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HYDROGEN ABSTRACTIONS FROM POLYARYLETHANES. EVIDENCE FOR ANCHIMERIC ASSISTANCE BY A MIGRATING PHENYL.

City University of New York PH.D. 1979

Hydrogen Abstractions From Polyarylethanes. Evidence For Anchimeric Assistance By A Migrating Phenyl

by

Veeramac V.K. Prasad

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1979

This dissertation has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

7 September 1979
date

Herbert Meislich
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Abstract

The reaction of 1,1,1,2-tetraphenylethane, UTPE 1 , with either Br_2 or with NBS yielded solely tetraphenylethylene, TPE 3 , under free radical conditions. The reaction of UTPE with chlorine or sulfuryl chloride , under similar conditions in CCl_4, however, gave little or no TPE. Starting material, UTPE, was recovered unchanged. The lack of reaction with chlorine atoms in CCl_4 is attributed to a complexation of the chlorine atoms to the phenyl rings of substrate as well as to an unique trapping of the chlorine atoms within the trityl moiety of the substrate. When the solvent was changed to benzene or to carbon disulfide, the solvent-complexed chlorine atoms were now able to convert UTPE to TPE in about 35-40% yield. Besides TPE, 9,10-diphenylphenanthrene, DPP, was also formed. In order to determine whether DPP was formed from the initially formed radical 1a , $Ph_3C\text{-}\dot{C}HPh$, or from the rearranged radical 1b , $Ph_2\dot{C}\text{-}CHPh_2$, it was necessary to generate radical 1b from an alternate source. To this end 1,1,2,2-tetraphenylethane, STPE, was subjected to the chlorination in benzene and in CS_2, since on hydrogen abstraction from STPE radical 1b is formed directly. Analysis of the product mixture however, showed the absence of DPP. Thus it may be inferred that the formation of DPP occurs from 1a rather than from 1b in the chlorination of UTPE. On this basis, the variance in product distribution in the reactions of UTPE with Br· and Cl· was attributed to the involvement of different intermediates. The first intermediate in the attempted chlorination of UTPE

is $Ph_3C\text{-}\dot{C}HPh$, 1a , but the first formed intermediate in the attempted bromination is either a phenyl-bridged radical or the rearranged radical 1b , formed by passing through a phenyl-bridged transition state.

Synchronous migration of phenyl was then tested for by comparing the rates of reaction of UTPE and neopentylbenzene, NPB, with bromine. Based on steric and electronic effects, the trityl group (larger and transition state destabilising) should slow down the rate compared to the t-butyl group (smaller and stabilising by electron donation). Contrary to expectations, the two substrates, UTPE and NPB, had almost identical rates. The unexpected rate enhancement observed in the case of UTPE is attributed to anchimeric assistance in the transition state due to the presence of a phenyl-bridged radical.

In a Hammett sigma-rho study, the bromination of 2-substituted tetraphenylethanes showed a rho value of -1.506 which was only 12% more negative than the rho value for the bromination of substituted toluenes. Since UTPE is an α-substituted toluene (the α-substituent being the trityl moiety) it was expected that on the basis of the steric bulk and the electron withdrawing character of the trityl group, the rho value would be considerably more negative. The smaller rho value obtained is consistent with the involvement of anchimeric assistance, which reduces the substituent dependency in a Hammett sigma-rho study.

The anchimeric assistance involved in the conversion of UTPE to TPE was then calculated to have a value of 210. This is a lower limit because in the calculations it was assumed that the steric effect of the trityl group and that of the t-butyl are about the same, when in reality the trityl group is known to be considerably larger.

In order to assess the importance of relief of steric strain that might be involved in the synchronous migration of the phenyl, the bromination of the closely related compound, 9-benzyl-9-phenylfluorene, BPF, was studied. Based on the relative stabilities of the initial and the corresponding rearranged radicals, a rearrangement involving an aryl or phenyl is more likely than in UTPE. Relief of steric strain, however, would not be an important factor in the case of BPF. Since BPF was found to brominate normally without rearrangement, the less favored rearrangement observed in the case of UTPE is therefore ascribed in part to relief of steric strain rather than solely to the relative stabilities of the initial and rearranged radicals, as is often the case in most radical rearrangements.

On the basis of the relative stabilities of initial and rearranged radicals, the 2,2,2-triphenylethyl radical should be extremely prone to rearrangement. An attempt was therefore, made to generate this radical by the reaction of 1,1,1,-triphenylethane with bromine. However, mostly starting material was only recovered. The lack of reaction is attributed

to deactivation of the methyl group by the electron-withdrawing trityl group.

The reaction of pentaphenylethane was also studied, since rearrangement in the intermediate penataphenylethyl radical is degenerate and its fate, therefore of interest. No brominated alkane was detected. Surprisingly products involving C-C bond cleavage of the starting material, viz. N-trityl succinimide and tetraphenylethane, were detected. Mechanisms for their formation are speculated upon.

Finally the bromination of UTPE and toluene was studied under conditions where oxygen was totally excluded. The rates of bromination in both cases were found to be slower than when the brominations were carried out under ambient conditions. It is postulated that the hydrogen bromide formed is oxidised to bromine by oxygen and, thus, additional bromine atoms further generated. The addition of epoxides, which trap HBr, under ambient conditions was found to slow down the rate of bromination, lending credence to the hypothesis.

Acknowledgements

Finished, it's finished, nearly finished,
it must be nearly finished.
Grain upon grain, one by one, and one day,
suddenly, there is a heap, a little heap,
the impossible heap.

Samuel Beckett, "Endgame"

I would like to express, first and foremost, my immense gratitude to my advisor, who was everything a mentor was supposed to be and more. I deem my growth as a thinking chemist and the training of my scientific wits under his guidance more important than the successful culmination of this research project.

I would like to thank the members of my committee, Professors N.Indictor, N.McKelvie, and M.H.J.Wijnen, for their many useful comments and advice.

To my co-Worker, Ms. Claude Gal, who helped create a working atmosphere that exemplified cooperation and, for supplying the French clues (among others) to the N.Y.Times Crossword puzzles, "merci"

Thanks are also due to Dr.T.Halgren for many useful and enlightening discussions on this research project.

Table of Contents

List of Tables

List of Spectrum

Historical

It has been shown that the reaction of 1,1,1,2-tetraphenylethane, UTPE 1 , with N-bromosuccinimide yields solely tetraphenylethylene, TPE 3 , instead of the expected bromo compound 2. The mechanism for the conversion of UTPE 1 to TPE 3 was postulated as shown below:[1]

$$\underset{\underline{1}}{Ph_3C\text{-}CH_2Ph} + Br\cdot \longrightarrow \underset{\underline{1a}}{Ph_3C\text{-}\dot{C}HPh} + HBr$$

$$\underline{1a} + Br_2 \not\longrightarrow \underset{\underline{2}}{Ph_3C\text{-}\underset{Br}{C}HPh} + Br\cdot$$

$$\underline{1a} \xrightarrow[\text{migration}]{\text{Phenyl}} \underset{\underline{1b}}{Ph_2\dot{C}\text{-}CHPh_2}$$

$$\underline{1b} \xrightarrow{Br\cdot \text{ or } Br_2} Ph_2C{=}CPh_2 + HBr$$

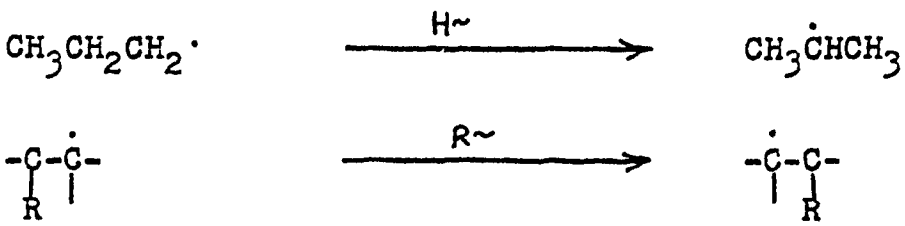
$$\underline{3}$$

Neopentylbenzene, NPB 4 , on the other hand, brominated normally to yield the expected 1-bromo-2,2-dimethyl-1-phenylpropane, 5 .[2]

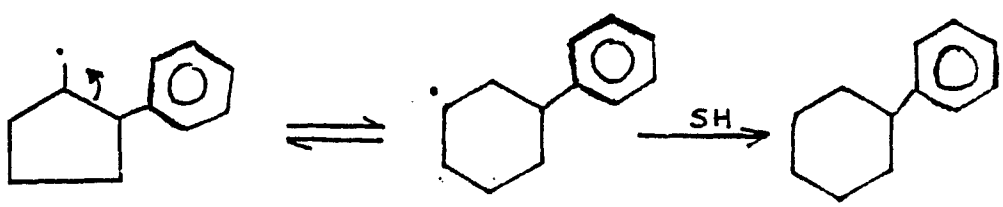
$$\underset{\underline{4}}{(CH_3)_3C\text{-}CH_2Ph} + Br\cdot \longrightarrow \underset{\underline{4a}}{(CH_3)_3C\text{-}\dot{C}HPh} + HBr$$

$$\underline{4a} + Br_2 \longrightarrow \underset{\underline{5}}{(CH_3)_3C\text{-}\underset{Br}{C}HPh} + Br\cdot$$

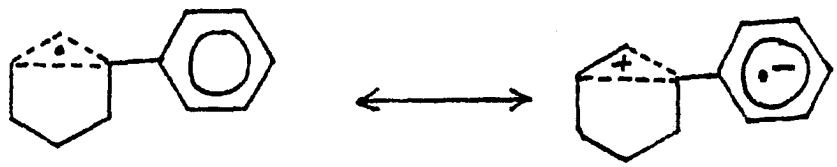
Rearrangements involving a 1,2-shift of a group or atom are fairly common in reactions involving cationic intermediates. However, such rearrangements are not as common in radical reactions. The only groups observed to undergo a 1,2-shift are aryl and vinyl groups, chlorine and bromine, and certain acyl functions.[3] A true 1,2-shift of a hydrogen atom or an alkyl has seldom been observed.



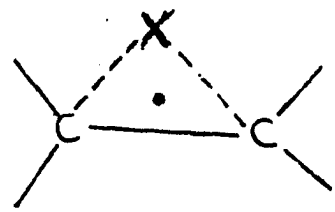
Recently, however, Walling and Cioffari claim to have provided the first clear-cut case of a simple radical rearrangement involving an intramolecular 1,2-alkyl migration in the example shown below:[4a]



However, they state that since rearrangement occurs here, but not in the several other alkyl systems they studied, the transition state for the migration may involve considerable carbonium ion character.



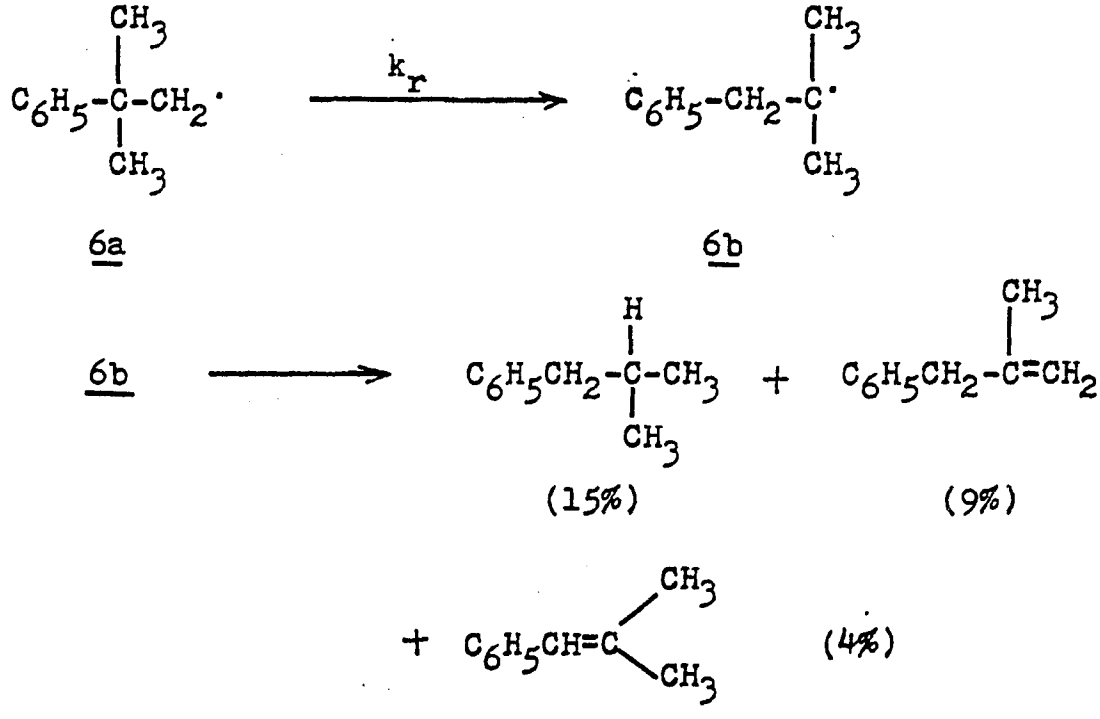
The reason why alkyl groups and hydrogen atoms fail to migrate has been attributed to the fact that such rearrangements would contravene the conservation of orbital symmetry.[4] In order for migration to occur there must exist some bridging of the migrating group X in the transition state as shown below:



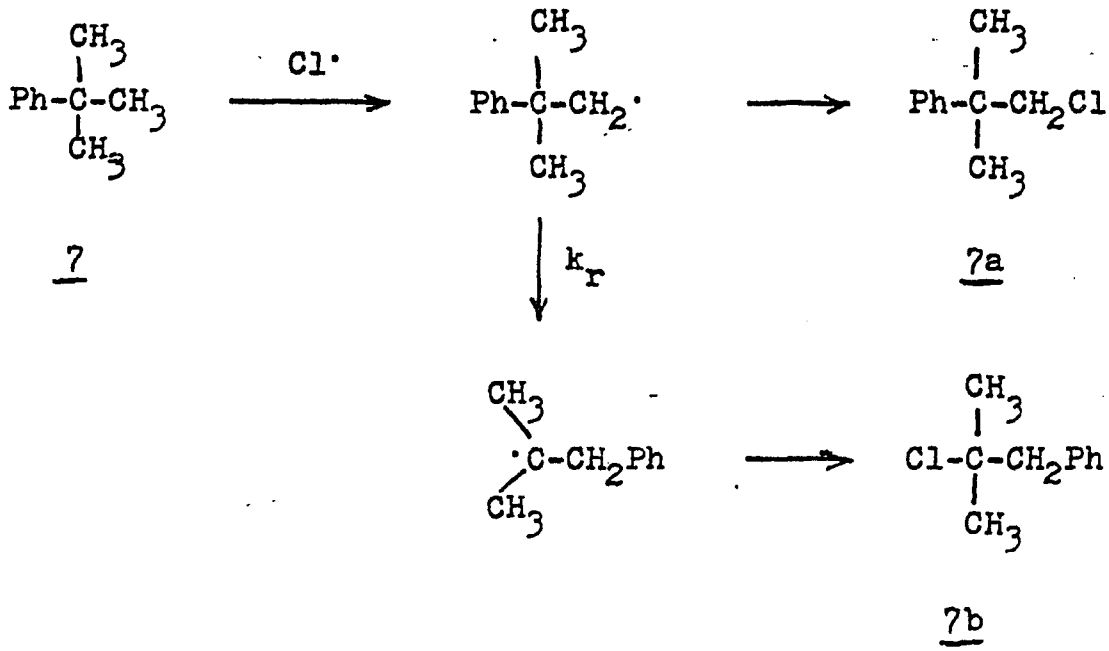
A bridged transition state involves one bonding and two antibonding orbitals.[4] Using this model the cationic migration of an alkyl group is permissible, the two electrons involved in the migration being placed in the bonding orbital. However, the extra electron of the radical species must be placed in the antibonding orbital and the energy of the transition state then becomes prohibitive. This restriction does not apply to aryl

vinyl groups, or to second-row elements because of their ability to provide low-energy molecular orbitals to accomodate the extra electron.

The first free radical rearrangement, the neophyl rearrangement was discovered by Urry and Kharasch in 1944.[5] They showed that neophyl chloride reacted vigorously in the presence of cobaltous chloride to give t-butylbenzene (27%), isobutylbenzene (15%), 2-methyl-3-phenylpropane (9%) and dimethylstyrene (4%). It was concluded that the neophyl radical, 6a , had rearranged to the 2,2-dimethylphenethyl radical, 6b .

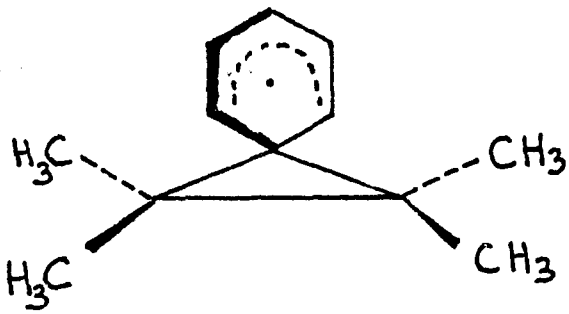


A 1,2-phenyl shift has also been proposed to occur during the photochlorination of t-butylbenzene 7 in the gas phase at 190-200° because a minor amount of rearranged chloride, 7b , was produced. [6]

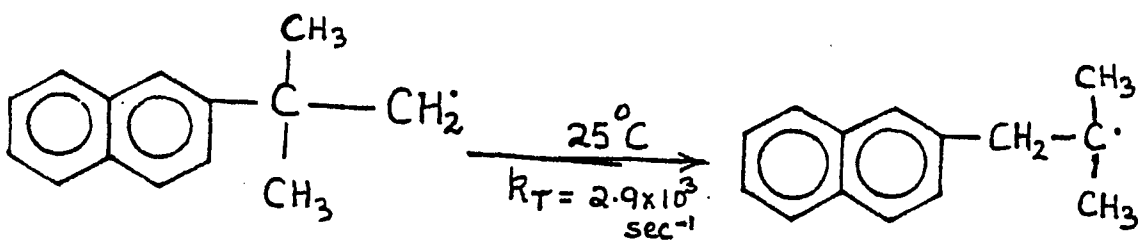


7 7a 7b

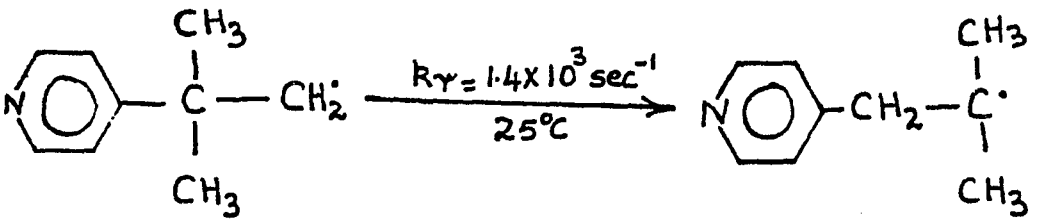
Although the neophyl rearrangement was the first free radical rearrangement to be discovered it requires quite a large activation energy (E_{act}=13.6 kcal/mol) and so it is a relatively slow process (k_r = 59 sec^{-1} at 25°C). The rearrangement of the phenyl proceeds through a spiro (2.5) octadienyl type of intermediate or transition state:



It is clear that this rearrangement ought to be accelerated if this structure were to be stabilised by better delocalisation of the unpaired electron into the aromatic ring. For this reason, the analagous rearrangements involving the naphthyl ring:



and the 4-pyridyl ring,



are appreciably faster than the neophyl rearrangement. [7]

Radical rearrangements during halogenation occur only under forcing conditions, as in the case of the photochlorination of t-butylbenzene around 200°. The liquid phase chlorination of t-butylbenzene, 7 , under less rigorous conditions, yields only the unrearranged chlorinated product. The absence of rearrangement has been explained as being due to the fact that the rate of interaction of the neophyl radical and sulfuryl chloride is faster than the rate of rearrangement.[8] Even rearrangements occuring during decarbonylation of aldehydes are strongly dependent on the lifetime of the initially formed radical. Thus Winstein, Heck, and Rapporte, [9] and Wilt and Phillip [10] have shown that the extent of rearrangement decreases on the addition of a good hydrogen donor e.g.thiophenol.

The occurence of rearrangement, moreover, is related to the stabilities (relative) of the rearranged and unrearranged radicals as shown in Table 1. In all cases, it will be noted that rearrangement occurs only when a more stable radical is formed.

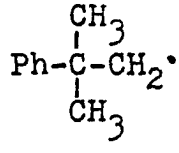
Table 1: 1,2-Phenyl Shifts During Decarbonylations

Initial Radical source	Rearranged Radical	% Rearrangement	Ref
$Ph_3C\text{-}CH_2^{\cdot}$	$Ph_2\dot{C}\text{-}CH_2Ph$	100	11
$Ph_2C(CH_3)\text{-}CH_2^{\cdot}$	$Ph\text{-}\dot{C}(CH_3)\text{-}CH_2Ph$	100	12
$Ph\text{-}C(CH_3)_2\text{-}CH_2^{\cdot}$	$(CH_3)_2\dot{C}\text{-}CH_2Ph$	57	13
$PhCH_2\text{-}\dot{C}(CH_3)$	$\dot{C}H_2\text{-}C(CH_3)_2(Ph)$	0	12

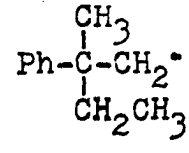
Table 1: 1,2-Phenyl Shifts During Decarbonylations

Initial Radical	Rearranged Radical	% Rearrangement
$Ph_3C-CH_2\cdot$	$Ph_2\dot{C}-CH_2Ph$	100 [11]
$Ph_2-\overset{H_3C}{\overset{\vert}{C}}-CH_2\cdot$	$Ph-\dot{\overset{H_3C}{\overset{\vert}{C}}}-CH_2Ph$	100 [12]
$(CH_3)_2\overset{Ph}{\overset{\vert}{C}}-CH_2\cdot$	$(CH_3)_2\dot{C}-CH_2Ph$	57 [13]
$PhCH_2-\dot{C}(CH_3)_2$	$(CH_3)_2\overset{Ph}{\overset{\vert}{C}}-CH_2\cdot$	0 [12]

A second factor which is known to promote rearrangement is the relief of steric crowding in the intial radical. This explains why the β-methyl radical 8 is more extensively rearranged than the neophyl radical 6a. [14]



6a



8

It is not clear as yet whether reactions involving aryl migrations proceed through a distinct bridged-radical intermediate or whether it merely proceeds through a bridged transition state. Thus Kochi and Krusic [15] failed to find evidence of a phenyl-bridged species, in a study of the esr spectrum of the 2-phenethyl radical.

In studies involving migratory aptitudes of various aryl groups, the p-nitrophenyl group was found to migrate about four times as fast as the phenyl group, [16] the β-naphthyl and p-diphenyl groups about six times times more readily than the phenyl. [17] The ability of the migrating group to delocalise an unpaired electron is the important factor in the ability of one group to migrate better than another. However, it has been demonstrated that any bridged-phenyl intermediate during a migration does not lend any anchimeric assistance in the formation of the radical. Thus the rates of decomposition of $[Ph\text{-}(Me)_2C\text{-}CH_2\text{-}CO_2]_2$, $[PhCH_2CH_2CO_2]_2$ and $[PhCH_2CH_2CH_2CO_2]_2$ were found to be comparable. [18] While the latter two peresters do not rearrange, the first perester yields the neophyl radical on decarbonylation and rearranges with migration of the phenyl. If migration of the phenyl occurred during the formation of the alkyl radical, an enhancement in the rate of decomposition would have been observed. Thus, "this evidence while not indicating unequivocally that a bridged radical intermediate (as opposed to a bridged transition state) is not formed, is consistent with the failure to obtain esr evidence for a bridged phenyl radical. [18a]

In summary, the conversion of UTPE to TPE, via the rearrangement of radical 1a to 1b,

$$\underset{\underline{1}}{Ph_3C\text{-}CH_2Ph} \longrightarrow \underset{\underline{1a}}{Ph_3C\text{-}\dot{C}H\text{-}Ph} \longrightarrow \underset{\underline{1b}}{Ph_2\dot{C}\text{-}CHPh_2} \longrightarrow \underset{\underline{3}}{Ph_2C{=}CPh_2}$$

is not surprising even though the conditions are ambient. The following summarises the factors possibly influencing the rearrangement:

a) Because of steric hindrance , the rate of interaction of radical 1a and the brominating agent, which generally is an encounter controlled process, is retarded, thus permitting the rearrangement to occur.

b) Rearrangement occurs because of greater stability of the rearranged radical, which is 3^{o} and benzhydrylic.

c) Driving force for the rearrangement may also be inherent in the relief of crowding that follows conversion of 1a to 1b .

d) Rearrangement may occur with anchimeric assistance by the migrating phenyl, even though there is no precedent for assistance.

Background

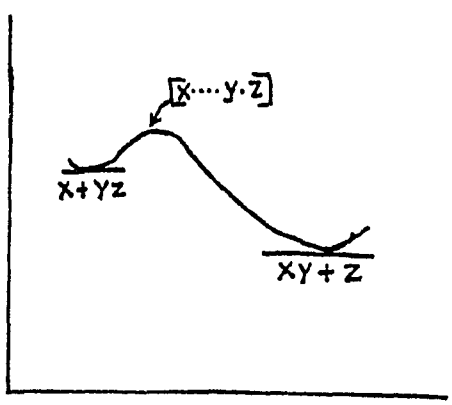
It was already known that 1,1,1,2-tetraphenylethane, UTPE , reacted with NBS to yield tetraphenylethylene, TPE , by a free radical pathway. The focus of this research project was to determine the generality of this conversion by studying the reaction of UTPE with other H-abstractors, normally used for the halogenation of alkanes. This study included the effect of the following factors, on the course of the reaction:

a) Nature of the transition state
b) Polar effects
c) Steric effects and,
d) Solvent effects

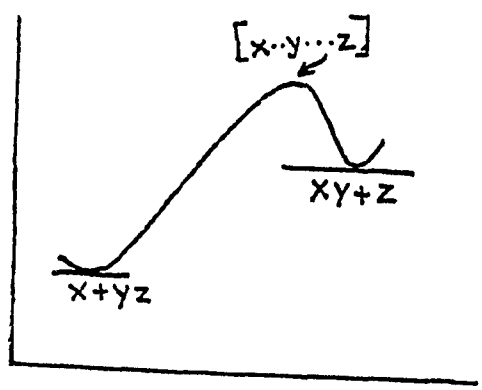
It was also the intent to elucidate whether or not the rearrangement of a phenyl, that occurs in the conversion of UTPE to TPE, was synchronous with abstraction of hydrogen. Towards this end other aralkanes were also to be studied in their reactivity towards NBS in order to obtain a composite picture of the factors governing the conversion of UTPE to TPE.

Nature of the Transition State

In terms of the concepts postulated by Hammond [19], the transition state of an exothermic reaction, e.g. abstraction of H by chlorine, will resemble more closely the reactants. This implies little bond-breaking and a long weak H-Cl bond, in the transition state. Since the carbon atom has very little radical character in the transition state, it has mainly sp^3 character. On the other hand, the transition state of an endothermic reaction, e.g. abstraction of H by a bromine atom, is reached comparitively late on the reaction pathway and it has greater resemblance to the intermediate radical than to the reactant. This implies greater C-H bond-breaking and a carbon atom with considerable sp^2 character. An energy diagram reflecting Hammond's postulate is shown below:



Low activation energy reaction



High Activation energy reaction

The postulate predicts large relative differences in reactivity for the reaction of C-H bonds of differing bond strengths (3^{o},2^{o},1^{o}) with bromine atoms; much smaller differences in reactivity are anticipated with chlorine atoms. The larger difference in reactivity (selectivity) between primary and tertiary hydrogens towards bromine atoms arises from the differences in the stability of the corresponding incipient radicals in the transition state. In chlorine atom abstractions, since the transition state involves less bond-breaking, less lowering of the activation energy due to the enhanced stability of the tertiary radical as compared to the primary radical would be anticipated.

Table 2: Relative Selectivity Values for Cl· and Br·[20]

	Cl·	Br·
CH_3-H	.004	.007
CH_3CH_2-H	1.0	1.0
$(CH_3)_2$CH-H	4.3	220
$(CH_3)_3$C-H	6.0	19,400

The reported kinetic isotope effects for toluene α-d are 1.3 for chlorination in CCl_4 and 4.6 for the corresponding bromination.[21] These values clearly indicate a more symmetri-

cal transition state for the thermoneutral hydrogen abstraction by Br· than for the exothermic hydrogen abstraction by chlorine atom:

C·····H·····Cl ; C·····H·····Br

Steric Effects

The attack by a radical on an alkane could occur either on hydrogen with displacement of the entire alkyl group, or on a carbon atom of the alkyl group with displacement of an alkyl fragment. Consider the displacement on a benzylic hydrogen of toluene with ethylbenzene in which displacement occurs on the β-carbon of ethylbenzene.

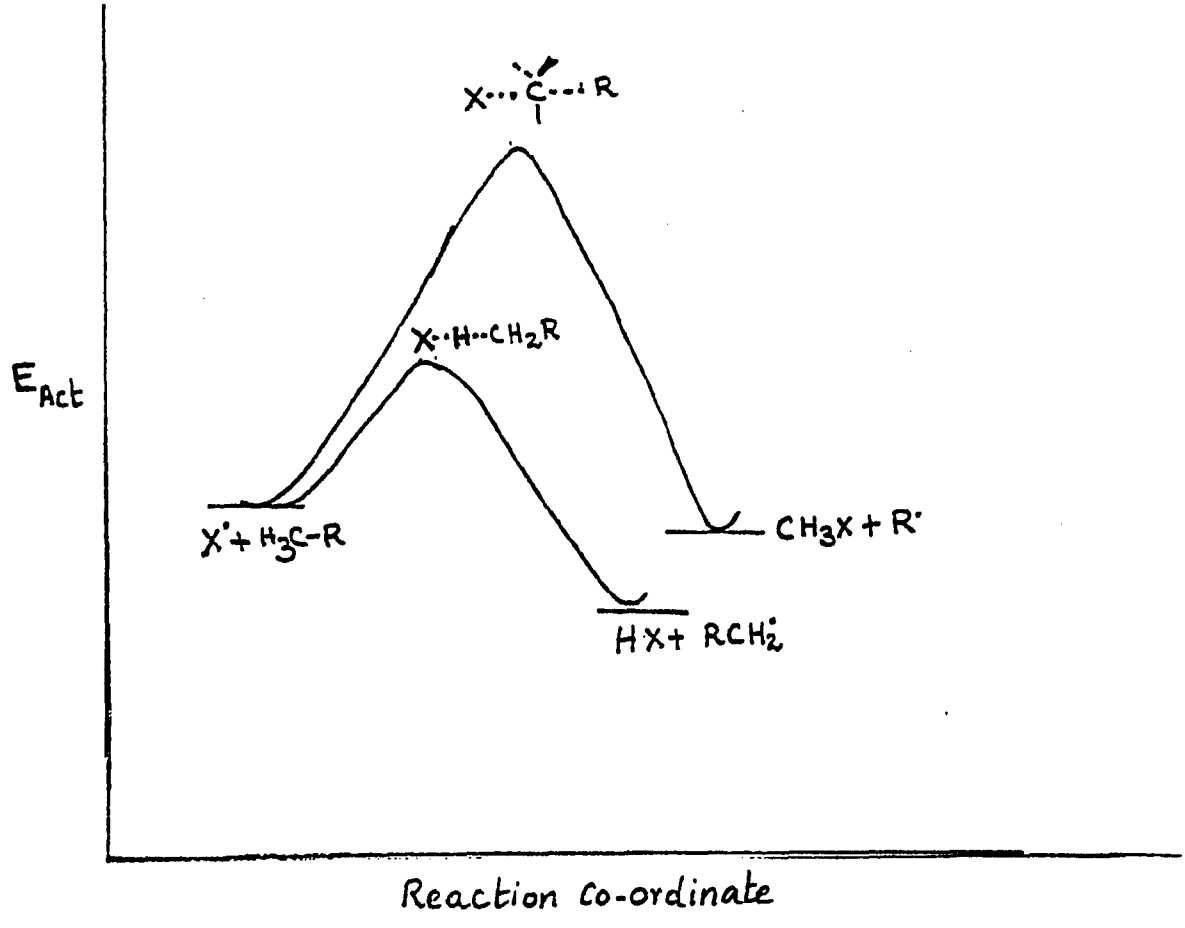
$$Cl\cdot + C_6H_5CH_3 \longrightarrow HCl + C_6H_5CH_2\cdot$$

Make H-Cl	=	-103 kcal/mole
Break $C_6H_5CH_2$-H	=	85 kcal/mole
ΔH	=	-18 kcal/mole

$$Cl\cdot + C_6H_5CH_2CH_3 \longrightarrow CH_3Cl + C_6H_5CH_2\cdot$$

Make CH_3Cl	=	-84 kcal/mole
Break $PhCH_2$-CH_3	=	70 kcal/mole
ΔH	=	-14 kcal/mole

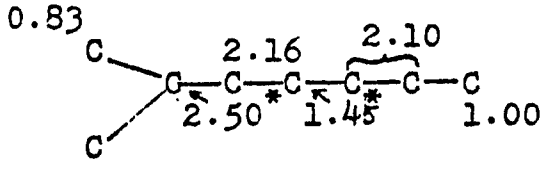
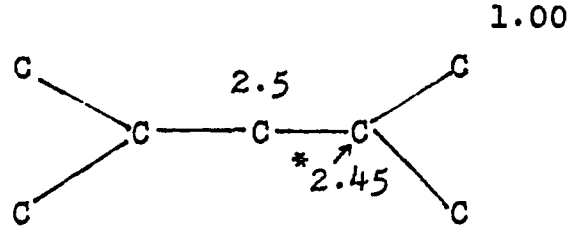
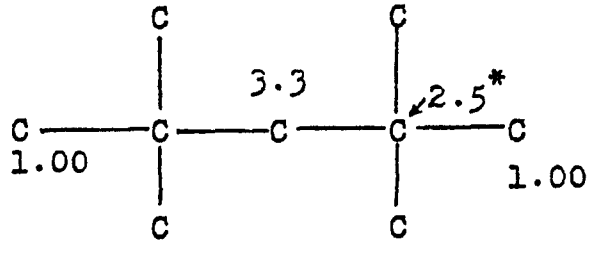
The enthalpic requirements for displacements on carbon are almost comparable with those on hydrogen. Yet, whereas displacements on hydrogen are a commonly encountered reaction, similar displacements on carbon are rare, exceptions being those involving cyclopropane compounds. This reflects the importance of steric effects in free radical reactions. The reaction most likely does not proceed with displacement on carbon because of a high activation energy requirement for such a displacement, caused by the sterically hindered approach of a free radical to an atom co-ordinated with two or more atoms or groups. [22] This is illustrated in the figure below:



Relative selectivity values of the type discussed so far (see Table 2) need not apply to larger molecules if steric effects were to play a role during hydrogen abstraction by halogen. The relative selectivity values for a number of branched alkanes for which complete product distributions have been determined are shown in Table 3. Certain low reactivities appear and these have been noted with an asterisk in the Table. These low reactivities have been attributed to steric inaccessablity of the hydrogens. [22,23,24] It is noted that since the neopentyl-like hydrogens in the alkanes studied exhibited normal reactivity, these effects are not of the type resulting from the interactions of nearby groups since the attack by chlorine is on hydrogen rather than on carbon.[25] They can be correlated more readily, on the other hand, with longer range nonbonded interactions which interfere with the approach of the chlorine atom to the hydrogen atoms in question.

Very little is known, however, about the complete product distributions for brominations of large chain paraffins. It has been suggested that bromination would be more susceptible to steric effects because of the inherently larger size of the bromine atom. [26]

Table 3: Relative Selectivities in Chlorination of Branched Alkanes

Substrate and RS values	Temp.	Ref
	20	22
	40	23
	85-90	24

Polar Effects

Halogenation of aralkanes can lead to either substitution in the aromatic nucleus or in the alkyl side chain, depending on the reaction conditions. Ring substitution, catalysed by Lewis acids, is enhanced by polar solvents, and is clearly an ionic process involving electrophilic attack of the halogen on the aromatic nucleus. Radical conditions favour side-chain halogenation. The relative reactivities of a series of meta- and para- substituted toluenes have been studied in order to identify the character of the transition state in these substitution reactions. [27,28] In both chlorination and bromination of the substituted toluenes, correlation of the rate constants with σ^+ was observed. This was taken to imply that the transition states of free radical reactions, normally considered to involve electrically neutral radicals, possessed "polar character". This polar effect may be the lowering of the energy of the transition state by an inductive effect of the substituent or else by participation of resonance structures in which the electron is transferred to the halogen: [29]

$$\underset{(A)}{R\text{-}H\ \cdot X} \longleftrightarrow \underset{(B)}{R^{+}\cdot H\ :X^{-}} \longleftrightarrow \underset{(C)}{R\cdot\ \ H\text{-}X}$$

It was also noted that electron-donating groups favoured hydrogen abstraction while electron-withdrawing groups retarded the rate of reaction. Polar effects are also clearly demonstrated by the low reactivity of chlorine atoms with fluoroform as compared to methane, despite the almost equal strengths of the bonds being broken. The polar effect is shown to be dependent on the nature of the attacking radical because methyl radicals, which are nucleophilic, react more rapidly with fluoroform than with methane. [30]

As already pointed out, the halogenation of substituted toluenes was found to correlate Hammett's sigma-rho equation:

$$\log k/k_o = \sigma \rho$$

Table 4 below lists some of the radicals that have been studied in the toluene series.

Table 4: Rho Values in the Halogenation of Toluenes

Abstractor	Temp.	ρ	Reference
Cl·	40	-0.66	31
Br·	80	-1.42	32
	80	-1.36	33
Cl_3C·	80	-1.46	34
t-BuO·	40	-0.83	35

The negative rho values clearly indicate that electron-releasing substituents in the aromatic ring facilitate hydrogen abstraction from the methyl group of toluene. The larger negative value of rho observed in brominations, in comparision to the rho value of the corresponding chlorination, is an indication of the greater electron-deficiency in the transition state for bromination, as would have been predicted from Hammond's postulate.

In general, in the case of reactive atoms like chlorine, the transition state will resemble structure A (page 19) which is reactant-like, and as the reactivity decreases, as in the case of Br·, the transition state will more closely resemble structure C, which is product-like. Since the bromine atom is also strongly electrophilic, resonance structures such as B, possible only when there is sufficient bond-breaking, may contribute to the transition state. The reactivity of RH, in this case, will hence be greatly affected by substituents on R which affect the ability of R to accomodate the positive charge. [36] Structure A would benefit very little, however from any resonance stabilisation.

The selectivity values of chlorine and bromine atoms towards aralkanes are shown in Table 5.

Table 4: Effect of Phenyl Groups on the Selectivity of C-H Bonds towards Halogen Atoms [37]

	Cl·	Br·
$C_6H_5CH_2CH_2$-H	1.3	64,000
$(C_6H_5)_2CH$-H	3.3	620,000
$(C_6H_5)_3C$-H	9.5	1,140,000
CH_3CH_2-H	1.0 [a]	1.0 [a]

a) Arbitrary Standard

In summary, therefore, attack of a chlorine atom on toluene, or similar aralkanes, which occurs with little bond-breaking in the transition state, is dominated by the polar effect. Attack by the bromine atom, which occurs with more development of radical character in the transition state, is dominated by radical stability effects. However, since a bromine atom is also elctrophilic and hence also subject to polar effects, it must be pointed out that the true resonance activating effect of the phenyl group must be larger than that judged from the observed data.

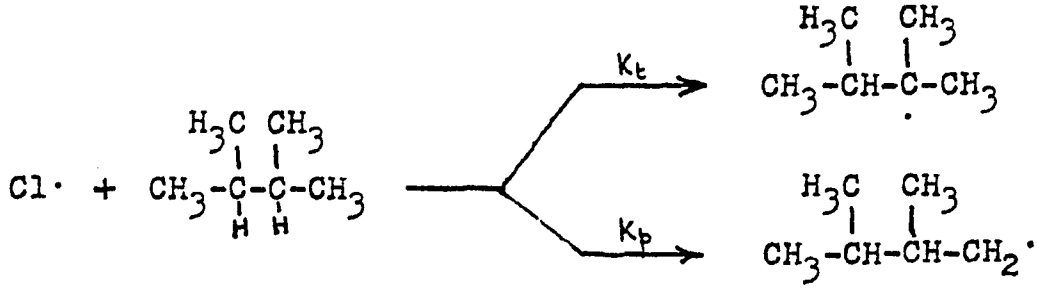
In 1972, Zavitsas and Pinto challenged the concept of polar effects and proposed that the reactivity of substituted toluenes parallels their benzylic bond dissociation energies (BDE) and vibrational stretching frequencies. To substantiate this proposal, a plot of ρ for abstraction of hydrogen from toluene

was plotted against ΔH and a linear plot obtained. [38] From this the authors concluded that positive values of rho would be impossible for abstraction of hydrogens from toluene. At that time, all the known values of rho for reactions with toluene were negative and, thus, could be rationalised by Zavitsas' BDE arguments. However, since then, positive values have been determined for hydrogen abstraction from substituted toluenes by nucleophilic radicals. [39,40] On this basis, Pryor has concluded that the importance of polar effects has not been disproved and suggests the following hypothesis, [40]

> "Hammett correlations of radical reactions may arise from two causes that may act in opposite directions. The first is that substituents alter the bond dissociation energy of the benzylic bond; since electron-donating substituents weaken the benzylic bond, this factor predicts a negative rho value, regardless of the nature of the attacking radical---- whether it is electrophilic or nucleophilic. This is the effect stressed by Zavitsas. However, since positive rho values have been obtained, notably in the case of isopropyl and t-butyl radicals, substituent effects must certainly perturb the BDE-determining rho, and is generally in accord with the usual representation of dipolar structures. It is therefore concluded that both SETS (substituent effects in the transition state) and effects of substituents on BDE should be considered in explaining the results of the Hammett equation correlations of these and other radical reactions."

Solvent Effects

Free radicals that are formed during the course of a reaction almost certainly encounter some sort of interaction with the solvent molecules. However, the nature of the interaction is often quite different in degree and kind from those observed for charged species. Most halogenations are, in general, slightly more selective in the gas phase. But a remarkable exception was found in the case of photochlorination in certain specific solvents by Russell [41, 42] and by Walling and Mayahi [43]. For example, chlorination of 2,3-dimethylbutane at 55° in the absence of any solvent (except the substrate itself) yields a mixture of 1-chloro-2,3-dimethylbutane and 2-chloro-2,3-dimethylbutane, the composition of which indicates the reactivity ratio k_t/k_p of 3.7 (statistically corrected).



Russell has observed that this reactivity ratio is markedly altered if the chlorination is carried out in solvents other than the alkane itself. Data on solvent effects is presented in Table 6.

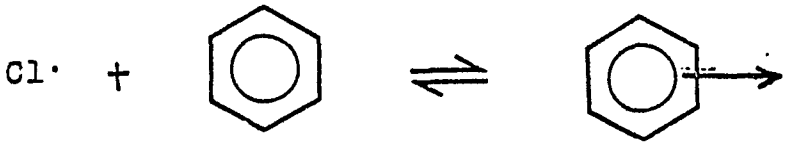
Table 5: Solvent Effects in the Chlorination of 2,3-Dimethylbutane at 55° [41]

Solvent	k_t / k_p
Neat	3.7
Carbon disulphide	15.0
Carbon tetrachloride	3.5
Dioxane	5.6
Nitrobenzene	4.9
Benzene	15.6
Anisole	18.4

In some solvents the reactivity ratio is larger, indicating that a greater degree of selectivity is being displayed by the chlorine atom as an abstractor. From the data above, it seems likely, therefore, that the chlorine atom is associated with the solvent in a fashion which renders it less reactive. The less reactive, solvated chlorine atom displays a higher degree of selectivity as a hydrogen abstractor. The transition state in this case, possesses more product-like character. As a consequence, both the polar characteristics and, to some extent, the resonance stabilisation of the alkyl radical formed, begin to play a more significant role in determining reactivities.

The nature of the interaction with the solvent is based on the ability of the chlorine atom to function as a Lewis acid and

form π-complexes with various solvent Lewis bases. The extent of such a complexation depends on both the strength of the Lewis base and its concentration. Russell [42] showed that the effectiveness of substituted aromatics increased with electron-donating groups, e.g. anisole $>$ benzene $>$ nitrobenzene. The effectiveness also showed an increase with increasing solvent concentration, often in more than linear fashion. The pronounced solvent effects observed in CS_2 possibly reflects a different kind of complexation, namely the formation of a σ-complex.



Cl· + S=C=S $\rightleftharpoons$ Cl-S-C=S (-complex)

Chlorine atoms are monomeric and, therefore, may be complexed by a single solvent molecule and still be able to participate in hydrogen abstraction reactions without encountering severe steric problems. The transition state for such reactions probably involves an approach to the hydrogen atom on which displacement is to occur, from the non-solvated side of the chlorine atom.

RH + [·Cl⟵solvent] ⟶ [R···H···Cl ⟵ solvent]

⟶ R· + HCl + solvent

It is quite possible, that at high solvent concentrations, the chlorine atom might become sandwiched between two solvent molecules and, thus become sterically hindered from any direct interaction with an alkyl hydrogen. In such a case, it would be necessary that some degree of desolvation occur before the transition state can be reached.

It has been shown that the selectivity or reactivity of Br· is unaffected by changes in solvent polarity.[43] Recently, however, some Russian investigators reported some dependence on solvent polarity during brominations. Their results are summarised in Table 6.

Table 6: Dependence of Rho on Solvent Polarity for the Free Radical Bromination of Toluenes at 40°. [44]

Solvent	Dielectric Constant (D)	Rho
CCl_4	2.238	1.72 ± 0.03
$CHCl_3$	4.806	1.69 ± 0.02
CH_2Cl_2	9.08	1.78 ± 0.04
CH_3CN	38.0	1.62 ± 0.03
CH_3NO_2	34.8	1.54 ± 0.03

From the above data, there seems to be a trend for rho to diminish as the dielectric constant of the medium decreases. However, CH_2Cl_2 is distinctly out of line and the differences are slight.

F. Halogenating Agents

Besides chlorine and bromine there are several reagents which will achieve substitutive halogenation by homolytic routes. These are of the general form QX, where X is a halogen atom and Q is a non-halogen atom or group of atoms capable of existing as a radical that can abstract hydrogen.

(i) t-Butylhypochlorite

Walling and his co-workers[45] were the first to show systematically that this was a synthetically useful chlorinating agent in the liquid phase. Reaction of toluene with the reagent was strongly inhibited by normal radical inhibitors and, produced benzyl chloride without significant ring attack. On this basis the following chain was proposed:

$$t\text{-BuOCl} \xrightarrow{h\nu} t\text{-BuO}\cdot + Cl\cdot$$

$$RH + t\text{-BuO}\cdot \longrightarrow R\cdot + t\text{-BuOH}$$

$$R\cdot + t\text{-BuOCl} \longrightarrow RCl + t\text{-BuO}\cdot$$

Since the bond strengths of t-BuO-H and H-Cl are almost the same (103 kcal/mole), the abstraction of hydrogen by t-BuO· is isoenergetic with the abstraction of hydrogen by chlorine atom. However, atom transfer with this reagent is more favorable because of the relatively weak O-Cl bond. At temperatures above 85°, fission of the alkoxy radical can become competetive:

$$(CH_3)_3C\text{-}O\cdot \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + CH_3\cdot$$

Under moderate conditions, such a complication is unlikely. From studies with model alkanes [45], selectivity values were determined (see Table)

Table7: Relative Selectivity in t-BuOCl chlorinations at 40°

	Paraffinic	Benzylic
Primary	1.0	10
Secondary	12.0	32
Tertiary	44.0	69

From the Table above, it is evident that the t-butoxy radical is more selective than the chlorine atom in response to radical selectivity. Similar conclusions were drawn by Kosugi and his co-workers who confirmed that the the t-butoxy radical is indeed more responsive to radical stability but shows similar response to polar factors as does chlorine.[46]

(ii) Sulfuryl Chloride

Many of the chlorinations possible with chlorine can be readily carried out by the use of the often more convenient sulfuryl chloride with traces of peroxidic initiators. Since it has been shown that this reagent shows greater selectivity for aliphatic substrates (RS_p^t of 10 for 2,3-dimethylbutane at 55°) than does chlorine,[47,48] the hydrogen abstraction step must involve some species besides chlorine atom. It is normally considered that an equilibrium exists between chlorine atom, sulfur dioxide, and chlorosulfonyl radical and that the latter can abstract hydrogen along with the chlorine atom. The following is the suggested mechanism for halogenations with sulfuryl chloride:

$$SO_2Cl_2 \xrightarrow{h\nu} SO_2Cl\cdot + Cl\cdot$$

$$SO_2Cl\cdot \rightleftharpoons SO_2 + Cl\cdot$$

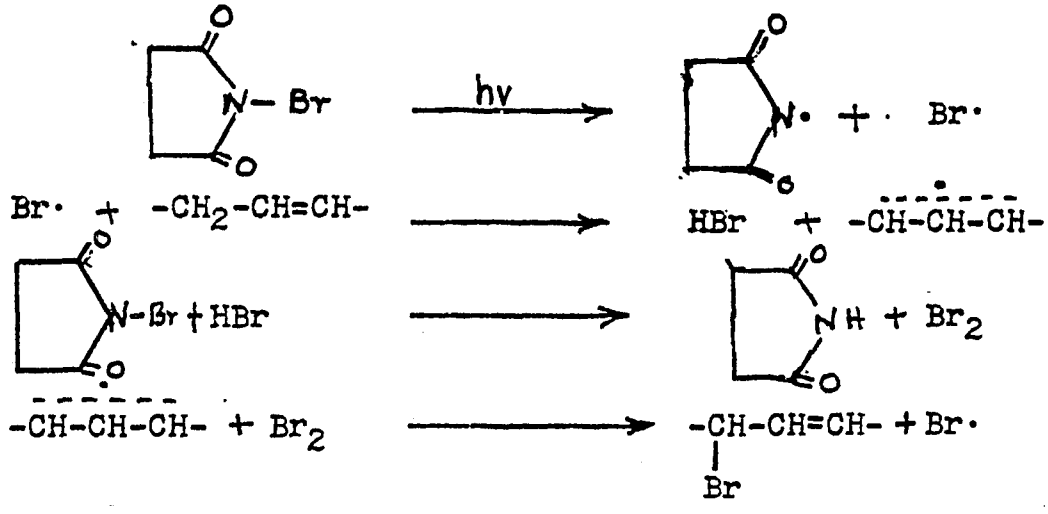
$$RH + Cl\cdot \longrightarrow R\cdot + HCl$$

$$RH + SO_2Cl\cdot \longrightarrow R\cdot + HCl + SO_2$$

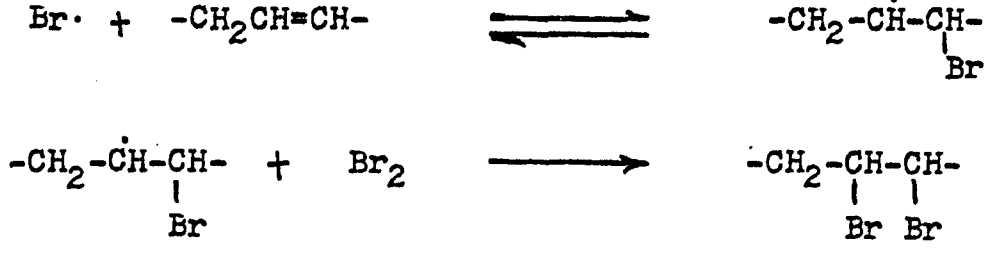
For aromatic substrates or for aliphatic substrates in aromatic solvents, the selectivity differences between chlorine and SO_2Cl_2 vanish and Russell suggests that in these cases the major abstracting species is neither the chlorine atom nor the chlorosulfonyl radical, but the aromatic-chlorine complex.

(iii) N-Bromosuccinimide; (NBS)

N-Bromosuccinimide has long been recognised as an effective allylic and benzylic brominating agent. The usual conditions employ refluxing carbon tetrachloride solvent, a medium in which NBS is somewhat soluble but the product succinimide is virtually insoluble. The mechanism of NBS bromination is shown below:[49]



The abstracting species is claimed to be the bromine atom and the role of NBS is to supply a steady but very low concentration of bromine by reaction with hydrogen bromide. To account for the specificity for allylic substitution, Goldfinger[50] pointed out that the abstraction step is operationally irreversible because the HBr formed is immediately scavenged, but that addition is reversible:



It has been subsequently demonstrated that allylic bromination can be achieved without any addition to the double bond with molecular bromine if it is introduced very slowly into an irradiated solution of olefin.[51,52] In support of the Goldfinger mechanism, Pearson and Martin[53] observed identical rho values not only for bromine and NBS but also for tetrafluoro- and tetramethyl N-bromosuccinimide.

Recently, however, it has been suggested that a hydrogen-abstracting species other than the Br· atom might be involved.[54] It is claimed that under conditions which suppress a bromine atom chain (e.g. ethylene which scavenges bromine atoms in acetonitrile) the succinimidyl radical becomes the abstracting species. This radical has been found to be a radical of low discrimination in hydrogen abstraction reactions, quite different from bromine atoms. The reaction with aralkanes is complicated by the formation of ring-substitution products and is currently being investigated in depth.

(iv) Bromotrichloromethane; $BrCCl_3$

Bromotrichloromethane is a very selective brominating agent in which the chain-carrying radical is trichloromethyl. For photoinitiated reactions with simple alkanes at 190° in the gas phase, RS_p^t is 2300 and RS_p^s is 80, values which are more selective than for bromine atom even though the abstraction is more exothermic than for bromine.[55] It is generally accepted that the bulk of the product comes from a chain initiated by $Cl_3C\cdot$ and that some bromine atom chains are also involved.

$$RH + BrCCl_3 \longrightarrow RBr + HCCl_3$$

Mechanism:

$$BrCCl_3 \xrightarrow{h\nu} Cl_3C\cdot + Br\cdot$$

$$RH + Cl_3C\cdot \longrightarrow HCCl_3 + R\cdot$$

$$R\cdot + Br\text{-}CCl_3 \longrightarrow RBr + Cl_3C\cdot$$

Results and Discussion

Reaction of UTPE with Free Radical H-Abstractors

1,1,1,2-tetraphenylethane, UTPE 1 , was synthesised in good yield by the reaction of trityllithium on benzyltrimethylammonium iodide (90%).

The reaction of UTPE with Br_2, NBS, or with $BrCCl_3$ gave solely TPE 3 , under free radical conditions. The mechanism for the formation of TPE from UTPE has already been discussed (see page 1). To ensure that the conversion of UTPE to TPE occurs solely by a free radical pathway, UTPE and NBS were sealed in the reaction tube (a Carius Combustion Tube) and placed in the dark at 40°C for 24 hours. Only starting material was recovered.

It might be suggested that 2-bromo-1,1,1,2-tetraphenylethane, 2 , is first formed by a typical free radical bromination, and that it then rearranges via a carbonium ion intermediate engendered by HBr or by succinimide acting as catalysts.

$$Ph_3C\text{-}CH_2Ph \xrightarrow{Br^{\bullet}} Ph_3C\text{-}\underset{Br}{CHPh}$$

2

$$\xrightarrow{-Br^{+}} Ph_3C\text{-}\overset{+}{C}HPh \longrightarrow Ph_2\overset{+}{C}\text{-}CHPh_2$$

$$\longrightarrow Ph_2C{=}CPh_2$$

3

In order to ensure that the formation of TPE is a primary process and not a secondary process, involving ionic intermediates, the reaction of UTPE with Br_2 in the presence of a) $CaCO_3$ and b) styrene oxide, which are known scavengers for any HBr produced,[56] was studied. There was no variation in the results. This eliminates the ionic pathway and reenforces the contention that the conversion of UTPE to TPE is an entirely free radical process. (It is to be noted that the reaction with NBS itself involves an inherent HBr trap in the form of NBS).

Solutions of UTPE were then irradiated in CCl_4 with equimolar quantities of a) Cl_2 b) SO_2Cl_2 c) t-BuOCl, after flushing the tube with nitrogen. The reaction of SO_2Cl_2 with UTPE was also studied in benzene and carbon disulphide. At the end of the reaction period, solutions were concentrated and analysed both by nuclear magnetic resonance (nmr) and by ultraviolet spectroscopy (uv) in order to determine the percent of TPE formed. Analysis by nmr is based on the change in concentration of starting material, from which the amount of TPE formed maybe deduced, assuming it is the only product. Analysis by uv is based directly on the concentration of the product, TPE, at its absorption maxima at 313nm. The results of both attempted brominations and chlorinations are summarised in Table 8.

Table 8: Reaction of UTPE with Halogenating Agents at 70°C. [a]

QX	Solvent	Time(h)	%UTPE (nmr)	%TPE (uv)
Cl_2	CCl_4	44	94 ± 2	-----
SO_2Cl_2	CCl_4	44	94 ± 2	10 ± 2
t-BuOCl	CCl_4	44	78 ± 2	------
SO_2Cl_2	C_6H_6	44	50 ± 4	------
SO_2Cl_2	CS_2	44	48 ± 3	------
Br_2	CCl_4	1	0	100
NBS	CCl_4	1	0	100
$BrCCl_3$	CCl_4	24	0	100

a) Molarity of both QX and UTPE was 0.05 in all runs except in the case of reaction with $BrCCl_3$ where the molarity of $BrCCl_3$ was 1.0 and that of UTPE 0.05.

It is immediately apparent from the Table that the rate of conversion of UTPE to TPE is faster when the less reactive species is the hydrogen abstractor. The normal order of reactivity of hydrogen abstractors towards toluene for instance, is $Cl\cdot > t\text{-}BuO\cdot > Br\cdot > Cl_3C\cdot$. In the case of UTPE however, the order of reactivity is $Br > Cl_3C\cdot > t\text{-}BuO\cdot > Cl\cdot$. In this context it should be noted that the solvent complexed species ($Cl\cdot$) is a less reactive species than an uncomplexed chlorine atom, and that the reactivity of $Cl\cdot$ in benzene and CS_2 correlates well with the observation that the more reactive species the less the rate of conversion of UTPE to TPE. The rate of reaction of UTPE with $X\cdot$ may be given by the equations:

$$Rate_{Cl\cdot} = k_{Cl} [UTPE] [Cl\cdot]$$

$$Rate_{Br\cdot} = k_{Br} [UTPE] [Br\cdot]$$

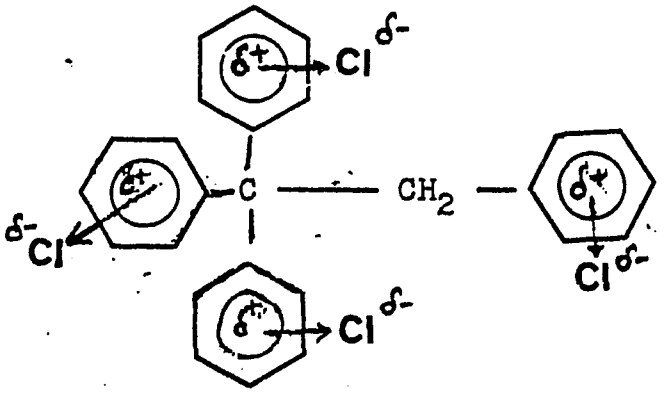
Variations in the reactivity of a substrate with different halogen atoms is dependent on the concentration of the halogen atom as well as the specific rate constants. In most cases, k_{Cl} is greater than k_{Br} and the overall rate of chlorination, as aleady stated, greater than the overall rate of bromination. In the case of UTPE, however, atypical reactivity is observed and $rate_{Br}$ is greater than $rate_{Cl}$. Hence it is concluded that $[Cl\cdot]$ is $\ll [Br\cdot]$. We suggest that in the reaction of UTPE with chlorine atoms, complexation

of the chlorine atoms to the substrate greatly diminishes its concentration. This is an important factor in the case of UTPE as there are four phenyl rings in the substrate. Since the concentration of the halogen species varies directly with the rate of reaction, complexation diminishes the rate of reaction. The less reactive species, $Br\cdot$ and $Cl_3C\cdot$, are less inclined towards π-complexation and the concentration is not affected as much, if at all.

The work of Gleicher and co-workers addresses itself to the importance of halogen complexation.[57, 57a] They showed that when hydrogen abstracting species complex with a substrate, intramolecular abstractions are still posibble. The reaction of $Cl_3C\cdot$ with $Ph\text{-}CH_2(CH_2)_n\text{-}Ph$ showed a rate maximum when $n=5$ and little or no enhancement was observed when $n=1$. It was concluded that this was not due to a simple statistical uncertainity but that an intramolecular transfer of a complexed radical was being observed. It is possible that the observed order of reactivity is based on the geometrical relationship of the complexed radical to the hydrogen being abstracted. In the case of bibenzyl ($n=1$) the proper geometry for an intramolecular abstraction is not present. It follows, therefore, that the proper geometry for abstraction of a hydrogen by a chlorine atom complexed to the substrate UTPE may likewise be absent.

In order to compensate for the low concentration of chlorine atoms ostensibly present when equimolar quantities of UTPE

and chlorine are reacted, the reaction of UTPE with excess sulfuryl chloride was studied. Even in this case, little or no conversion of UTPE to TPE was noted. Mostly starting material was recovered. The absence of reaction even with excess sulfuryl chloride can now no longer be attributed to a low concentration of chlorine atoms. Instead, the modified nature of the substrate, on complexation with chlorine atoms, is likely to be responsible for the lack of reaction. This is on account of the fact that complexation with the phenyl rings renders the phenyl rings more electron-withdrawing and hence transition state destabilising. An extreme case where all phenyl rings are involved in complexation and become strongly deactivating towards charge development is shown below:



When the reaction of UTPE with Cl_2 or with SO_2Cl_2 was then studied in benzene or CS_2, the amount of TPE isolated increas-

ed considerably. Both of the above solvents are good complexors and would hence disfavour complexation with the substrate. Unlike the substrate-complexed chlorine atom, the solvent complexed obviously does not suffer from the geometrical restrictions imposed on the former.

In retrospect, it seems illogical that complexation with the substrate, when UTPE is reacted with an equimolar amount of SO_2Cl_2, should be entirely responsible for the low conversion of UTPE to TPE (ca.5%). Since an equilibrium exists between π-complexed chlorine atoms and uncomplexed chlorine atoms, there should be at all times, a sufficient concentration of chlorine atoms for the reaction to proceed. It appears, therefore, that some structural feature unique to the substrate, UTPE, might also be playing an additional retarding role. To test this hypothesis the chlorination of toluene in the presence of UTPE was studied---- UTPE being already known to be inert under the reaction conditions.

The chlorination of toluene with SO_2Cl_2 in CCl_4 was carried out by irradiation for a short period. The ratio of product, benzyl chloride, to starting material may be estimated by nmr. The chlorination was then repeated in the presence of added UTPE. As a standard, the chlorination was also studied in the presence of an equimolar quantity of phenyl rings (as there are 4 phenyl rings per mole of UTPE) by the addition of the appropriate amount of benzene. The results are shown in Table 9.

Table 9: The Chlorination of Toluene with 0.1M SO_2Cl_2 [a,b]

Moles SH [c,d]	RH added [e]	Moles RH	% Benzyl chloride [f]
10^{-3}	-----	-----	51 2
10^{-3}	UTPE	0.5×10^{-3}	25 3
10^{-3}	Benzene	2×10^{-3}	50 2

a) At 65°

b) In CCl_4 solvent.

c) SH = Toluene ; d) 0.1M conc.

e) RH = Added non-reactant.

f) Each run in triplicate.

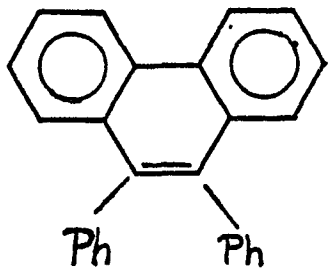
The presence of UTPE in the toluene-sulfuryl chloride system resulted in a significant rate retardation, while the presence of benzene, in the quantities used, had no measurable effect at all. On this basis it is hypothesised that the propeller-like conformation of the three phenyls of the trityl group is responsible for trapping chlorine atoms in irreversible fashion.

[A similar series of experiments were also carried out for the bromination of toluene. The ratio of rates of the reactions of toluene and UTPE with bromine, when measured independent of one another, was almost the same as when they were allowed for the same bromine atom.]

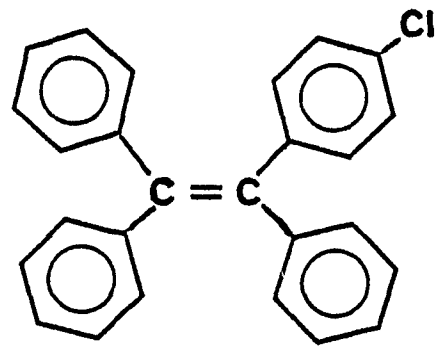
Product Distribution:

When UTPE was reacted with Br_2, NBS, or with $BrCCl_3$, tetraphenylethylene, TPE, was formed almost exclusively. Trace amounts of p-(bromophenyl)-triphenylethylene were also present but not isolated. The complete conversion of UTPE to TPE was monitored by nmr, using t-butylbenzene as an internal standard, and was indicated by the disappearance of the singlet signal due to the benzylic protons of the starting material. The alkene, TPE, gives essentially a singlet in the aromatic region. Its presence was verified and quantified by its uv absorption at 313 nm.

In contrast to the reaction of UTPE with "brominating agents", the reaction with either SO_2Cl_2 or Cl_2 in benzene or carbon disulphide gave a crude product which showed three spots on a tlc plate, besides one for starting material. Column chromatography led to the isolation of three products, the major component being TPE. The other products were identified from their spectral data and melting point as 9,10-diphenylphenanthrene, DPP 9, and p-(chlorophenyl)-triphenylethylene, 10. The comparitive results are shown in Table 10.



DPP 9

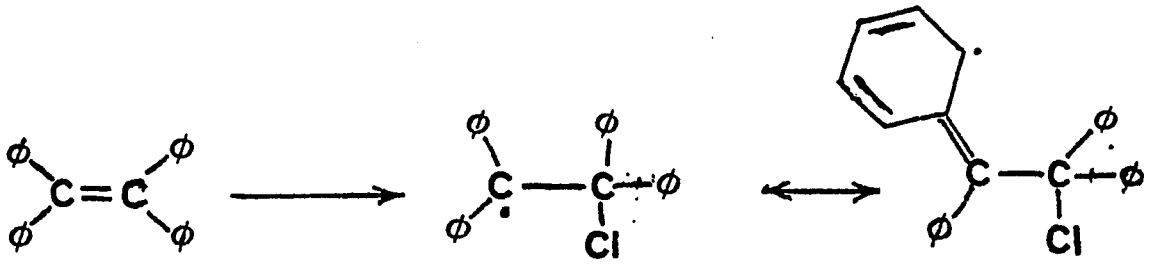


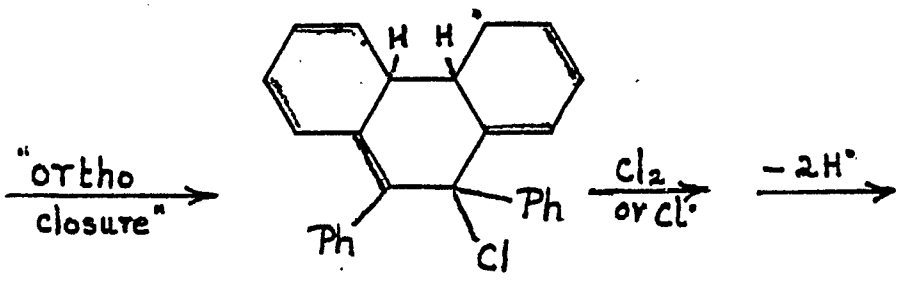
10

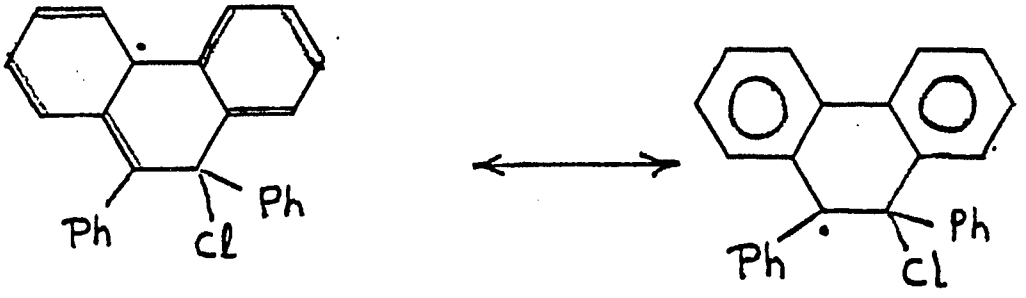
Table 10: Results of the Attempted Halogenations of UTPE

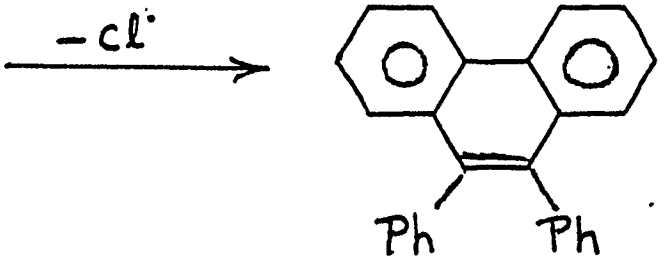
X·	Solvent	% TPE	% DPP, 9	% 10	% UTPE
Br·	CCl_4	99	0	0	0
Cl_3C·	----	99	0	0	0
Cl·	CS_2	28	9	16-19	42
Cl·	C_6H_6	25	12	11	45

It is conceivable that both DPP and 10 are not primary products of the reaction but actually secondary products of the reaction derived from the initially formed alkene, TPE, by the pathway outlined on the next page.



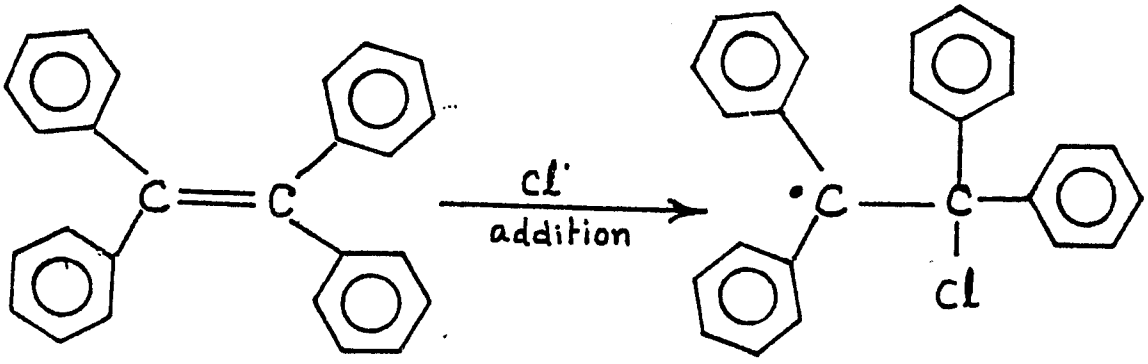




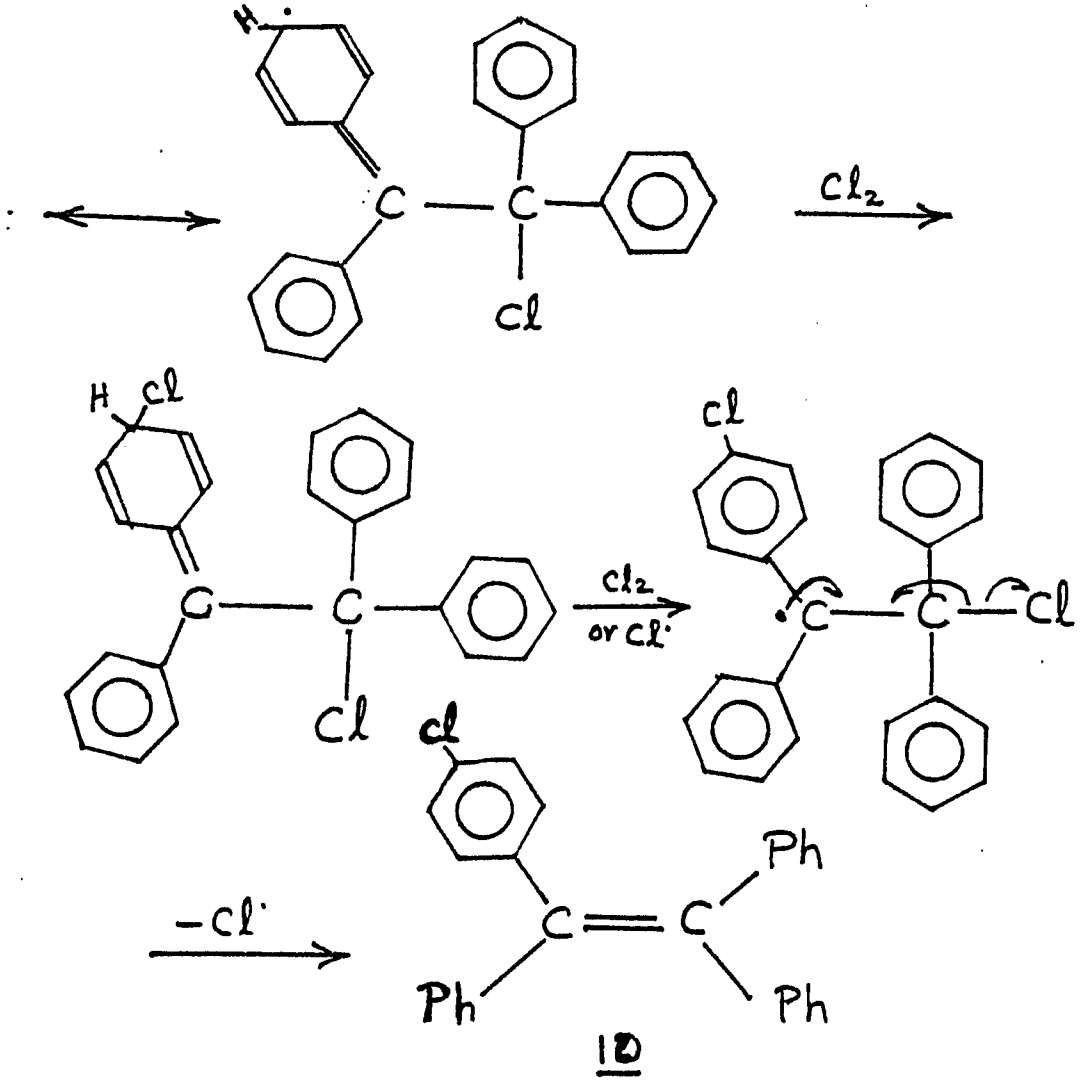


DPP 9

Mechanism for the formation of 10 from TPE, 3

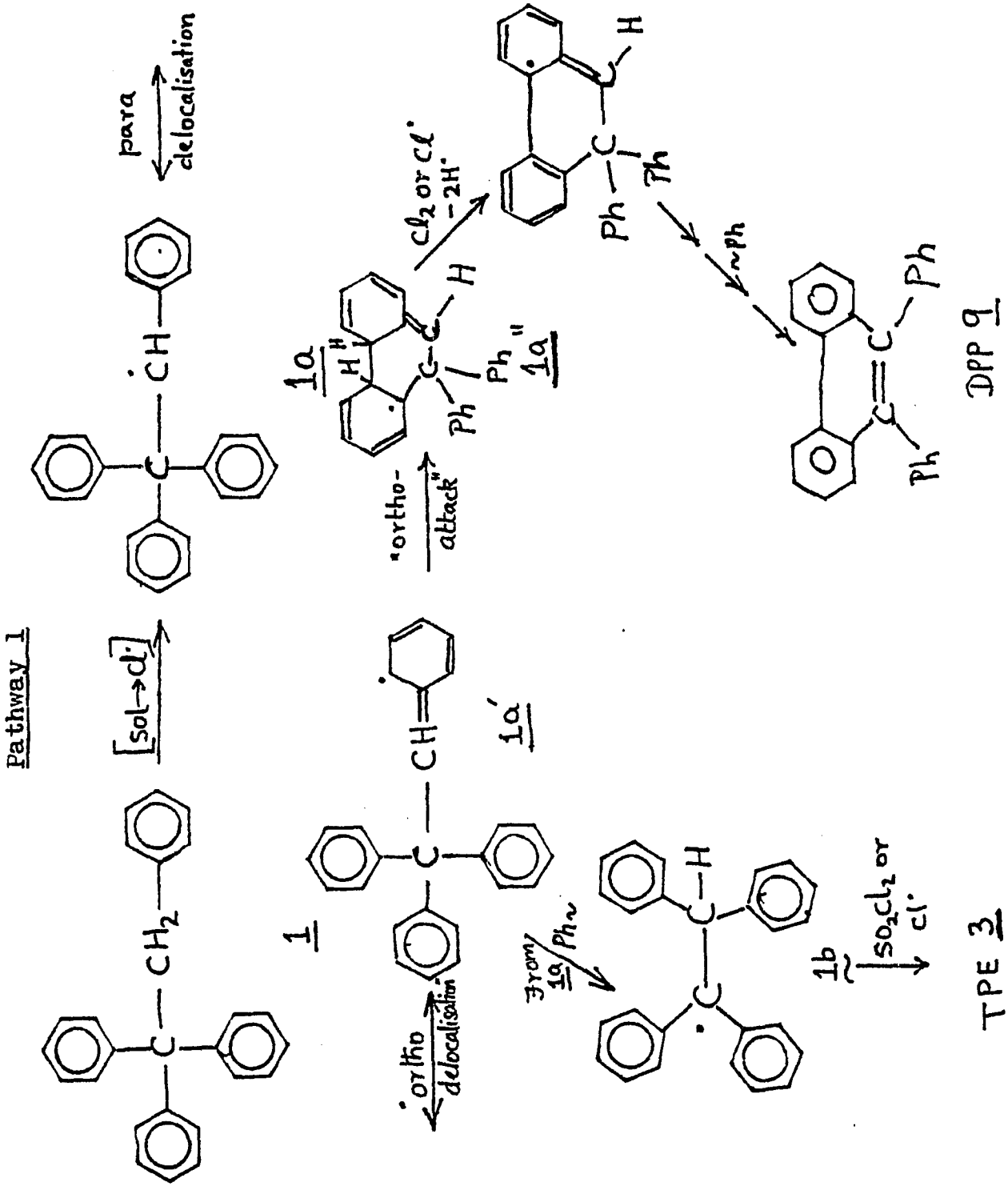


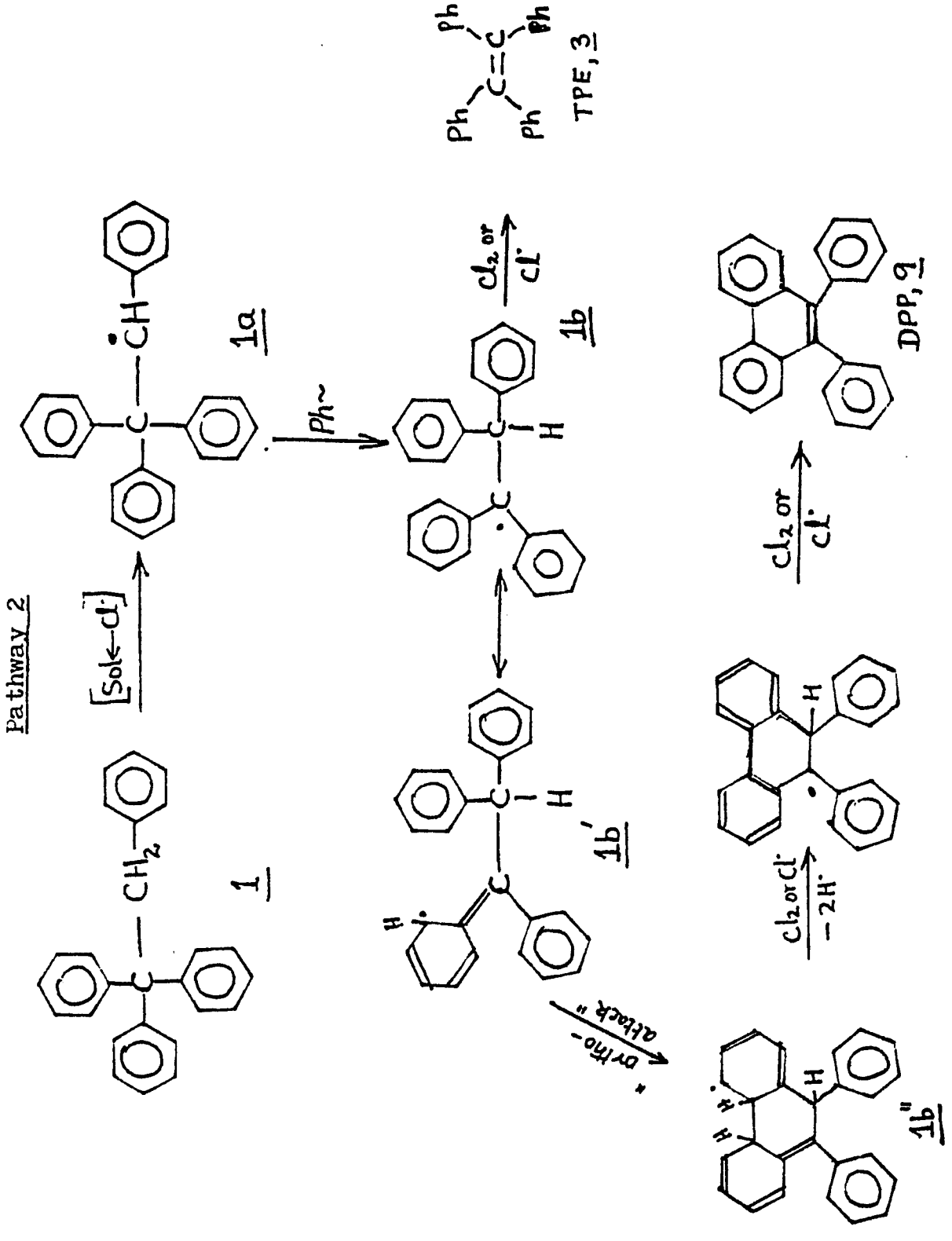
TPE, 3



10

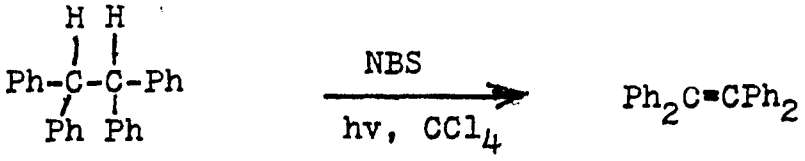
In order to ascertain whether or not DPP, 9 , and compound 10 were indeed secondary products as postulated above, a control wherein TPE was reacted with an equimolar amount of SO_2Cl_2 in benzene was performed. While some 15-20% of compound 10 was isolated, no DPP was detected. Thus compound 10 may or may not be a primary product of the reaction . However, since no DPP, 9 , was formed from the primary product, TPE, it must itself be a primary product of the reaction. Two likely pathways for the formation of DPP directly from UTPE are shown on pages 47 and 48.





If we assume that intermediate 1a can be formed by abstraction of H from UTPE by Br·, its fate---- whether it rearranges or undergoes cyclisation ---- should be independent of the nature of the halogen. The conversion of radical 1b to TPE (pathway 2), however, is dependent on the nature of the halogen species though its alternate fate, viz. cyclisation to DPP, is independent of the halogen. Therefore, if pathway 2 is operative, then it would be possible to rationalise the differences in product distribution in the reactions of UTPE with Cl· and Br· . It was, therefore, necessary to generate radical 1b from an alternate source and see if under the conditions of the reaction above, any DPP could be detected. Towards this end 1,1,2,2-tetraphenylethane, STPE 11 , was synthesised.

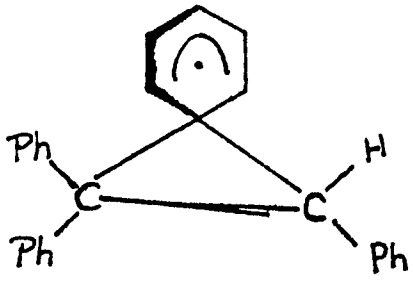
STPE like UTPE reacted rapidly with NBS to yield TPE as the sole product, via the intermediacy of radical 1b



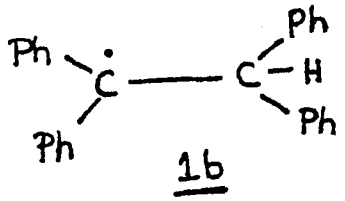
STPE, 11 TPE, 3

STPE was then reacted with SO_2Cl_2 in benzene and in CS_2

under conditions identical to those which resulted in the formation of DPP from UTPE. The crude product was then analysed as usual and, while 15-18% of compound 12 was detected, no 9,10-diphenylphenanthrene was detected. This means that any DPP that was formed had to originate from the initially formed radical 1a. However, since no DPP was formed in the reaction of UTPE with Br· and it has already been pointed out that the fate of radical 1a is independent of the nature of the halogen species, it is concluded that different intermediates are involved in the reactions of UTPE with Cl· and Br· . It is suggested that the intermediate in the reaction of UTPE with Cl· is 1a and the intermediate in the corresponding reaction with Br· is either the bridged radical 1c or the rearranged radical 1b:



1c

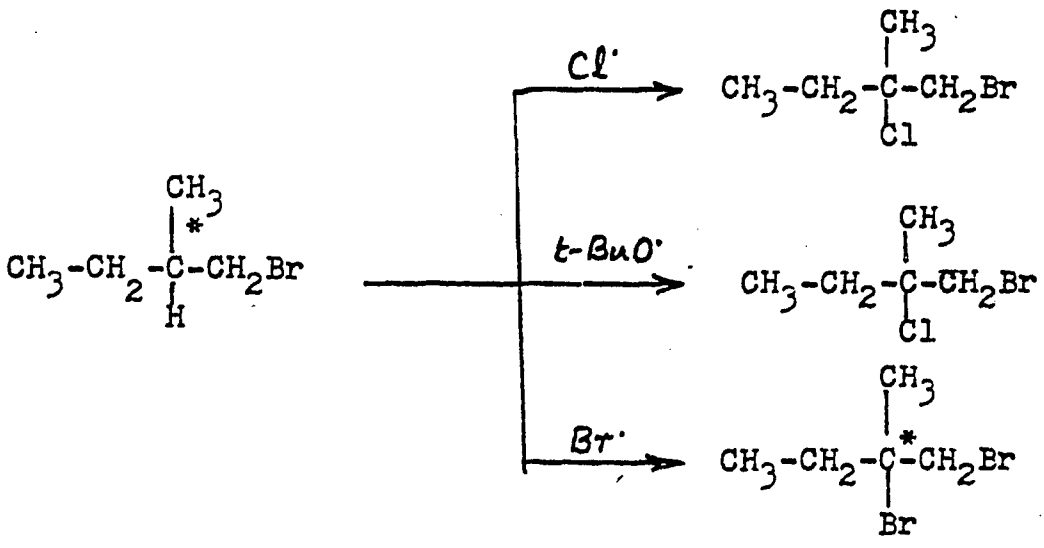


1b

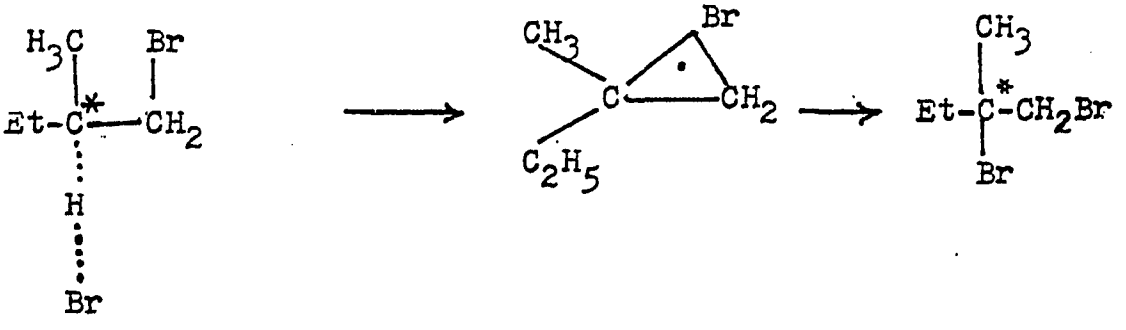
Detection of Assistance

In order for 1b or 1c to be the first formed intermediates, in the conversion of UTPE to TPE with Br·, the migration of the phenyl has to begin synchronously with the abstraction of hydrogen, in order to bypass 1a as an intermediate. (If 1b is the first formed intermediate then the migration of the phenyl must perforce be complete when the abstraction of the hydrogen is total). A synchronous migration of the phenyl implies neighbouring group participation. It has already been shown that 1b is not a precursor to DPP, 9 . It must be also assumed that if 1c , and not 1b ,is the intermediate in the reaction of UTPE with Br·, 1c similarly cannot be a precursor to DPP, since no DPP is formed in the reaction. At this point no conclusions can be drawn as to whether the actual intermediate in the reaction with Br· is 1b or 1c.

In the halogenations of alkyl bromides, bridging and anchimeric assistance has been clearly demonstrated . The extent of bridging, in this case by a halogen atom, and hence the extent of anchimeric assistance is dependent on the nature of the transition state.[58] Consider the set of reactions shown below:



The high degree of stereochemical control observed in the reaction with bromine atom (100% retention of optical activity) is attributed to bridging in the transition state by the 1-bromo group, forcing further reaction of the radical to occur from the side opposite the bridge. This leads to retention of configuration.



In the abstractions involving exothermic transition states, as in the reactions with Cl· and t-BuO·, the tertiary halide formed was optically inactive. Moreover, substitution occurred at all C-H bonds. The lack of special reactivity at the tertiary hydrogen and the lack of stereochemical control, in these exothermic abstractions, is attributed to the nature of the transition state. In the reactant-like transition state of exothermic abstractions, wherein little bond-breaking has occurred, bridging by an adjacent bromo group cannot take place. This is due to the fact that there is little development of a free p-orbital on the carbon atom being displaced to allow for bridging. Abstraction by Br·, on the other hand, being an endothermic process, proceeds through a transition state wherein extended bond-breaking has occurred and the carbon atom being displaced is almost sp^2-hybridised. Bridging and anchimeric assistance are hence only noticeable when the abstraction of the hydrogen by the attacking radical is an endothermic process. [58] In the reactions of UTPE with radicals involving a reactant-like transition state, e.g. with Cl·, no bridging would be possible for the reasons cited above. The existence of a bridged intermediate would, however, be possible for abstraction of hydrogen by a bromine atom. Just as two different intermediates have been postulated in the reactions of optically active isoamylbromide with Cl· and Br· to account for the differences in the optical nature of the products, the existence

of two different intermediates in the reactions of UTPE with Cl· andBr· is also possible.

Demonstration of Anchimeric Assistance with the formation of a phenyl-bridged species in the reaction of UTPE with Br·

Kinetic evidence for the existence of anchimeric assistance in the reaction of UTPE with NBS was obtained by a comparision of it rate of reaction with the rate of reaction of neopentylbenzene, NPB 4 .

Neopentylbenzene was synthesised by the reaction of t-butyllithium with benzyl chloride, in a yield of about 63%. Rate analyses were done by nmr and were based on the disappearance of starting material. These rates were then compared to the rates of bromination of toluene and ethylbenzene, also performed under the same conditions. The results are shown in Table 11.

Table 11: Relative Rates of Bromination of α-substituted Toluenes[a] I

α-Group	Rate	
H	1.0	
CH_3	19.8	
$(CH_3)_3C$	0.42	$(0.45)^2$
$(Ph)_3C$	0.43	

a) At 70°C and 0.1 M concentration in substrate and halogen.

It is evident from the above results that the rates of reaction of both UTPE and NPB are approximately the same. This is surprising in view of their opposing polar effects. The electron relesing t-butyl group would be expected to stabilise developing electron deficiency in the transition state and thus enhance the rate compared to toluene (ignoring steric effects for the moment). The electron-withdrawing trityl group on the other hand would be expected to be a destabilising influence in the transition state and retard the rate relative to toluene. Steric effects are certainly expected to be involved. Normally steric sizes of groups can be desribed in terms of A-values, which correspond to a free-energy difference of a substitiuent in an axial and in an equatorial position on a cyclohexane ring. The use of these values in the case of substituted ethanes would be incorrect. So, for the moment if we can consider the steric bulks of both the trityl and t-butyl groups to be approximately equal, then the almost equal rates of reaction of UTPE and NPB is unexpected on the basis of their opposing polar effects. This implies that some rate accelerating factor is operative in the reaction of NBS with UTPE, but not with NPB. This rate acceleration may be due to anchimeric assistance in the abstraction of hydrogen from UTPE.

If indeed anchimeric assistance is present in the reaction of UTPE with NBS (or Br_2) , it is possible to calculate

a value for the implied assistance, provided we can estimate the "inductive" deactivating value for the trityl group. This value was calculated in a manner similar to the calculation of anchimeric assistance in the brominations of alkyl bromides as described below.[59]

By use of an inductive deactivating factor of 0.14 for β-bromine atoms, anchimeric assistance in alkyl bromides has been found to vary from3 to 820.[59,60] The deactivating factor of 0.14 was calculated as follows :

The observed rate of bromination at the 3-position of 1-bromobutane is 0.37 times that of the secondary carbon of propane as determined experimentally. The sites being compared are indicated by asterisks:

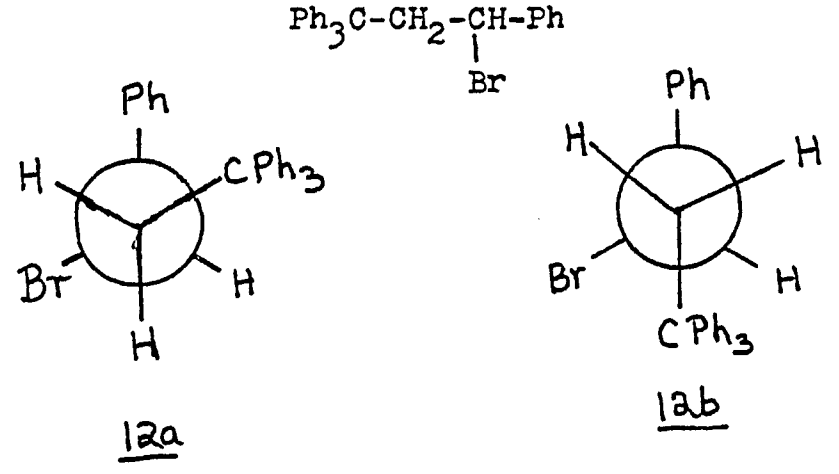
$$CH_3\overset{*}{C}H_2-CH_2-CH_2Br \qquad\qquad CH_3\overset{*}{C}H_2-CH_3$$

The enhancement of this deactivation at the next closer position to the deactivating substituent is 1/2.7 ------ the Taft factor.[61] Thus at a position β to a non-participating bromine atom the rate should be (1/2.7 x 0.37) or 0.14 times the rate for butane, the corresponding alkane. The anchimeric effect, in this case, is then defined as the ratio of the observed rate, k_{Br}, to that calculated for a non-participating bromine, k_H ;

$$\text{Anchimeric Assistance} = \frac{k_{Br}}{k_H}$$

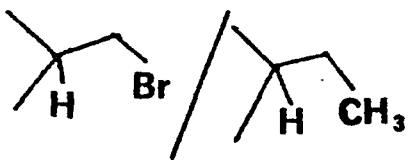
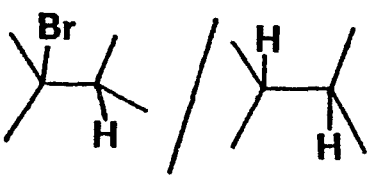
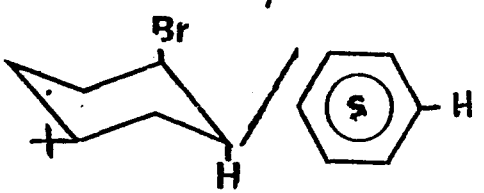
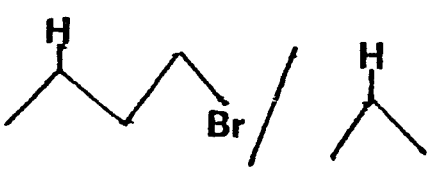
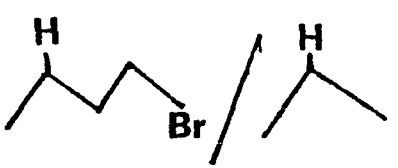
Several examples of anchimeric effects calculated in the manner described above are shown in Table 12 on the next page.

In order to calculate in a similar fashion the magnitude of the anchimeric assistance that seems to be indicated in the conversion of UTPE to TPE on reaction with NBS or Br_2, one would have to first estimate the deactivating effect of the trityl moiety. Towards this end 1,1,1,3-tetraphenylpropane was synthesised and its rate of reaction with NBS studied under the usual conditions. The crude product from the reaction has the nmr spectrum shown on page and is consistent with the structure 12, which is the product of normal bromination. The pattern of the H^1, H^2, H^3 protons is a typical AMX pattern expected from either of the two likely conformers 16a and 16b.



12a 12b

Table : Relative Rates of Hydrogen Abstraction by Bromine Atoms [61]

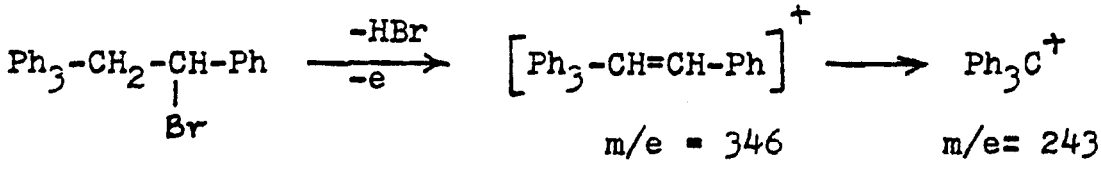
Reactants	Temp-erature	$(k_{Br}/k_H)_{obs}$	$(k_{Br}/k_H)_{perH}$	Anchimeric effect
	35	8	8	57
	35	12.5	25	179
	27	19.2	115	820
	60	1.4	1.4	10
	30	2.5	2.5	18
	0	4.1	4.1	30
	60	0.35	0.35	1.0

The mass spectrum of the crude, however, showed no peak where the parent ion would be expected at 414 & 412. Instead the peaks shown below were obtained.

Table 13: Mass Spectral Data for Compound 16

m/e	Intensity
347	1.7
346	7.7
243	9.0
82	92.3
81	45.1
80	100
79	48.1

The base peak at 80 and its isotopic counterpart (for Br) at 82 is due to $H^{79}Br^+$ and $H^{81}Br^+$ respectively. Evidently HBr is being eliminated with remarkable facility. The fragment at m/e 346 is due to the alkene formed after HBr loss in the mass spectrometer, and the fragment at m/e 243 is due to the trityl cation.



Attempts to purify the crude bromide, 12 , by column chromatography yielded a compound 13, whose nmr and mass spectra are consistent with the alkene formed after loss of HBr:

$$Ph_3C\text{-}CH{=}CH\text{-}Ph$$

13

The rate of bromination of 1,1,1,3-tetraphenylpropane, TPP 12, was determined as usual by nmr, by monitoring the disappearance of starting material against an internal standard, t-butylbenzene. The comparitive rates of bromination of TPP, ethylbenzene, toluene and UTPE under similar conditions are shown in Table 14

Table 14: Relative Rates of Bromination of Substituted Toluenes, II [a]

Reactant [b]	Rate
$PhCH_2\text{-}H$	1.0
$PhCH_2\text{-}X$	0.43
$PhCH_2\text{-}CH_2\text{-}H$	22.2
$PhCH_2\text{-}CH_2\text{-}X$	1.72

a) At 70° and 0.1M conc. in both substrate and halogen and statistically corrected

b) X= $C(Ph)_3$

The replacement of the β-hydrogen of ethylbenzene by a trityl group, the last two entries in the Table, results in a rate retardation of 0.080. Using the Taft argument, if the trityl group were moved one place closer to the site of bromination, as in UTPE, the deactivating effect of the trityl group would be magnified by a factor of 2.7. In other words, the expected rate of bromination of UTPE would be 0.080/2.7 or 0.03 times slower than that of the appropriate alkane, which in this case is toluene. The experimentally determined rate is, however, 0.43. Thus the experimental rate exceeds the theoretical rate by a factor of 14. This factor only reflects part of the anchimeric assistance, as in the calculation of the theoretical rate no computation was made for steric effects. If steric effects could be assessed, the calculated rate will be smaller than 0.03, and the the ratio of experimental rate to theoretical rate would be larger. The anchimeric assistance then would be 14X, where X is no less than one.

Andrew, Keefer, Friedrich, and their co-workers have determined the relative rates of hydrogen abstraction from the benzyl position of several α-substituted toluenes.[61a] Surprisingly they obtained a good correlation of relative rates of hydrogen abstraction by bromine atom with the parameters of the substituents. The large negative rho value of -2.47 that was obtained in the correlation was taken as

evidence for both appreciable charge development in the transition state and for the possibility of direct resonance interaction between the substituent and the incipient radical. Although it was stated that steric factors were unimportant in this system, subsequent work by Gleicher and Totherow,[2] indicated that steric factors could indeed influence the rate. In order to correlate both steric and inductive effects an expanded form of the Taft equation was utilised:

$$\log \frac{k_x}{k_H} = \sigma^+\rho + sE_s$$

Both reaction parameters, ρ and s, was evaluated by an iterative method using the data of Friedrich et al,[61a] to give the final expression shown below.

$$\log \frac{k_x}{k_H} = -2.47\sigma^+ + 0.53E_s$$

Using the above equation, Gleicher and Totherow determined a t-butyl group has a rate retarding effect of 10. Certainly a similar steric retarding effect should be manifested when the α-substituent is a trityl group and this would be a lower limit since we expect the trityl group to be larger than a t-butyl group. Thus from earlier calculations shown on page 61, we would expect the anchimeric assistance to be no less than 140.

Recently, Charton has refined the E_s parameter and defined a new steric constant, ν, also based on van der Waal's radii. A few characteristic values for substituents based on this constant are shown below in Table 15.

Table 15: Values of steric constants of Substituents

Group	ν
CH_3	0
CH_3CH_2	0.52
Ph	0.58
CH_2Ph	0.70
t-Bu	1.24
$(Ph)_3C-$	2.92*

* Private communication from M.S.Charton

As the substituent constant for the trityl group indicates that it is considerably larger than the t-butyl group, we expect the steric retardation to be greater than 10, and the anchimeric assistance to be greater than 140. The lack of a published σ-value for the trityl group precludes the calculation of a more precise value fro the total anchimeric assistance.

Hammett Sigma-Rho Study

Further evidence that anchimeric assistance is involved in the conversion of UTPE to TPE with Br· was obtained from a Hammett sigma-rho study.

It is known that as alkyl substituents are introduced at the benzylic carbon of toluene the rho value for the abstraction of benzylic hydrogen from toluene decreases in absolute magnitude. When bromine atoms from NBS are generated at 70° a rho value of -1.39 is found for the series,[63] while the allylbenzenes and ethylbenzenes have values of -0.76 and 0.69 respectively.[64,65] These values are in keeping with the expectation that electron-releasing groups at the reaction site should stabilise the transition state and decrease the substituent effect for the series.

Rho values are also dependent on steric effects. Destabilisation of the transition state due to unfavorable interactions between alkyl groups at the reaction site and the attacking radical increases the substituent dependence for the reaction. A larger absolute value of rho indicates a greater selectivity on the part of the attacking radical. Gleicher[66] and Minisci and co-workers [67] have noted instances of radical selectivity increasing at hindered sites.

In the case of UTPE, the substitution of the deactivating group (trityl) for benzylic hydrogen of toluene should lead to destabilisation of the transition state and increase the substituent effect for the series relative to toluene.

If anchimeric assistance was involved in the abstraction of hydrogen, a lowering in the substituent dependance would be noted. It was, therefore, hoped that a study of the relative rates of reaction of 2-aryl-1,1,1-triphenylethanes towards NBS would shed some light on the effect of anchimeric assistance for the series. Hence, for this study 2-aryl-1,1,1-triphenylethanes were synthesised, as usual, by the reaction of tritylllithium with the appropriately substituted benzyl chlorides.

The relative rates of reaction of the various substituted tetraphenylethanes were determined by direct competition between pairs of substrates using NBS as the source of bromine atoms. Analysis of the extent of reaction was determined by gas chromatography as a function of the product ratios, except in the case of 2-p-methylphenyl-1,1,1,-triphenylethane. In the case of the latter, extent of alkene formation was determined by Uv, with appropriate correction for reaction at the p-methyl group. The results of these experiments are presented in Table 16.

It is immediately apparent that electron-withdrawing substituents greatly retard the rate of reaction. Application of the Hammett equation using both σ and σ^+ values gave rho values as shown in Table 17. Better correlation with σ^+ constants was noted.

Table 16: Relative Rates of Alkene Formation from Substituted Tetraphenylethanes with NBS at 70°

Substituent	σ [a]	σ^+ [b]	k_x/k_H
p-t-C_4H_9	-0.197	-0.256	2.90 ± 0.12
p-CH_3 [c]	-0.170	-0.311	2.55 ± 0.15
H	0	0	1.00
p-F	0.06	-0.07	0.93 ± 0.04
p-Cl	0.227	0.114	0.75 ± 0.03
m-CF_3	0.430	0.520	0.155 ± 0.01

a) J.E.Leffler and Grunwald, "Rates and Equilibria of Organic Reactions", John Wiley & Sons, New York, 1963, p173

b) H.C.Brown and Y.Okamoto, J.Am.Chem.Soc., 80, 4979, 1958

c) Corrected for reaction at both benzylic positions.

Table 17: ρ Values for Hydrogen Abstraction from Substituted Tetraphenylethanes at 70° with NBS

Substituent Constant	ρ	r (Correlation Constant)
σ	-1.519	-0.882
σ^+	-1.506	-0.986

The rho value for this reaction was found to be merely 12% more negative than the rho value for toluene. Certainly a much greater increase in substituent dependency

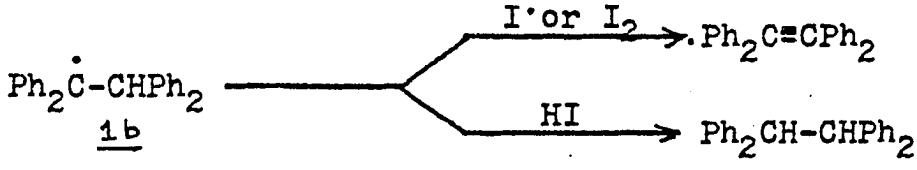
should have been observed. On the basis of steric effects alone an 80% increase in the rho values for ethylbenzenes was noted when comparing the selectivities of bromine atoms and trichloromethyl radicals, the trichloromethyl group being bulkier and having the more negative rho value.[2] If one considers that a value of -1.52 has been obtained by Russian chemists for the NBS halogenation of toluene at 70°C,[44] the value of -1.506 obtained for the reaction of tetraphenylethane with NBS, also at 70°, is all the more remarkable. It is therefore concluded that anchimeric assistance is definitely involved in the reaction of UTPE with NBS and that the magnitude of this assistance appears to be just enough to offset the inductive and steric effects present in the series.

Iodination of UTPE

The iodination of alkanes is very difficult to achieve homolytically, even when the hydrogen being abstracted is benzylic. The enthalpy of activation from benzylic sites is +14 kcal/mole, while the corresponding value for abstraction by a bromine atom is -2 kcal/mole. On account of the unfavorably large endothermicity of the abstraction step, the abstraction is readily reversible. Homolytic iodination is, therefore, rarely attempted.

$$RH + I\cdot \rightleftharpoons R\cdot + HI$$

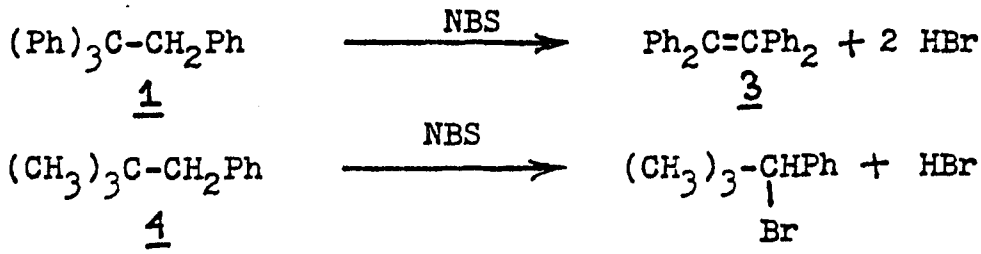
Since the formation of the intermediate R· in the reaction of UTPE with Br· has been shown to occur with anchimeric assistance (R· possibly being a bridged species) it was hoped that anchimeric assistance would compensate for the unfavorable endothermicity of abstraction of hydrogen by I· . (The radical (R·) would be formed in a product-like transition state, in this case, and anchimeric assistance would be possible.). Radical 1b , formed after mig- of the phenyl is complete, could then be further oxidised to TPE 3 or react with the HI formed and form 1,1,2,2-tetraphenylethane.



When equimolar quantities of iodine and UTPE were irradiated under the usual conditions, no decoloration of the solution was observed. Workup of the reaction mixture showed that only starting material was present. It is therefore, concluded that the initial abstraction of hydrogen from UTPE never does occur in the first place, and that the lowering of the energy of activation expected due to relief of steric strain and anchimeric assistance is not sufficient to offset the high activation energy.

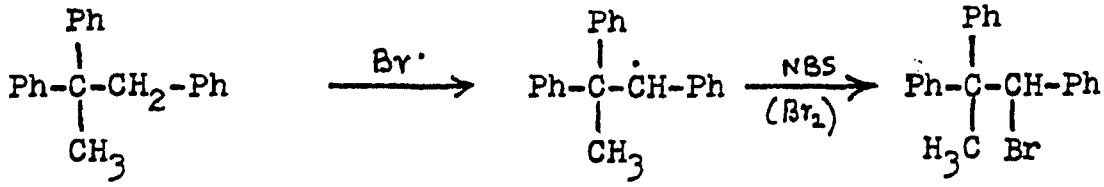
Steric Effects and Relief of Steric Strain

As already stated, UTPE 1 , is converted to TPE 3 , while neopentylbenzene, NPB 4 , is brominated normally on reaction with NBS.



The normal bromination observed in the case of neopentylbenzene is due to the forbidenness of an alkyl migration rather than due to the fact that the t-butyl group is less bulkier than the trityl group and can brominate normally.

It is also to be noted that 1,2,2-triphenylpropane 14 , where one of the phenyls of UTPE has been replaced by a methyl group, was brominated normally to yield a product characterised as 1-bromo-1,2,2-triphenylpropane 15 .[1]



14 14a 15

The lack of rearrangement in this particular case may be

rationalised as follows:

a) The free radical intermediate 14a, arising from abstraction of hydrogen from 14 , may not be as sterically hindered towards bromine insertion as the intermediate 1a (even assuming no assistance in the case of UTPE) resulting from UTPE, as the E_s values shown in Table 15 seem to indicate.

b) The energy of activation for the 1,2-migration of a phenyl group in 14a is greater than that for a phenyl migration in 1a because, although the rearranged radical is tertiary in both cases, the former is stablilised by only one phenyl while the latter is stabilised by two phenyls.

c) The stability of radical 1a is affected by the degree of overlap of the p-orbital on the benzylic carbon with the aromatic π-cloud. If this overlap is reduced due to interaction of the trityl group with the lone phenyl group, resulting in non-planarity of the lone phenyl group, then the stability of radical 1a would be reduced. Relief of steric strain might then become an additional driving force for the rearrangement. In 14a there is less steric congestion and the benzylic radical may be delocalised in a normal manner.

A note: The isolation of 1-bromo-1,2,2-triphenylpropane from the treatment of 1,2,2-triphenylpropane 14 with NBS is further tangible evidence that TPE 3 is formed from UTPE 1 by a free radical rearrangement rather than an ionic

In order to test how important a role the steric factor plays in precluding normal bromination and influencing the rearrangement of UTPE to TPE, 9-benzyl-9-phenylfluorene was synthesised. This compound is very similar to UTPE in terms of polar effects. A study of models indicates that tying back two of the phenyls of the trityl group of UTPE in the form of a fluorenyl ring should deprive this system of the steric acceleration, if any, that might be inherent in the rearrangement of radical 1a to 1b. 9-benzyl-9-phenylfluorene, 9-BPF , might, therefore undergo normal bromination without rearrangement .

---

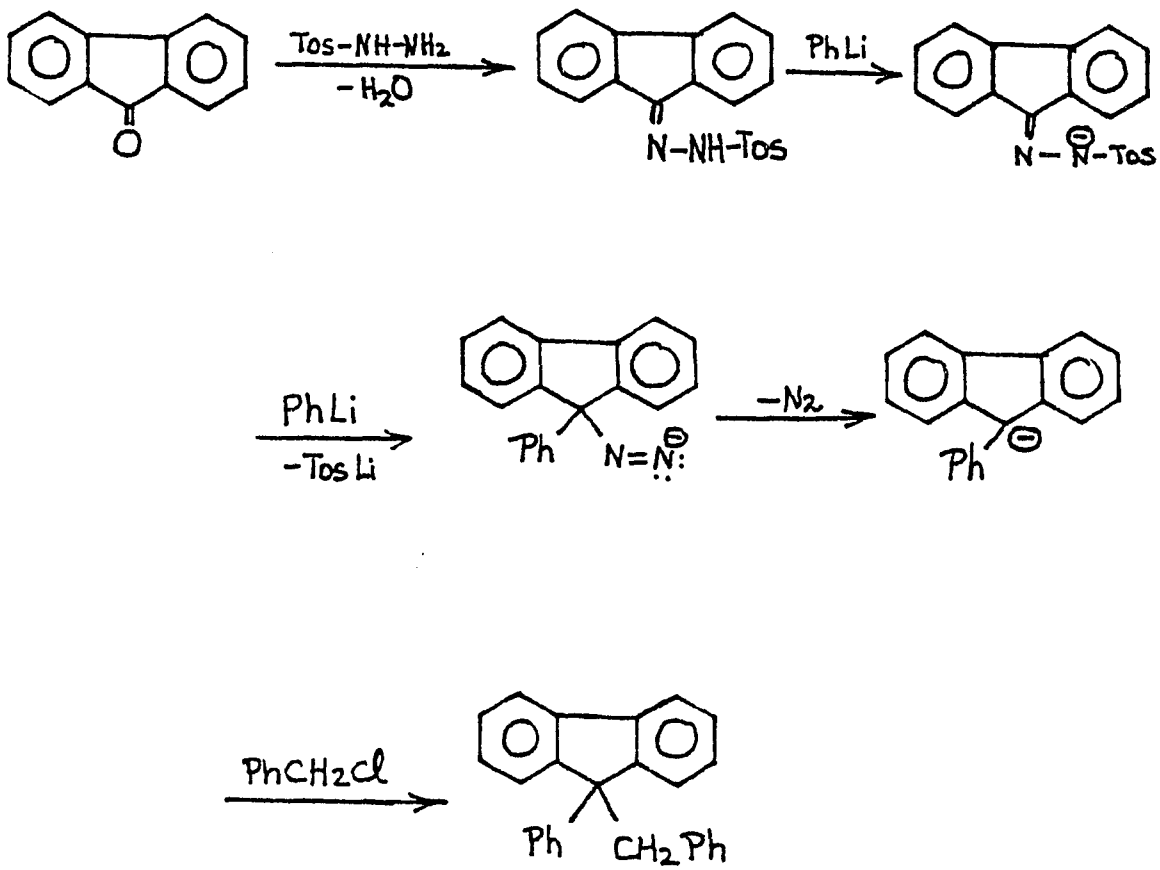
rearrangement, on ionisation of an initially formed brominated compound 2 (vide infra). If under the conditions of the reaction with NBS, the brominated compound 2 had been formed and had been converted to a carbocation, there is no reason why a carbocation could not likewise be formed from 14 . The 1,1,2-triphenylethyl carbocation is known to rearrange even though the rearranged ion is degenerate with the original ion.[68]

$$(Ph)_2CH\text{-}\overset{+}{C}H(Ph) \rightleftharpoons PhCH\text{-}\overset{+}{C}H(Ph)_2$$

A 1,2,2-triphenylpropyl carbocation would certainly, therefore, be more likely to rearrange.

$$(Ph)_2\overset{+}{C}\text{-}CH(Ph) \longrightarrow Ph\text{-}\overset{+}{C}(CH_3)\text{-}CH(Ph)_2$$

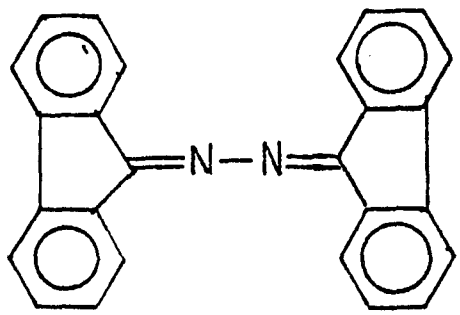
The synthetic route attempted in the preparation of 9-BPF, 15, is shown below:



9-BPF, 15

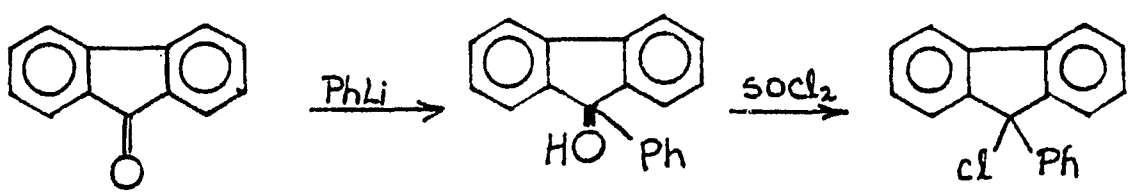
The analagous conversion of tosylhydrazone of 9-PBF to 9,9-dimethylfluorene had been achieved by using two moles of methyllithium and alkylating the intermediate 9-methylfluorenyl carbanion with methyl iodide.[69]

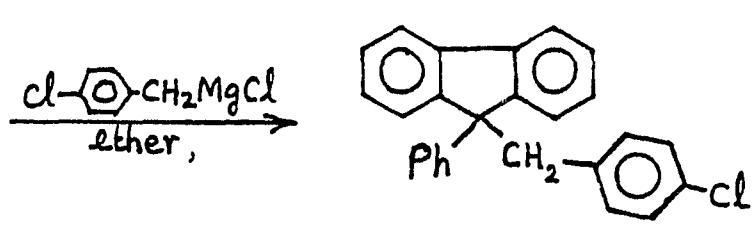
When the alkylation of the intensely colored carbanion was attempted with benzyl chloride, the expected decoloration was not observed. From the reaction mixture was obtained a compound, on the basis of whose spectrum (mass) the azine structure shown below is assigned. Precedence for a similar reaction with formation of an azine is known.[70] None of the expected product, 9-benzyl-9-arylfluorene was obtained.



"Azine"

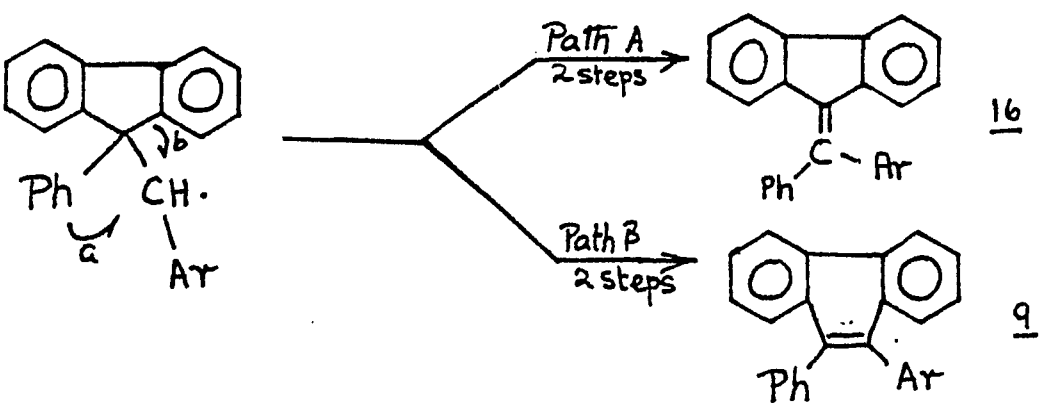
Eventually the desired product 15 was synthesised in low yield by the reaction of p-chlorobenzylmagnesiumchloride with 9-chloro-9-phenylfluorene.



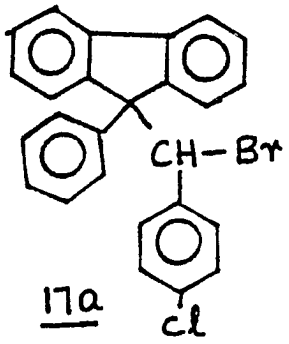


15

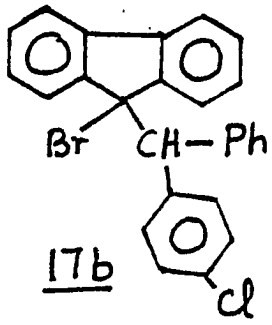
If 9-PBF, like UTPE, does not undergo normal bromination and instead rearranged, two possible products, 9,9-diphenylphenanthrene, DPP 9 , or the "fulvene" compound 16 , would be anticipated from two possible modes of rearrangement:



9-PBF, 15 , was irradiated with NBS for a short period and the crude product analysed by uv, nmr, and mass spectroscopy. The presence of a labile hydrogen was detected by treatment with alcoholic KOH. The nmr spectrum of the product revealed a singlet at 6.05δ indicative of a methine hydrogen, in this case, attached to a carbon atom with electron-withdrawing groups. On this basis, one of the two possible structures shown, was assigned to the product.

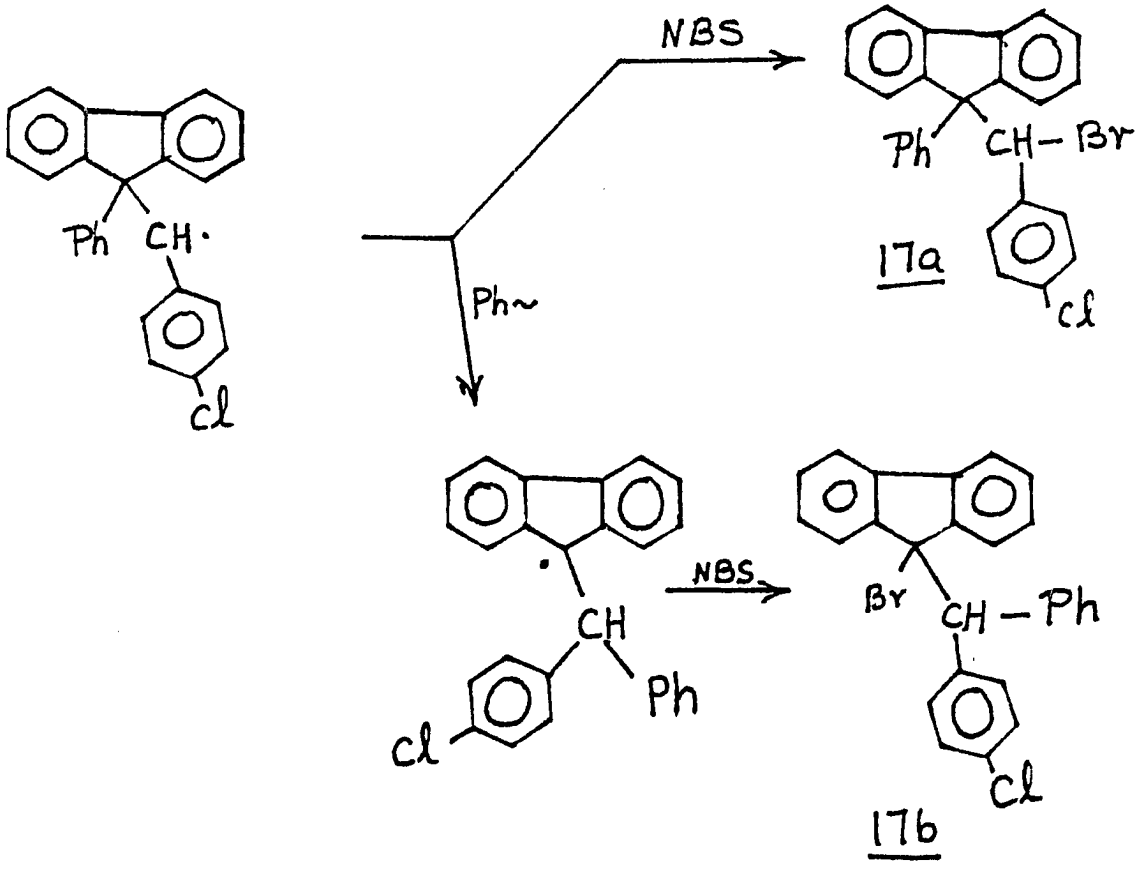


17a



17b

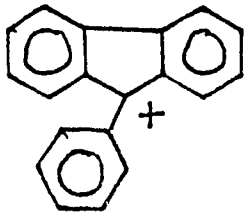
Compound 17a is the product of normal bromination. Compound 17b is formed after rearrangement of a phenyl group has occurred.



17a

17b

The structure 17a was finally assigned to the product on the basis of its mass spectrum. A base peak at 241 indicated that the 9-phenylfluorene moiety was retained in the product.



m/e = 241

One concludes, therefore , that the lack of steric hindrance to normal bromination and the absence of any F-strain in the ground state of the molecule makes any sort of rearrangement a comparitively high energy process. This stands in contrast to the total rearrangement observed, under similar conditions, when UTPE is reacted with NBS, thus conforming our assertions that, in this case, rearrangement is not solely dictated by the relative stabilities of the rearranged and initial radicals.

Reaction of Pentaphenylethane with NBS

One of the reasons why UTPE, 1 , does not undergo normal bromination is that the initially formed radical can rearrange to a more stable and,as already indicated, part of the driving force for the rearrangement is also derived from the simultaneous relief of steric crowding. In this context it seemed appropriate to study the bromination of pentaphenylethane. If abstraction of hydrogen from pentaphenylethane, PPE , does take place, inspite of the considerable steric hindrance to attack on the hydrogen, then, since rearrangement is degenerate, it would be interesting to see if normal bromination might occur

$$(Ph)_3C\text{-}CH(Ph)_2 \longrightarrow (Ph)_3C\text{-}\dot{C}(Ph)_2 \longrightarrow (Ph)_2\dot{C}\text{-}C(Ph)_3$$

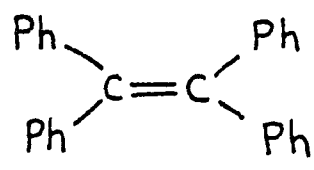
18

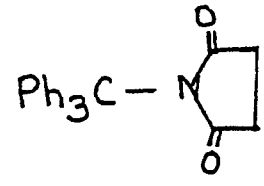
Pentaphenylethane was synthesised in good yield by the reaction of tritylllithium and benzhydrylbromide.

Pentaphenylethane is known to dissociate into trityl and benzhydryl radicals at temperatures above 110°.[71] To ensure that no dissociation was occurring at 70°, under the conditions of the reaction to be studied, PPE was irradiated without any halogen in CCl_4 at 70° and the solution analysed. PPE was recovered unchanged.

PPE was then irradiated with an equimolar amount of NBS under the usual conditions for a period of 24 hours. Thin layer chromatography of the crude showed four spots, one of which was starting material. Column chromatography gave a solid of m.p. 148-151 whose nmr showed a signal at 5.82 δ. It had a parent at m/e of 408. No other significant data was obtained. At this point no structural assignment can be made to this product.

The other compounds isolated by column chromatography were:





N-Trityl succinimide was isolated in low yield (2-3%) and its structure assigned on the basis of a parent ion at m/e 341 and a base peak corresponding to the trityl moiety at m/e 243.

Tetraphenylethylene was identified by its mass spectrum and its characteristic uv absorbance at 313 nm.

Since no attempt was made to study this reaction to study this reaction more thoroughly, it is quite possible that other products might have been present, since the chromatographic solvent mixture was not varied.

Possible mechanisms to account for the formation of TPE from pentaphenylethane are shown below:

Mechanism I:

$$Ph_3C\text{-}CH(Ph)_2 \xrightarrow{Br^\cdot} Ph_3C\text{-}\dot{C}(Ph)_2$$

$$\xrightarrow{-Ph^\cdot} Ph_2C{=}CPh_2$$

TPE

Mechanism II:

$$Ph_3C\text{-}CH(Ph)_2 \xrightarrow{Br^\cdot} Ph_3C\text{-}\dot{C}Ph_2$$

$$\longrightarrow \left[Ph_3C^\cdot : CPh_2\right]$$

$$\longrightarrow Ph_3C^\cdot + Ph_2C:$$

$$Ph_2C: \xrightarrow{\text{dimerisation}} Ph_2C{=}CPh_2$$

TPE

Halogenation of 1,1,1-Triphenylethane

If abstraction of a hydrogen from the methyl group of triphenylethane can be accomplished, the resulting triphenylethyl radical should be more prone to rearrange than than the radical 1a (from UTPE). on account of the greater stability to be gained by the conversion of the 1° radical 19a to the tertiary radical stabilised by two phenyls.

$$Ph_3C\text{-}CH_3 \longrightarrow Ph_3C\text{-}CH_2\cdot \longrightarrow Ph_2C\text{-}CH_2Ph$$

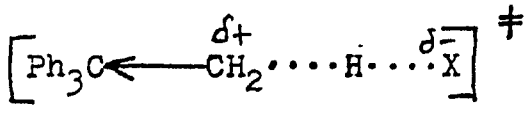
19 19a 19b

The generation of the 2,2,2-triphenylethyl radical has been accomplished several ways, and in all cases led to products which resulted from the rearranged radical, 19b. The various methods employed so far have been a) aldehyde decomposition [72] b) decomposition of azo compounds [73] c) peroxide decomposition [11] d) Hunsdiecker reaction [74] and e) Kolbe electrolysis. [75] No attempt has been made so far to generate the radical 19a by abstraction of a hydrogen by halogen.[76]

1,1,1-triphenylethane was synthesised by the method of Gilman and Gaj, from trityllithium and trimethylphosphate.[77]

Equimolar quantities of 19 and bromine in carbon tetrachloride were irradiated as usual for 24 hours. Analysis of the crude product showed only starting material

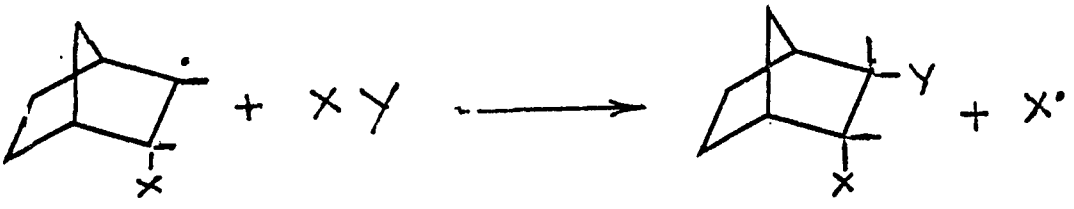
Even employing a four fold excess of bromine had no effect. Similarly photochlorination also yielded mostly starting material (95%). It appeared that the rest of the crude product consisted of products of nuclear halogenation of the phenyl rings. The reasons for the lack of direct halogenation are not exactly clear but steric factors can certainly be ruled out as being a dominant factor here as attack of the halogen atom is on hydrogen rather than on carbon. Moreover, abstraction of hydrogen does take place from UTPE, whose hydrogens are more shielded. It appears that a strong polar effect due to the deactivating influence of the trityl group must certainly be involved and be one of the chief factors in the lack of reaction.



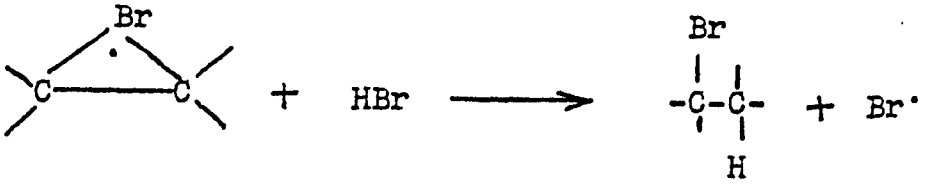
A destabilised transition state, such as the one shown above, could only be achieved if sufficient activation energy is supplied, as in the modes of generation already described.[11; 72-76] Halogenation under ambient conditions is concluded to be impossible under free radical conditions.

Reaction of Tetraphenylethylene (TPE) with Bromine

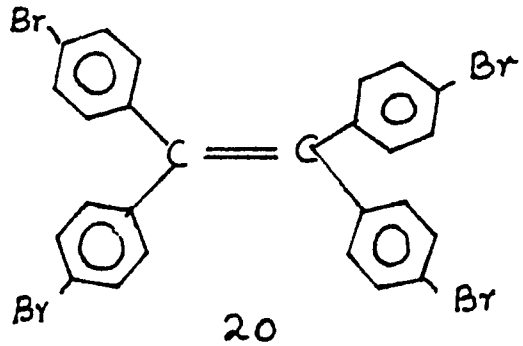
A characteristic test for alkenes is their ability to decolorise a solution of bromine in CCl_4, unless the double bond is highly deactivated towards addition of bromine. Steric effects have been observed and accorded an important function in a number of free radical addition reactions. However, they involve mostly the governing of stereochemistry of the chain transfer step in free radical additions. For example, addition to norbornylene seems to be governed by the unhindered angle of approach which permits chain transfer from the exo-side but not easily from the endo-side (cis addition frequently occurs in this case)



Other steric influences include bridging of olefinic bonds as a rationale for the trans-addition observed for such reactions as the HBr addition to olefins.[78]



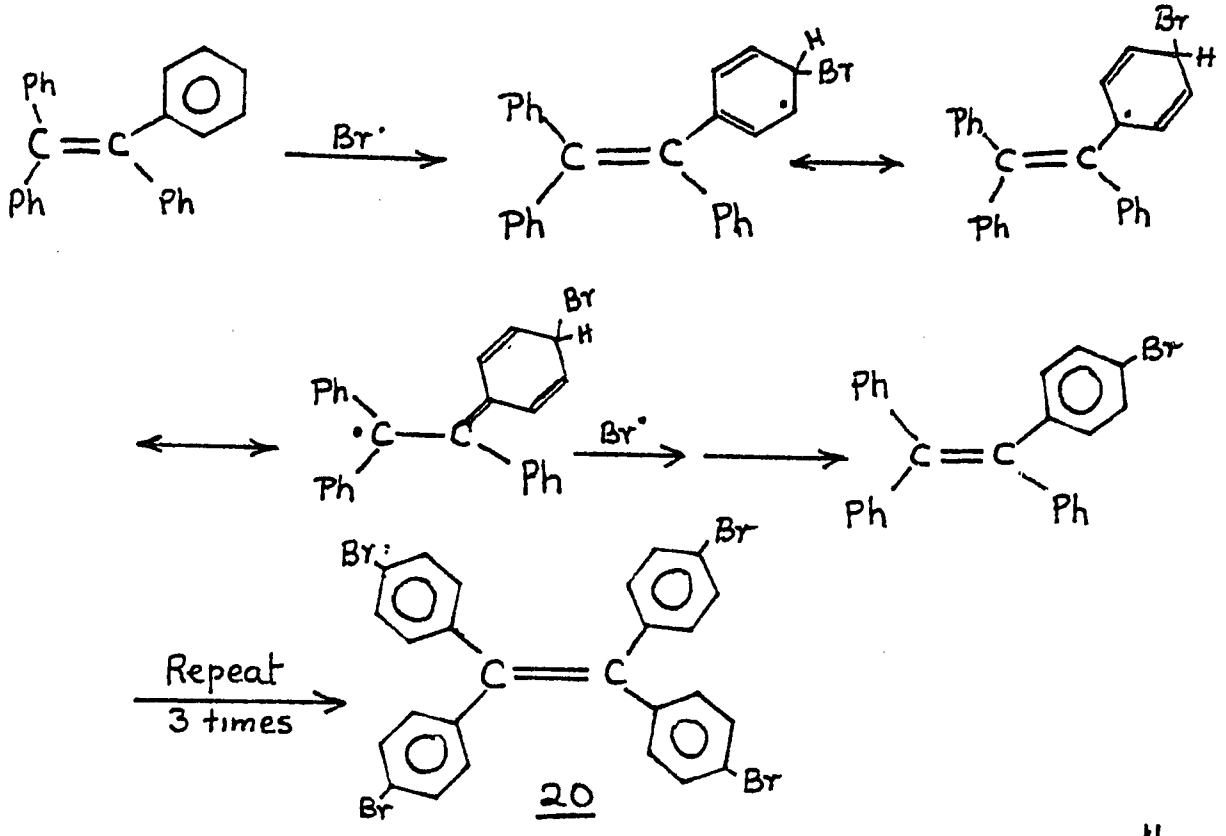
Few cases are known, however, where addition is completely precluded due to inaccessibility of the double bond. Tetraphenylethylene, 3 , is an instance where shaking with a solution of bromine in CCl_4 produces no decoloration due to the steric hindrance present. On the other hand, when a 5-6 molar excess of bromine and TPE were irradiated together, a crude product was obtained, whose mass spectrum showed upto 7 bromine atoms. This could be crystallised to yield a compound melting sharply at 248°. This compound was characterised by its mass spectrum, which revealed the presence of 4 bromine atoms and by its literature m.p. of 249°. [79] Its nmr spectrum also correlated well with the assignment of the structure as, tetrakis-p-bromo-tetraphenylethylene, 20:



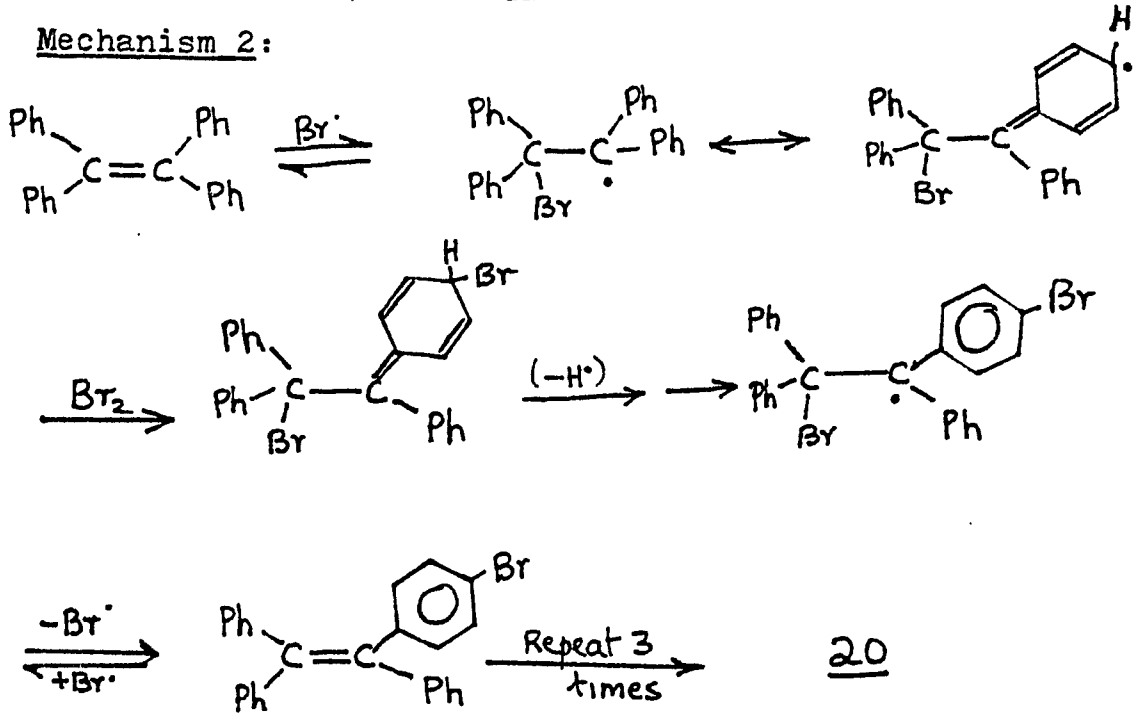
20

Under the conditions of the experiment, which involves non-polar solvent and irradiation by light, it can be safely concluded that the bromination of the phenyl rings is not polar in character. The following mechanisms are suggested:

Mechanism 1:



Mechanism 2:



Role of Oxygen in the Photobromination of UTPE

It has been thoroughly demonstrated that the photochlorination of toluene and other hydrocarbons, in both the gas phase as as well as in solution, is inhibited markedly by traces of oxygen.[80] The bromination of hydrocarbons is similarly inhibited by oxygen in the gas phase.[81,82] In solution, however, it has been shown by Kharasch, White and Mayo,[83] that the photobromination of toluene, and other hydrocarbons, was activated by oxygen. It was, therefore, of interest to study the effect of oxygen on the photobromination of UTPE.

The photobromination of UTPE with Br_2 was carried out both under ambient conditions (20% oxygen) and under nitrogen, after thoroughly degassing by the freeze-thaw method. It was observed that:

a) Bromination was about 30% faster under ambient conditions than when the bromination was conducted in an oxygen-free atmosphere.

b) The decoloration of the UTPE-Br_2-Oxygen always started at the surface and proceeded downward through the solution. A similar observation was reported by Kharasch and co-workers[83]

From this it is concluded that the reaction of UTPE with Br_2 involves free radical intermediates. This conclusion is also supported by the observation of a slight decrease in the rate of reaction (8-12%) of UTPE with SO_2Cl_2 in benzene under ambient conditions. Rates in all cases were determined by nmr.

It is generally accepted that the inhibitory effect of oxygen in photochlorinations is due to the fact that oxygen terminates the chain reaction by reacting with hydrocarbon radicals .[84,85]

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

The peroxy radical itself is unlikely to initiate chains on its own accord by direct abstraction of hydrogen from the hydrocarbon. Absolute reactivities of organic substrates towards their own peroxy radical reveal them to be comparitively unreactive radicals.[86]

A similar inhibition would also be expected of the corresponding photobrominations. Since the rate is enhanced, we surmise that the peroxy radical as well as oxygen react with the HBr formed to produce additional bromine atoms.

$$ROO\cdot + HBr \longrightarrow ROOH + Br\cdot$$

$$O_2 + 4HBr \longrightarrow 2H_2O + 4\ Br\cdot$$

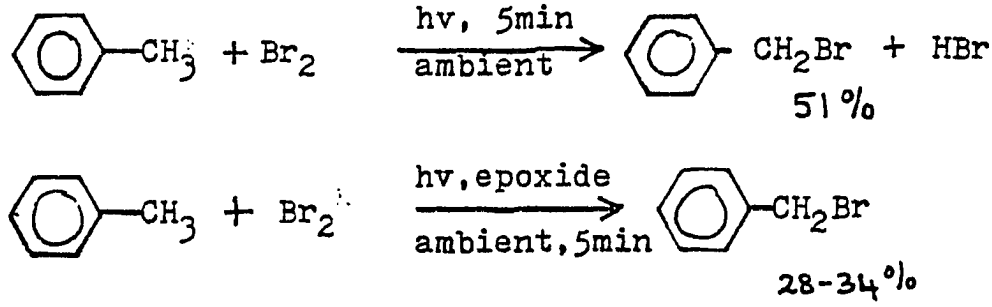
The strength of the ROO-H bond has been estimated to be 88 kcal/mole.[87] Thus the interaction of the peroxy radical with HBr would be almost thermoneutral and likely to occur. The corresponding reaction with HCl would be considerably endothermic and unlikely to occur. Moreover, the hydroperoxide that is formed from the reaction with HBr could activate the reaction further, in a manner similar to the acti-

vating effect of peroxides.

In summary, the formation of the peroxy radical represents a chain terminating step in photochlorinations, on account of its inability to initiate further reaction. However, in photobrominations the peroxy radical can react with the HBr to produce additional bromine atoms, which become chain-propagating species, and an activating effect is seen.

In order to test the hypothesis that the HBr formed during photobrominations is functioning as a source of additional bromine atoms, either by reaction with peroxy radicals or by direct reaction with the oxygen present, we restudied the bromination of toluene in the presence of 1,2-butene oxide. Epoxides are known to be excellent scavengers of HBr and its presence in the bromination system should deprive the system of additional active bromine atoms, on the basis of our hypothesis. The scavenging of HBr should, therefore lead to a decrease in the rate of bromination of toluene.

By monitoring the rate of disappearance of toluene as well as the rate of formation of benzyl bromide, by nmr, it was possible to determine the rate of conversion of toluene to benzyl bromide. It was found that the presence of epoxide in the toluene-bromine-oxygen system resulted in a rate decrease of 38-45 % in comparision to the reaction where no epoxide was present.



An alternate hypothesis [88] for the inhibitory effect of oxygen during chlorinations is based on the equation below:

$$Cl\cdot + O_2 \longrightarrow ClO_2$$

Because oxygen does not inhibit the bromination of toluene, Kharasch, White, and Mayo [83] made the assumption that $BrO_2\cdot$ is not stable. However this does not explain the activation observed during the bromination of toluene. We feel that the hypothesis of Kharasch and co-workers [83] that HBr was functioning as an additional source of bromine atoms has been validated by our results and is the best rationalisation of the activating effect of oxygen during photobrominations.

Conclusions

The reaction of 1,1,1,2-tetraphenylethane, UTPE 1 , with either NBS, Br_2, or with $BrCCl_3$, gave tetraphenylethylene, TPE, as the sole product. The mechanism for the conversion of UTPE to TPE was postulated to involve a 1,2-phenyl shift followed by subsequent oxidation along a free radical pathway. 9-Benzyl-9-phenylfluorene which should have been more prone to rearrange than UTPE, instead gave the normal brominated product. The facile rearrangement observed, instead of the expected normal bromination, in the case of UTPE, was attributed to:

a) Relief of steric strain

b) The formation of a more stable radical than the initial radical.

When UTPE was reacted with SO_2Cl_2 or Cl_2 in CCl_4, however, little or no reaction occured. The trapping of the reactive chlorine atoms by the substrate, both by the normal π-complexation with a phenyl ring as well as to an unique trapping within the trityl moiety, was deemed to be the main reason for the unusually low reactivity of UTPE towards chlorine atoms. When the solvent was changed from CCl_4 to either benzene or CS_2, both of which are good π-complexors, much greater reactivity was, paradoxically, observed. This was attributed to the fact that the chlorine atoms were no longer being trapped by the substrate and that the π-complexed

chlorine atoms were capable of hydrogen abstraction unlike the substrate-complexed ones. Interestingly, 9,10-diphenylphenanthrene was also formed besides TPE in the reaction of UTPE with SO_2Cl_2 in benzene or CS_2. The variance in the reactions of UTPE with Br_2, where TPE was the sole product, and π-complexed chlorine atoms, was attributed to the involvement of different intermediates. A phenyl-bridged intermediate was proposed for the reaction with Br·, while the classical radical was proposed as an intermediate for the reaction with Cl· .

The formation of the phenyl-bridged radical intermediate, in the reaction of UTPE with bromine or NBS, was shown to occur with anchimeric assistance in the transition state. Thus, a Hammett sigma-rho study for the series of 2-substituted-1,1,1-tetraphenylethanes gave a rho value of -1.50 The rho value for the reaction of toluene with NBS was shown by Walling and co-workers to be about -1.36. Russian chemists, recently, have calculated a value of -1.55 for the reaction of toluene with NBS. Regardless of which of the two values are accurate, the rho value obtained for the reaction of UTPE with NBS is considerably less negative than expected. A greater substituent dependancy was expected since the trityl group is considerably deactivating by induction as well as being extremely bulky. It was concluded that anchimeric assistance counterbalances, to a large extent, the steric and inductive effects that should have resulted in a considerable increase in substituent dependance in a

Hammett sigma-rho study.

An experiment was designed to enable the calculation of the magnitude of the anchimeric assistance. By comparing the rates of reaction of UTPE and 1,1,1,3-tetraphenylpropane with NBS, an estimate of the destabilising inductive effect of a trityl group was possible. By assuming that the steric bulk of the trityl group and a t-butyl group were the same, when in fact the trityl group is more bulky, a lower limiting value, for the anchimeric assistance, of 210 was obtained.

It was also concluded that the activation observed when the bromination of UTPE was carried out under ambient conditions, relative to bromination under nitrogen, was due to HBr being oxidised to additional bromine atoms.

Experimental

Section A. Preparations

Preparation of 1,1,1,2-tetraphenylethane, UTPE, 1 .

In a three-neck flask fitted with gas inlet, gas outlet and a pressure equalising funnel, was placed 4.88g triphenylmethane (0.02 mole). 100ml of freshly distilled THF (distilled over barium oxide)was added and the resulting solution stirred magnetically, under an atmosphere of nitrogen. The entire contents of the flask had been pre-cooled to $0^{o}C$. N-Butyllithium (2ml; 0.021 mole) was then added dropwise with rapid stirring. The resulting red solution was then stirred magnetically for an hour.

To the solution of trityllithium, being maintained at $0^{o}C$, was added benzyl trimethylammonium bromide in small portions. When the red color of the trityllithium disappeared,the ice-bath was removed and the solution stirred at room temperature for 10 minutes. The solution was then poured into about 100ml saturated NH_4Cl and the organic layer separated. The aqueous layer was extracted with 25 ml CH_2Cl_2 and the extract combined with the organic layer. After washing with 5% HCl and neutralising with 5% NaOH, the organic layer was dried over anhydrous $MgSO_4$. Upon removal of solvent a crude solid was obtained which was recrystallised from benzene/ methanol. Yields were generally around 90%.

Data: m.p. $143-44^{o}$ (Lit.m.p.$142-43^{o}$)[89]

nmr -- singlet at 7.05 δ (20 H); 3.84 δ (2H)

mass spectrum -- parent at 334 (m/e)

Preparation of 1,1,2,2-tetraphenylethane, STPE, 11 .

In a three-neck flask fitted with gas inlet, gas outlet and addition funnel was added magnesium turnings (1,13g.; 0.05 mole). The flask was thoroughly flushed with nitrogen. A few drops of a solution of benzhydrylbromide (12.0g; 0.05 mole) in about 75 ml anhydrous ether was added to initiate the formation of the Grignard. Once a vigorous reaction had started, the remainder of the benzhydryl solution was added over a period of 15 minutes. After the exothermic reaction had subsided, the flask was heated at reflux for 15 minutes. The solution was dark green at this point.

To the solution of benzhydrylmagnesiumbromide was then added 8-10 mgs of cuprous chloride and an additional 11.7 g of benzhydryl bromide (0.045 mole) in 50 ml of anhydrous ether. The reaction mixture was refluxed for 20 minutes, poured into cold water and the ether layer separated and washed repeatedly with saturated solution of sodium chloride. The washings were extracted with CH_2Cl_2 and combined with the ether extract. The solution was then dried over anhydrous $MgSO_4$. The solvent was then evaporated on a rotary evaporator, and the resulting solid recrystallised from toluene/methanol. Yield of product is 8.0-8.15 g (40-43%).

Data: m.p. 210-211° (lit. m.p.211°)[90]
nmr --- singlet at 7.05 δ (20H); 4.78 δ(2H)
mass spectrum--- parent at m/e 334

Preparation of 2-p-chlorophenyl-1,1,1-triphenylethane

The synthesis of the title compound was achieved by the reaction of trityllithium with p-chlorobenzyl chloride in the manner described for the preparation of UTPE. Upon removal of the solvent the solid obtained was recrystallised from methanol. Yields were generally around 80-88%.

Data: m.p.176-177°(lit.m.p.174-175°)[91]

nmr--- complex pattern at 7.07-6.65 δ(20H); singlet at 3.86 δ(2H)

mass spectrum: parent at m/e 370, 368 (Chlorine isotope)

Preparation of neopentylbenzene, NPB, 4 .

The synthesis was achieved by the reaction of t-butyllithium with benzyl chloride.

To a solution of benzyl chloride at 0° and under nitrogen, an equimolar amount of t-butyllithium in hexane was added dropwise. The color of the solution at the end of the reaction period was a faint red and and as usual a precipitate of LiCl was formed. The solution was then allowed to warm to room temperature before being gently refluxed for an hour. The resulting solution was poured into 100ml of saturated NH_4Cl and worked up as described earlier. The oily residue obtained after work-up was distilled under reduced pressure. Yield of product was around 65%

Data; b.p. 85°C/12mm (lit.b.p.185°)[92]
nmr--- singlets at 7.02 δ(5H); 2.46δ(2H);
0.98δ(2H)
mass spectrum: parent at m/e 148

Preparation of 1,1,1,3-tetraphenylpropane

The synthesis of the title compound was achieved by the reaction of trityllithium and 2-phenethylbromide, by the general procedure already outlined for the synthesis of UTPE.

To a solution of trityllithium (0.02 mole), 2 ml of phenethylbromide (0.015 mole) was added dropwise at 0°C, under nitrogen. Within 5 minutes the red color of the solution was discharged and the solution turned milky white. Workup as usual gave a yellow oil which when treated with hot methanol gave a yellow solid. The crude solid was recrystallised from toluene/methanol to yield white crystals. Yield of product is generally around 90%.

Data: m.p. 120-121° (lit.m.p.124-125°)[93]
nmr --- see spectra on page 115
mass spectrum-- parent at m/e 346

Preparation of 9-phenyl-9-benzylfluorene, 9-PBF

The synthesis was achieved by the coupling of benzylmagnesium chloride and 9-chloro-9-phenylfluorene.

9-Phenylfluorenol, synthesised by the method of Ullmann and Wurstenberger,[94] was converted to the chloride with conc. HCl and acetyl chloride. The chloride was repeatedly cryst-

allised from pentane and had a melting point of 77-78°.[95]

Benzylmagnesium chloride was prepared as described earlier. To approximately 0.01mole of the Grignard was added 9-chloro-9-phenylfluorene (2.25 g; 0.008 mole) and the ether solution refluxed, after the exothermic reaction had subsided, for an hour. After the usual workup, the product obtained was an oil which was then chromatographed on a silica gel column (1'x1") using a solvent mixture of 95% Hexane and 5% methylene chloride. A white solid obtained (0.36g; 15% yield) had the spectral characteristics of the desired product.

Data: m.p. 132-33°(lit m.p.135-36°)[96]
nmr---3.96δ; 7.0-7.15δ(18H) - see page 116
mass spectrum: Parent at 332 (4% of base peak at 241)

Preparation of 1,1,1-triphenylethane

Approximately 0.01 mole of trityllithium was prepared by the reaction of 2.4g (0.01 mole) of triphenylmethane and 0.011 mole of n-butyllithium, as already described.

Trimethylphosphate (1.4g, 0.01 mole) in 20 ml of anhydrous THF was added to the ice-cold solution of trityllithium and stirring was continued an additional 15 minutes after the red color of the trityllithium was discharged.

Workup as usual gave a solid which on recrystallisation from ethanol yielded 1.7 g of white crystals of m.p. 93-94° (lit. m.p.93-94°)[97]

Preparation of 2-p-Methylphenyl-1,1,1-triphenylethane

The title compound was synthesised by the reaction of p-tolylmagnesium chloride with triphenylmethyl chloride, by the general procedure already outlined. It was recrystallised from benzene/methanol and had a m.p. of 158-59° (lit.[97a] m.p. 160-61°)

Preparation of 2-p-Fluorophenyl-1,1,1-triphenylethane

The title compound was synthesised by the reaction of p-fluorobenzyl chloride with tritylllithium by the general procedure already outlined. It was recystallised from benzene/methanol and had a m.p. of

Preparation of 2-m-Trifluoromethylphenyl-1,1,1-triphenylethane.

The title compound was synthesised by the reaction of m-trifluoromethylbenzylmagnesium chloride, prepared from trifluoromethylbenzyl chloride (PCR Chemicals, Florida) and trityl chloride by the procedure already outlined. It was recrystallised from methanol and had a m.p. of 113-15°.

Preparation of 2-p-t-Butylphenyl-1,1,1-triphenylethane

The title compound was prepared by the reaction of tritylllithium and p-t-butylbenzyl chloride, as described. Yield of product is quantitative. The product was re-

crystalised from benzene/methanol and had a m.p. of 156-159°.

Preparation of Pentaphenylethane

The title compound was prepared by the reaction of trityllithium and benzhydryl bromide in over 90% yield, by the procedure outlined. The crude product was crystallised from cold chloroform and had a m.p. of 156-59° (lit.[98] m.p. 159-161°)

Reaction of 1,1,1,2-tetraphenylethane, UTPE 1 , with NBS under free radical conditions.

To a solution of 1,1,1,2-tetraphenylethane (0.334 g; 1 mmol) dissolved in 20 ml of CCl_4, in a specially designed glass tube (see page 112 for illustration), was added 0.180 g of NBS (1 mmol). The tube was evacuated and nitrogen was led in to maintain a positive pressure. The tube was then irradiated at a distance of 2" from a 300 watt GE sunlamp for a period of one hour. The temperature of the solution, read immediately on opening the tube, was 69-70°. Total conversion of NBS to succinimide was observed to have taken place. The solvent was then removed on a flash evaporator to yield a yellow powder. The nmr of this crude product showed peaks only in the aromatic region. Tlc on a silica gel (Q 4F; Quantum Industries) plate showed only a single spot. Solvent systems used in the development of the plate were a) Hexane b) 3:1 Hexane/Benzene and c) 8:1 Hexane/Methylene chloride. The crude was recrystallised from methanol to yield 0.32 g (98%) of a solid melting at 220-21°, uv max 311 nm (log 4.2). It gave a parent ion at m/e 332 in the mass spectrum. The product was characterised as tetraphenylethylene, TPE 3 , (lit [99] m.p.221°). This identification was confirmed by oxidation with potassium permanangate to an oil which gave an orange 2,4-dinitrophenylhydrazone derivative melting at

232-35° (lit.[100] m.p. 237° for the DNPH of benzophenone).

Reaction of 1,1,1,2-tetraphenylethane with Bromine

When equimolar quantities of 1,1,1,2-tetraphenylethane and bromine were reacted, under the conditions described above, a quantitative yield of tetraphenylethylene was obtained. The mass spectrum of the crude product indicated the presence of 1-p-bromophenyl-1,2,2-triphenylethylene in trace quantities, by the presence of the characteristic bromine isotopic pattern at 410 & 412.

Reaction of 1,1,1,2-tetraphenylethane with $BrCCl_3$

0.334 g of 1,1,1,2-tetraphenylethane (1 mmol) was dissolved in 15 ml of CCl_4 and 5 ml of bromotrichloromethane was added. About 10 mg of benzoyl peroxide was added and the solution irradiated as described. At the end of 24 h, the crude product, obtained by rotary evaporation of the solvent, was determined by spectral analysis to be exclusively tetraphenyletnylene.

Reaction of 1,1,1,2-tetraphenylethane with Bromine in the presence of HBr scavengers.

The reaction of 1,1,1,2-tetrphenylethane with bromine was carried out as described above, with the addition of equimolar quantities of a) $CaCO_3$ and of b) Styrene oxide. At the end of the reaction period (1h) the solutions were

analysed for TPE by uv. Results were the same as in the reaction carried out in the absenceof these HBr scavengers.

Reaction of 1,1,1,2-Tetraphenylethane with Chlorine in CCl_4

To a solution of 0.334g of 1,1,1,2-tetraphenylethane (1 mmol) in 19 ml of CCl_4 was added 1 ml of a 1M solution of chlorine (1 mol). About 10 mg of benzoyl peroxide was added and the solution irradiated as described above, under nitrogen. When analysed at the end of one hour by nmr and uv, it appeared that only starting material was present. Irradiation was then carried out for 42h more. When analysed again, the amount of TPE present was estimated as being no more than 8-10%, the rest being starting material.

Reaction of 1,1,1,2-tetraphenylethane with SulfurylChloride in Carbon Tetrachloride

Equimolar quantities of SO_2Cl_2 and 1,1,1,2-tetraphenylethane in CCl_4 (0.05M) were irradiated as described above. Analysis at the end of 43h by nmr and uv indicated that about 6-9% of tetraphenylethylene was present, the rest being unreacted starting material.

Reaction of 1,1,1,2-tetraphenylethane with Sulfuryl Chloride in Benzene.

Equimolar quantities of 1,1,1,2-tetraphenylethane and sulfuryl chloride (0.5 mmol) in 10 ml of benzene were irradiated as usual for a period of one hour. Nmr and uv analysis showed that only starting material was still present. Irradiation was therefore continued an additional 43 h . Temperature of the solution at the end of the reaction period was 68-69°.

Tlc of the crude on a silica gel plate showed the presence of 3 products besides unreacted starting material. The four spots had r_f values of 0.72, 0.70, 0.67 and 0.52. The crude product was then chromatographed on a 2" x 1" alumina column and eluted with heptane, 10:1 heptane/benzene, 8:1 heptane/benzene and finally with 8:1 heptane/ethyl acetate. Changes in solvent composition were made every 200 ml. Ten ml fractions were collected. The first compound eluted from the column had a m.p. of 234°, uv max at 308 nm. This compound was characterised by its nmr, uv, & mass spectrum (parent ion at m/e 330) as 9,10-diphenylphenanthrene (lit.[101] m.p.234°). The second compound eluted had a melting point of 128-133° and was shown to be starting material, UTPE. The third fraction gave a product of m.p. 211-215°. From its mass spectrum and uv, this compound was identified as tetraphenylethylene. The last

fraction gave a product melting at 162-65°. Its mass spectrum revealed a parent ion at m/e 366 with the characteristic chlorine isotopic pattern. On this basis it was assigned the structure, p-chlorophenyl-triphenylethylene, (lit.[102] m.p.165-67°). Typical recovery yields from 160 mg of crude and percentages on starting material are shown below:

9,10-diphenylphenanthrene	38-42 mg	ca.12%
1,1,1,2-tetraphenylethane	130-150 mg	ca.45%
tetraphenylethylene	72-76 mg	ca.25%
p-chlorophenyl-TPE	34-38 mg	ca.11%

Methodology of the nmr analysis of the conversion of 1,1,1,2-tetraphenylethane to tetraphenylethylene.

0.5 ml of t-butylbenzene was introduced at the start of the reaction to the solution of reactants (20 ml of a 0.05M solution) and served as internal standard. The ratio of the area of the singlet peak for the t-butyl group and the area of the singlet peak for the benzylic protons of starting material, at 3.84δ was determined prior to irradiation. After the desired time interval, an aliquot was withdrawn for analysis. The singlet signal at 3.84δ diminishes in intensity relative to the t-butyl group signal 0.95δ, as starting material is converted to product. A comparision

of the new ratio of the areas of the t-butyl group of the internal standard and the diminished area of the signal at 3.84 δ of starting material served as a measure of the extent of reaction.

Uv Analysis of the Conversion of 1,1,1,2-Tetraphenylethane to Tetraphenylethylene.

Solutions for uv analysis were made up in CCl_4, in view of the fact that reactions were generally done in CCl_4 and direct analyses of aliquots of reaction mixtures could be performed without evaporation of the CCl_4 and substituting hexane or other solvents generally recommended for recording uv spectra. Interference from CCl_4 is negligible at 312nm. A standard curve using varying proportions of UTPE and TPE was obtained at λ_{max} 312 nm. It was necessary to to include UTPE in the analysis as the concentration of UTPE affected the extent of absorption of TPE at 312 nm. The solution mixtures had the following concentrations per 2 ml.

a) 25×10^{-8} mole UTPE
b) 20×10^{-8} mole UTPE and 5×10^{-8} mole TPE
c) 15×10^{-8} mole UTPE and 10×10^{-8} mole TPE
d) 10×10^{-8} mole UTPE and 15×10^{-8} mole TPE
e) 5×10^{-8} mole UTPE and 20×10^{-8} mole TPE
f) 25×10^{-8} mole TPE

After the desired time interval, a 0.1ml aliquot of the 0.05 M solution of substrate was withdrawn and diluted to 100ml, its absorbance measured and its concentration determined from the standard curve.

Reaction of 1,1,2,2-tetraphenylethane, STPE, with NBS

Equimolar quantities of STPE and NBS (0.5 mmol) in 10 ml of CCl_4 were irradiated by the general procedure outlined. A quantitative yield of tetraphenylethylene, TPE , was isolated, within 30 minutes.

Reaction of 1,1,2,2-tetraphenylethane with Bromine

Equimolar quantities (0.05 mmol) of 1,1,2,2-tetraphenylethane and bromine in 10 ml CCl_4 were irradiated as usual. At the end of 30 minutes a quantitative yield of tetraphenylethylene was isolated.

Reaction of 1,1,2,2-tetraphenylethane with Sulfuryl Chloride in Benzene

Equimolar quantities of 1,1,2,2-tetraphenylethane (1mmol) were dissolved in benzene (20 ml) and irradiated under the usual conditions for 44 hours. Nmr analysis showed that 42-48 % of unreacted starting material was present. Mass spectral analysis indicated the presence of both p-chlorophenyl-triphenylethylene (m/e at 366 & 368) and tetraphenylethylene (m/e at 332). Tlc also showed the presence of only two products besides starting material.

Reaction of 1,1,1,3-Tetraphenylpropane with NBS

Equimolar quantities (1 mmol) of 1,1,1,3-tetraphenylpropane and NBS were irradiated by the GE sunlamp as described earlier, for a period of one hour. The succinimide was filtered off after cooling in ice and the solution concentrated. Tlc of the solution showed that all the starting material had reacted and that there was a single product present. The nmr spectrum (see page 115) showed doublets at 4.9-4.8, 4.35-4.15, and 3.8-3.7 ppm in an integral ratio of 1:1:1. The product obtained by complete evaporation of the solvent gave an intense green flame in the Beilstein's test. It did not crystallise and it decomposed on attempted vacuum distillation. Mass spectrum, however, gave a parent at m/e 346 which resulted from a facile HBr loss. Column chromatography on an alumina column using 9:1 hexane/methylene chloride gave a white powder of m.p.116-118° whose nmr spectrum had no peaks in the alifatic region between 6.0 - 1.0 ppm. This compound was characterised as trans-β-tritylstyrene.[103]

Reaction of Pentaphenylethane, PPE, with NBS

Equimolar quantities (0.5 mmol) of PPE and NBS in 10 ml CCl_4 were irradiated by the GE sunlamp for a period of 24 h. Over 65% of the NBS was recovered unchanged. Tlc of the crude using 9:1 hexane/methylene chloride revealed the presence of

four spots with r_f values of 0.715, 0.65, 0.35 and 0.05 when visualised under uv light.

Column chromatography on neutral alumina (60-200 mesh) using a 6:1 heptane/methylene chloride solvent mixture resulted in the isolation of tetraphenylethylene (the second fraction) , charaterised by its nmr, uv and mass spectrum. The first fraction was starting material.

The final fraction eluted with 100% methylene chloride was analysed mass spectrally and shown to possess a parent at m/e 341 and a base peak at m/e 243. It had an nmr signal at 3.60 ppm and a uv absorbance at 202 nm. This was characterised as N-tritylsuccinimide.

Determination of the Relative Rates of Reaction of the Various Arylalkanes

The rates (relative) of reaction of UTPE,toluene, ethylbenzene and tetraphenylpropane, were measured by monitoring a characteristic signal in the nmr spectrum of the compound relative to an internal standard, t-butylbenzene. For neopentylbenzene, however, no internal standard was required. The rate of conversion of neopentylbenzene to product was determined instead by using the t-butyl protons of the starting material as an internal standard,since it remains constant throughout the reaction.

Determination of the Relative Rates of 2-Aryl-1,1,1-triphenylethanes for a Hammett Sigma-Rho Study

Solutions of pairs of tetraphenylethanes and NBS were prepared in the molar ratio of 4:4:1. Irradiation was carried out till conversion of NBS to succinimide was almost complete. Analysis of the mixtures was carried out by GC. The ratio of the areas of the products was used as a measure of the relative rates. All determinations were run in triplicate. The substituted tetraphenylethane competed directly with tetraphenylethane, UTPE, for the abstracting radical. In the case of the p-fluoro derivative it was necessary to determine its relative reactivity to the m-trifluoromethyl derivative. The rate constants thereby obtained were converted to the desired form through the expression:

$$\frac{k_F}{k_{CF_3}} = \frac{K_{CF_3}}{k_H} \times \frac{k_F}{k_{CF_3}}$$

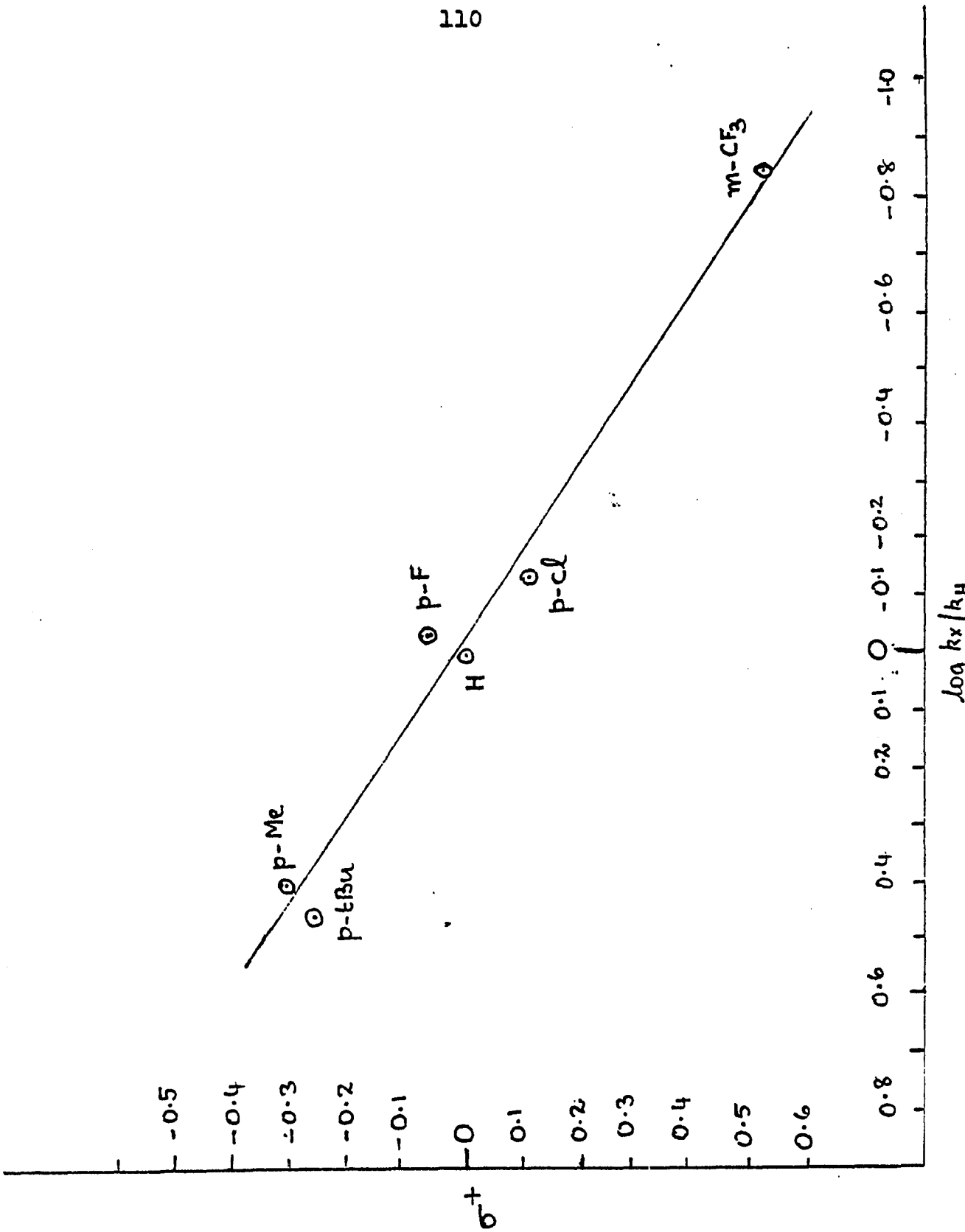
Chromatographic Conditions were as described on the next page.

Column:	18" x 0.12" (glass)
Support:	1% Dexsil 300 on Supelcoport
Detection:	Flame Ionisation
Injector:	300°
Column Temp.	Rate from 160° to 250° @ 4°/min
Detector Temp.	325°
Helium Flow Rate	42 ml/min

Table 18: Retention Times[a] of 2-Aryl-1,1,1-triphenylethanes and Corresponding Alkenes

Substituent	Alkane	Alkene
H	14.8	11.2
m-CF_3	13.7	9.8
p-Cl	17.1	15.6
p-F	14.8	11.2
p-tBu	17.2	15.8

a) In minutes

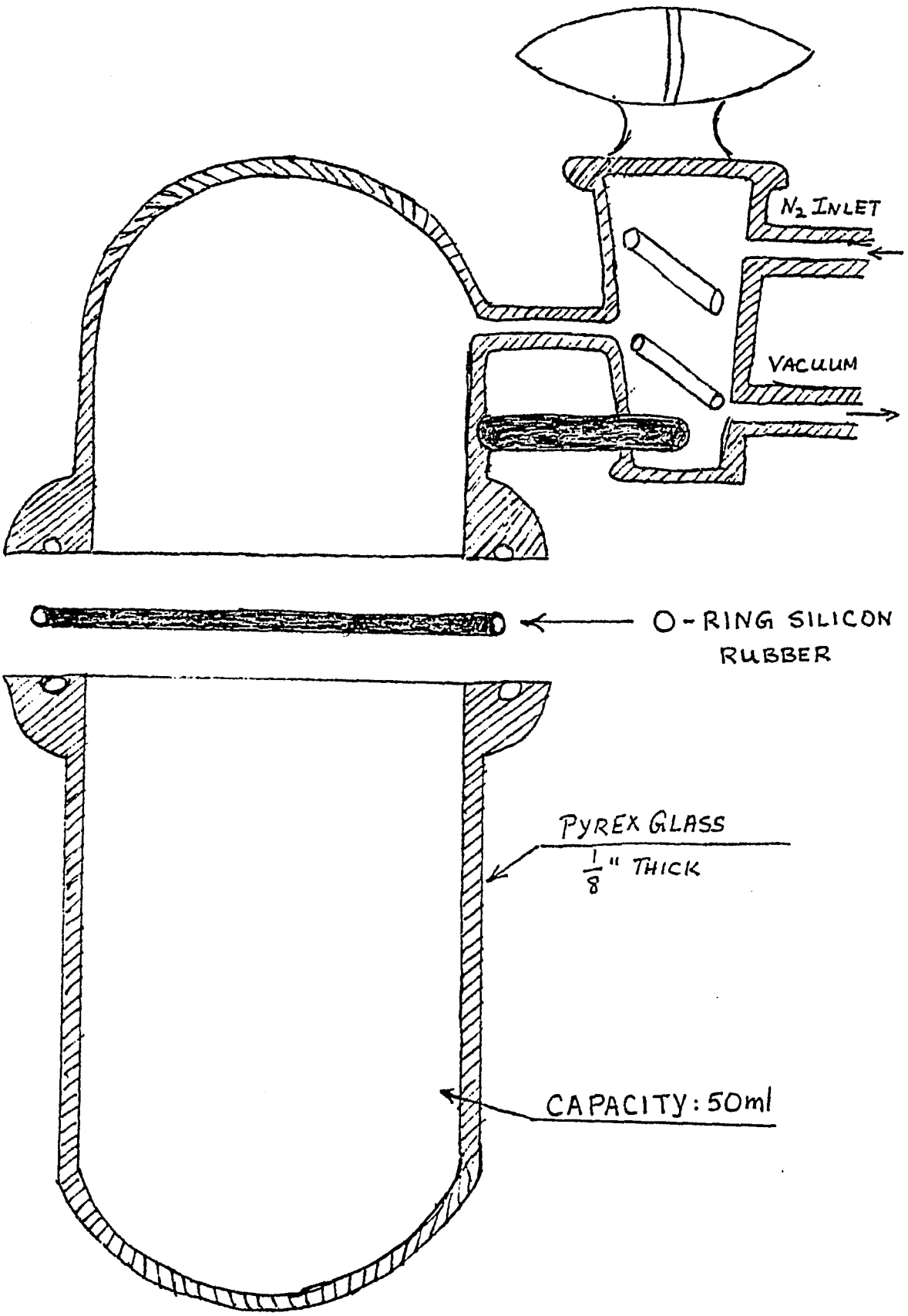


Reaction of 1,1,1-Triphenylethane with Bromine or SO_2Cl_2

Equimolar quantities (1 mmol) of the triphenylethane and halogen in 10 ml of CCl_4 were irradiated under the usual conditions, for a period of 24 h. The solvent was concentrated down and the nmr of the solution taken. Only starting material was present.

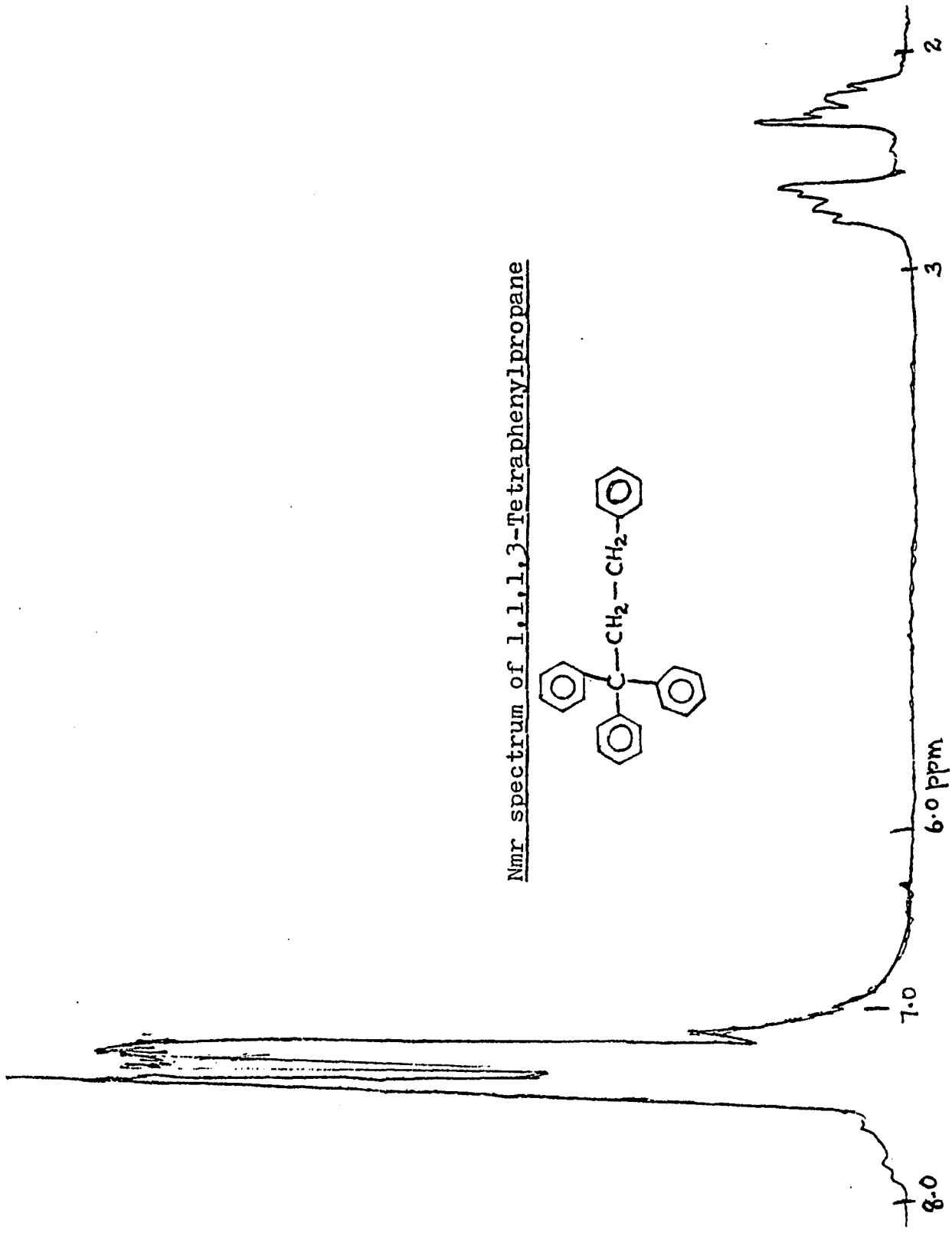
Reaction of Tetraphenylethane with Excess Bromine

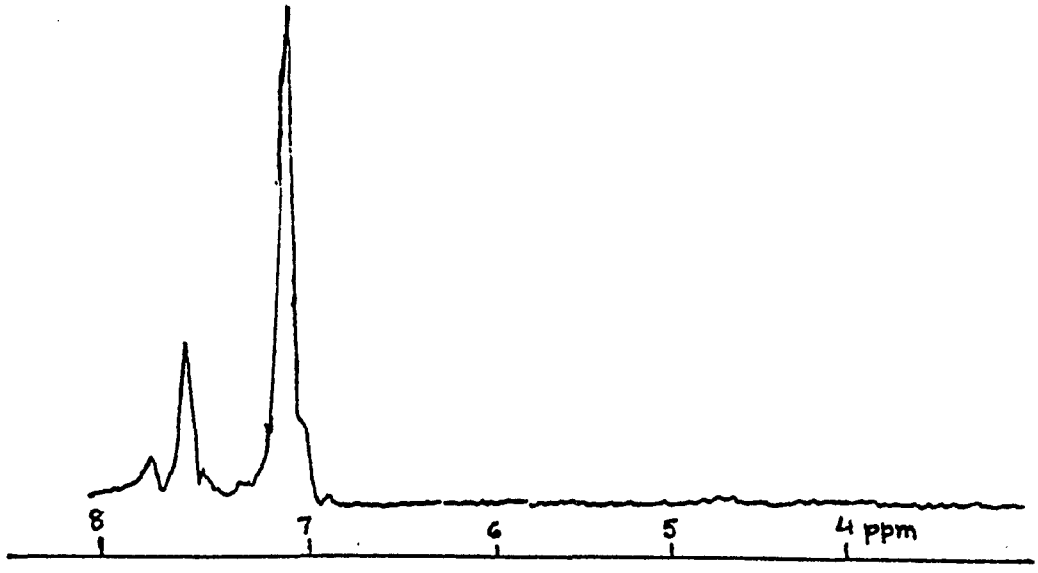
1 mmol of tetraphenylethylene (0.332g) and 5 mmol of bromine in 20 ml of CCl_4 was irradiated as usual, for 24h. Temperature at the end of the reaction period was 20°C. Removal of the solvent gave approximately 0.710g of a yellow-green solid. Tlc revealed this product to consist of a single compound with considerable fluoresence when viewed under a uv lamp. It had a strong uv absorbance at 328 nm. Mass spectral analysis showed the presence of 6 bromine atoms. This crude product when recrystallised from methanol/chloroform gave a white solidmelting at 254-55° (lit.[104] 258°). On the basis of the above data this product was assigned the structure of tetrkis-p-bromo-tetraphenylethylene.



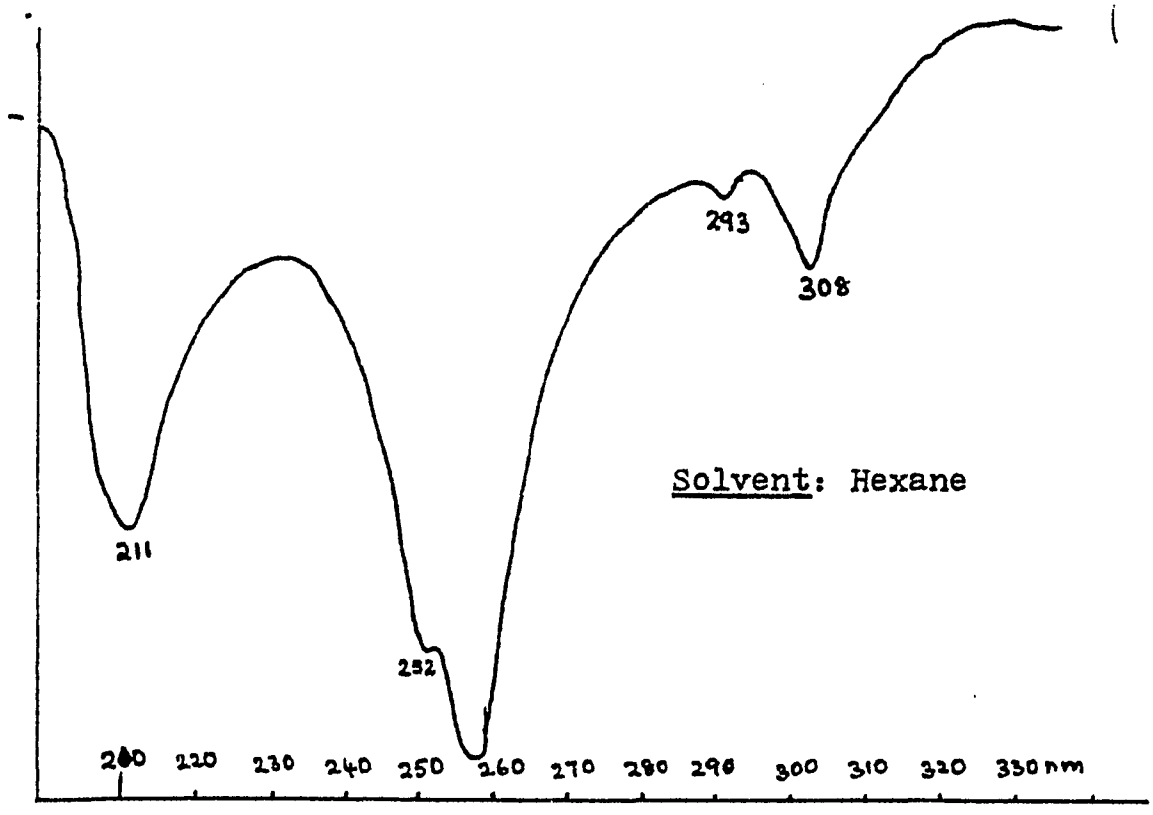
Reaction Vessel used for Halogenations

Nmr spectrum of 1,1,1,3-Tetraphenylpropane

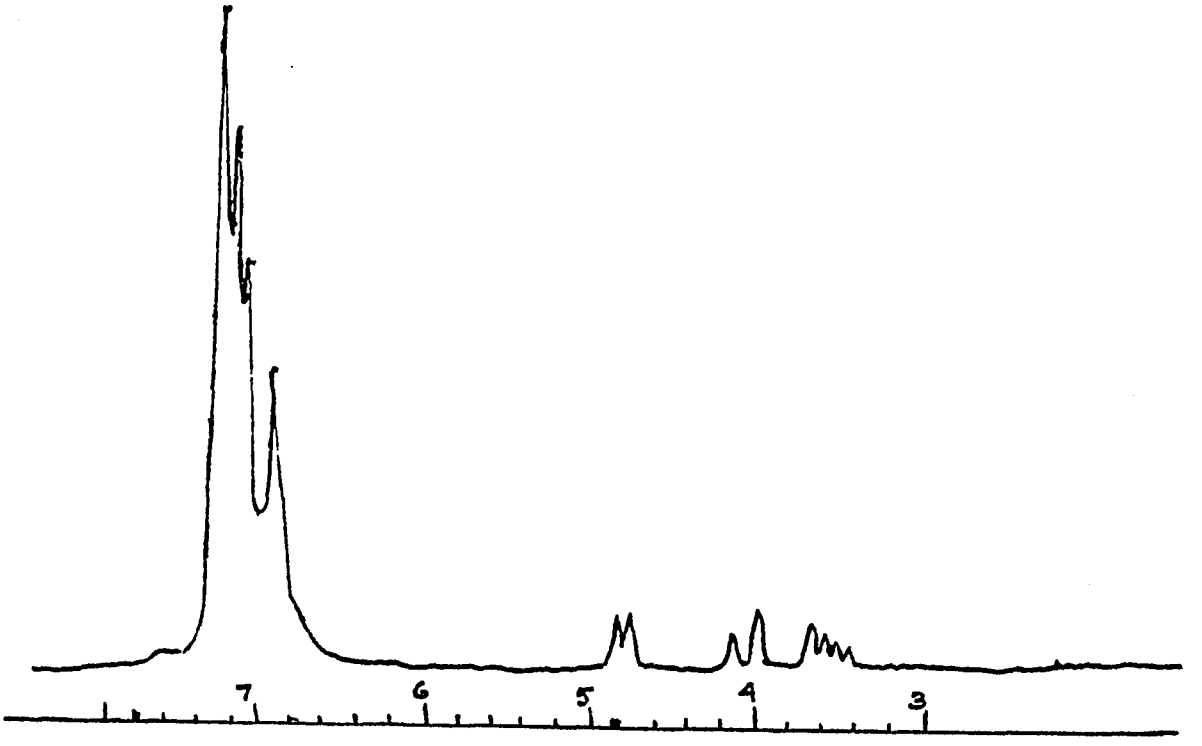




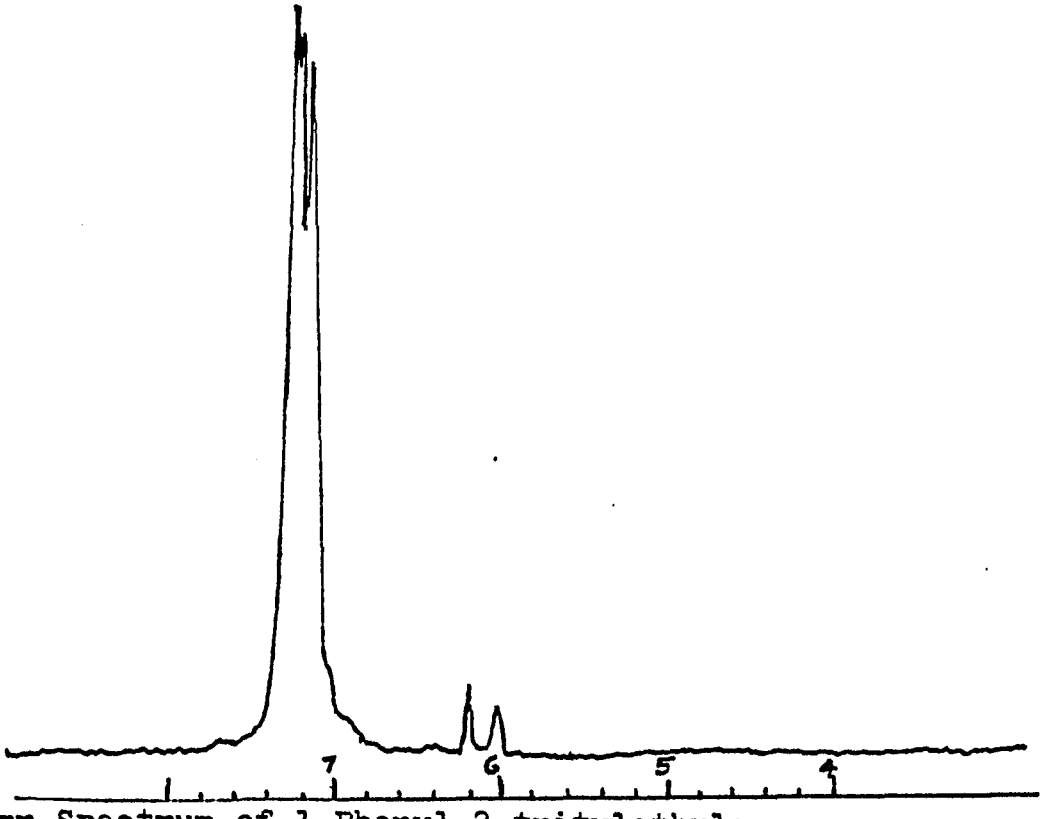
1: Nmr Spectrum of 9,10-Diphenylphenanthrene, DPP, 9.



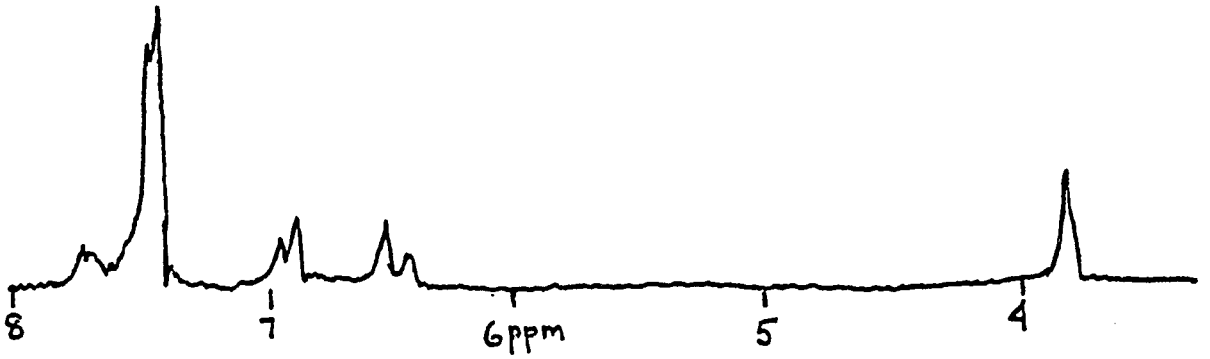
2: Uv Spectrum of 9,10-Diphenylphenanthrene, DPP



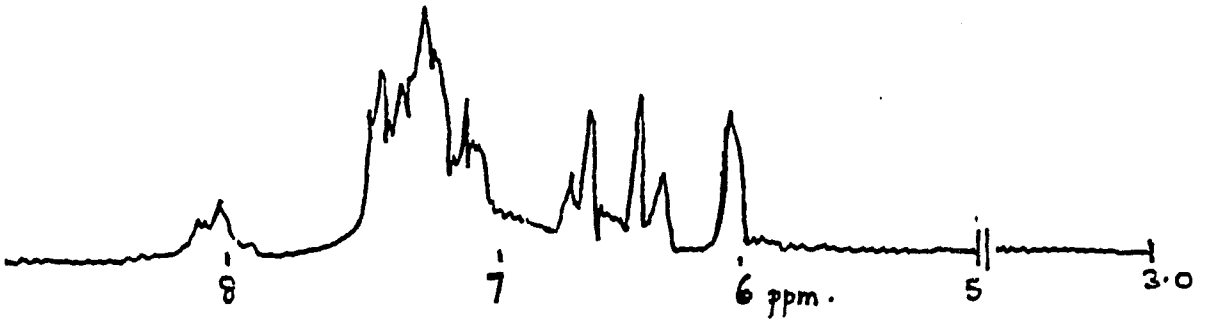
3: Nmr Spectrum of 3-Bromo-1,1,1,3-tetraphenylpropane



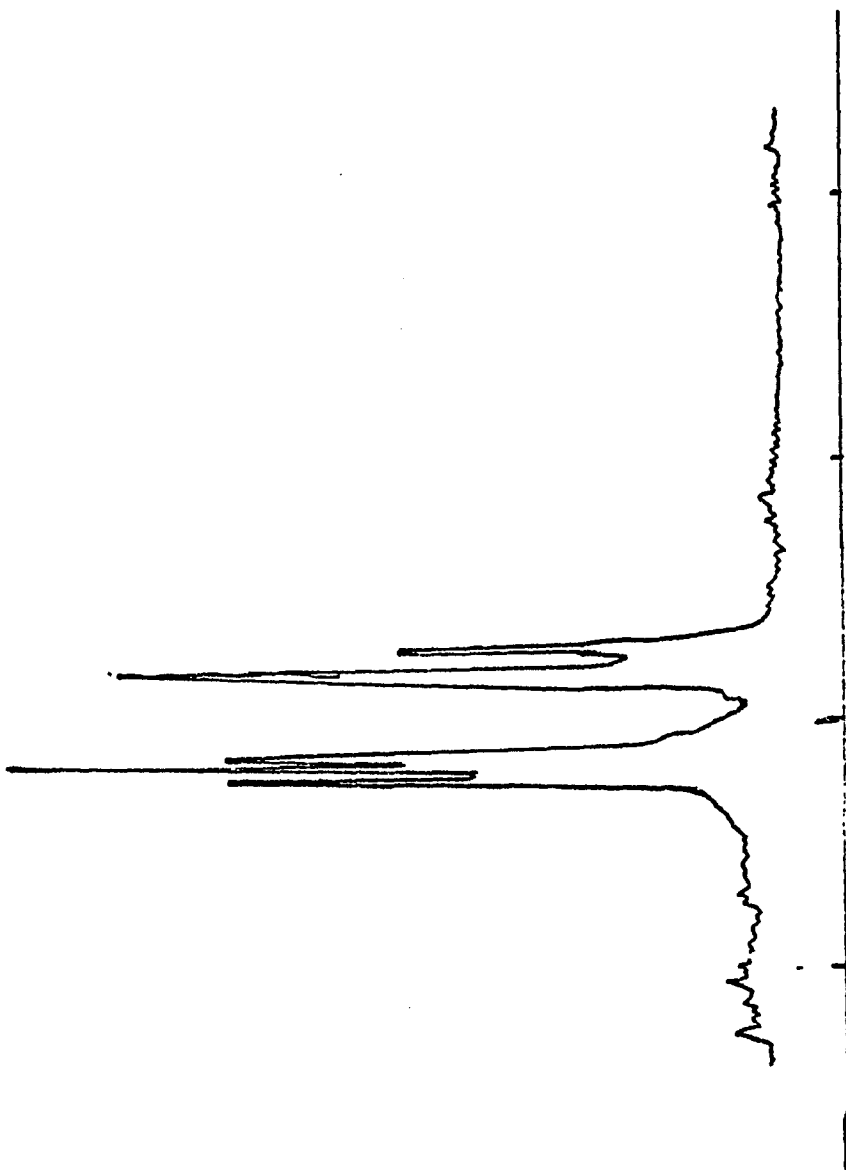
4: Nmr Spectrum of 1-Phenyl-2-tritylethylene



5: Nmr Spectrum of 9-p-chlorobenzyl-9-phenylfluorene, 15



6: Nmr Spectrum of 9-(α-Bromo-p-chlorobenzyl)-9-phenylfluorene



8: Nmr Spectrum of Tetrakis-p-bromo-tetraphenylethylene

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