and the organic acids removed from the solution by thorough extraction with ether. Removal of the solvent left a crystalline mixture of acids (0.078 g., 93%). Fractional crystallization from water gave the less soluble o-toluic acid (0.030 g.), m.p. 103°, and the much more soluble phenylacetic acid (0.031 g.), m.p. 76°. The identity of both acids was confirmed by their infrared spectra and by mixed melting point determinations with authentic samples.

The cleavage reaction described above was effected also by 0.1 N aqueous sodium hydroxide at room temperature, but required about 5 days for completion. On the other hand, 2 N hydrochloric acid had no effect upon the ketone under these conditions: it was recovered unchanged (isolation as the 2,4-dinitrophenylhydrazone).

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# Condensed Cyclobutane Aromatic Compounds. X. Naphtho[b]cyclobutene

BY M. P. CAVA AND R. L. SHIRLEY

Naphtho[b]cyclobutene has been synthesized starting from 2,3-dimethylnaphthalene by pyrolysis of a sulfone intermediate VI. The mechanism of the pyrolysis of this sulfone is discussed.

In a recent paper of this series,[1] a fundamentally new synthesis of benzocyclobutene (I) was described by the pyrolytic decomposition of 1,3-dihydroisothianaphthene 2,2-dioxide (II). The extension of this sulfone pyrolysis method to the synthesis of the hitherto unknown naphtho[b]cyclobutene (III) is now reported.
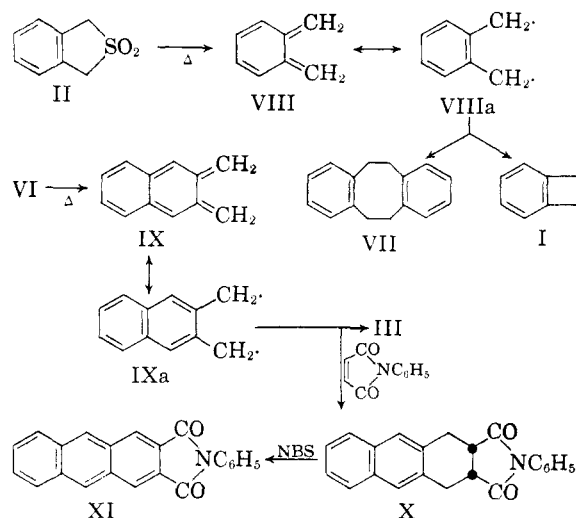
The reaction of 2,3-bis-(bromomethyl)-naphthalene[2](IV) with aqueous alcoholic sodium sulfide proceeded readily to give, in 65% yield, the cyclic sulfide 1,3-dihydronaphtho[2,3-c]thiophene (V). Oxidation with cold peracetic acid converted V, in 86% yield, to the corresponding sulfone, 1,3-dihydronaphtho[2,3-c]thiophene 2,2-dioxide (VI).
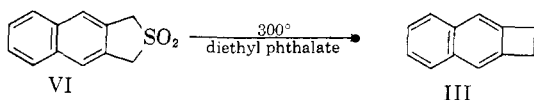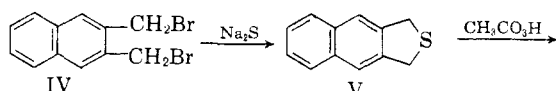
The pyrolysis of sulfone VI in boiling diethyl phthalate solution led to the formation, in over 60% yield, of the crystalline naphtho[b]cyclobutene (III), m.p. 86.5°. The ultraviolet spectrum of this new hydrocarbon is very similar to that of 2,3-dimethylnaphthalene (Fig. 1), the principal difference being the higher intensity absorption exhibited by III beyond 260 mμ. A similar enhanced absorption in the ultraviolet has been noted previously for the simpler benzocyclobutene.[3]

Although the pyrolysis of the simple sulfone II to benzocyclobutene (I) proceeds very satisfactorily under low pressure in the gas phase, only 1,2,5,6-dibenzocyclooctadiene (VII) was obtained in boiling diethyl phthalate solution.[1] The formation of only the monomeric pyrolysis product III in the 2,3-dimethylnaphthalene series under conditions which give a dimeric product VII in the benzene series may be rationalized by a comparison of the expected stabilities of the reaction inter-

(1) M. P. Cava and A. A. Deana, THIS JOURNAL, 81, 4266 (1959).
(2) M. F. Hebbelynck and R. H. Martin, Bull. soc. chim. Belges, 59, 206 (1950).
(3) M. P. Cava and D. R. Napier, THIS JOURNAL, 80, 2255 (1958).

mediates VIII and IX. The 2,3-naphthoquinodimethane (IX), which is an analog of the un-

known 2,3-naphthoquinone, would be expected to be a structure of higher energy relative to its aromatic diradical resonance form IXa than is the case in the benzene series (VII vs. VIIIa). Or stated in a slightly different manner, the diradical IXa in the naphthalene series is stabilized less by its polyene resonance contributor IX than is the case for its benzene analog VIIIa. A consequence of the higher degree of diradical character of IX compared to VIII could be rapid intramolecular ring closure of IX to III under conditions in which VIII is sufficiently stable to undergo dimerization, or intermolecular reaction.

The intermediate IX, however, is sufficiently stable to enable it to be trapped by a dienophile scavenger, in the same manner employed previously to trap o-quinodimethane (VIII).[1] Pyrolysis of the sulfone VI in the presence of N-phenylmaleimide gave, in 82% yield, the colorless adduct N-phenyl-1,2,3,4-tetrahydro-cis-2,3-anthracenedicarboximide (X). Aromatization of X by N-bromosuccinimide gave the yellow N-phenyl-2,3-anthracenedicarboximide (XI). As expected, the adduct X exhibited a chromophore in the ultraviolet similar to 2,3-dimethylnaphthalene, whereas
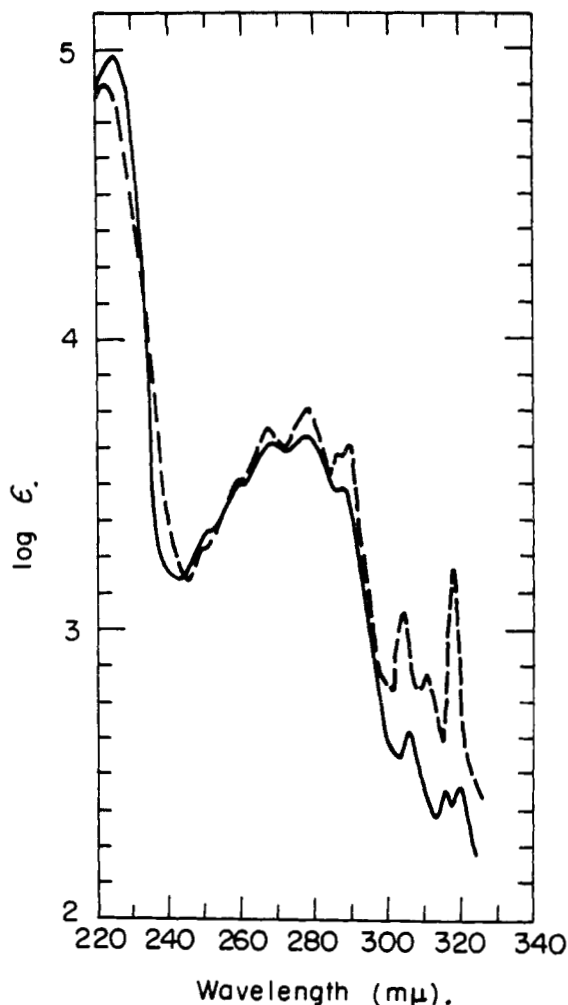
Fig. 1.—Ultraviolet absorption spectra of: ————, 2,3-dimethylnaphthalene; – – – –, naphtho[b]cyclobutene.

the aromatized product XI showed a very different and very intense untraviolet absorption due to its conjugated anthracene system (Fig. 2).

Some chemical transformations of naphtho[b]-cyclobutene will be discussed in a subsequent paper.

Acknowledgment.—We should like to thank the National Science Foundation for a grant in support of this work.

Experimental[4]

1,3-Dihydronaphtho[2,3-c]thiophene (V).—A mixture of finely ground 2,3-bis-(bromomethyl)-naphthalene[2] (IV, 52.0 g.), sodium sulfide nonahydrate (156 g.) and 95% ethanol (1000 ml.) was refluxed for one hour. The solution was diluted with cold water (ca. 2000 ml.) and the yellow solid removed by filtration after chilling for two hours in the refrigerator. The dried precipitate was dissolved in methylene chloride and the solution passed through a column of neutral alumina (Woelm). Evaporation of the eluate and sublimation of the residual solid at 145° (2.5 mm.) afforded the crude sulfide V (20.0 g., 65%), m.p. 154–163°, which was sufficiently pure for oxidation to the corresponding sulfone. The pure sulfide, m.p. 169.5–170.5°, was obtained as pale yellow plates after several crystallizations from ethanol.

Anal. Calcd. for $C_{12}H_{10}S$: C, 77.40; H, 5.41; S, 17.19. Found: C, 77.31; H, 5.29; S, 17.40.

(4) Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected unless stated otherwise.
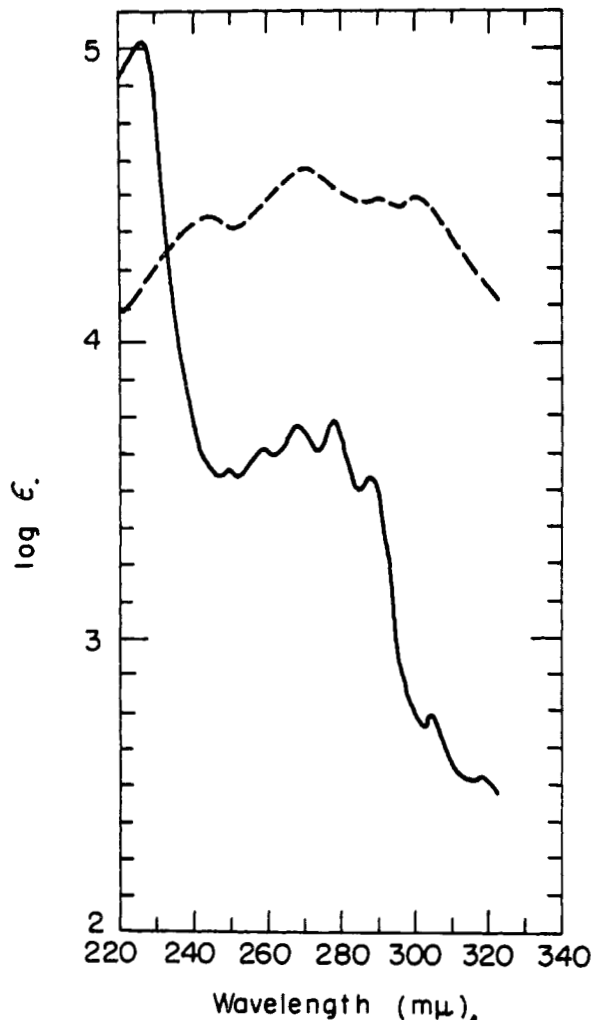

Fig. 2.—Ultraviolet absorption spectra of: ————, 1,2,3,4-tetrahydro-N-phenyl-2,3-anthracenedicarboximide; – – – –, N-phenyl-2,3-anthracenedicarboximide.

1,3-Dihydronaphtho[2,3-c]thiophene 2,2-Dioxide (VI).—A mixture of commercial (Becco) 40% peracetic acid (60 g.) and acetic acid (70 ml.) was added over a 30-minute period to a stirred suspension of sulfide V (20.0 g.) in acetic acid (300 ml.), the reaction temperature being maintained at 15–20° by external cooling during the addition. The cooling bath was removed and stirring was continued for 4 hours at room temperature. The glistening white solid (20.2 g., m.p. 251–255°) was filtered, washed with aqueous sodium bicarbonate, then water, and dried. Concentration of the acetic acid filtrate afforded an additional 3.1 g. of product. Upon crystallization from chloroform the sulfone VI (20.1 g., 86%) formed voluminous white needles, m.p. 254–256° dec. The analytical sample melted at 255–257° dec. after a further crystallization from dimethylformamide-benzene.

Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 66.05; H, 4.62; S, 14.67. Found: C, 65.82; H, 4.56; S, 14.69.

Naphtho[b]cyclobutene (III).—A mixture of sulfone VI (9.00 g.) and diethyl phthalate (120 ml.) was heated to boiling with a free flame. The phthalate solution was distilled slowly (evolution of sulfur dioxide) until only a small amount of dark residue remained behind in the pot. The colorless distillate was stirred at 90° with 10% aqueous sodium hydroxide (500 ml.) until all of the diethyl phthalate was hydrolyzed. Most of the ethanol liberated upon hydrolysis was distilled out on the steam-bath and the remaining suspension, after cooling, was extracted with four 40-ml. portions of methylene chloride. The combined and dried extracts were evaporated, and the residue was triturated

several times with 30–60° petroleum ether, leaving an insoluble residue (0.91 g.) of sulfone VI (identified by melting point and infrared spectrum). The petroleum ether extract, after treatment with charcoal (Darco), was concentrated and cooled to give white prisms of naphtho[b]cyclobutene, m.p. 84.5–86° (3.49 g., 61% based on unrecovered sulfone). In a number of similar preparations the yield of III varied from 60 to 75%. Chromatographic investigation of the dark pot residues from the pyrolysis of sulfone VI afforded no crystalline by-products. The analytical sample of III, m.p. 86.5° (cor.), was obtained by decomposition (on alumina) of the purified picrate (see below); ultraviolet spectrum(ethanol): λ_{max} 223 (log E 4.88), 267 (3.68), 278 (3.78), 290 (3.63), 304 (3.06), 311 (2.85), 318 (3.21); shoulders at 250, 259 and 286 mμ (see Fig. 1).

Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54; mol. wt., 154. Found: C, 93.37; H, 6.65; mol. wt. (isothermal distillation in methylene chloride), 154.

The picrate of III, m.p. 139.5–140.5°, crystallized from ethanol in long yellow needles.

Anal. Calcd. for $C_{18}H_{13}O_7N_3$: C, 56.40; H, 3.43; N, 10.96. Found: C, 56.26; H, 3.45; N, 10.82.

The orange **2,4,7-trinitrofluorenone complex of III**, m.p. 146–148°, was crystallized from benzene–petroleum ether.

Anal. Calcd. for $C_{25}H_{15}O_7N_3$: C, 63.97; H, 3.22; N, 8.95. Found: C, 63.78; H, 3.25; N, 9.08.

N-Phenyl-1,2,3,4-tetrahydro-*cis*-2,3-anthracenedicarboximide (X).—A mixture of sulfone VI (2.00 g.), N-phenylmaleimide (2.40 g.) and diethyl phthalate (25 ml.) was heated to boiling and distilled slowly until almost 20 ml. of distillate was collected. The distillation residue was cooled in the refrigerator; the white solid which crystallized was triturated with cold benzene, filtered, washed with cold benzene and dissolved in methylene chloride. The solution was placed on a column of alumina (neutral Woelm, activity 1) and the column eluted with methylene chloride. Passage of the product through the column was observed easily as the movement of a bluish fluorescent zone. Concentration of the eluate and crystallization from methylene chloride–benzene afforded the imide X as tiny white crystals (2.30 g., 82%), m.p. 230–233°. The analytical sample, m.p. 233–234.5°, was recrystallized from chloroform–benzene.

The identical imide X was obtained in 61% yield by pyrolysis of a mixture of sulfone VI and N-phenylmaleimide in the absence of diethyl phthalate. The ultraviolet spectrum of X (Fig. 2) was very similar to that of 2,3-dimethylnaphthalene (Fig. 1).

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.71; H, 5.24; N, 4.28. Found: C, 81.14; H, 5.18; N, 4.77.

N-Phenyl-2,3-anthracenedicarboximide (XI).—A mixture of imide X (0.33 g.), N-bromosuccinimide (0.36 g.), benzoyl peroxide (*ca.* 20 mg.) and chloroform (4 ml.) was refluxed for 15 hours while irradiated by an ordinary 100-watt lamp. The chloroform was evaporated and the solid residue was crystallized twice from dimethylformamide to give imide XI as fine orange–yellow leaflets (0.22 g., 68%), m.p. 355–358°. A dilute benzene solution of XI exhibited an intense blue fluorescence; its ultraviolet spectrum (Fig. 2) revealed an intensely absorbing chromophore different from that of imide X.

Anal. Calcd. for $C_{22}H_{13}O_2N$: C, 81.72; H, 4.05; N, 4.33. Found: C, 81.63; H, 4.23; N, 4.40.

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Some Evidence Regarding Free Radical Rearrangement Reactions

BY WILLIAM B. SMITH AND JAMES D. ANDERSON

Treatment of 2-phenyl-1-bromopropane and 2-phenyl-1-bromoethane-1-C^{14} with magnesium and cobaltous bromide in refluxing ether has been used to produce the respective free radicals. In the former case the monomeric products showed 40% rearrangement, while in the latter case rearrangement amounted to *ca.* 20%. The mechanistic implications of these results are considered.

Introduction

A number of free radical rearrangement reactions are now known which proceed at least to a certain extent with the 1,2-shift of an aryl group. It has been well established in analogous carbonium ion rearrangements that the neighboring aryl group may contribute to the driving force for the reaction through aryl-bridged transitions states and subsequent formation of "non-classical" aryl-bridged carbonium ions. While qualitative considerations suggest that neighboring aryl-group participation should be equally likely in free radical rearrangement reactions, the fact remains that existent evidence in the literature strongly argues against the formation of such "non-classical" radical intermediates except as possible stages in the conversion of one conventional open radical to another.

The first evidence of phenyl migration during a free radical reaction was obtained by Urry and Kharasch[1] who found that the treatment of 1-chloro-2-phenyl-2-methylpropane (neophyl chloride) with phenylmagnesium bromide and cobaltous bromide produced a mixture of hydrocarbons corresponding to about 50% migration of the phenyl group. Winstein and Seubold[2] subsequently obtained essentially the same result during the decarbonylation of 3-phenyl-3-methylbutanal. Arguments in favor of a phenyl-bridged intermediate were refuted by Seubold[3] who showed that the precentage rearrangement in the decarbonylation reaction was a function of the life time of the radical intermediate, increasing beyond 50% when the reaction mixture was diluted with an inert solvent.

Further evidence regarding the nature of the radical intermediate in reactions involving the migration of an aryl group was reported by Urry and Nicolaides[4] who found that the 2-*p*-tolyl-2-methylpropyl radical produced either from the bromide *via* the Grignard reagent–cobaltous halide reaction or by the decarbonylation of the appropriate aldehyde formed monomeric prod-

(1) W. H. Urry and M. S. Kharasch, THIS JOURNAL, **66**, 1438 (1944).

(2) S. Winstein and F. H. Seubold, *ibid.*, **69**, 2916 (1947).

(3) F. H. Seubold, *ibid.*, **75**, 2432 (1953).

(4) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).