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# THE THERMAL REACTION OF PHENYLAZOTRIPHENYLMETHANE AND NAPHTHYLAZOTRIPHENYLMETHANE DERIVATIVES WITH SULPHUR DIOXIDE

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**Abstract**—The thermal reaction of phenylazotriphenylmethane, (I), with $SO_2$ in benzene or n-heptane gives triphenylmethyl phenyl sulphone (II) in good yield. This reaction is suppressed by a radical scavenger such as n-butylmercaptan to give n-butyl triphenylmethyl sulphide. The kinetic data obtained from the decomposition of I in liquid $SO_2$ does not differ much from the data in toluene. However, when two crossed reactions were carried out using two chemically labelled azo compounds in each case, the respective crossover compounds were not observed, although the two azo compounds chosen decomposed at approximately the same rate. Moreover, the intermolecular coupling product, diphenyl disulphone, was not formed. These facts suggest that the formation of II is not a 4-center type configuration or an intermolecular radical mechanism, but through an intramolecular radical reaction due to a special cage of $SO_2$.

The evidence that II could be derived from the phenylsulphonyl radical rather than from the triphenylmethylsulphonyl radical was obtained from the fact that the triphenylmethyl radical (π-character radical) formed from 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene (Gomberg's trityl) does not react with $SO_2$, but does react with $O_2$ to give bis-triphenylmethyl peroxide.

On the other hand, the reaction of I with $SO_2$ in the presence of $O_2$ yields *p*-hydroxytetraphenylmethane and benzenesulphonic acid, but neither II nor bis-triphenylmethyl peroxide are formed, suggesting that the reaction in the presence of $SO_2$ and $O_2$ is ionic.

Also, the addition of iodine to the system (I-$SO_2$-benzene or n-heptane) does not suppress the formation of II. This may be interpreted that iodine does not act as a scavenger, since iodine forms a complex with $SO_2$

Moreover, phenylazotriphenylmethane and naphthylazotriphenylmethane derivatives when treated with $SO_2$ in benzene give the corresponding sulphones. In these reactions, it was shown that σ-character radicals (*p*-methoxy, *p*-chloro, and *m*-nitrophenyl radicals, or α- and β-naphthyl radicals) react with $SO_2$ to give sulphonyl radicals. In this case, the α-naphthyl radical reacts sluggishly owing to the steric effect of the *peri*-position of naphthalene ring.

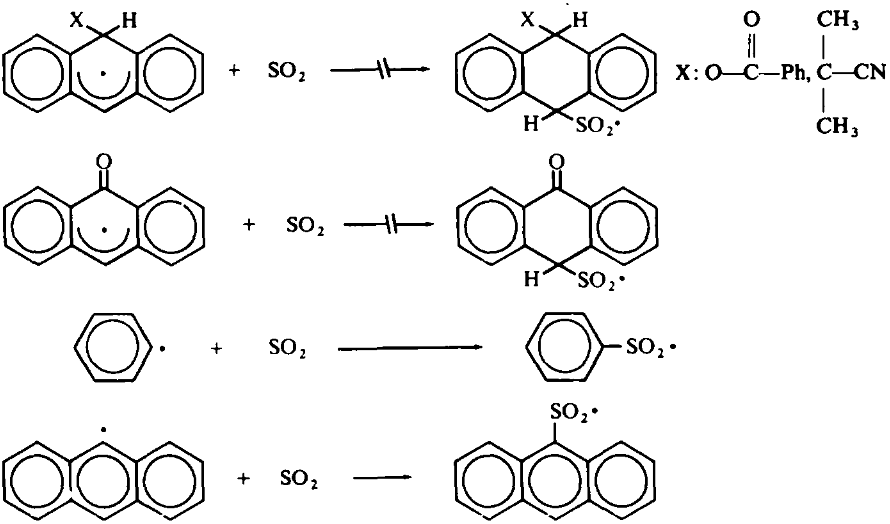
## INTRODUCTION

IN PREVIOUS PAPERS,[1,2] the reaction of anthracene with sulphur dioxide in the presence of benzoyl peroxide or azobisisobutyronitrile (AIBN), suggests that the π-character radicals (such as 9,10-dihydro-9-2′-cyano-2′-propylanthryl and anthronyl radicals) do not react with $SO_2$, whereas σ-character radicals (such as the phenyl and the anthryl radicals) react with $SO_2$ to form the sulphonyl radicals. (Scheme I).

In the present investigation, phenylazotriphenylmethane (I) was chosen as the radical source since this compound is able to liberate both π- and σ-character radicals (triphenylmethyl and phenyl radicals). The reaction of I with $SO_2$ was found to give triphenylmethyl phenyl sulphone (II) nearly quantitatively.

Baeyer and Villiger reported[3] the preparation of II from the reaction of $Ph_3CCl$ with $PhSO_2Na$. Since in the present method of preparation, II is formed almost quantitatively, this new synthetic approach should arouse interest in the mechanism.

Scheme I

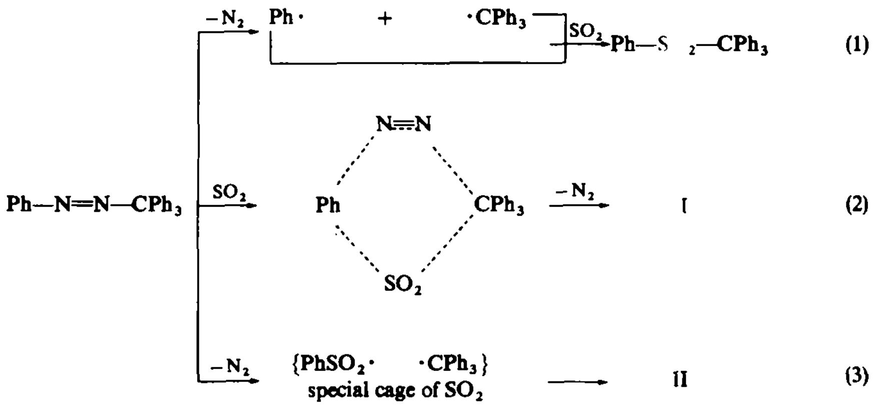


## RESULTS AND DISCUSSIONS

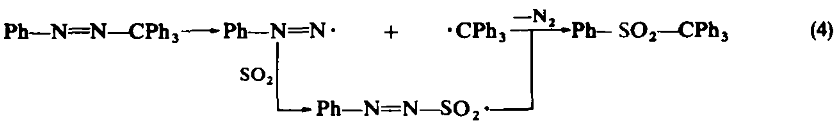
### *The thermal reaction of phenylazotriphenylmethane* (I) *with* $SO_2$

As the reaction of I with $SO_2$ in benzene or *n*-heptane gives triphenylmethyl phenyl sulphone (II) in good yield, three possible pathways are visualized in Scheme II.

Scheme II



An alternative pathway—the reaction of the intermediate azo-radical with $SO_2$ (route 4)—was not considered as the loss of nitrogen from the intermediate azo-radical is probably exceedingly fast as indicated by Denny and Newman.[4]



(a) *The decomposition rate of* I. The yield of II in the reaction of I with $SO_2$ is nearly quantitative, and neither an intermolecular coupling product such as diphenyl disulphone* nor a cage reaction product such as tetraphenylmethane† are formed. These results suggest a 4-center type process such as Eq. 2 or an intermolecular cage reaction such as Eq. 3.

If this reaction proceeds via pathway 2, the activation parameters of the decomposition rate of I in liquid $SO_2$ should differ considerably from those in toluene.[7] The rates of decomposition of the azo compound (I) in liquid $SO_2$ were determined at two temperatures by measurement of the volume of nitrogen evolved as a function of time ($V_t$). Linear plots of ln $V_\infty/(V_\infty - V_t)$ vs time were obtained in duplicated runs, indicating that the decompositions are of the first-order law (Fig. 1). Rate constants were determined from the slopes of the plots. The activation energies, $E_A$, were calculated from the rate constants at the two temperatures by application of the Arrhenius equation, and entropies of activation, $\Delta S^\ddagger$, were calculated according to the equation derived from transition state theory. The results are summarized in Table 1.

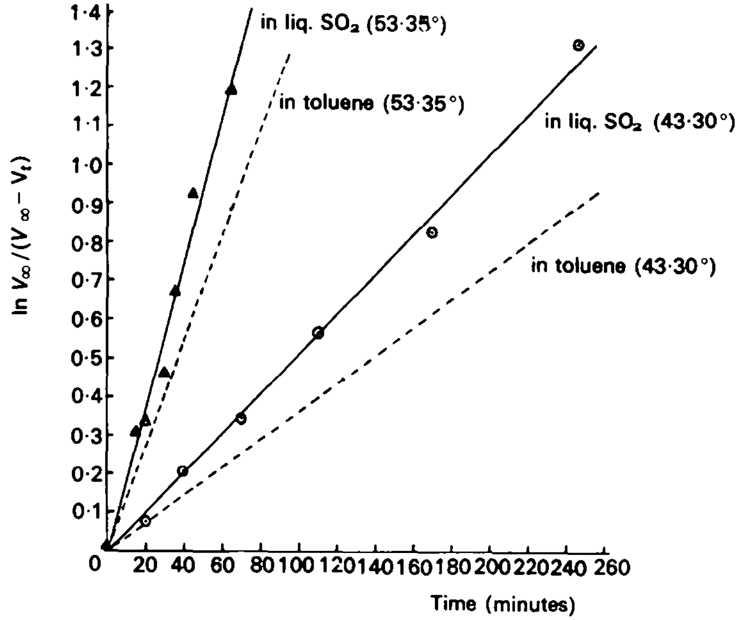


FIG. 1. Decomposition rates of I.

It is evident that the values, $E_A$ and $\Delta S^\ddagger$ in liquid $SO_2$ do not vary much from those in toluene. Since solvation of I at initial state is larger in an electron rich solvent than in an electron poor solvent,[8] the degree of the desolvation in the transition state will be greater in toluene than in liquid $SO_2$. In this case, the compensation of $E_A$ and $\Delta S^\ddagger$ will be operating.[9] Therefore, the small difference of activation parameters depends upon the ordinary solvent effect in which the transition state is solvated and to a lesser extent in the initial state.[9] This result rules out the 4-center type reaction (Eq. 2), and pathway 3 is indicated.

* The formation of diphenyl disulphone from the reaction of BPO with $SO_2$ in benzene soln has been reported.[5]

† It was reported that tetraphenylmethane (5%) was obtained in the cage decomposition of I.[6a] Also, it has been discussed that the decomposition of I in aromatic solvents undergoes about 10% cage recombination.[6b,c]

TABLE 1

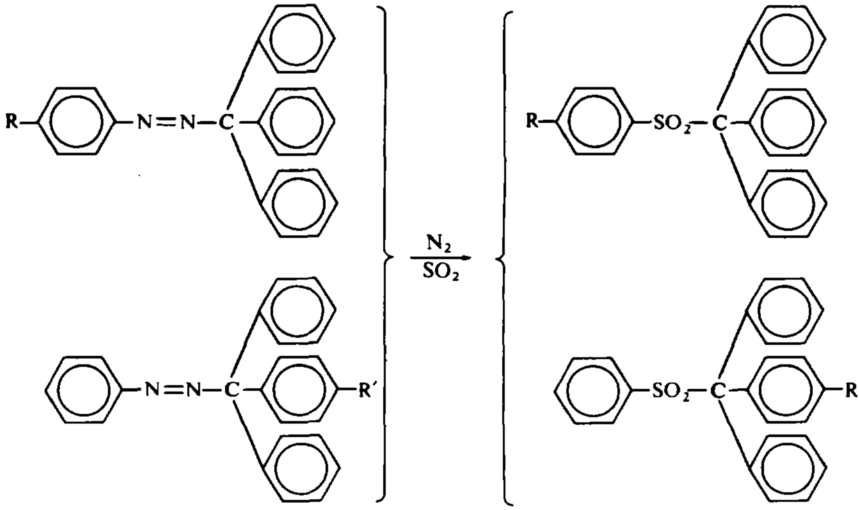
| | °C | $k_1 \times 10^4$ $sec^{-1}$ | $E_A$ kcal/mole | $\Delta S^{\ddagger}$ e.u. |
|---|---|---|---|---|
| in liq. $SO_2$ | 53·35 | 3·10 | 26·5 | 3·7 |
| | 43·30 | 0·85 | | |
| in toluene* | 53·35 | 2·25 | 27·4 | 4·8 |
| | 43·30 | 0·60 | | |

* Data are cited from Ref. 7.

(b) *The crossover experiments.* As the formation of II appears to be via pathway 3, two crossed experiments were carried out to see if the formation of II is too rapid to give crossover compounds formed between two chemically labelled azo compounds. In each crossed reactions, the two azo compounds chosen decomposed at approximately the same rate: *p*-anisylazotriphenylmethane (III); $2{\cdot}13 \times 10^{-4}$ $sec^{-1}$ (54·0°), and phenylazo-*p*-chlorophenyldiphenylmethane (VII); $2{\cdot}28 \times 10^{-4}$ $sec^{-1}$ (53·2°), or *p*-chlorophenylazotriphenylmethane (IV); $1{\cdot}41 \times 10^{-4}$ $sec^{-1}$ (54·6°), and phenylazo-*p*-anisyldiphenylmethane (VI); $1{\cdot}87 \times 10^{-4}$ $sec^{-1}$ (53·2°). Furthermore, it was verified that non-crossover compounds were formed nearly quantitatively in the reaction of the corresponding azo compounds with $SO_2$ as shown in Exps. 9–15.

In one case, III and VII were treated with $SO_2$ in benzene as described in Exp. 14. The crossover compounds could not be isolated by recrystallization or silica gel column chromatography, and further TLC revealed two spots of non-crossover compounds but no spots corresponding to crossover compounds.

SCHEME III



i: R = OMe, R' = Cl
ii: R = Cl, R' = OMe

Similarly, in the treatment of IV and VI as described in Exp. 15, both TLC and mass spectral analyses failed to show the presence of the crossover compounds.

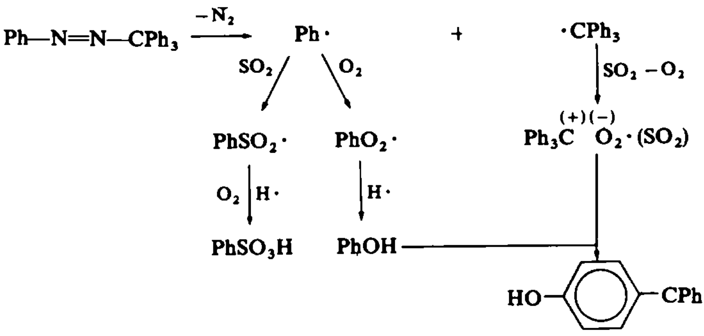
As these observations indicate an intramolecular process, the reaction could be *via* the special cage which consists of the interaction of $SO_2$ with the phenyl rings of I as shown in Eq. 3. This special cage should result in the recombination[10] of radical pairs[11] formed on nearby $SO_2$ molecules.

(c) *The effect of scavengers.* (1) *The addition of* n-*butylmercaptan.* Although this reaction was suppressed by a radical scavenger such as n-butylmercaptan(n-BuSH)* to give n-butyl triphenylmethyl sulphide as the main product, the addition of four equivalents of n-BuSH to I were required to completely suppress the formation of II. The addition of two equivalents of n-BuSH to I (initial concn of 0·3 mole/l) resulted in the formation of about 10% of II and therefore the n-BuSH competes against the geminate recombination.

(2) *The addition of iodine.* As shown in Exp. 6, a scavenger† such as iodine did not suppress the formation of II in benzene or n-heptane soln, and even in the addition of 1/10 equivalent of iodine to I the violet colour of iodine did not disappear. Exp. 7 shows that II was not formed through some iodine containing compounds. Consequently, iodine does not act as a scavenger, since iodine forms a complex with $SO_2$.[14]

(d) *The effect of oxygen in the reaction of* I *with* $SO_2$. In exp. 4, the reaction of I with $SO_2$ in benzene in the presence of $O_2$ gave *p*-hydroxytetraphenylmethane (XI), benzenesulphonic acid and a small amount of phenol, but neither II § nor bis-triphenylmethyl peroxide (X) was found, although the reaction of I with only $O_2$ gave X without formation of XI (Exp. 3). These results suggest that this reaction involves the following ionic mechanism:

SCHEME IV



XI

Russel *et al.*[15] reported that the reaction of radicals with $O_2$ involves an ionic mechanism as shown below:

$$R\cdot + O_2 \xrightarrow{k_0} [R\cdot O_2 \leftrightarrow \overset{(+)}{R}\ \overset{(-)}{O_2}\cdot \leftrightarrow R\text{—}O_2\cdot] \rightarrow \rightarrow$$

$$R\cdot + R'H \xrightarrow{k_H} RH + R'\cdot$$

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* The addition of about one equiv of n-BuSH to AIBN (initial concentration 0·2 mole/l.) in $CCl_4$ soln scavenges the free radicals escaped from cage.[12]

† It has been well known that iodine is a good scavenger of phenyl radical in the decomposition of I.[13]

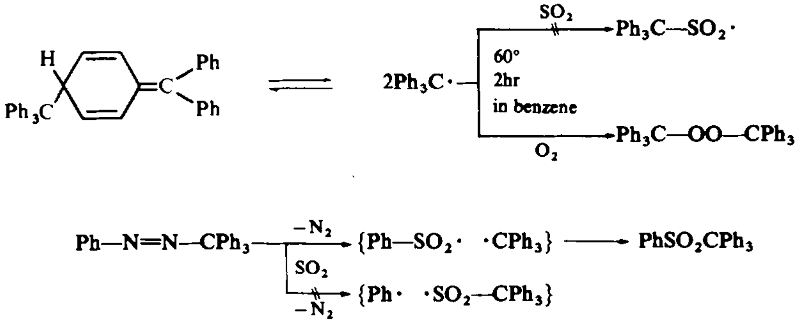
§ No formation of II was reproducible, although Exp. 4 was repeated four times. However, under the condition without stirring, about 40% of II was obtained.

They proposed that the difference between $k_O/k_H$ for phenyl ($10^3$) and benzylic type radicals ($10^{10}$) could be the result of a higher energy content of phenyl carbonium ions than benzylic type carbonium ions.

If this reaction involves the ionic intermediate, the mechanism in Exp. 4 can be interpreted. Actually, Busch and Knoll[16] reported a 98% yield of XI from the reaction of $Ph_3CCl$ with PhOH. The formation of the electron transfer species shown in Scheme IV has been recognized[17] as reasonable in the presence of $SO_2$ and $O_2$.

(e) *The reaction of triphenylmethyl radical with* $SO_2$. The triphenylmethyl radical (π-character radical)* formed from 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene[19] (Gomberg's trityl) does not react with $SO_2$ (Exp. 16), but reacts with $O_2$ to form X. This indicates that II may be derived from the phenylsulphonyl radical rather than from the triphenylmethylsulphonyl radical (Scheme V).

SCHEME V



### *The thermal reaction of phenylazotriphenylmethane derivatives with* $SO_2$

In order to demonstrate the electronic effects in substituted phenyl radicals (σ-character radicals),† the reaction of phenylazotriphenylmethane derivatives with $SO_2$ (Exps. 9–13) was investigated.

It was shown that the phenyl radicals having electron attracting groups (*p*-chlorophenyl and *m*-nitrophenyl radicals) react with $SO_2$ to form the phenylsulphonyl radicals in almost quantitiative yield.

### *The thermal reaction of naphthylazotriphenylmethane derivatives with* $SO_2$

In Exps. 17 and 18 compounds VIII and IX with σ-character radicals α-naphthyl and β-naphthyl were allowed to react with $SO_2$.

The yield of triphenylmethyl α-naphthyl sulphone, (56·5%) in Exp. 17 is lower than that of triphenylmethyl β-naphthyl sulphone, (92·5%) in Exp. 18, and suggests a steric interference§ between bulky sulphonyl group and the H · atom in the *peri*-position.

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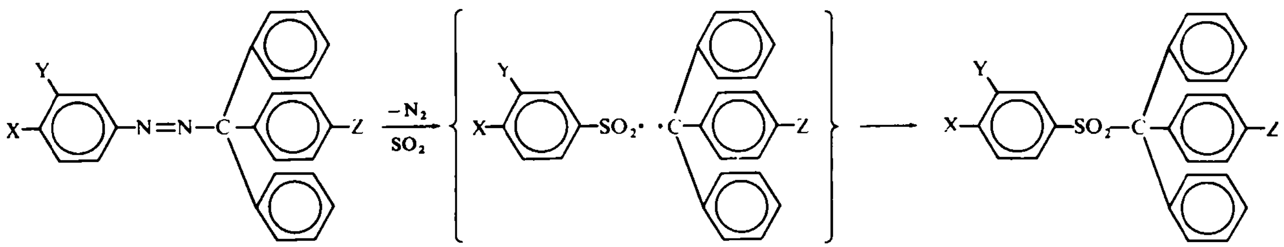
* In a radical such as triphenylmethyl in which the unpaired electron is oriented so as to hybridized completely with the aromatic π-electron system, the hyperfine splitting constants for the observed ESR spectrum is in good agreement with the simple valence bond approximation.[18]

† The odd electron of phenyl radical replaces a σ—C—H bond oriented in the plane of the benzene ring, the splitting constants of ESR spectra being $a_o = 18{\cdot}1$, $a_m = 6{\cdot}4$ and $a_p =$ zero gauss.[20]

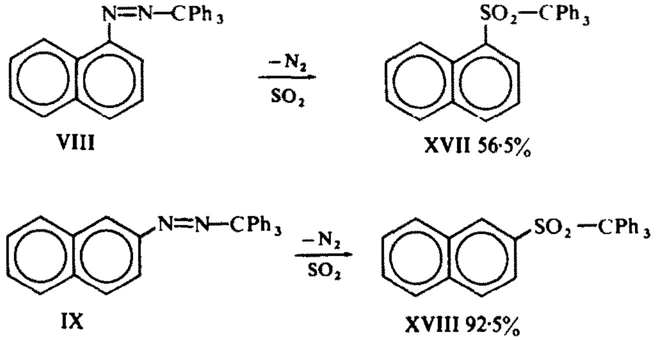
§ The similar steric effect in nucleophilic displacement of naphthalene series has been reported by Berliner *et al.*[21]

SCHEME VI



| | | | | | | |
|---|---|---|---|---|---|---|
| X | H | OMe | Cl | H | H | H |
| Y | H | H | H | $NO_2$ | H | H |
| Z | H | H | H | H | OMe | Cl |

SCHEME VII



This steric effect is confirmed by the more rapid decomposition of VIII than IX as shown in Table 2, by virtue of the evolution of nitrogen and the resonance instability of the initial state due to noncoplanarity for steric reasons.

TABLE 2

| | °C | $k \times 10^4$ sec$^{-1}$ | $E_A$ Kcal/mole | $\Delta S^\ddagger$ e.u. |
|---|---|---|---|---|
| VIII | 53·10 | 1·63 | 31·0 | 15·5 |
| | 60·10 | 4·30 | | |
| IX | 53·35 | 0·74 | 40·4 | 50·6 |
| | 60·05 | 2·60 | | |

## EXPERIMENTAL

*Apparatus.* IR spectra were run on a EPI-S2 type Hitachi IR spectrometer. NMR spectra were obtained with a Japan Electron Optics Lab. spectrometer. UV spectra were taken with a EPS-3 Hitachi recording spectrometer.

*Materials.* Liquid $SO_2$ was dehydrated with $P_2O_5$ and distilled. n-Hexane and benzene were purified by ordinary methods.

Phenylazotriphenylmethane (I): m.p. 111° dec,[22] *p*-anisylazotriphenylmethane (III): m.p. 113° dec,[23] *p*-chlorophenylazotriphenylmethane (IV): m.p. 107° dec,[24] and *m*-nitrophenylazotriphenylmethane (V): m.p. 109° dec,[22] were synthesized by the method of Cohen and Wang.[7]

*Phenylazo-p-anisyldiphenylmethane* (VI). Treatment a soln of anisol and benzoyl chloride in $CS_2$ with $AlCl_3$, yielded *p*-methoxybenophenone[25] which crystallized from ether, m.p. 61°. Diphenyl-*p*-anisylcarbinol was prepared[26] by interaction of PhMgBr in ether and *p*-methoxybenzophenone, and crystallized from ether–pet ether, m.p. 81°. This carbinol and phenylhydrazine in acetic acid was allowed to stand for one week in contact with air, and VI was crystallized from ether, m.p. 112° dec.[23]

*Phenylazo-p-chlorophenyldiphenylmethane* (VII). *p*-Chlorobenzophenone was synthesized[27] and after crystallization (m.p. 75°) from ether–EtOH was treated[28] with PhMgBr in ether. The mixture was shaken with $NH_4Cl$ aq, washed with $H_2O$, dried and yielded diphenyl-*p*-chlorophenylchloromethane[27] after treatment with dry HCl and crystallization from ligroin, m.p. 83°. N-Phenyl-N'-diphenyl-*p*-chlorophenylmethylhydrazine was prepared from 17·7 g (53·4 mmole) diphenyl-*p*-chlorophenylchloromethane and 12 g

(111 mmole) phenylhydrazine in 100 ml anhyd ether by heating under reflux for 1 hr. The mixture was filtered off and concentrated, and the hydrazo compound was crystallized from pet ether, 13·2 g, 64·5% yield, m.p. 109°. VII was prepared by treatment of 6·0 g of the above hydrazo compound in 80 ml ether with 40 ml sat $Na_2CO_3$aq and 30% $H_2O_2$ (18 ml) with stirring at room temp for 7 hr. The ether was evaporated and the azo compound crystallized from ether–EtOH, 4·8 g, 80·5% yield, m.p. 99° dec.[28] (Found: C, 78·49; H, 4·95; N, 7·54; Cl, 9·38. Calc. for $C_{25}H_{19}N_2Cl$: C, 78·42; H, 5·00; N, 7·32; Cl, 9·26%).

*α-Naphthylazotriphenylmethane* (VIII). α-Naphthylhydrazine, 7·8 g (49 mmole) was dissolved in 35 ml dry pyridine and treated with a soln of 13·7 g (49 mmole) trityl chloride in 35 ml dry pyridine, first at 0°, then at 25° for 1 hr. The mixture was diluted with 100 ml ether, washed with $H_2O$ repeatedly, and the insoluble material washed with MeOH and ether, 10·9 g, 55% yield, m.p. 155°.[23] This hydrazo compound (10·0 g) was dissolved 500 ml $CHCl_3$, converted to VIII by oxidation with 30% $H_2O_2$ (40 ml) and 200 ml sat $Na_2CO_3$aq with stirring at room temp for 7 hr. The soln was evaporated and the azo compound crystallized from benzene–MeOH, 4·0 g, 40% yield, m.p. 113° dec.[22]

*β-Naphthylazotriphenylmethane* (IX). β-Naphthylhydrazine (8·0 g) was converted to N-β-naphthyl-N′-triphenylmethylhydrazine (crystallized from EtOH–pet ether, 8·0 g, 41% yield, m.p. 105°) as described above. This hydrazo compound was dissolved in 60 ml ether–20 ml $CHCl_3$ and oxidized with 30% $H_2O_2$ (15 ml) and 35 ml sat $Na_2CO_3$aq for 4 hr. The solvent was evaporated and the residue was crystallized from benzene–MeOH, 3·0 g, 36% yield, m.p. 116° dec. (Found: C, 87·51; H, 5·59; N, 7·01. $C_{29}H_{22}N_2$ requires: C, 87·41; H, 5·57; N, 7·03%).

*Experiment* 1

Compound I (45 mmole) was dissolved in 300 ml benzene, and the soln heated at 60° for 2 hr while 85 g of $SO_2$ was passed through. The solvent was distilled under reduced press and residue showed an IR spectrum identical with that of an authentic II.[3] The above reaction products were chromatographed over silica gel, using benzene as the solvent.

The following compounds were isolated and identified:

*Triphenylmethyl phenyl sulphone* (II), m.p. 167° (recrystallized from benzene–ether), 95%; $\nu_{max}^{Nujol}$ 1300, and 1130 $cm^{-1}$ ($\nu_{SO_2}$). (Found: C, 78·18; H, 5·44. Calc. for $C_{25}H_{20}O_2S$: C, 78·10; H, 5·24%). It showed no depression of mixed m.p. and had an identical IR spectrum with that of an authentic sample.[3] This product was hydrolyzed by active $Al_2O_3$ chromatography to triphenylcarbinol.

*Triphenylmethane*, m.p. 92° (recrystallized from MeOH), 3·3%. NMR: τ; 4·5 (methine, singlet, 1H), 2·5–3·2 (aromatic, multiplet, 15H). (Found: C, 93·23; H, 6·93. Calc. for $C_{19}H_{16}$: C, 93·40; H, 6·60%).

*Bis-triphenylmethyl peroxide* (X), m.p. 183° (crystallized from toluene), trace. NMR: τ; 2·6–2·9 (aromatic, multiplet). (Found: C, 88·12; H, 5·59. Calc. for $C_{38}H_{30}O_2$: C, 88·00; H, 5·85%). This showed no depression of the mixed m.p. with an authentic sample[19] and had an identical IR spectrum.

*Experiment* 2

n-Heptane was used as the solvent in place of benzene. The reaction mixture was treated as mentioned in Exp. 1. From the distillate, benzene (2·2%) was identified by comparison of UV spectrum with an authentic specimen. The other products were obtained in nearly the same yield as in Exp. 1.

*Experiment* 3

Compound I (15 mmole) was dissolved in 100 ml benzene, and the soln was heated at 60° for 2 hr while $O_2$ was passed through. The benzene was distilled under reduced press. The reaction mixture was chromatographed over silica gel using benzene as the solvent, and the following compounds were isolated and identified: Bis-triphenylmethyl peroxide (41·3%) and triphenylmethane (2·1%) were confirmed as described above.

*Biphenyl*, m.p. 69–71°, 6·0%. This compound had the same IR spectrum as an authentic specimen and showed no depression of m.p.

*Triphenylcarbinol*, m.p. 164°, 16·1%. The IR spectrum of this compound coincided with that of a specimen synthesized by another method, and this was confirmed by a mixed m.p.

*Phenol*. A trace was confirmed by phenol tests with nitrous acid and $FeCl_3$.

*Experiment* 4

Compound I (21 mmole) was dissolved in 140 ml benzene, and the soln was heated at 60° for 2 hr with stirring while 70 g of gaseous $SO_2$ and $O_2$ were passed through. The following compounds were isolated and identified: Triphenylmethane (5·4%) phenol (trace) were confirmed as described above.

*Benzenesulphonic acid,* 61·0%. After the reaction mixture was extracted with water, the water soluble fraction was concentrated, converted to its Na-salt, and confirmed by comparison of the IR spectrum with an authentic sample.

*p-Hydroxytetraphenylmethane* (XI), m.p. 280° (recrystallized from $CHCl_3$–pet ether), 24·0%, $\nu_{max}^{Nujol}$ 3550 $cm^{-1}$ ($\nu_{OH}$). It showed no depression of the mixed m.p. and had an identical IR spectrum with that of an authentic sample.[16]

*Experiment* 5

n-Butylmercaptan (2 mole equivs to I) was used as the radical scavenger in Exp. 1. The following compounds were isolated and identified: II (10·1%) was confirmed as described above.

*n-Butyl triphenylmethyl sulphide,* m.p 47·5° (recrystallized from MeOH), 76·5%, NMR: τ; 9·0–9·4 (methyl, 3H), 8·4–9·0 (β- and γ-methylene, 4H), 7·7–8·1 (α-methylene, 2H), 2·5–3·0 (aromatic, 15H). Mass spectrum: *m/e*; 275, 243, 165, 56. (Found: C, 83·01; H, 7·17. $C_{23}H_{24}S$ requires: C, 83·08; H, 7·28%).

While the experiment of the addition of 4 equivs n-BuSH to I under a similar conditions did not afford II.

*Experiment* 6

Iodine (1 mole equiv to I) was used in place of n-BuSH in Exp. 5. In this experiment, II was obtained nearly quantitatively. In this case, even if n-heptane was used as the solvent instead of benzene, the reaction mixture did not change. Also, when $I_2$ ($\frac{1}{10}$ mole equiv to I) was used in benzene, the violet colour of $I_2$ did not disappear.

*Experiment* 7

I (7·5 mmole) and $I_2$ (7.5 mmole) were dissolved in 50 ml n-heptane, and soln was heated at 60° for 1 hr. As the reaction proceeded, the violet colour due to $I_2$ decreased. Successively, 16 g of gaseous $SO_2$ was passed through at 60° for 1 hr. In this experiment, II was not formed.

*Experiment* 8

Compound II (3·4 mmole) was dissolved in 50 ml benzene, and soln was heated at 60° for 2 hr with stirring while 30 g of gaseous $SO_2$ and $O_2$ were passed through. II was obtained unchanged.

*Experiments* 9–13. (The substituted azo compounds were used in place of I in Exp. 1)

*Exp.* 9. (Compound III was used in place of I in Exp. 1)

*Triphenylmethyl p-methoxyphenyl sulphone* (XII), m.p. 157° (recrystallized from benzene), ~100%, $\nu_{max}^{Nujol}$ 1300, 1130 $cm^{-1}$ ($\nu_{SO_2}$), NMR: τ; 6·2 (OMe, 3H), 2·3–3·4 (aromatic, 19H). (Found: C, 75·15; H, 5·54; S, 7·53. $C_{26}H_{22}O_3S$ requires: C, 75·34; H, 5·35; S, 7·74%).

*Exp.* 10. (Compound IV was used in place of I in Exp. 1)

*Triphenylmethyl p-chlorophenyl sulphone* (XIII), m.p. 156° (recrystallized from benzene), ~100%, $\nu_{max}^{Nujol}$ 1304, 1140 $cm^{-1}$ ($\nu_{SO_2}$). (Found: C, 72·39; H, 4·77; S, 7·11; Cl, 8·43. $C_{25}H_{19}O_2SCl$ requires: C, 71·67; H, 4·57; S, 7·65; Cl, 8·46%).

*Exp.* 11. (Compound V was used in place of I in Exp. 1. In this experiment, reaction temp was 65°)

*Triphenylmethyl m-nitrophenyl sulphone* (XIV), m.p. 152° (recrystallized from benzene–ether), ~100%, $\nu_{max}^{Nujol}$ 1305, 1140 $cm^{-1}$ ($\nu_{SO_2}$). (Found: C, 69·88; H, 4·54; N, 3·14; S, 7·74. $C_{25}H_{19}O_4NS$ requires: C, 69·91; H, 4·46; N, 3·26; S, 7·47%).

*Exp.* 12. (Compound VI was used in place of I in Exp. 1)

*Diphenyl-p-anisylmethyl phenyl sulphone* (XV), m.p. 151° (recrystallized from benzene–ether), 96%, $\nu_{max}^{Nujol}$ 1300, 1130 $cm^{-1}$ ($\nu_{SO_2}$), NMR: τ; 6·2 (OMe, 3H), 2·3–3·4 (aromatic, 19H). (Found: C, 75·71; H, 5·40; S, 7·93. Calc. for $C_{26}H_{22}O_3S$: C, 75·34; H, 5·35; S, 7·74%).

*Exp.* 13. (Compound VII was used in place of I in Exp. 1)

*Diphenyl-p-chlorophenylmethyl phenyl sulphone* (XVI), m.p. 145° (recrystallized from benzene–ether), 99%, $\nu_{max}^{Nujol}$ 1300, 1130 cm$^{-1}$ ($\nu_{SO_2}$). (Found: C, 72·07; H, 4·65; S, 7·80; Cl, 7·92. $C_{25}H_{19}O_2SCl$ requires: C, 71·67; H, 4·57; S, 7·65; Cl, 8·46%).

*Experiment* 14

Compound III (6·3 mmole) and VII (6·3 mmole) were dissolved in 85 ml benzene and the soln was heated at 60° for 2 hr while 24 g of gaseous $SO_2$ was passed through. XII, 67·4% based on III and XVI, 54·5% based on VII, were isolated and identified as described above. In this experiment, the crossover sulphones were not obtained, though the reaction mixture was chromatographed over silica gel. Further TLC using silica gel (Wakogel B-5) and benzene as the adsorbent and solvent did not show the spots of the crossover compounds (II; $R_f$ = 0·48), but did show two spots of non-crossover compounds (XII; $R_f$ = 0·45, XVI; $R_f$ = 0·55).

*Experiment* 15

Compound IV (3·4 mmole) and VI (2·6 mmole) were dissolved in 40 ml benzene, and the soln was heated at 50° for 6 hr while 66 g of gaseous $SO_2$ was passed through. The analyses by TLC and mass spectrometry showed no crossover compounds, while two spots (XIII; $R_f$ = 0·44, XV; $R_f$ = 0·30) and mass spectral peaks corresponding to non-crossover compounds were revealed.

TLC was confirmed that the above sulphones did not decompose into the corresponding carbinols.

*Experiment* 16

1-Diphenylmethylene-4-trityl-2,5-cyclohexadiene (Gomberg's trityl)[29] was dissolved in 80 ml benzene, and the soln was heated at 60° for 2 hr while 30 g $SO_2$ was passed through. The reaction mixture gave negative sulphur tests.

*Experiments* 17 *and* 18. (In place of I in Exp. 1, VIII and IX were used and the following compounds were isolated and identified)

*Triphenylmethyl α-naphthyl sulphone* (XVII), m.p. 145° (recrystallized from benzene–ether), 56·5%, $\nu_{max}^{Nujol}$ 1300, 1125 cm$^{-1}$ ($\nu_{SO_2}$), $\lambda_{max}^{EtOH}$ 287 mμ (log ε 3·82). (Found: C, 80·03; H, 5·14; S, 7·42. $C_{29}H_{22}O_2S$ requires: C, 80·15; H, 5·10; S, 7·38%).

*Triphenylmethyl β-naphthyl sulphone* (XVIII), m.p. 164·5° (recrystallized from benzene), 92·5%, $\nu_{max}^{Nujol}$ 1300, 1125 cm$^{-1}$ ($\nu_{SO_2}$), $\lambda_{max}^{EtOH}$ 260 and 267 mμ (log ε 3·72). (Found: C, 80·13; H, 5·12; S, 7·06. $C_{29}H_{22}O_2S$ requires: C, 80·15; H, 5·10; S, 7·38%).

*Kinetic measurement*

Compound I (350 mg) was dissolved in 7 ml liquid $SO_2$ in a pressure vessel. A number of the above-mentioned identical mixtures were made up, the individual mixtures taken one by one at fixed times during the course of the reaction at 43·3° and 53·35°, and the liquid $SO_2$ evaporated completely. Then, each mixture was dissolved in 10 ml toluene and the unchanged azo compound was determined by measurement of the volume of evolved $N_2$.

Compound VIII (300 mg) or IX (300 mg) was dissolved in 15 ml benzene. The rates of decomposition of each azo compound were determined at two temps by measurement of the volume of evolved $N_2$ as a function of time.

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