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A Novel Photorearrangement of Benzyl Phenyl Sulfone Encapsulated in β-Cyclodextrin

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Abstract: Solid ß-cyclodextrin complex of benzyl phenyl sulfone, upon irradiation, undergoes a unique intramolecular rearrangement yielding exclusively *ortho*-methyldiphenyl sulfone as the product.

Mechanistic studies on photochemistry of sulfonyl derivatives have not been explored extensively, in comparison with the attention received by the analogous carbonyl compounds. Cava *et al.*[1] first reported the photoactivity of aryl sulfones, which upon excitation loose SO_2 (photoextrusion) and yield products typical of radical coupling reactions. Mechanism of photoextrusion of SO_2 from aryl methyl sulfones in homogeneous[2] and micellar media[3] have been investigated using both steady-state and time-resolved techniques. In recent years cyclodextrins (CDs) are used as popular microvessels for photochemical studies and the utility lies in their potential for providing reaction control, mechanistic information and molecular recognition[4]. Our interest[5-7] in employing CD to achieve selectivity in organic reactions prompted us to investigate the photolysis of benzyl phenyl sulfone, (1), encapsulated in ß-CD and the results are discussed below.

ß-CD complexes of (1) containing both equal and excess of cyclodextrin (ß-CD:(1) = 1:1 and 5:1) were prepared as reported for other organic substrates[5-7] and photolysed at 254nm (64 W) in aqueous solutions (8 hours; in nitrogen atmosphere). The solid 1:1 complex of (1) with ß-CD was irradiated for 100 hours. For comparison, photolysis of (1) in isotropic solvents such as methanol, benzene and acetonitrile (8 hours; in nitrogen atmosphere) were also studied.

Formation of an inclusion complex of (1) with ß-CD was inferred by comparison of ^1H- and ^{13}C-NMR data, X-ray diffraction pattern and also by the IR spectra of ß-CD, (1), ß-CD complex of (1) and a physical mixture of ß-CD and (1). Notable differences[6,7] in ^{13}C-NMR, X-ray diffraction pattern as well as the IR spectra are observed between the ß-CD complex of (1) and its physical mixture with ß-CD. ^1H-NMR data also provide further information. The chemical shifts (in Hz) given for CD protons are in the order H_1, H_2, H_3, H_4, H_5 and H_6: for pure CD protons 2065.7, 1502.9, 1628.6, 1471.4, 1582.9 and 1591.4; and for ß-CD-(1) complex 2065.5, 1503.1, 1584.8, 1471.3, 1584.8 and 1623.8. The data show significant upfield shift for H_3 and downfield shift for H_6 protons. Such changes in chemical shift values are felt as a the consequence of anisotropic effects of the aromatic ring residing inside the cavity and considered[8] to be evidence for inclusion complex formation in aqueous CD solution. By employing absorption spectrophotometry (Benesi-Hildebrand method[9]), the dissociation constant of the complex has been found to be 3.2×10^{-4} M.

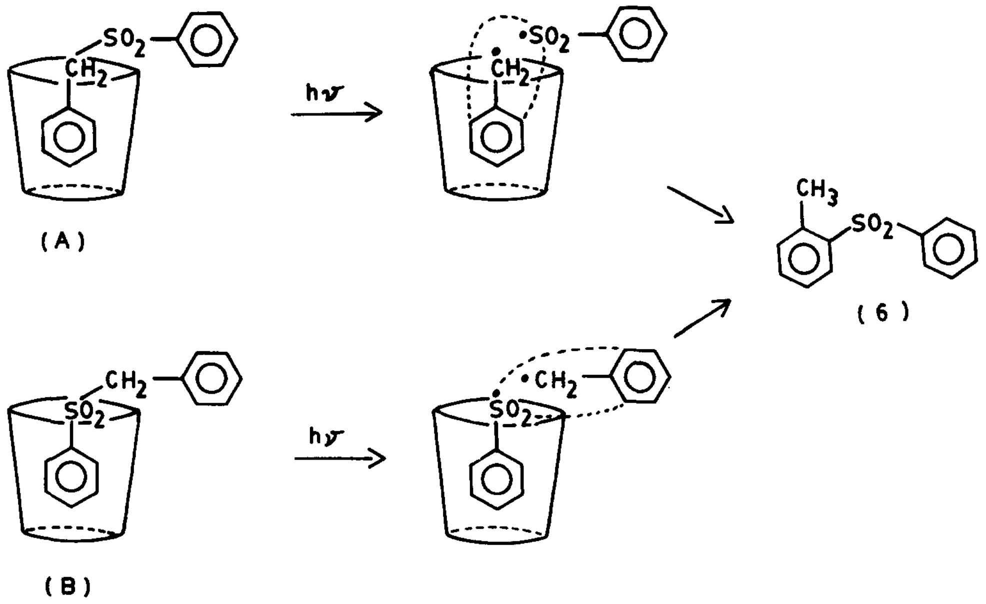
Photoproducts were identified using GC by coinjection of authentic samples synthesised separately and also by their ^{1}H-NMR spectra (in $CDCl_3$, δ) [e.g; dibenzyl: 7.25 (10H,s), 2.9 (4H,s); diphenylmethane: 7.3 (10H,s), 3.95 (2H,s); and for *ortho*-methyldiphenyl sulfone: 8.15 (1H,m), 7.8 (2H,m), 7.45 (6H,m), 2.4 (3H,s)].

The data in Table 1 indicate that photolysis of (1) in benzene, methanol and acetonitrile results in products derived primarily from the radical pair, namely $C_6H_5SO_2^{\bullet}$ and $C_6H_5CH_2^{\bullet}$, formed upon photolysis of (1). In benzene and methanol, dibenzyl, (4) is obtained as the major product and *ortho*-methyldiphenyl sulfone has not been detected. Irradiation of aqueous solutions of ß-CD complexes of (1) (1:1 and 5:1) yield mainly benzenesulfonic acid and this may be due to the reaction of benzenesulfonyl radical with water.

Table 1. Results of Irradiation of Benzyl Phenyl Sulfone (1).[a]

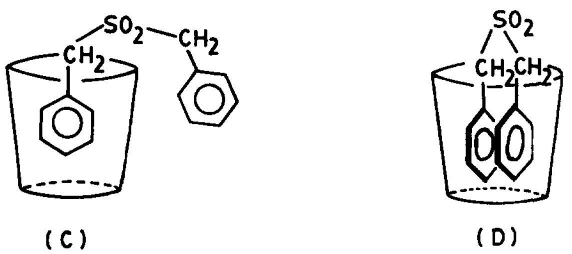
Medium	Percentage conversion	% Yield of photoproducts[b]					
		(2)	(3)	(4)	(5)	(6)	(7)
Methanol	49	-	7	26	-	-	16
Benzene	74	8	4	43	-	-	19
Acetonitrile	27	4	3	5	-	-	15
ß-CD-(1) (1:1) complex/water	33	-	5	-	20	-	8
ß-CD-(1) (5:1) complex/water	81	-	4	-	59	-	18
ß-CD-(1) (1:1) solid complex	37	-	-	-	-	37	-

[a] Error limit ± 5% ; analysed by GC. [b] (2) Biphenyl. (3) Diphenylmethane. (4) Dibenzyl. (5) Benzenesulfonic acid. (6) *ortho*-Methyldiphenyl sulfone. (7) To be characterised.



Scheme 1.

The remarkable feature of the present study is the exclusive formation of *ortho*-methyldiphenyl sulfone, (6), during the photolysis of solid β-CD complex of (1) and this may be explained as follows. Benzyl phenyl sulfone encapsulated in β-CD (structures (A) or (B) in Scheme 1) upon photolysis, produces a radical pair. This pair as a result of the geometric restriction imposed by the host β-CD, experiences restricted rotational motion and diffusion. Thus, the radicals may either couple again to give (1) or can undergo an intramolecular rearrangement involving attack at the nearby *ortho*-position (Scheme 1) yielding (6). Absence of *para*-isomer formation, evidenced from NMR data, may be explained as due to the loss of freedom of the radical pair and the greater protection for *para*-position in (1) of the complex.



Structures of* ß*-CD complexes of dibenzyl sulphone.

However, we do not observe any similar intramolecular rearrangement with dibenzyl sulfone, (**8**). When solid *β*-CD complex of (**8**) is photolysed at 254 nm (100 hours), (**4**) was identified as the major product. It has already been reported[2] that photolysis of (**8**) in benzene and 1,4-dioxane gives only (**4**). We also observe that photolysis of (**8**) in benzene, methanol, acetonitrile, 1,4-dioxane and also as their solid *β*-CD complex yields only (**4**). Two structures (C) and (D) are possible for (**8**) encapsulated in *β*-CD cavity. The absence of any intramolecular rearrangment in (**8**) may be attributed to a faster rate of photoextrusion of SO_2 as it leads to more stable benzyl radical pair and this is more likely in (D) in which both the aryl rings penetrate into the cavity. Structure similar to (D) involving inclusion of both phenyl rings has been proposed by Ramamurthy and co-workers[4,10] in the photobehaviour of *α*-alkyldibenzyl ketones in *β*-CD. The exclusive formation of (**4**) in the present work also supports the structure (D) for *β*-CD complex of (**8**).

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REFERENCES

1. Cava, M.P.; Schlessinger, R.H.; Van Meter, J.P. *J. Am. Chem. Soc.* **1964**, *86*, 3173-3174.
2. Givens, R.S.; Hrinczenko, B.; Liu, J.H.-S.; Matuszewski, B.; Tholen-Collison, J. *J. Am. Chem. Soc.* **1984**, *106*, 1779-1789.
3. Gould, I.R.; Chen-ho Tung, Turro, N.J.; Givens, R.S.; Matuszewski, B. *J. Am. Chem. Soc.* **1984**, *106*, 1789-1793.
4. Ramamurthy, V.; Eaton, D.F. *Acc. Chem. Res.* **1988**, *21*, 300-306.
5. Pitchumani, K.; Durai Manickam, M.C.; Srinivasan, C. *Tetrahedron Lett.* **1991**, *32*, 2975-2978.
6. Pitchumani, K.; Velusamy, P.; Sabithamala, S.; Srinivasan, C. *Tetrahedron*, **1994**, *50*, 7903-7912.
7. Pitchumani, K.; Velusamy, P.; Srinivasan, C. *Tetrahedron*, **1994**, *50*, 12979-12988.
8. Demarco, P.V.; Thakkar, A.L. *J. Chem. Soc., Chem. Commun.* **1970**, 2-4.
9. Benesi, H.A.; Hildebrand, J.H. *J. Am. Chem. Soc.* **1949**, *71*, 2703-2707.
10. Nageshwer Rao, B.; Syamala, M.S.; Turro,N.J.; Ramamurthy, V. *J. Org. Chem.* **1987**, *52*, 5517-5521.

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