94
6525	0.451	25.67	5700	0.110	6.26			
6500	0.460	26.18	5650	0.103	5.86			
6475	0.457	26.01	5600	0.087	4.95			

These results are plotted on Graph 10.

Graph 10

Absorption of 2-chloro-2-nitroso-norcamphane in EtOH



$C = 0.01757\,M$

$\varepsilon_{max} = 26.18$

$\lambda_{max} = 6500\,Å$