BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1117—1119 (1972)

The Photochemical Degradation of Diphenyl Sulfone-1-^{14}C

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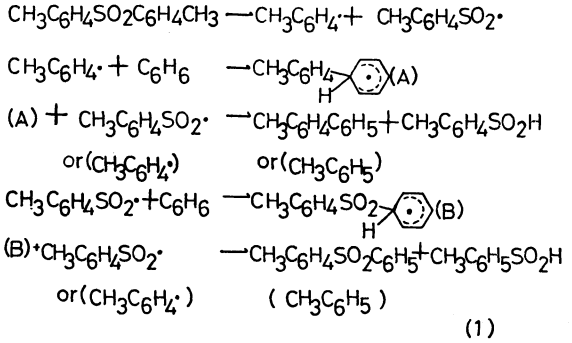
(Received May 26, 1971)

The photolysis of diphenyl sulfone-1-^{14}C upon irradiation with 2537 Å light in benzene gave biphenyl-1-^{14}C and benzenesulfinic acid-^{14}C. The yields of both compounds were estimated by means of an isotope dilution method. The ^{14}C activity of the sulfone recovered was equal to that of the sulfone employed, while that of biphenyl formed was found to have nearly one half of the ^{14}C activity. These results reveal that the phenylation reaction by phenyl radical formed by the photolytic cleavage of the C–S bond of the sulfone is an intermolecular reaction in which benzenesulfonyl radical appears to abstract hydrogen from the intermediate cyclohexadienyl radical rather than attacking benzene. The ^{14}C distribution indicates that the ^{14}C activity at 1-position was found to remain at the same position of biphenyl after photolysis of the sulfone. Thus, the photolysis of diaryl sulfones in benzene followed by the oxidation of biphenyl derivatives obtained would be a convenient method for the degradation of diaryl sulfones.

Degradation of ^{14}C-labeled diphenyl sulfone was previously carried out by way of initial alkaline fusion of the sulfone, followed by the subsequent cleavage of the phenol obtained, but the method was tedious. We sought to find a simple and more convenient degradative method of sulfone or sulfide, especially in our studies on the mechanisms of the reactions of diphenyl sulfone and related compounds with either sulfur[1] or diaryl disulfide[2], possible migration of phenyl group in the treatment of diphenyl sulfide with aluminum chloride[3] and also the alkali fusion of these compounds.[4] Recently, Kharasch and Khodair[5] reported that the photolysis of diaryl sulfone, sulfoxide, and sulfide in benzene produces aryl radicals which give the corresponding biphenyl in good yield. They proposed the following intermolecular mechanism since the photolysis of bis-*p*-tolyl sulfone in benzene gave only 4-methylbiphenyl and no 4,4′-dimethylbiphenyl.



(1)

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[*] Present address: Ube Industries Ltd., Ube, Yamaguchi.

[1] S. Oae and S. Kawamura, This Bulletin, **36**, 163 (1963).

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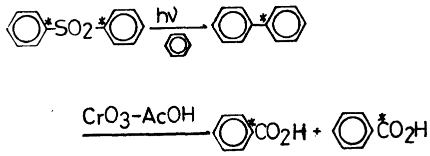
[5] N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, **1967**, 98.

Thus, the photolysis of diphenyl sulfone seems to be a convenient method for the degradation of diphenyl sulfone if there is no skeletal rearrangement. In order to confirm the absence of skeletal rearrangement during the reaction so that the method can be used for the degradation of diphenyl sulfone and sulfide conveniently, the photolysis of diphenyl sulfone-l-^{14}C was carried out, followed by the degradation of the biphenyl-*x*-^{14}C formed.

This paper describes a detailed account and implications of experimental observations.

Results and Discussion

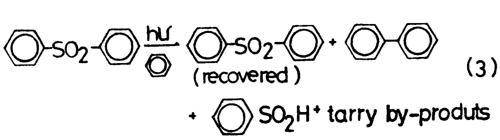
The synthesis of diphenyl sulfone-l-^{14}C has been described.[6] The rather low yield (27%) of biphenyl formation is due to the low efficiency of irradiation and our efforts to minimize any further reaction. Biphenyl formed by photolysis was diluted with an aliquot of inactive biphenyl and then oxidized with CrO_3 in acetic acid at 70—75°C (Eq. (2)). The activity of benzoic acid thus obtained was compared with that of biphenyl. The percentage rearrangement of the activity at 1-position of the sulfone was calculated. The result reveals that more than 99% ^{14}C activity remained in the original position. Thus, the photolysis of diphenyl sulfone is shown to be a convenient method for the degradation to determine the ^{14}C activity at 1-position of diphenyl sulfone, sulfoxide and sulfide.



(2)

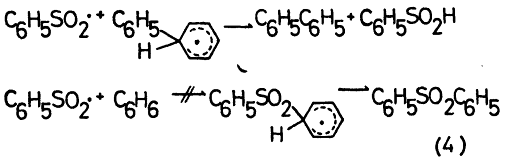
In order to shed further light on the mechanism of the photolysis of diaryl sulfone in benzene a more detailed analysis of products was performed by using the ^{14}C-labeled diphenyl sulfone.

A benzene solution of diphenyl sulfone-l-^{14}C (0.0224 M) was irradiated with 2537 Å light at room temperature for 20 hr. After the reaction, unchanged diphenyl sulfone was recovered while biphenyl formed was isolated and subjected to ^{14}C activity measurement. Determination of the yield of a possible product, benzenesulfinic acid, was carried out by means of isotope dilution. (Eq. (3)). The result of the photolysis is shown in Table 1.



(3)

The following conclusion may be drawn from the data in Table 1. Firstly, the activity of diphenyl sulfone recovered is equal to that of the starting material. Benzenesulfinic acid appears to be formed by the hydrogen atom abstraction from the intermediate cyclohexadienyl radical with benzenesulfonyl radicals produced by the initial C–S bond cleavage of the sulfone, while there is no addition of benzenesulfinyl radical to benzene to reproduce diphenyl sulfone as shown by Eq. (4). If the sulfonyl radical attacks the solvent benzene, the ^{14}C activity of the recovered sulfone would be less than that of the starting sulfone. Secondly, the fact that the activity of biphenyl formed is nearly one half of that of diphenyl sulfone used reveals that phenyl radical produced reacts with benzene to yield biphenyl, *viz.*, the process is an intermolecular free radical arylation reaction of benzene. That the ^{14}C activity of biphenyl (47%) is slightly less than the theoretical value might be due to the isotope effect during the initial C–S bond cleavage of the sulfone-^{14}C.



(4)

Thus, the photolysis of diphenyl sulfone in benzene is considered to proceed through the mechanistic route proposed earlier by Kharasch and Khodair as shown by the following equation. Consequently, the photolysis of diphenyl sulfone is found to be a simple

TABLE 1. PHOTOLYSIS OF DIPHENYL SULFONE-1-^{14}C

	Diphenyl sulfone (Starting material)	Diphenyl sulfone (Recovered)	Biphenyl	Benzenesulfinic acid
Activity	8.26×10^5	8.31×10^5	3.88×10^5	1.02×10^4 a)
(dpm/mmol)		(100.6%)	(47.0%)	
Yield	Conversion:			
	58.7%	(41.3%) d)	71.0% b)	6.8% c)

a) Three fifths of the resulting benzene solution diluted with 0.755 g of inactive sulfinic acid.

b), c) Based on the amount which actually underwent photolysis and on the assumption that one mol of diphenyl sulfone yielded one mol of biphenyl.

d) Recovered yield.

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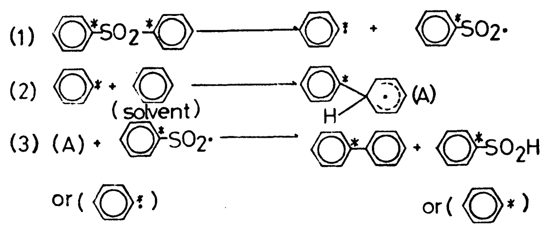
[6] S. Oae, N. Furukawa, M. Kise, and M. Kawanishi, This Bulletin, **39**, 1212 (1966).

and convenient method of degradation of ^{14}C labeled diphenyl sulfone.



(5)

Experimental

Preparation of Diphenyl Sulfone-1-^{14}C. Diphenyl sulfone–1–^{14}C was synthesized through 9 steps starting from barium carbonate-^{14}C. The synthetic method has been given.[6]

The Photolysis of Diphenyl Sulfone-1-^{14}C. The photolysis of sulfone (1.223 g) was carried out in 250 m*l* of benzene at room temperature for 15 hr by the irradiation of 2537 Å light of a low-pressure cold cathode mercury lamp. The reaction mixture turned brown and then become tarry material which coated the lamp reducing the efficiency of prolonged irradiation. The benzene solution was divided into two parts. Three fifths of the contents of the flask was used for the measurement of the activity of diphenyl sulfone recovered and biphenyl formed *in situ* and the rest was subjected to the determination of the yields of the compounds listed in Table 2 by means of an isotope dilution method. The benzene solution was washed with 5% alkali solution to remove the acidic components including benzenesulfinic acid. After evaporation of benzene, both biphenyl and diphenyl sulfone were isolated and separated by means of silica gel column chromatography. Benzenesulfinic acid was extracted with ether from the aqueous layer after acidified with hydrochloric acid. Crude biphenyl thus obtained was purified by recrystallization from water-alcohol and then by sublimation twice. Diphenyl sulfone and benzenesulfinic acid isolated were purified by recrystallization twice from benzene-*n*-hexane and ether-*n*-hexane, respectively. Diphenyl sulfone, biphenyl, and benzenesulfinic acid thus obtained were subjected to the counting of ^{14}C activity.

Oxidation of Biphenyl. An aliquot amount of biphenyl (0.4 g) was dissolved in 5 m*l* of acetic acid, and to this solution was added a solution of 5 g of anhydrous chromic acid in 2 m*l* of water and 5 m*l* of acetic acid dropwise with stirring at 70—75°C. Carbon dioxide evolved during the oxidation. After the oxidation was completed, the content of the flask was stirred for 30 min at 70—75°C. The reactant was then poured into 40 m*l* of water and the whole mixture was extracted with ether. The ether layer was washed with water three times to remove acetic acid and then re-extracted with 5% alkali solution. The alkali solution was reacidified and the benzoic acid precipitated was purified by sublimation. The yield was about 20%. Both benzoic acid and biphenyl were subjected to the counting of ^{14}C activity. The specific activities of both biphenyl-*x*-^{14}C and benzoic acid-^{14}C were found to be the same. Thus no ^{14}C rearrangement occurred during photolysis and oxidation. The benzoic acid obtained was degraded according to the known method[7] and was found to have ^{14}C activity at its 1 position.

Measurement of the ^{14}C Activities. Activities of all the compounds were counted with a liquid scintillation counter (TEN) in toluene solution using POPOP as a scintillator.

We wish to thank Dr. M. Hamada of the Radiation Center of Osaka Prefecture for his advice and for affording facilities for the measurements.

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[7] J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith, and C. W. Vaughan, *J. Amer. Chem. Soc.*, **75**, 3290 (1953); J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956).