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THESIS

submitted to

THE UNIVERSITY OF GLASGOW

in fulfilment of the
requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

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SEPTEMBER, 1964

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S U M M A R Y

Some chemical investigations of 1-thia-4-pyrone have been carried out. In experiments with hydroxylamine and hydrazines, 1-thia-4-pyrone was shown to react somewhat similarly to 4-pyrone. Thus 4-hydroxylaminopyridine-N-oxide was obtained from the reaction of 1-thia-4-pyrone and hydroxylamine, and with hydrazine a pyrazole derivative was obtained. In contrast, little or no reaction was observed with phenyl and p-nitrophenylhydrazines; with 2,4-dinitrophenylhydrazine 1-thia-4-pyrone-2,4-dinitrophenylhydrazone was obtained. Methyl magnesium iodide and cyclopentadienyl sodium did not condense with 1-thia-4-pyrone. No evidence of nuclear bromination was found. 1-Thia-4-pyrone with bromine in various solvents gave a complex to which is assigned the formula $C_5H_4OS.HBr.3Br_2$. Numerous attempts to synthesise metal carbonyl derivatives of 1-thia-4-pyrone were unsuccessful. The n.m.r. spectrum of 1-thia-4-pyrone has been studied.

Several routes to a tricyclo[9,3,0,0^{4,8}]tetradecane system were attempted using cis,cis-1,5-cyclo-octadiene as starting material. The tetrabromo-derivative, 1,2:5,6-tetrabromocyclo-octane was unreactive to sodio- and magnesio-malonic esters. Friedel-Crafts reactions of 1,5-cyclo-octadiene with ethyl malonyl chloride and β -chloropropionyl chloride were unsuccessful. Possible reasons were suggested.

Synthesis and subsequent transformations of several tropyphenols have been studied. From p-tropyphenol via triphenylmethyl perchlorate dehydrogenation and basification, tropilidene-p-quinone was obtained which was unstable to air and could not be purified. Ditropyl ether and thiophenol afforded tropyphenyl phenyl thioether which reacted with triphenylmethyl perchlorate to give tropylium perchlorate and triphenylmethyl phenyl thioether. Dehydrogenation of o-tropyphenols which were obtained by the action of ditropyl ether on the corresponding phenol afforded benzo[b]cycloheptatrieno[d]furans which could be further dehydrogenated to benzofuranotropylium salts. Basification of the latter afforded three products. The first was the original benzo[b]cycloheptatrieno[d]furan. The other two were benzofuranotropone isomers whose structures are assigned on the basis of n.m.r. spectra.

SUMMARY

Some chemical investigations of 1-thia-4-pyrone have been carried out. In experiments with hydroxylamine and hydrazines, 1-thia-4-pyrone was shown to react somewhat similarly to 4-pyrone. Thus 4-hydroxylaminopyridine-N-oxide was obtained from the reaction of 1-thia-4-pyrone and hydroxylamine, and with hydrazine a pyrazole derivative was obtained. In contrast, little or no reaction was observed with phenyl and p-nitrophenylhydrazines; with 2,4-dinitrophenylhydrazine 1-thia-4-pyrone-2,4-dinitrophenylhydrazane was obtained. Methyl magnesium iodide and cyclopentadienylsodium did not condense with 1-thia-4-pyrone. No evidence of nuclear bromination was found. 1-Thia-4-pyrone with bromine in various solvents gave a complex to which is assigned the formula $C_5H_2OS.HBr.3Br_2$. Numerous attempts to synthesise metal carbonyl derivatives of 1-thia-4-pyrone were unsuccessful. The n.m.r. spectrum of 1-thia-4-pyrone has been studied.

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A C K N O W L E D G E M E N T S

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SOME STUDIES IN THE FIELD OF
NON-BENZENOID AROMATIC COMPOUNDS

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INTRODUCTION

Aromaticity

It was by coincidence that among the many odoriferous compounds listed by Loschmidt² in 1861, most contained the benzene nucleus. The term 'aromatic' then meant literally 'of pleasant smell or taste'. A few years later, Kekule,^{2 '5} recognizing the structure of the benzene nucleus, proposed that this objective qualitative feature should be the defining criterion for aromatic compounds. It was only months, however, before Erlenmeyer⁴ introduced the point of view that aromaticity encompassed substances of similar behaviour rather than substances with a common structural feature.

There followed a vigorous development of the chemistry of benzenoid compounds, the structure of the benzene molecule being the subject of a large number of hypotheses⁶ the majority of which now enjoy only historical interest.

A number of properties became recognized as being common to benzenoid aromatic molecules, such as the stability of the system, apparent from its ease of formation, and the difficulty of effecting addition reactions at the double bonds. The hydrogen atoms on

the ring, on the other hand, were easily replaced by various groups in electrophilic substitution reactions, e.g. nitration, sulphonation, halogenation, acylation etc. Substituents in aromatic systems appeared to have characteristic properties e.g. acidic properties of phenols, the weakened basicity of the amino group, the ability to undergo azo-coupling, the lack of reactivity of halogen.

Of striking significance, however, was the theory of the 'aromatic sextet' postulated by Armit and Robinson⁶ in 1925, which stated that six electrons of the benzene nucleus formed a stable system responsible for the aromatic character of the substance.

Although this proposition provided no physical explanation, it immediately found support in enabling a common factor to be found in the structure of benzene and aromatic heterocycles and also explained, if only formally, the absence of aromaticity in cyclobutadiene and cyclo-octatetraene.

Then, in a short period around 1930, the evolution of the quantum theory revolutionised the whole approach to the problem of aromaticity. The application of molecular-orbital and valence-bond methods to cyclic conjugated systems, as well as providing a physical basis for

the 'aromatic sextet', allowed the calculation of thermochemical resonance energy, an experimentally-measurable quantity. Agreement between calculated and experimental values proved the fundamental adequacy of the quantum-mechanical methods although their application to problems clearly bound up with aromatic character, such as reactivities and electronic spectra, has never produced such clear and simple agreements with experiment as has the calculation of resonance energies.

A major contribution to the founding of the modern theory of aromaticity was made by Huckel^{7 '32 '33} who was first to apply the molecular-orbital method to aromatic systems.

To apply this method, the π -electrons of a conjugated system are regarded as being common to all the carbon atoms of the system, and occurring in common molecular orbitals.

Three types of molecular orbital are possible. These are the bonding orbitals, in which electrons have less energy than in the atomic orbitals and consequently their occurrence in these orbitals makes the system more stable. There are non-bonding orbitals in which the energy of the

4

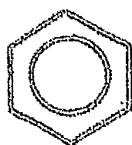
electrons is the same as that in atomic orbitals. Finally, there are anti-bonding orbitals in which the energy of electrons is greater than that in atomic orbitals and hence the occurrence of electrons in these orbitals is energetically undesirable. To conform with the Pauli principle, not more than two electrons can be allocated to each such molecular orbital.

Solution of the wave equation for a given aromatic system determines the numbers of each type of orbital.

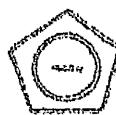
Calculations by this approach show that benzene contains three bonding and three anti-bonding molecular orbitals, and in the ground state the six π -electrons of the system occupy the most favourable lowest energy levels, which are the three bonding orbitals. It can be shown by analogous calculations that in the case of three isolated double bonds the energy of the $3 \times 2 \pi$ -electron system is about 39 k.cal mole more than that in the common π -molecular orbital system.

The stability of the benzene nucleus (I) is thus explained by a closed six π -electron system which may be compared with the specially stable electron shell of the inert gases, in that entry or removal of an electron requires the expenditure of energy.

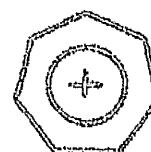
By application of this concept of a closed π -electron shell in aromatic systems, Huckel was able to show theoretically that not only benzene but also five- and seven-membered rings possessing conjugated systems of 6π -electrons and bearing a negative and positive charge respectively, giving the $C_5H_5^-$ anion (II) and the $C_7H_7^+$ cation (III), could be aromatic and energetically stable.



(I)



(II)



(III)

Thus the remarkable properties of the cyclopentadienyl anion (II) prepared so much earlier by Thiele^{10,11} found satisfactory theoretical explanation and in 1954, Doering and Knox¹² obtained the tropylium (cycloheptatrienylum) cation.

As a further consequence, the aromatic character of five-membered heterocyclic rings could be explained, since these contain six π -electrons, four electrons from double bonds and two unshared electrons of the hetero-

atom, in three bonding molecular orbitals.

Hückel's approach finally allowed the question of the aromaticity of a wide variety of cyclic systems to be elucidated even without numerical calculations, and a general rule which he derived states that 'monocyclic conjugated polyolefins having the symmetry of a regular polygon possess a closed electron shell and consequently aromatic stability if the number of π -electrons is $(4n + 2)$ (where n is an integer)'.

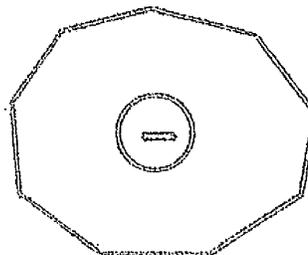
Other aromatic systems were thus predicted.

The parent cyclopropenylum ion (IV), which satisfies the ' $(4n + 2)$ rule' where $n = 0$, is not yet known but Breslow,¹³ in 1957, obtained the first derivative of the system by synthesising triphenylcyclopropenylum tetrafluoroborate.

Only very recently, Katz¹⁴ reported the preparation of the cyclononatetraenyl anion (V).



(IV)



(V)

Thus aromatic character has received various definitions and explanations since its original concept. The most recent attempts to define aromatic character rest their arguments on physical rather than chemical properties.

Volpin,¹⁵ in 1960, wrote 'aromatic compounds are those unsaturated cyclic compounds in which all the ring atoms take part in the formation of a single conjugated system, and the π -electrons of this system form a closed electron shell'.

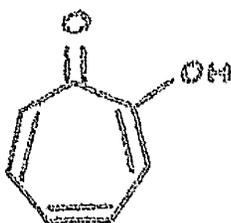
Even more recently, Elvidge and Jackman,¹⁶ in 1961 wrote 'We can define an aromatic compound, therefore, as a compound which will sustain an induced ring current. The magnitude of the ring current will be a function of the delocalisation of π -electrons around the ring and therefore a measure of aromaticity'.

The most recent comment, however, by Hafner¹⁷ states 'A high degree of electron delocalisation, i.e. a strong ring current of the π -electrons does not always guarantee benzene-like reactivity and stability. It therefore appears justified to distinguish between 'aromatic character' of the ground state and 'aromatic' reactivity and stability'.

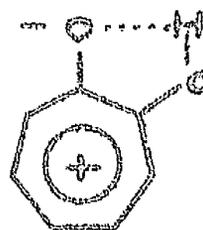
Lloyd¹⁸ also appreciated the significance of such an approach when he concluded 'In considering the aromaticity of any compound, it is best to recognize that both the classical concept, based on chemical analogies with benzene, and the modern one based on physical factors should be taken into account, and that a compound may not satisfy both criteria equally well'.

The Tropylium Cation and Tropylation.

Although, as has been stated, it was not until 1954 that the tropylium cation was recognized the conception of a stable $C_7H_7^+$ moiety was successfully applied by Dewar¹⁹ to elucidate the properties and structure of the naturally occurring tropolones. Thus the properties of tropolone (VI) and its derivatives were explained by a structure based on a seven-membered aromatic system (VII).

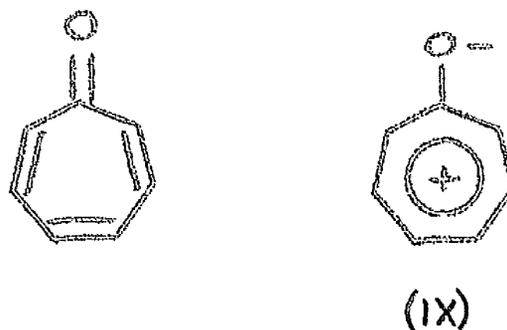


(VI)



(VII)

Similarly tropone (VIII) can be described by approximation to a dipolar structure (IX).



Physical evidence became available to confirm these hypotheses when Robertson,²⁰ by X-ray study of the copper salt of tropolone, showed the seven-membered ring to be a planar almost regular polygon, the lengths of the carbon-carbon bonds averaging 1.40 Å. The carbon-carbon bond length in tropone was shown to be 1.41 Å.²¹ These interatomic carbon-carbon distances correspond to a bond order intermediate between that of a single and double bond confirming the aromatic character of the rings concerned.

Support for a degree of electronic polarisation was obtained by measurement of dipole moments. Thus tropone was shown to have a dipole moment of 4.50 D,^{22 23} which can be compared with that of cycloheptanone which is only 5.04 D.²⁴

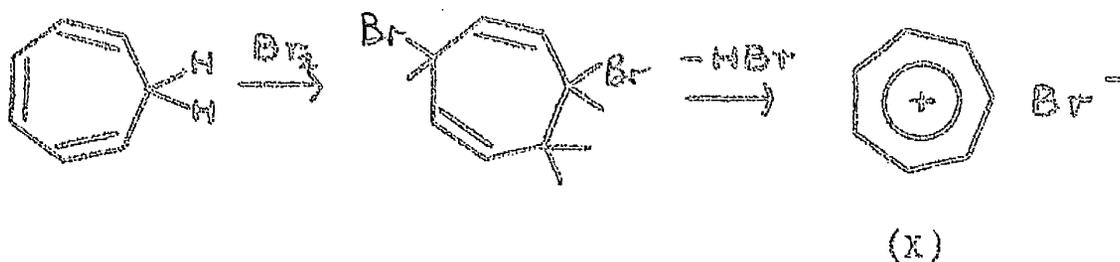
Chemical evidence displays beyond doubt the aromatic character of the tropolones which behave very much like phenols. Tropolones readily undergo various electrophilic substitution reactions such as nitration, sulphonation,

nitrosation, halogenation, hydroxymethylation and coupling with arene diazonium salts.

The aromatic character of tropones, however is not so evident and has indeed been disputed by Buchanan and Lockhart²⁵ who state, 'the case for aromaticity in tropones, in terms of chemical evidence rests entirely on amination by hydrazine or hydroxylamine'. Tropone in fact forms a semicarbazone and a 2,4-dinitrophenyl hydrazone as shown by Nozoe.²⁶

The chemistry of tropones and tropolones has been reviewed by Pauson²⁷ and Nozoe.²⁸

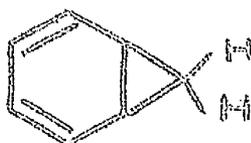
Doering and Knox¹² obtained the unsubstituted tropylium cation as tropylium bromide (X) by thermal elimination of hydrogen bromide from dibromocycloheptatriene as follows:



This reaction had been carried out by Merling²⁹ as early as 1891 but the product was then considered to be a solid isomer of dibromocycloheptatriene.

Various methods have now been devised for the

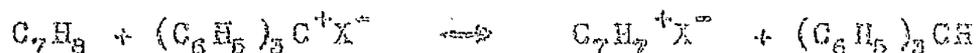
synthesis of the tropylium ion. Notable are those by Dewar and Pettit^{30,31} based on the facile isomerisation of the norcaradiene system (XI), and by Gamellini and Pettit³² who obtained the tropylium ion, though only in 5% yield, by permanganate oxidation of cyclooctatetraene.



(XI)

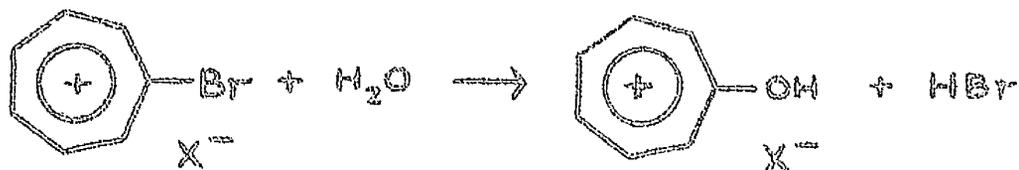
The stability of the tropylium ion itself proved to be a sufficient driving force for the removal of a hydride ion from cycloheptatriene by strong Lewis acids and the method of Kursanov and Vol'pin³³ using phosphorus pentachloride presented a convenient laboratory preparation.

More recently, Dauben et al.^{34,35} synthesised tropylium salts in almost quantitative yield from triphenylmethyl salts and cycloheptatriene in solvents of high dissociation power i.e.



The physical and chemical properties of the tropylium ion have received an intensive study which will undoubtedly continue. They have been reviewed by Vol'pin¹⁵ and Nozoe³⁶.

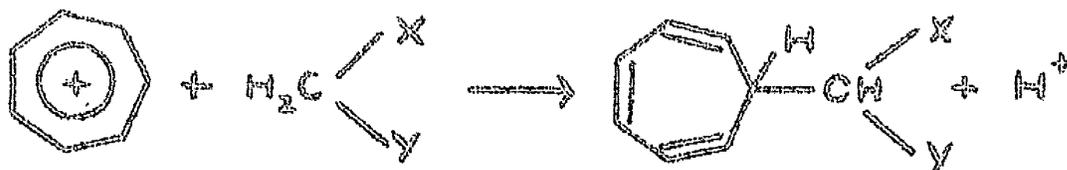
A considerable amount of attention has been devoted to tropylation reactions where the troyl ring is introduced into other organic molecules. It is the most characteristic property of the troylium cation that it undergoes easy reaction with various nucleophilic reagents. In the majority of cases this leads to addition of the attacking agent or, in other words, the introduction of the troyl ring to that agent i.e. troylation. Nevertheless examples are known of nucleophilic exchange reactions in the troyl nucleus. For example, chloro- and bromotroylium salts, on treatment with water, extremely readily exchange the halogen atom for a hydroxyl group.^{37,38}



As might be expected, electrophilic reactions diagnostic of benzenoid aromatic systems such as nitration, sulphonation, and acylation have not been induced in troylium salts.

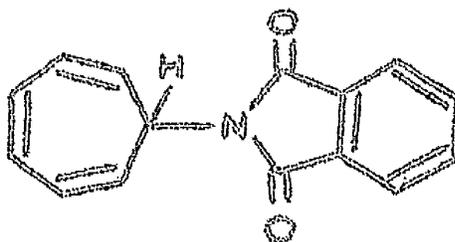
The unusually high electrophilic properties of the troylium ion were first reported by Vol'pin et al.³⁹ who

stated that tropylium salts could alkylate compounds with active hydrogen atoms according to the general equation



where X and Y could be $-\text{COOH}$, $-\text{COOC}_2\text{H}_5$, $-\text{COCH}_3$, $-\text{NO}_2$, $-\text{CN}$ etc. Where the methylene group had high reactivity such as in β -keto-esters and β -diketones, the reactions proceeded very readily in the cold and even with the evolution of heat.

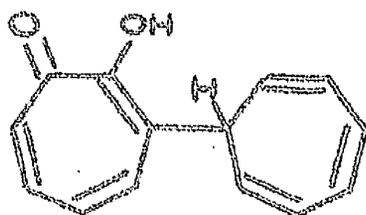
The same authors⁴⁰ showed that aliphatic aldehydes undergo similar reactions and that alkyl and alkyl aryl ketones react with the tropylium ion only on heating. Jordan and Elliot⁴¹ prepared N-tropylphthalimide (XII) from tropylium bromide and potassium phthalimide



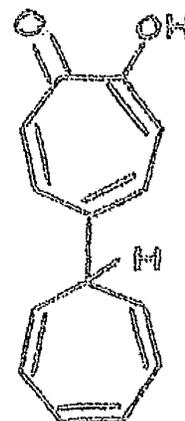
(XII)

Vol'pin et al. reported that aromatic compounds such as phenol, quinol, phloroglucinol, resorcinol and α - and β -naphthols also react with the tropylium ion and Nozoe⁴² reported the reaction of tropylium ion with sodium phenoxide and sodium β -naphtholate.

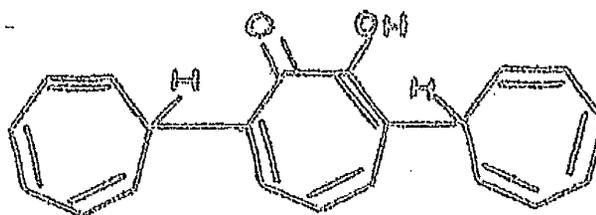
Very recently, Nozoe et al.⁴³ reported the reaction of tropylium bromide with sodium tropolonate to give 3-(7-trotyl)- (XIII), 5-(7-trotyl)- (XIV) and 3,7-di-(7-trotyl) tropolone (XV).



(XIII)

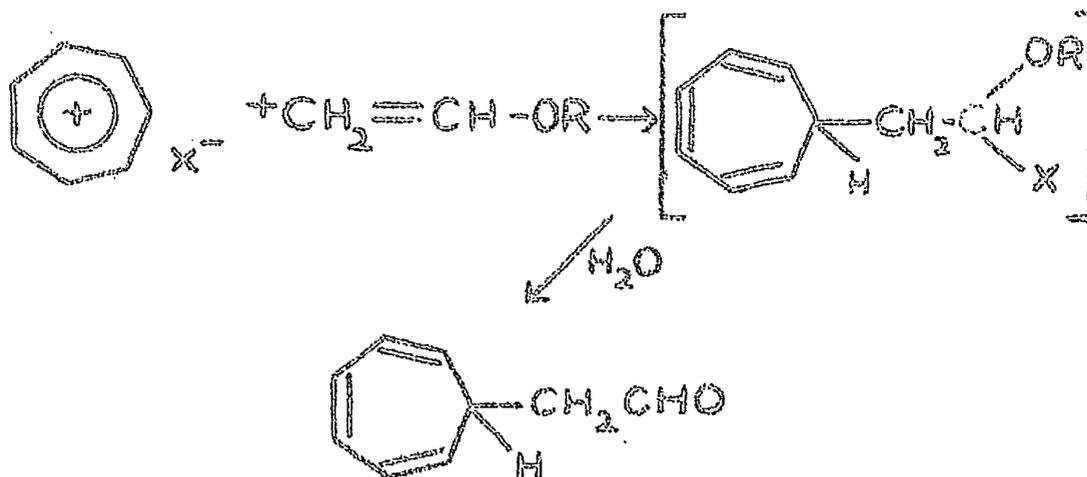


(XIV)

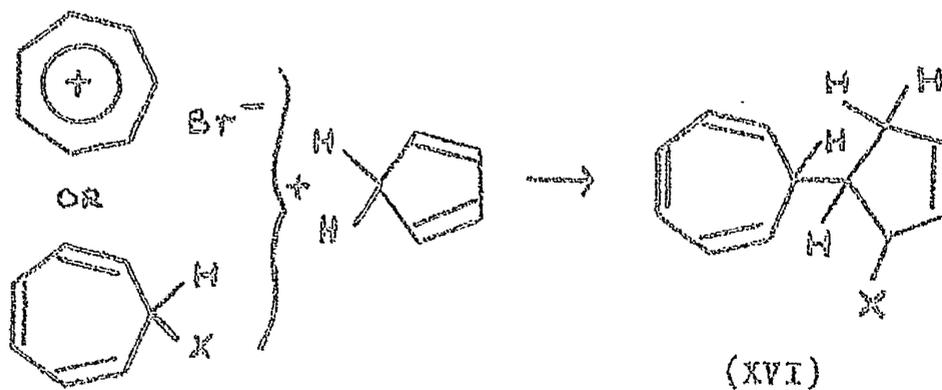


(XV)

Reactions with several compounds having activated double bonds have also been reported,⁴⁴ e.g. vinyl ethers,

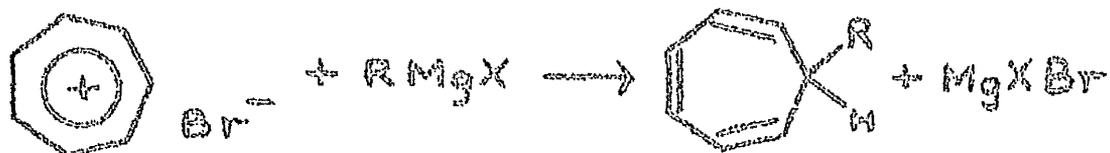


With cyclopentadiene³⁹ tropylium salts readily give tropylium derivatives (XVI).

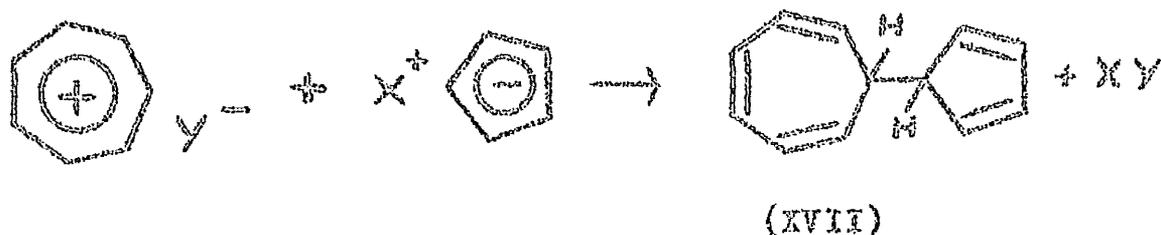


where $X = -OC_2H_5, -OH, -O.CO.CH_3$

Reaction of organometallic compounds with tropylium salts has also been studied. Alkyl and aryl tropilidenes are readily obtained by treatment of the appropriate Grignard reagent or organolithium compound with the tropylium ion.^{37,45,46}

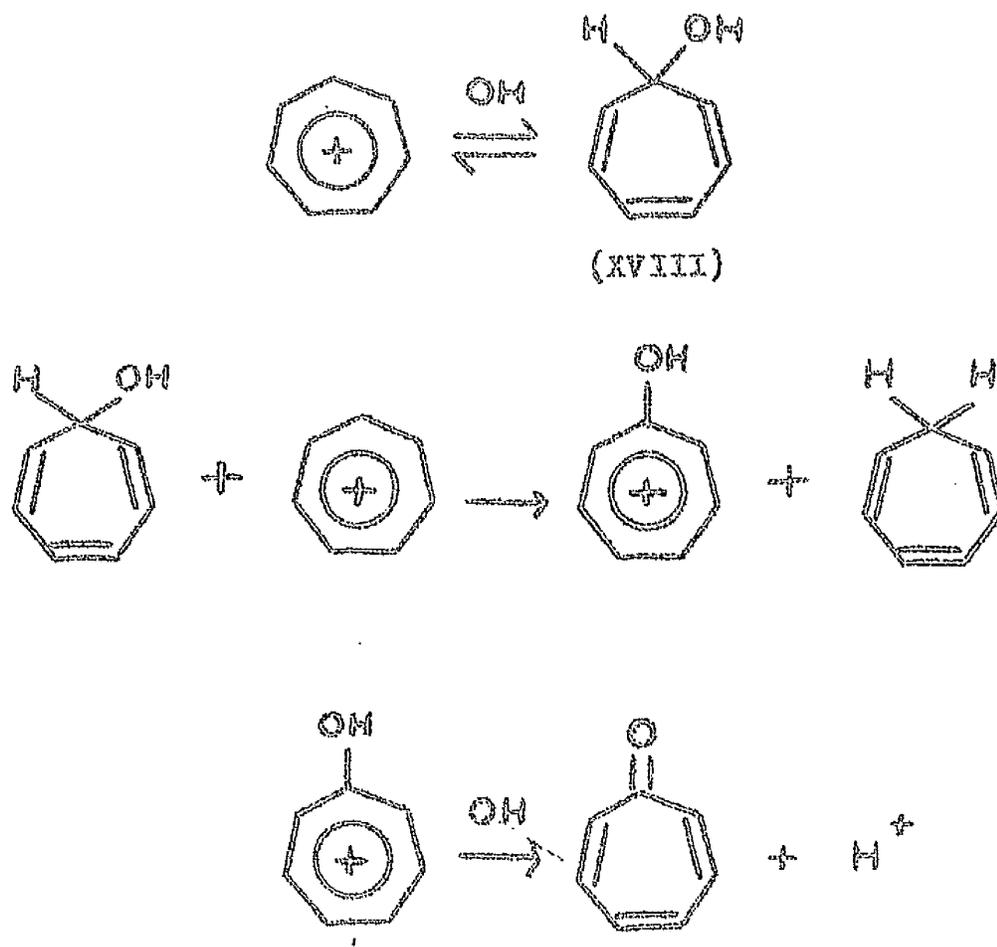


With cyclopentadienyl sodium or lithium^{57 547}, tropylium salts give, not the salt $\text{C}_5\text{H}_5^- \text{C}_7\text{H}_7^+$, but the covalent compound, cyclopentadienyl cycloheptatriene (XVII)

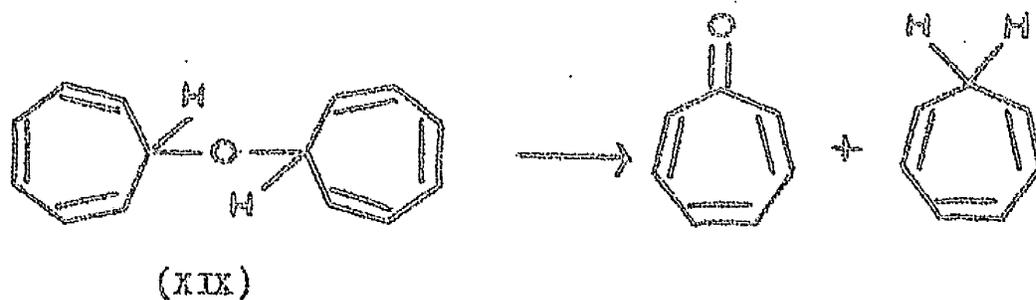


The simplest of the reactions between the tropylium ion and a nucleophilic reagent is that with the hydride ion to give cycloheptatriene. Such a reaction is obtained with sodium borohydride or lithium aluminium hydride.⁴⁹

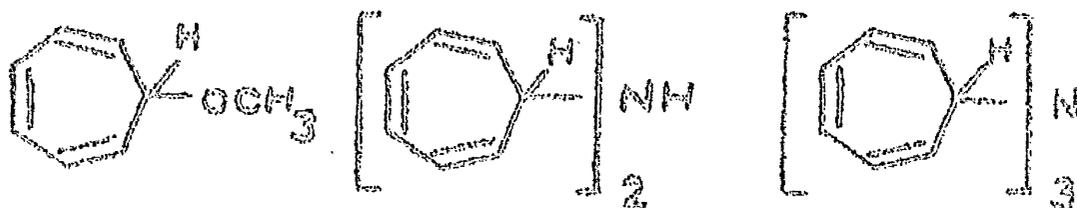
In fact, the tropylium ion can abstract hydride ions from easily oxidisable compounds. For example, on slow neutralisation of an aqueous solution of a tropylium salt with sodium bicarbonate, tropone is formed by dehydrogenation of trotyl alcohol (XVIII) originally formed from the cation in the aqueous medium^{50 51}



Similarly ditropyl ether (XIX), in the presence of tropylium ions or a trace of hydrochloric acid, which generates ions from the ether, disproportionates into tropone and cycloheptatriene.^{50 51}



Doering and Knox^{46 1952} have reported the reaction of tropylium salts and the methoxide ion to give 1-methoxy cycloheptatriene (XX) and with sodium bicarbonate to give ditropyl ether (XIX). With aqueous ammonia ditropylamine (XXI) is formed and, in ethereal solution, ammonia and tropylium salts form tritropylamine (XXII).



That ditropyl ether and alkyl ethers are extremely easily cleaved by mineral acids to give the more stable tropylium ion^{47 1948 1950 1951} explains why the tropylation reaction is also a property of these ethers.

Nozoe and Kitahara⁵³ reported the exothermic reaction of ditropyl ether and ethyl tropylium ether with phenol by merely mixing without solvent to give *o*- and *p*-tropylium phenol and ditropyl phenol.

2,6-Xylenol was tropyliated in the *p*-position with ditropyl ether.⁵⁴ Very recently Juts and Voithen-leitner⁵⁵ prepared a whole series of *p*-substituted tropylium benzenes using methyl tropylium ether and the Grignard reagent of the corresponding *p*-substituted bromobenzenes.

Polycyclic Aromatic Systems

Huckel's rule for the stability of a system of $(4n + 2)\pi$ -electrons was derived for monocyclic molecules only.

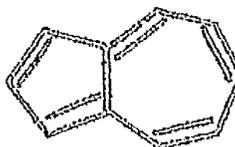
However the fact that numerous bicyclic and polycyclic molecules were known whose aromatic character was undisputed, such as naphthalene, anthracene and phenanthrene, and which satisfied the '(4n + 2) rule', prompted Vol'pin¹⁵ to modify the rule to include polycyclic systems, accepting that bridging bonds could be neglected.

Vol'pin stated that 'any plane (or nearly plane) fused system containing no atoms common to more than two rings will be aromatic if the number of π -electrons in it is equal to $4n + 2$ (where n is a whole number)'. An added and obvious criterion was that the rule related only to systems in which the bridge contains no additional atoms, i.e. in the Baeyer nomenclature, to systems containing a zero atom bridge.

The possible fused bicyclic combinations, of five- and seven-membered rings only, are as follows



(XXIII)



(XXIV)



(XXV)

Of these, only azulene (XXIV) satisfies the ' $4n + 2$ ' rule⁵⁶ for aromaticity. It was first characterised by Pfan and Plattner⁵⁶ in 1936 and is indisputably aromatic.⁵⁷

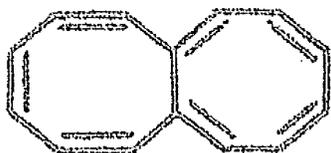
Correspondingly, pentalene (XXIII) and heptalene (XXV) were not expected to be aromatic. It was not until 1961, that the synthesis of heptalene by Dauben and Bartelli⁵⁸ provided experimental confirmation of this theoretical prediction.

It is perhaps significant, too, that pentalene has not yet been synthesised.

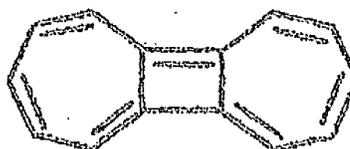
Using the generalised ' $4n + 2$ ' rule⁵⁶, a series of fused bi- and polycyclic systems which might be expected

to display aromatic character have been predicted.^{15 95 9}

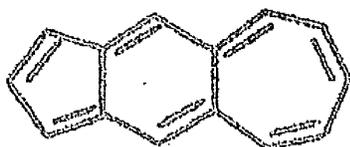
This series included the following,



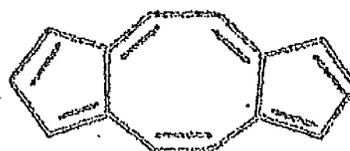
(XXVI)



(XXVII)



(XXVIII)

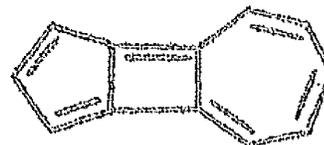


(XXIX)

By the same rule, systems which might not be expected to display aromatic character such as (XXX) and (XXXI) were predicted.¹⁵



(XXX)

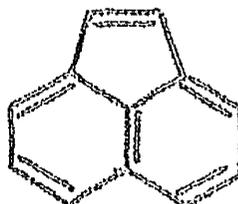


(XXXI)

Suffice it to say that of these systems
Suffice it to say that of these systems

(XXVI-XXXI) S-indacene has since been synthesised by Hafner⁶⁰ who showed it to be non-aromatic as predicted.

With tri- and polycyclic systems having atoms common to three rings, the '(4n + 2) rule' no longer applies. For example, acenaphthylene (XXXII) has 12 electrons and therefore does not conform to the '(4n + 2)rule' although it is aromatic.



(XXXII)

With such systems calculations are necessary by the molecular-orbital method already described to determine whether the molecule contains a closed π -electron system.

As early as 1951, however, Craig⁶⁹ presented a theory to distinguish between molecules which might be expected to show normal aromatic behaviour and those which might not. The classification, based on the symmetry of the electronic ground state, could be applied

to molecules having one or more twofold axes passing through to molecules having one or more twofold axes passing through at least two of the π -centres. Thus molecules not having these axes of symmetry could not be classified and could only be dealt with by an actual calculation of energy levels.

Predictions thus possible need bear no relation to the number of π -electrons, except in monocyclic hydrocarbons where all molecules having $4n$ π -electrons are not aromatic. It does therefore explain the aromatic character of such molecules as acenaphthylene (XXXII).

Heterocyclic Aromatic Compounds.

It has long been recognised that benzenoid aromatic character is exhibited by six-membered heterocyclic compounds such as pyridine (XXXIII) and pyrimidine (XXXIV) where $=CH-$ is replaced by $=N-$.



(XXXIII)



(XXXIV)

As Baker^{61 1962} pointed out, a $=CH=CH-$ group may be replaced by hetero- atoms having a lone pair of p-electrons

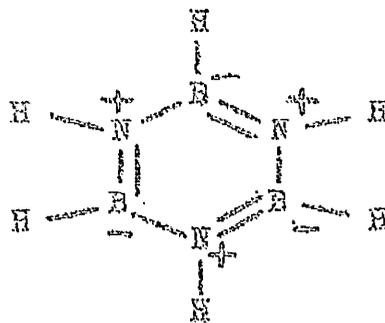
Thus substitution by $-NH-$ gives pyrrole (XXXV, $X = -NH-$), substitution by $-O-$ gives furan (XXXV, $X = -O-$), and by $-S-$ gives thiophen (XXXV, $X = -S-$).



(XXXV)

In all these cases, the sextet of π -electrons is maintained by the contribution of the hetero-atom.

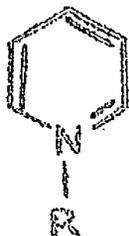
It is interesting to note that examples are known, e.g. triborane triamine (XXXVI),⁶⁸ where all the carbon atoms are replaced giving purely inorganic compounds with aromatic benzenoid structures.



(XXXVI)

Compounds such as pyridine (XXXIII) retain their aromatic character in the form of salts or quaternary derivatives (XXXVII) since their formation involves only the unshared pair of electrons on the nitrogen atom.

In the same way a positive oxonium atom $=\overset{+}{O}-$ can also replace $=C-$ in the benzene ring to give the pyrylium cation (XXXVIII, X = O). By analogy, the thiapyrylium cation can also be obtained (XXXVIII, X = S).



(XXXVII)



(XXXVIII)

Baker laid down certain limitations to these substitutions, some of which have since been criticised by Vol'pin.¹⁵ However, Baker did state that 'If a group carrying an electric charge is introduced the result will be an ion... A neutral molecule will also result if some exocyclic atom or group, is attached which has an opposite charge'.

Thus, attachment of a negative oxygen atom to the p-position of structure (XXXVIII) gives the dipolar form (XXXIX), which can resonate with the neutral structure (XL) of e.g. 1,4-pyrone (XL, X = O) and 1-thia-4-pyrone (XL, X = S).



(XXXIX)



(XL)

Thus 1,4-pyrones (XXXIX = XL; X = O) and 1-thia-4-pyrones (XXXIX = XL; X = S) may be expected to display to some extent the characteristics of a closed π -electron shell.

1-Thia-4-pyrone.

Because of their wide distribution in nature, pyrans, pyrylium salts and pyrones have been the subject of an immense amount of chemical research, as recourse to text-books^{64 '65} on the subject will show. They are to be found in carbohydrates, chromones, flavones, anthocyanins and alkaloids.

The sulphur analogues on the other hand are almost entirely of synthetic origin and have received considerably less attention.

Thus, despite an appreciable amount of research devoted to synthetic routes to 1-thia-4-pyrones, no

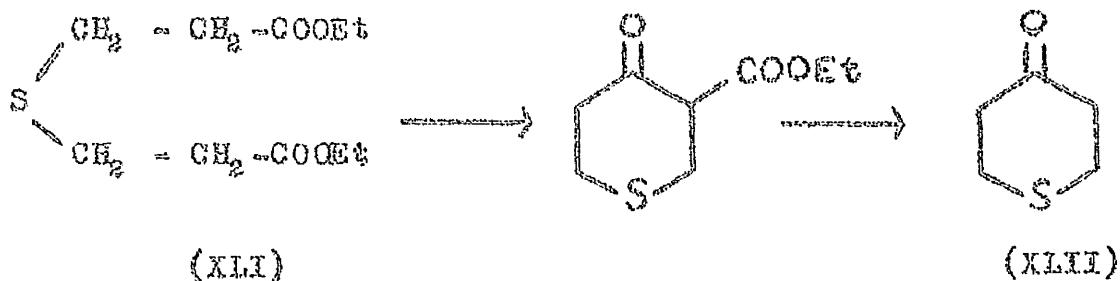
detailed chemical investigations on 1-thia-4-pyrone have been reported. Some interest in its physical properties has been shown (see below).

The first derivatives of the 1-thia-4-pyrone system were prepared as early as 1904 by Apitzsch⁶⁶ by the action of carbon disulphide and alkali on ketones of the general structure RCH_2COCH_2R



1-Thia-4-pyrone itself was first prepared by Arndt and Bekir⁶⁷ in 1930 by dehydrogenation of tetrahydro-1-4-pyrone (XLI) with phosphorus pentachloride.

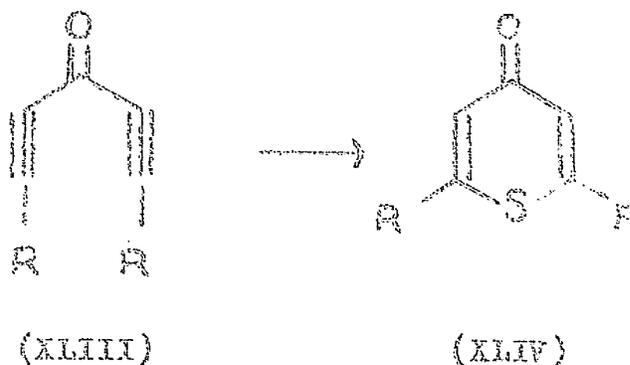
Tetrahydro-1-thia-4-pyrone had been prepared a few years earlier by Bennett and Scora⁶⁸ from diethyl $\beta\beta'$ -thiodipropionate (XLI) by Dieckmann cyclisation and treatment of the product with hot dilute acid or cold dilute alkali



Since then numerous routes to tetrahydro-1-thia-4-pyrone and its derivatives, and hence 1-thia-4-pyrone and its derivatives by phosphorus pentachloride dehydrogenation, have been established^{69 '70 '71 '72 '73 '74}

The last decade has produced routes to 1-thia-4-pyrones which avoid going through the tetrahydro-stage.

In 1954, Bardone⁷⁵ obtained 2,6-disubstituted 1-thia-4-pyrones (XLIV) by treatment of di-(β -substituted)-ethynyl ketone (XLIII) with hydrogen sulphide in a sealed tube at 100°.



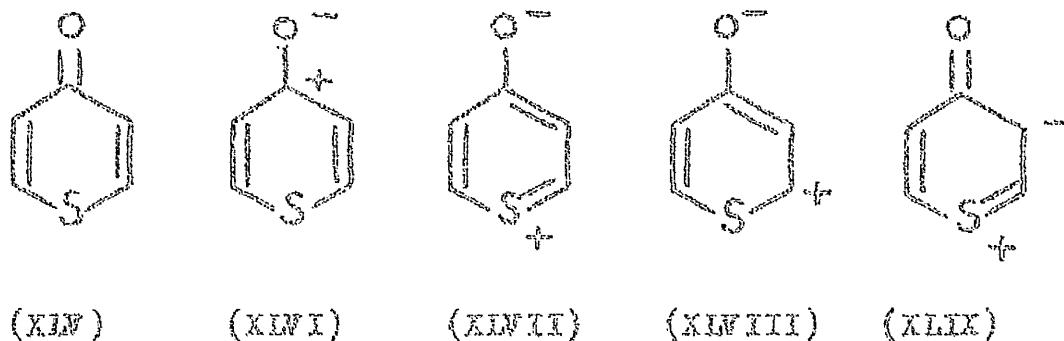
Mayer^{76 '77} prepared 1-thia-4-pyrone itself from 1,4-pyrone by treatment with sodium hydrogen sulphide by simply exchanging the ring oxygen for sulphur.

Physical measurements on 1-thia-4-pyrone and its derivatives have shown that the structure of the molecule as depicted in form (XLIV) does not explain the results obtained.

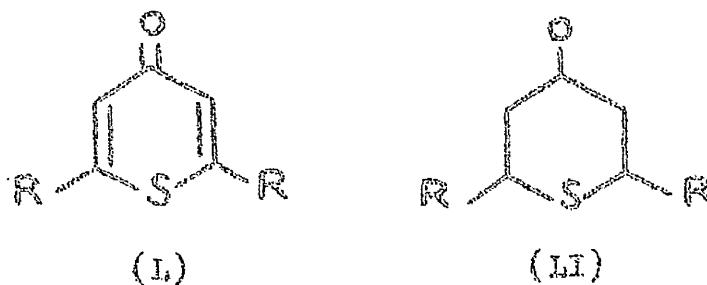
Interaction between the carbon-oxygen double bond and the unshared electrons of the ring sulphur atom

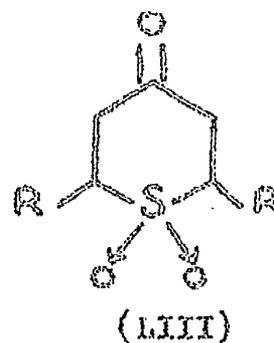
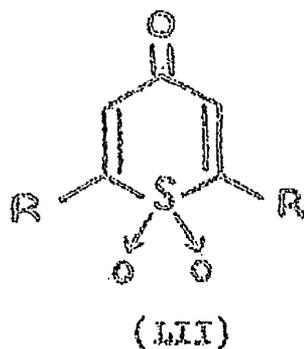
through the two nuclear double bonds can be initiated by the tendency of the carbonyl group to form the dipole $\text{>C}^+ - \text{O}^-$.

The following resonance forms (XLIV-XLIX) are therefore possible and the 1-thia-4-pyrone molecule is considered to be a hybrid of these forms.



The first physical evidence obtained was by measurement of heats of combustion of 2,6-diphenyl-1-thia-4-pyrone (I, R = Ph) its tetrahydro derivative, (LI, R = Ph) and the corresponding sulphones, (LII, LIII; R = Ph).⁷²⁰⁷⁹





The values obtained indicated a resonance energy in (L) of 32.7 k.cals mole.

These compounds were also subjected to dipole moment studies⁷⁹ and the results together with the results of more recent studies on the parent 1-thia-4-pyrone molecule by Traverso⁸⁰ indicate electronic departure from structure (XLV). From structure (XLV), neglecting any interaction through the double bonds, the dipole moment might reasonably be equated to the difference in the moments of the $\begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} = \text{O}$ and $\begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{S} \end{array}$ groups. Taking the moments of benzophenone (3.0 D) and diphenyl sulphide (1.5 D) as being representative of these, the calculated moment for 1-thia-4-pyrone is 1.5 D. The observed value is 3.96 D, indicating some interaction through the double bonds. However, in the extreme dipole structure of form (XLVII), the calculated moment is about 20 D. The large difference in this calculated moment and the observed moment of 3.96 D is to be expected since dipolar structures,

even though otherwise favoured, become increasingly unstable with increased separation of charge.

Tarbell and Hoffman⁸¹ studied the infrared spectrum of 1-thia-4-pyrone and of some of its derivatives. The spectrum showed a strong carbonyl peak at 1609 cm.^{-1} whereas resonance form (XIV) might be expected to show an absorption band in the 1660 cm.^{-1} region typical of a conjugated carbonyl group. Of added significance was the fact that 1-thia-4-pyrone sulphone (LII, R = H) showed normal carbonyl absorption at 1657 cm.^{-1} and sharp bands in the carbon-carbon double bond region. In the sulphone contributions from resonance forms similar to (XIVII) and (XLIX) are no longer possible since the sulphur atom no longer has unshared electrons to donate to the ring system.

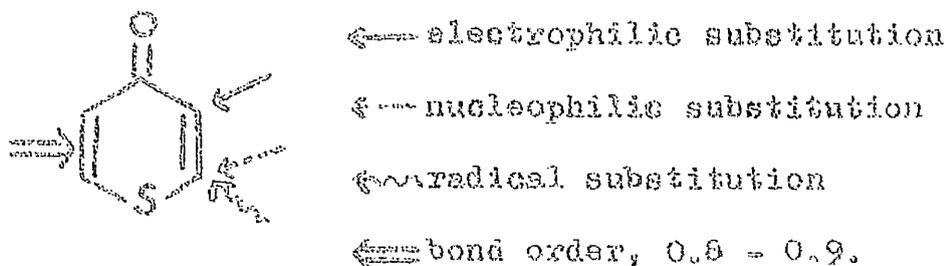
The ultraviolet spectrum of 1-thia-4-pyrone has also been studied.^{82, 83} Maxima at 290 $\text{m}\mu$ (ϵ , 19,500) and 299 $\text{m}\mu$ (ϵ , 15,850) are obtained. This also represents a shift to higher wavelengths since normal $\alpha\beta$ -unsaturated carbonyl compounds are expected to absorb between 220 and 250 $\text{m}\mu$.⁸⁴

One piece of chemical evidence to show that resonance within the 1-thia-4-pyrone nucleus involved the

unshared electrons of the sulphur atom was presented by Arndt and Bekir⁶⁷ who showed that although tetrahydro-1-thia-4-pyrone (LI, R = H) could be oxidised by hydrogen peroxide to the sulphone (LIII, R = H), 1-thia-4-pyrone was not oxidised under similar conditions and more vigorous treatment led to its destruction.

Traverso⁷⁵ has since been able to obtain a trace of the sulphone by direct oxidation of 1-thia-4-pyrone by treatment with hydrogen peroxide for 5 days at -5°.

The 1-thia-4-pyrone molecule has received a theoretical analysis by Zahradnik and Kortecky.⁸⁵ By mathematical study of π -electron density, free valence and bond order, theoretical predictions are made for the centres of electrophilic, nucleophilic and radical reactivities as follows:



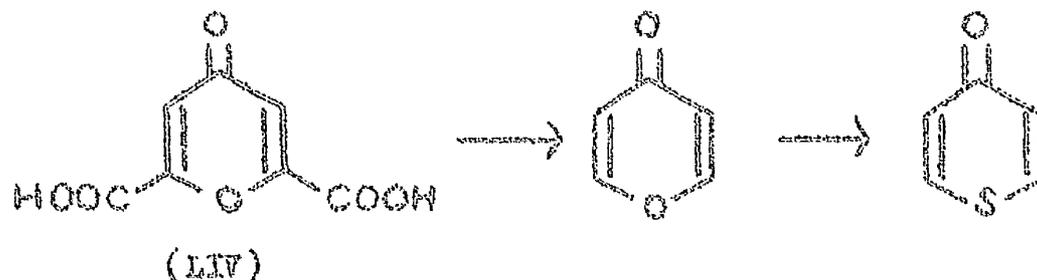
DISCUSSION

CHAPTER I

Some Chemical Investigations of 1-Thio-4-pyrone

Preparation of 1-Thia-4-pyrone.

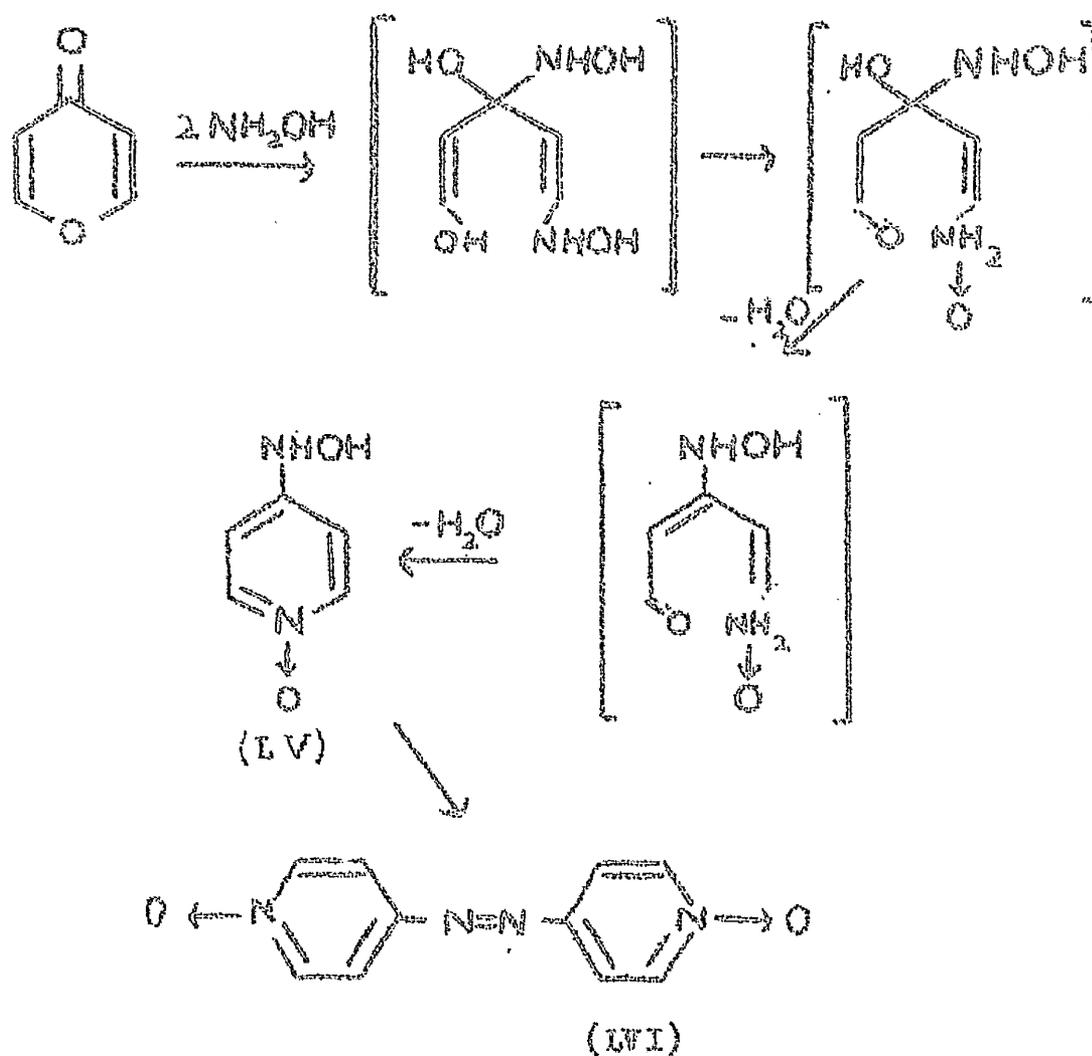
A study of the known routes already described in the introduction for the synthesis of 1-thia-4-pyrone indicated that it would be most conveniently prepared by a two-stage process from commercially obtainable chelidonic acid (LIV) by decarboxylation to 4-pyrone and conversion of the latter to 1-thia-4-pyrone by Mayer's method^{26, 27} using sodium hydrogen sulphide. The decarboxylation of chelidonic acid by pyrolysis with copper powder which had been carried out by Willstätter and Pummerer²⁸ and later refined by Cornubert and Robinet,²⁹ was modified to a simple laboratory preparation.



Carbonyl Group Reactivity

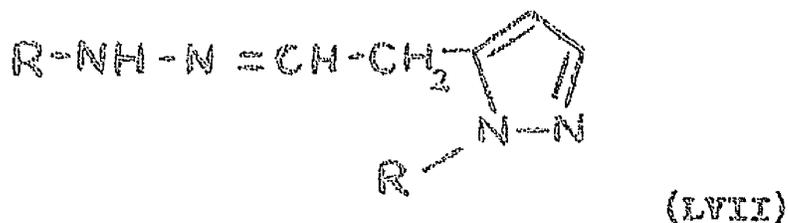
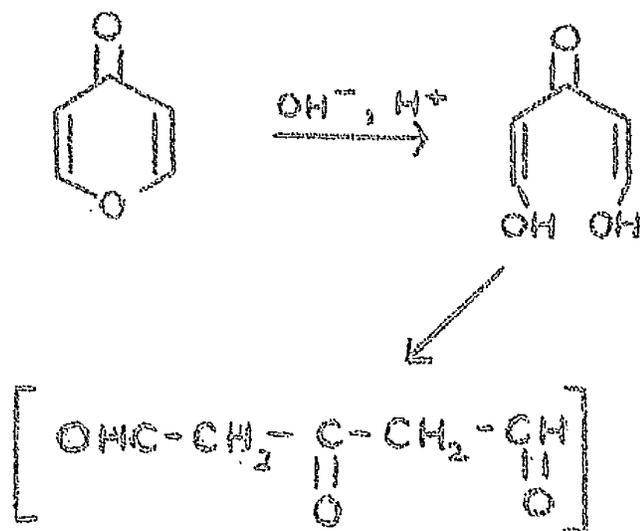
Initial chemical investigations of the 1-thia-4-pyrone molecule were concentrated on the reactivity of the carbonyl group toward hydroxylamine and various hydrazines.

In its reaction with hydroxylamine, 1-thia-4-pyrone was shown to behave like 4-pyrone as studied by Parisi *et al.*²⁸ From 4-pyrone and hydroxylamine they isolated 4-hydroxylaminopyridine-1-oxide (LV). To explain its formation they proposed a ring opening sequence followed by elimination of water and ring closure. The product on treatment with sodium hydroxide solution yielded 4,4'-azopyridine-1,1'-dioxide (LVI) thus:-



1-Thia-4-pyrone yielded the same products (LV and LVI) probably by a similar mechanism involving in this case the elimination of hydrogen sulphide.

Jones et.al.¹⁹³⁰ studied the reaction of 4-pyrone with hydrazine, phenylhydrazine and p-nitrophenylhydrazine. In each case, ring opening took place followed by further reaction and cyclisation to give the corresponding pyrazolyl derivative (LVII) as formulated below:-



where R = H, phenyl and p-nitrophenyl

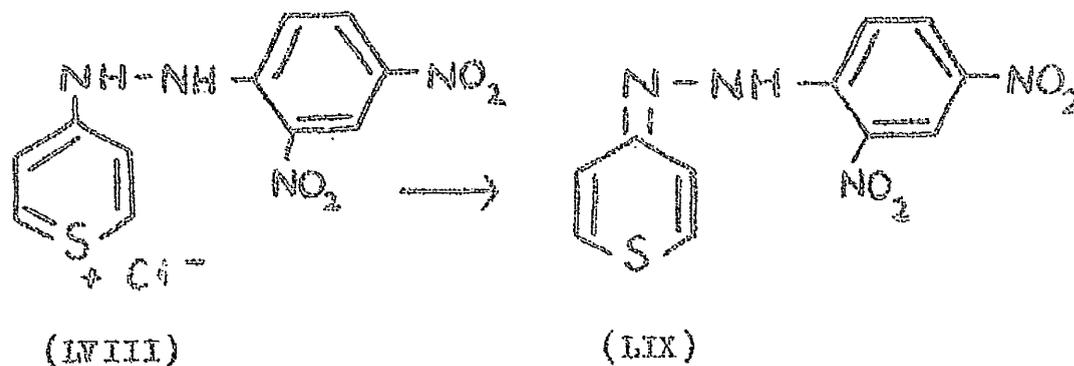
1-Thia-4-pyrone reacted rapidly with hydrazine, hydrogen sulphide being evolved. After potassium permanganate oxidation of the reaction mixture according to the method of Jones and Mann,⁸⁹ pyrazole-3-carboxylic acid⁹⁰ was isolated confirming reaction similar to that obtained with 4-pyrone.

By contrast, however, phenyl- and p-nitrophenyl-hydrazine reacted extremely slowly, if at all, with 1-thia-4-pyrone, the only evidence obtained to suggest reaction being the slight evolution of hydrogen sulphide after prolonged refluxing of the reaction mixture, which might indicate the ring opening mechanism to pyrazoles.

For the sake of comparison, the reaction of 4-pyrone with p-nitrophenylhydrazine in glacial acetic acid⁹⁰ was repeated. The expected pyrazole derivative, 1-(p-nitrophenyl)-5-pyrazolylacetaldehyde p-nitrophenylhydrazone (LVII, R = p-nitrophenyl) was formed in a few moments. A similar experiment with 1-thia-4-pyrone yielded only 1-acetyl-2-(p-nitrophenyl)hydrazine.

With 2,4-dinitrophenylhydrazine in ethanol a true carbonyl derivative was obtained which was isolated as the hydrochloridesalt (LVIII). This gave the free base,

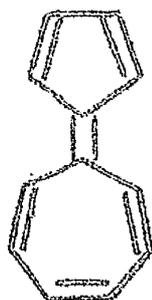
1-thia-4-pyrone 2,4-dinitrophenylhydrazone (LVIII), on treatment with water.



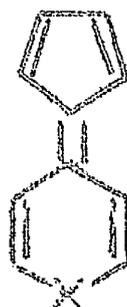
The hydrazone (LVIII) was also obtained in glacial acetic acid along with 1-acetyl-2-(2',4'-dinitrophenyl)hydrazine.

Attempted Reaction with Organometallic Reagents.

Initiated by a contemporary interest in the preparation of new non-benzenoid aromatic systems, investigations were focussed on the introduction of alkyl groups, and in particular the cyclopentadienyl group, to the 4-position of 1-thia-4-pyrone with a view to preparing the unknown 4-cyclopentadienyldene-1-thiapyran (LXI, X = S) analogous to sesquifulvalene (cyclopentadienyldene-cycloheptatriene) (LX).



(LX)

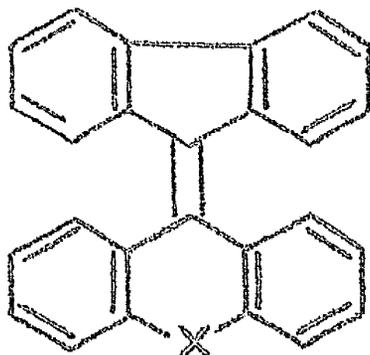


(LXI)

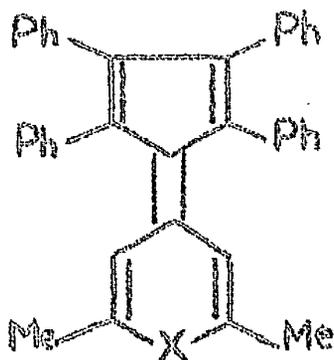
Sesquifulvalene (LX) is not yet known although tetrabenzo⁹² and tetraphenyl⁹³ derivatives have been reported. More recently Prinzbach⁹⁴ prepared a mono-substituted derivative.

The first simple 4-cyclopentadienylidene-dihydropyridine derivative (LXI, X = N-CH₂-C₆H₃Cl₂-2,6) was prepared in 1956⁹⁵ and other derivatives have since been prepared.⁹⁶ The parent compound (LXI, X = NH) is not yet known.

In the analogous oxygen and sulphur systems, tetrabenzo-derivatives (LXII, X = O, S) were obtained by Schönberg et al.⁹⁷ in 1959 from the reaction of thioxanthene and thio-thioxanthene with 9-diazofluorene. More recently Lloyd and Wasson⁹⁸ used this same principle to obtain the first derivatives without fused rings (LXIII, X = O, S)

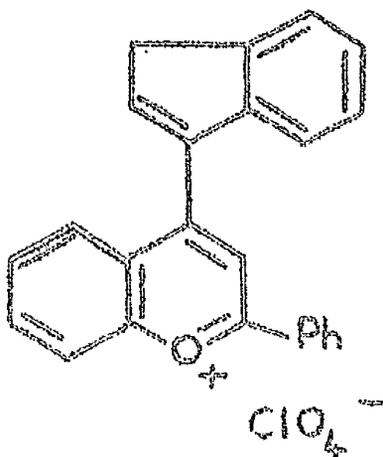


(LXII)

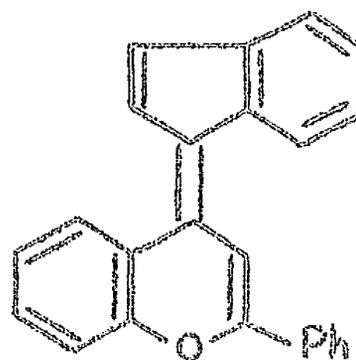


(LXIII)

Boyd^{96'99} presented another route by preparing 4-1'-indenylidene-flav-2-ene (LXV) via the corresponding pyrylium salt (LXIV) by merely treating the latter with sodium hydroxide or water.



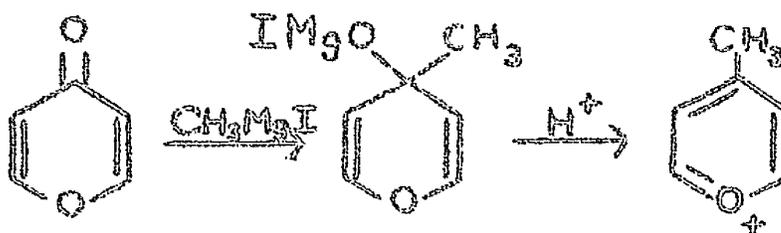
(LXIV)



(LXV)

A route to the parent 4-cyclopentadienylidene 1-thiapyran (LXI, X = S) using this principle was considered. It was hoped to obtain 4-cyclopentadienyl-1-thiapyrylium salts from 1-thia-4-pyrone and cyclopentadienyl sodium.

Kobrich²⁰⁰ had reported the preparation of methylpyrylium salts by the action of methyl magnesium iodide on 4-pyrone as follows:-



However similar attempts to prepare the analogous thiapyrylium salts were unsuccessful and equally abortive were attempts to obtain the cyclopentadienyl-thiapyrylium salts using cyclopentadienyl sodium. Acidification of the reaction mixture in each case yielded the 4-hydroxythiapyrylium salt which was precipitated out as the perchlorate and also as the the tri-iodide, which latter was converted to the simple iodide.

Identical salts were obtained from 1-thia-4-pyrone and the corresponding acid.

An attempt to obtain 4-cyclopentadienylidene-1-thiapyran (LXI, X = S) using potassium *t*-butoxide, cyclopentadiene and 4-methoxythiapyrylium perchlorate⁷⁵ by the procedure employed by Boyd¹⁰¹ to obtain 4-cyclopentadienylidene-dihydropyridine derivatives led only to the recovery of 4-methoxythiapyrylium perchlorate.

Reaction of 1-Thia-4-pyrone with Bromine.

Although 4-pyrone is reported to brominate in the 3- and 5-positions to give both the mono- and di-bromo products¹⁰² no evidence of nuclear bromination of 1-thia-4-pyrone was obtained. In various solvents and under varying conditions an orange-red complex was obtained.

The complex, on heating in water and more rapidly in the presence of acetone, was converted to 4-hydroxy-1-thiapyrylium bromide identified as the hydrate from which thiapyrone could be recovered in almost quantitative yield by basification and extraction with chloroform. An identical salt was obtained from 1-thia-4-pyrone and hydrogen bromide.

Nosce²⁶ reported a complex obtained from tropone and bromine which he formulated as $2C_7H_6O \cdot 3Br \cdot 5H_2O$ using volumetric analysis. This compound could be converted to 2,7-dibromotropone by heating in water.

Volumetric analysis of the 1-thia-4-pyrone complex with bromine carried out on a freshly prepared sample showed reasonable agreement for the formula $C_5H_4OS \cdot HBr \cdot 3Br_2$. Further determinations on samples allowed to stand exposed to air indicated that bromine was readily lost to the atmosphere. The results are shown in Table I.

TABLE I

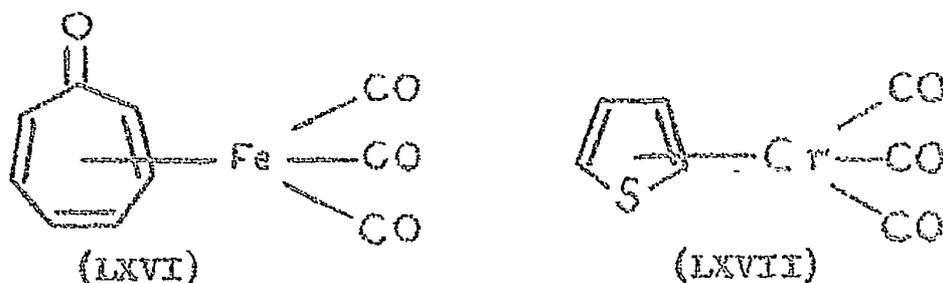
	Calc. for $C_5H_4OS \cdot HBr \cdot 3Br_2$	Freshly Prepared Sample	4 Hr. After Preparation	24 Hr. After Preparation
% Br	71.25	70.04	64.10	59.82
%HBr	12.03	14.96	16.29	17.70

Nuclear magnetic resonance spectra were obtained for the thiapyrone-hydrogen bromide-bromine complex and for the 4-hydroxy-1-thiapyrylium salt obtained from it. These were consistent with the proposed structures. Resonance values integrals and assignments are reported in the Appendix.

Parkenyi and Zahradnik¹⁰⁵ have claimed that 3-bromo-4-hydroxy-1-thiapyrylium bromide was obtained when 1-thia-4-pyrone and bromine were allowed to react for two days in glacial acetic acid. Their experiment was therefore repeated and the same orange-red 1-thia-4-pyrone-hydrogen bromide-bromine complex as that already described was obtained, from which 1-thia-4-pyrone could be recovered by basification and extraction with chloroform.

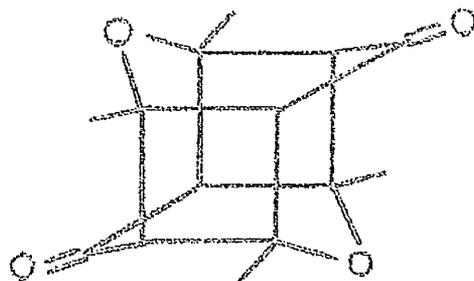
Attempted Reaction of 1-Thia-4-pyrone with Metal Carbonyls.

The fact that tropone, a non-benzenoid aromatic compound could form an iron tricarbonyl complex (LXVI)¹⁰⁴ and that thiophen, a heterocyclic aromatic compound could form a chromium tricarbonyl complex¹⁰⁵ (LXVII) prompted attempts to prepare organometallic complexes of 1-thia-4-pyrone.

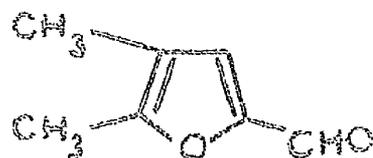


However, attempts to obtain metal carbonyl derivatives with iron pentacarbonyl, iron dodecarbonyl, cobalt octacarbonyl, nickel tetracarbonyl, chromium hexacarbonyl and molybdenum hexacarbonyl under varying conditions were unsuccessful, 1-thia-4-pyrone being recovered from the reaction mixture in all cases.

One of these attempts involved ultraviolet irradiation of 1-thia-4-pyrone in ether in the presence of iron pentacarbonyl. Yates *et al.* reported that irradiation of 2,6-dimethyl-4-pyrone in the solid state gave a dimer (LXVIII)¹⁰⁶. In high dilution (aqueous) a furfuraldehyde derivative (LXIX)¹⁰⁷ was obtained in small yield along with the dimer (LXVIII).



(LXVIII)

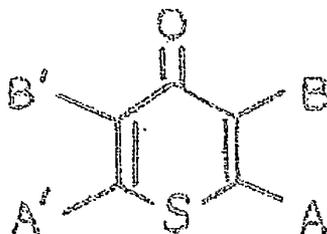


(LXIX)

A check on 1-thia-4-pyrone, however, showed that it was recovered unchanged after irradiation for 10 hr. in ether.

Nuclear Magnetic Resonance Spectrum of 1-Thia-4-pyrone.

The N.M.R. spectrum of 1-thia-4-pyrone was studied in deuteriochloroform. Two multiplets were obtained centred at 2.11 τ and 2.91 τ

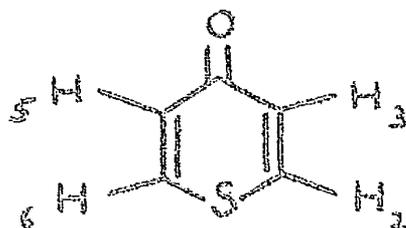


Under high resolution a multiplet pattern was obtained which was characteristic of an A_2B_2 system as expected.

The lower multiplet is attributed to the hydrogen atoms adjacent to the sulphur atom by analogy with furan and thiophen¹⁰⁸ which have signals centred at 2.58 τ and 3.63 τ and at 2.70 τ and 2.90 τ respectively.

Comparison of these τ -values with those of 1-thia-4-pyrone indicates that the magnitude of the ring current of delocalised π -electrons in the ground state of the latter is comparable with that in furan and thiophen whose aromatic character is undisputed.

Bladon and Brown in unpublished work have analysed the spectrum of 1-thia-4-pyrone. The coupling constants are as shown below. The larger of the two meta-coupling constants is assigned to that through the hetero-atom (i.e. $J_{2,6}$). This assignment is based on a study of the spectra of 4-pyrone, 4-thiopyrone, 1-thia-4-pyrone, and 1-thia-4-thiopyrone and is consistent with the observed coupling constants through the hetero-atoms of furan and thiophen.



$$J_{2,3} = 10.39 \text{ c/s}$$

$$J_{2,5} = 0.48 \text{ c/s}$$

$$J_{2,6} = 4.06 \text{ c/s}$$

$$J_{3,6} = 1.97 \text{ c/s}$$

$$S = 31.90 \text{ c/s}$$

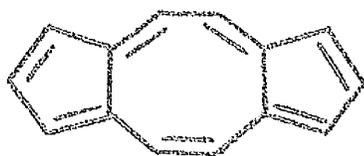
CHAPTER II

Some Attempted Routes to a Tricyclo

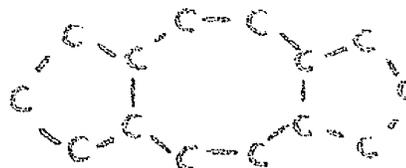
[9,3,0,0^{4 16}] tetradecane system

As has been described in the introduction to this thesis, a number of fully conjugated fused polycyclic systems were predicted by Vol'pin some of which were expected to display aromatic character and some not. It remains for organic chemists to synthesise these compounds and prove or disprove the theoretical predictions.

Among the structures considered was compound (XXIX). Some routes to this compound were therefore considered, the initial objective being the formation of compounds with the required carbon skeleton (LXX).

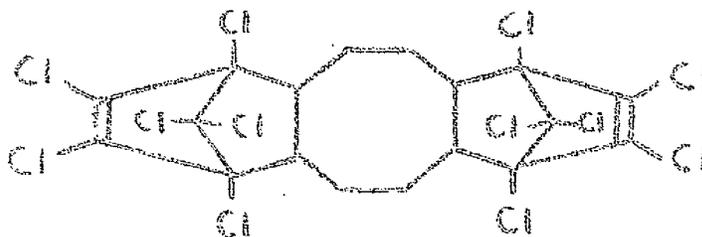


(XXIX)



(LXX)

Strictly speaking, it would be untrue to say that such a carbon skeleton is unknown for it has been reported although only in a more complicated form in compound (LXXI)¹⁰⁹



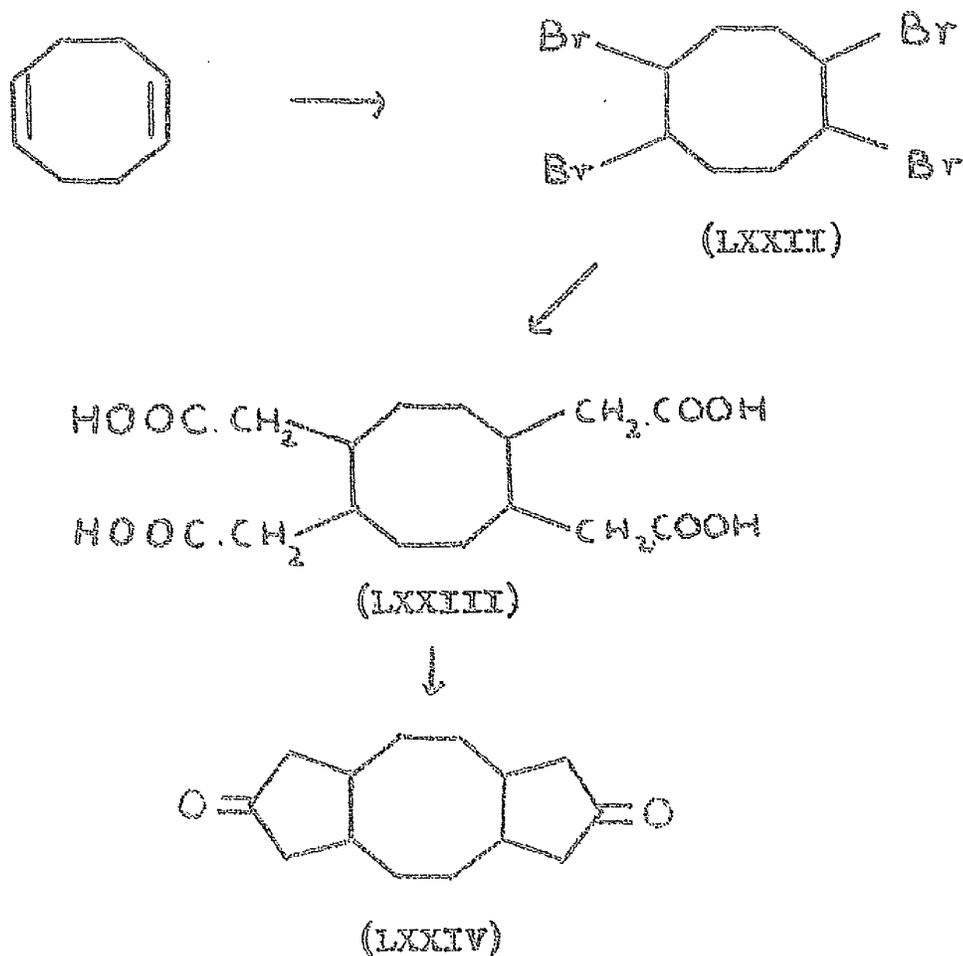
(LXXI)

Since it presented functional groups at the required 1,5-positions in an eight-membered ring, the readily available compound, cis,cis-1,5-cyclo-octadiene, was considered as a possible starting material. Several experimental routes were attempted to obtain compounds with the required carbon skeleton (LXX) from it.

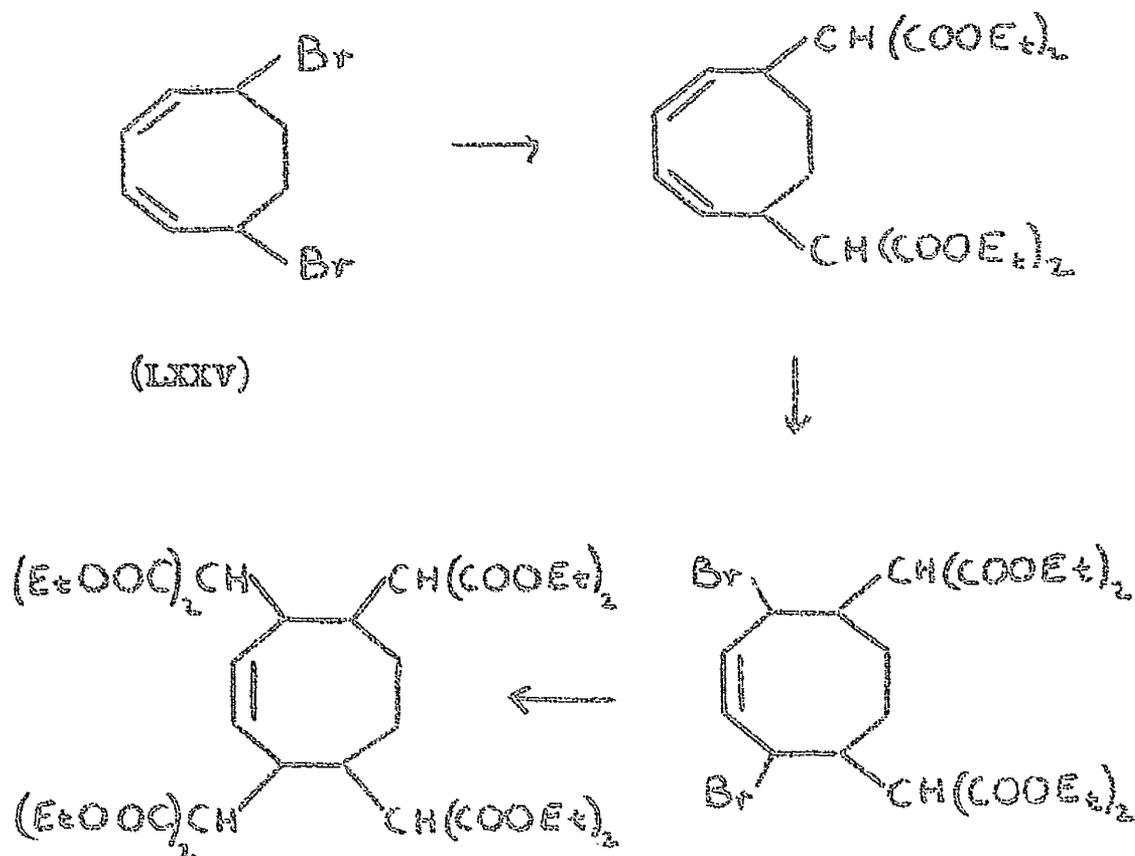
The first route considered was by bromination of 1,5-cyclo-octadiene to the 1,2:5,6-tetrabromo derivative (LXXII), already carried out by Ziegler and Wilms,¹¹⁰ and then replacement of the bromine atoms by acetic acid residues via reaction with sodiomalonic ester, hydrolysis and decarboxylation to give the 1,2:5,6-tetra acetic acid derivative (LXXIII). From this it was hoped to proceed by Dieckmann cyclisation or similar methods to the diketone (LXXIV).

The tetrabromo compound (LXXII), however, was recovered after treatment under varying conditions of solvent and temperature with sodiomalonic ester or with the magnesio-malonic ester which gives better yields in the case of ethylene bromide.^{111 112}

The lack of reactivity of the bromine atoms in 1,2:5,6-tetrabromocyclo-octane was attributed to steric hindrance and the use of 5,8-dibromo-1,3-cyclo-octadiene (LXXV)

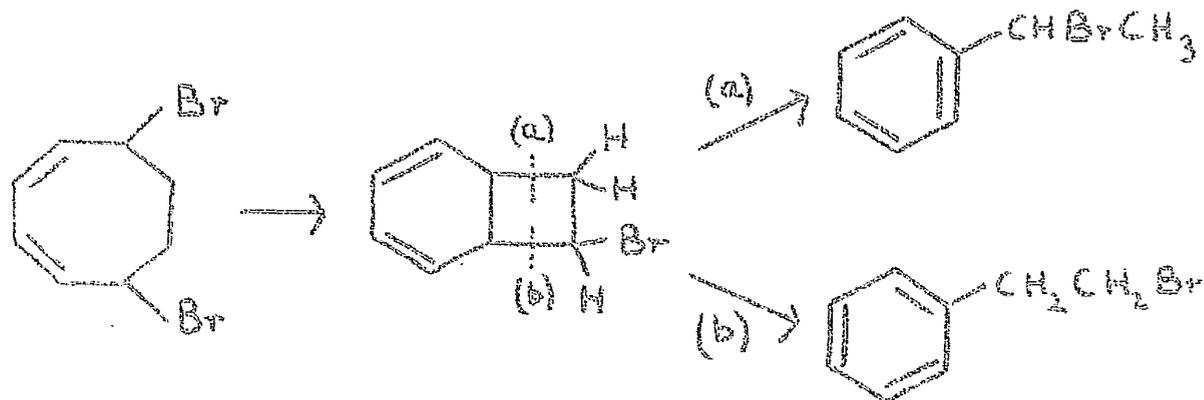


was therefore examined. Cope et al.^{113, 114} showed that the bromine atoms being allylic were reactive and could be replaced for example by dimethylamino groups. It was therefore hoped to obtain a 1,2:5,6-tetra-acetic acid derivative via the following steps.



However reaction of 5,8-dibromo-1,3-cyclo-octadiene with sodiomalonic ester gave a mixture of products together with a large amount of intractable oil. The vacuum-distillable material showed ester carbonyl absorption in the infrared. Attempts to obtain by fractional distillation a product giving satisfactory analysis were unsuccessful.

Cope et al.¹¹⁴ found that 5,8-dibromo-1,3-cyclo-octadiene on rapid distillation at atmospheric pressure lost hydrogen bromide to give a mixture of isomers which included α - and β -phenylethyl bromides, indicating a rearrangement similar to that which occurs with cyclo-octatetraene and hydrogen bromide¹¹⁵ i.e.



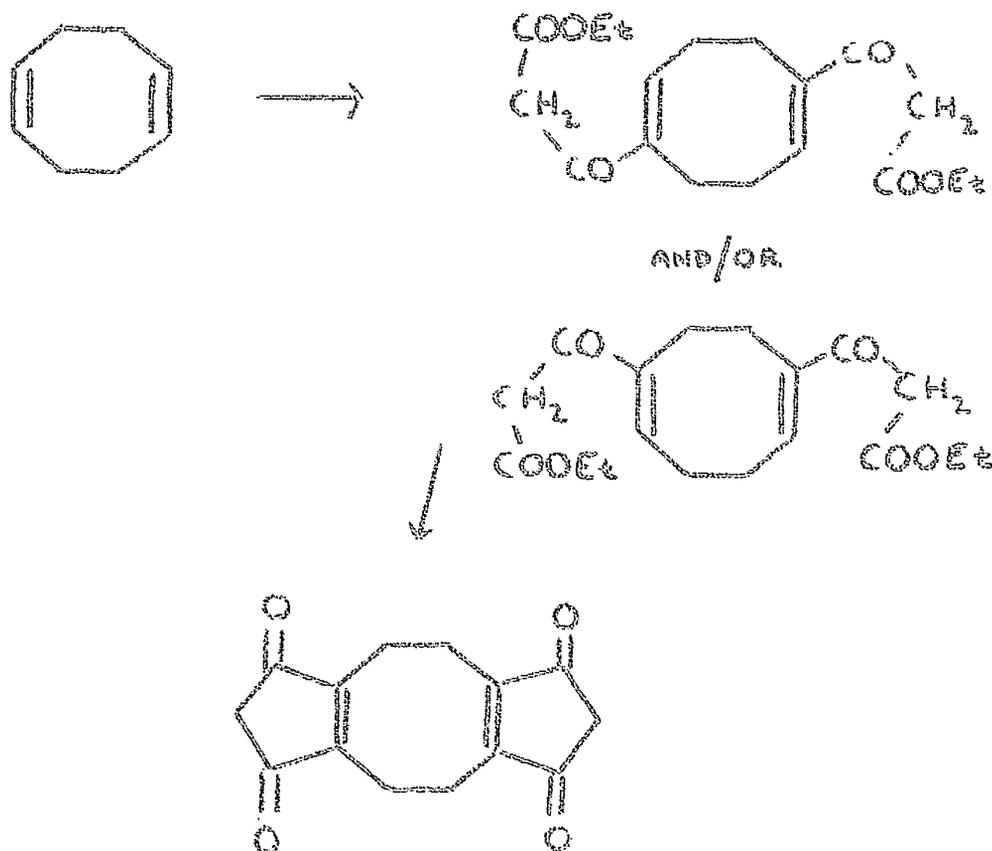
It is not inconceivable that similar rearrangements might take place under the basic conditions of the reaction with sodium ethoxide and diethyl malonate. Classical allylic rearrangements of course are also possible.

Attention was next directed to the possibility of Friedel-Crafts reactions with 1,5-cyclo-octadiene. Ruzicka and Bosrkenoogen¹¹⁶ acetylated cyclo-octene using acetyl chloride and aluminium chloride according to Darzens' method.¹¹⁷

More recently, Jones et al.¹¹⁸ acetylated and benzoylated cyclo-octene using an improved method employing the acyl chloride-aluminium chloride complex in methylene chloride.

Syntheses were considered, therefore, involving the di-acylation of 1,5-cyclo-octadiene with 3-carbon acyl moieties such as ethyl malonyl chloride and β -chloropropionyl chloride with a view to cyclisation of the products obtained to give compounds with the required tricyclic skeleton (LXX).

A synthetic route using ethyl malonyl chloride was considered as follows:



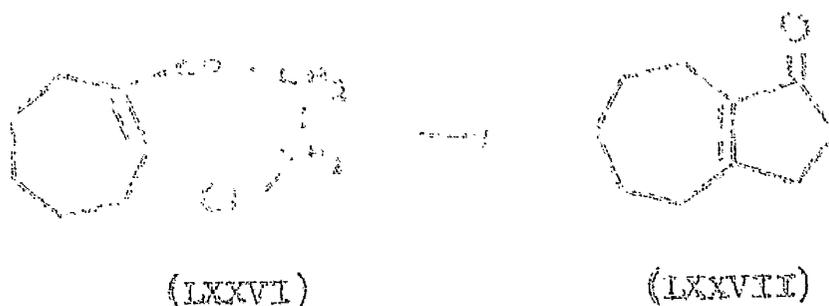
Ethyl malonyl chloride was obtained in a much improved yield from ethyl potassium malonate by modification of the method of Oddo and Albanese.¹¹⁹

Treatment of 1,5-cyclo-octadiene with ethyl malonyl chloride and aluminium chloride by the method of Jones et al.¹¹⁸ resulted only in polymerisation. Royals and Henary¹²⁰ in studying the acetylation of cyclohexene pointed out that of aluminium chloride, zinc chloride and stannic chloride, the latter was 'easier to handle and gave the smoother reaction'.

1,5-Cyclo-octadiene was therefore treated with ethyl malonyl chloride in the presence of stannic chloride. A distillable product was thus obtained as a colourless liquid mixture. Chromatography gave an oil (\approx 5%) which displayed ester carbonyl absorption in the infrared. Analyses were not in satisfactory agreement with the theoretical values.

It would appear therefore that the presence of the desired product cannot be precluded, but the poor yield and the difficulty of obtaining a pure sample for identification made this route an impracticable proposition.

Jones et al.¹¹⁸ acylated cycloheptene with β -chloropropionyl chloride and cyclised the product (LXXVI) with phosphoric acid-formic acid to give bicyclo[5,30]dec-1(7)-en-8-ene (LXXVII).



An analogous condensation of two β -alkoxypropionic fragments with 1,5-cyclo-octadiene was therefore attempted.

With aluminum chloride, as before, no distillable product was obtained, but stannic chloride gave a distillable product which was chromatographed to give an oil displaying ester carbonyl absorption in the infrared. As before, however, analysis did not agree with the theoretical values and the yields were extremely small (< 3%).

The fact that aluminum chloride and stannic chloride are polymerising agents for olefins has long been recognised^{121, 122} and this alone could explain the extremely low yields obtained in these reactions.

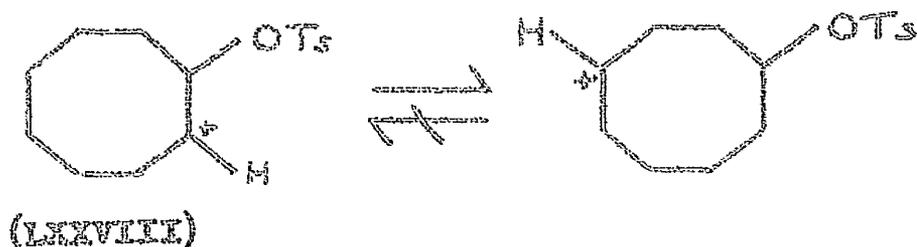
However, work on large numbered rings, including the eight-membered ring, reviewed by Sicher¹²³ indicates the possibility that transannular side reactions may also be taking place which could explain the complex mixtures obtained in these reactions.

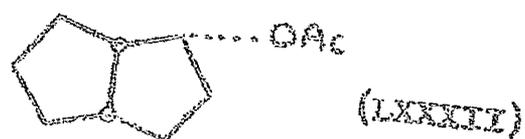
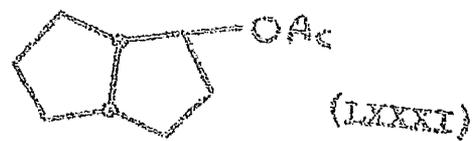
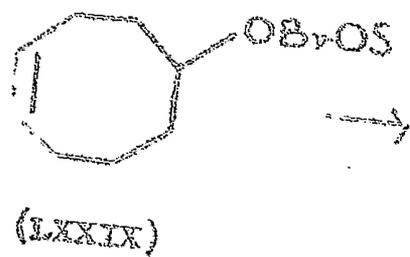
For example, Cope *et al.*¹²⁴ showed that cis- and trans-cyclo-octane-1,2-diol ditosylate on acetolysis gave products formed by transannular hydride shift from the original carbonium ion (LXXVIII).

Acylation of olefins is considered to pass through a carbonium ion stage and therefore the possibility of such transannular hydride shifts in the acylation of cyclo-octadiene cannot be ignored.

Sicher¹²⁵ states of carbonium ions in eight- to eleven-membered rings 'The positively charged centre in such ions is held in close proximity to the hydrogen atoms on the opposite side of the ring so that intramolecular hydride shifts from these positions to the carbonium ion are possible. The overall result of this type of reaction is that the substituent does not enter on the atom carrying the leaving group but on a carbon placed on the opposite side of the ring'.

Transannular double-bond participation has also been reported. For example, Cope and Peterson¹²⁶ showed that solvolysis of 4-cyclo-octen-1-yl p-bromobenzenesulphonate (LXXIX) produced cis-bicyclo[5,3,0]-octane derivatives (LXXX-LXXXII).

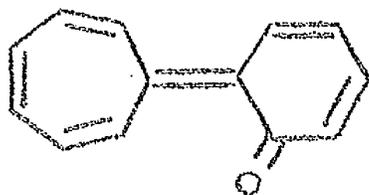




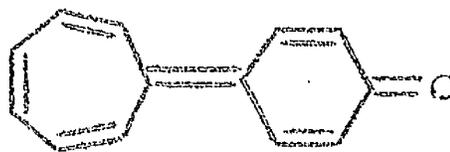
CHAPTER III
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Some Studies of Propylated Phenols

Following on the report by Nozoe and Kitahara⁵⁵ that phenol and ditropy^l ether reacted to give o- and p-tropy^lphenols the syntheses of tropilidene-o- and p-quinones (LXXXIII and LXXXIV respectively) which were then unknown, was considered.



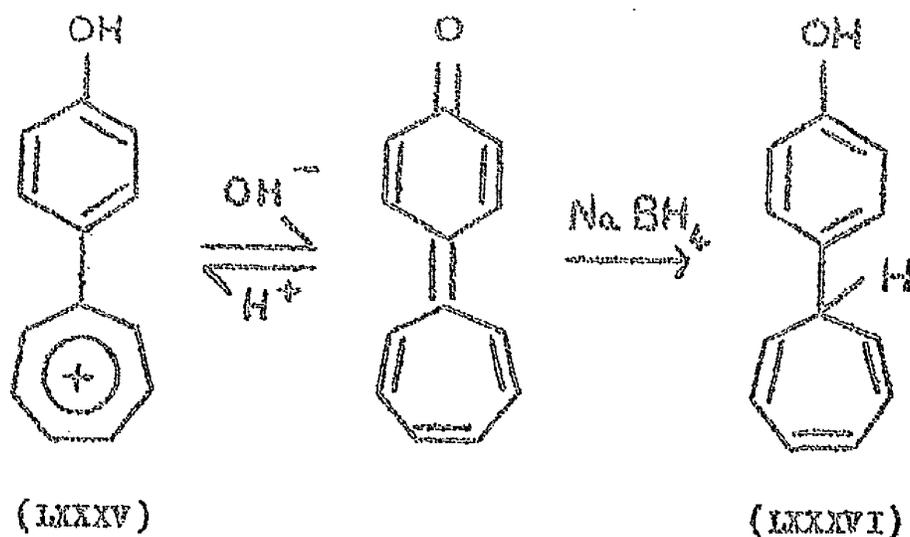
(LXXXIII)



(LXXXIV)

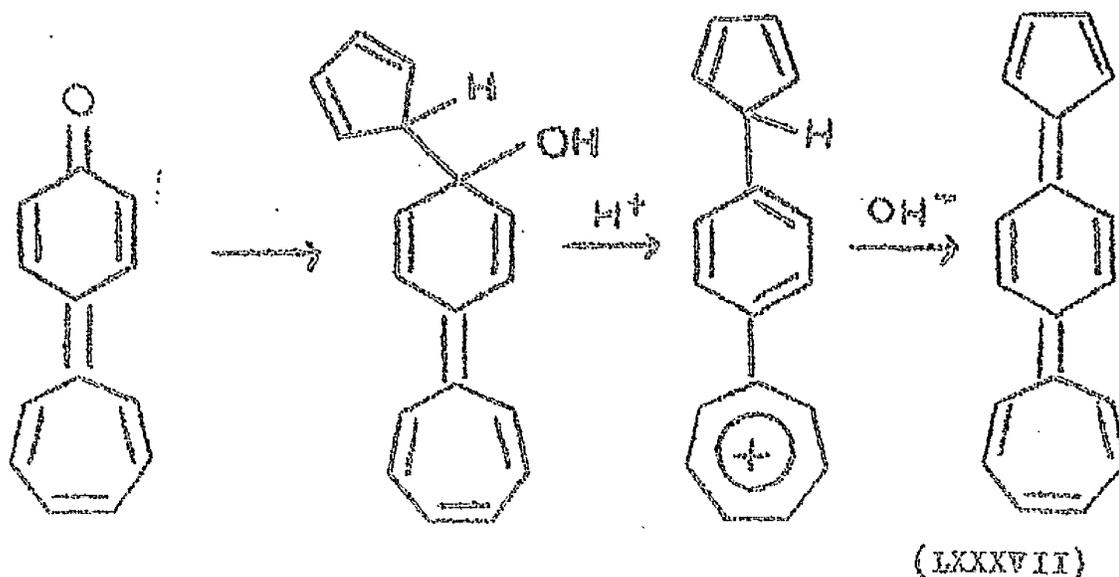
Treatment of p-tropy^lphenol with triphenylmethyl perchlorate gave the p-hydroxyphenyltropy^lium ion (LXXXV) as the perchlorate, which on basification with sodium bicarbonate solution gave a deep violet-red colour. The violet-red product was extractable with chloroform giving a deep purple non-crystalline solid which was unstable to air and gave unsatisfactory analysis and n.m.r. spectrum. This product, however, is considered to be impure tropilidene-p-quinone (LXXXIV) (*4*-cycloheptatrienylydene cyclohexa-2,5-dien-1-one).

Treatment of the purple solid with sodium borohydride



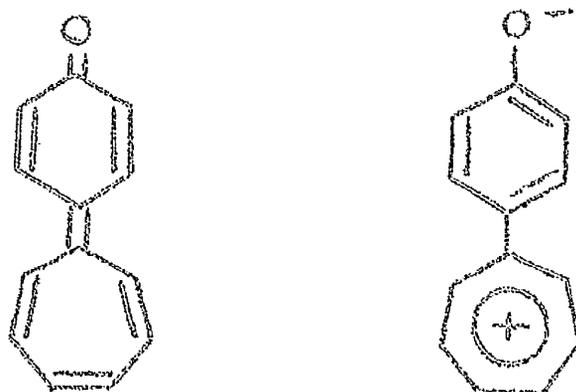
gave *p*-tropylphenol (LXXXVI), and with perchloric acid *p*-hydroxyphenyltropylium perchlorate was obtained.

The possibility was considered of replacing the oxygen atom of the tropilidene-*p*-quinone system by a cyclopentadienyliidene group to give the sesquifulvalene system separated by a six-membered ring i.e. 1-cycloheptatrienyliidene-4-cyclopentadienyliidene cyclohexa-2,5-diene (LXXXVII). The route to be attempted was as follows.



Tropilidene-p-quinone was unchanged, however, after treatment with methyl magnesium iodide or cyclopentadienylsodium.

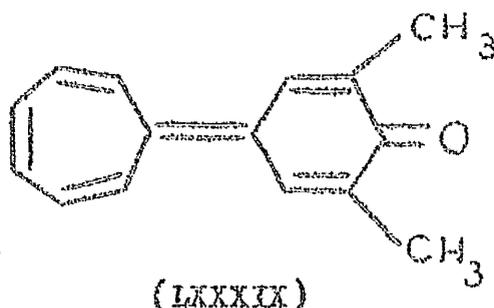
This apparent lack of reactivity of the carbonyl group is supported by the inability to obtain a 2,4-dinitrophenyl hydrazone from tropilidene-p-quinone. A probable explanation is the tendency for electrons in the molecule to be delocalised towards the charged structure (LXXXVIII) containing the stable tropylium ion as in tropone.



Further support for this is the position of the carbonyl peak in the infrared at 1600 cm.^{-1} whereas an $\alpha\beta$ -unsaturated carbonyl group shows absorption in the 1660 cm.^{-1} region.

Tropilidene-p-quinones have been reported in the literature. Van Helden *et al.*⁵⁴ tropyliated 2,6-xyleneol with ditropyl ether in a heterogeneous medium of acetic acid, water and n-hexane to give 2,6-dimethyl-4-tropylphenol (21%) from

which they obtained the corresponding perchlorate (15%) by treatment with perchloric acid in glacial acetic acid. The perchlorate on basification or by heating at 200° in a stream of nitrogen yielded a purple unstable solid which they assumed to be the tropilidene-p-quinone derivative (LXXXIX)

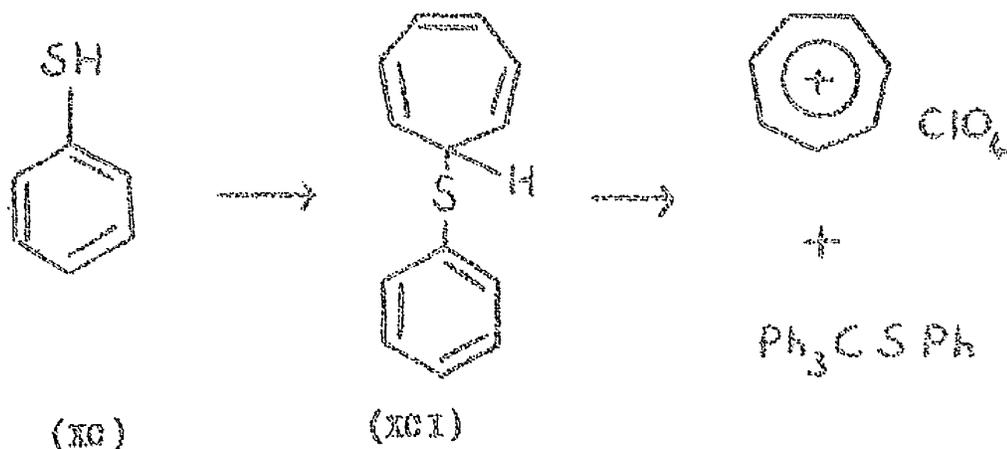


With the hope that the n.m.r. spectrum of this product might be more enlightening, 2,6-dimethyl-4-tropylphenol was obtained (> 50%) from the reaction of 2,6-xyleneol and ditropyl ether without solvent. This gave the corresponding perchlorate (> 80%) on treatment with triphenylmethyl perchlorate. The tropilidene-p-quinone derivative (LXXXIX) obtained on basification however, gave no satisfactory n.m.r. spectrum on account of its instability and poor solubility.

The parent tropilidene-p-quinone (LXXXIV) has also been prepared very recently by Jutz and Voithenleitner⁵⁵ by the route already described (i.e. LXXXVI → LXXXV → LXXXIV).

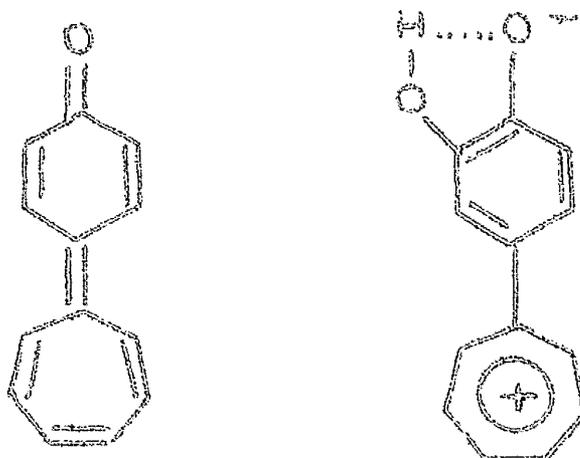
Again their attempts to obtain a pure sample were unsuccessful.

The reaction of ditropyl ether on thiophenol (XC) was investigated with a view to obtaining the thio-analogue of tropilidene-p-quinone. The product obtained however was troyl phenyl thio-ether (XCI) which on treatment with triphenylmethyl perchlorate afforded troylium perchlorate and triphenylmethyl phenyl thio-ether.¹²⁶



Degani and Fochi¹²⁷ have obtained a series of troyl thioethers, including troyl phenyl thioether, from troylium chloride and the sodium salt of the corresponding mercaptan and have shown that these reacted with acids to give the original troylium salt and mercaptan.

Attention was directed to attempting the troylation of catechol with a view to dehydrogenation of troylcatechol as before to the troylidene quinone structure (XCII) bearing structural analogy to tropelone as does troylidene-p-quinone to tropone.



(XCII)

Ditropyl ether reacted extremely rapidly with catechol giving a non-distillable product from which no pure product could be obtained by chromatography. With guaisacol, the monomethyl ether of catechol, and ditropyl ether, however, tropylation was effected and only one monotropyguaisacol could be isolated.

Treatment of this tropyguaisacol with triphenylmethyl perchlorate afforded the corresponding tropylium salt which on basification gave a pale yellow oil.

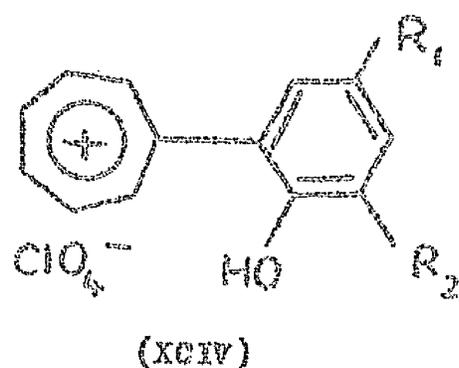
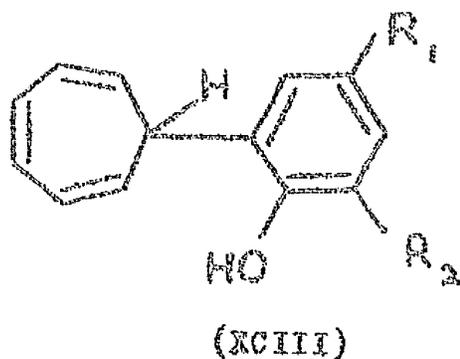
From both 4- and 6-tropyguaisacols the corresponding tropilidene-*o*- and *p*-quinone derivatives might now be expected to be highly coloured. However it was suspected that with the perchlorate obtained from *o*-tropyguaisacol, the proximity of the hydroxyl group to the tropylium ion might allow their

interaction to yield a product other than a tropilidenequinone. The position of the troyyl group was therefore considered to be ortho to the hydroxyl group and an n.m.r. spectrum of troyyl-guaiacol indicated a triplet at 6.98 τ which compares with that in o-troyylphenol at 7.09 τ ,⁸⁸ p-troyylphenol showing a triplet at 7.75 τ .

That only the 6-troyyl guaiacol was isolated from the troyylation of guaiacol would appear to contradict the recognised path of electrophilic aromatic substitution. A literature study of such reactions on guaiacol, however, indicates that the positions of substitution and their relative proportions follow no predictable sequence. For example, nitration of guaiacol¹³⁰ gives almost twice as much 6-nitro as 4-nitro derivative. Alkylation¹³¹ and acylation¹³⁰ give mainly the 4-substituted derivative while by halogenation depending on the reagents used 5-halogeno-derivatives can be isolated as the only monosubstituted product obtained,^{131 132} in contrast to 4- and 6-halogeno-derivatives by other methods.¹³³

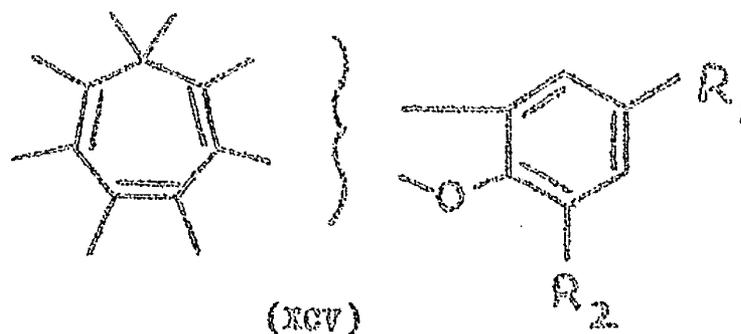
It was therefore decided to investigate more closely the basification of 2-hydroxyphenyltroylium perchlorates. Since o-troyylphenol (XCIII, $R_1 = R_2 = H$) was not very readily obtainable it was decided to attempt the troyylation of p-cresol where the ortho-troyyl derivative was the only mono-substituted derivative expected. This proved to be the case and o-troyyl-

-p-cresol (XCIII, $R_1 = \text{CH}_3$, $R_2 = \text{H}$) was obtained in relatively good yield (34.8%). An n.m.r. spectrum consistent with this structure was obtained displaying a triplet at 7.06 τ for the tertiary hydrogen atom of the tropylium ring ortho to the hydroxyl group (see Appendix). This product was readily converted to the tropylium salt (XCIV, $R_1 = \text{CH}_3$, $R_2 = \text{H}$) whose n.m.r. spectrum showed a hydroxyl hydrogen at 3.5 τ which is considerably lower than that for the p-hydroxyphenyltropylium salt (5.7 τ) indicating the proximity of the hydroxyl group in the former to the charged tropylium ring with the resulting deshielding effect. The salt on basification gave a pale yellow oil as before.

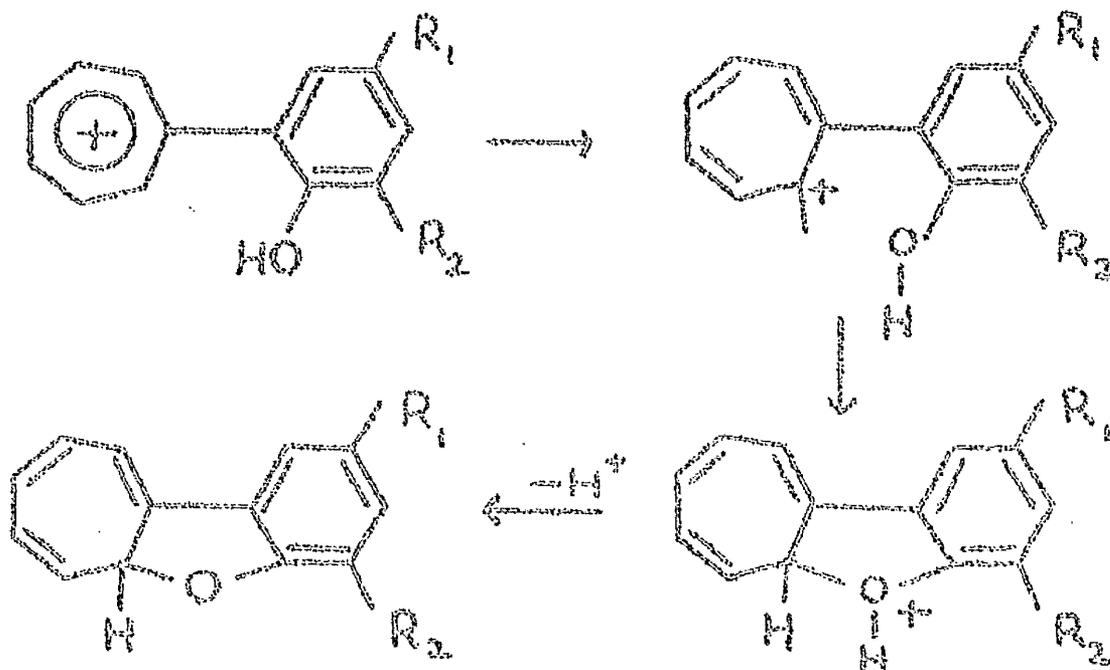


An infrared spectrum of this oil showed no hydroxyl stretching frequency nor carbonyl frequency. However a strong sharp peak was observed at 1190 cm^{-1} which was considered to indicate an ether linkage. Benzofuran,¹⁸⁴ itself, displays an ether peak at 1250 cm^{-1} . The product was therefore considered to be 3-methylbenzo[b]cycloheptatrieno[d]furan (XCV, $R_1 = \text{CH}_3$,

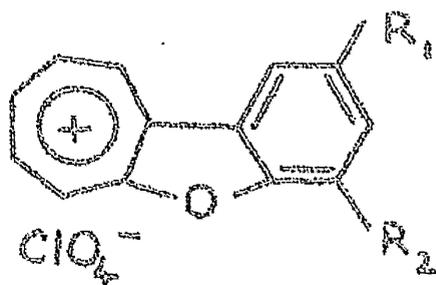
$R_2 = H$). An n.m.r. spectrum was not consistent with any one of the possible isomers and suggested the presence of a mixture.



The following possible mechanistic route to this product is suggested.



Since the cycloheptatriene moiety was still present in this compound, further dehydrogenation with triphenylmethyl perchlorate to the tropylium salt was possible and gave (3-methylbenzofurano)tropylium perchlorate (XCVI, $R_1 = CH_3$, $R_2 = H$).



(XCVI)

An n.m.r. spectrum confirmed this structure (see Appendix).

This series of reactions was repeated with *o*-tropyliphenol itself (XCVIII, $R_1 = R_2 = H$) and analogous products were obtained. Returning to tropyliguaiacol, the perchlorate (XCIV, $R_1 = H$, $R_2 = OMe$) obtained directly with triphenylmethyl perchlorate showed a hydroxyl hydrogen peak at 3.70 τ in the n.m.r. spectrum which is consistent with the values for the other two (2-hydroxyphenyl) tropylium salts (3.5 τ and 3.85 τ).

By analogy the oil obtained on basification was considered to have the other structure (XCV, $R_1 = H$, $R_2 = OMe$). Two strong sharp peaks were obtained in the infrared at 1687 cm.^{-1} and 1266 cm.^{-1} , carbonyl and hydroxyl bands again being absent. The higher value is considered to be that of -OMe on the benzene ring by analogy with guaiacol¹⁸⁶ itself

($\sim 1270 \text{ cm.}^{-1}$). This product as expected, therefore, reacted with triphenylmethyl perchlorate to give the tropylium salt (XCVI, $R_1 = H$, $R_2 = OMe$).

Basification of the perchlorates (XCVI) was next considered. In the previous examples with 2- and 4-hydroxyphenyltropylium salts a labile hydrogen atom was present attached to the oxygen atom so that basification brought about the abstraction of a proton. With these perchlorates (XCVI), however, no such proton is present and the addition of OH^- was therefore expected.

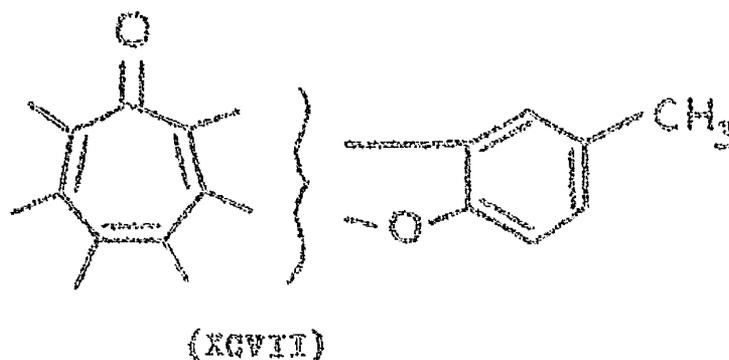
From the basification of (3-methylbenzofurano)tropylium perchlorate, three products were isolated by chromatography.

The first product (A) was a pale yellow oil which was identified as 3-methylbenzo[b]cycloheptatrieno[d]furan (XCV, $R_1 = CH_3$, $R_2 = H$) already prepared, which could be converted to the corresponding perchlorate (XCVI, $R_1 = CH_3$, $R_2 = H$).

The other two products were crystalline solids (B and C).

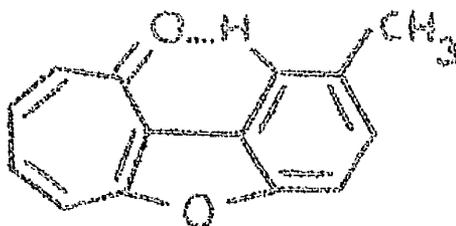
From the presence of the cycloheptatrienofuran (XCV, $R_1 = CH_3$, $R_2 = H$) among the products it was suspected that the basification of the tropylium salt had followed the reaction path obtained with the unsubstituted tropylium ion. This gives ditropyl ether, followed by disproportionation to give cycloheptatriene and tropone (see introduction).

By analogy, therefore, corresponding tropone derivatives (XCVII) were looked for.



The first solid (B) and its 2,4-dinitrophenylhydrazone which formed slowly, analysed correctly for structure (XCVII) and its 2,4-dinitrophenylhydrazone. The infrared spectrum showed a band at 1623 cm.^{-1} (medium) and 1575 cm.^{-1} (strong). The former is attributed to $\text{>C}=\text{C}<$ stretching vibrations and the latter to the carbonyl group by analogy with recent assignments for tropone itself based on solvent effects.¹⁸⁶ An n.m.r. spectrum (see Appendix) showed a peak at 7.5 τ corresponding to β -methyl protons, a series of peaks at 2.2-3.5 τ corresponding to 6 protons and a peak at 1.5 τ corresponding to 1 proton. This latter peak was not affected after 24 hr. treatment with D_2O .

Since the 2,4-dinitrophenylhydrazone was formed only slowly and from the presence of 1 proton at 1.5 τ in the n.m.r. spectrum it was thought that hydrogen bonding was taking place and solid (B) is assigned structure (XCVIII).

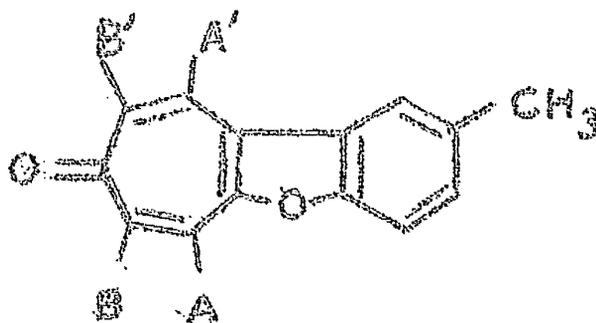


(XCVIII)

An n.m.r. spectrum in trifluoroacetic acid was obtained which was consistent with this (see Appendix).

The second solid (E) and its 2,4-dinitrophenylhydrazones which formed with ease also analysed correctly for structure (XCVII) and its 2,4-dinitrophenylhydrazones. The infrared spectrum showed bands at 1608 cm.^{-1} (medium) and 1515 cm.^{-1} (strong). Again the former is attributed to $>C=C<$ stretching vibrations and the latter to the carbonyl group. An n.m.r. spectrum showed a peak at 7.51τ corresponding to 3 methyl protons and a series of peaks at $2.1-3.2 \tau$ corresponding to 7 protons. When the spectrum was obtained in trifluoroacetic acid however, there was obtained a peak at 7.28τ corresponding to 3 protons, a peak at 2.08τ corresponding to 2 protons and a series of peaks at $0.3 - 1.9 \tau$ corresponding to 5 protons. This last series of peaks was representative of 4 hydrogen atoms in

two superimposed AB systems with an additional hydrogen further superimposed (see Appendix). This is only consistent with structure (XCIK) which is therefore assigned to solid (C).



(XCIK)

EXPERIMENTAL

Experimental Procedures

Melting Points. These were determined on a Kofler melting point apparatus and are uncorrected.

Nuclear Magnetic Resonance Spectra were measured on a Perkin-Elmer 40 M/c spectrometer.

Reagents. The silica gel used for chromatography was Hopkin and Williams, M.F.C. Grade.

The nitrogen used in reactions involving organometallic compounds was deoxygenated with Fieser's solution and dried with concentrated sulphuric acid.

CHAPTER I

Some Chemical Investigations of 1-Thia-4-pyrone

4-Pyrone by Decarboxylation of Chelidonic Acid.

A small retort (100 ml. bulb with delivery tube of length 12") was charged with chelidonic acid (20 g., predried at 140°) and dry precipitated copper powder (40 g., commercial quality). This was fitted by ground glass joints to a receiver flask with the open end protected by a calcium chloride tube. The bulb of the retort was immersed in a Wood's metal bath which was then heated to 220° in 20 min., to 280° in a further 25 min. and then to 340-350° after a total of 1 hr., this latter temperature being maintained for 10 min. The crude 4-pyrone (7.0 g., 67%) which distilled over was dried by refluxing with benzene in a 'Dean and Stark' apparatus and finally distilled at 97°/5 mm.

1-Thia-4-pyrone

Mayer's method^{76 '77} was modified as follows:-
 4-pyrone (20 g., 0.21 mole) in water (80 ml.) was treated with excess sodium hydrogen sulphide prepared from sodium sulphide (40 g., 0.46 mole) saturated with hydrogen sulphide at 100° for 1 hr. The resulting mixture was refluxed for 30 min. with hydrogen sulphide bubbling through it. The hydrogen sulphide flow was then stopped and refluxing continued for a further 15 min. The solution was cooled, sodium sulphate and sodium chloride added, and extraction

carried out with chloroform. The product obtained from the dried (Na_2SO_4) extract by removal of solvent was recrystallised from carbon tetrachloride to give 1-thia-4-pyrone (4.5 g., 19.3%) as colourless needles, m.p. 110° [lit.⁶⁷ m.p. 110°] (Found: C, 53.8; H, 3.7; S, 28.6. $\text{C}_5\text{H}_4\text{OS}$ requires C, 53.5; H, 3.6; S, 28.6%)

Reaction of 1-Thia-4-pyrone with Hydroxylamine.

A solution of 1-thia-4-pyrone (300 mg., 2.7 mmole) and hydroxylamine hydrochloride (600 mg., 8.6 mmole) in ethanol (3 ml.) and pyridine (3 ml.) was refluxed on a water bath for 3 hr. By removal of most of the solvent in vacuo and addition of water there was obtained 4-hydroxylaminopyridine-N-oxide (216 mg., 64%), identified by comparison of its infrared and ultraviolet spectra with published data.⁸⁸ (Found: C, 47.4; H, 4.9. $\text{C}_5\text{H}_6\text{N}_2\text{O}_2$ requires C, 47.6; H, 4.8%).

The product (100 mg.) was dissolved in hot water which was then made alkaline with sodium hydroxide solution. Extraction with chloroform and recrystallisation of the product from benzene gave 4,4'-azopyridine-1,1'-dioxide (55mg., 64.2%) as red crystalline needles, m.p. 260° [lit.⁸⁸ m.p. $246-247^\circ$] identified by comparison of infrared and ultraviolet spectra with published data.⁸⁸ (Found: C, 55.0; H, 3.7. $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2$ requires C, 55.6; H, 3.7%)

Reaction of 1-Thia-4-pyrone with Hydrazine.

1-Thia-4-pyrone (200 mg., 1.8 mmole) was treated with hydrazine hydrate (1 g., 20 mmole) in ethanol (1 ml.). After the initial exothermic reaction had subsided, the mixture was warmed for 3 hr. on a steam bath. Potassium permanganate (1.25 g., 7.9 mmole) in water (20 ml.) was added and the solution was refluxed for a further 30 min., cooled and filtered. The filtrate was acidified with dilute hydrochloric acid and evaporated to dryness. The residue was extracted with acetone to yield pyrazole-3-carboxylic acid (127 mg., 63%) m.p. 212° λ_{max} (EtOH) 214 μ (log. ϵ , 3.96). [lit.⁹⁴ m.p. $212-213^{\circ}$, λ_{max} (EtOH) 214 μ (log. ϵ , 3.96)].

Reaction of 1-Thia-4-pyrone with Phenylhydrazine.

A solution of 1-thia-4-pyrone (100 mg., 0.9 mmole) and phenylhydrazine hydrochloride (300 mg., 2.1 mmole) in ethanol (5 ml.) was refluxed for 3 hr. on a steam bath. Cooling afforded only phenylhydrazine hydrochloride identified by melting point (247°) and mixed melting point with an authentic sample.

Reaction of 4-Pyrone with p-Nitrophenylhydrazine.

A solution of 4-pyrone (1.0 g., 0.01 mole) and p-nitrophenylhydrazine (3.1 g., 0.02 mole) in glacial acetic acid (10 ml.) was heated for 1 hr. on a steam bath

Cooling gave a product which was recrystallised from pyridine to give 1-(p-nitrophenyl)-5-pyrazolylacetaldehyde p-nitrophenylhydrazone as a yellow crystalline solid, m.p. 242° [lit.⁹¹ m.p. 242-243°] (Found: C, 55.6; H, 3.7. $C_{17}H_{14}N_6O_4$ requires C, 55.7; H, 3.5%).

Reaction of 1-Thia-4-pyrone with p-nitrophenylhydrazine.

A solution of 1-thia-4-pyrone (500 mg., 4.5 mmole) and p-nitrophenylhydrazine (1.5 g., 9.8 mmole) in glacial acetic acid was heated for 3 hr. on a steam bath. Cooling gave a yellow crystalline product which was recrystallised from methanol to give 1-acetyl 2-(p-nitrophenyl)hydrazine as yellow needles, characterised by analysis, melting point (212°) and mixed melting point with the product obtained by heating p-nitrophenylhydrazine with glacial acetic acid (Found: C, 49.6; H, 4.3. $C_8H_9N_2O_3$ requires C, 49.3; H, 4.6%).

Reaction of 1-Thia-4-pyrone with 2,4-Dinitrophenylhydrazine.

(a) To a filtered solution of 2,4-dinitrophenylhydrazine (1.0 g., 5.0 mmole) in ethanol (50 ml.) and concentrated hydrochloric acid (1.5 ml.) was added 1-thia-4-pyrone (500 mg. 4.5 mmole). The mixture was warmed for 15 min. on a steam bath. Cooling gave yellow crystals of 1-thia-4-pyrone 2,4-dinitrophenylhydrazone hydrochloride,

m.p. 223° (1.0 g., 70%) (Found: C, 39.9; H, 3.1; Cl, 11.0; N, 17.0; S, 9.6. $C_{12}H_9N_4O_2SCl$ requires C, 40.2; H, 2.8; Cl, 10.0; N, 17.0; S, 9.8%).

This product on addition to water gave a dark red crystalline compound which was recrystallised from methanol to give 1-thia-4-pyrone-2,4-dinitrophenylhydrazones, as dark red needles, m.p. 224°. (Found: C, 44.8; H, 3.3; N, 18.9. $C_{11}H_8N_4O_2S$ requires C, 45.2; H, 2.8; N, 19.2%).

(b) 1-Thia-4-pyrone (500 mg., 4.5 mmole) and 2,4-dinitrophenylhydrazine (1.5 g., 7.5 mmole) were refluxed for 1 hr. in glacial acetic acid (10 ml.). Cooling gave two products separated by fractional crystallisation from methanol to give 1-thia-4-pyrone-2,4-dinitrophenylhydrazones identified by melting point and mixed melting point with the compound obtained in the previous experiment. The second product was 1-acetyl-2(2,4'-dinitrophenyl)hydrazine, m.p. 198° identical to that obtained by refluxing 2,4-dinitrophenylhydrazine in glacial acetic acid (Found: C, 40.1; H, 3.6. $C_9H_8N_4O_5$ requires C, 40.0; H, 3.4%).

Reaction of 1-Thia-4-pyrone with Methyl Magnesium Iodide.

(a) To methyl magnesium iodide at 0° [from magnesium (0.22 g., 90 mmole) and methyl iodide (excess)] under nitrogen in dry ether (20 ml.) was added dropwise 1-thia-4-pyrone (1 g., 9.0 mmole) in dry ether (100 ml.).

After stirring for 15 min., the resulting mixture was poured into dilute hydrochloric acid and treated with potassium tri-iodide solution (excess) to give 4-hydroxythiapyrylium tri-iodide (3.5 g., 80%) which was recrystallised from water to give green needles, m.p. 95° (Found: C, 12.2; H, 1.1; $C_5H_5I_3OS$ requires C, 12.2; H, 1.0%).

Slow evaporation of an aqueous solution of the tri-iodide brought about conversion to 4-hydroxy-1-thiapyrylium iodide. This process was accelerated by addition of acetone. Recrystallisation from acetone gave white dichroic plates, m.p. 173° (Found: C, 25.3; H, 2.5. C_5H_5IOS requires C, 25.0; H, 2.1%).

Treatment of an acidified solution of 1-thia-4-pyrone with potassium tri-iodide solution gave the same tri-iodide, m.p. and mixed m.p. 95°, which could be converted as above to the same mono-iodide, m.p. and mixed m.p. 173°.

(b) To methyl magnesium iodide at 0° [from magnesium (0.11g., 4.5 mmole) and methyl iodide (excess)] under nitrogen in dry ether (10 ml.) was added dropwise 1-thia-4-pyrone (0.5 g., 4.5 mmole) in dry ether (50 ml.). After stirring for 30 min., the solution was cooled to -40° and treated with perchloric acid (5 ml. of 72% solution) in dry ether (10 ml.) also cooled to -40° to yield 4-hydroxythiapyrylium perchlorate as colourless hygroscopic crystals, m.p. 240°.

identical to the product obtained from 1-thia-4-pyrone and perchloric acid. A mixed melting point was undepressed.

Attempts to recrystallise this product from methanol for analysis yielded 4-methoxy thiapyrylium perchlorate as colourless needles, m.p. 122° [lit.⁷⁵ m.p. 125°] (Found: C, 31.5; H, 3.4; Cl, 15.8; S, 13.8. $C_6H_7ClO_5S$ requires C, 31.8; H, 3.1; Cl, 15.6; S, 14.2%).

Reaction of 1-Thia-4-pyrone with Cyclopentadienyl Sodium

A solution of cyclopentadienyl sodium [from sodium (0.42 g., 18 mmols) and cyclopentadiene monomer (excess)] in dry tetrahydrofuran (5 ml.) was added under nitrogen at -70° to 1-thia-4-pyrone (2 g., 18 mmole) in dry tetrahydrofuran (100 ml.). After 1 hr., the mixture was concentrated in vacuo and poured into dilute hydrochloric acid. Addition of potassium tri-iodide solution to the resulting mixture gave 4-hydroxythiapyrylium tri-iodide as previously.

Reaction of 1-Thia-4-pyrone with Bromine.

(a) To 1-thia-4-pyrone (300 mg., 2.7 mmole) in water (5 ml.) at 0° was added a solution of bromine (1.4 g., 8.8 mmole) in water (5 ml.) containing potassium bromide (1 g.). An orange-red crystalline product (600 mg.) was obtained m.p. 110-120°.

(b) To 1-thia-4-pyrone (200 mg., 1.8 mmole) in carbon tetrachloride (10 ml.) was added bromine (900 mg.,

5.6 mmole) in carbon tetrachloride (5 ml.). The orange-red product (250 mg.) which was slowly precipitated, showed no depression of melting point with that obtained in (a).

(c) 1-Thia-4-pyrone (50 mg., 0.45 mmole) in glacial acetic acid (1 ml.) treated with bromine (250 mg., 1.6 mmole) slowly yielded the same orange-red compound.

(d) No other product was obtained from numerous attempts similar to (a), (b), and (c), but including refluxing in the presence of halogenation catalysts such as ferric halides, and ultraviolet irradiation.

Heating this orange-red complex in water and evaporating to dryness or warming slightly in acetone gave a white crystalline solid, m.p. 190°, which was shown to be 4-hydroxythiapyrylium bromide hydrate by identification with that obtained from 1-thia-4-pyrone and hydrogen bromide/acetic acid in acetone. (Found: C, 29.0; H, 3.3. $C_5H_7BrO_2S$ requires C, 28.5; H, 3.3%).

Treatment of this product (100 mg.) with sodium bicarbonate solution (excess) and extraction with chloroform gave 1-thia-4-pyrone (quantitative) identified by melting point and mixed melting point with an authentic sample.

The composition of the orange-red 1-thia-4-pyrone/bromine complex was determined by dissolving a weighed amount

(25-30 mg.) in water (10 ml.) containing potassium iodide (0.5 g.) and titrating the liberated iodine with sodium thiosulphate (0.01N solution) to obtain the free bromine value. Further titration with sodium hydroxide (0.01N solution) allowed the calculation of the percentage of hydrogen bromide present.

Attempted Reactions of 1-Thia-4-pyrone with Metal Carbonyls.

1-Thia-4-pyrone was recovered after treatment with the following metal carbonyls under the conditions specified.

- (a) Iron pentacarbonyl in refluxing benzene for 12 hr.
- (b) Iron pentacarbonyl at 160° for 6 hr. in an autoclave (40 ml.) under carbon dioxide.
- (c) Iron pentacarbonyl in refluxing ether for 4 hr. under ultraviolet irradiation (Hanovia 500 w. lamp)

1-Thia-4-pyrone was recovered after irradiation for 10 hr. of its solution in ether.

- (d) Iron dodecacarbonyl at 160° for 6 hr. in an autoclave (40 ml.) under carbon dioxide.
- (e) Iron dodecacarbonyl in refluxing toluene for 8 hr. and in refluxing diglyme for 3 hr.
- (f) Cobalt octacarbonyl in refluxing tetrahydrofuran for 2 hr.
- (g) Nickel tetracarbonyl in refluxing methylene chloride.

- (h) Nickel tetracarbonyl at 70° for 4 hr. in an autoclave (40 ml.) under carbon dioxide.
- (i) Chromium hexacarbonyl for 20 hr. in refluxing petroleum ether (b.p. $100-120^{\circ}$)
- (j) Chromium hexacarbonyl at 200° for 4 hr. in an autoclave (40 ml.) under carbon dioxide.
- (k) Molybdenum hexacarbonyl for 3 hr. in refluxing diglyme.

CHAPTER II

Some Attempted Routes to a Tricyclo

[9,3,0,0^{4 96}] tetradecane system

1,2:5,6-Tetrabromocyclo-octane

The method of Ziegler and Wilms¹¹⁰ was used to obtain 1,2:5,6-tetrabromocyclo-octane (66.7%) as an isomeric mixture, m.p. 100-122° [lit.¹¹⁰ m.p. 105-124°] (Found: C, 22.9; H, 2.7. $C_8H_{12}Br_4$ requires C, 22.5; H, 2.8%).

Reaction of 1,2:5,6-Tetrabromocyclo-octane with Sodio-malonic Ester.

To sodium metal (1.9 g., 0.08 mole) dissolved in ethanol (40 ml.) was added with stirring diethyl malonate (13 g., 0.08 mole) in benzene (75 ml.). 1,2:5,6-Tetrabromocyclo-octane (8.5 g., 0.02 mole) in benzene (25 ml.) was then added and the resulting mixture refluxed for 6 hr. The benzene was then distilled off to small bulk and the residue poured into water and extracted with ether. The ether was dried (Na_2SO_4) and worked up to give a product which yielded diethyl malonate on distillation, the residue being 1,2:5,6-tetrabromocyclo-octane. Varying the solvent, reaction time and temperature gave the same result.

Reaction of 1,2:5,6-Tetrabromocyclo-octane with Magnesiummalonic Ester.

Magnesium metal (5 g., 0.21 mole) was stirred and refluxed in absolute ethanol (50 ml.) until dissolved (6 hr.). After the addition of diethyl malonate (65 g., 0.41 mole), the mixture was refluxed for 4 hr., 1,2:5,6-tetrabromocyclo-octane (40 g.,

0.09 mole) in absolute ethanol (200 ml.) and dry dioxan (100 ml.) was then added and the whole stirred and refluxed for a further 60 hr. The bulk was reduced by distillation of solvent and the residue poured into dilute hydrochloric acid. Extraction with ether and working up gave starting materials as in the previous experiment.

5,8-Dibromo-1,3-cyclo-octadiene.

The method of Cope et al¹¹² was used to obtain 5,8-dibromo-1,3-cyclo-octadiene (86.6%) b.p. 100-105° 0.3 mm.

Reaction of 5,8-Dibromo-1,3-cyclo-octadiene with Sodiomalonic Ester.

To sodium metal (4.2 g., 0.18 mole) dissolved in ethanol (100 ml.) was added with stirring diethyl malonate (30 g., 0.19 mole). 5,8-Dibromo-1,3-cyclo-octadiene (24 g., 0.09 mole) was added dropwise when an exothermic reaction took place. After stirring for 2 hr., the solution was concentrated by distillation poured into water and extracted with ether. The extract was dried (Na_2SO_4) and the solvent removed to give a dark-red oil (37 g.). Distillation gave fractions as follows:-

(1) 40-80°/0.1 mm (10 g.), (2) 80-110°/0.1 mm (2 g.),
 (3) 110-140°/0.1 mm (12 g.), leaving an intractable residue (13 g.)

The first fraction proved on re-distillation to be mainly diethyl malonate. The remaining fractions were redistilled to

give a colourless oil, b.p. 120-13°/0.1 mm which displayed ester carbonyl absorption in the infrared at 1720 cm.⁻¹

(Found: C, 66.9; H, 7.3. C₂₂H₂₂O₂ requires C, 62.2; H, 7.6%).

Ethyl Malonyl Chloride

The method of Oddo and Albanese¹¹⁹ was modified as follows: To ethyl potassium malonate¹¹⁹ (40 g., 0.24 mole) in dry ether (200 ml.) at -15° was added cautiously thionyl chloride (45 g., 0.38 mole). The mixture was refluxed for 3 hr. and filtered through a sinter (porosity 3). The ether was removed under vacuum and the residue distilled to give a colourless liquid, b.p. 35°/0.1 mm. (24.5 g., 69.2%).

Reaction of 1,5-Cyclo-octadiene with Ethyl Malonyl Chloride.

(a) To aluminium chloride (14 g., 0.1 mole) in methylene chloride (30 ml.) was added dropwise with stirring ethyl malonyl chloride (12.5 g., 0.08 mole) in methylene chloride (20 ml.). The product was filtered through glass wool and the filtrate treated slowly with stirring at -15° with 1,5-cyclo-octadiene (4.4 g., 0.04 mole). The resulting solution was poured into ice dilute hydrochloric acid and the organic layer separated, dried (Na₂SO₄) and worked up to give an opaque 'rubbery' gum.

(b) To 1,5-cyclo-octadiene (8.4 g., 0.08 mole) and ethyl malonyl chloride (24 g., 0.16 mole) at -15° was added dropwise over 4 hr. stannic chloride (10 ml.). The product was poured

into ice-dilute hydrochloric acid and the mixture extracted with ether. The ether extract was washed with sodium bicarbonate solution, dried (Na_2SO_4) and worked up to give an oil (15.1 g.) which was distilled from sodium carbonate to give a colourless oil (5.0 g.). Redistillation of this oil gave fractions as follows:-

- (1) 0.54 g. up to $32^\circ/0.1$ mm., (2) 1.38 g. up to $85^\circ/0.1$ mm.,
 (3) 2.21 g. up to $105^\circ/0.1$ mm.

All attempts by distillation and chromatography to obtain a product giving satisfactory analysis were unsuccessful. Chromatography of (3) on silica gel with benzene-ether gave an oil (1.38 g., 5.3%) (Found: C, 65.8; H, 7.1. $\text{C}_{19}\text{H}_{24}\text{O}_6$ requires C, 64.3; H, 7.2%).

Reaction of 1,5-Cyclo-octadiene with β -chloropropionyl Chloride.

(a) To aluminium chloride (17 g., 0.13 mole) in methylene chloride (50 ml.) was added dropwise with stirring β -chloropropionyl chloride (12.8 g., 0.10 mole) in methylene chloride (20 ml.). The product was filtered through glass wool and the filtrate treated slowly with stirring at -15° with 1,5-cyclo-octadiene (5 g., 0.05 mole) in methylene chloride (50 ml.). The product was poured into ice-dilute hydrochloric acid and the organic layer separated, dried (Na_2SO_4) and worked up to give a thick dark oil which gave no product on attempted distillation

from sodium carbonate.

(b) To 1,5-cyclo-octadiene (7.9 g., 0.07 mole) and β -chloro-propionyl chloride (19.5 g., 0.15 mole) at -15° was added dropwise over 2 hr. stannic chloride (10 ml.). The product was poured into ice-dilute hydrochloric acid and the mixture extracted with ether. The ether extract was washed with sodium bicarbonate solution, dried (Na_2SO_4) and worked up to give an oil (9 g.) which was distilled from sodium carbonate to give a colourless oil (3.7 g.). Redistillation of this oil gave fractions as follows:-

- (1) 0.83 g. up to $90^\circ/0.08$ mm., (2) 0.74 g., up to $102^\circ/0.08$ mm.,
 (3) 1.43 g. up to $110^\circ/0.08$ mm.

All attempts by distillation and chromatography to obtain a product giving satisfactory analysis were unsuccessful. Chromatography on silica gel with benzene gave an oil (0.56 g., 2.7%) (Found: C, 60.0; H, 8.5. $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{O}_2$ requires C, 58.2; H, 6.5%).

CHAPTER III
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Some Studies of Tropyliated Phenols

Tropylation of Phenol.

o- and *p*-tropylyphenols were prepared by Hosoe's method as follows:-

When ditropyl ether (8 g., 0.04 mole) was added to phenol (7.6 g., 0.08 mole) an exothermic reaction took place. Distillation gave unreacted phenol and a pale yellow oil (7.0 g.), b.p. 105-125°/0.1 mm. which slowly crystallised. Chromatography on silica gel with benzene gave *o*-tropylyphenol (1.9 g., 12.8%) and then *p*-tropylyphenol (3.4 g., 22.9%).

p-Hydroxyphenyltropylium Perchlorate.

To *p*-tropylyphenol (0.5 g., 2.7 mmole) in glacial acetic acid (5 ml.) was added triphenylmethyl perchlorate (1.0 g., 2.9 mmole) and the mixture warmed for 10 min. on a steam bath. The yellow crystalline precipitate obtained was filtered off, washed with ether and dried to give *p*-hydroxyphenyltropylium perchlorate (650 mg., 84.7%) which was recrystallised from water to give red needles (600 mg., 76.2%), m.p. 200-201°, $\lambda_{\text{max.}}(\text{H}_2\text{O})$ 430 m μ [lit.⁶⁵ m.p. 201-202°, $\lambda_{\text{max.}}$ 435 m μ] (Found: C, 55.5; H, 3.7; Cl, 12.3. $\text{C}_{13}\text{H}_{11}\text{ClO}_5$ requires C, 55.2; H, 3.9; Cl, 12.5%).

Tropilidene-*p*-quinone.

An aqueous solution of *p*-hydroxyphenyltropylium perchlorate (170 mg., 0.6 mmole) was treated with sodium

bicarbonate solution (excess). A deep violet-red solution was obtained, λ_{max} 525 m μ [lit.⁵⁶ 530 m μ], which was extracted with chloroform. The organic layer was dried (Na_2SO_4) and worked up to give a dark purple solid (95 mg., 86.7%), which was sensitive to air and would not redissolve completely in chloroform or methylene chloride. Attempted recrystallisations to obtain a pure sample for analysis were unsuccessful. [ν_{max} (in nujol) 1600 cm^{-1} (m)]

Reduction of Tropilidene-p-quinone with Sodium Borohydride.

To tropilidene-p-quinone (55 mg., 0.3 mmole) in ethanol (5 ml.) was added sodium borohydride (116 mg., 3 mmole). The mixture was left overnight, poured into water and extracted with chloroform. The chloroform extract was dried (Na_2SO_4) and worked up to give a colourless crystalline compound which was recrystallised from petroleum ether (b.p. 60-80°) to give p-tropylphenol (21 mg., 37.8%) identified by melting point (78°) and mixed melting point (78°) with an authentic sample.

Reaction of Tropilidene-p-quinone with Perchloric Acid.

Treatment of tropilidene-p-quinone (23 mg., 0.13 mmole) with perchloric acid (1 ml. of 72% solution) and water (1 ml.) gave a yellow crystalline solid which was recrystallised from water to give red needles of p-hydroxyphenyltropylium perchlorate (14 mg., 39.2%) identified by infrared spectrum, melting point

(200°) and mixed melting point (200°) with an authentic sample.

Reaction of Tropilidene-p-quinone with Methyl Magnesium Iodide.

A dried (Na_2SO_4) ether solution of tropilidene-p-quinone, prepared from p-hydroxyphenyltropylium perchlorate (565 mg., 2 mmole) by basification and ether extraction, was added with stirring to a solution of methyl magnesium iodide (in ether under nitrogen) prepared from magnesium (50 mg., 2.1 mmole) and methyl iodide (excess). The mixture was stirred for 2 hr. and poured into dilute hydrochloric acid. Ether extraction gave a small amount of unidentified oil (100 mg.). The yellow acid layer on basification gave a deep violet-red colour, giving an ultraviolet absorption maximum at 525 m μ characteristic of tropilidene-p-quinone. Reacidification gave the original yellow solution showing an ultraviolet absorption maximum at 430 m μ characteristic of the p-hydroxyphenyltropylium ion.

Reaction of Tropilidene-p-quinone with Cyclopentadienylsodium

A solution of tropilidene-p-quinone in tetrahydrofuran prepared from p-hydroxyphenyltropylium perchlorate (565 mg., 2 mmole) as before was added to cyclopentadienyl sodium prepared from sodium (46 mg., 2 mmole) and cyclopentadiene monomer (excess) under nitrogen. The mixture was stirred for 1 hr. and poured into dilute hydrochloric acid. Ether extraction

gave no identifiable product. The acid solution, however, on basification gave a violet-red solution as before.

(3,5-Dimethyl-4-hydroxyphenyl)tropylium Perchlorate.

2,6-Xylenol (4 g., 33 mmole) was treated with ditropylium ether (3.3 g., 16 mmole). The slight exothermic reaction which took place was accelerated by heating for 1 hr. on a steam bath. Unreacted 2,6-xylenol was removed by distillation and the residue distilled to give an oil (3.6 g., 51.8%), b.p. 125° 0.09 mm. which crystallised to give 4-tropyl-2,6-xylenol, m.p. 62-67° [lit. m.p. 67-67.5°].

This product (530 mg., 2.5 mmole) in glacial acetic acid (10 ml.) was treated with triphenylmethyl perchlorate (860 mg., 2.5 mmole). The mixture was heated on a steam bath for 10 min., cooled and filtered to give a reddish-brown crystalline compound (630 mg., 81.2%) which was recrystallised from water to give (3,5-dimethyl-4-hydroxyphenyl)tropylium perchlorate hydrate m.p. 222° (Found: C, 55.4; H, 5.5; Cl, 11.0. $C_{15}H_{17}ClO_3$ requires C, 54.8; H, 5.2; Cl, 10.8%).

Treatment of this compound with sodium bicarbonate solution gave a deep violet-red solution. Extraction with carbon tetrachloride and working up gave an unstable purple residue which could not be purified.

Reaction of Ditropyl Ether with Thiophenol.

Thiophenol (9.3 g., 0.088 mole) was treated with ditropyl ether (9 g., 0.045 mole). An exothermic reaction took place. The mixture was heated at 100° for 30 min. and allowed to cool. Distillation gave tropylyl phenyl thioether (13.94 g., 82.5%) as a very pale yellow oil b.p. 98°/0.1 mm. (Found: C, 76.6; H, 6.3; S, 16.6. $C_{13}H_{12}S$ requires C, 77.9; H, 6.0; S, 16.0%). This compound formed a complex with mercuric chloride to give very pale green crystalline plates of tropylyl phenyl thioether bis-(mercuric chloride), m.p. 198° (Found: C, 20.9; H, 1.8. $C_{13}H_{12}Cl_2Hg_2S$ requires C, 21.0; H, 1.6%).

Reaction of Tropylyl Phenyl Thioether with Triphenylmethyl Perchlorate.

Tropylyl phenyl thioether (1.97 g., 9.8 mmole) in glacial acetic acid (10 ml.) was treated with triphenylmethyl perchlorate (3.47 g., 10 mmole). The mixture was warmed for 10 min. on a steam bath, cooled and filtered. A warm aqueous extract of the crystalline product obtained yielded, on cooling, tropylium perchlorate identified by melting point and infrared spectrum comparison with an authentic sample. The residue from the aqueous extract was warmed with petroleum ether (b.p. 60-80°) which was then worked up to give triphenylmethyl phenyl thioether as colourless prisms, m.p. 107.5° [lit.^{12a} m.p. 106°] (Found:

C, 84.9; H, 5.9; S, 9.4. $C_{25}H_{20}S$ requires C, 85.2; H, 5.7; S, 9.1%)

Tropylation of Catechol.

Catechol (5.5 g., 0.05 mole) was treated with ditropyl ether (5 g., 0.025 mole). A very rapid exothermic reaction took place giving a thick oil which would not distil.

Attempts to obtain single substances by chromatography were unsuccessful.

Tropylation of Guaiacol.

To guaiacol (8.3 g., 0.067 mole) was added ditropyl ether (6.6 g., 0.033 mole) and the mixture was heated for 15 min. on a steam bath. Distillation of the product gave a pale yellow oil (5.73 g.), b.p. 120-130°/0.01 mm. Chromatography on silica gel with benzene gave 2-methoxy-6-tropylphenol as colourless crystal, m.p. 50° (2.7 g., 18.8%) (Found: C, 78.2; H, 6.6. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%). Further elution slowly yielded an oily mixture (0.9 g.) which could not be purified on rechromatography.

Tropylation of p-Cresol.

To p-cresol (21.6 g., 0.2 mole) was added ditropyl ether (19.8 g., 0.1 mole) and the mixture heated for 1 hr. on a steam bath. The product was chromatographed on silica gel with benzene to give a colourless crystalline solid (13.8 g., 34.8%) which was recrystallised from petroleum ether (b.p. 60-80°)

to give 2-tropyl-4-methylphenol, m.p. 65°. Analysis indicated that this compound crystallised as a hydrate ($\frac{1}{2}$ mole H_2O) (Found: C, 81.1; H, 7.2. $C_{12}H_{14}O \cdot \frac{1}{2}H_2O$ requires C, 81.1; H, 7.3%). An n. s. r. spectrum confirmed this. (See Appendix).

(2-Hydroxy-5-methylphenyl)tropylium Perchlorate.

2-Tropyl-4-methylphenol (1.19 g., 6 mmole) in methylene chloride (5 ml.) was treated with triphenylmethyl perchlorate (2.06 g., 6 mmole) in methylene chloride (50 ml.) and the mixture left overnight in a refrigerator. Filtration yielded (2-hydroxy-5-methylphenyl)tropylium perchlorate, as orange platelets, m.p. 172° (Found: C, 56.4; H, 4.3; Cl, 12.1%. $C_{14}H_{13}ClO_6$ requires C, 56.7; H, 4.4; Cl, 12.0%).

(2-Hydroxyphenyl)tropylium Perchlorate.

A mixture of o-tropylphenol (1.84 g., 0.01 mole) in methylene chloride (5 ml.) and triphenylmethyl perchlorate (3.43 g., 0.01 mole) in methylene chloride (75 ml.) was left in a refrigerator overnight. Filtration gave a yellow crystalline solid (1.73 g., 61.2%) which was recrystallised from methylene chloride to give (2-hydroxyphenyl)tropylium perchlorate m.p. 162° (Found: C, 54.6; H, 4.0; Cl, 13.0. $C_{13}H_{11}ClO_6$ requires C, 55.2; H, 3.9; Cl, 12.5%).

(2-Hydroxy-3-methoxyphenyl)tropylium Perchlorate.

To 2-methoxy-6-tropylphenol (0.86 g., 4 mmole) in

methylene chloride (5 ml.) was added triphenylmethyl perchlorate (1.4 g., 4.1 mole) in methylene chloride (40 ml.) and the mixture left overnight in a refrigerator. Filtration yielded (2-hydroxy-3-methoxyphenyl)-tropylium perchlorate (760 mg., 61%) as orange-yellow needles, recrystallisable from methylene chloride, m.p. 182°. (Found: C, 53.3; H, 4.5; Cl, 10.8. $C_{14}H_{13}ClO_6$ requires C, 53.8; H, 4.2; Cl, 11.3%).

3-Methylbenzo[b]cycloheptatrieno[d]furan.

(2-Hydroxy-5-methylphenyl)tropylium perchlorate (0.99 g., 3.3 mmole) was shaken well with sodium bicarbonate solution (excess) and the product extracted with methylene chloride. The extract was dried (Na_2SO_4) and worked up to give a yellow-brown oil which was distilled to give 3-methylbenzo[b]cycloheptatrieno[d]furan (0.58 g., 88.6%) as a pale yellow oil which darkened on exposure to air for a few days, b.p. 130-140°/0.05 mm. (Found: C, 85.0; H, 6.5. $C_{14}H_{12}O$ requires C, 85.7; H, 6.2%) ν_{max} . (liquid film) 1190 cm^{-1} (C-O).

Benzo[b]cycloheptatrieno[d]furan.

(2-Hydroxyphenyl)tropylium perchlorate (1.41 g., 5 mmole) was shaken well with sodium bicarbonate solution (excess). The product was extracted with methylene chloride the extract dried (Na_2SO_4) and worked up to give a dark brown

oil which was distilled to give benzo[b]cycloheptatrieno[d]furan (0.47 g., 51.7%) as a pale yellow oil, unstable to air, b.p. 130-140° 0.2 mm. (Found: C, 86.3; H, 6.3. $C_{15}H_{10}O$ requires C, 85.7; H, 5.5%) $\nu_{max.}$ (liquid film) 1117 cm^{-1} (C-O).

1-Methoxybenzo[b]cycloheptatrieno[d]furan.

2-Hydroxy-3-methoxyphenyl)tropylium perchlorate (1.25 g., 4 mmole) was shaken well with sodium bicarbonate solution (excess) The product was extracted with methylene chloride, the extract dried (Na_2SO_4) and worked up to give a brown oil which was distilled to give 1-methoxybenzo[b]cycloheptatrieno[d]furan (700 mg., 82.5%), as a pale yellow unstable oil, b.p. 150-160° 0.06 mm. $\nu_{max.}$ (liquid film) 1087 cm^{-1} (cyclic C-O) 1266 cm^{-1} (-O-Me).

(3-Methylbenzofurano)tropylium Perchlorate.

3-Methylbenzo[b]cycloheptatrieno[d]furan (500 mg., 2.5 mmole) in methylene chloride (2 ml.) was treated with triphenylmethyl perchlorate (880 mg., 2.6 mmole) in methylene chloride (25 ml.) and the mixture left overnight in a refrigerator. Filtration gave (3-methylbenzofurano)tropylium perchlorate (720 mg., 81.3%) as orange-yellow needles, m.p. 192° (Found: C, 56.8; H, 3.8; Cl, 12.0. $C_{14}H_{11}ClO_5$ requires C, 57.1; H, 3.8; Cl, 12.0%).

Benzofuranotropylium Perchlorate.

When benzo[b]cycloheptatrieno[d]furan (425 mg., 2.3 mmole) in methylene chloride (2 ml.) was treated with triphenylmethyl perchlorate (800 mg., 2.3 mmole) in methylene chloride (25 ml.), a yellow crystalline precipitate was obtained almost immediately. Filtration gave benzofuranotropylium perchlorate, m.p. 200° (610 mg., 92.9%) (Found: C, 55.0; H, 3.2; Cl, 12.8. $C_{13}H_9ClO_5$ requires C, 55.6; H, 3.2; Cl, 12.6%).

(1-Methoxybenzofurano)tropylium Perchlorate.

When 1-methoxybenzo[b]cycloheptatrieno[d]furan (507 mg., 2.4 mmole) in methylene chloride (2 ml.) was treated with triphenylmethyl perchlorate (820 mg., 2.4 mmole) in methylene chloride (25 ml.) an immediate yellow crystalline precipitate was obtained. Filtration gave (1-methoxybenzofurano)tropylium perchlorate (705 mg., 95.1%), m.p. 203°. (Found: C, 53.7; H, 3.6; Cl, 11.5. $C_{14}H_{11}ClO_5$ requires C, 54.1; H, 3.6; Cl, 11.4%).

Basification of (3-Methylbenzofurano)tropylium Perchlorate

(3-Methylbenzofurano)tropylium perchlorate (7.43 g., 25.2 mmole) was shaken well with sodium bicarbonate solution (excess) and the product extracted with methylene chloride. The extract was dried (Na_2SO_4) and worked up to give a dark-brown oil (5.24 g.). This product was chromatographed on silica gel with benzene to give product A, a brown oil (2.12 g.)

When the eluant was changed to benzene-10% ether a pale yellow solid (product B) was obtained (0.98 g.), m.p. 130°, and then a very pale yellow solid (product C, 0.87 g.), m.p. 139°. No other product was obtained on further elution.

Product A. The brown oil was distilled to give a pale yellow oil (1.50 g.) b.p. 92°/0.02 mm., which was identified as 3-methylbenzo[b]cycloheptatrieno[d]furan. (Found: C, 85.1; H, 6.0. $C_{14}H_{12}O$ requires C, 85.7; H, 6.0%).

This product on treatment with triphenylmethyl perchlorate in methylene chloride gave (3-methylbenzofurano) tropylium perchlorate identified by infrared spectrum, melting point (192°) and mixed melting point (192°) with the product obtained previously.

Product B: This product was purified by sublimation at 120-130°/0.1 mm. to give pale yellow plates, m.p. 130° (Found: C, 79.9; H, 4.8. $C_{14}H_{10}O_2$ requires C, 80.0; H, 4.8%).

$\nu_{\max.}$ (KCl) 1625 cm^{-1} (medium) 1575 cm^{-1} (strong).

Product B (50 mg., 0.24 mmole) in ethanol (2.5 ml.) and concentrated hydrochloric acid (0.15 ml.) was refluxed for 8 hr. with 2,4-dinitrophenylhydrazine (70 mg., 0.35 mmole). Filtration gave dark purple (almost black) crystalline needles m.p. 302° (67 mg., 72.5%) (Found: C, 61.5; H, 4.3; N, 14.5. $C_{20}H_{14}N_4O_6$ requires C, 61.5; H, 3.6; N, 14.4%).

Product C: Sublimation of this product at 130-140°/ 0.1 mm. gave very pale yellow crystalline plates, m.p. 139° (Found: C, 79.6; H, 4.7. $C_{14}H_{10}O_2$ requires C, 80.0; H, 4.8%) $\nu_{\max.}$ (KCl) 1608 cm^{-1} (medium), 1515 cm^{-1} (strong).

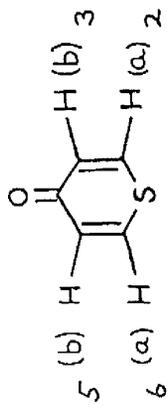
Product C (50 mg., 0.24 mmole) in ethanol (2.5 ml.) and concentrated hydrochloric acid (0.15 ml.) was warmed with 2,4-dinitrophenylhydrazine (70 mg., 0.35 mmole). An orange-yellow precipitate was rapidly formed which on filtration and washing with warm ethanol lost hydrochloric acid to give dark purple (almost black) needles, m.p. 291° (70 mg., 75.0%) (Found: C, 62.0; H, 3.8; N, 14.6. $C_{20}H_{14}N_2O_5$ requires C, 61.5; H, 3.6; N, 14.4%).

A P P E N D I X

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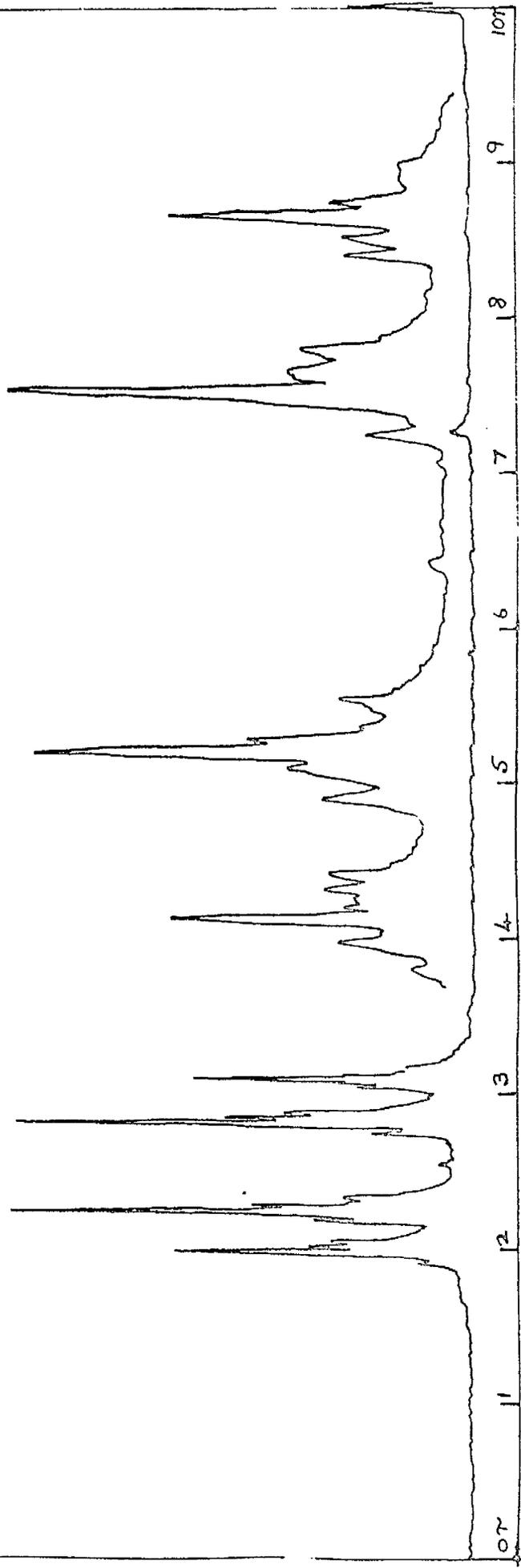
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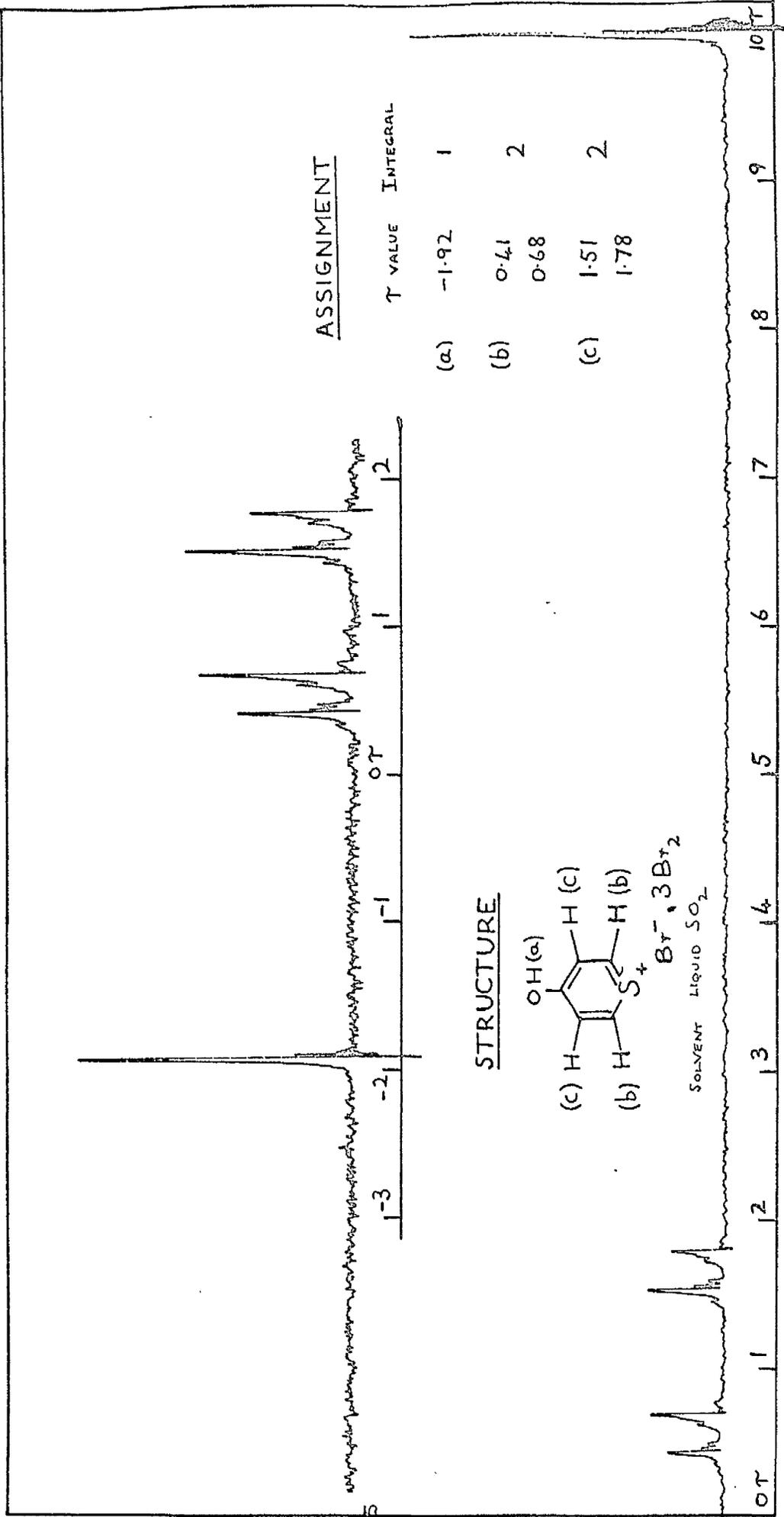


SOLVENT CDCl₃

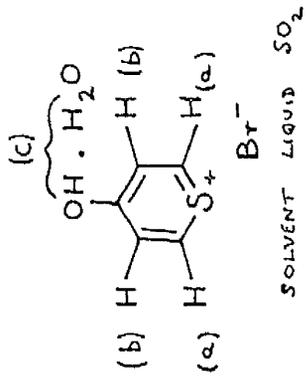
ASSIGNMENT

τ-VALUE	INTEGRAL	COUPLING CONSTANTS
(a) ~ 2.11	2	J _{2,3} - 10.39 c/s
(b) ~ 2.91	2	J _{2,5} - 0.48 c/s
		J _{2,6} - 4.06 c/s
		J _{3,5} - 1.97 c/s
		δ = 31.90 c/s



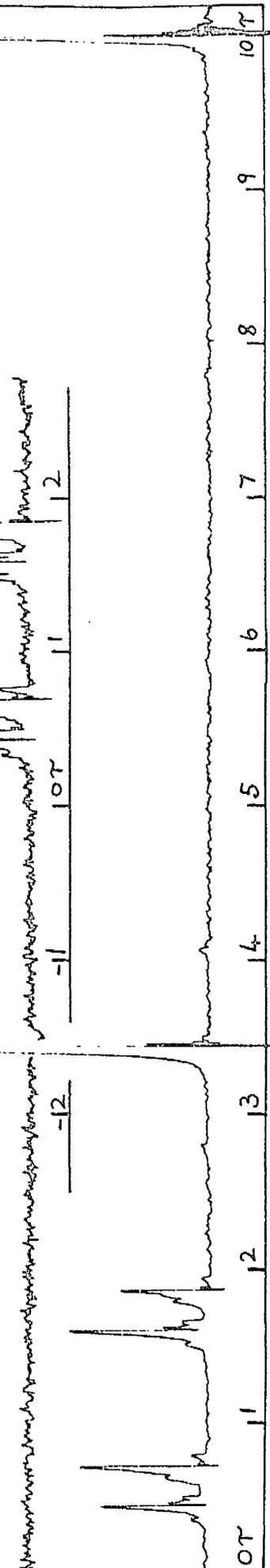


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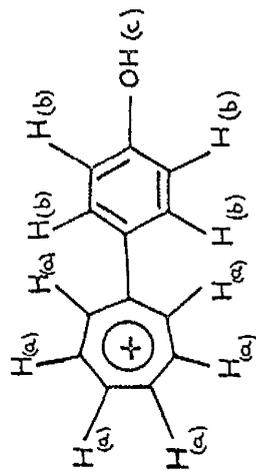


ASSIGNMENT

	τ VALUE	INTEGRAL
(a)	0.44	2
(b)	0.70	2
(c)	1.59 1.85	3



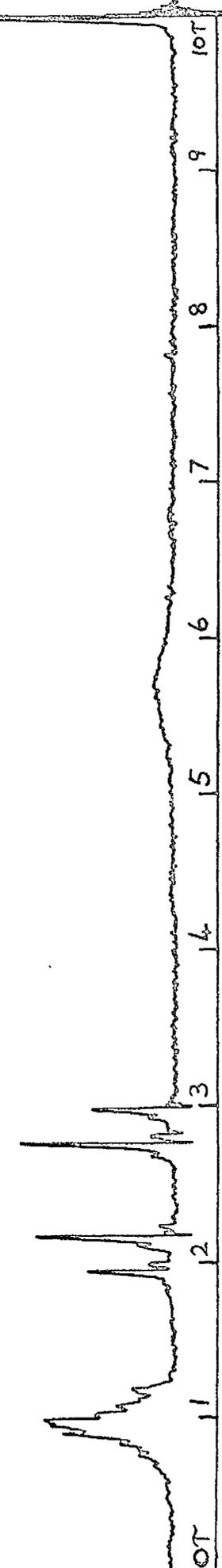
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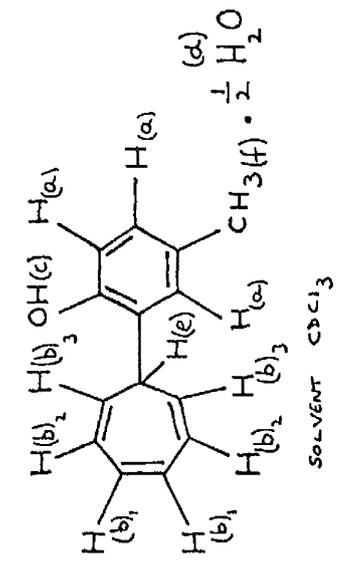
ClO_4^-
SOLVENT LIQUID SO_2

ASSIGNMENT

	<u>T-VALUE</u>	<u>INTEGRAL</u>
(a)	~ 0.96	6
(b)	~ 2.45	4
(c)	~ 5.70	1

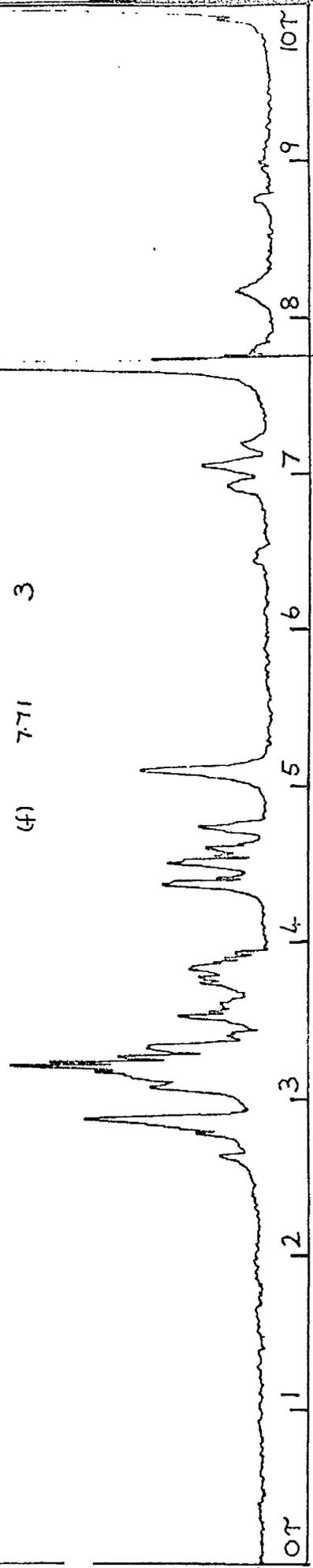


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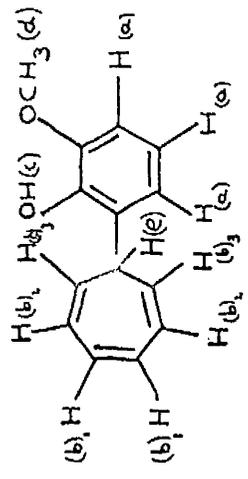


ASSIGNMENT

	τ -VALUE	INTEGRAL
(a)	~2.5 - 3.5	10
(b) _{1,2,3}	~3.3 - 4.8	
(c)	4.37	1
(d)	5.10	1
(e)	7.06	1
(f)	7.71	3



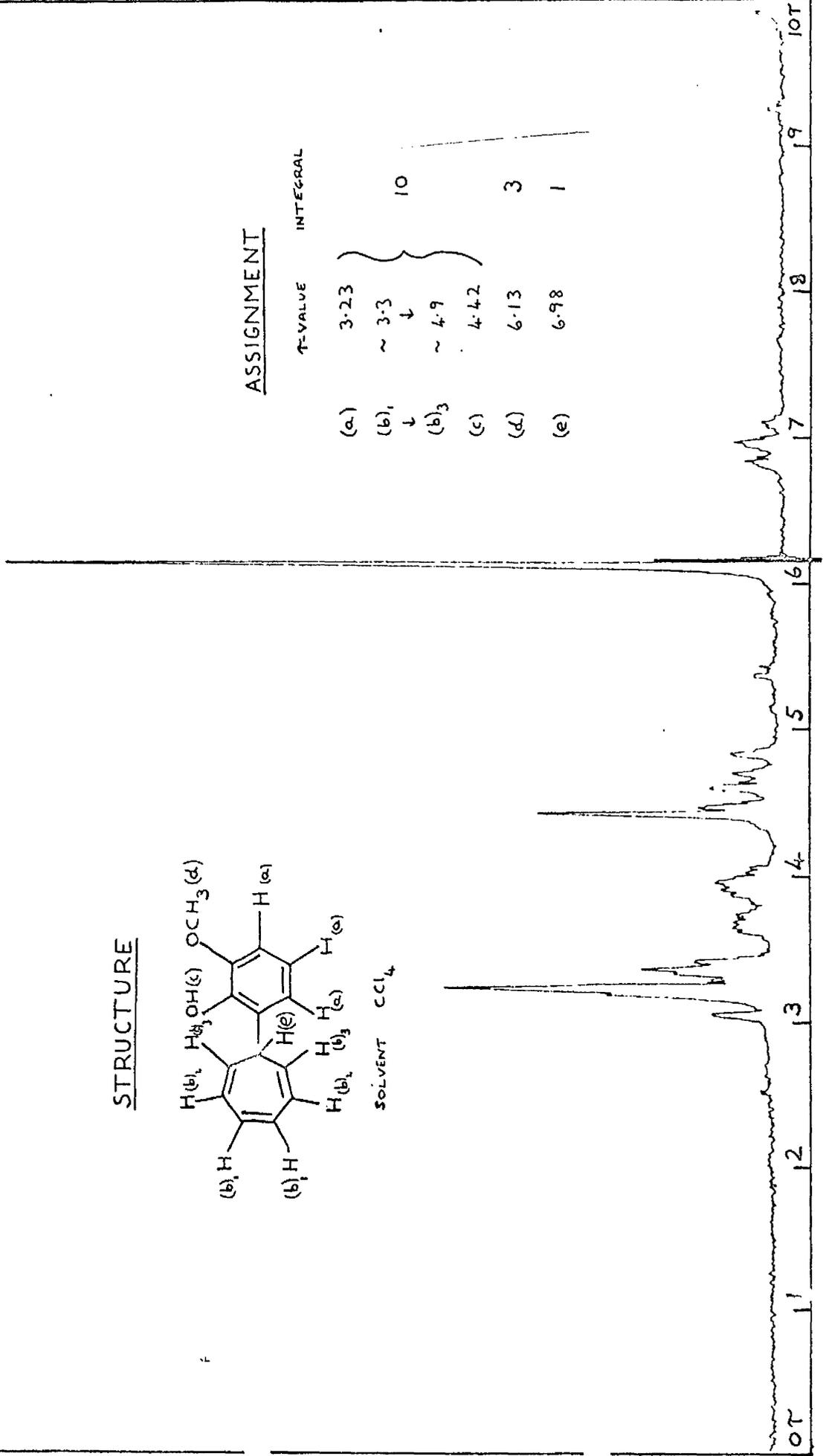
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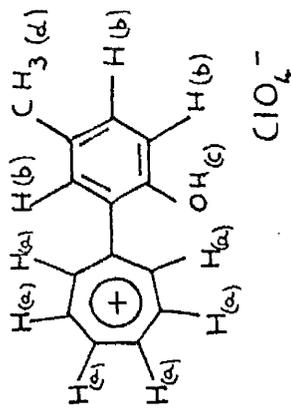
SOLVENT CCl₄

ASSIGNMENT

	τ-VALUE	INTEGRAL
(a)	3.23	10
(b) ₁	~ 3.3	
↓	↓	
(b) ₃	~ 4.9	3
(c)	4.42	
(d)	6.13	1
(e)	6.98	



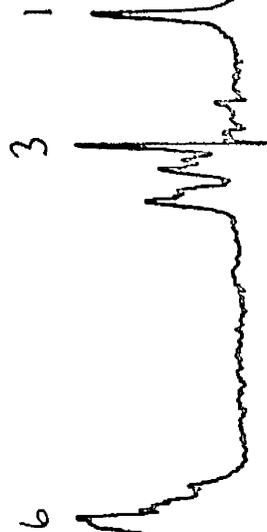
STRUCTURE



SOLVENT LIQUID SO₂

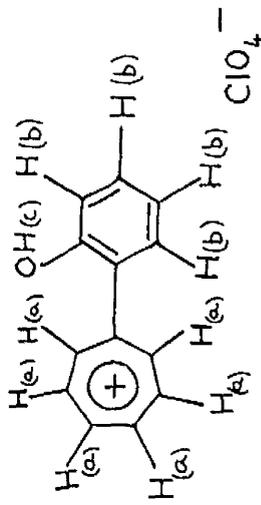
ASSIGNMENT

	T-VALUE	INTEGRAL
(a)	~0.89	6
(b)	~2.70	3
(c)	3.50	1
(d)	7.64	3



11 12 13 14 15 16 17 18 19 10T

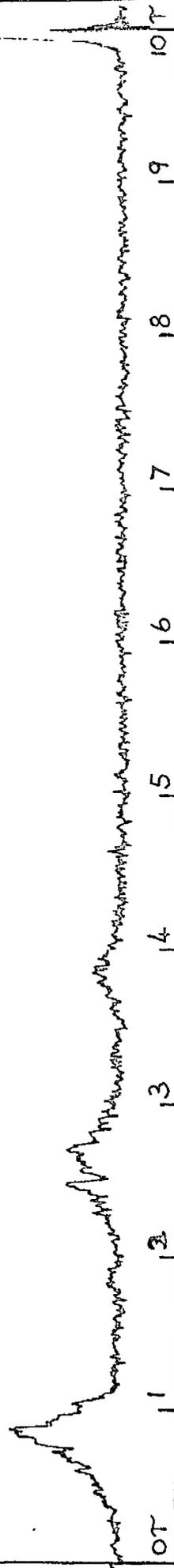
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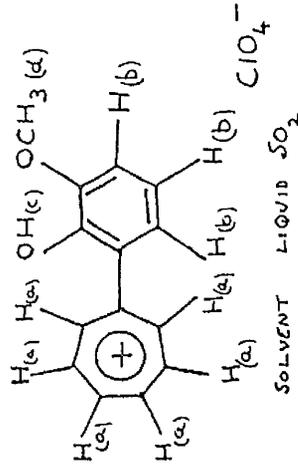
SOLVENT LIQUID SO₂

ASSIGNMENT

	τ -VALUE	INTEGRAL
(a)	~ 0.87	6
(b)	~ 1.60	4
(c)	~ 3.85	1

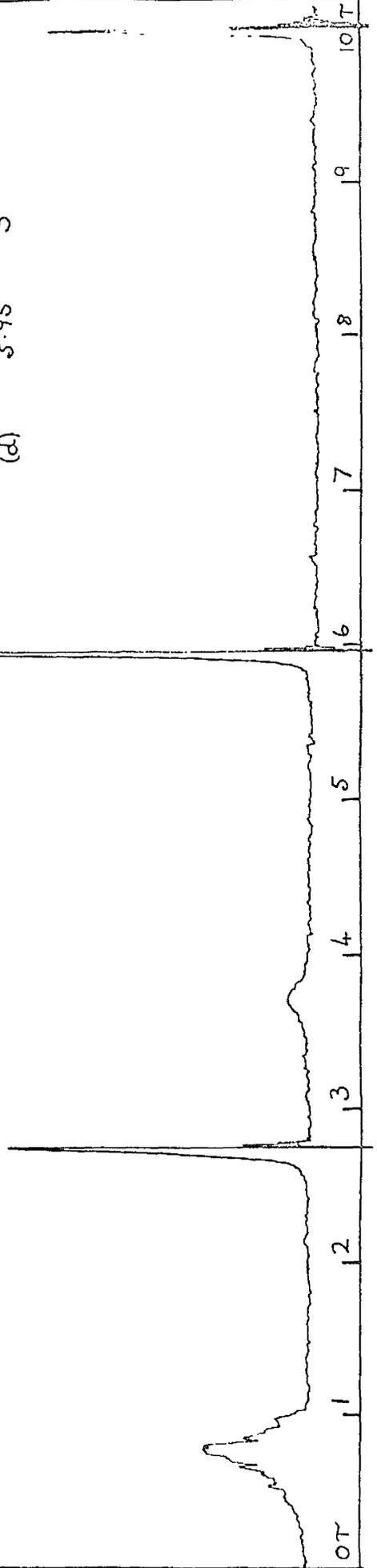


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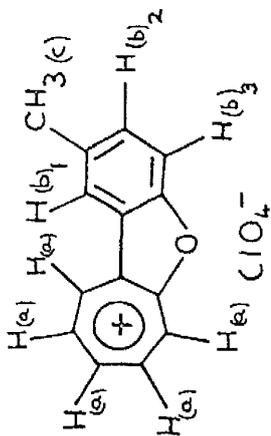


ASSIGNMENT

	τ -VALUE	INTEGRAL
(a)	~ 0.79	6
(b)	2.74	3
(c)	3.70	1
(d)	5.95	3



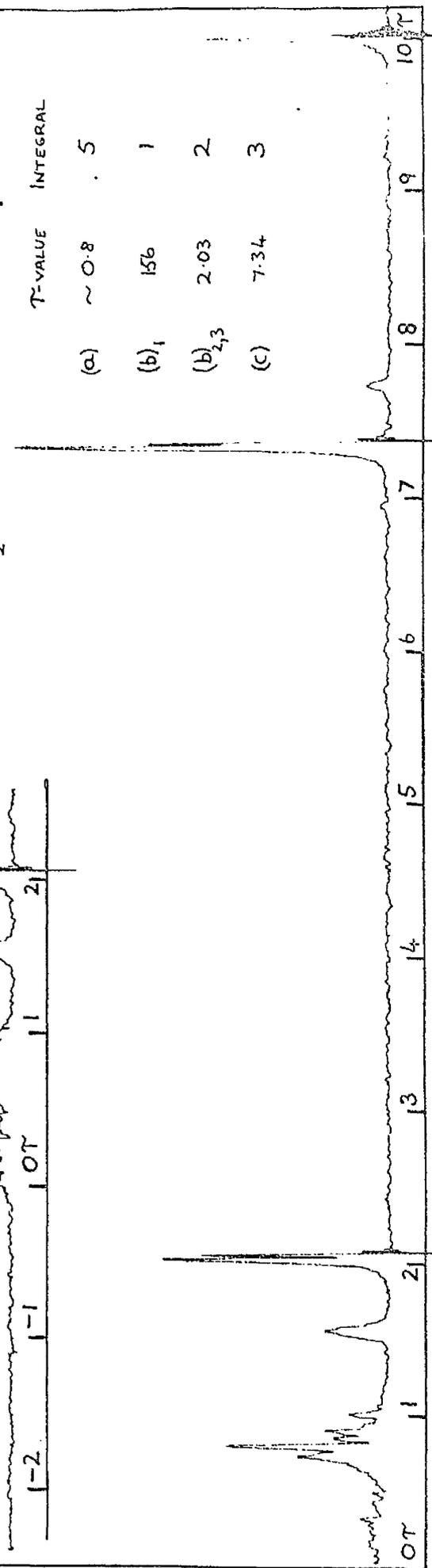
STRUCTURE



SOLVENT LIQUID SO_2

ASSIGNMENT

	τ -VALUE	INTEGRAL
(a)	~ 0.8	5
(b) ₁	156	1
(b) _{2,3}	2.03	2
(c)	7.34	3



OT

3

4

5

6

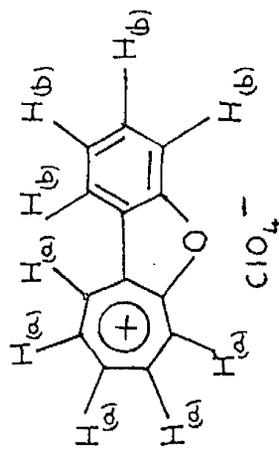
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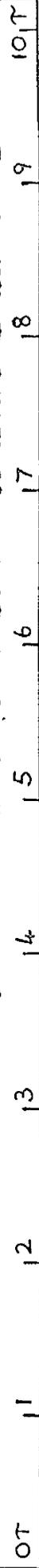
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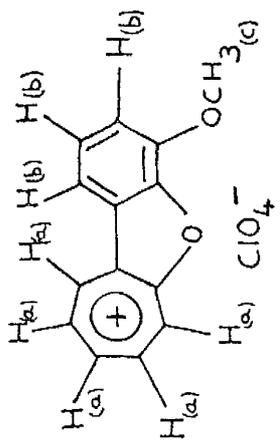
SOLVENT LIQUID SO₂

ASSIGNMENT

	τ -VALUE	INTEGRAL
(a)	0.75	5
(b)	1.85	4



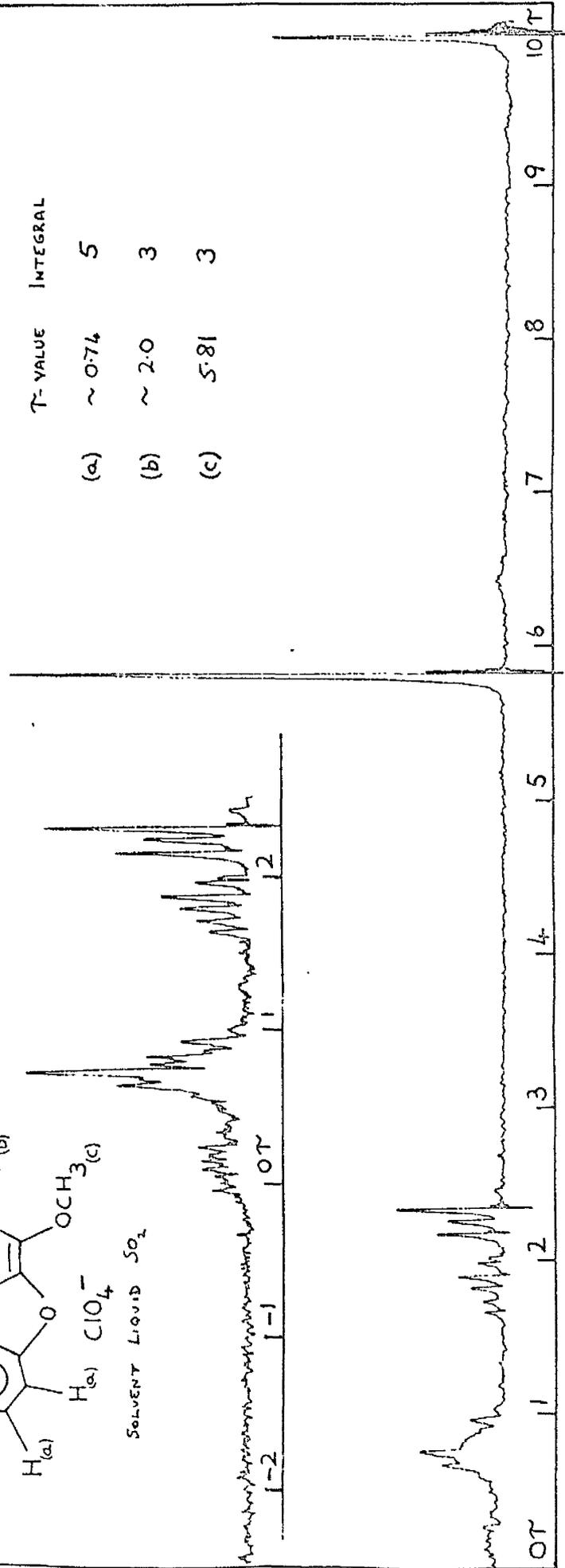
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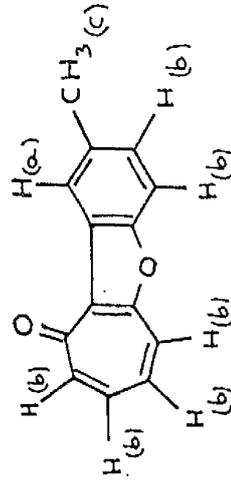
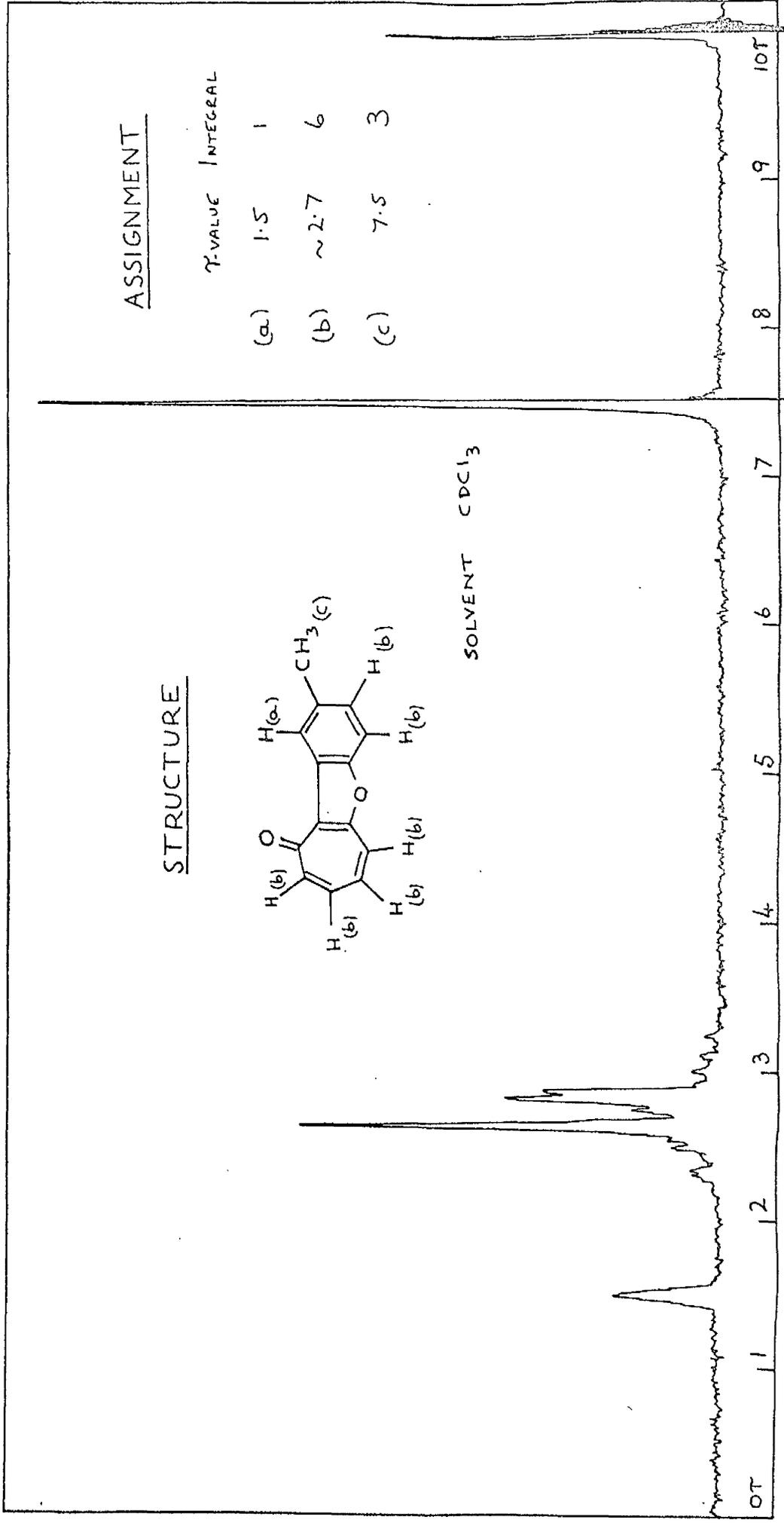


SOLVENT LIQUID SO_2

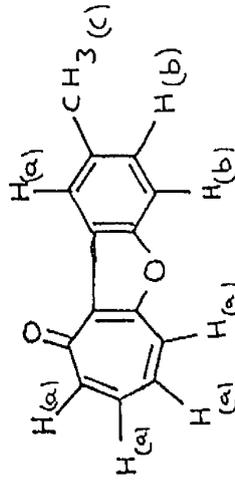
ASSIGNMENT

	T-VALUE	INTEGRAL
(a)	~ 0.74	5
(b)	~ 2.0	3
(c)	5.81	3





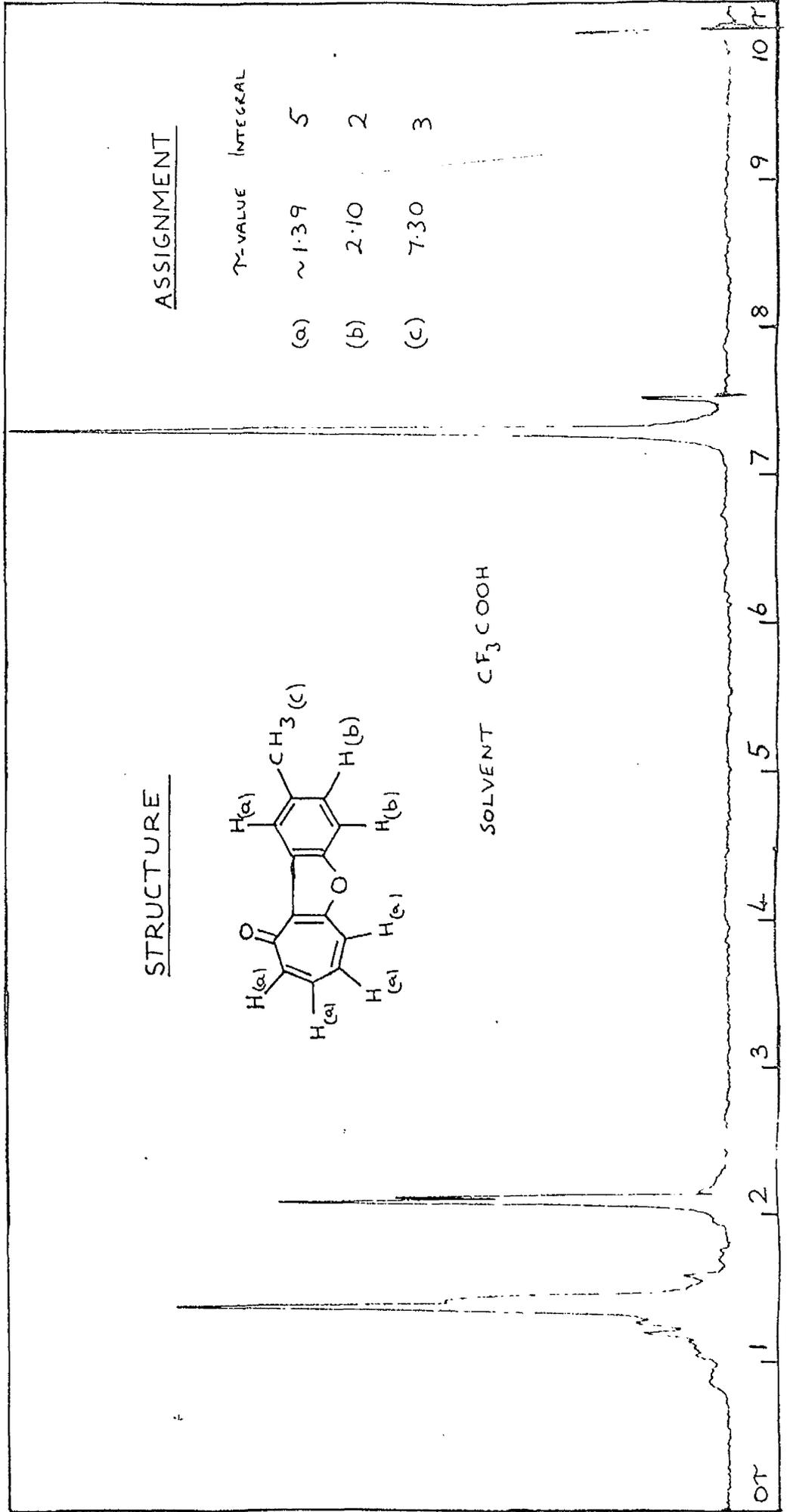
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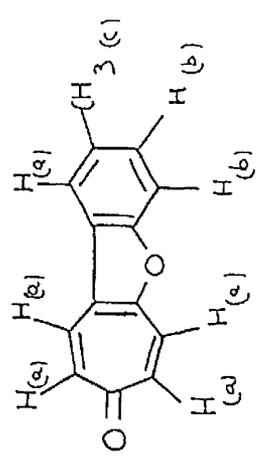
SOLVENT CF₃COOH

ASSIGNMENT

	τ -VALUE	INTEGRAL
(a)	~1.39	5
(b)	2.10	2
(c)	7.30	3



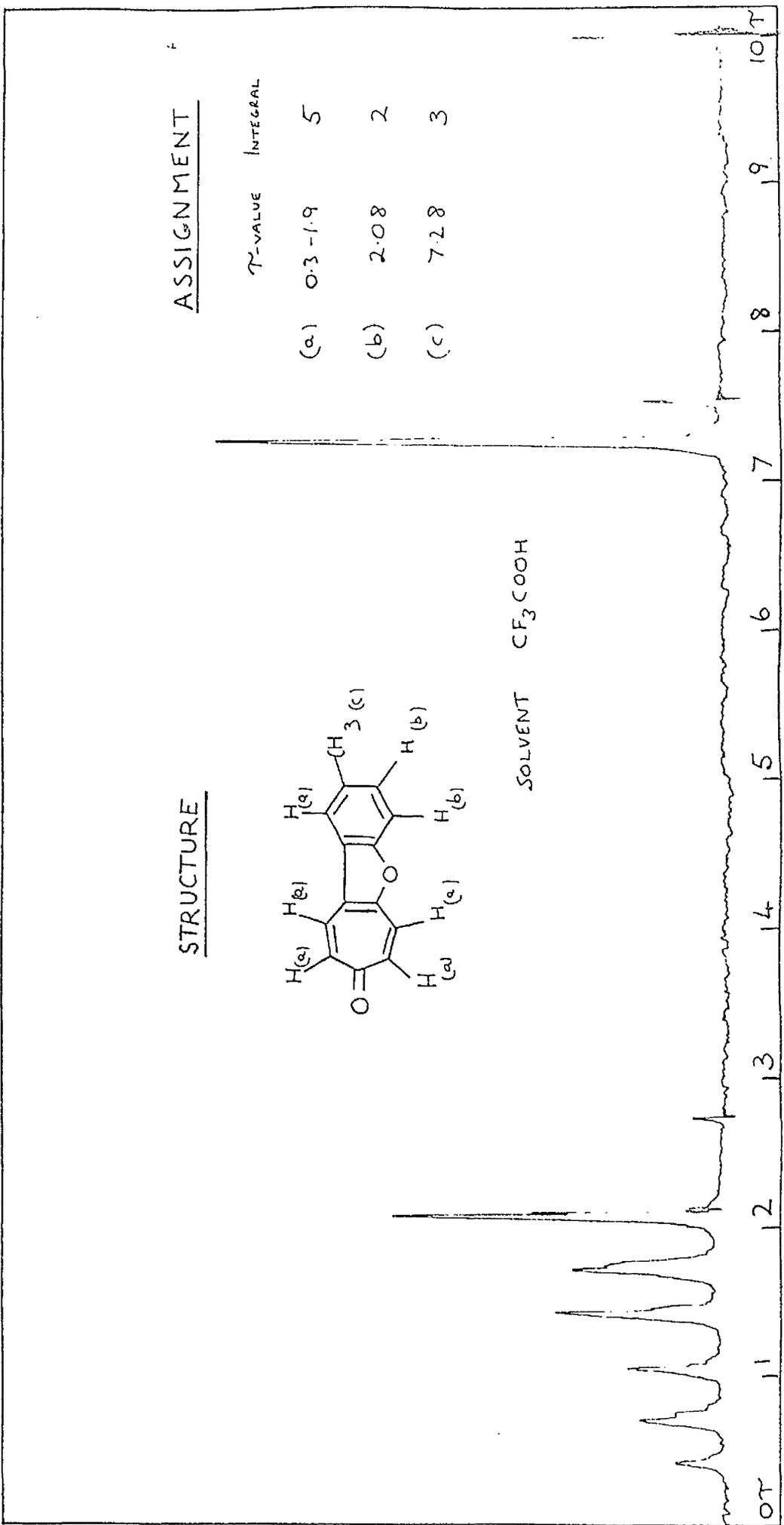
STRUCTURE



SOLVENT CF₃COOH

ASSIGNMENT

	τ -VALUE	INTEGRAL
(a)	0.3 - 1.9	5
(b)	2.08	2
(c)	7.28	3



B I B L I O G R A P H Y

1. Loschmidt, cited in Noller, 'Textbook of Organic Chemistry' Saunders, 1951.
2. Kekule, Bull. Soc. chim. France, 1865, 3, 98.
3. Kekule, Annalen, 1866, 137, 129.
4. Erlenmeyer, Annalen, 1866, 137, 327.
5. Wittig, 'Stereochemie', ONTI, 1934.
6. Armit and Robinson, J. Chem. Soc., 1919, 437.
7. Huckel, Z. Physik, 1931, 70, 204.
8. Huckel, 'Grundzuge der Theorie Ungesattigter und Aromatischer Verbindungen' m Verlag, Chemie, Berlin, 1938.
10. Thiele, Ber., 1900, 33, 666.
11. Thiele, Annalen, 1901, 319, 226.
12. Doering and Knox, J. Amer. Chem. Soc., 1954, 76, 167.
13. Breslow, J. Amer. Chem. Soc., 1957, 79, 5318.
14. Katz and Garratt, J. Amer. Chem. Soc., 1963, 85, 2852.
15. Vol'pin, Russ. Chem. Rev., 1960, 29, 129.
16. Elvidge and Jackman, J. Chem. Soc., 1961, 859.
17. Hafner, Angew. Chem. Internat. Edit., 1964, 3, 165.
18. Lloyd, 'Alicyclic Compounds', Edward Arnold, London, 1963.
19. Dewar, Nature, 1945, 155, 50.
20. Robertson, J. Chem. Soc., 1951, 1222.
21. Kimura, Sasaki, Kimura and Kubo, J. Chem. Phys., 1957, 727, 320.

22. Giacomo and Smyth, J. Amer. Chem. Soc., 1952, 74, 4411.
23. Kurita, Sato, Nozoe, and Kubo, Bull. Chem. Soc., Japan, 1953, 26, 272.
24. Gunthard and Gaumann, Helv. Chim. Acta, 1951, 34, 39.
25. Buchanan and Lockhart, J. Chem. Soc., 1959, 3586.
26. Nozoe, Mukai, and Takase, Sci. Reports Tohoku Univ., 1956, 39, 164.
27. Pauson, Chem. Rev., 1955, 55, 9.
28. Nozoe, in Ginsburg ed., 'Non-benzenoid Aromatic Compounds' 1959, p.339.
29. Merling, Ber., 1891, 24, 3108.
30. Dewar and Pettit, Chem. and Ind., 1955, 199.
31. Dewar and Pettit, J. Chem. Soc., 1956, 2021.
32. Ganellin and Pettit, J. Amer. Chem. Soc., 1957, 79, 1767.
33. Kursanov and Vol'pin, Doklady Akad. Nauk. S.S.S.R., 1957, 113, 339.
34. Dauben, Gedecki, Harmon and Pearson, J. Amer. Chem. Soc., 1957, 79, 4557.
35. Dauben, Honnen and Harmon, J. Org. Chem., 1960, 25, 1442.
36. Nozoe, in Cook and Carruthers Eds., Progr. Org. Chem., 1961, 5, 132.
37. Doering and Krauch, Angew. Chem., 1956, 68, 661.
38. Vol'pin, Akhrem and Kursanov, Izvest. Akad. Nauk, S.S.S.R., Otdel Khim. Nauk, 1957, 760.

39. Idem, ibid., 1957, 1501.
40. Idem, Zhur. Obshchei Khim., 1959, 29, 2855
41. Jordan and Elliot, J. Org. Chem., 1962, 27, 1445.
42. Nozoe, Ito and Tezuka, Chem. and Ind., 1960, 1088.
43. Nozoe, Tezuka and Mukai, Bull. Chem. Soc., Japan, 1963, 36, 1470.
44. Vol'pin, Akhrem and Kursanov, Doklady Akad. Nauk S.S.S.R., 1958, 120, 531.
45. Vol'pin et al., Doklady Akad. Nauk, S.S.S.R., 1958, 120, 531.
46. Doering and Knox, J. Amer. Chem. Soc., 1957, 79, 352.
47. Vol'pin, Akhrem and Kursanov, Khim. Nauka i Prom., 1957, 2, 656.
48. Idem, Zhur. obshchei Khim., 1958, 28, 330.
49. Parnes, Vol'pin and Kursanov, Tetrahedron Letters, 1960, 21, 20.
50. Ikemi, Nozoe and Sugirjama, Chem. and Ind., 1960, 932.
51. Ter. Bogg, Van Helden, Rickel, Renold, and Dreiding, Helv. Chim. Acta, 1960, 43, 457.
52. Doering and Knox, J. Amer. Chem. Soc., 1954, 76, 3202.
53. Nozoe and Kitahara, Chem. and Ind., 1962 1192.

54. Van Helden, Ter Borg and Bickel, Rec. Trav. chim.,
1962, 81, 599.
55. Jutz and Voithenleitner, Chem. Ber., 1964, 97, 29.
56. Pfau and Plattner, Helv. Chim. Acta, 1936, 19, 858.
57. Heilbronner, in Ginsburg ed., 'Non-benzenoid Aromatic
Compounds', 1959, p.171.
58. Dauben and Bartelli, J. Amer. Chem. Soc., 1961, 83, 4657.
59. Craig, J. Chem. Soc., 1951, 3175.
60. Hafner, et al., Angew. Chem. Internat. Edit., 1963, 2, 123.
61. Baker and McOmie, in Cook ed. Progr. Org. Chem., 1955, 3, 44.
62. Baker in Todd ed., '-Perspectives in Organic Chemistry',
New York and London, 1956, p.28.
63. Sidgwick, 'Chemical Elements and their Compounds', Oxford,
1950.
64. Fried, in Elderfield ed., 'Heterocyclic Compounds', Vol. 1
p.343.
65. Campbell, in Rodd ed., 'Chemistry of Carbon Compounds'
Vol. IV, p.809.
66. Apitzsch, Ber., 1904, 37, 1599; 1905, 38, 2888;
1908, 41, 4028.
67. Arndt and Bekir, Ber., 1930, 63B, 2393.
68. Bennett and Scorsch, J. Chem. Soc., 1927, 194.
69. Arndt, Schwarz, Martins and Aron, Rev. Fac. Sci. Istanbul,
1948, A13, 57.

70. Barkenbus, Midkiff and Newman, J. Org. Chem., 1951, 16,
232 and 1047.
71. Rollo, Senesi and Traverso, Ann. Chim. (Rome), 1952, 42,
507.
72. Horak and Cerny, Chem. Listy, 1952, 46, 1716.
73. Traverso, Chem. Ber., 1958, 91, 1224.
74. Horak, Zavada and Piskala, Chem. and Ind., 1958, 1113.
75. Bardone, Compt. rend., 1954, 238, 1716.
76. Mayer, Chem. Ber., 1957, 90, 2362.
77. Mayer, Chem. Tech (Berlin), 1958, 10, 418.
78. Lorenz-Oppan and Sternitzke, Z. Elektrochem., 1954, 40,
501.
79. Arndt, Martin and Partington, J. Chem. Soc., 1935, 602.
80. Rollo, Senesi and Traverso, Ann. Chim. (Rome), 1952, 42,
673.
81. Tarbell and Hoffman, J. Amer. Chem. Soc., 1954, 76, 2451.
82. Franzosini, Traverso and Senesi, Ann. Chim. (Rome), 1956,
46, 582.
83. Rollo and Franzosini, Ann. Chim. (Rome), 1956, 46, 582.
84. Gillam and Stern, 'Electronic Absorption Spectroscopy',
London, 1958.
85. Zahradnik and Koutecky, Tetrahedron Letters, 1961, 18,
632.

86. Willstatter and Pummerer, Ber., 1904, 37, 3745;
1905, 38, 1461.
87. Cornubert and Robinet, Bull. Soc. chim. France, 1933, 565,
1950, 36.
88. Parisi, Bovina and Quilico, Gazzetta, 1960, 90, 903.
89. Jones and Mann, J. Amer. Chem. Soc., 1953, 75, 4048.
90. Ainsworth and Jones, J. Amer. Chem. Soc., 1954, 76, 3172.
91. Dal Monte, Mangini and Passerini, Gazzetta, 1956, 86, 797.
92. Pullman et al., Bull. Soc. chim. France, 1952, 19, 73.
93. Prinzbach, Angew. Chem., 1961, 73, 169.
94. Prinzbach and Rossway, Tetrahedron Letters, 1963, 19
1217.
95. Kohnke, Ellegast and Bertram, Annalen, 1956, 600, 176.
96. Boyd and Jaekman, J. Chem. Soc., 1963, 458 and references
therein.
97. Schonberg and Sidky, J. Amer. Chem. Soc., 1959, 81, 2259.
98. Lloyd and Wasson, Chem. and Ind., 1963, 38, 1559.
99. Boyd, Proc. Chem. Soc., 1959, 93.
100. Kobrich, Annalen, 1961, 648, 114.
101. Boyd, Proc. Chem. Soc., 1960, 253.
102. Feist and Baum, Ber., 1905, 38, 3562.
103. Parkany1 and Zahradnik, Coll. Czech. Chem. Comm., 1962,
27, 1355.
104. Hubel and Weiss, Chem. and Ind., 1959, 703.

105. Fischer and Ofele, Chem. Ber., 1958, 91, 2395.
106. Yates and Jorgensen, J. Amer. Chem. Soc., 1958, 80, 6150.
107. Yates and Still, J. Amer. Chem. Soc., 1963, 85, 1208.
108. Bhacca, Johnson and Shoolery, 'N.M.R. Spectra Catalog',
Varian Associates, Vol. 1., 1962.
109. Ziegler, Annalen, 1954, 589, 157.
110. Ziegler and Wilms, Annalen, 1950, 567, 39.
111. Noyes and Kyriakides, J. Amer. Chem. Soc., 1910, 32, 1057.
112. Meincke, Cox and McElwain, J. Amer. Chem. Soc., 1935, 57,
1134.
113. Cops et al., J. Amer. Chem. Soc., 1948, 70, 2305.
114. Idem, ibid., 1950, 72, 2510.
115. Reppe, Schlichting, Klager and Topol, Annalen, 1948, 560, 1.
116. Ruzicka and Boerkenoogan, Helv. Chim. Acta, 1931, 14, 1319.
117. Darzens, Compt. rend., 1910, 150, 707; 151, 758.
118. Jones, Taylor and Rudd, J. Chem. Soc., 1961, 1342.
119. Oddo and Albanese, Gazzetta, 1927, 57, 827.
120. Royals and Hendry, J. Org. Chem., 1950, 15, 1147.
121. Thomas, 'Anhydrous Aluminium Chloride in Organic Chemistry',
Reinhold, 1947.
122. Wakeman, 'The Chemistry of Commercial Plastics', Reinhold,
1947.
123. Sieber, Progr. Stereochem., 1962, 3, 202.

124. Cope, Moon and Peterson, J. Amer. Chem. Soc., 1959, 81, 1650.
125. Cope and Peterson, ibid., 1959, 81, 1643.
126. Finzi and Bellavita, Gazzetta, 1932, 62, 699.
127. Degani and Fochi, Boll. sci. Fac. Chim. ind. Bologna, 1962, 20, 139; Chem. Abs., 1963, 59, 3829.
128. Klemenc, Monatsh., 1912, 33, 701.
129. Dat-Kuang et al., Bull. Soc. Chim. France, 1961, 1136.
130. Nakazawa, J. Pharm. Soc. Japan, 1954, 74, 836.
131. Sato and Mikawa, Bull. Chem. Soc. Japan, 1960, 33, 1736.
132. Yanovskaya et al., Zhur. obshchei Khim., 1952, 22, 1594.
133. Robertson, J. Chem. Soc., 1908, 23, 788.
134. Entel et al., J. Amer. Chem. Soc., 1951, 73, 4152.
135. Rosenwald, J. Amer. Chem. Soc., 1952, 74, 4602.
136. Goety, Heilbronner, Katritzky and Jones, Helv. Chim. Acta, 1961, 44, 387.