Photochemical Rearrangement of Phenyl Benzenesulphonates

By **Yoshiro Ogata,*** **Katsuhiko Takagi,** and **Shin Yamada,** Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, 464 Japan

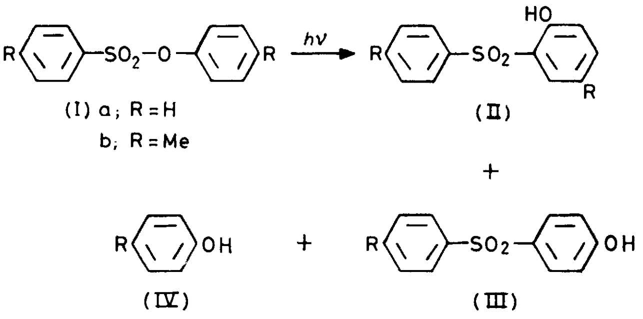
Phenyl benzenesulphonate (Ia) is converted into *o*- and *p*-hydroxyphenyl phenyl sulphones and phenol by u.v. irradiation. Quenching and sensitising studies suggest that the rearrangement proceeds *via* an excited singlet state or *via* a short-lived triplet. The rearrangement proceeds predominantly *via* an intramolecular path in view of the results of a mixed reaction involving both (Ia) and *p*-tolyl toluene-*p*-sulphonate (Ib) and the effect of radical scavenger. A mechanism involving ' cage radical pair ' is proposed.

PHOTOCHEMICAL Fries rearrangement has been reported,[1] with some aromatic esters,[2-7] carbonates,[8-10] ethers,[11,12] and amides.[13-15] These involve the migration of the acyl, carboxylate, or aryl group to the *ortho*- and *para*-positions of the aromatic ring with accompanying formation of phenol or aniline.

The migration of the sulphonyl group, however, has hardly been observed except for the thermal reaction of phenyl toluene-*p*-sulphonates [16] and the photoreaction of arylsulphonanilides.[17] In the course of our investigation of the photoelimination of the sulphonyl group, we found that phenyl benzenesulphonate (Ia) gave *o*- (IIa) and *p*-hydroxyphenyl phenyl sulphones (IIIa), together with phenol (IVa). We now report the behaviour and mechanism of this kind of reaction.

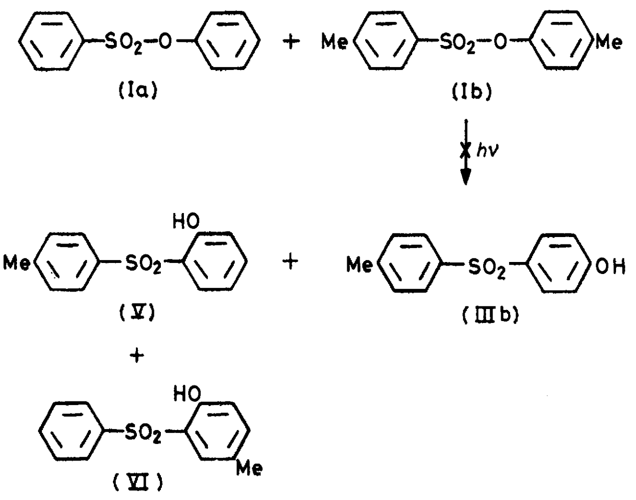
RESULTS AND DISCUSSION

Irradiation of an ethanol solution of phenyl benzenesulphonate (Ia) afforded (IIa) (15.3% †), (IIIa), (31.1%), and (IVa) (17.4%) together with a small amount of diphenyl ether. No trace of benzene was formed. A considerable amount of polymeric deposit was also obtained.



SCHEME 1

The photolysis of *p*-tolyl toluene-*p*-sulphonate (Ib) in ethanol gave only the *ortho*- (IIb) (16.0%) but not the *para*-isomer together with *p*-cresol (IVb) (23.4%); hence the alkyl group blocks migration to the substituted position.



SCHEME 2

An equimolar mixture of (Ia and b) was irradiated in ethanol solution to examine the crossed rearrangement. As shown in Scheme 2, independent rearrangement products, (IIa), (IIIa), and (IIb), were detected, but no hybrid products were detectable.

Furthermore, on irradiation of a solution containing phenol and *p*-tolyl toluene-*p*-sulphonate (Ib), no intermolecular hybrid products (IIIb) and (V) were detected by g.l.c. These results suggest an intramolecular mechanism similar to the photo-Fries rearrangement.[3-5]

The ratio of *para* (IIIa) to *ortho* (IIa) from (Ia) varies between 2.0 and 3.3 depending on the irradiation times as shown in the Figure. This indicates that (IIa) and

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† All yields were calculated on the basis of consumed starting material.

[1] For a comprehensive review, see for example (*a*) D. Bellus and P. Hrdlovic, *Chem. Rev.*, 1967, **67**, 599; (*b*) V. I. Stenberg, in ' Organic Photochemistry,' ed. O. L. Chapman, Dekker, New York, 1967, vol. 1, p. 127.

[2] J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, 1960, 217.

[3] H. Kobsa, *J. Org. Chem.*, 1962, **27**, 2293.

[4] J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1963, 1781.

[5] R. A. Finnegan and J. J. Mattice, *Tetrahedron*, 1965, **21**, 1015.

[6] M. R. Sandner, E. Hedaya, and D. J. Trecker, *J. Amer. Chem. Soc.*, 1968, **90**, 7249.

[7] J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, **94**, 2219.

[8] C. Pac and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1964, **37**, 1392.

[9] A. Davis and J. H. Golden, *J. Chem. Soc.* (*B*), 1968, 425.

[10] E. A. Caress and I. E. Rosenberg, *J. Org. Chem.*, 1971, **36**, 769.

[11] D. P. Kelley, J. T. Pinhey, and R. D. G. Rigby, *Tetrahedron Letters*, 1966, 5953.

[12] Y. Ogata, K. Takagi, and I. Ishino, *Tetrahedron*, 1970, **26**, 2703.

[13] D. Elad, *Tetrahedron Letters*, 1963, 873.

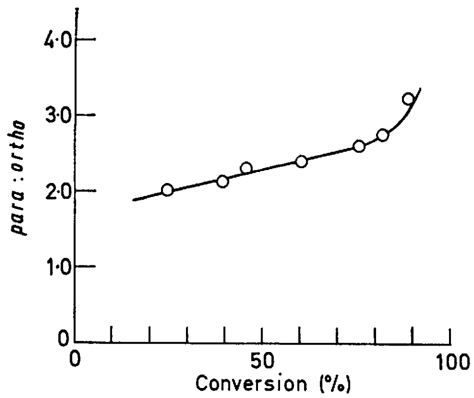
[14] D. Elad, D. V. Rao, and V. I. Stenberg, *J. Org. Chem.*, 1965, **30**, 3252.

[15] H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Japan*, 1969, **42**, 409.

[16] A. R. Parikh, K. A. Thaker, and R. D. Desai, *J. Inst. Chem., Calcutta*, 1973, **45**, 914 (*Chem. Abs.*, 1974, **80**, 59,619).

[17] H. Nozaki, T. Okada, R. Noyori, and M. Kawanisi, *Tetrahedron*, 1966, **22**, 2177.

(IIIa), once formed, are further photodecomposed, since no photolytic interconversion between (IIa) and (IIIa) occurs.



Correlation between conversion (%) and *para* : *ortho* ratio for the photolysis of phenyl benzenesulphonate (Ia) in ethanol

Then the effect of Bu^{n}SH (a radical scavenger) on photolysis of (Ia) was examined (Table 1). The yield of *para*-isomer decreases as the concentration of Bu^{n}SH increases, especially in the case of the neat reagent. On the other hand, the yield of *ortho*-isomer remains nearly constant or tends to rise slightly on addition of the radical scavenger. The formation of (IIa) may be intramolecular but that of (IIIa) is, at least partly, intermolecular. Then phenomena may be correlated with the formation of phenol favourably in a high concentration of Bu^{n}SH. Hence, (Ia) may decompose into 'a radical pair' in a solvent cage, and then may undergo subsequent coupling.

TABLE 1

Effect of n-butyl mercaptan on photolysis of phenyl benzenesulphonate [a]

Bu^{n}SH (M)	Conversion (%)	Yield (%) *ortho*-Isomer (IIa)	*para*-Isomer (IIIa)	Phenol (IVa)	Isomer ratio (*para* : *ortho*)
Solvent	28.9	15.6	9.0	48.8	0.6
1.40	52.1	14.9	19.0	15.7	1.3
0.70	53.6	11.7	18.1	11.8	1.6
0.12	67.1	7.7	17.9	12.1	2.3
0.06	70.3	5.8	16.9	12.5	2.9
	73.8	6.1	17.6	13.1	2.9

[a] Concentration 4.4 × 10^{-2}M in ethanol. All irradiation times are 16 h except Bu^{n}SH as solvent (25 h).

In addition, if the reaction were intermolecular, the formation of rearranged products would be essentially inhibited on addition of Bu^{n}SH. Therefore, this transformation proceeds predominantly *via* an intramolecular path and in part *via* an intermolecular path especially with (IIIa).

Phenyl benzenesulphonate (Ia) was irradiated in various solvents, acetonitrile, methanol, ethanol, isopropyl alcohol, t-butyl alcohol, benzene, and n-hexane (Table 2). It is apparent that the yield of rearranged products depends on the nature of the solvent. Examination of these data reveals that yields of this photo-Fries reaction depend on the solvent polarity rather than viscosity. Sandner *et al.*[6] have reported the viscosity effect on the photoreaction of *para*-substituted phenyl esters. However, the photoreaction of (Ia) in this study is little affected by solvent viscosity in passing from acetonitrile (0.33 cP) to t-butyl alcohol (2.95 cP) in spite of a marked effect of polarity on this photolysis. Lowering of the polarity of the solvent results in a lower *para* : *ortho* ratio. For example, no *para*-isomer was observed in n-hexane but the *para* : *ortho* ratio is 3.1 in EtOH, and this suggests that the intermediate radical is polar, especially for *para*-substitution. This is against Plank's result [18] on the polar effect on photolysis of phenyl benzoate *i.e.* lowering the polarity results in a higher *para* : *ortho* ratio.

To establish the multiplicity (*S* or *T*) of this rearrangement, quenching and sensitising experiments were carried out. Neither the rate of disappearance of (Ia) nor of formation of (IIa) and (IIIa) was affected by a triplet quencher (penta-1,3-diene).

Furthermore, an equimolar mixture of (Ia) and various sensitisers, *e.g.* benzophenone (E_T 68.6 kcal mol^{-1}) was irradiated. The radiation was filtered through Pyrex to remove light (<300 nm) absorbed by (Ia), and to ensure selective excitation of the sensitiser. However, there was no effect upon addition of sensitiser on the reaction.

TABLE 2

Photolysis of phenyl benzenesulphonate (Ia) in various solvents [a]

Solvent	Dielectric constant	Viscosity (cP) at 25°	Conversion (%)	Yield (%) *ortho*-Isomer (IIa)	*para*-Isomer (IIIa)	Phenol (IV)	Isomer ratio (*para* : *ortho*)
Acetonitrile	37.5	0.33	69.7	8.0	16.4	11.0	2.1
Methanol	32.63	0.611	65.3	8.5	19.5	12.4	2.3
Ethanol	24.30	1.19	62.6	6.2	19.3	13.2	3.1
Isopropyl alcohol	18.3	1.76	58.8	6.6	19.5	15.3	3.0
t-Butyl alcohol [b]	10.9	2.95	70.9	4.5	17.3	13.7	3.8
Benzene	2.284	0.65	49.1	23.8	16.5	11.4	0.7
n-Hexane	1.890	0.32	18.5	30.0		4.2	0.0

[a] Concentration 2.1 × 10^{-2}M for 10 h at 20°. [b] For 15 h at 30°.

These results show that the overall process is unaffected by triplet quenchers and sensitisers, and that the reaction occurs *via* a lowest excited singlet state or *via* a triplet manifold at a rate exceeding the diffusion control.

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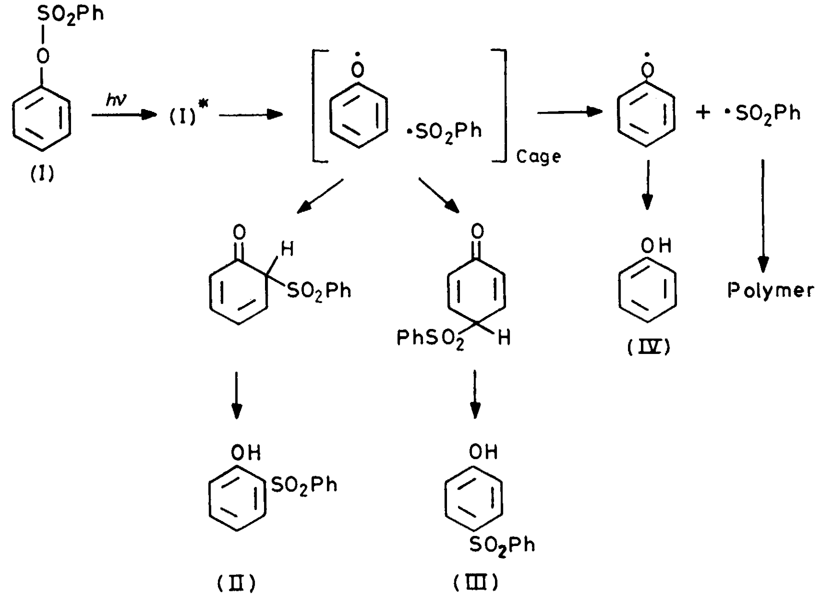
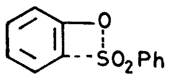
[18] D. A. Plank, *Tetrahedron Letters*, 1968, 5423.

Kobsa[3] has proposed a mechanism for the photo-Fries reaction which involves homolytic cleavage of the C–O bond of the ester into radical pair (ArO· + ·COR), held together in a solvent cage, followed by migration. An analogous mechanism is plausible for our reaction, since we could detect diphenyl ether which is the coupling product of phenyl and phenoxyl radicals. This mechanism suggests an intramolecular mechanism.

The excitation by absorption of a photon by (I) results in the S–O bond cleavage to give radicals within a solvent cage. Recombination of two radicals at the *ortho*- and *para*-positions results in the formation of the cyclohexadienones, which enolises to the hydroxyphenyl phenyl sulphones. Diffusion from the solvent cage permits the formation of phenol by abstracting a hydrogen atom from the solvent, *etc.*; the other fragment, $PhSO_2\cdot$, may eject SO_2 to yield phenyl radical. These radicals, $PhSO_2\cdot$ *etc.*, may form polymeric material.



SCHEME 3



(VII)

However, since the *para* : *ortho* ratio tends to decrease with decreasing polarity of the solvent, the *ortho*-isomer may be formed, at least partly, *via* less polar or concerted * transition states such as (VII) instead of the solvent cage reaction. On the other hand, the solvation of polar radical should favour the migration of radicals to longer distance giving the *para*-isomer.

EXPERIMENTAL

M.p.s were measured by a Yanagimoto microapparatus, and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer model 337 grating spectrophotometer and u.v. spectra on a Hitachi double-beam instrument, model 124. N.m.r. spectra were determined by a Hitachi high resolution spectrophotometer, model R-24B. Quantitative analysis of photolysates was done by a Yanagimoto gas chromatograph having a flame ionisation detector, model GCG-550F, employing two 1.0 m × 1.5 mm columns packed with Apiezon L grease and PEG 20M on Chamelite at 100—300°.

Materials.—The sulphonates (Ia and b) were prepared by condensation of aromatic sulphonyl chloride and phenols in the presence of pyridine. Phenyl benzenesulphonate (Ia) has b.p. 161—162° at 2 mmHg (lit.,[19] 191—192° at 10 mmHg); $\lambda_{max.}$ (MeOH) 272, 265, 259, and 253sh nm (log ε 2.95, 3.06, 2.97, and 2.83); $\nu_{max.}$ (neat) 1 370 cm^{-1} (SO_2). *p*-Tolyl toluene-*p*-sulphonate (Ib) shows m.p. 70° (lit.,[20] 69°); $\nu_{max.}$ (KBr) 1 390 (SO_2) and 831 cm^{-1} (*para*-substitution); $\delta(CDCl_3)$ 2.17 (3 H, s, Me), 2.30 (3 H, s, Me), and 6.62—7.60 (8 H, m, 2 Ph).

General Procedures.—All experiments were carried out in a cylindrical quartz tube (15 × 200 mm and 10 × 150 mm) or a Pyrex tube (15 × 200 mm), except for preparative experiments. Irradiations were carried out using a Halos high-pressure 300 W mercury lamp with a water-cooled quartz jacket, whose total relative energy of radiation below 300 nm was *ca.* 90% of that of 365—366 nm.

Photolysis of Phenyl Benzenesulphonate (Ia).—An ethanolic solution of (Ia) (5.33 g, 0.022 8 mol) was irradiated at 20° for 40 h. The solution gradually turned yellow. After completion of the reaction, the solvent was evaporated and the residue was dissolved in ether, and then extracted with aqueous KOH. The ether solution gave unchanged starting material (1.75 g, 32.8%). The aqueous KOH layer was extracted with ether after acidification (HCl), and the ether was then evaporated. A portion (2.5 g) of this residue

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* 1,3-Sulphonyl migration is a photochemically allowed reaction.

[19] W. F. Fower, jun., C. C. Unruh, P. A. McGee, and W. O. Kenyon, *J. Amer. Chem. Soc.*, 1947, **69**, 1636.

[20] Chem. Fabr. v. Heyden, Deutsches Reichspatent, 1931/532403.

was passed through a 450 × 15 mm column packed with 100 mesh silica gel. Elution with benzene–ethyl acetate gave (IIa) (15.3%), (IIIa) (31.1%), and (IVa) (17.4%). Products were identified by i.r., m.p., n.m.r., and u.v. spectra, and also g.l.c. in comparison with authentic specimens. *o*-Hydroxyphenylphenyl sulphone (IIa) shows m.p. 94—95° (lit.,[21] 96—98°); $\lambda_{max.}$ (EtOH) 291 (log ε 3.66), 274sh (3.40), 232sh (4.06), and 218 nmsh (4.24); $\lambda_{max.}$ (aqueous NaOH) 325 nm (log ε 3.75); $\nu_{max.}$ (KBr) 3 370 (OH) and 1 310 cm^{-1} (SO_2); δ([$^2H_6$]DMSO) 10.55sh (1 H, OH), and 7.93—6.72 (9 H, m, ArH). *p*-Hydroxyphenylphenyl sulphone (IIIa) shows m.p. 134—135° (lit.,[22] 137°); $\lambda_{max.}$ (EtOH) 255 nm (log ε 4.18), $\lambda_{max.}$ (aqueous NaOH) 290 nm (log ε 4.26); $\nu_{max.}$ (KBr) 3 370 (OH), 1 300 (SO_2), and 842 cm^{-1} (*para*-substitution); δ([$^2H_6$]DMSO) 10.54br (1 H OH), 7.91—6.74 (9 H, m, ArH).

Cross Reactions.—(1). A mixture of (Ia) (2.3 g, 0.01 mol) and (Ib) (2.6 g, 0.01 mol) in EtOH (500 ml) was irradiated for 45 h. The reaction mixture was condensed by evaporation and analysed by g.l.c. The products, (IIa), (IIIa), (IIb), (IVa), and (IVb), were identified by comparison of their retention times with those of authentic samples. No hybrid products (IIIb), (V), and (VI), were detected.

(2). Irradiation of an ethanol solution (12 ml) of (Ib) (0.36 mmol) and phenol (0.34, 0.90, and 1.80 mmol) for 5 h gave (IIb) (7.3, 10.5, and 10.0%, respectively) and (IVa), but no cross-products (IIIb) and (V). Yield was determined by g.l.c. using bibenzyl as internal standard.

Quenching Studies.—An ethanol solution (12 ml) containing 2.9 × 10^{-2}M-sulphonate (Ia) and varying amount of penta-1,3-diene was placed in a quartz tube. The tubes were irradiated by a Halos 300 W high-pressure mercury lamp on a rotating turntable apparatus.

Sensitising Studies.—Phenyl benzenesulphonate (Ia) (0.39 mmol) and various sensitisers, *i.e.* benzophenone (0.38 mmol; E_T 68.6 kcal mol^{-1}), xanthone (0.39 mmol, E_T 74.0 kcal mol^{-1}), acetophenone (0.45 mmol; E_T 73.7 kcal mol^{-1}), and *p*-methoxyacetophenone (0.39 mmol, E_T 71.8 kcal mol^{-1}), were irradiated in benzene (12 ml). A Halos 300 W high-pressure mercury lamp with a Pyrex tube, which cut off light shorter than 300 nm, was used as a light source. Light of wavelength longer than 300 nm was absorbed by sensitisers (>99%). Irradiation of (Ia) for 15 h gave neither (IIa) nor (IIIa) at all, although (Ia) was consumed during irradiation.

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[21] E. D. Amstutz, I. M. Hunsberger, and J. J. Chessick, *J. Amer. Chem. Soc.*, 1951, **73**, 1220.

[22] M. E. Heppenstall and S. Smiles, *J. Chem. Soc.*, 1938, 899.