

Photoreactions of Some Benzylic Sulphones

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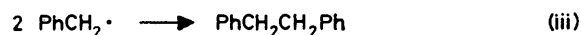
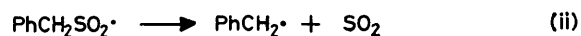
Formation of a mixture of three bibenzyl derivatives by irradiation of benzyl 4-chlorobenzyl sulphone proves that desulphonylation of acyclic dibenzyl sulphones is an intermolecular process. Irradiation of benzyl t-butyl sulphone gives bibenzyl and 2-methylpropane-2-sulphonic acid.

In photoreactions of sulphonocleavages,¹ cleavage of one or both bonds on either side of the $-\text{SO}_2-$ group may occur. Reaction is more efficient when stabilised (*e.g.* particularly benzylic) radicals are formed.² Desulphonylation gives rise to hydrocarbon products from cyclic^{2,3} or acyclic⁴⁻⁶ sulphones, but sulphonic acids have also been obtained from photoreactions of diphenyl sulphone⁷ (in benzene) and β -oxo-sulphones, *e.g.* (1)⁶ (in methanol, but not in benzene). Photoisomerisation of (1) to isopropenyl toluene- α -sulphonate (6) also occurs.⁶ We describe here results obtained with some acyclic benzylic sulphones, including the formation of a sulphonic acid from compound (5).

The photoreaction of dibenzyl sulphone (2) to give bibenzyl (7) was presumed to involve loss of sulphur dioxide.⁵ However, we have been unable to identify the latter as a by-product, and we find that the yield of (7) is little more than half the molar quantity of the sulphone consumed, which suggests a fate of the radicals $\text{PhCH}_2\text{SO}_2\cdot$ other than desulphonylation [step (ii)]. An

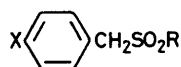
1.0:1.8:0.9. The departure from the statistically expected ratio (1:2:1) possibly reflects a slight preference for formation of benzyl rather than 4-chlorobenzyl radicals in the primary step of decomposition. The proportions of chlorinated bibenzyls (8) and (9) decreased with increasing time of irradiation, owing to their secondary photolysis which has been studied independently.⁸

The photoreaction of benzyl phenyl sulphone (4) was examined in the expectation that α -cleavage of the



benzyl group would pre-empt the formation of phenyl radicals and that the radicals $\text{PhSO}_2\cdot$ might give rise to benzenesulphonic acid. The latter was suggested as a by-product of the photoreaction of diphenyl sulphone,⁴ but it was subsequently identified only by an isotope dilution method.⁷ Notwithstanding, irradiation of (4) in benzene gave a complex mixture of products, which included hydrocarbons (biphenyl, diphenylmethane, and bibenzyl) and diphenyl sulphone. This last is presumably formed by reaction of the radicals $\text{PhSO}_2\cdot$ with benzene, although others have concluded that this reaction is unimportant.^{4,9} Deoxygenation products were also observed from the photoreaction of (4): benzyl phenyl sulphide, and diphenyl sulphide and sulphoxide (*cf.* the formation of dimethyl disulphide, dimethyl sulphide, and dimethyl sulphone in the photoreaction of dimethyl sulphoxide¹⁰).

Irradiation of benzyl t-butyl sulphone (5) afforded bibenzyl (7) and 2-methylpropane-2-sulphonic acid; the latter was identified by comparison of its *S*-benzylthio-uronium salt with an authentic sample. The formation of a sulphonic rather than a sulphinic acid is unexpected, but it apparently occurs during the photoreaction since no reducing properties were observed in the acidic material before work-up. Methanesulphonic acid is



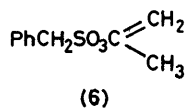
(1) X = H, R = CH_2COMe

(2) X = H, R = CH_2Ph

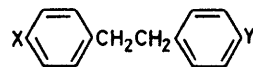
(3) X = Cl, R = CH_2Ph

(4) X = H, R = Ph

(5) X = H, R = Bu^t



(6)



(7) X = Y = H

(8) X = H, Y = Cl

(9) X = Y = Cl

acidic residue possibly contains toluene- α -sulphonic acid, but this could not be characterised.

The formation of bibenzyl (7) is expected to be an intermolecular process, involving combination of benzyl radicals from different sulphone molecules [step (iii)]. Thus, irradiation of benzyl 4-chlorobenzyl sulphone (3) gave a mixture of bibenzyl (7) and its 4-chloro- and 4,4'-dichloro-derivatives (8) and (9) initially in the ratio

¹ J. D. Coyle, *Chem. Soc. Rev.*, 1975, **4**, 523.

² M. P. Cava, R. H. Schlessinger, and J. P. Van Meter, *J. Amer. Chem. Soc.*, 1964, **86**, 3173; P. M. Weintraub, *Chem. and Ind.*, 1970, 1296.

³ J. Saltiel and L. Metts, *J. Amer. Chem. Soc.*, 1967, **89**, 2232; F. G. Bordwell, J. M. Williams, jun., E. B. Hoyte, jun., and B. B. Jarvis, *ibid.*, 1968, **90**, 429.

⁴ N. Kharasch and A. I. A. Khodair, *Chem. Comm.*, 1967, 98.

⁵ T. Sato, Y. Goto, T. Tohyama, S. Hayashi, and K. Hata, *Bull. Chem. Soc. Japan*, 1967, **40**, 2975.

⁶ C. L. McIntosh, P. de Mayo, and R. W. Yip, *Tetrahedron Letters*, 1967, 37.

⁷ M. Nakai, N. Furukawa, S. Oae, and T. Nakabayashi, *Bull. Chem. Soc. Japan*, 1972, **45**, 1117.

⁸ G. E. Robinson and J. M. Vernon, *J.C.S. Perkin I*, 1972, 1277.

⁹ J. M. Squire and W. A. Waters, *J. Chem. Soc.*, 1962, 2068.

¹⁰ K. Gollnick and H.-U. Stracke, *Pure Appl. Chem.*, 1973, **33**, 217; *cf.* C.-T. Chen and S.-J. Yan, *Tetrahedron Letters*, 1969, 3855.

formed in the photoreaction of dimethyl sulphoxide, supposedly *via* disproportionation or oxidation (by dimethyl sulphoxide) of methane-sulphenic and -sulphinic acids.¹⁰ Corresponding deoxygenated sulphur-containing by-products from (5) were sought, but not identified. Only a small amount of diphenylmethane [as in the prolonged photoreaction of the sulphone (2), it is probably formed by reaction of benzyl radicals with solvent benzene] and traces of benzaldehyde and neopentylbenzene were detected.

EXPERIMENTAL

Photoreactions were conducted in a Hanovia photochemical reactor with a 100 W medium-pressure mercury arc lamp in a water-cooled quartz jacket, immersed in a solution of the substrate under bubbling nitrogen. Volatile products were identified by comparison of g.l.c. retention times (on 1.5 m × 4 mm columns packed with silicone gum rubber SE 30 on Celite) and mass spectra of g.l.c. peaks (obtained on an A.E.I. MS 12 spectrometer operating at 70 eV) with those of authentic compounds.

Dibenzyl sulphone (2) was prepared by oxidation of the sulphoxide with hydrogen peroxide and acetic acid at 60–70 °C. Benzyl phenyl sulphoxide and the sulphones (3)–(5) were obtained by similar oxidation of the corresponding sulphides. M.p.s of all these compounds agreed with those reported.¹¹

Photoreactions.—*Dibenzyl sulphone* (2). The sulphone (2) (1.0 g) in benzene (110 ml) was irradiated for 46 h. The exit stream of nitrogen was examined for sulphur dioxide by i.r. spectroscopy and by passing through acidified potassium permanganate solution, which was subsequently tested for sulphate anions: results of both tests were negative. A sticky film adhering to the wall of the u.v. lamp jacket after the photoreaction was partly soluble in a little water, and the solution gave an acidic reaction and a white precipitate with aqueous barium chloride, but an *S*-benzylthiuronium derivative was not obtained. The benzene solution contained unchanged (2) (10%), bibenzyl (7) (51% based on a 1:1 correlation with sulphone consumed), and traces of diphenylmethane.

The photoreaction of the sulphone (2) (3.0 g) in ethanol (1 l) was cleaner. After 13 h g.l.c. analysis showed that only 6% of (2) remained. The solution was evaporated to dryness, the residue was extracted with light petroleum at its b.p. (60–80 °C), and the extract was filtered through a short column of alumina. Bibenzyl (7) (0.5 g), m.p. and mixed m.p. 47–49 °C (from isopentane), was obtained.

¹¹ R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060; F. G. Bordwell and B. M. Pitt, *ibid.*, 1955, **77**, 572; G. S. Misra and R. S. Asthana, *J. prakt. Chem.*, 1957, [4] **4**, 270.

Benzyl 4-chlorobenzyl sulphone (3). The sulphone (3) (0.4 g) in benzene (110 ml) was irradiated and samples of the solution were withdrawn at intervals for g.l.c. analysis. The molar ratios of bibenzyl (7) to 4-chlorobibenzyl (8) and 4,4'-dichlorobibenzyl (9) were plotted against time and extrapolated back to 1.0 : 1.8 : 0.9 at zero time. After 1 h the ratios were 1.0 : 1.7 : 0.8, and the proportions of (8) and (9) showed a progressive decrease during 49 h of irradiation.

Benzyl phenyl sulphone (4). The sulphone (4) (1.0 g) in benzene (110 ml) was irradiated for 24 h. The solution contained biphenyl, diphenylmethane, and bibenzyl (molar ratios *ca.* 3 : 1 : 2) and smaller amounts of diphenyl sulphide, sulphoxide, and sulphone, and benzyl phenyl sulphide. Another possible product, benzyl phenyl sulphoxide, was not separated from the sulphone (4) under the conditions used for g.l.c., and could not be identified from the mass spectrum in the presence of (4).

*Benzyl *t*-butyl sulphone* (5). During irradiation of the sulphone (5) (1.0 g) in benzene (110 ml) a brown solid was deposited on the wall of the u.v. lamp jacket. The extent of decomposition of (5) was thus highly variable in different runs, and dependent on the frequency with which this film was removed. Bibenzyl (7) and diphenylmethane were identified by g.l.c. analysis of the solution, and (7), m.p. 50–52 °C, was isolated as described for the reaction of dibenzyl sulphone (2). Traces of benzaldehyde and neopentylbenzene were also present; the g.l.c. peak of the latter was incompletely separated.

The combined solid material (0.1 g) scraped at intervals from the u.v. lamp jacket during a 100 h photoreaction was deliquescent, dissolving in water to give an acidic solution. It was recrystallised repeatedly from acetone–isopentane (charcoal) to give hydrated 2-methylpropane-2-sulphonic acid, m.p. 93–94°, which was dried *in vacuo* for analysis (Found: C, 30.6; H, 7.7; S, 20.4. Calc. for C₄H₁₀O₃S·H₂O: C, 30.7; H, 7.7; S, 20.5%). Another sample of the crude sulphonic acid was dissolved in water; the solution was filtered and the filtrate afforded the *S*-benzylthiuronium salt, m.p. 199–201 °C (lit.,¹² 202 °C) (Found: C, 47.4; H, 6.3; N, 9.1; S, 21.2. Calc. for C₁₂H₂₀N₂O₃S₂: C, 47.4; H, 6.6; N, 9.2; S, 21.1%), identical [m.p., mixed m.p., and i.r. spectrum (Nujol)] with a sample prepared independently.¹²

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¹² H. J. Backer and P. L. Stedehouder, *Rec. Trav. chim.*, 1933, **52**, 437; E. S. Balakirev, G. N. Anisimova, and N. S. Malyshova, *Probl. Poluch. Poluprod. Prom. org. Sin., Akad. Nauk S.S.S.R., Otdel. Obshchei Tekh. khim.*, 1967, 5 (*Chem. Abs.*, 1968, **68**, 12,626a).