Photolysis of *N*-Arylsulphonyl-*SS*-dimethylsulphoximides in Aromatic Solvents. Photoisomerisation of Methylbiphenyls[1]

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Photolysis of the title compounds in benzene or toluene gives biphenyls in reasonable yields, probably *via* aryl radicals. *o*- and *m*-Methylbiphenyl are photoisomerised to give mixtures of the three isomers in which the *meta*-isomer predominates; the *para*-isomer is photostable under these conditions as are the terphenyls. No sulphonylnitrenes were formed in these reactions.

SULPHONYLNITRENES have almost invariably been generated by thermolysis of sulphonyl azides at 120 °C or higher.[2] The observation [3] that *N*-sulphonylazepines are the products of kinetic control of the reaction of singlet sulphonylnitrenes with aromatic substrates whereas *N*-phenylsulphonamides are the products of thermodynamic control made it desirable to develop a method of generating sulphonylnitrenes at low (preferably ambient, or below) temperatures. Unfortunately, photolysis of aliphatic and aromatic sulphonyl azides (except for ferrocenylsulphonyl azide [4]) in nonprotic, nonpolar solvents such as benzene or cyclohexane, or in a polar solvent such as pyridine, produced insoluble high-melting materials that were not characterised.[5-7] When photolysis of methanesulphonyl azide was carried out in benzene at 25 °C, so that the walls of the photolysis apparatus did not become coated with tar, a very small amount of *N*-methylsulphonylazepine was isolated.[6,8] The main product was a yellow, amorphous solid which exhibited NH, SO$_2$, and azide bands in the i.r. and which was not characterised. No *N*-methylsulphonylaniline was detected. Other attempts to generate singlet sulphonylnitrenes at low temperatures were equally unencouraging.[8] Following reports that a number of nitrene derivatives were produced by photolysis of appropriate pyridinium *N*-ylides [9-12] we examined the photolysis of *N*-sulphonyliminopyridinium ylides at various wavelengths and in different solvent systems.[13] In no case was any evidence obtained for the formation of singlet sulphonylnitrenes, although the sulphonamides obtained could arise from triplet nitrene.

The photolysis of *N*-arylsulphonyl-*SS*-dimethylsulphoximides (1) was examined in the hope that this might lead to singlet nitrenes, though compounds (1) can themselves be generally obtained in poor yield by photolysis (with a low pressure mercury lamp) or thermolysis of sulphonyl azides in sulphoxides.[5] We now report a study of the photolysis of compounds (1) in aromatic solvents, which did not result in the production of sulphonylnitrenes but did lead to aryl radicals.

When *SS*-dimethyl-*N*-phenylsulphonylsulphoximide (1; R = H) was irradiated in benzene (quartz vessel; 2537 Å radiation) at room temperature a 74.5% yield of biphenyl (2; R = H) was obtained, together with *SS*-dimethylsulphoximide (3) (7%), dimethyl sulphoxide (0.03%), dimethyl sulphone (trace), and SO$_2$ (7%). The remaining sulphur-containing fragments could not be accounted for. No diphenyl sulphone was isolated (the latter was shown to be stable under the photolysis conditions). Similarly, photolysis of (1; R = Me) in benzene gave a 79.6% yield of a mixture of 4-methyl-

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[1] Preliminary communication, R. A. Abramovitch and T. Takaya, *Chem. Comm.*, 1969, 1369.

[2] R. A. Abramovitch and R. G. Sutherland, *Fortschr. Chem. Forsch.*, 1970, **16**, 1.

[3] R. A. Abramovitch and V. Uma, *Chem. Comm.*, 1968, 797.

[4] R. A. Abramovitch, C. I. Azogu, and R. G. Sutherland, *Chem. Comm.*, 1969, 1439.

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[7] W. Lwowski and E. Scheiffele, *J. Amer. Chem. Soc.*, 1965, **87**, 4359.

[8] R. A. Abramovitch, T. D. Bailey, T. Takaya, and V. Uma, *J. Org. Chem.*, 1974, **39**, 340.

[9] J. Streith, A. Blind, J.-M. Cassal, and C. Sigwalt, *Bull. Soc. chim. France*, 1969, 948.

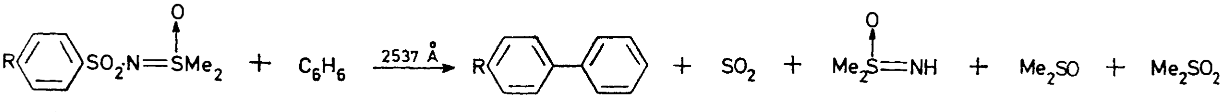
[10] T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, 1970, **35**, 426.

[11] V. Snieckus, *Chem. Comm.*, 1969, 831; V. Snieckus and G. Kan, *ibid.*, 1970, 172.

[12] C. W. Bird, I. Partridge, and D. Y. Wong, *J.C.S. Perkin I*, 1972, 1020.

[13] R. A. Abramovitch and T. Takaya, *J. Org. Chem.*, 1973, **38**, 3311.

biphenyl (2; R = Me) and biphenyl (2; R = H) in the molar ratio of 96 : 4. Irradiation of (1; R = H) in benzene, toluene, or toluene–acetonitrile in a Pyrex vessel for 24 h with 3 000 Å radiation led to almost total recovery (92—97%) of starting material. Under the same conditions but with pyridine as solvent an 86% recovery of (1) was achieved; this was also the result when the photolysis was carried out in benzene for 50 h with 3 500 Å radiation and benzophenone as sensitiser.



(1) (2) (3)

Photolysis of (1; R = H) in toluene for 34 h (2 537 Å) gave a mixture of *o*-, *m*-, and *p*-methylbiphenyls (48—53%) in the ratio 11.3 : 48.5 : 40.5. No biphenyl or bibenzyl was detected. A competitive phenylation of toluene and benzene gave a total rate ratio of 1.95 : 1. Variation of the ratio of the two solvents did not change ${}^{\mathrm{Me}}{}_{\mathrm{H}}K$, indicating that no selective solvation occurs.

At first sight, the isomer and total rate ratios are inconsistent with the known behaviour of aryl radicals or aryl cations (Table 1), though the total rate ratio is identical with that determined from the photolysis of triphenylbismuth. Another similarity between the two photochemical reactions is that no bibenzyl was formed in either case. The differences in the isomer ratios were much too great to be accounted for by differences in methods of analysis [i.r. and partial analysis by g.l.c. in Ph_3Bi photolyses, complete g.l.c. analysis in photolysis of (1)]. It was found, however, that *o*- and *m*-methylbiphenyl are each isomerised under the reaction conditions to a mixture of all three isomers in which the *meta*- predominates (Table 2). The *para*-isomer (2; R = Me), on the other hand, was not isomerised on irradiation at 2 537 Å for 24 h, though it was recovered in only 87% yield (Table 2). The observed isomer ratio (Table 1) is not, therefore, a reflection of the intermediacy of a species other than a phenyl radical. No such photoisomerisation was observed under the conditions used in the photolysis of triphenylbismuth. The results clearly indicate that the *ortho*-isomer is the most photolabile. Since the *para*-isomer is stable under these conditions it should serve as a ' sink ' in these rearrangements and, given long enough, both *ortho*- and *meta*-isomers should eventually rearrange completely to the *para*-, barring side reactions [these are apparent from the yields of recovered mixed biphenyls (Table 2)].

TABLE 1

Isomer and total rate ratios in phenylation of toluene

Source of phenyl	(1; R = H)	$PhN_2^+BF_4^-$ † [a]	$PhN_2^+BF_4^-$–C_5H_5N ‡ [b]	$(PhCO_2)_2$ § [c]	Ph_3Bi ¶ [d]
${}^{\mathrm{Me}}{}_{\mathrm{H}}K$	1.98	1.07	1.26	1.29	1.99
% *ortho*	11.1	47.1	60.7	57.4	56.6
% *meta*	48.5	27.2	22.2	24.6	27.1
% *para*	40.5	25.4	17.1	18.1	16.3

† At 65 °C in tetramethylene sulphone. ‡ At 60 °C in tetramethylene sulphone. § At 80 °C. ¶ Photolysis at 80 °C.

[a] R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc.* (*B*), 1968, 497. [b] R. A. Abramovitch and O. A. Koleoso, *J. Chem. Soc.* (*B*), 1968, 1293. [c] G. H. Williams, ' Homolytic Aromatic Substitution,' Pergamon, Oxford, 1960; D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 1955, 7. [d] D. H. Hey, D. A. Shingleton, and G. H. Williams, 1963, 5612.

TABLE 2

Photoisomerisation of methylbiphenyls (2 537 Å for 24 h)

Starting MeC_6H_4Ph	Isomer ratio (%) *o*-	*m*-	*p*-	Total yield (%)
o-	1.70	64.0	34.5	50.1—58.6
m-	1.97	76.9	21.0	56.0—60.1
p-			100	87.2

At least two possible explanations can be put forward to account for the high value of ${}^{\mathrm{Me}}{}_{\mathrm{H}}K$ obtained in the photolysis experiments. The first is that excited phenyl radicals are produced and that these are more selective (or electrophilic) than those generated thermally. The other is that the high values reflect photochemical ' shunting ' of biphenyl to side products (tars) faster than methylbiphenyls. A decision between these (or other) possibilities will have to await further work.

Isomerisation of the xylenes, mesitylene, and the di- and tri-t-butylbenzenes on irradiation is well known.[14] Subsequent to our original communication,[1] Mende, Laseter, and Griffin [15] reported the photorearrangement of bitolyls. They observed that those isomers having at least one *ortho*-methyl group are most reactive and rearrange in a highly selective manner, whereas 3,3′-, 3,4′-, and 4,4′-dimethylbiphenyl were comparatively photostable. Their results are in qualitative agreement with our more limited photochemical data in that the results in Table 2 suggest that the 2-isomer is photoisomerised the most readily, and the 4-isomer not at all (under these conditions). We also agree with Griffin and his co-workers in suggesting that the isomerisations probably involve a benzvalene intermediate leading to sequential 1,2-shifts of the substituent. Benzvalene formation probably also occurs in the unsubstituted ring but this does not lead to isomerisation (though it could lead to by-product formation). 4-Methylbiphenyl is either not appropriately photoexcited to the benzvalene

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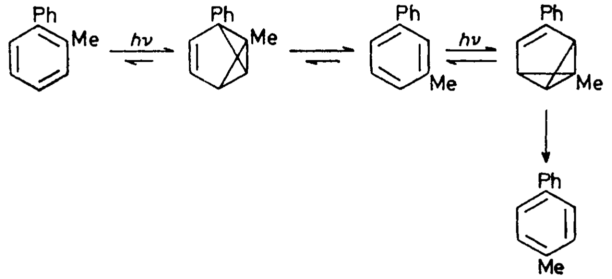
[14] K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1965, **87**, 4004, and references cited therein; H. R. Ward, *ibid.*, 1967, **89**, 2367; A. W. Burgstahler and P. L. Chien, *ibid.*, 1964, **86**, 2940.

[15] U. Mende, J. L. Laseter, and G. W. Griffin, *Tetrahedron Letters*, 1970, 3747.

under these conditions, or else the excited state is quenched or undergoes intersystem crossing before it can rearrange.



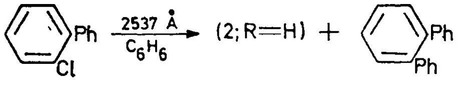
The aryl radicals may well result from photochemical S–N bond cleavage in (1) to give sulphur dioxide and (4):

$$(1)\xrightarrow{h\nu}\underset{(4)}{Me_2S(O){=}N\cdot}+ArSO_2\cdot\longrightarrow Ar\cdot+SO_2$$

the latter could abstract hydrogen from the σ-complex formed from Ar· and C_6H_6 to give (2) and (3), or, to a much lesser extent, from solvent benzene to give phenyl radicals. This latter pathway would explain the formation of small amounts of biphenyl in the photolysis of (1; R = Me) in benzene. The formation of dimethyl sulphoxide and dimethyl sulphone could be accounted for by secondary photolysis of initially formed (3). Thus, irradiation (2 537 Å) of a solution of (3) in benzene for 24 h gave dimethyl sulphoxide (10%) and dimethyl sulphone (0.4%): 74.5% of (3) was recovered. The photodisproportionation of a sulphoxide has been observed.[16] The formation of aryl radicals from $ArSO_2\cdot$ has precedent.[17]

Photolysis of (1; R = H) in bromobenzene gave an extremely low (0.24%) overall yield of products consisting of biphenyl and *o*-, *m*-, and *p*-bromobiphenyls in the molar ratio of 14.4 : 49.4 : 20.2 : 16.0. Most of (1) (93%) was unchanged. That these products did not arise mainly from (1) was shown by irradiation of neat bromobenzene, which gave the same overall yield of the same four products but in the ratio 4.07 : 57.0 : 23.9 : 15.1, respectively. Other still more minor products included a terphenyl and two isomeric bromoterphenyls (see below), which were also obtained in the reaction in the presence of (1). Similar results were obtained using chlorobenzene except that the yields of products were even smaller (<0.1%). When (1) was present in the chlorobenzene it was recovered in 92% yield.

Irradiation of 2-chlorobiphenyl (5) in benzene (2 537 Å) gave mainly biphenyl (2; R = H) (35.9%) and *o*-terphenyl (6) (4.2%). No *m*- and *p*-terphenyl were detected. Similar irradiation of *o*-terphenyl (6) in benzene did not lead to its isomerisation to *m*- and *p*-terphenyl. We conclude that the biphenyl formed in the photolyses of chloro- and bromo-benzene results from the secondary decomposition of the chloro- and bromobiphenyls initially formed (hydrogen abstraction from solvent or from either intermediate σ-complexes or cyclohexadiene derivatives). The chloro- and bromobiphenyls are produced by attack of phenyl radicals upon solvent: photolysis of aryl bromides is known to give aryl radicals.[18] The bromoterphenyls are undoubtedly produced as secondary products from the initially formed bromobiphenyls and solvent bromobenzene *via* biphenylyl radicals, as exemplified by (5) ⟶ (6). It appears that in these media the solvent is probably either absorbing all the radiation or is quenching excited (1) before it can decompose. The same was true in nitrobenzene or pyridine solution, no photodecomposition of (1; R = H) occurring in these solvents.



(5) (6)

EXPERIMENTAL

Reagents and Reference Compounds.—All solvents were purified and degassed by standard procedures and their purity was checked by g.l.c. The methylbiphenyls were purified by g.l.c. on a 12 ft × 1/4 in column packed with 10% SE-52 on Chromosorb W at 190 °C (helium flow rate 60 ml min^{-1}), followed by recrystallisation. Biphenyl and bibenzyl (reagent grade) were recrystallised from light petroleum. *o*- and *m*-Chlorobiphenyl and *o*- and *m*-bromobiphenyl were purified by g.l.c. on a 12 ft × $\frac{1}{4}$ in column packed with 25% Apiezon L on Anakrom. *p*-Chloro- and -bromo-biphenyl were recrystallised, as were the *o*-, *m*-, and *p*-terphenyls.

SS-Dimethyl-*N*-phenylsulphonylsulphoximide, m.p. 119—120° was prepared by the method of Carr, Seden, and Turner [19] (lit.,[19] m.p. 115°), and *SS*-dimethyl-*N*-*p*-tolylsulphonylsulphoximide, m.p. 174—175°, was prepared similarly (lit.,[19] m.p. 170°). *SS*-Dimethylsulphoximide, m.p. 51—52°, was prepared by the hydrolysis [20] of the *N*-*p*-tolylsulphonyl derivative (lit.,[20] m.p. 52—53°).

Photolysis of SS-*Dimethyl*-N-*phenylsulphonylsulphoximide* —(a) *In benzene*. A solution of the sulphoximide (0.3 g) in dry degassed benzene (200 ml) was irradiated for 24 h in a water-cooled quartz vessel under oxygen-free dry nitrogen in a Rayonet reactor with 2 537 Å lamps. The sulphur dioxide evolved (6.8%) was trapped with aqueous 5% potassium hydroxide and analysed as barium sulphate. The solvent was evaporated off and the residue chromatographed on a column of alumina. Elution with chloroform gave starting material (167 mg). Prior elution with light petroleum–ether (1 : 1 v/v) and ether gave the combined products, which were analysed by g.l.c. on a 6 ft × $\frac{3}{16}$ in column packed with 20% HI-EFF 8BP on GasChrom Q at

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[16] R. A. Archer and B. S. Kitchell, *J. Amer. Chem. Soc.*, 1966, **88**, 3462.

[17] F. A. Drahowzal in 'Organic Sulfur Compounds,' ed. N. Kharasch, vol. 1, Pergamon, New York, 1961, p. 372; R. A. Abramovitch, C. I. Azogu, and I. T. McMaster, *J. Amer. Chem. Soc.*, 1969, **91**, 1219.

[18] N. Kharasch, R. K. Sharma, and H. B. Lewis, *Chem. Comm.* 1966, 418; T. Matsura and K. Omura, *Bull. Chem. Soc. Japan*, 1966, **9**, 944.

[19] D. Carr, T. P. Seden, and R. W. Turner, *Tetrahedron Letters*, 1969, 477.

[20] H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 1950, 2081.

175 °C and a helium flow rate 60 ml min^{-1} with 3-bromobiphenyl as internal standard. The products were collected as they were eluted from the column and their i.r. spectra were compared with those of authentic samples. Thus were obtained biphenyl (74.9%), dimethylsulphoximide (6.9%), dimethyl sulphoxide (0.03%), and dimethyl sulphone (trace).

(b) *In toluene.* A solution of (1) R = H (300 mg) in dry toluene (200 ml) was irradiated as above. Work-up by chromatography and g.l.c. on a 12 ft × $\frac{1}{4}$ in 25% Apiezon L on Anakrom column at 225 °C with 2-fluorobiphenyl as internal standard gave *o*-, *m*-, and *p*-methylbiphenyl in yields of 5.5, 24.8, and 20.7%, respectively (isomer ratio $o:m:p$ 11.1 : 48.5 : 40.5) (average of 2 runs).

Competitive Phenylation of Benzene and Toluene.—These experiments were carried out under the same conditions as above except that mixtures (200 ml) of benzene and toluene in various molar proportions were used. The quantitative analyses for biphenyl and 2-methylbiphenyl were carried out on a 6 ft × $\frac{3}{16}$ in column packed with 20% HI-EFF 8BP on GasChrom Q (60—100 mesh) at 185 °C, and 3- and 4-methylbiphenyl were analysed on a 12 ft × $\frac{1}{4}$ in 25% Apiezon L on Anakrom (60—100 mesh) column at 225 °C. 3-Bromobiphenyl was used as internal standard in both cases. The results are summarised in Table 3 and are the averages of three determinations each on two separate runs.

TABLE 3

Competitive phenylation of benzene and toluene

[PhH] : [PhMe]	${}^{\mathrm{Me}}_{\mathrm{H}}K$
1 : 1	1.95
2 : 1	2.04
5 : 1	2.02
6 : 1	1.92
1 : 5	2.00
Average	1.98 ± 0.08

Photolysis of SS-*Dimethyl*-N-p-*tolylsulphonylsulphoximide in Benzene.*—The sulphoximide (300 mg) was suspended in dry benzene (150 ml) and irradiated as above. The yellow solution was evaporated and the residue chromatographed on neutral alumina. Elution with chloroform gave a mixture of biphenyl and 4-methylbiphenyl, m.p. 38—41°. This was separated on a column (12 ft × $\frac{1}{4}$ in) of 10% SE-52 on Chromosorb W (60—80 mesh) at 190 °C with 3-bromobiphenyl as internal standard. The ratio of biphenyl to 4-methylbiphenyl (3 runs) was 3.7 ± 0.2 : 96.2 ± 0.1. The overall yield was 79.6% (based on sulphoximide consumed). The products were identical (m.p., i.r.) with authentic samples.

Continued elution of the alumina column gave starting sulphoximide (157 mg). From the photolysis residues which were extracted with methanol and chromatographed on alumina were obtained starting material (36 mg), dimethylsulphoximide, dimethyl sulphoxide, and dimethyl sulphone in very low yields.

Photolysis of Bromobenzene.—(a) *In the presence of the Sulphoximide* (1a). A solution of (1a) (300 mg) was irradiated as above. Work-up as before and g.l.c. on a 12 ft × $\frac{1}{4}$ in 25% Apiezon L on Anakrom column (2-nitrobiphenyl internal standard) gave biphenyl and *o*-, *m*-, and *p*-bromobiphenyl in the molar ratio 14.4 : 49.2 : 20.2 : 16.0 in 0.24% overall yield. A mixture of terphenyls (mainly *o*-isomer) (2% of total), *m/e* 230 ($M^{+\cdot}$), and two isomeric bromoterphenyls [*m/e* 310/308 ($M^{+\cdot}$)] were also obtained. Starting sulphoximide (279 mg, 93%) was recovered.

(b) *In the absence of the sulphoximide* (1a). Neat bromobenzene was irradiated and worked up as above to give biphenyl and *o*-, *m*-, and *p*-bromobiphenyl in the molar ratio 4.1 : 57.0 : 23.9 : 15.1 in 0.24% overall yield. Another seven peaks were observed on g.l.c. including *o*-terphenyl (g.l.c. retention time, i.r.), and two isomeric bromoterphenyls (*m/e* 310/308).

Photolysis of Chlorobenzene.—This was carried out as in the case of bromobenzene; the same g.l.c. conditions were used for quantitative analysis (4-bromobiphenyl internal standard). Biphenyl and *o*-, *m*-, and *p*-chlorobiphenyl were obtained in the molar ratio 6.14 : 32.3 : 31.3 : 30.5 and the overall yield was <0.1%. Traces of *o*-terphenyl also appeared to be formed.

Similar results were obtained when (1a) was present except that the ratio of biphenyl and *o*-, *m*-, and *p*-chlorobiphenyl was now 4.0 : 25.7 : 33.5 : 36.8. Starting sulphoximide (92%) was recovered.

Photolysis of 2-*Chlorobiphenyl in Benzene.*—A solution of 2-chlorobiphenyl (96 mg) in dry benzene (200 ml) was irradiated and worked up as above. Quantitative analysis on a 12 ft × $\frac{1}{4}$ in 25% Apiezon L on Anakrom column at 225 °C (4-bromobiphenyl as internal standard) gave biphenyl (35.9%) and *o*-terphenyl (4.2%), identical with authentic samples. No *m*- and *p*-terphenyls were detected. Irradiation of *o*-terphenyl in benzene under the same conditions did not give any *m*- and *p*-terphenyls.

Photoisomerisation of Methylbiphenyls.—A solution of a methylbiphenyl (100 mg) in dry degassed toluene (150 ml) was irradiated as above for 24 h. Analysis of the products was carried out on a 12 ft × $\frac{1}{4}$ in 25% Apiezon L on Anakrom column at 225 °C using 3-bromobiphenyl as internal standard. Duplicate runs and triplicate analyses were carried out. The results are summarised in Table 2.

Photolysis of SS-*Dimethylsulphoximide in Benzene.*—A solution of dimethylsulphoximide (46 mg) in dry degassed benzene (200 ml) was irradiated under nitrogen for 24 h. The products were analysed by g.l.c. on a 6 ft × $\frac{3}{16}$ in column packed with 20% HI-EFF 8BP on GasChrom Q (3-bromobiphenyl internal standard). Dimethyl sulphoxide (10%), dimethyl sulphone (0.4%), and starting sulphoximide (74.5%) were obtained.

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