Kinetic and Mechanistic Studies on Compounds with Strained Rings

by

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Acknowledgements.

I should like to thank my supervisor, Professor B. Capon, for his help and guidance and the staff and students of the Department of Organic Chemistry for putting up with a "Geordie Sassenach" in their department. Also, I should like to thank the University of Glasgow for financing these studies and Mrs. N. Watson for the expert typing of this thesis despite being one of the fortunate members of society who have little to do with Chemistry. Last but not least, I should like to thank my mother without whom this thesis would not have been possible.

CONTENTS

SUMMARY

A theory explaining the stabilisation of carbonium ion intermediates, termed "vertical stabilisation", has been put forward by T.G. Traylor and co-workers. Vertical stabilisation has been defined as that stabilisation in $Y\text{-}CH_2^+$ or $Y\text{-}CH_2^\bullet$ which is afforded while the internal geometry of Y and the Y-C bond length remain essentially as they were in the reactant. Traylor suggests that vertical stabilisation is a form of σ-π conjugation (hyperconjugation) and that it may be determined whether a group acts to stabilise a positive charge by internal nucleophilic displacement or by σ-π conjugation by studying the effect of that group in a vertical process. The reaction studied by Traylor was the charge transfer between substituted benzenes and a standard acceptor, tetracyanoethylene (T.C.N.E.). A relationship has been shown by various workers to exist between ionisation potentials and reactivity, i.e. σ^+, in another vertical process, gas-phase removal of an electron. Traylor believes that as the absorption frequencies of the charge transfer complexes are directly related to ionisation potentials then a relationship should be apparent between charge transfer frequency and σ^+. Evidence is given by Traylor for a linear correlation between absorption frequency and reactivity and it is postulated that a method of directly estimating the σ^+ constant for a particular substituent is possible by determining the charge transfer absorption frequency for the respective substituted benzene - T.C.N.E. complex.

In particular, Traylor has suggested that strained cyclic substituents should exhibit vertical stabilisation in

reactions involving carbonium ion formation. Traylor has attempted to demonstrate this theory of stabilisation by comparing the rates of solvolysis of various cyclic substituted carbinyl derivatives relative to the neopentyl derivative with the charge transfer frequencies of their respective substituted benzene - T.C.N.E. complexes. A plot of log relative rate of solvolysis against charge transfer frequency obtained by Traylor is shown. Using this plot Traylor has predicted the rate of solvolysis of the 1-norcaryl-and homocubyl-carbinyl systems.

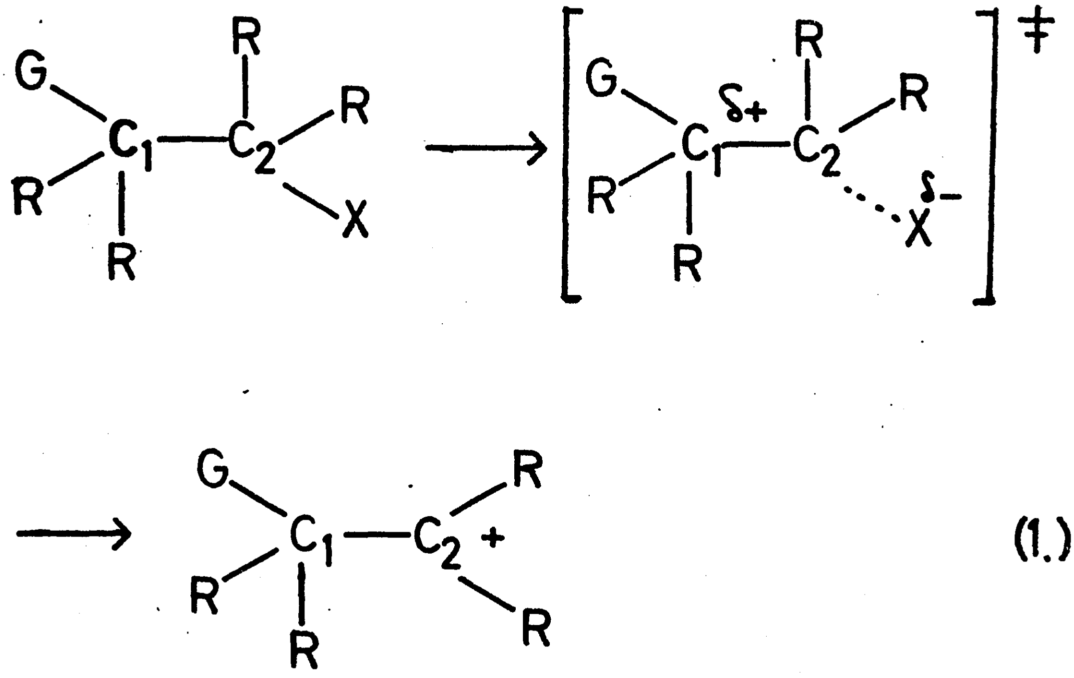
The scope of the present work has been to test this theory by determining the kinetics of electrophilic aromatic substitution of these cyclic substituted benzenes to see if, in fact, the rates predicted by Traylor are correct. Also, the homocubyl carbinyl compound was synthesised and the kinetics of solvolysis of the 3,5-dinitrobenzoate derivative in aqueous acetone were determined. Finally, the charge transfer absorption spectra of the cyclic substituted benzenes were recorded to see how accurately the absorption frequency could be determined for a particular substituent and to corroborate Traylor's results.

The results obtained in this work suggest that Traylor's hypothesis of a method of estimating reaction rates by measuring the absorption maxima of the charge transfer complexes with T.C.N.E. needs to be taken with a great deal of reservation for several reasons. Firstly the inability to estimate accurately enough the exact position of the charge transfer absorption maxima. Secondly, the fact that the results of the electrophilic aromatic substitution reaction studied in this work, i.e.

nitration, do not corroborate Traylor's theory. Finally, the rate of solvolysis of the homocubyl carbinyl system is much slower than that predicted by Traylor.

INTRODUCTION.

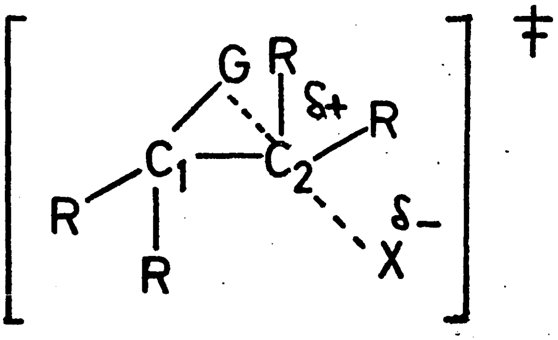
The stabilisation of carbonium ions by neighbouring group participation has aroused considerable interest over the years.(1,2). A large variation in the rate of reaction (1) may be achieved when the nature of group G is changed.



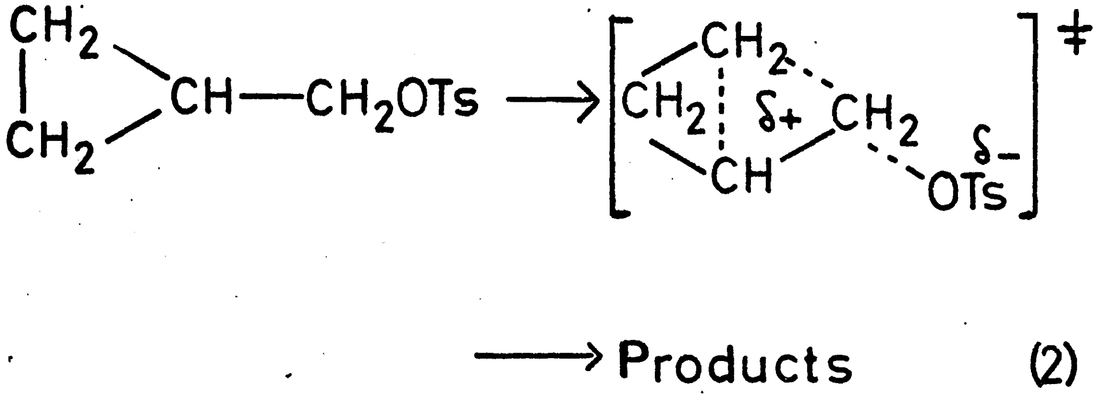
(1.)

When G is a known nucleophilic group containing lone pairs (e.g. $-O^-$, $-SR$, $-NR_2$, $-C(=O)O^-$, $-NHC(=O)R$, etc) then the mechanism is usually agreed to involve formation of a bridged-ion transition state (3). As the $C_2 - X$ bond ionises the nucleophilic group, -G, moves closer to C_2 and forms a partial σ bond with this carbon.

i.e.



However, when G is a strained ring, aryl, metal group, etc. then a variety of mechanisms have been put forward involving some or no nuclear movement of Group G. Examples of bridging-type mechanisms (internal nucleophilic displacement) which have been postulated are shown in the following solvolyses :



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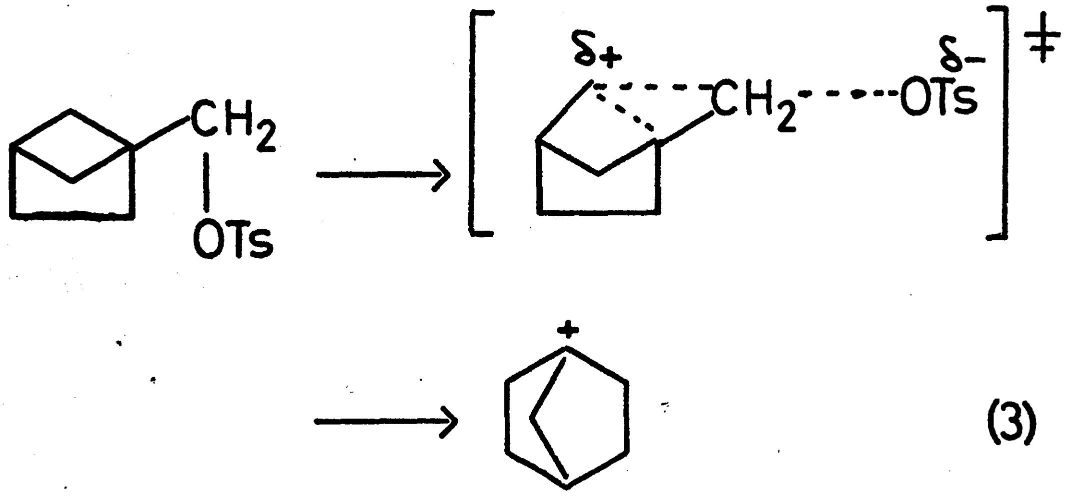
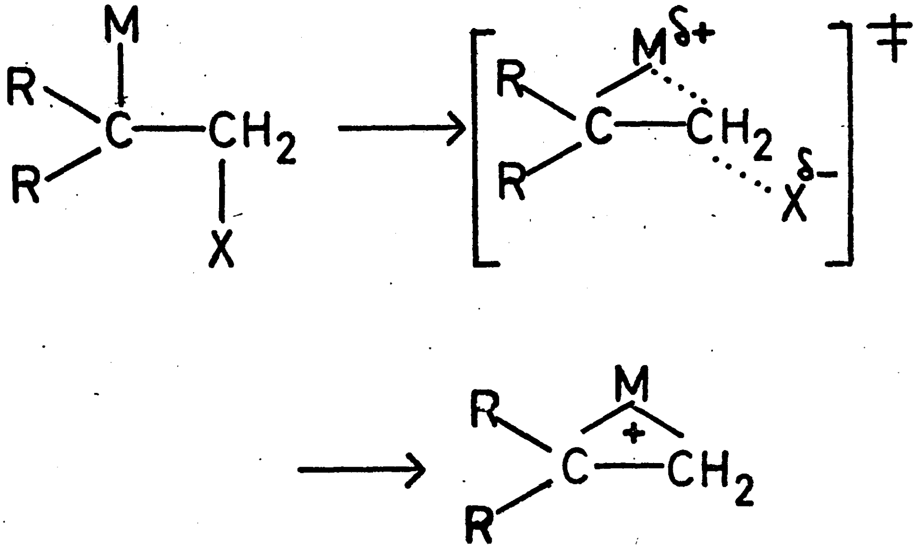


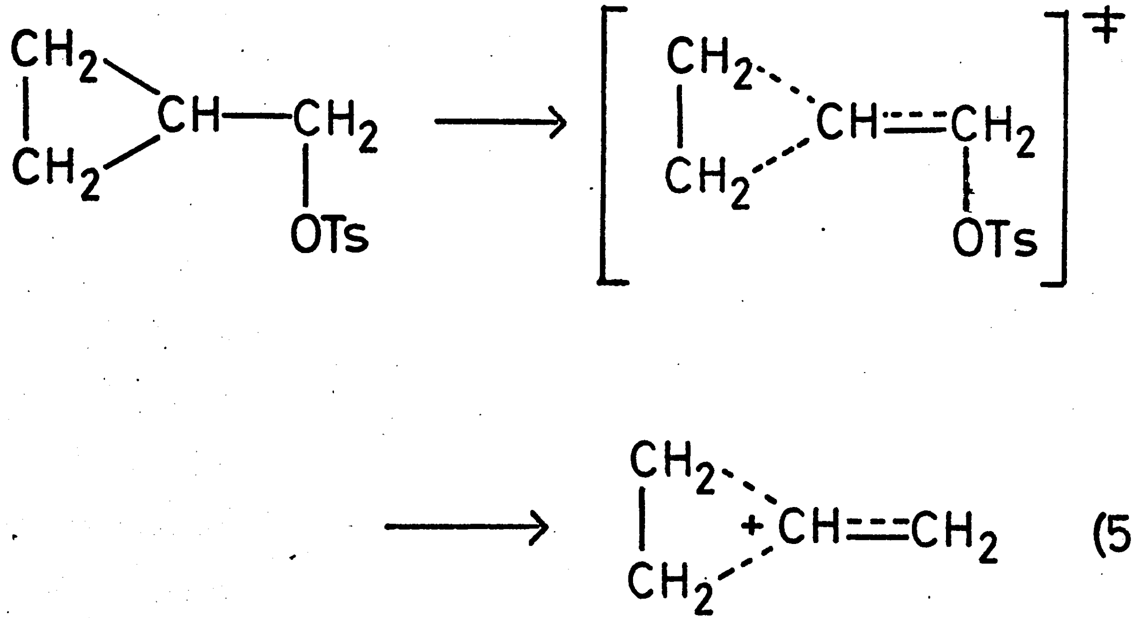
(3)



(4)

M=Metal

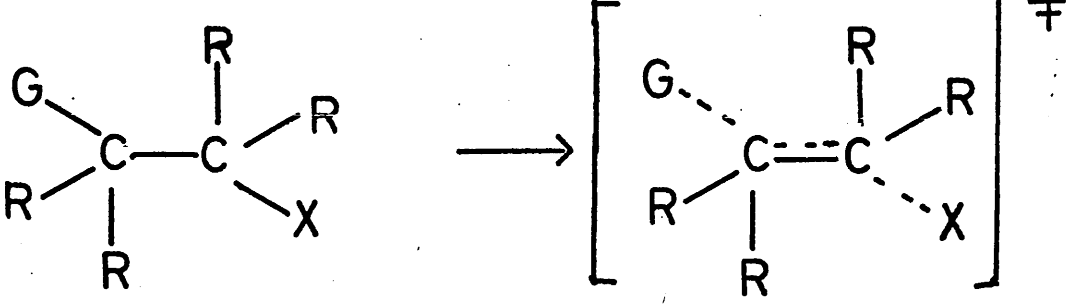
An alternative mechanism for reaction (2) involving no nuclear movement of the cyclopropyl ring is as follows :



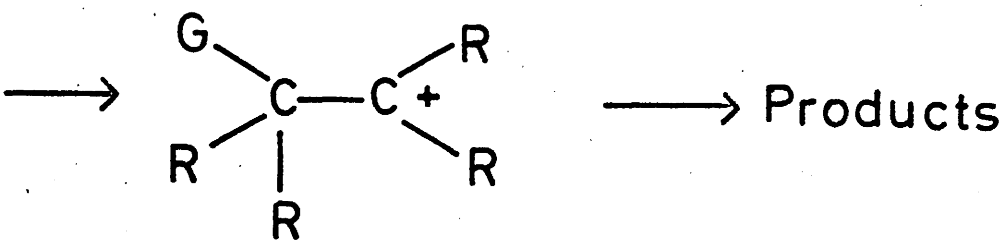
(5)

This involves delocalisation of carbon-carbon σ bonds, called σ-π conjugation (or hyperconjugation).

One of the strongest advocates of σ-π conjugation has been Traylor who, in a series of papers (9-12), has put forward a theory of stabilisation of carbonium ions, termed "vertical stabilisation". Vertical stabilisation has been defined by Traylor as "that stabilisation which the group R supplies to a cation, $R-\overset{+}{C}R_2$ or radical, $R\dot{C}R_2$, (or the corresponding transition states), without any nuclear movement within the Group R." This can be illustrated by the solvolysis of alkyl systems as shown:

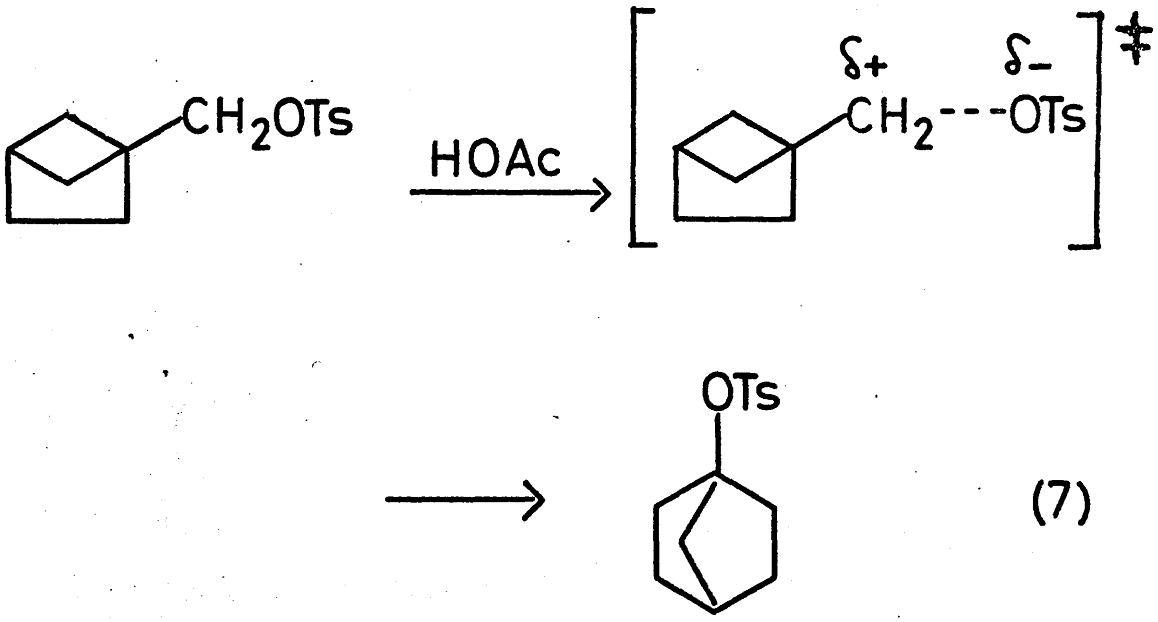


I



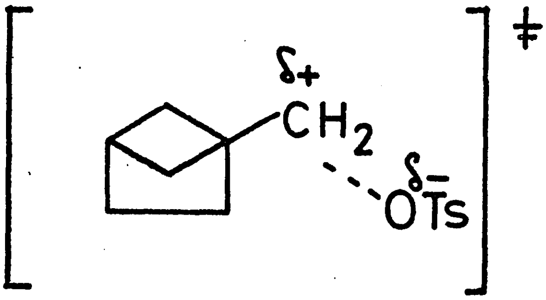
(6)

Such conjugation does not require either changes in the G-C bond length or any movement of the stabilising group G toward the positive centre. Hence, the structure of the transition state I may be differentiated from other postulated transition states i.e. for the solvolysis of 1-[2.1.1] bicyclohexyl methyl tosylate.



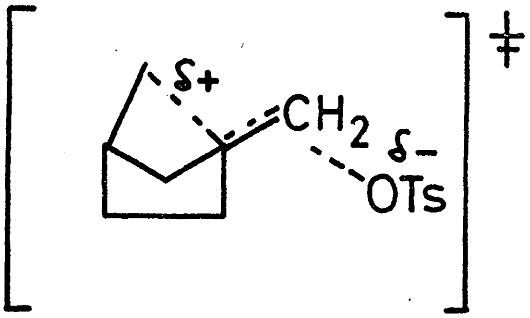
(7)

Four different transition states have been suggested :



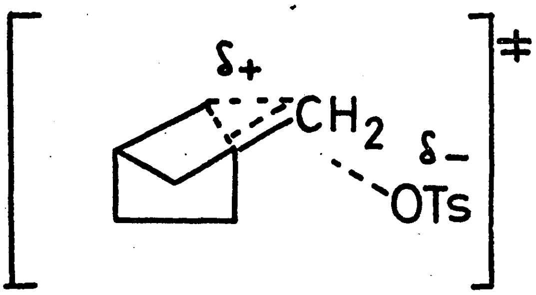
II

Classical Ionisation[13,14]



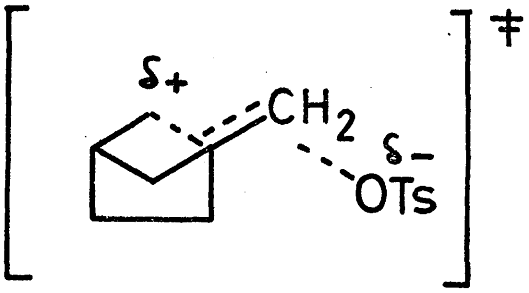
III

Fragmentation[15]



IV

Bridging[16]



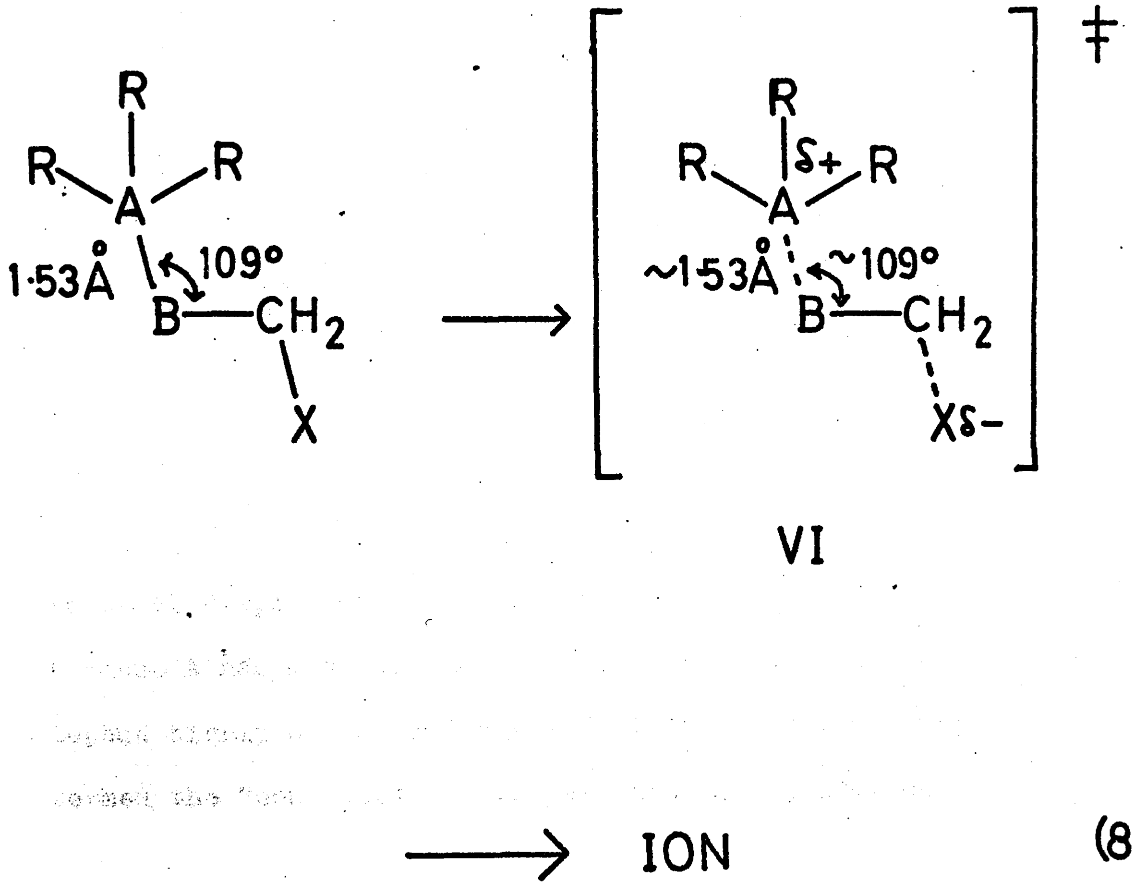
V

Vertical Delocalisation[9]

Structure II is different from structures III, IV and V in that there is no σ bond delocalisation. Also, structure V differs from III and IV because both III and IV require nuclear movement in the strained system and can be classified as "non-vertical stabilisation". Traylor does not suggest that cations cannot be bridged but that because most of the stabilisation energy may be provided without nuclear movement, very little is gained by moving atoms. For example, structure IV and V are not resonance forms since the geometry changes. It is argued that the energies of IV and V differ very little and that the actual geometry looks more like V than IV at the transition state.

Definition of a σ-π conjugation

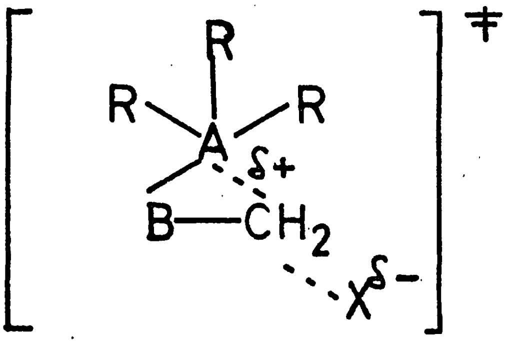
As has been stated above, simple σ-π conjugation has been interpreted as a vertical stabilisation in which the σ bond is delocalised without changing its bond length or angle. For example, the cation $R_3ABCH_2^+$ might be formed as shown below:



VI

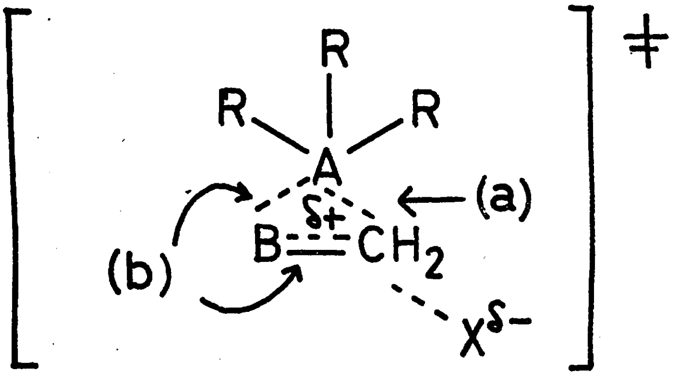
(8)

Formulation VI represents a limiting behaviour achieved only in vertical processes, and that, between this and the formulation VII which attributes all the driving force to internal



VII

displacement, there are various intermediate cases having contributions from both kinds of driving force. The formulation VIII implies contributions from both σ-π conjugation (b) and from

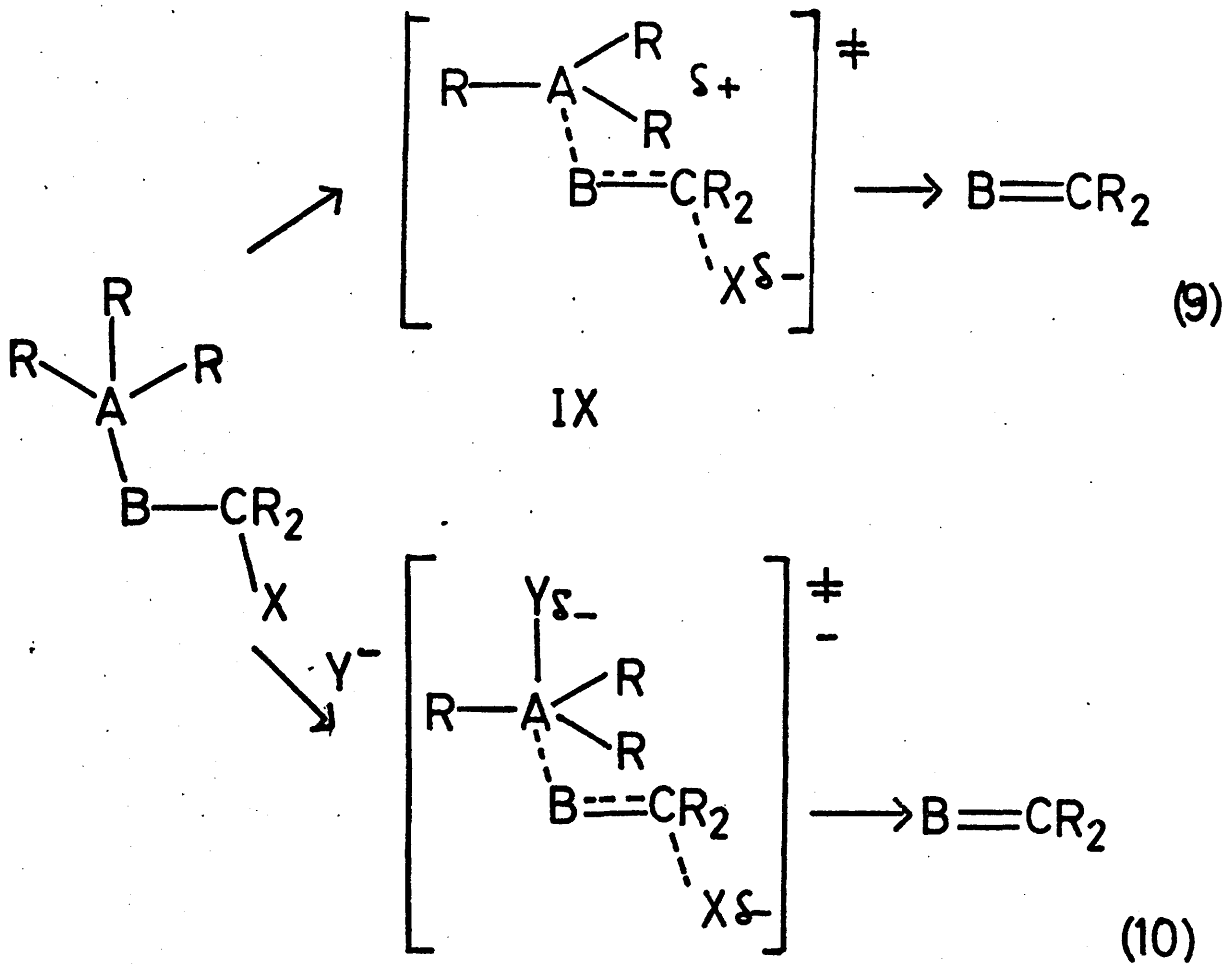


VIII

internal displacement (a) but this stabilisation is not vertical because A has moved. However, the (b) contribution need not depend highly on the ABC angle and, therefore, (b) may be loosely termed the "contribution from vertical stabilisation". This contribution would be expected to reveal itself in a vertical or Franck-Condon process as electronic excitation.

A second kind of non-vertical acceleration is fragmentation (or other eliminations) in which the AB bond lengthens and considerable rehybridisation occurs at A.

Fragmentation



(9)

IX

(10)

X

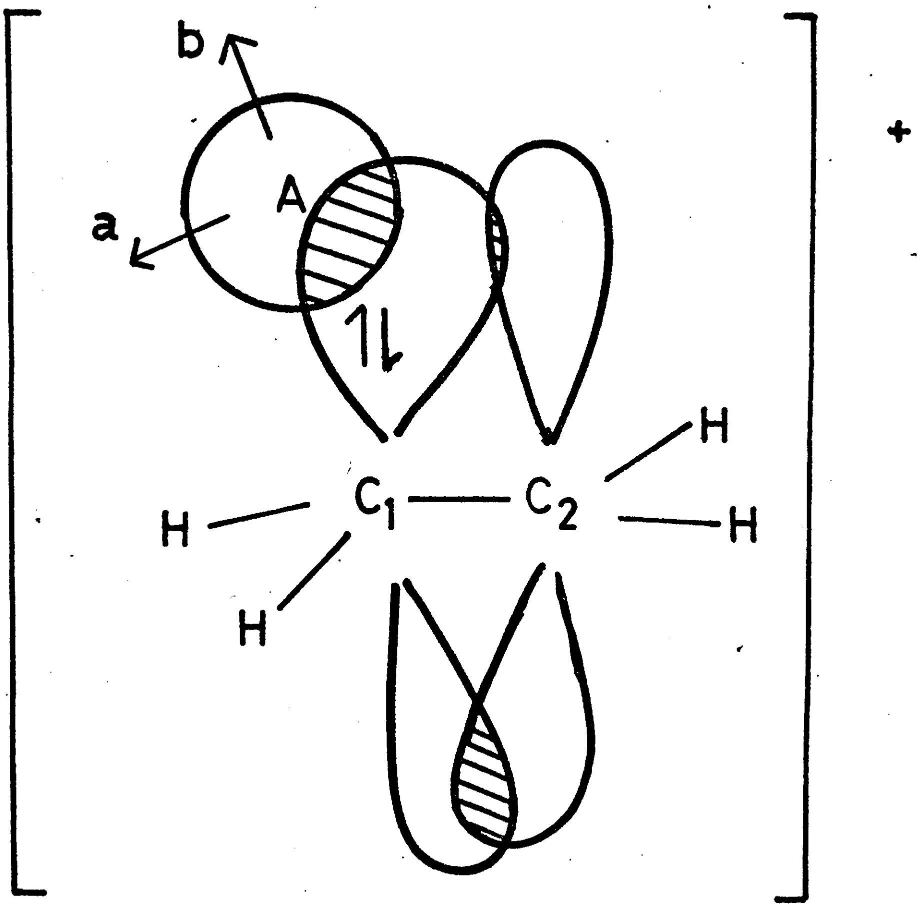
E2 Elimination

These processes, like internal displacement, should not correlate with any actual vertical processes.

Traylor suggests that if a test is developed which demonstrates that all the stabilisation of a transition state which could be VI, VII, VIII, IX or X is available in a Franck-Condon process then that stabilisation is "limiting vertical" as in VI. If such vertical stabilisation is undetectable then the stabilisation is "limiting non-vertical" as in VII, IX or X.

Factors which influence σ-π conjugation.

It has been proposed by Traylor that since the stabilisation provided to the transition state VI accrues from delocalising the AB σ bond and from formation of a B = CH_2 π bond then this conjugation should be enhanced by any structural change which makes the AB σ bond more delocalisable (polarisable) or increases the strength of the B = CH_2 π bond. The possible σ-π conjugation effects may be visualised in the atomic orbital diagram for A CH_2 CH_2^+ shown below:

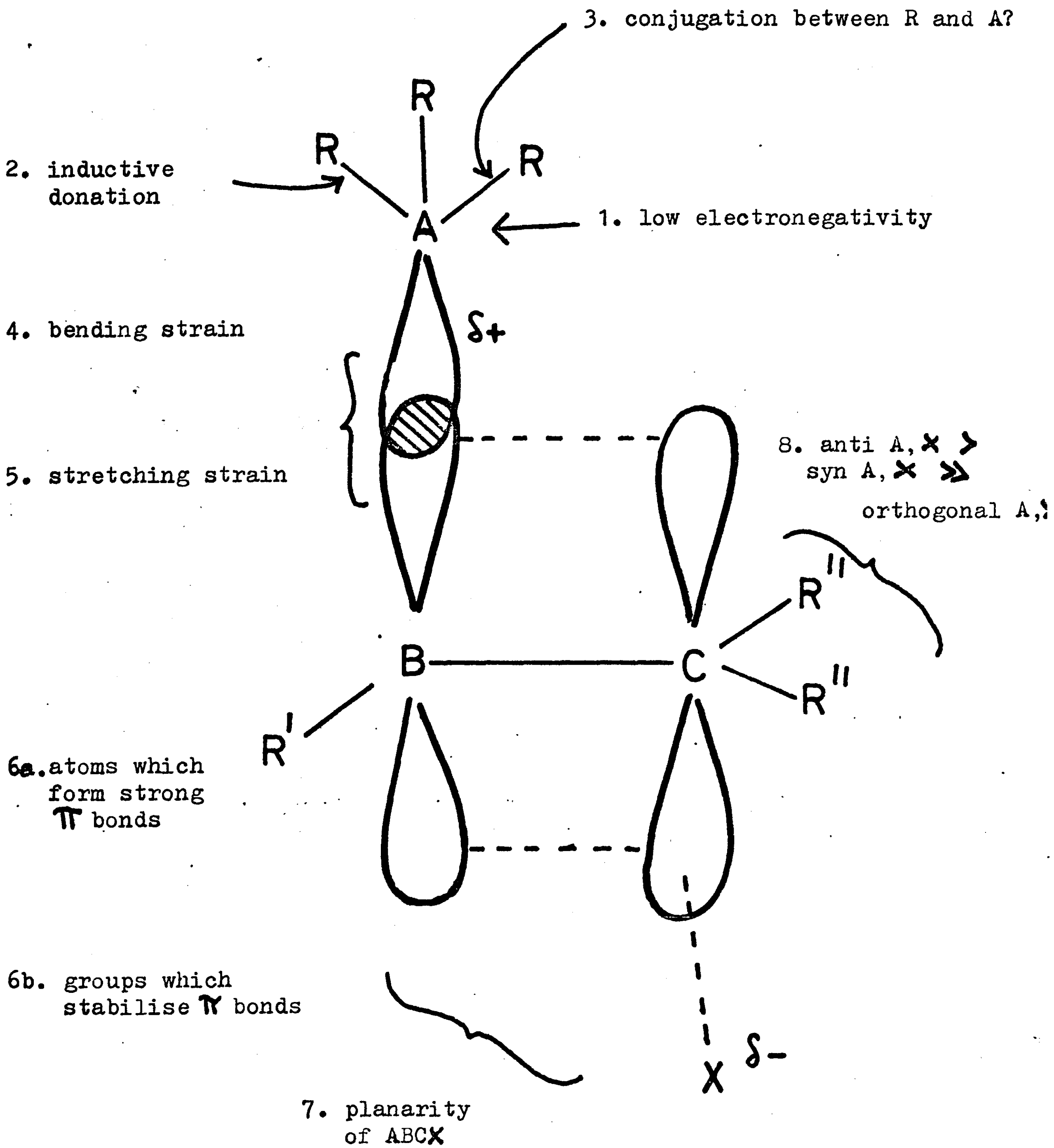


XI

The sp^3 hybrid orbital on C_1 may overlap with the p orbital on C_2 but the extent of this interaction will depend upon the position and the electronegativity of A. The σ orbital will overlap less with A and more with C_2 if A is, by some geometrical restraint, forced away from a normal equilibrium position. Either bending (direction a) or stretching (direction b) the AC_1 bond should have this effect. On the other hand, lowering the electronegativity of A decreases the probability that the electrons ($\uparrow\downarrow$) will be near A and results in better C_1C_2 π bonding. Alteration of C_1 or C_2 to atoms having different inherent π overlap should also alter the extent of σ-π conjugation, everything else remaining constant.

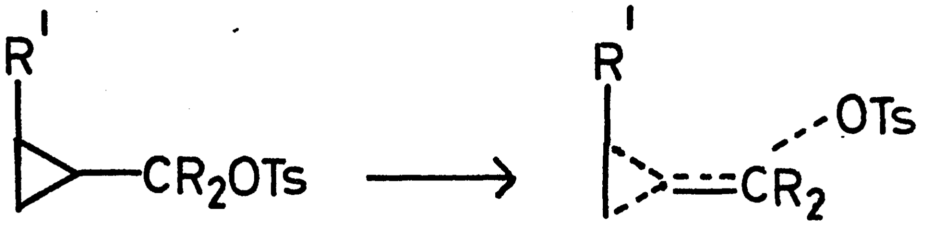
Traylor has illustrated these effects in Chart I for the solvolysis of $R_3AB(R')C(R'')_2X$:

CHART I



(1) The polarisation of the $A^+ - B^-$ bond is brought on by having the electronegativity of A lower than that of B. An example given by Traylor is that the Pb-C bond is much more polar than the H-C bond and thus more delocalisable. Correspondingly, the ionisation potential of $(C_6H_5)_3$ Pb CH_2 C_6H_5 is lower than that of H $CH_2C_6H_5$ by about 1eV.

(2) Donation to A by the groups R would lower the electronegativity of A and increase the polarity of the A-B bond (if B is C, N or O). For example, the rates of solvolysis of the cyclopropyl carbinyl compounds below increase as $R^1 = CH_3$. (17)



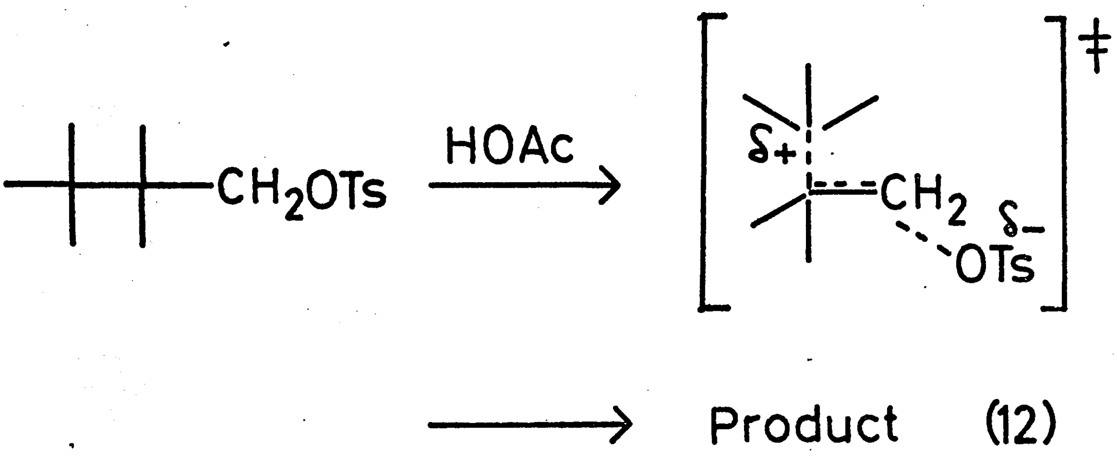
(11)

(3) Traylor considers that though there is still argument concerning cross-conjugation in cyclopropyl groups, cross-conjugation through σ bonds has been shown to be absent in other systems. (18) A possible reason, which he puts forward, is the requirement of a rehybridisation of the R_3A system to achieve good R_3A^+ delocalisation (19), such rehybridisation being a non-vertical process.

(4) As mentioned earlier, bending of the A-B bond should give less overlap of the A-B σ bond and greater π overlap between atoms B and C. Examples of systems constrained in this way would be strained rings such as cyclopropyl (eq.11). Evidence given by

Traylor for vertical stabilisation in strained ring systems is recorded further on.

(5) An example given by Traylor to illustrate the importance of stretching strain is that the central bond length in hexamethyl ethane is 1.578°A compared to 1.57°A for the 1,7 bond and 1.55°A for the 1,2 bond in norbornane. Thus, he states that the central bond in hexamethylethane should be delocalisable and may account for the accelerated solvolysis shown in equation (12).



(12)

He also states that strained rings delocalise readily and should provide considerable stability to cations without changing their geometry.

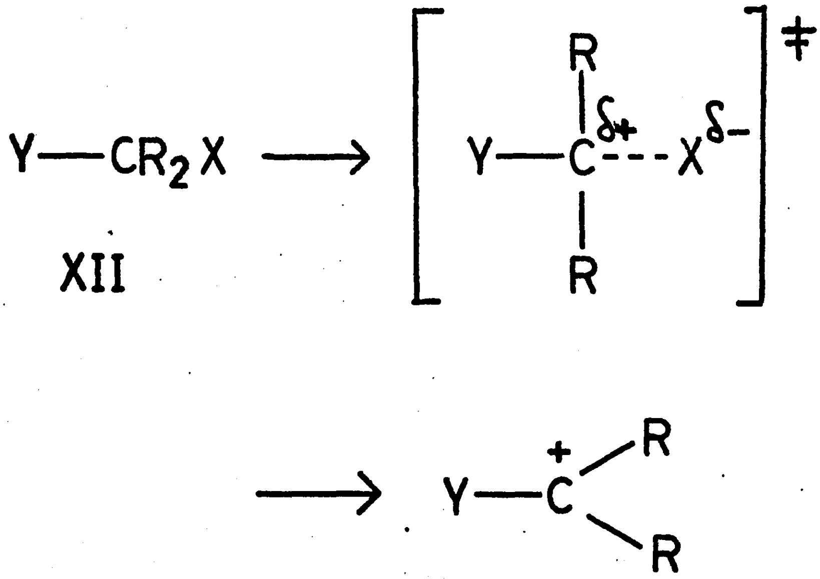
(6) Atoms B and C should form good π bonds as delocalisation depends upon good overlap between the A-B σ bond and the p orbital on C of $\overset{''}{CR_2}$. Therefore, for maximum σ-π conjugation, B should be C, N or O.

(7) A coplanar arrangement of ABCX is preferred as for all concerted processes involving the formation or breaking of two adjacent bonds e.g. Diels-Alder reaction, hydroboration, xanthate

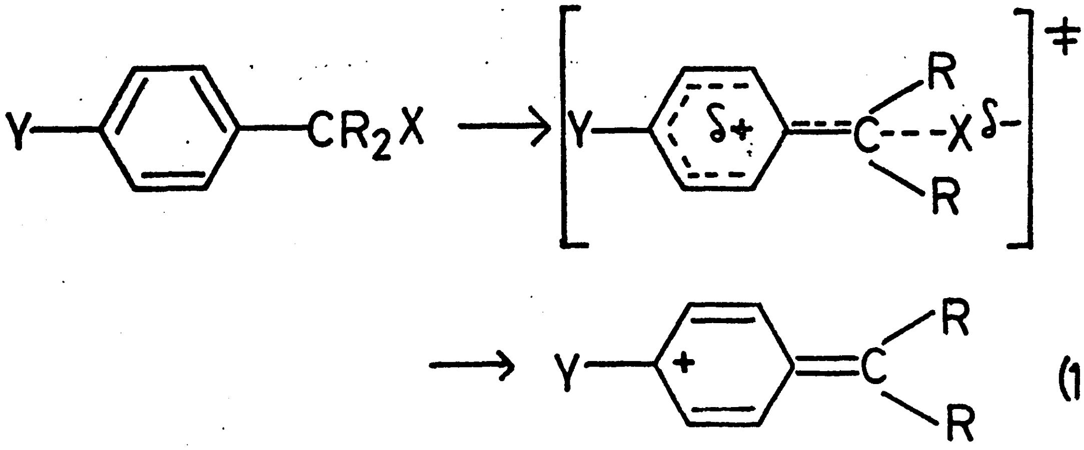
pyrolysis, etc. Any other arrangement would reduce the B-C π overlap.

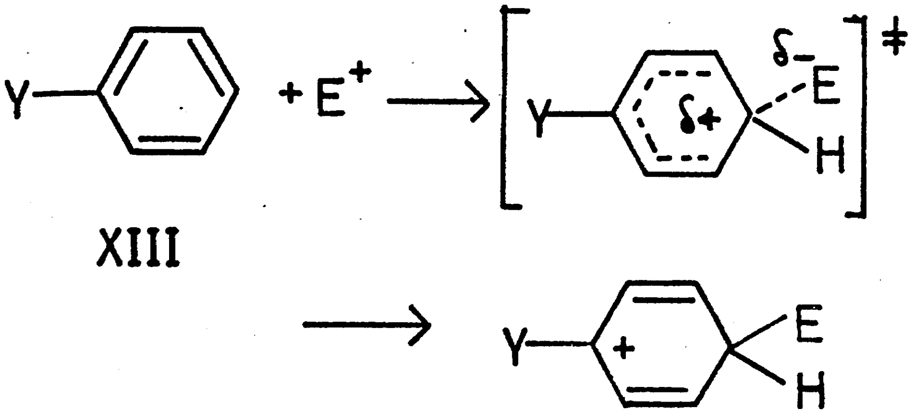
(8) Also, ionic processes such as electrophilic addition, elimination, etc. proceed much faster when the two leaving or entering groups are anti than when they are syn. It is suggested that σ-π conjugation would have the same preferred geometry.

Traylor has proposed that one method of deciding whether a group acts to stabilise a positive charge by internal nucleophilic displacement (bridging, etc) or by σ-π conjugation is to study the effect of that group in a vertical (Franck-Condon) process. Such processes would occur too rapidly to allow nuclear movements. Thus, the energy of a vertical process could not be lowered by internal displacement but could be by conjugation. He has been concerned with the following types of reaction:-


XII

(13)

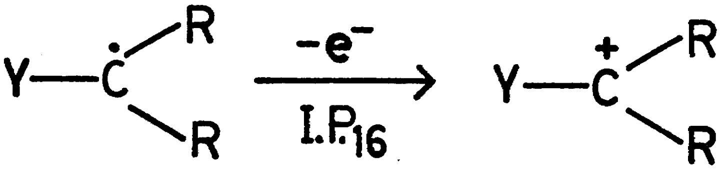

(14)



XIII

(15)

One vertical process related to the carbonium ion forming reactions shown above is the gas-phase removal of an electron. Many of the groups Y which accelerate the solvolysis of XII also lower the ionisation potentials of the related free radicals and olefins.



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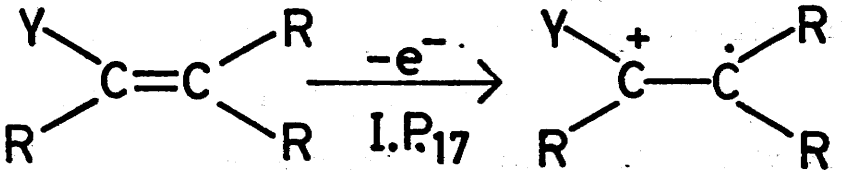
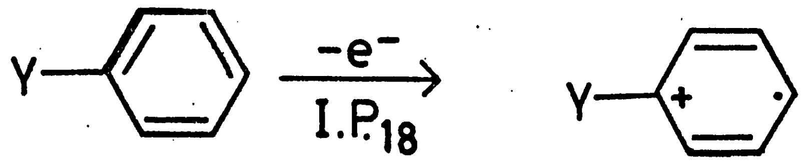


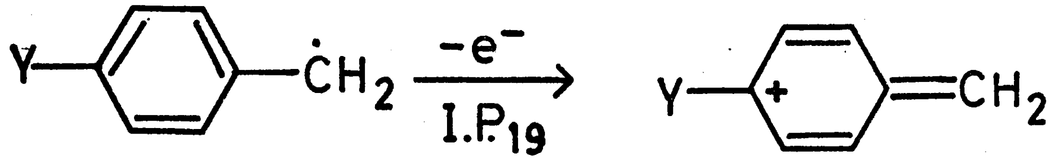
(17)

XIV

Similarly Y groups which accelerate the rates of reactions (14) and (15) also lower the ionisation potential.



(18)



(19)

The ionisation potentials from (17), (18) and (19) correlate with σ^{+} (calculated using the rates of reaction (14)).

i.e.

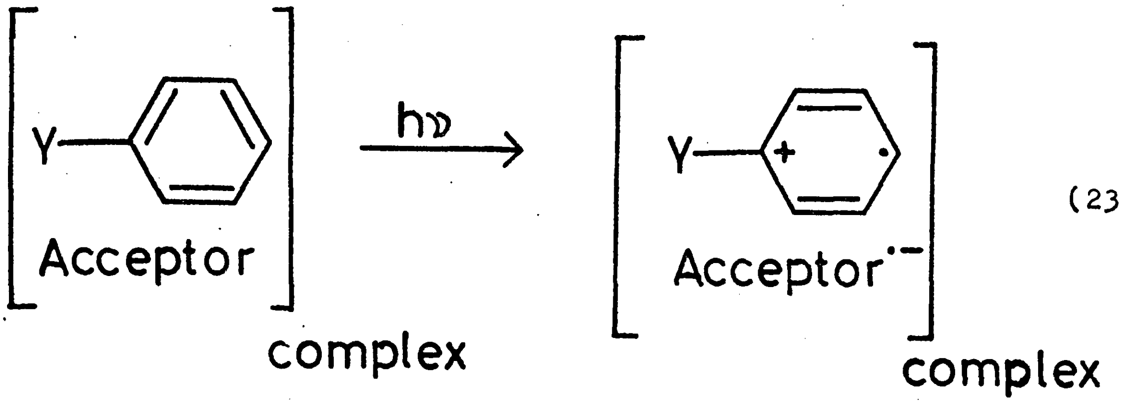
$I.P._{16} \cong -45\ \sigma^{+}$ + constant (20) (22)

$I.P._{18} = -17.4\ \sigma^{+}$ + constant (21) (23)

$I.P._{19} = -19\ \sigma^{+}$ + constant (22) (24)

Traylor suggests that these correlations can be used to distinguish stabilisation involving internal nucleophilic displacement from other types of stabilisation.

The vertical process studied by Traylor was the charge-transfer (25) between the donors XIII or XIV and two standard acceptors, tetracyanoethylene (T.C.N.E.) (26), (27) and dichloromaleic anhydride (D.C.M.A.). Some positive charge is placed on the carbon α to the Y substituent in the absorption process shown in equation (23).



(23)

Traylor believes that as the absorption frequencies of the charge-transfer complexes are known to be directly related to the ionisation potentials for the respective donors then a relationship between charge-transfer frequency and σ^{+} should be apparent.

Table I lists some of the charge-transfer frequencies of a variety of monosubstituted benzenes complexed with T.C.N.E. or with D.C.M.A. obtained by Traylor. (9)

TABLE I

Frequencies for Charge-Transfer Absorptions in Complexes of T.C.N.E. or D.C.M.A. with substituted benzenes.[a]

π base	λmax (mμ) (TCNE)	ν TCNE (cm^{-1})	ν DCMA (cm^{-1})
Ph-H	387	25,800	
Ph-t-Bu	415	24,100	
Ph-i-Pr	415	24,130	
Ph-Et	412	24,200	
Ph-Me	411	24,300	33,560
Ph-NHCOCH$_3$	480	20,800	
Ph OCH$_3$	507	19,700	28,600
Ph CH$_2$HgCH$_2$Ph	635	15,780	24,940
Ph CH$_2$SiMe$_3$	486	20,100	29,940
Ph NMe$_2$	520	19,200	21,230
7-Ph-norcarane	500	20,000	
Ph-cyclopropane	470	21,300	

a) Solvent CH_2Cl_2 ; temperature 25° C.

Plots of these charge-transfer frequencies with both acceptors against σ_p^+ for the groups Y, which stabilise positively charged carbon by inductive or resonance effects are shown in Figure I (9).

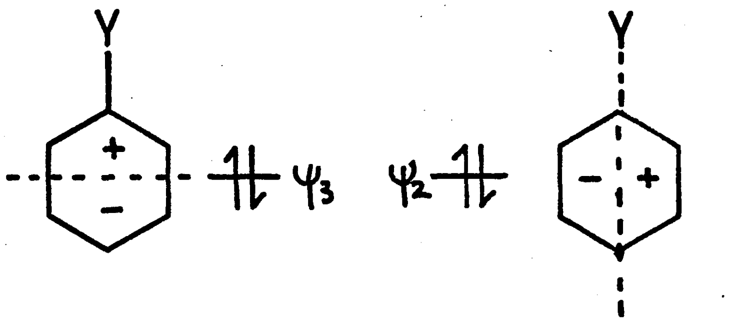
Using these plots Traylor obtained the following equations (9) for each line :

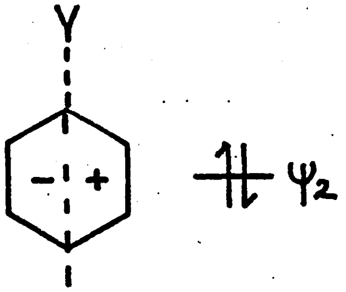
$$\nu_{T.C.N.E.} = (9{,}300\,\sigma^+ + 26{,}200) \pm 500\ \mathrm{cm}^{-1} \quad (24)$$

$$\nu_{D.C.M.A.} = (10{,}400\,\sigma^+ + 36{,}400) \pm 600\ \mathrm{cm}^{-1} \quad (25)$$

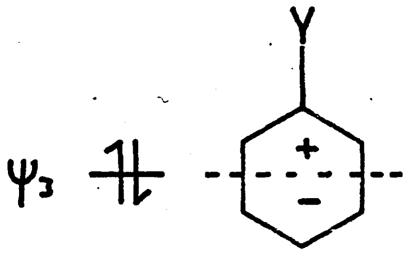
The following limitations have been placed by Traylor on these Hammett relationships. The validity of these plots depend on the assumption that the orbital from which the electron is removed by charge transfer has the same symmetry as the orbital which participates in para attack of reaction (15). This assumption fails in the following instances :-

(1) When Y is an electron-withdrawing substituent. This is illustrated by the energy levels of the highest filled orbitals of monosubstituted benzenes shown below :





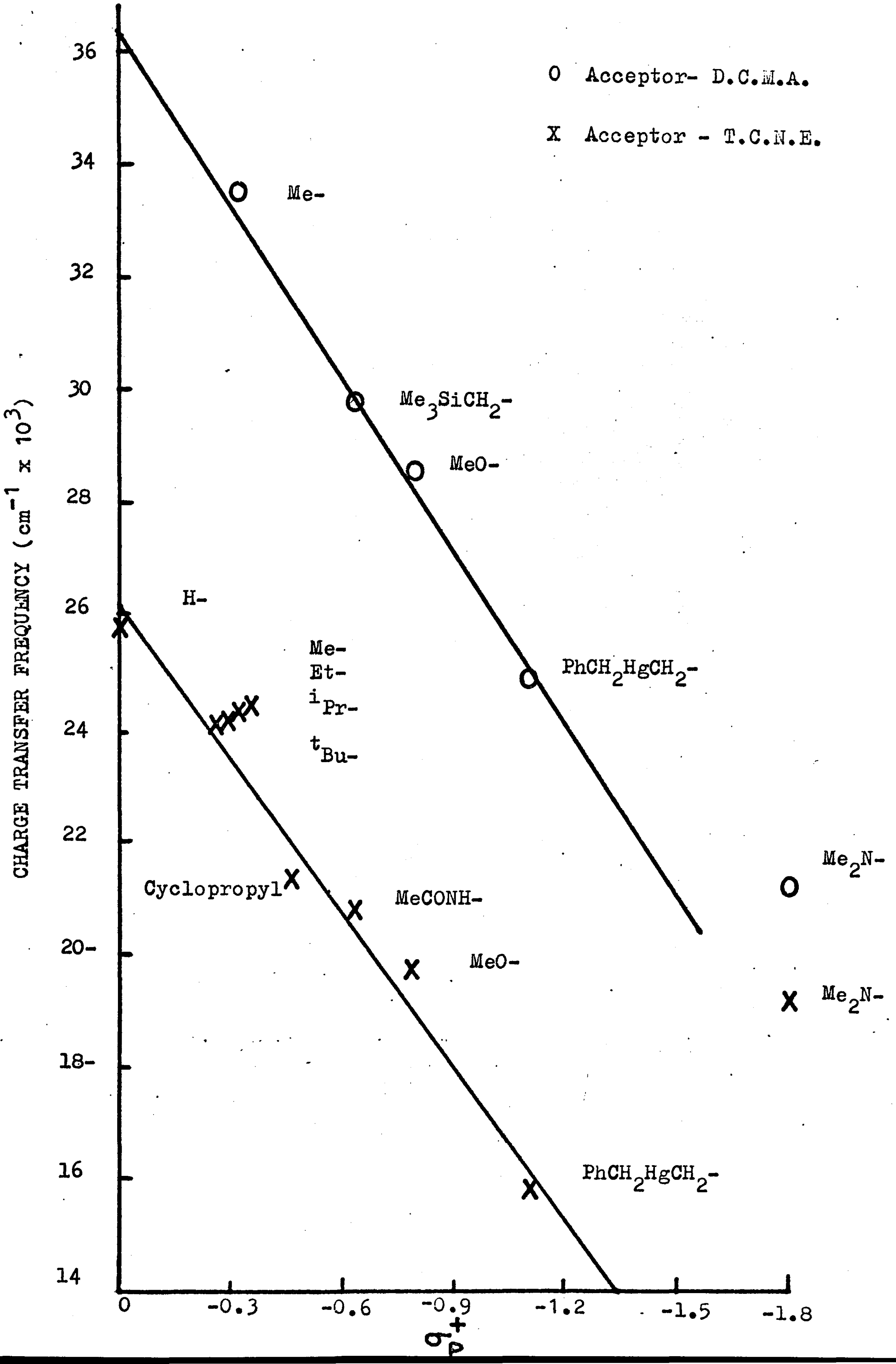
electron-donating Y



electron-withdrawing Y

FIGURE I

Plots of charge-transfer frequencies of Y C_6H_5 -Acceptor complexes against σ_p^+ of Y. Identity of Y is shown adjacent to each point.



Although para electrophilic attack always involves ψ_3 regardless of the nature of Y, the electron will be removed from ψ_3 by charge transfer only when Y is an electron-donating substituent.

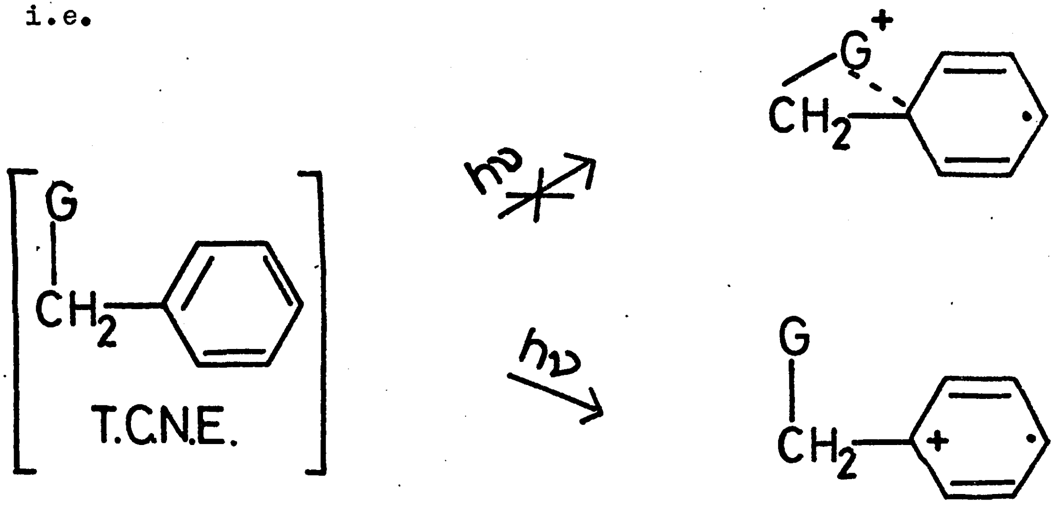
(2) When the ionisation potential of an aliphatic analogue R-Y is equal to or lower than that of benzene. The ionisation of Y-Ph is then likely to involve an electron from Y itself or from the Y-C σ bond. In either case the π electrons (i.e. ψ_2 and ψ_3) of the benzene ring may not be strongly involved in the ionisation.

Thus, the ionisation potentials or charge transfer frequencies may be treated by a Hammett equation when Y causes only a small perturbation on the benzene ring i.e. the substituents must not severely alter the symmetry of the π orbitals.

Traylor also mentions that, occasionally, charge transfer frequencies, although being easier to measure than ionisation potentials, are not accurate measures of the ionisation potentials. This arises when there is strong bonding between the donor and acceptor in the ground state.(25) The excitation process then removes an electron from this bond rather than from the "free" donor. This situation only occurs when the aromatic donors are alkyl anilines or other C_6H_5Y in which σ_Y^+ is more negative than -1.4. Therefore, only substituents having values of σ_Y^+ between 0 and -1.4 have been studied by Traylor.

Although a method of directly testing reactions to see whether a group Y actually does accelerate solvolysis by vertical stabilisation has not been devised, Traylor proposes that it can be determined whether a group is capable of vertical stabilisation by determining its effect on a known vertical process. If the group displays vertical stabilisation in one process then he infers that it probably displays the vertical stabilisation to a similar extent in another process which places positive charge in the same position. Substituents which accelerate solvolyses by resonance or inductive effects have large effects on vertical processes (charge transfer spectra; see Figure I) whereas neighbouring nucleophilic groups, which undergo internal displacement, do not display any of their stabilising influences on charge transfer spectra.

i.e.



(26)

The capability of Y in stabilising positively charged transition states is measured by the well-known linear free-energy (Hammett) relationships based on equations (13), (14) or (15). The Hammett relationships for charge-transfer spectra (equations (24) and (25)) are used to measure the capability of Y in stabilising the charge transfer excited states. Traylor suggests that if σ^+_Y obtained from reactions is the same as that obtained from charge transfer spectra, then internal nucleophilic displacement does not occur in the reactions.

Traylor has attempted to demonstrate his findings by comparing the relative rates of solvolysis of alkyl systems containing a variety of strained-ring substituents with the charge transfer spectra of the respective phenyl derivatives. Using the example of the solvolysis of 1- [2.1.1] bicyclohexyl-methyl tosylate, recorded earlier (equation 7), he suggests that if the classical mechanism, structure II, were applicable and the solvolysis of the tosylate were faster than the solvolysis of neopentyl tosylate because of steric effects, then the charge transfer frequency should increase with increasing strain in R of RC_6H_5 because the increasing S character in the R-C bond causes inductive electron withdrawal. If mechanism V were important then the frequency should decrease with increasing strain. The contribution to rate acceleration from bond stretching (fragmentation) III, or bond making (bridging) IV, would not be detected in the charge transfer spectra (vide supra).

The charge transfer frequencies of a series of RC_6H_5 obtained by Traylor, together with relative rates of solvolysis of RCH_2X are shown in Table II.(10).

Traylor's plot of log relative solvolysis rates of R CH_2X against the charge transfer frequencies of the complexes RC_6H_5-tetracyanoethylene is shown in Figure II.(10)

The linear correlation obtained in Figure II implies, according to Traylor, that acceleration of the reaction (equation 7) is primarily due to a vertical electronic effect involving conjugation of one or more of the strained bonds. He goes on to suggest that strained or polarised σ bonds can therefore afford enormous stabilisation of neighbouring cations without any change in the structure of R to relieve the strain.

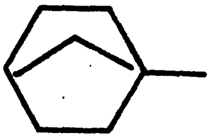
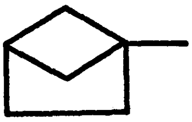
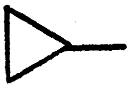
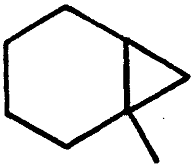
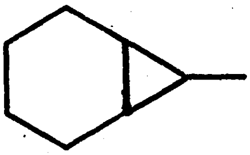
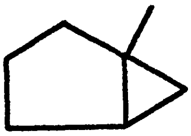
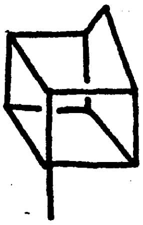
From these studies Traylor draws two conclusions.

(1) A carbonium ion generated α to a strained σ bond is delocalised (non-classical) in proportion to the strain. There are no "classical" carbonium ions having such strain.

(2) The stabilisation may be vertical or near-vertical and thus probes for migration to differentiate classical from non-classical

TABLE II

Charge transfer frequencies for RC_6H_5 with T.C.N.E. [a] compared with relative rates of solvolysis of R CH_2 X.

R.		λ(nm)	ν(cm^{-1} x 10^3)	krel	log krel	σ^+_R [b]
1.	t-Bu	438	22.8	1	0	-0.3
2.		450	22	8	0.9	-0.4
3.		465	21.5	190	2.28	-0.5
4.		475	21	$5x10^4$	4.7	-0.54
5.		485	20.6			-0.60
6.		505	19.8	$1.1x10^7$	7.04	-0.69
7.		510	19.6	$3x10^7$	7.48	-0.71
8.		520	19.2			-0.75

a. Solvent CH_2Cl_2, room temperature.

b. Most of the σ^+ values appear to have been calculated from the charge transfer frequency using equation (24)

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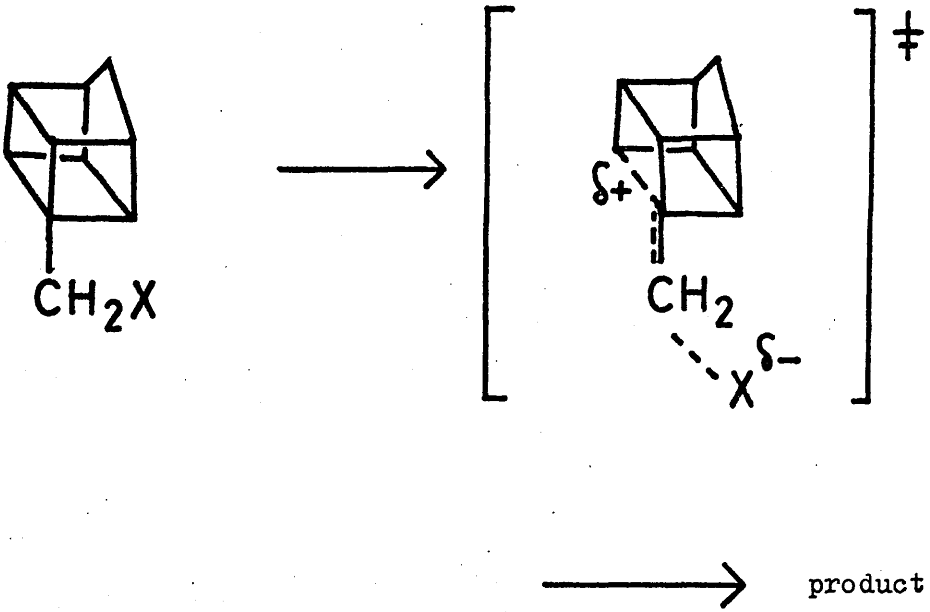
behaviour may be inconclusive.

This correlation has also been claimed by Traylor to provide a simple means of predicting relative solvolysis rates. By measuring the charge transfer spectrum of RC_6H_5 - T.C.N.E. he suggests that the rate of solvolysis of $R\,CH_2\,X$ may be estimated.

The rates of solvolysis of the homocubyl and 1-norcaryl carbinyl systems have been predicted by him in this way. (10) i.e.

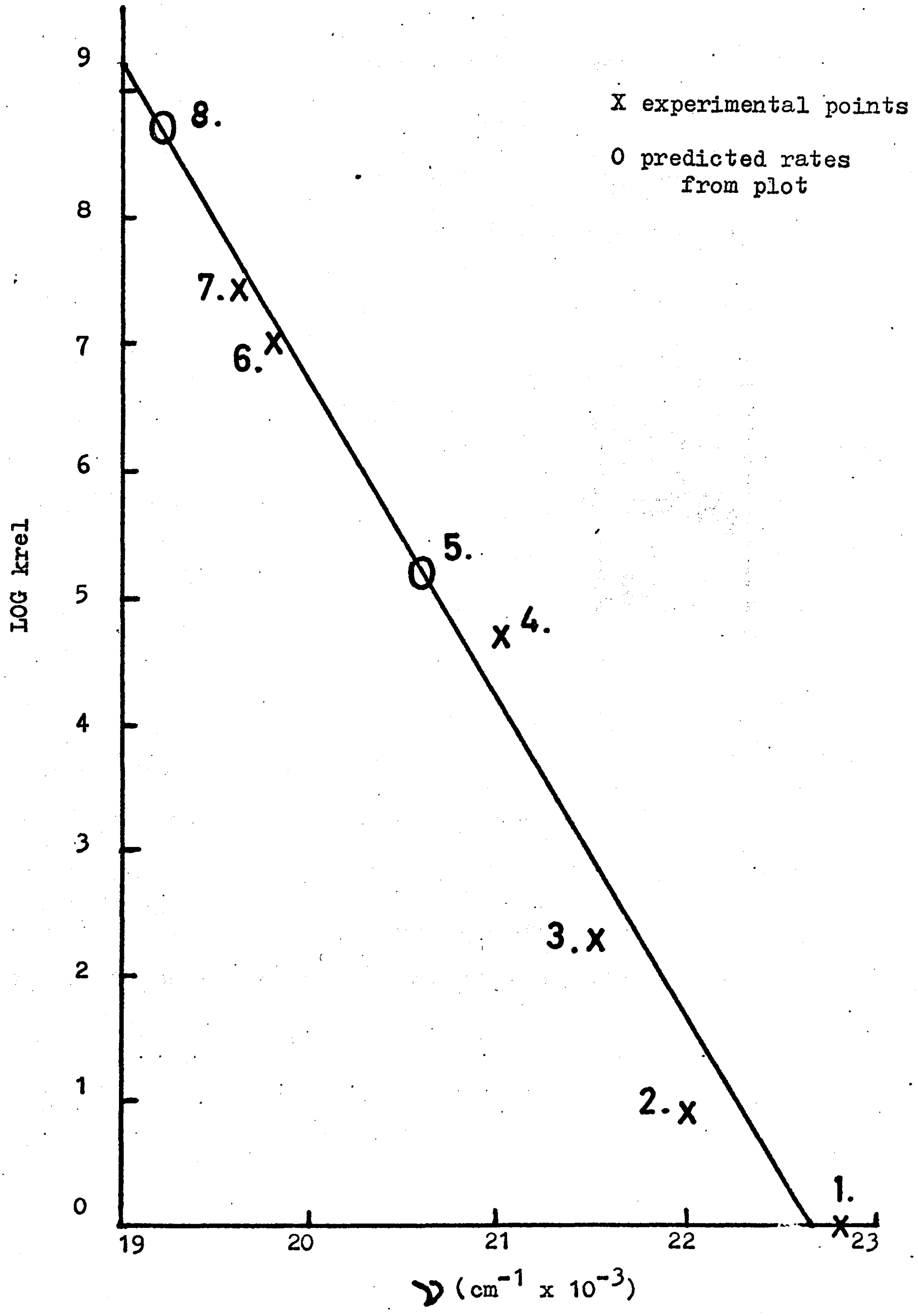


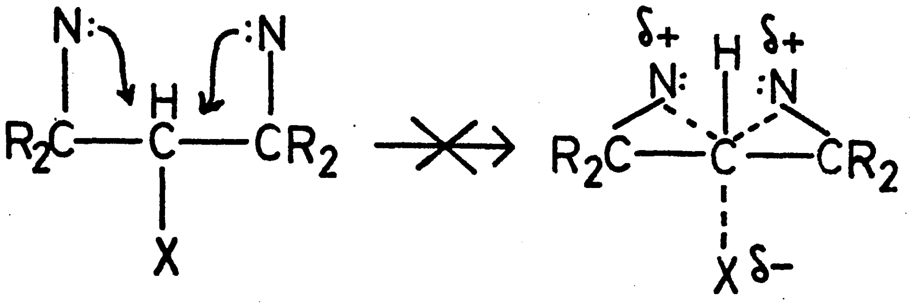
(27)

Further evidence for σ-π conjugation quoted by Traylor is the effect of having more than one nucleophilic group attached to a substrate. In reactions such as (28) internal nucleophilic displacement would be competitive because steric effects prevent significant simultaneous attack by the two nucleophiles.

FIGURE II

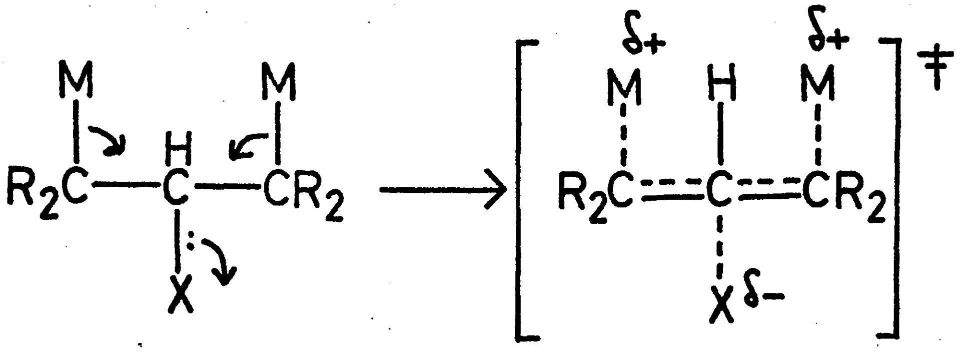
Log relative solvolysis rates of R CH_2 X against charge transfer frequencies of R C_6 H_5 - T.C.N.E.





(28)

On the other hand, there is no such severe restriction on σ-π conjugation and such groups will act co-operatively, equation (29).



(29)

Therefore, for the general reaction

$$(M\ CH_2)_n(CH_3)_{3-n}CX \rightarrow (M\ CH_2)_n(CH_3)_{3-n}C^+ + X^- \qquad (30)$$

an internal nucleophile would be expected to accelerate the ionisation by approximately $n\Delta$ and a σ-π conjugating group by about $(\Delta)^n$, where Δ is the acceleration for one such group. Traylor illustrates evidence for this postulate by mentioning that aryl groups (M = aryl) have been observed to accelerate (28) such reactions by $n\Delta$ whereas cyclopropyl groups (29) appear to accelerate the reaction by $(\Delta)^n$. Previous work (9) by Traylor on the charge transfer complexes of diphenylmethane and triphenylmethane with T.C.N.E. seems to indicate that there is no vertical stabilisation in these complexes whereas the charge transfer spectrum of cyclpropyl benzene points to vertical σ-π conjugation (vide supra).

In conclusion, Traylor's theory of "vertical stabilisation" describes a mechanism whereby polarisable σ bonds may stabilise neighbouring cationic centres without altering the length or angles around such bonds as the transition state is approached. Thus, a cyclopropyl group, for example, may stabilise a cation by vertical delocalisation in the same way that a vinyl group does. The "strain" in both the cyclopropyl and vinyl groups makes the electrons more delocalisable, but these systems need not be "relieved" by nuclear movements in order to afford stabilisation or stereochemical control. It is not suggested that the cations which are intermediates in solvolysis reactions are not bridged, but that because all, or nearly all, of the stabilisation of cations as measured by solvolysis reactions is also seen in vertical processes, such bridging contributes very little to the stabilisation at the transition state, Thus, Traylor states "that σ-π conjugation is not simply an excuse for drawing different dotted lines but is phenomenologically very different from either internal displacement or fragmentation".

DISCUSSION.

The scope of the present work was to test Traylor's hypothesis of "vertical stabilisation" in several ways.

(1) By synthesising the phenyl derivatives of the strained ring systems 4 - 7 in Table II and measuring the charge transfer spectra of the complexes formed by the addition of tetracyanoethylene (T.C.N.E.) to these substituted benzenes, thus confirming or denying Traylor's values for the charge transfer frequencies.

(2) By the experimental determination of the kinetics of electrophilic aromatic substitution in these phenyl derivatives it was hoped that the accuracy of Traylor's σ^+ values, estimated from the charge transfer frequencies using equation (24) could be verified.

(3) By the synthesis of the homocubyl carbinol system XXI (4-hydroxymethylpentacyclo $[4.3.0.0.^{2,5}.0.^{3,8}.0.^{4,7}]$ nonane) and the determination of the rate of solvolysis of the 3.5-dinitrobenzoate derivative in aqueous acetone. The experimental rate constant could be compared with that predicted by Traylor from Figure II.

Details of the synthetic work, kinetics and charge transfer measurements are contained in the experimental section.

1) Charge-Transfer Measurements

The charge transfer spectra, recorded using an Unicam SP8000 U.V. recording spectrophotometer, for the following substrates: phenyl cyclopropane, 1-phenyl norcarane, 7-phenyl norcarane, 1-phenyl bicyclo [3.1.0] hexane, and, also, for toluene are shown in the experimental section, p. 85-89.

It was decided to check the experimental procedure employed to measure the spectra by first using toluene as the substrate. As can be seen from the Unicam chart a reasonable spectrum was obtained with a single peak, having $\lambda_{max.}$ at 410 nm, being visible. The Cary Model 14 spectrophotometer gave a spectrum of identical shape and $\lambda_{max.}$ This value compares favourably with that obtained by Traylor (411 nm)[9] and also that obtained by Merrifield and Phillips (406 nm)[26].

The spectrum for the phenyl-cyclopropane - T.C.N.E. complex shows two peaks, the shorter wavelength peak being centred on $\lambda_{max.}$ 404 nm. while the second, longer wavelength peak merges with the first peak to form a broad plateau-shaped peak. This makes the estimation of $\lambda_{max.}$ rather difficult although it appears to be in the range 465 -480 nm. Traylor, also, seems to be indecisive as to the true position of $\lambda_{max.}$ as he records a value of 470 nm. in one publication[9] and a value of 475 nm. in another paper[10].

The spectrum for the 1-phenyl norcarane - T.C.N.E. complex again shows two peaks, the shorter wavelength peak being centred at $\lambda_{max.}$ 400 nm. and the longer wavelength peak being much broader at approximately λ_{max}. 550 nm. The broadness of this second peak makes the determination of $\lambda_{max.}$ difficult but does not explain the value of $\lambda_{max.}$ obtained by Traylor (485 nm)[10].

The 7-phenyl norcarane - T.C.N.E. complex gave a spectrum containing a single, fairly broad peak centred on λ_{max}. 408 nm. Again, this value does not agree with Traylor's results. Traylor, again, quotes two values, 500 nm. in one publication [9] and 505 nm. in another communication[10].

Finally, the spectrum obtained from the complex of 1-phenyl bicyclo $[3.1.0]$ hexane and T.C.N.E. shows two peaks of similar appearance to the spectrum of phenyl cyclopropane - T.C.N.E. The shorter wavelength peak is centred on $\lambda_{max.}$ 405 nm. and is fairly well-defined but the longer wavelength peak is broad and overlaps the first peak, causing the determination of λ_{max}. to be difficult. Traylor has quoted [10] a value for $\lambda_{max.}$ of 510 nm. but from the Unicam spectrum the value could be anywhere between 480 nm and 520 nm.

In all the above-mentioned cases identical spectra were obtained using a Cary Model 14 ultra-violet recording spectrophotometer, both in shape and position of $\lambda_{max.}$ as for the Unicam SP8000 charts shown.

Traylor, also, appears to have difficulty in deciding the position of $\lambda_{max.}$ for the t-butyl benzene - T.C.N.E. complex. He quotes values of 415 nm[9] and 438 nm [10] in separate papers, although he does mention that the estimation of $\lambda_{max.}$ for shorter wavelengths ($<$ 450 nm) is rather inaccurate due to the fact that the longer wavelength maxima are broad and overlap the second maxima. A difference in $\lambda_{max.}$ of 23 nm. makes a substantial difference in the value of σ^+ calculated from equation (24) (vide infra).

This, in effect, illustrates the main weakness in Traylor's experimental findings. Although it is reasonable to assume a relationship between charge transfer absorption frequencies and ionisation potentials, as postulated by previous workers,[27,30] and hence, the ability of a particular group to stabilise carbonium ions, if the frequency of absorption cannot be determined with a high degree of accuracy, then this method of determining σ^+ values and relative rates of reaction is going to be rather unreliable. Traylor does not reproduce the spectra obtained by his co-workers but the spectra in the present work seem to indicate that, for strained ring systems at least, the charge transfer absorption frequencies cannot be determined accurately enough to be employed in the estimation of reaction rates or σ^+ constants.

Closer examination of Traylor's results show further discrepancies. For example, the graph of charge transfer frequency, ν_{TCNE}, against σ^+_p drawn by Traylor (Figure I)[9] gives a value for ν_{TCNE} for the dimethylamino group of approximately 14,800 cm^{-1} and, yet, Table I in the same paper quotes ν_{TCNE} as being 19,200 cm^{-1}. Also, Traylor quotes σ^+_R values in Table II[10], presumably calculated using equation (24) although he does not make this clear. The recalculated σ^+ values using Traylor's results for ν_{TCNE} from equation (24) are shown against the values calculated by Traylor in Table III.

As can be seen, there appears to be some difference between the σ^+ values reported by Traylor and those calculated using his results, especially for those substrates where Traylor is indecisive as to the exact position of ν_{TCNE}. It is interesting to note that the σ^+ value for the cyclopropyl group obtained by Traylor is approximately 0.08 more negative than that obtained from the solvolysis of t-cumyl chlorides, i.e. the cyclopropyl group should be more reactive than is found

TABLE III

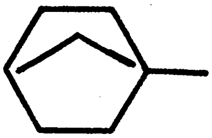
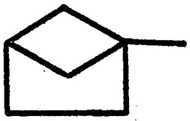
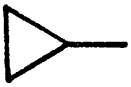
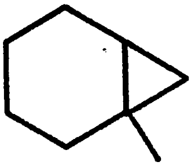
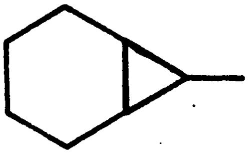
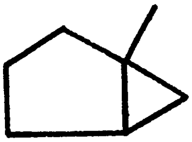
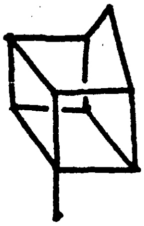
R	ν_{TCNE} (cm^{-1} x 10^3)	σ^+_R(calc)[a]	σ^+_R(Traylor)[b]	σ^+_R (lit)
1. t-Bu	24.1 [c] 22.8 [d]	- 0.226 - 0.366	- 0.3	- 0.256 [e]
2. 	22 [d]	- 0.452	- 0.4	
3. 	21.5 [d]	- 0.501	- 0.5	
4. 	21.3 [c] 21.0 [d]	- 0.527 - 0.559	- 0.54 [f]	- 0.46 [g]
5. 	20.6 [d]	- 0.602	- 0.60	
6. 	20.0 [c] 19.8 [d]	- 0.667 - 0.688	- 0.69	
7. 	19.6 [d]	- 0.710	- 0.71	
8. 	19.2 [d]	- 0.753	- 0.75 [h]	

TABLE III - continued

a) Calculated using Traylor's values for ν_{TCNE} as shown from equation (24).

b) Calculated by Traylor, see reference 10.

c) Reference 9.

d) Reference 10.

e) Reference 33.

f) Traylor quotes a value of - 0.52 in references 9, 31.

g) Reference 33. Reference 32 gives values for σ^+ ranging from - 0.41 to -0.47, averaging out at - 0.45.

h) Also quoted in reference 31.

experimentally. Also, calculation of σ^+ for the methyl group using Traylor's value [9] for ν_{TCNE} of 24,300 cm^{-1} gives σ^+ as -0.20 compared with an accepted value of -0.311 [33]. Thus, Traylor implies that the methyl group is less reactive than the t-butyl group, i.e. the reverse of the Baker-Nathan order of reactivities.

Hence, it can be seen from the above table that Traylor not only has difficulty in obtaining a consistent value for the charge transfer frequencies for several of the substrates but, also, appears to have either inaccurately calculated or mis-quoted values for some of the σ^+ constants. Yet, in a further paper [31] he gives some of these σ^+ values as if they were established figures ! It seems that the linear relationships between charge transfer frequency and reactivity (Figures I and II) shown by Traylor must be regarded with a certain amount of reservation until a more accurate method of determination of the charge transfer absorption frequencies of these cyclic substrates is found.

2) Electrophilic Aromatic Substitution

The choice of electrophilic substitution reaction was influenced by a variety of factors. A reaction was required which would be reasonably sensitive to changes in substituents in the benzene ring, i.e. a large, negative rho value for the reaction was needed. Also, the reaction must involve total or near-total substitution in the benzene ring with no or negligible substitution in the group attached to the aromatic ring. For this reason acetylation [34] and bromination [35,36] were excluded as both these reactions involve cleavage of the cyclopropyl ring in phenyl cyclopropane. Finally, the measurement of the kinetics of reaction should be relatively straightforward, preferably involving a continuous method such as visible/ultra-violet spectroscopy.

Initially, it was decided to use molecular chlorination as the electrophilic reaction, the ρ value being approximately -10.0. The procedure of Keefer and Andrews [37] was employed. The reaction was carried out in acetonitrile at 25° C ± 0.1° C, the substrate being 10^{2} M excess over chlorine to ensure monosubstitution. The change in absorbance of the chlorine solution was followed using a Cary Model 14 ultra-violet recording spectrophotometer at a wavelength of 330 nm. At first, toluene was tried as the substrate to check the procedure, a rate constant of approximately 10^{-3} s^{-1} being obtained, in reasonable agreement to that obtained by Keefer and Andrews. However, when the more reactive substrates, possessing strained-ring substituents, were tried the reaction was found to be too rapid to measure spectrophotometrically. On reducing the concentration of these substrates to lower the rate of chlorination it appeared that a consecutive reaction was occurring, approximately three equivalents of chlorine reacting for each equivalent of substrate.

Next, it was decided to use nitration as the electrophilic substitution reaction, the ρ value being -6.0 [33]. Both toluene [68] and phenyl cyclopropane [38-41] give little or no substitution in the alkyl substituent. The procedure of Hartshorn, Moodie and Schofield [68] was employed (see experimental). The results are shown in Table VI (experimental section).

Before the kinetics of nitration are discussed it is necessary to mention one or two reservations about the results obtained. Firstly, the products of nitration were not determined for the reactions and, hence, it has been necessary to assume that all or most of the nitrating agent reacts via electrophilic aromatic substitution, the cyclic substituents remaining untouched. As stated previously, phenyl cyclopropane gives mainly aromatic substitution products so it is reasonable to assume that the other substrates, which, in effect, can be compared with cyclopropane rings with alkyl substituents attached, should react in a similar manner. Baas and Wepster [39] quote yields of 97.7% of the aromatic nitration product for phenyl cyclopropane and 96.1% for 2-methylcyclopropyl benzene. Consequently, product ratios have not been determined for the substrates and so the reaction rates quoted are overall rates and not partial rate factors. Secondly, the standard deviations calculated for the weighted averages of the rate constants vary between 3.39% and 17.46%. This means that, although the rate constants are of the right order the figures mentioned should not be taken too literally.

Despite these reservations, however, the rate measurements show an interesting trend. The kinetics of nitration of benzene and toluene were measured in order to check the procedure, solutions, etc. The rate constants obtained compare favourably with those obtained by Schofield et al [68] following the same procedure and using the same conditions (a slightly modified version of the procedure used for the determination of the kinetics of reaction of toluene was employed for benzene rather than Schofield's aliquot method). This gives a relative rate for toluene against benzene of 51.2, compared to 50 ± 6 obtained by Schofield. Other workers have obtained relative rate ratios ranging from 17 [33] to 90 [38], depending on the conditions of reaction and method of determination, so the figures obtained in the present work appear to be reasonable.

The relative rate for phenyl cyclopropane against benzene is about 243, using the experimental results recorded in this work. This compares with figures quoted by Baas and Wepster [39] of greater than 100 (these workers have estimated the rate to be seven times greater than that of the isopropyl group which gives a relative rate of 182), by Stock [35] of 912, and that calculated by Shechter [38] of approximately 700, using data from the solvolysis of t-cumyl chlorides, bearing in mind the differing conditions employed by these workers. If the ortho: para product ratio for nitration of phenyl cyclopropane is assumed to be 74:26 (similar ratios were obtained by Shechter [38] and by Baas and Wepster [39]) then a relative rate of 243 gives a partial rate factor for the para position of 379 which yields a σ_p^+ value of - 0.43 for the cyclopropyl group. This figure compares favourably with those quoted by other workers [32], ranging from - 0.41 to - 0.47.

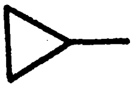
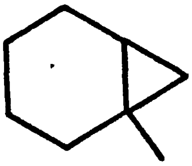
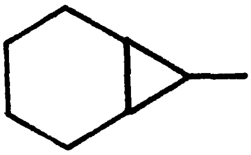
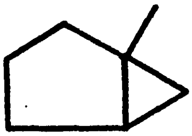
Thus, the rate constants measured for benzene, toluene and phenyl cyclopropane appear to be in reasonable agreement with the work of other authors. By comparing the experimental rates for substrates 5 - 7 (in Table II) with either that measured for benzene or that of phenyl cyclopropane it should be possible to corroberise Traylor's order of reactivities shown in Table II. As can be seen from the results, the order of reactivity obtained experimentally is 7-phenyl norcarane > 1-phenyl bicyclo [3.1.0] hexane > phenyl cyclopropane > 1-phenyl norcarane compared to Traylor's order of 1-phenyl bicyclo [3.1.0] hexane > 7-phenyl norcarane > 1-phenyl norcarane > phenyl cyclopropane. These relative reactivities can be compared to those obtained by Stock [35] for the nitration of methyl-substituted cyclopropyl benzenes. Stock has found that the (1-methyl cyclopropyl) benzene is approximately one third slower than phenyl cyclopropane in the nitration of the benzene ring. 1-phenyl norcarane would be expected to react similarly to the 1-alkyl substituted compound and, in fact, the rate of nitration is again approximately one third that of phenyl cyclopropane. The 1-phenyl bicyclo [3.1.0] hexane compound would be expected to react somewhat faster than the 1-alkyl cyclopropyl benzene due to increased strain in the five-membered ring, which it does, almost twice the rate of phenyl cyclopropane. Finally, the 7-phenyl norcarane compound can be compared to cis-2,3-dimethylcyclopropyl benzene. The anti compound reacts approximately 3.5 times as fast as phenyl cyclopropane whereas 7-phenyl norcarane reacts approximately four times faster than phenyl cyclopropane. Thus, it seems reasonable to propose that for nitration, at least, the order of reactivities obtained in the present work is the correct one and Traylor's order of reactivity incorrect.

Further evidence of this is shown by using Traylor's σ^+ values, quoted in Table II, to calculate partial rates of nitration for the para positions in the substituted benzenes (it is assumed that the σ^+_R values quoted by Traylor are in fact σ^+_p values although he does not make this clear). Table IV shows the results of these calculations.

Thus, it can be seen that for all four substrates the rate constants for the para position calculated using Traylor's σ^+ values are greater than the overall rate constants determined experimentally. Obviously, it would be expected that the para rate constants should be approximately given by the overall rate constant minus twice the ortho partial rate factor. The most likely conclusion one can draw from this is that the σ^+ values are at fault.

However, to continue the comparison of these cyclic compounds with the methyl-substituted cyclopropyl systems, it is interesting to note that the relative rates of solvolysis of the 3,5-dinitrobenzoate derivatives of the methylcyclopropyl carbinyl compounds in aqueous acetone [17] at 100° C are as folows : anti-cis-2,3-dimethylcyclopropyl carbinyl, 110; 1-methylcyclopropyl carbinyl, 5; cyclopropyl carbinyl, 1.0. In other words, by analogy, the 7-phenyl substituted ring system should solvolyse fastest, followed by the 1-phenyl substituted ring system with phenyl cyclopropane slowest. This, in effect, is the order suggested by Traylor for 7-phenyl norcarane, 1-phenyl norcarane, and phenyl cyclopropane (it is difficult to fit 1-phenyl bicyclo [3.1.0] hexane into this analogy due to the increased

TABLE IV

R	σ_p^+ [a]	fp	Estimated rate constant for para position (S -1) [b]	Overall rate constant obtained experimentally (S -1)
	-0.54	1.738×10^{3}	8.151×10^{-3}	1.14×10^{-3}
	-0.60	3.981×10^{3}	1.867×10^{-2}	0.441×10^{-3}
	-0.69	1.738×10^{4}	8.151×10^{-2}	4.84×10^{-3}
	-0.71	1.82×10^{4}	8.537×10^{-2}	1.96×10^{-3}

a Traylor's σ_R^+ values from Table II

b Calculated using $k = 4.69 \times 10^{-6}\ s^{-1}$ for benzene.

ring strain of the system from the five-membered ring).

A possible explanation for these apparently anomalous results is suggested by Stock [35]. He proposes that destabilising steric interactions combine with stabilising charge delocalisation effects to reduce the rate factors for the methylated cyclopropyl substituents. The cyclopropyl carbinyl systems are affected by electronic factors only so that additional methyl groups enhance delocalisation of positive charge to the cyclopropane ring in the preferred bisected conformation, thus, giving the enhanced rates shown. On the other hand, methyl groups exert a different influence on the reactivity of the cyclopropyl benzenes. Stock suggests that steric effects increase the energy of the bisected conformation of the cyclopropane ring, due to non-bonded interactions between, for example, the methyl groups and the ortho hydrogens of the benzene ring. Thus, the nitration data for the methylated cyclopropyl substituents reflect conflicting steric and electronic factors.

In the case of the bicyclic compounds 5 - 7 the magnitude of the steric effects increases in the order 7-phenyl norcarane $<$ 1-phenyl bicyclo $[3.1.0]$ hexane $<$ 1-phenyl norcarane on examination of models of these compounds. Therefore, Stock's explanation of conflicting steric and electronic effects may account for the reactivities obtained experimentally.

In conclusion, it appears that the σ_R^+ values calculated by Traylor do not fit the data for aromatic nitration particularly well, although some of the discrepancies observed could well be accounted for by Stock's theory of conflicting steric and electronic effects. However, not all the differences can be due to steric interactions as even the σ_R^+ constant for phenyl cyclopropane itself (which would not be subjected to any steric effects) obtained by Traylor, is higher than that calculated from the nitration data or that recorded by other workers. Stock and Brown in their work [33] on substituent effects state that the σ^+ constants obtained for solvolyses should be the same as those obtained through electrophilic aromatic substitution reactions so that a correlation should exist between the data obtained from aromatic nitration and that from the solvolyses of the carbinyl compounds.

3) Solvolysis of 4-(3,5-dinitrobenzoyl) oxymethylpentacyclo $\left[4.3.0.0.^{2,5}.0.^{3,8}.0.^{4,7}\right]$ nonane, XXII

One of the interesting points in Traylor's series of papers on vertical stabilisation is his prediction of the rate of solvolysis of various alkyl systems. He has suggested that measurement of the charge transfer absorption frequency of the alkyl-substituted benzene - T.C.N.E. complex correlates directly with the rate of solvolysis of the alkyl carbinyl system. The linear correlation obtained by Traylor is shown in Figure II, p.28.

The rates of solvolysis of two of the cyclic carbinyl systems have been predicted by him on the basis of the charge transfer measurements of the ring-substituted benzene - T.C.N.E. complexes. In particular, the rate predicted for the homocubyl carbinyl system seems to be quite large.

Traylor obtains a value for the charge transfer absorption frequency of 19,200 cm^{-1} for the phenyl homocubane - T.C.N.E. complex. By using this result, a figure for log relative rate for the homocubyl carbinyl system may be estimated from Figure II. This gives log rate of the homocubyl system relative to the t-butyl carbinyl system as being 8.75. Thus, the homocubyl system solvolyses 5.62×10^{8} times faster than the t-butyl system, according to Traylor. The relative rate of solvolysis of the cyclopropyl carbinyl system is given by Traylor as being 5×10^{4} times faster than the t-butyl carbinyl system, and, as the rate of solvolysis of the 3,5-dinitrobenzoate derivative of cyclopropyl carbinol in 60% aqueous acetone at 100° C is known, the predicted rate of solvolysis of the 3,5-dinitrobenzoate derivative of the homocubyl carbinol under the same conditions may be calculated. Von R. Schleyer and Van Dine [17] give the rate of solvolysis of the cyclopropyl carbinyl 3,5-dinitrobenzoate under the above condition as 4.3×10^{-7} s^{-1}. Thus, the calculated rate of solvolysis of the homocubyl carbinyl 3,5-dinitrobenzoate in 60% aqueous acetone at 100° C works out to be 4.83×10^{-3} s^{-1}, using the results of Traylor's studies.

It was decided to synthesise the 3,5-dinitrobenzoate derivative of homocubyl carbinol and to measure its rate of solvolysis in aqueous acetone to see if Traylor's prediction does, in fact, hold. The synthetic work is recorded in the experimental section. Examination of the analytical data, in particular the n.m.r. spectrum, suggests that the ester of the primary alcohol has been produced rather than a rearranged product such as a bishomocubyl system [42] which would be a tertiary alcohol derivative.

Details of the kinetic studies are shown in the experimental section. The ampoule method was employed, determinations being carried out in duplicate in 80% aqueous acetone at 90° C. As can be seen from the results, the solvolysis appears to be very slow, there being only about 10% reaction after seven days. Because of the small degree of reaction and, hence, the lowness of the titres of the 0.01M sodium hydroxide, the accuracy of the figures is probably not as high as one would have liked. However, despite this, considering the variation in the length of time that the reaction has been allowed to continue, ranging from eighteen hours to seven days, the rate constants calculated for each kinetic run, using the usual first order rate equation, are reasonably constant at approximately 2×10^{-7} s^{-1}.

The figures quoted for the rate constants in Table VII have been measured in 80% aqueous acetone at 90° C. In order to compare these results with the calculated rate constant using Traylor's figures (vide supra), it is necessary to allow for the differing conditions employed. On changing the solvent from 80% aqueous acetone to 60% aqueous acetone it has been estimated [43,44] that the rate of solvolysis increases by a factor of 26. The rate measurements in the present work were carried out at 90° C. Ideally, in order to convert the rate constants measured at this temperature to the values for 100° C, the Arrhenius parameters for the reaction are required in order to use the standard Arrhenius equation. As the rate of solvolysis of this compound has only been carried out at one temperature, the Arrhenius parameters cannot be calculated. However, it is generally agreed that on changing the temperature of a reaction by 10° C the rate of reaction varies by a factor of two to three times. Allowing for the maximum change, this means that the rate constants obtained experimentally must be tripled on going from 90° C to 100° C. The recalculated experimental rate constants for the solvolysis of the 3,5-dinitrobenzoate derivative of homocubyl carbinol in 60% aqueous acetone at 100° C are shown in Table V.

Therefore, the experimentally determined rate constant for the solvolysis under the above-mentioned conditions is of the order of 2×10^{-5} s^{-1}. As mentioned previously, Traylor predicted the rate constant for solvolysis to be 4.83×10^{-3} s^{-1}, which means that the actual rate of solvolysis is approximately 240 times slower than that predicted by Traylor. Thus, a substantial difference exists between Traylor's predicted rate of solvolysis and that measured experimentally which suggests that the σ_R^+ value predicted by Traylor for the homocubyl system of -0.75 is considerably more negative than the actual value. On the assumption that the value for the charge transfer frequency measured by Traylor is correct, this means that the calculation of σ^+ from the charge

TABLE V

Time	k_1[a] expt. (s^{-1})	k_2[b] expt. (s^{-1})
18 hours	1.762×10^{-7}	1.374×10^{-5}
24 hours	3.306×10^{-7}	2.579×10^{-5}
7 days	1.782×10^{-7}	1.390×10^{-5}

a) experimental rate constant measured at 90° C in 80% aqueous acetone.

b) experimental rate constant after conversion to 60% aqueous acetone at 100° C.

transfer frequency of the substituted benzene - T.C.N.E. complex, using equation (24), is invalid for the homocubyl system at least. Also, the prediction that the rate of solvolysis of a particular compound may be estimated from the colour of the substituted benzene - T.C.N.E. complex appears to be untenable.

Conclusion

Traylor, in his theory of vertical stabilisation, in effect, suggests the following proposals.

(1) That a relationship exists between the charge transfer absorption spectrum of a particular substituted compound and the σ^+ value for the substituent of that compound.

(2) If the σ^+ value obtained from the charge transfer frequency, using equation (24), is the same as measured by reactions such as solvolysis, electrophilic aromatic substitution, etc. then the stabilisation afforded by the substituent is "vertical", i.e. it involves no movement of the atoms in the group.

(3) Measurement of the charge transfer frequency of substituted benzene - T.C.N.E. complexes gives a means of directly estimating the rates of solvolyses of the respective substituted carbinols.

The first proposal that a relationship exists between σ^+ and ν_{TCNE} is, on the face of it, a reasonable assumption. As mentioned previously, a relationship between charge transfer frequencies and ionisation potentials has been postulated by several workers and, since ionisation potentials correlate with σ^+ values (see introduction), then the ability of a group, R, to stabilise the positive charge in the RC_6H_5 - T.C.N.E. complex should be similar to that for the stabilisation of other carbonium ions such as those in equations (13) and (15) etc. However, the practical application of this correlation relies on the necessity of the charge transfer frequencies to be measured accurately. The charge transfer measurements in the present work suggest that the frequencies cannot be measured sufficiently accurately to be used in a comparison with σ^+ constants; Traylor, himself, seems to find difficulty in deciding which is the true value for some of the substrates. In fact, the values for the charge transfer frequencies of 1-phenyl norcarane and 7-phenyl norcarane do not agree with Traylor's figures at all. Thus, it appears that the linear relationship shown by Traylor in Figure I should be treated with a great deal of reservation.

The second point that Traylor mentions is that if σ^+ calculated using equation (24) from charge transfer data is the same as that obtained from reactions then the reactions involve vertical stabilisation. The reaction studied in the present work was nitration, i.e. electrophilic aromatic substitution. Use of Traylor's σ^+ values, from charge transfer data, gave partial rate factors for nitration of the para position which were higher than the overall rate measured experimentally. In fact, the order of reactivity of the strained ring compounds differed substantially from that predicted by Traylor. According to Traylor's postulate, this would imply that the stabilisation afforded in the transition state in nitration is non-vertical, but, it is interesting to examine the results obtained for phenyl cyclopropane. The cyclopropyl group has been suggested by several workers to stabilise carbonium ions without change in the geometry of the ring atoms so that it would be expected that the figures for the nitration of phenyl cyclopropane should indicate vertical stabilisation in the transition state. However, the σ_p^+ obtained in the present work is about - 0.43 compared to Traylor's predicted value of

- 0.54. This suggests that the σ^+ values calculated by Traylor are somewhat inaccurate and appear to be more negative than experimental results indicate.

Finally, Traylor has proposed that measurements of the charge transfer absorption frequency for a substituted benzene - T.C.N.E. complex enables the rate of solvolysis of the respective carbinyl system to be estimated. The results obtained for the solvolysis of the homocubyl carbinol system in the present work gave the rate to be 240 times slower than that predicted by Traylor. This suggests that the correlation in Figure II quoted by Traylor between relative rates of solvolysis and charge transfer frequency is incorrect, at least for the homocubyl system.

Ideally, the charge transfer spectrum of phenyl homocubane should be measured and, also, the kinetics of solvolysis of the 1-phenyl norcarane system to see if these fit in with Traylor's data. Also, the σ^+ constants for the various strained rings should be calculated from data for an alternative reaction, such as the solvolysis of the t-cumyl chlorides, in order to compare these with Traylor's predicted values.

Thus, it appears that the results of this present work contradict those of Traylor and bring into question his theory of vertical stabilisation but, until further work, such as that mentioned above, has been carried out, definite conclusions as to the validity of Traylor's hypothesis cannot be made. Support for Traylor's work has been given by Hoffmann, Radom, Pople, Von R. Schleyer, Hehre and Salem[45] in their study of the conformational consequences of hyperconjugation. They state that "on theoretical grounds there is no dichotomy between participation with and without bridging. The hyperconjugative interaction will always be accompanied by geometrical adjustment, but the extent of that deformation may be small or large". However, it must be remembered that other theories have been put forward which explain the observed facts reasonably well, such as Dauben's [46,47] idea of relief of strain providing the driving force in reactions involving cyclic substituted compounds. Dauben has suggested that, for cyclopropyl carbinyl type systems, fragmentation, involving bond-lengthening leading to relief of strain, is the major pathway in solvolysis reactions.

EXPERIMENTAL

PREPARATIVE EXPERIMENTAL

Melting points were measured on a Kofler-Reichart hot stage melting-point apparatus and are uncorrected.

Infra-red spectra were recorded using a Perkin-Elmer 237 spectrophotometer, wavelengths being in units of $cm.^{-1}$ The following abbreviations are used: s = strong; m = medium; w = weak; sh = shoulder.

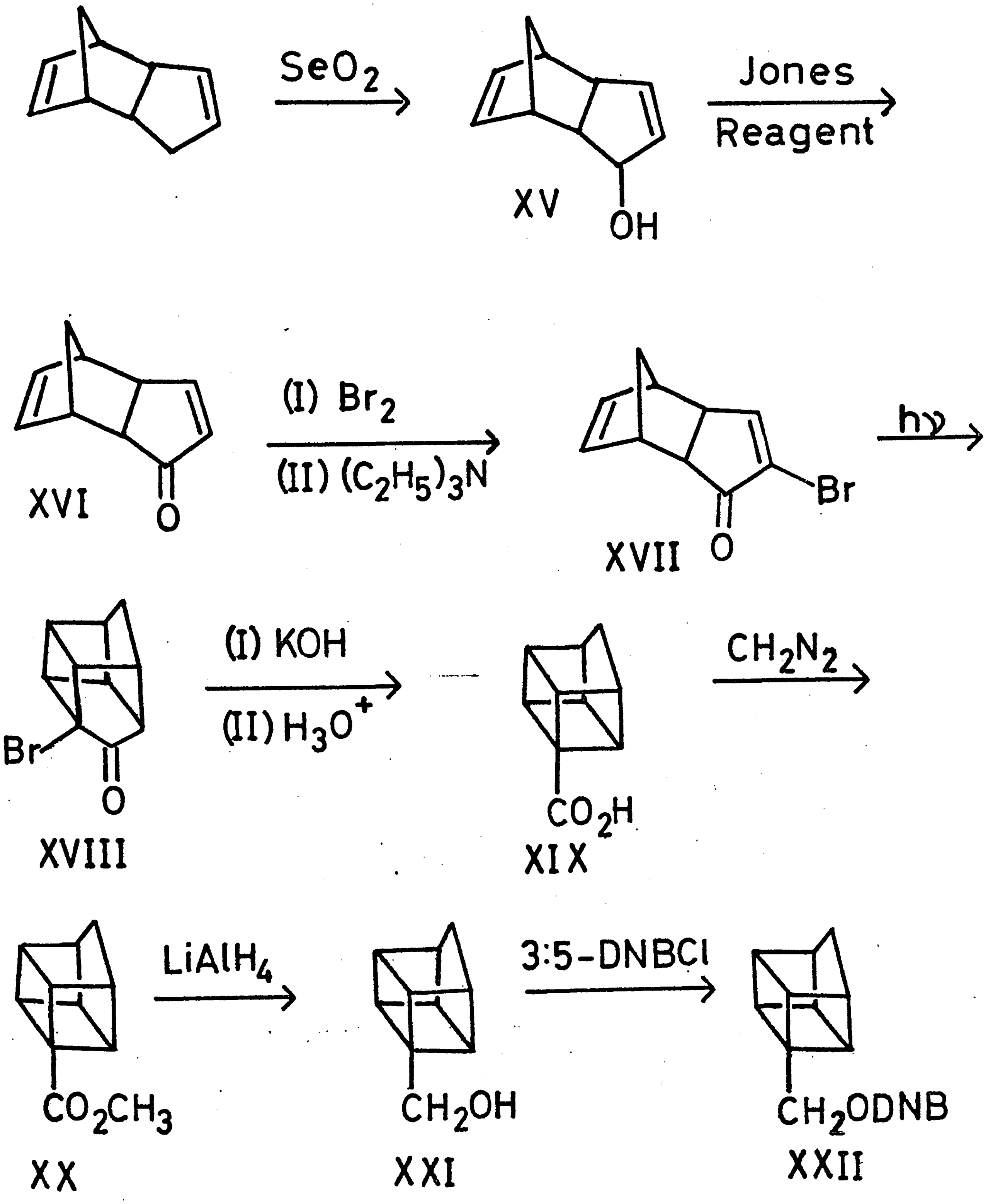
N.M.R. spectra were determined as approximately 10% solutions on a 60 MHz Varian T-60 instrument. Chemical shifts were measured downfield from internal T.M.S. and are quoted as delta values. The following abbreviations are used: s = singlet; d = doublet; t = triplet; m = multiplet.

Mass spectral analysis was performed on an A.E.I. M.S.12 mass spectrometer.

Elemental analyses were determined by Mrs. G. Harkness of the University of Glasgow and are quoted as percentages.

Preparation of 4 -(3.5-dinitrobenzoyl) oxymethylpentacyclo $[4.3.0.0.^{2,5}.0.^{3,8}.0.^{4,7}]$ nonane

The above compound was synthesised by the following method:-



DNB=3:5Dinitrobenzoyl

Preparation of α-1-hydroxydicyclopentadiene (XV)

This was prepared according to the method of Woodward and Katz(48) as follows :-

Freshly distilled dicyclopentadiene (186g) was dissolved in 500 mls dioxan in a one litre three-necked flask equipped with a Hershberg stirrer and reflux condenser. Water (50 mls) and potassium dihydrogen phosphate (20g) were added, and, while the solution was stirred and heated on a steam bath, selenium dioxide (80g) was added. After three hours the mixture was cooled, the precipitated selenium was filtered immediately with suction, and the precipitate was washed with ether. The filtrate was shaken with 1 l. of saturated sodium chloride solution. The aqueous solution was drawn off and washed three times with 300 ml. portions of ether. The combined organic solutions were then washed with 250 mls of 5% aqueous sodium hydroxide and 500 mls saturated brine. The emulsion which formed was broken by filtration through Celite 535. The organic phase was washed twice more with brine and dried over sodium sulphate. The solvent was removed at reduced pressure and the residual oil was distilled (b.p. 80° C at 0.8 mm).

The alcohol was obtained as a pale yellow oil which solidified on standing. Alder (49) reported obtaining the alcohol as a waxy mass, m.p. 40° - 50°, Rosenblum (50) as an oil, b.p. 84° at 3 mm and Woodward (48) as an oil which after distillation (67° at 0.1 mm) yielded slightly yellow waxy crystals.

Phenyl Urethane Derivative.

Prepared according to the method given in Vogel, Practical Organic Chemistry.

m.p. 139.5° - 140.5° (lit. m.p.[48,49] 139.6° - 140.0°, 142°)

I.R. (liquid film)

3320 (s), 3030 (m), 2960 (s), 2930 (sh), 2890 (m).
2860 (sh), 1620 (w), 1340 (m), 1100 (w), 730 (m) cm.$^{-1}$

N.M.R. ($CDCl_3$)

δ_{TMS} 6.0 - 5.4 (4 H, m)
4.1 (1H, broad s)
3.50 - 2.35 (4 H,m)
1.75 - 1.25 (3 H,m)

Preparation of Endo-3a, 4, 7, 7a-tetrahydro - 4.7 - methanoinden - 1 - one (XVI)

This was prepared using the procedure of Paquette and Ward (51) as follows :-

A solution of 40g of α-1-hydroxydicyclopentadiene (0.27 mol) in 500 mls. acetone was cooled in an ice-bath and titrated with a total of 170 mls. of Jones reagent (CA.0.2M) prepared as shown below. The reaction mixture was added to 1 l. of brine and extracted with ether. The combined organic extracts were washed with water and dried. Evaporation of the solvent left an oily residue which solidified on standing. Recrystallisation of the solid from pentane gave white crystals (m.p. 55° - 57°).

Rosenblum (50) obtained an oil, b.p. 82° - 87° at 4 mm. which crystallised on cooling to give colourless plates, m.p. 59.0° -

- 59.5°. Paquette (51) obtained white crystals, m.p. 80°.

Preparation of Jones reagent (52)

70g of chromium trioxide (0.7 mol) were dissolved in 100 mls water in a 500 mls beaker. The beaker was immersed in an ice-bath and 112g (61 ml, 1.1 mol) of concentrated (18 M) sulphuric acid, followed by 200 mls of water were added cautiously with manual stirring. The solution was cooled to 0° - 5°.

I.R. (K.Br disc)

3030 (m), 2980 (s), 2940 (sh), 2870 (m), 1690 (s), 1550 (w), 1350 (m), 1330 (m), 1218 (m), 1195 (m), 895 (m), 775 (m), 733 (m), 718 (m), 643 (w) cm^{-1}.

Preparation of Endo-2-bromo-3a, 4, 7, 7a - tetrahydro - 4, 7 - methanoinden - 1 - one (XVII)

The method of Paquette and Ward (51) was used to synthesise the above compound as follows :-

A solution of bromine (20.1g, o.126 mol) in 200 mls of carbon tetrachloride was added rapidly to a vigorously stirred solution of ketone XVI (18.3g, 0.126 mol) in 500 mls of the same solvent. This was quickly followed by the addition of triethylamine (25g, 0.25 mol) in 100 mls carbon tetrachloride. The reaction mixture was warmed on a steam bath for 30 minutes and then stirred for a final 1.5 hours. The precipitate was separated by filtration and the filtrate was washed with water. The aqueous washings were extracted with ether and the combined organic layers were dried and evaporated. Short path distillation of the residue gave the ketone as a yellow oil, b.p. 130° at 2 mm.

which solidified on standing, m.p. of crude material 48° - 50°.

Paquette (51) obtained a pale yellow oil, b.p. 95° - 100° at o.1 mm, which gave a crystalline solid, m.p. 55° - 57°, on cooling. Dunn, Dipasquo and Hoover (53) obtained a solid m.p. 56° - 57°.

I.R. (nujol)

3030 (w), 2920 (s), 2850 (sh), 1720 (s), 1580 (m), 1460 (s) cm $^{-1}$.
cf. reference 53   1735 (c = o), 1590 (c = c)

NMR ($CDCl_3$)

δ_{TMs}	7.40	(1H, d)
	6.01-5.75	(2H,m)
	3.50-3.20	(2H, m)
	3.20-2.90	(2H, m)
	1.95-1.55	(2H, complex triplet)

cf. reference 53   7.56, 3.52-3.18, 3.18-2.75, 1.71.

Preparation of 5-Bromopentacyclo$[5.3.0.0.^{2,5}.0.^{3,9}.0.^{4,8}]$decan-6-one (XVIII)

The method of Dunn, Dipasquo and Hoover (53) was employed as follows :-

A solution of ketone XVII (5.28g) in ethyl acetate (220 mls) was irradiated with a 450-W Hanovia medium pressure mercury vapour lamp for 32 hours in a pyrex immersion photolysis apparatus. The solvent was removed in vacuo and the dark residue heated with boiling petroleum ether (100 mls). The insoluble dark solid remaining was removed by filtration; the filtrate was treated with activated charcoal and then cooled in a freezer. The desired product was collected as off-white crystals, m.p. 35° - 37°.

Dunn, Dipasquo and Hoover (53) obtained colourless crystals, m.p. 39° - 40°. After filtration of the products, more crystals could be produced by concentration of the remaining petroleum ether solution and further freezing.

I.R. (K.Br. disc)

2990 (m), 2960 (sh), 2920 (sh), 2850 (w), 1800 (sh), 1780 (sh), 1760 (s), 1240 (m), 1030 (m), 960 (m), 750 (m) cm^{-1}.

cf. reference 53 (c = o) 1800 (m), 1785 (sh), 1775 (s) 1765 (s), 1755 (s).

NMR. ($CDCl_3$)

δ_{TMS} 3.50 - 2.72 (6H.m)

2.55 - 2.20 (1H.m)

1.77 (2H, broad singlet)

cf. reference 53 3.68-2.72 (6H.m), 2.4 (1H.m) AB pattern at 1.79 (broad singlet).

Preparation of Pentacyclo $[4.3.0.0.^{2,5}.0.^{3,8}.0.^{4,7}]$ nonane-4-carboxylic acid (XIX)

This was prepared using the procedure of Dunn, Dipasquo and Hoover (53) as follows :-

A solution of ketone XVIII (21g, 0.093 mol) in hot 30% aqueous potassium hydroxide (350 mls) was heated at reflux for 4 hours. After cooling to room temperature, the solution was extracted with ether and then acidified with dilute hydrochloric acid. The mixture was extracted with ether, the combined extracts were dried, treated with activated charcoal and then evaporated in vacuo to give the acid as white crystals, m.p. 90° - 92° (lit. (53) m.p. 93° - 95°).

I.R. (K.Br. disc)

2990 (s), 2600 (m), 1670 (s), 1420 (s), 1320 (s), 1240 (s), 940 (m), 710 (m), cm^{-1}.

cf. reference 53 1675 cm^{-1} (acid c = o).

N.M.R. ($CDCl_3$)

δ_{TMS} 10.50 (1H.s) - disappeared on shaking with D_2O

3.60-3.10 (7H,m)

1.68 (2H,s)

cf. reference 53 11.45 (1H,s), 3.72-3.05 (7H,m) 1.72 (2H,s).

Preparation of 4-hydroxymethylpentacyclo[4.3.0.0.^{2,5}.0.^{3,8}.0.^{4,7}] nonane (XXI)

It was decided that, instead of reducing the acid XIX directly to the alcohol XXI, as carried out by Paquette et al (54) the methyl ester XX would first be prepared and then this reduced using the procedure of Paquette, Ward, Boggs and Farnham (54). In this way higher yields of alcohol were produced.

a) Methylation of Pentacyclo[4.3.0.0.^{2,5}.0.^{3,8}.0.^{4,7}]nonane-4-carboxylic acid.

Methylation of the carboxylic acid was carried out quantitatively using diazomethane, (55, 56).

The diazomethane was prepared as follows :-
15 mls. of diethyl ether, 15 mls. of ethyl digol and 5 mls of concentrated sodium hydroxide were placed in a 50 ml round-bottomed, long-necked flask connected by glass tubing to a 250 ml conical flask containing approximately 20 mls diethyl ether (the glass tubing in the second flask being below the level of the ether). The round-bottomed flask was gently heated using a water bath and the conical flask cooled by immersion in an ice-salt mixture. Nitrosan (bis-(N-methyl-N-nitroso) terephthalimide) was carefully added in small portions to the reaction mixture, the liberated diazomethane being carried over into the cooled flask by the ether vapour. The reaction was continued until the ethereal solution in the conical flask was bright yellow (ca.0.04M diazomethane) and then the flask was substituted by another and so on until sufficient diazomethane was produced.

The carboxylic acid XIX was added slowly to the yellow solution until there was only a slight excess of diazomethane present (nitrogen was liberated). The flask was allowed to stand for 30 minutes and then the ethereal solution was dried over magnesium sulphate and the ether removed in vacuo. The methyl ester XX, in the form of an oil, was sufficiently pure for use in the next step.

N.M.R. ($CDCl_3$)

δ_{TMS}	3.62	(3H,s)
	3.60-3.0	(7H,m)
	1.65	(2H,s)

b) Reduction of ester to alcohol XXI

The ether used in the reduction was dried by refluxing overnight with lithium aluminium hydride and then distilled.

To 2g of lithium aluminium hydride in 60 mls anhydrous ether was added with stirring (magnetic) a solution of 5g of homocubane-4-carboxylic acid methyl ester XX in 60 mls anhydrous ether. Upon completion of the addition, the mixture was stirred at room temperature for 2 hours and heated to reflux for 3 hours. With cooling, water was introduced until a white granular precipitate formed. The solid was separated by filtration, the dried filtrate was evaporated, and the residue was distilled to give the alcohol as a colourless oil, b.p. 75° - 80° at 0.2 mm (lit.[54] 65° - 67° at 0.05 mm).

N.M.R. ($CDCl_3$)

δ_{TMs}	3.60	(2H,s)
	3.50 - 3.0	(7H,m)
	1.63	(3H,s)

cf. reference 54 δ_{Tms} 3.60 (S.2); 3.0-3.5 (m.7); 2.0 (S.1); 1.7 (S.2).

Preparation of 4 -(3.5-dinitrobenzoyl) oxymethylpentacyclo $[4.3.0.0.^{2,5}.0.^{3,8}.0.^{4,7}]$ nonane (XXII)

This was prepared using the method given in Vogel, Practical Organic Chemistry, as follows :-

To 1g of 3.5 - dinitrobenzoyl chloride was added 0.5 ml of alcohol XXI in a conical flask. The flask was loosely corked and heated on a water bath for 10 minutes. After the mixture was cooled, 10 mls of saturated sodium bicarbonate solution were added, the resulting solid ester was broken up using a stirring rod and filtered. The solid was washed with a little sodium bicarbonate solution, followed by water and then sucked as dry as possible. The crude ester was dissolved in the minimum volume of hot ethanol and hot water was added dropwise with agitation until the solution just developed a slight turbidity that did not disappear on shaking (the mixture being immersed in a hot water bath during the recrystallisation). The solution was allowed to cool slowly, the resulting crystals filtered off and dried upon a few thicknesses of filter paper. The ester was recrystallised from 40/60 petroleum ether to give off-white crystals, m.p. 83° - 84°.

<u>I.R.</u> (K.Br disc)

3090 (w), 2970 (m), 1725 (s), 1625 (m), 1600 (w), 1540 (s), 1340 (s), 1270 (s), 1160 (m), 720 (sh), 710 (s), cm $^{-1}$.

<u>N.M.R.</u> ($CDCl_3$)

δ_{TMS}	9.30	(m,3)	Aromatic protons
	4.50	(s,2)	$-CH_2-O-$
	3.60-3.0	(m,7)	acyclic -CH-
	1.70	(s,2)	bridge $-CH_2-$

Microanalysis

Calculated for $C_{17}H_{14}N_2O_6$: C, 59.60; H, 4.19; N, 8.19

Found C, 60.00; H, 4.25; N, 7.93

Mass Spectrum

m/e M^+ 342, $C_{12}H_8N_2O_6$ 276, $C_7H_3N_2O_5$ 195

Preparation of 1 - phenyl bicyclo [4.1.0] heptane

The above compound was prepared from 1-phenyl cyclohexene by a Simmons-Smith type reaction (57) using methylene iodide and zinc-copper couple. The zinc-copper couple was prepared as follows, using LeGoff's procedure (58) :-

To a hot rapidly stirred solution of 0.5g cupric acetate monohydrate in 50 mls glacial acetic acid was added 30-35g zinc granules. This was shaken for 1-3 minutes, the solution being kept hot. The couple was allowed to settle and then as much of the acetic acid as possible was decanted taking care not to lose the couple. The dark reddish-grey couple was then washed with one 50 ml portion of acetic acid, followed by 3 x 50 mls portions of ether, the flask being shaken with each wash for 0.5 - 1 minutes. The couple was then ready for use in the next step.

64.5g of zinc-copper couple (0.50 mol) were placed in a conical flask fitted with a condenser, dropping funnel and magnetic stirrer. 100 mls. of ether were added, followed by a few mls. of methylene iodide. While the stirred suspension was kept at a gentle reflux a mixture of 39.5g phenyl cyclohexene (0.25 mol) and the remainder of the methylene iodide 60.7g total (0.35 mol) was added dropwise over a period ranging from 0.5-2 hours. The reaction mixture was stirred and refluxed for 5 days.

The ether solution was then slowly decanted from the unchanged couple into a separatory funnel containing a mixture of ice and 1 N hydrochloric acid. The ethereal solution was separated, washed with a second portion of ice - 1N hydrochloric acid, washed 3 times with water and finally dried over potassium carbonate. The ether was removed in vacuo and the product distilled to give a colourless liquid, b.p. 84° at 0.7 mm (lit. (59) b.p. 104° - 105° at 3 mm).

The reaction was much slower than expected compared with other methods quoted in the literature (58, 59), despite the addition of a crystal of iodine in later attempts to help speed the formation of the norcarane.

N.M.R. ($CDCl_3$)

δ_{TMS} 7.5 - 7.1 (m,5)

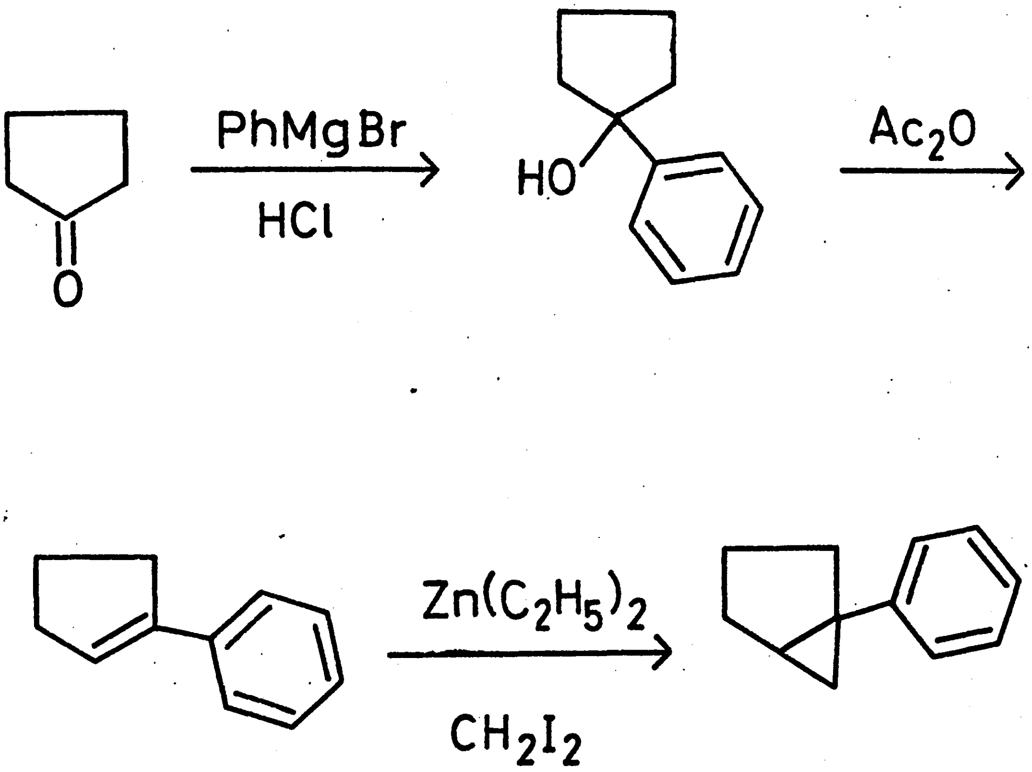
2.55 - 0.5 (m,11)

Microanalysis

Calculated for $C_{13}H_{16}$:	C, 90.64;	H, 9.36.
Found	C, 90.4;	H, 9.2.

Preparation of 1-phenyl bicyclo [3.1.0] hexane

This compound was prepared by the following synthetic scheme :



a) Preparation of 1-phenyl cyclopentene (61)

The Grignard reagent used in the first step was prepared (60) as follows :-

In a three-necked flask fitted with a separatory funnel, reflux condenser and stirrer were placed 11g magnesium. A mixture of 12g bromobenzene and 30 mls dry ether was run in and the flask was warmed gently until the reaction became rapid. Stirring was then started and the vessel was surrounded by a dish of cold water. A mixture of 63g bromobenzene and 145 mls dry ether was run in at such a rate as to cause vigorous refluxing; when the addition was complete (1 hour) the whole was stirred for ten minutes.

As soon as the reaction was completed in the Grignard preparation a solution of 33.6g (0.4 mol) cyclopentanone in 60 mls ether was added from a dropping funnel as rapidly as possible so that vigorous refluxing was maintained; about thirty minutes were required. The reaction mixture was then heated under reflux for an additional 30 minutes and allowed to stand for one hour. The magnesium complex was decomposed by the addition of 250g of ice and 40 mls concentrated hydrochloric acid. The ether layer was separated, dried with calcium chloride, filtered and the ether removed in vacuo. The resulting 1-hydroxy-1-phenyl cyclopentane was checked by n.m.r.

<u>N.M.R.</u> ($CDCl_3$)

δ_{TMS}	7.5 - 7.1	(m,5)
	2.1 - 1.8	(m,8)
	1.7	(s,1) - singlet at 1.7 disappeared on checking with D_2O

20 mls of acetic anhydride was then added to the 1-hydroxy-1-phenyl cyclopentane and the flask and contents were heated in a steam bath for 20-25 minutes. The mixture was finally distilled under reduced pressure through a Vigreux column, giving a colourless liquid, b.p. 75° - 80° at 0.5 - 0.8 mm.

I.R. (liquid film)

3080-3020 (m), 2950 (s), 2840 (s), 1600 (w), 1495 (s), 1445 (m), 755 (s), 695 (s) cm^{-1}.

N.M.R. ($CDCl_3$)

δ_{TMS} 7.5 - 7.1 (m,5)

6.1 - 6.0 (m,1)

2.9 - 2.3 (m,4)

2.3 - 1.8 (m,2)

b) Cyclisation

Synthesis of the bicyclic system proved to be much more difficult in the case of 1-phenyl cyclopentene than for the corresponding 1-phenyl cyclohexene (vide supra). LeGoff's method (58) using granular zinc-copper couple or the more reactive powdered couple failed to give significant amounts of the required product. A couple prepared according to the method of Shank and Shechter (57) also did not give the bicyclic compound. An alternative method (62) employing iodomethyl zinc iodide, prepared from zinc iodide and diazomethane failed to give the required product. Finally, reaction of the olefin with diethyl zinc was found to be successful in giving the bicyclic compound.

The diethyl zinc was prepared (63) as follows :-

In a 250 mls flask, provided with a reflux condenser (fitted with a drying tube) and a magnetic stirrer was placed 65g powdered zinc-copper couple. To this was added 78g ethyl iodide; the stirrer was started and the mixture heated to refluxing. After 0.5 hour, the reaction started and the heating was switched off. The flask was left a further 0.5 hour;

on cooling to room temperature the mixture solidified.

Rather than attempt to isolate the diethyl zinc by distillation it was decided to use the solid immediately in the next step. The procedure of Furukawa, Kawabata and Nishimura (64) was employed with some modifications :

A solution of 5g (0.04 mol) of 1-phenyl cyclopentene in 50 mls benzene was added to the reaction flask, containing the diethyl zinc from the previous step. Methylene iodide (28g, 0.10 mol) was added dropwise with stirring to the mixture under nitrogen at 60° C during 8 - 10 hours. The heating was continued overnight. 50 mls of 1% aqueous hydrochloric acid were added to the cooled reaction mixture with stirring and the remaining zinc-copper couple was filtered off. The organic layer was separated, washed with 1% aqueous hydrochloric acid, water, and dilute aqueous sodium bicarbonate and dried over molecular sieves. The solvent was removed in vacuo and the product distilled to give a colourless liquid, b.p. 55° - 60° at 1 mm. (lit. (59) b.p. 93° - 94° at 3 mm).

N.M.R. ($CDCl_3$)

δ_{TMS}	7.40 - 7.15	(m,5)
	2.1 - 1.2	(m,7)
	1.0 - 0.6	(m,2)

Microanalysis

Calculated for	$C_{12}H_{14}$:	C, 91.08;	H, 8.92
Found		C, 90.45;	H, 9.20

Preparation of Phenyl cyclopropane

Phenyl cyclopropane was synthesised (65) by first preparing 5-phenyl-2-pyrazoline from cinnamaldehyde and hydrazine and then carrying out a Kishner-Wolf reduction using potassium hydroxide as a catalyst.

a) Preparation of 5-phenyl-2-pyrazoline

Freshly distilled cinnamaldehyde (13.2g) was added to a mixture of 90% hydrazine (12 mls) and ethanol (40 mls). Alteration of this order causes precipitation of a large amount of azine. The mixture was refluxed for one hour, ethanol was distilled off in vacuo and the residue was dissolved in ether and washed with water. Distillation gave a yellow oil, b.p. 100° at 0.8 mm, which was a mixture of 5-phenyl-2-pyrazoline and cinnamaldehyde hydrazone. Redistillation gave the pure product as a colourless oil, b.p. 87° at 0.2 mm (lit. (65) b.p. 135-8° at 9 mm).

The product gave no precipitate with ethanolic cinnamaldehyde and when dissolved in cold, dilute hydrochloric acid, the addition of sodium nitrate produced the nitroso derivative as a pale yellow precipitate, m.p. 70° - 71°.

N.M.R. ($CDCl_3$)

δ_{TMS}	7.4 - 7.2	(m,5)
	6.8	(m,1)
	5.8 - 5.2	(broad s, 1)
	4.85 - 4.55	(3 singlets integrating as 1 proton)
	3.4 - 2.4	(6 multiplets integrating as 2 protons)

Microanalysis

Calculated for $C_8H_{10}N_2$:	C, 73.96;	H, 6.85;	N, 19.18.
Found	C, 74.12;	H, 6.74;	N, 18.75.

b) Reduction to phenyl cyclopropane

The pure pyrazoline (15.6g) was heated under reflux at 200° C with potassium hydroxide (0.1g) for 1.5 hours. The product was shaken with dilute hydrochloric acid; the neutral fraction gave phenyl cyclopropane as a colourless liquid, b.p. 72° at 20 mm (lit. (65) b.p. 172° - 174°).

N.M.R. ($CDCl_3$)

δ_{TMs}	7.05	(m,5)
	1.85	(m,1)
	0.98	(m,2)
	0.75	(m,2)

cf Varian N.M.R. spectra catalogue, Vol. 2 spectrum 528.

Microanalysis

Calculated for C_9H_{10}	C, 91.47;	H, 8.53
Found	C, 91.5;	H, 8.6.

Preparation of 7-phenyl norcarane

7-phenyl norcarane was prepared by the method of Hodgkins, Woodyard and Stephenson (66), involving the formation of 7-chloro-7-phenyl norcarane from cyclohexene and benzal chloride in the presence of strong base and then reduction of the chloro compound to the required products with activated zinc in the presence of sodium ethoxide.

a) Preparation of 7-chloro-7-phenyl norcarane.

Potassium t-butoxide was prepared by adding 500 mls of dry t-butyl alcohol to a 1 litre four-necked flask equipped with a condenser fitted with a calcium chloride tube, mechanical stirrer, thermometer and a stopper. The temperature was adjusted to approximately 75° C and then potassium metal (10g, 0.256 mol) was added in small pieces. After completion of the reaction, the excess t-butyl alcohol was distilled in vacuo.

7-chloro-7-phenyl norcarane was prepared by adding cyclohexene (200 mls) to the potassium t-butoxide prepared above. Purified benzal chloride (41g, 0.255 mol) was added to the stirred refluxing solution dropwise through a dropping funnel over a period of 1.5 hours. The reaction mixture was refluxed for an additional 6 hours, cooled and 250 mls of water added. The organic layer was separated and washed with water until the aqueous layer was neutral and then it was washed with a saturated solution of sodium chloride and dried over calcium chloride. The excess cyclohexene was distilled in vacuo and as the product is unstable at high temperature (67), the resulting residue was distilled at low pressure to give a colourless liquid, b.p. 90° at 0.4 mm (lit. (66) b.p. 170° - 173° at 33 mm).

N.M.R. ($CDCl_3$)

δ_{TMS} 7.6 - 7.4 (m,5)
2.4 - 1.75 (m,4)
1.75 - 1.20 (m,4)
1.15 - 0.70 (m,2)

b) Reduction to 7-phenyl norcarane

Activated zinc dust was prepared by adding hydrochloric acid (4N) to zinc dust which had been placed in a beaker. The mixture was stirred for 1 minute and then filtered and washed quickly with large volumes of 10% sodium hydroxide, water, 25% ethanol, absolute ethanol, acetone, absolute ether and then dried under vacuum on a hot plate at 200° C for 1 hour.

The 7-chloro-7-phenyl norcarane was reduced using zinc dust as follows :-

A 5% solution of sodium ethoxide was prepared from 300 mls of ethanol and 12g (0.522g.atom) of sodium. After completion of the reaction, 35g of activated zinc dust and 25g (0.121 mol) of 7-chloro-7-phenyl norcarane were added. The mixture was refluxed with vigorous stirring for 40 hours, cooled and filtered. Water was added to the filtrate and the aqueous solution extracted with ether. The ethereal extract was washed with water and dried over calcium chloride. The ether was evaporated in vacuo and the residue distilled to give 7-phenyl norcarane as a colourless liquid, b.p. 108° at 3 mm (lit. (66) b.p. 127° - 128° at 13 mm) having a characteristic odour.

N.M.R. ($CDCl_3$)

δ_{TMs} 7.4 - 7.0 (m,5)

2.1 - 1.5 (m,4)

1.5 - 1.0 (m,4)

1.0 - 0.6 (m,3)

Microanalysis

Calculated for	$C_{13}H_{16}$	C, 90.64;	H, 9.36.
Found		C, 90.59;	H, 9.2

Kinetic Experimental

a) Aromatic Nitration

Reagents

Analar acetic anhydride was used without further purification. Toluene was washed with concentrated sulphuric acid, water, dilute sodium hydroxide, dried over molecular sieves, and distilled twice through a 6" column filled with glass beads. Analar benzene was used without further purification. The remaining substrates were distilled at least twice through a 6" Vigreux column and checked by n.m.r. for trace impurities.

Pure nitric acid was prepared according to the method given in Vogel, - Practical Organic Chemistry, as follows :-

Nitric acid was distilled at reduced pressure from a 50/50 mixture of fuming nitric acid (S.G.1.5) and concentrated sulphuric acid as a red-brown liquid. This was treated with urea and nitrogen was bubbled through at 60° until the liquid became colourless. Further distillation from concentrated sulphuric acid at reduced pressure gave a pale yellow liquid. On repeating the treatment of bubbling nitrogen through, while heating at 60° C, for approximately two hours, followed by distillation at reduced pressure pure nitric acid as a colourless liquid was obtained. This was stored in a sealed, brown bottle at 0° C.

Kinetic Measurements

The procedure of Schofield et al (68) was employed. Rate constants were determined using a Cary Model 14 spectrophotometer, thermostatted at 25° C ± 0.1° c, the temperature being checked before and after each kinetic run. 10 mm Spectrosil quartz U.V. cells, fitted with Teflon stoppers, were used.

Acetyl nitrate solutions (approximately 0.3 M) were prepared by weighing the required amounts of nitric acid into known volumes of acetic anhyrdride, the solutions being kept at room temperature for 15 minutes before use. First-order kinetics were obtained by using an excess of acetyl nitrate over aromatic compound.

Stock solutions of substrates were prepared by measuring the required amount of hydrocarbon into known volumes of acetic anhydride; 10^{-1} M for toluene, 0.5 M for benzene and 5×10^{-2} M for the remaining aromatic compounds.

The following procedure was used for all substrates except benzene :

2.5 mls of acetyl nitrate solution were pipetted into a U.V. cell; the cell was stoppered and thermostatted at 25° C. 25 μls of stock solution were injected, giving a substrate concentration of 10^{-3} M for toluene and 5×10^{-4} M for the other compounds; the solution was stirred using a glass rod and the change in absorbance at 340 nm wavelength was measured, acetic anhydride being used as a blank.

As the nitration of benzene proceeded much more slowly than for the other substrates the above method had to be modified. It was found that the absorbance of the acetyl nitrate solution varied slightly over long periods of time. To counteract this, 2.5 mls of the same acetyl nitrate solution were pipetted into the blank cell as in the reaction cell. Hence, any change in absorbance was due to nitration of the substrate alone. 25 μl of benzene stock solution (0.5 M) were injected into the reaction cell, giving a substrate concentration of 5×10^{-3} M, the change in absorbance being measured as previously. The runs were followed for 48 hours.

For the shorter kinetic runs 35-45 values were used, taken directly from the chart. However, for the longer runs (i.e. benzene) the output from the recorded was fed into a Solartron Compact Data Logger which digitised the absorbance reading, the values (200-220) being punched on 5-channel paper tape. The first order rate constants were determined using a generalised least-squares program, written by Professor B. Capon, following the procedure of Wentworth (69) and Deming (70). Evaluation was performed on a Digico Micro 16-P computer.

b) Kinetics of Solvolysis of 4-(3.5-dinitrobenzoyl)oxymethyl pentacyclo$[4.3.0.0.^{2,5}.0.^{3,8}.0.^{4,7}]$nonane (XXII)

Reagents

0.01 M sodium hydroxide was prepared by diluting 10 mls of a standard, carbonate-free, molar solution of sodium hydroxide (supplied by Hopkin and Williams) to one litre using distilled water which had been degassed. The solution was stored in an aspirator fitted with a soda-asbestos filter. The molarity of this solution was checked by titration against a 0.01 M solution of 3,5-dinitrobenzoic acid, prepared by dissolving recrystallised and dried 3,5-dinitrobenzoic acid in 80% acetone-water.

80% acetone-water was prepared by refluxing Analar acetone over calcium chloride for 2 hours, then distilling through a Vigreux column, the centre cut being taken. Four volumes of dried acetone were added to one volume of degassed, distilled water.

The ester XXII was recrystallised twice from 40/60 petroleum ether before use. A 0.01 M solution of the ester was prepared by dissolving a known weight of the ester in 80% aqueous acetone. This was stored in a sealed flask at 0° C.

Kinetic Measurements

The ampoule method (71) was used. A thermostatted oil bath, heated by 2 immersion heaters controlled by a relay system and contact thermometer, was set at 90° C. 5 mls of 0.01 M solution of the ester were pipetted into a glass ampoule which was then sealed, covered with wire gauze and placed in the oil bath. After a certain time the ampoule was removed, cooled in a solid carbon-dioxide -acetone bath, broken and the contents emptied into a 10 ml beaker. The solution was titrated against standard 0.01 M sodium hydroxide using a Radiometer type T.T.T.1 automatic titrator, set at an end-point setting of pH 7.7. A glass/calomel electrode system was used.

The rate constant was estimated using the standard first-order rate equation.

Results

a) Aromatic Nitration

TABLE VI

Substrate	Rate Constant (s^{-1})	Weighted Average of rate constants (s^{-1})	Standard Deviation (%)	k, rel
Benzene	4.641×10^{-6} 4.374×10^{-6} 5.246×10^{-6}	4.690×10^{-6}	9.67	1
Toluene	2.373×10^{-4} 2.471×10^{-4} 2.490×10^{-4}	2.402×10^{-4}	3.39	51
Phenyl Cyclopropane	1.086×10^{-3} 1.040×10^{-3} 1.441×10^{-3} 1.268×10^{-3}	1.141×10^{-3}	17.46	243
1-Phenyl Norcarane	4.094×10^{-4} 4.688×10^{-4} 4.735×10^{-4} 4.000×10^{-4} 3.872×10^{-4} 4.299×10^{-4} 4.672×10^{-4} 4.018×10^{-4}	4.412×10^{-4}	8.47	94
7-Phenyl Norcarane	4.870×10^{-3} 4.975×10^{-3} 4.502×10^{-3}	4.839×10^{-3}	5.33	1031
1-Phenyl Bicyclo [3.1.0] hexane	2.083×10^{-3} 1.834×10^{-3} 1.722×10^{-3} 2.306×10^{-3}	1.955×10^{-3}	13.49	417

b) Solvolysis of ester XXII

TABLE VII

Time	Titre (mls)	pH at end-point	Rate constant[a] (s^{-1})
18 hours	0.11 0.09	8.75 7.80	1.762×10^{-7}
24 hours	0.16 0.12	9.1 8.9	3.306×10^{-7}
7 days	0.59 0.43	7.65 8.10	1.782×10^{-7}

a 80% aqueous acetone at 90° C. Rate constant calculated by averaging titres and substituting in first-order rate equation.

Charge-Transfer Measurements

The charge-transfer complexes were prepared according to the procedure of E.M. Voigt and C. Reid (27).

Reagents

Tetracyanoethylene was recrystallised twice from chlorobenzene and dried. The hydrocarbons were twice distilled through a Vigreux column before use. Dichloromethane was purified by washing with 5% sodium carbonate solution, followed by water, dried over anhydrous calcium chloride, and then fractionated twice.

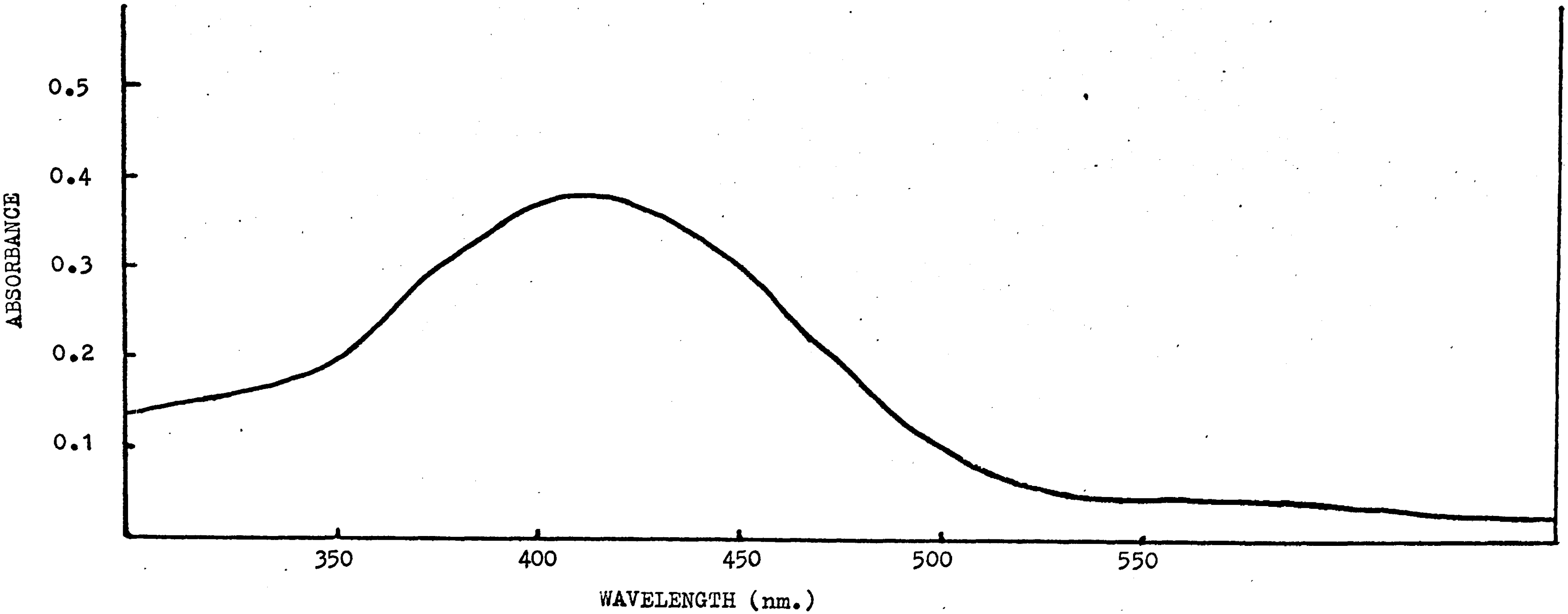
Procedure

A 2×10^{-2} M stock solution of T.C.N.E. in dichloromethane and a 10^{-1} M stock solution of each of the substrates were prepared. 1.25 mls of the hydrocarbon stock solution were pipetted into a 10 mm quartz U.V. cell followed by 1.25 mls of the T.C.N.E. stock solution. The cell was stoppered and the spectrum of the resulting coloured solution was recorded using an Unicam SP8000 U.V. recording spectrophotometer and a Cary Model 14 recording spectrophotometer, thermostatted at 25° C $\pm$ 0.1° C, against a blank of the hydrocarbon stock solution diluted to the same concentration of hydrocarbon (5×10^{-2} M) as in the sample cell using dichloromethane.

The spectra recorded on the Unicam SP8000 spectrophotometer for toluene, phenyl cyclopropane, 1-phenyl norcarane, 7-phenyl norcarane and 1-phenyl bicyclo [3.1.0] hexane are shown overleaf.

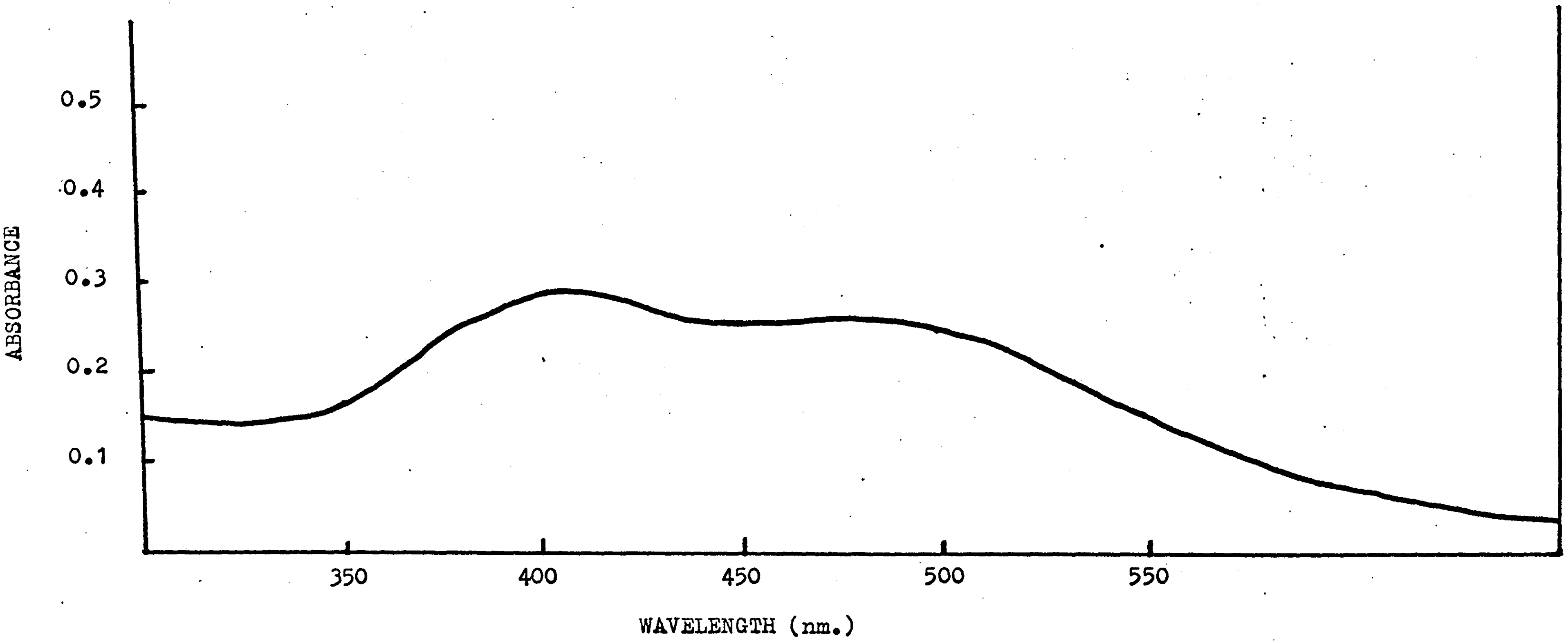
1. <u>CHARGE TRANSFER SPECTRUM OF TOLUENE-T.C.N.E. COMPLEX</u>

(Recorded using an Unicam SP8000 U.V. Spectrophotometer).



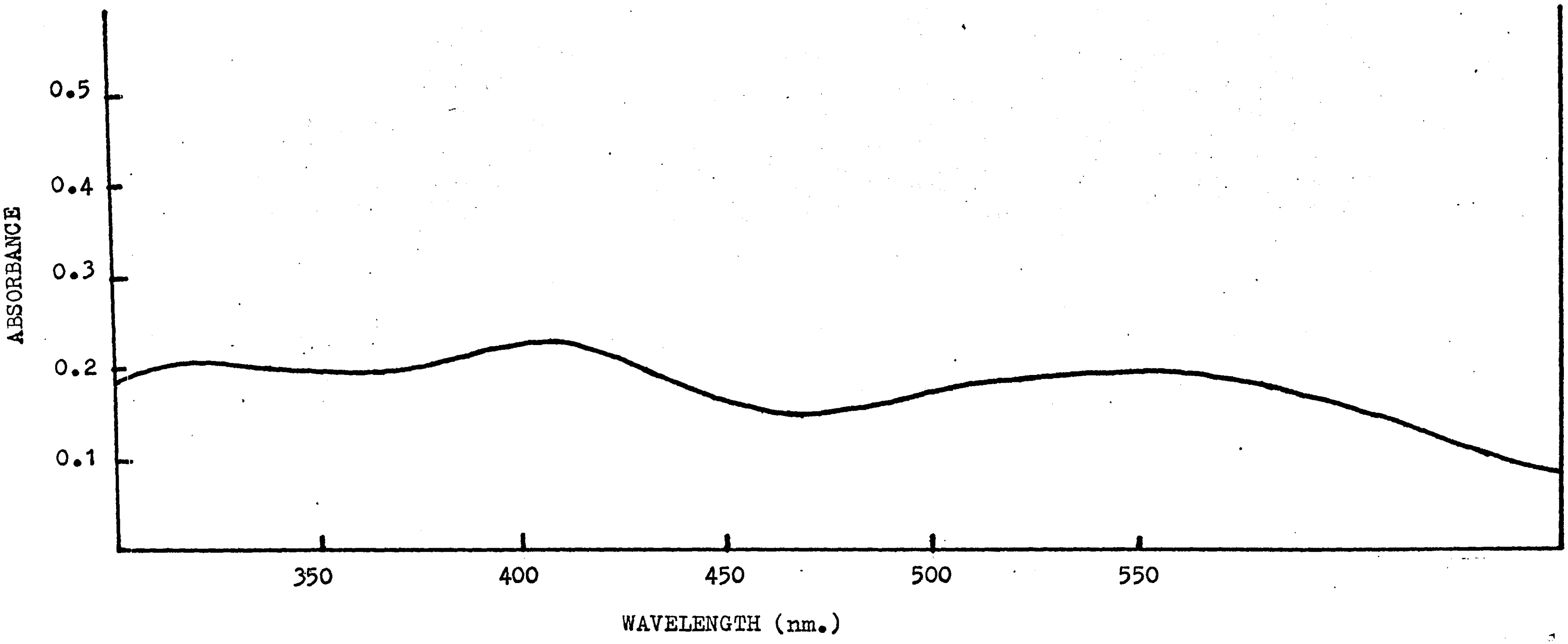
2. CHARGE TRANSFER SPECTRUM OF PHENYL CYCLOPROPANE-T.C.N.E. COMPLEX

(Recorded using an Unicam SP8000 U.V. Spectrophotometer).



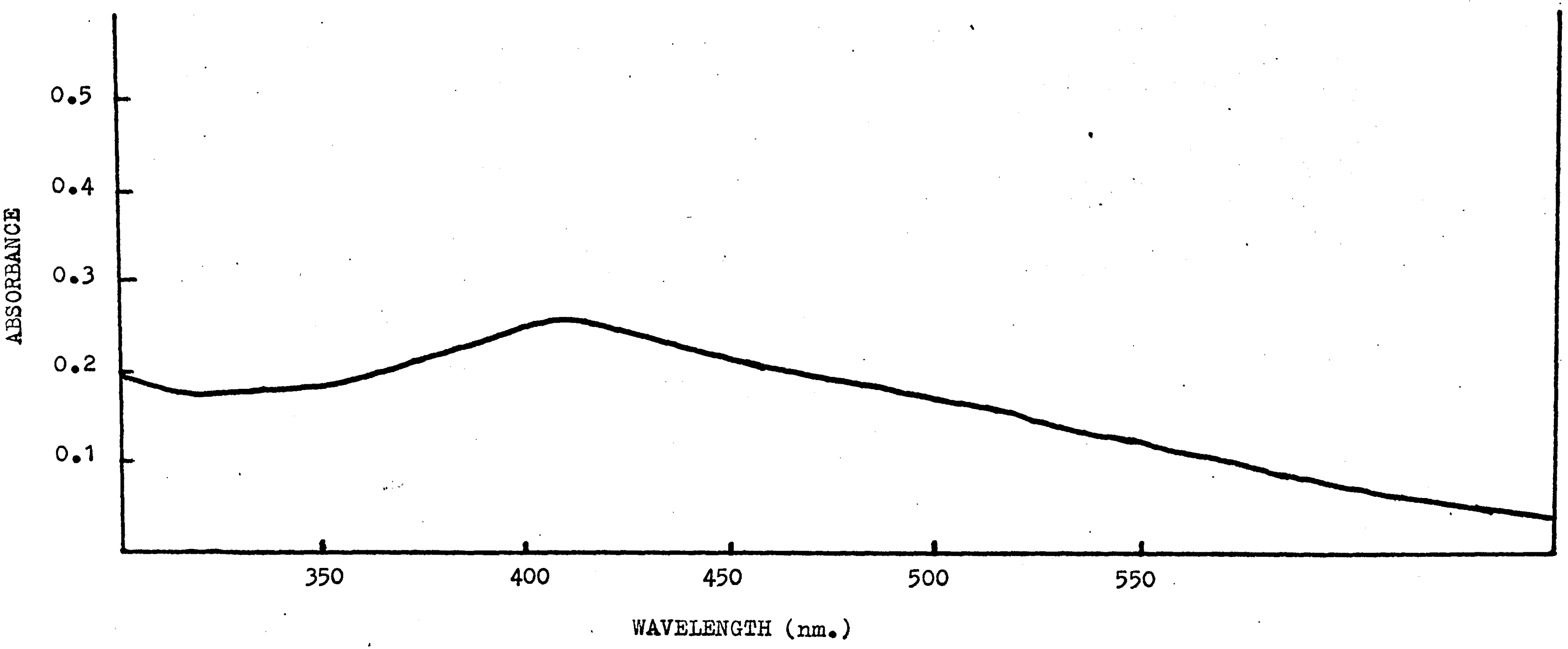
3. <u>CHARGE TRANSFER SPECTRUM OF 1-PHENYL NORCARANE-T.C.N.E. COMPLEX</u>

(Recorded using an Unicam SP8000 U.V. Spectrophotometer).



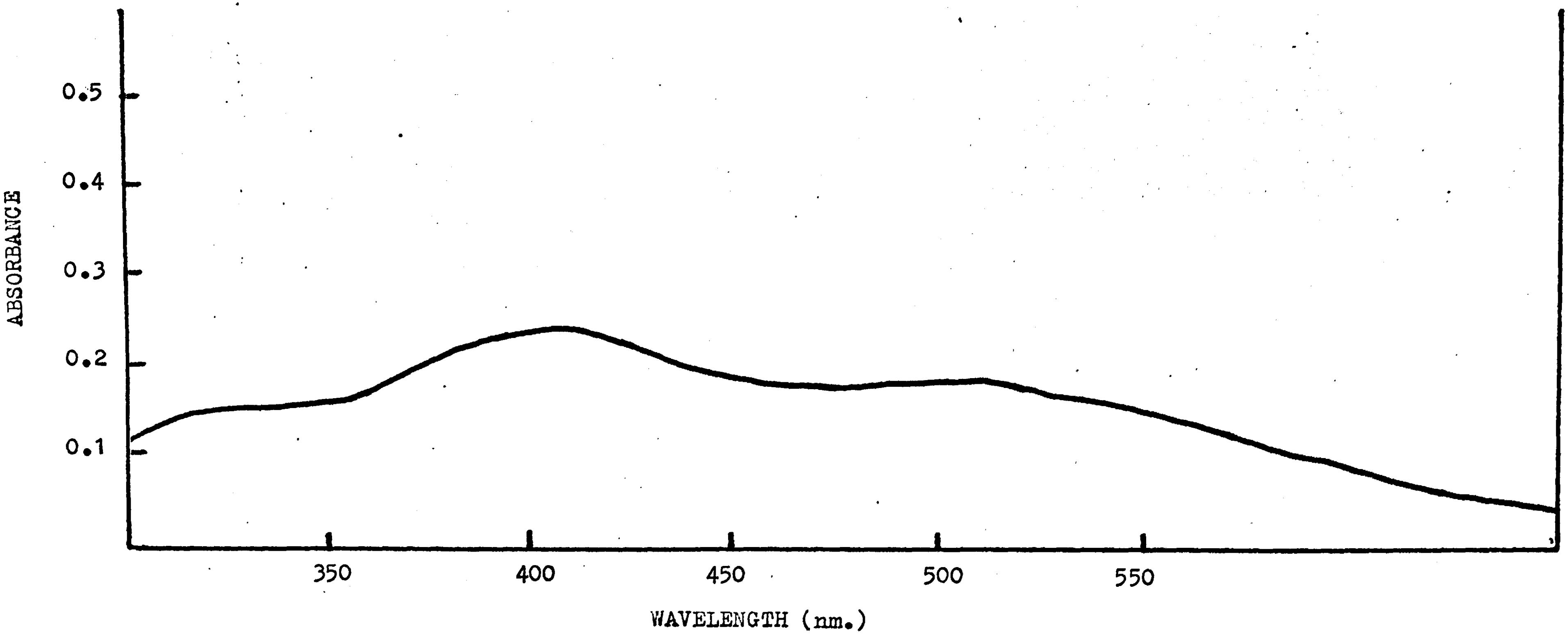
4. CHARGE TRANSFER SPECTRUM OF 7-PHENYL NORCARANE-T.C.N.E. COMPLEX

(Recorded using an Unicam SP8000 U.V. Spectrophotometer).



5. <u>CHARGE TRANSFER SPECTRUM OF 1-PHENYL BICYCLO [3.1.0] HEXANE-T.C.N.E. COMPLEX</u>

(Recorded using an Unicam SP8000 U.V. Spectrophotometer)



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