Synthesis of Benzocyclobutene by Photochemical Desulfonylation

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As part of the investigation of the synthesis of cyclic compounds, studies of the decarbonylation of cycloalkanones[1,2] and the denitrogenation of diazo-cycloalkanones[3-8] by photochemical reaction have been extensively carried out by several groups of workers in recent years. Little attention has, however, been paid to the synthesis of cyclic compounds by the photo-desulfonylation of the cyclic sulfone; up to the present, no reports along this line have been made.

On the other hand, concerning the desulfonylation of cyclic sulfone, it has been shown in earlier papers[9,10] that a few cyclic compounds were produced by pyrolyses of the corresponding cyclic sulfones. On the whole, however, not only were the pyrolytic conditions employed in the above experiments very drastic, but also the yields of the resulting cyclic compounds were rather insignificant. For example, the pyrolysis of 1, 3-dihydroisothianaphthene-2, 2-dioxide in the molten state at temperatures between 280°C and 300°C[7] gave a mixture of *o*-xylene, benzocyclobutene and 1, 2, 5, 6-dibenzocycloöctadiene in yields as low as 3.2, 12.8 and 4.0% respectively.

It was well known that the aromatic compounds containing a sulfonyl group exhibit intense absorption in the ultraviolet region. Therefore, it might be expected that the desulfonylation of aromatic sulfone would be photochemically accelerated by the collisional transfer of vibrational energy from excited molecules to foreign molecules.

The present investigation was undertaken to confirm the feasibility of the synthesis of the benzocyclobutene ring system by the photolysis of 1, 3-dihydroisothianaphtene-2, 2-dioxide.

Results and Discussion

The results of the formation of benzocyclobutene by the decomposition of the sulfone are listed in Table I.

TABLE I. DECOMPOSITION OF 1, 3-DIHYDROISOTHIANAPHTHENE-2, 2-DIOXIDE[a]

Expt. No.	Temp. °C	Irradiation	Benzocyclobutene yield,[b] %
1	200	−	2.6
2	200	+	4.0
3	250	−	17.5
4	250	+	24.9
5	300	−	30.7
6	300	+	39.2
7	350	−	42.0
8	350	+	53.2

a) Each experiment was carried out in the reduced pressure system.
b) Based on total amount of the sulfone used.

In each case, benzocyclobutene was obtained as the major product, together with small amounts of 1, 2, 5, 6-dibenzocycloöctadiene; in addition, the molar ratios of benzocyclobutene and 1, 2, 5, 6-dibenzocycloöctadiene were approximately between 3.9 and 4.1. In some cases, however, with irradiation (Expt. 4 and 6), the products were contaminated by a trace amount of *o*-xylene. From the above results, it may be concluded that the temperature change, within the range of 200∼350°C, has an obvious effect on the conversion of the sulfone and that the irradiation considerably accelerates the desulfonylation of the sulfone. As has been described earlier, in every reaction under reduced pressure it has been observed that the ultraviolet-light has no remarkable effect on the molar ratio of benzocyclobutene and 1, 2, 5, 6-dibenzocycloöctadiene. On the other hand, in the reaction under the atmospheric pressure (Expt. 9), the formation of 1, 2, 5, 6-dibenzocycloöctadiene increases, while the formation of benzocyclobutene, on the contrary, decreases, the formation of a small amount of *o*-xylene being clearly observed, as is shown in Table II.

Although one would expect that, from the stand point of chemical equilibrium, reducing

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TABLE II. EFFECT OF REACTION PRESSURE ON THE COMPOSITION OF PRODUCT

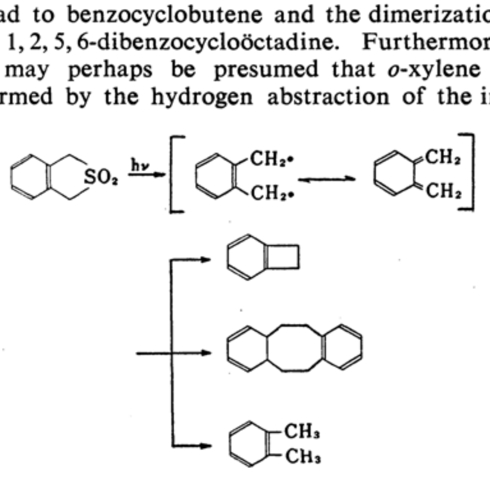
Expt. No.	Temp. °C	Press. mmHg	Yield,[a] %		
			Benzocyclobutene	Dibenzocycloöctadiene	*o*-Xylene
5	300	12∼15	30.7	8.1	—
9[b]	300	760	7.8	28.3	2.0

a) Based on total amount of the sulfone.
b) In the absence of ultraviolet-light.

the pressure would accelerates the desulfonylation considerably, the total amount of the decomposition product was nearly equal to the amount of the reaction product under the reduced pressure. Moreover, in order to ascertain the thermal behavior of benzocyclobutene, a further experiment was carried out. When benzocyclobutene was heated under atmospheric pressure at 300°C for 2 hr., 1, 2, 5, 6-dibenzocycloöctadiene was formed in a 57.1% yield, along with a trace amount of *o*-xylene.

In view of the above facts, the most reasonable conclusions to be drawn are that the rate of desulfonylation is independent of the reaction pressure, and that the reaction pressure plays a very important role in the further reaction of the intermediate *o*-xylylene biradical generated by the desulfonylation of the sulfone. Namely, as soon as benzocyclobutene is formed by desulfonylation under reduced pressure, it is immediately removed from the reaction vessel without collision with the other. Consequently, the dimerization of benzocyclobutene was considerably suppressed.

It seems to be more reasonable to consider that the decomposition of 1, 3-dihydroisothianaphthene-2, 2-dioxide may proceed through the intermediate *o*-xylylene biradical, which may be a mesomeric species, and be generated by the desulfonylation of the above sulfone. The intramolecular cyclization of the biradical will lead to benzocyclobutene and the dimerization to 1, 2, 5, 6-dibenzocycloöctadine. Furthermore, it may perhaps be presumed that *o*-xylene is formed by the hydrogen abstraction of the intermediate biradical from the sulfone or the above cyclic products.



Further investigations into the photochemical desulfonylation of various cyclic sulfones are being carried out in this laboratory.

Experimental

Materials. — Forty grams of 1, 3-dihydroisothianaphthene, prepared according to the directions of Cava et al.,[10] were added drop by drop, over a period of 3.5 hr., into 11.3% peracetic acid (930 ml.) with stirring. The temperature was maintatined at 5∼10°C during the addition of the sulfide, and after the addition was complete, the mixture was allowed to stand at room temperature for 1 day. After cold water (1000 ml.) had then been stirred into the above mixture, the crude sulfone was precipitated, collected by filtration, and dried. The concentration of the mother liquors in vacuo gave an additional sulfone. Three recrystallizations from benzene-petroleum ether gave 44.6 g. (90.3%) of 1, 3-dihydroisothianaphthene-2, 2-dioxide, m. p. 148.5∼149.0°C.

Found: C, 57.08; H, 4.81. Calcd. for $C_8H_8 \cdot O_2S$: C, 57.14; H, 4.80%.

Apparatus and Procedure.—The photolyses were conducted in a reaction vessel connected by a stopcock to a manometer, two traps and a vacuum pump. The reaction vessel, containing a thermometer and the low pressure mercury resonance lamp (100 W.), was a cylindrical glass cell, with an internal diameter of 8.0 cm. and a length of 25 cm.; it was coiled with the flexible heater and placed on the shaking machine. Pulverized 1, 3-dihydroisothianaphthene-2, 2-dioxide (5.0 g.) was placed in the reaction tube, and a considerable volume of glass-wool was stuffed into the output-part of the reaction vessel to avoid trouble due to the sublimation of the starting material. Before the reaction began, the system was swept by nitrogen gas and evacuated to 12∼15 mmHg. The reactions, regardless of the presence or absence of the ultraviolet-light, were carried out at 200∼350°C with shaking at the reduced pressure of 12∼15 mmHg for 5 hr.

After the reaction was complete, the volatile product, which had been collected in traps cooled at −78°C by a dry-ice-acetone bath was, analyzed by gas chromatography, using a 3 m. tricresyl phosphate column at 110°C; it was thus confirmed to be usually composed of only one component, except for the rare case when that component is accompanied by a trace of *o*-xylene. The volatile product was distilled under reduced pressure, giving a colorless benzocyclobutene, b. p. 52.0~52.5°C/22 mmHg, n_D^{21} 1.5405 (Lit.11) b. p. 50.5~51.0°C/20 mmHg ; n_D^{20} 1.5421). It showed infrared absorption bands at 1580, 1545, 1475, 778 and 717 cm^{-1} (*o*-disubstituted benzene) ; the ultraviolet spectrum of this compound was in full accordance with that described in the literature.

A mixture of 0.5 g. of benzocyclobutene and 0.6 g. of maleic anhydride in 1.5 ml. of benzene was heated in a sealed tube at 130°C for 30 hr. After the reaction mixture had been distilled under reduced pressure to remove any unchanged substances, the residual solid was sublimed at 150~165°C/3 mmHg. Recrystallization of the sublimate from benzene gave 0.55 g. of 1,2,3,4-tetrahydronaphthalene-*cis*-2,3-dicarboxylic anhydride as white needles, m. p. 188.0~188.5°C (Lit.12) m. p. 189°C).

The brownish residue in the reaction vessel was extracted with a large amount of petroleum ether as completely as possible. The ethereal extract was then dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was dissolved in benzene - light-petroleum ether (1 : 10) and chromatographed over alumina. The evaporation of the solvent from the effluent left colorles crystals. Recrystallization from ethyl alcohol afforded 1,2,5,6-dibenzocycloöctadiene as white needles, m. p. 108°C (Lit.10) m. p. 109~110°C).

Found : C, 92.38 ; H, 7.41. Calcd. for $C_{16}H_{16}$: C, 92.26 ; H, 7.74%.

It showed infrared absorption bands at 1595, 1585, 1485, 755 and 733 cm^{-1} (*o*-disubstituted benzene) ; and at 3000 cm^{-1} (=C-H). Moreover, in its ultraviolet spctrum, the maximum absorptions were present in 264.0 mμ (log ε 2.965) and 272.0 mμ (log ε 2.667) in 95% ethyl alcohol.

Summary

The synthesis of benzocyclobutene by the photochemical desulfonylation of 1,3-dihydroisothianaphthene-2,2-dioxide has been studied and the following results obtained ; 1) The irradiation considerably accelerates the desulfonylation of the sulfone, while the ultraviolet-light has no remarkable effect on the molar ratio of the formed benzocyclobutene and 1,2,5,6-dibenzocycloöctadiene. 2) The rate of desulfonylation is independent of pressure, and the reaction pressure plays a very important role in the further reaction of the intermediate *o*-xylylene biradical produced by the desulfonylation.

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