of magnitude expected from random exchange with a molecule without active hydrogen atoms. These small exchanges provide strong evidence that transmission of conjugative effects in the transition state for carbanion formation are small indeed in comparison with those commonly observed for analogous α,β-unsaturated esters, nitriles and ketones. Furthermore, they explain the failure to isolate products from the reactions attempted earlier since carbanion formation is an essential step in these reactions.

Experimental

The preparation of the cyclopropanes has been described.[14]

Deuterium oxide (>99.5%) was purchased from the Stuart Oxygen Co., San Francisco, Calif.

General Procedure for Attempted Acylation and Alkylation Reactions.—The reaction flask was fitted with a Hershberg stirrer, a reflux condenser protected with a drying tube and a dropping funnel. Sodium amide and sodium hydride were weighed and transferred and triphenylmethylsodium[15] was siphoned into the reaction flask under an atmosphere of nitrogen. Anhydrous ether was used as the solvent in all experiments except no. 5 (*t*-butyl alcohol). A solution of the cyclopropane was added dropwise to the stirred suspension of the base, and the reaction mixture was refluxed with stirring when the addition had been completed. After the specified reaction time a solution of the alkyl halide, or ester, was added dropwise and refluxing continued for the indicated period. The reaction mixture was cooled in an ice-bath and the excess base was decomposed by the cautious addition of ice. The mixture was acidified, the layers separated, and the aqueous phase extracted with solvent. The combined organic phase was washed with sodium bicarbonate and water and dried. After removal of solvent the reaction mixture was fractionated. The results of these attempted reactions are summarized in Table I.

Cyanoethylation reactions were carried out according to the directions of Bruson[16] for the cyanoethylation of diethyl malonate.

Deuterium Exchange.—The procedure described is typical of the exchange reactions. To a stirred suspension of 1.56 g. (0.04 mole) of sodium amide in 150 ml. of dry ether was added 3.3 g. (0.031 mole) of 1-cyano-1,2,2-trimethylcyclopropane (IX). After refluxing for 24 hours, the reaction mixture was cooled in ice and 1.02 g. (0.05 mole) of deuterium oxide was added. The ice-bath was removed and stirring was continued for 3 hours. The ether solution was then dried by the addition of 1 g. of anhydrous sodium sulfate. After removal of the ether, the residue was fractionated through a Todd column (reflux ratio 100:1) yielding 2.1 g. of nitrile, b.p. 66° (29.5 mm.), $n^{25}\text{D}$ 1.4285.

Deuterium Analyses.—About 500 mg. of each compound was combusted according to the procedure of Niederl and Niederl[17] using the universal packing. The water produced in the combustion was collected and purified by the procedure described by Doering and Hoffmann.[18] The deuterium analyses were done at Yale University by the falling drop method.[19]

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(14) G. W. Cannon, A. A. Santilli and P. Shenian, This Journal, **81**, 1660 (1959).

(15) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

(16) H. A. Bruson in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 79.

(17) J. B. Niederl and V. Niederl, "Organic Quantitative Microanalysis," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 108.

(18) W. von E. Doering and A. K. Hoffmann, This Journal, **77**, 521 (1955).

(19) A. S. Keston, D. R. Henberg and R. Schonheimer, *J. Biol. Chem.*, **122**, 227 (1937). The authors are grateful to Prof. Doering for the use of their falling drop apparatus and to Mr. Marvin Lehr for his invaluable assistance in the actual deuterium determinations.

Amherst, Mass.

[Contribution from the McPherson Chemical Laboratory of The Ohio State University]

Condensed Cyclobutane Aromatic Compounds. VI. The Pyrolysis of 1,3-Dihydroisothianaphthene-2,2-dioxide: A New Synthesis of Benzocyclobutene[1]

By M. P. Cava and A. A. Deana

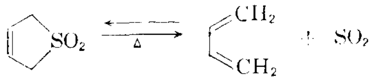
Received February 2, 1959

The pyrolysis of 1,3-dihydroisothianaphthene-2,2-dioxide (V) in the molten state at 280–300° gives sulfur dioxide and low yields of a mixture of *o*-xylene, benzocyclobutene (VI) and 1,2,5,6-dibenzocycloöctadiene (VII). In boiling diethyl phthalate solution, the only hydrocarbon formed from V is the octadiene VII. In contrast, decomposition of V in the gas phase over a hot wire at 460–670° gives pure benzocyclobutene in good yield. The primary pyrolysis product of V is *o*-quinodimethane (VIII), as was shown by trapping VIII with N-phenylmaleimide to give the N-phenylimide of tetralin-*cis*-2,3-dicarboxylic acid (IX).

The synthesis of the benzocyclobutene ring system has been reported by only two routes: the reaction of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene with sodium iodide,[2–4] and the photolysis of α-diazoindanones.[5,6]

A new synthesis of this system now has been achieved.[7]

It is well known that sulfur dioxide can add to butadiene to give 2,5-dihydrothiophene-1,1-dioxide (I),[8] a reaction which can be reversed with ease by heat.



I

The investigation reported here was carried out in order to determine the feasibility of extending the reverse reaction to the cyclic aromatic analog of I, 1,3-dihydroisothianaphthene-2,2-dioxide (V). Only one report of the thermal decomposition of a derivative of V is to be found in the literature: 1,1,3-tri-

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(1) Presented before the Division of Organic Chemistry at the 134th National Meeting of the American Chemical Society in Chicago, Ill., September 8, 1958.

(2) H. Finkelstein, Inaugural Dissertation, Strassbourg, 1910.

(3) M. P. Cava and D. R. Napier, This Journal, **79**, 1701 (1957).

(4) For a closely analogous synthesis from a dibromo-*o*-xylene derivative; see F. R. Jensen and W. E. Coleman, *ibid.*, **80**, 6149 (1958).

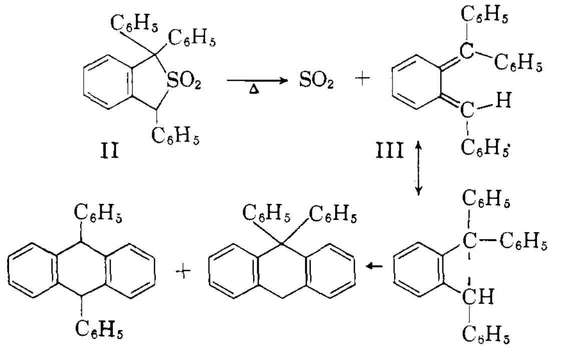
(5) M. P. Cava, R. L. Litle and D. R. Napier, *ibid.*, **80**, 2257 (1958).

(6) L. Horner, W. Kirmse and K. Muth, *Chem. Ber.*, **91**, 430 (1958).

(7) An additional synthesis of benzocyclobutene, starting with cycloheptatriene, was reported very recently; A. P. ter Borg and A. F. Bickel, *Proc. Chem. Soc.*, 283 (1958).

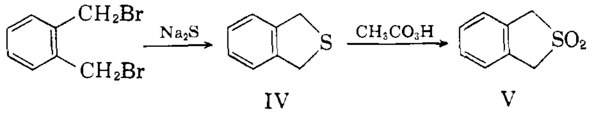
(8) E. H. Rodd, ed., "Chemistry of Carbon Compounds," Vol. IV, Part A, Elsevier Publishing Co., New York, N. Y., 1957, p. 221.

phenyl-1,3-dihydroisothianaphthene-2,2-dioxide (II) liberates sulfur dioxide slowly at 150° to give a mixture of anthracene derivatives.[9,10] The primary course of events may be explained as



It may be noted that the contribution of the *o*-quinoid form III to the above resonance hybrid should be negligible, since obvious steric factors prevent it from achieving an even approximately planar configuration.[11]

The preparation of 1,3-dihydroisothianaphthene-2,2-dioxide was carried out by a modification of the method described in the literature,[12] the intermediate 1,3-dihydroisothianaphthene (IV) being oxidized to the sulfone by peracetic acid.

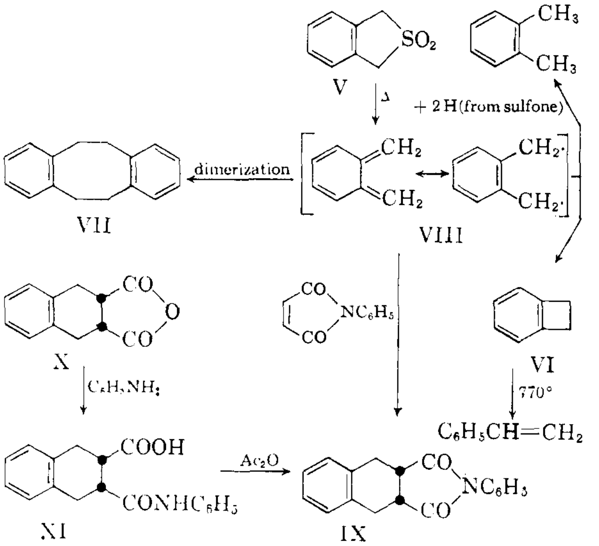


When the sulfone V was heated in the molten state to about 280°, sulfur dioxide was evolved at a moderate rate and a volatile liquid distilled over. This liquid, formed in 16% yield, was shown by infrared analysis and gas chromatography to be a mixture containing 80% of benzocyclobutene (VI) and 20% of *o*-xylene. From the polymeric pyrolysis residue was isolated, in 4% yield, 1,2,5,6-dibenzocycloöctadiene (VII). All three of these hydrocarbons can be explained as rational transformation products of the very reactive *o*-quinodimethane (VIII), a substance predicted to have a high degree of free radical character at the terminal methylene groups.[13] Thus, intramolecular cyclization of VIII would lead to benzocyclobutene, dimerization to 1,2,5,6-dibenzocycloöctadiene and hydrogen abstraction (from unchanged sulfone V) to *o*-xylene.

Indeed, when the pyrolysis was carried out in such a manner that the molten sulfone was not the solvent, the formation of *o*-xylene was suppressed entirely. Pyrolysis of V in a solution of boiling diethyl phthalate (300°) led to no significant production of volatile hydrocarbons. However, the yield of 1,2,5,6-dibenzocycloöctadiene (VII) rose to 48%, making this procedure a very convenient synthesis of the latter hydrocarbon. When the sulfone was pyrolyzed at 460–670° in the vapor phase in a low pressure nitrogen atmosphere, monomeric ring closure predominated and pure benzocyclobutane was formed in 59–63% yield. When the temperature of the Nichrome heating coil was raised to 770°, the yield of benzocyclobutene remained excellent (67%), but the product became contaminated by a small amount (2%) of styrene, probably resulting from a pyrolytic rupture of benzocyclobutene.

A final confirmation of the primary formation of *o*-quinodimethane in the pyrolysis of V was obtained by fusing the sulfone at 260° in the presence of N-phenylmaleimide. Under these conditions no hydrocarbon products were formed, but the expected Diels–Alder adduct of *o*-quinodimethane and N-phenylmaleimide, N-phenyl-1,2,3,4-tetrahydronaphthalene-*cis*-2,3-dicarboximide (IX), was obtained in 78% yield. The structure of this product was confirmed by an independent synthesis from aniline and 1,2,3,4-tetrahydronaphthalene-*cis*-1,2-dicarboxylic anhydride (X).[14]

Experiments designed to extend this sulfone pyrolysis method to the synthesis of substituted benzocyclobutenes and to the naphthocyclobutenes are in progress and will be reported in future papers of this series.



Experimental[15]

1,3-Dihydroisothianaphthene (IV).—A solution of anhydrous sodium sulfide (1 mole) in ethanol was prepared in the following manner. Sodium (23 g., 1 mole) was dissolved in absolute ethanol (500 ml.), and the resulting solution was saturated with hydrogen sulfide while cooling the mixture in an ice-bath. The sodium hydrosulfide solution thus formed was neutralized, with cooling, by the slow addition of a sodium ethoxide solution prepared from sodium (23 g., 1 mole) and absolute ethanol (500 ml.). To the resulting sodium sulfide solution was added, with stirring, finely powdered α,α'-dibromo-*o*-xylene (263 g., 1 mole) in small portions during 45 minutes. The hot reaction mixture was allowed to cool to room temperature, water (500 ml.) was

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[9] H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).

[10] H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **71**, 1235 (1952).

[11] However, both the *cis* and *trans* isomers of 1,3-diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide, which could pyrolyze to a planar intermediate, give 9-phenyl-9,10-dihydroanthracene on heating; ref. 4, and unpublished experiments of M. P. Cava, A. A. Deana, M. J. Mitchell and E. S. Lipinsky.

[12] W. Autenrieth and A. Bruning, *Ber.*, **36**, 183 (1903).

[13] J. D. Roberts, A. Streitwieser and C. M. Regan, This Journal, **74**, 4579 (1952).

[14] R. D. Haworth and F. H. Slinger, *J. Chem. Soc.*, 1321 (1940).

[15] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected.

added and the solution was filtered to remove an amorphous gray precipitate. The filtrate was extracted several times with 1000-ml. portions of 30–60° petroleum ether. Evaporation of the combined extracts and distillation of the residual oil at 2 mm. afforded 1,3-dihydroisothianaphthene, b.p. 62–72° (59.7 g., 44%). The crude product, which solidified readily below 20°,[12] was satisfactory for direct oxidation to the sulfone.

1,3-Dihydroisothianaphthene-2,2-dioxide (V).—A solution of crude IV (59.7 g.) in acetic acid (40 ml.) was added dropwise with stirring to 40% peracetic acid (180 g.). The temperature of the peracid was maintained at 5–10° by external cooling during the addition of the sulfide, which required three hours. After the addition was complete, stirring was continued for 40 hours at room temperature. The mixture was diluted with cold water (50 ml.) and the white crystalline sulfone V, m.p. 150–151° (61.0 g.), was removed by filtration and dried. By concentration of the mother liquors *in vacuo* an additional 4.8 g. was obtained (total yield 65.8 g., 89%). The sulfone was recrystallized from methylene chloride–petroleum ether as white needles, m.p. 150–151° (reported[12] 150–152°).

Pyrolysis of 1,3-Dihydroisothianaphthene-2,2-dioxide (V). (a) **Direct Distillation Method.**—The sulfone V (5.0 g.) was placed in a small distilling flask and heated cautiously with a bunsen burner. At 280° sulfur dioxide began to be evolved and a colorless liquid distilled over slowly. After 20 minutes of intermittent heating (necessary to prevent sublimation of the sulfone) the decomposition was complete and 0.9 g. of oil had collected in the receiver. Petroleum ether (30–60°) was added to precipitate some unchanged starting material which had distilled over. Evaporation of the solution and distillation of the residue gave a mixture (0.52 g., 16%) of benzocyclobutene (VI) and *o*-xylene. Infrared analysis indicated 80% of VI and 20% of *o*-xylene to be present. The hydrocarbons were separated by vapor phase chromatography, which indicated also that no other volatile components were present. Distillation of the residue from the sulfone pyrolysis at 175–185° (7 mm.) gave a yellow gum which was taken up in petroleum ether (30–60°) and chromatographed on a column of alumina. Evaporation of the eluate gave a crystalline residue which was recrystallized from ethanol to give dibenzocyclooctadiene (VII, 0.14 g., 4%), m.p. 109–110°. The infrared spectrum was identical with that of an authentic sample (kindly supplied by Prof. A. C. Cope) and the melting points of the two samples were not depressed upon admixture.

(b) **Gas Phase Pyrolysis.**—The sulfone V was placed in a 125-ml. round-bottomed flask, above which was connected a Pyrex sleeve containing a Nichrome coil. Above the coil sleeve was a cold-finger Dry Ice trap. The system was flushed with nitrogen and evacuated to 2 mm., the nitrogen flow being continued at a very slow rate at this pressure. The wire was heated electrically (previously calibrated by use of a thermocouple) and the sulfone was sublimed slowly, by gentle heating, through the hot wire chamber during a period of 40 minutes. The cold finger was removed from the trap and allowed to warm up to room temperature, when the solid condensate liquefied. Redistillation of this liquid at atmospheric pressure gave a colorless oil, b.p. 149–150°, identical in its infrared spectrum[16] and vapor chromatographic behavior with pure benzocyclobutene. From the distillation residue unchanged sulfone was recovered in some experiments. The results of four experiments are tabulated below (the percentage yields of benzocyclobutene are based on unrecovered sulfone).

Wire temperature (±25°)	460	560	670	770
Amount sulfone used, g.	1.0	1.5	1.0	1.0
Amount sulfone recovd., g.	0.10	0.11	0.01	0.00
Benzocyclobutene formed, g.	0.34	0.51	0.39	0.42
Yield, %, of benzocyclobutene	60	59	63	67

The hydrocarbon formed in the 770° pyrolysis contained styrene, detectable in the infrared spectrum. The amount of styrene was estimated as 2% by gas chromatography.

(c) **Pyrolysis in Solution.**—The sulfone V (2.50 g.) was added to diethyl phthalate (20 ml.) contained in a distilling flask. The mixture was heated to boiling (300°) for one hour, during which time sulfur dioxide was evolved but no volatile hydrocarbons were collected. The entire reaction mixture was hydrolyzed by warming with 15% sodium hydroxide for 24 hours. Extraction of the hydrolysate with petroleum ether, concentration of the extract and chromatography on alumina afforded dibenzocyclooctadiene (VII) which, after crystallization from petroleum ether (30–60°) at −78°, formed colorless prisms (0.74 g., 48%), m.p. 108–110°. The infrared spectrum was identical with that of the authentic sample (see part a).

Pyrolysis of 1,3-Dihydroisothianaphthene-2,2-dioxide (V) in the Presence of N-Phenylmaleimide.—A mixture of V (2.0 g., 0.012 mole) and N-phenylmaleimide (3.0 g., 0.017 mole) was placed in a small flask which was heated in a salt-bath at 240–260° for 15 minutes, during which time sulfur dioxide was evolved. After heating at 300° for a further 15 minutes, the mixture was cooled and the glassy product was taken up in a small volume of benzene and adsorbed on a column of alumina. Elution of the column with ether removed a crystalline solid which crystallized in colorless needles (2.58 g., 78%, IX), m.p. 130–131°.

Anal. Calcd. for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.13; H, 5.27; N, 5.25.

N-Phenylimide of 1,2,3,4-Tetrahydronaphthalene-*cis*-2,3-dicarboxylic Acid (IX).—To a solution of 1,2,3,4-tetrahydronaphthalene-*cis*-1,2-dicarboxylic anhydride[14] (0.43 g.) in benzene (5 ml.) was added aniline (0.20 ml.) and the mixture was refluxed for 15 minutes. The white precipitate (0.64 g.) of the monoanilide of 1,2,3,4-tetrahydronaphthalene-*cis*-2,3-dicarboxylic acid was filtered and dried; m.p. 137–139°.

Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 72.92; H, 5.59; N, 5.07.

A mixture of the above monoanilide (0.50 g.), anhydrous sodium acetate (0.12 g.) and acetic anhydride (5 ml.) was heated for 30 minutes on the steam-bath. Cold water was added and, after several hours, the white N-phenylimide was filtered, dried and recrystallized from benzene–petroleum ether to give white needles, 0.33 g., 70%, m.p. 130–132°. The melting point was not depressed by the sulfone-phenylmaleimide pyrolysis product, and the infrared spectra of both samples were identical.

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(16) M. P. Cava and D. R. Napier, THIS JOURNAL, **80**, 2255 (1958).