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

Condensed Cyclobutane Aromatic Compounds. XVII. Naphtho[*a*]cyclobutene

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A synthesis of naphtho[*a*]cyclobutene from 1,2-dimethylnaphthalene is described. The relative thermal stabilities of naphthto[*a*]cyclobutene and naphtho[*b*]cyclobutene are discussed, and some Diels-Alder adducts of 1,2-naphthoquinodimethane are reported.

A synthesis of naphtho[*b*]cyclobutene[1] (I) and some reactions of this compound[2] have been described recently. A synthesis of the isomeric naphtho[*a*]cyclobutene (II) is now reported.

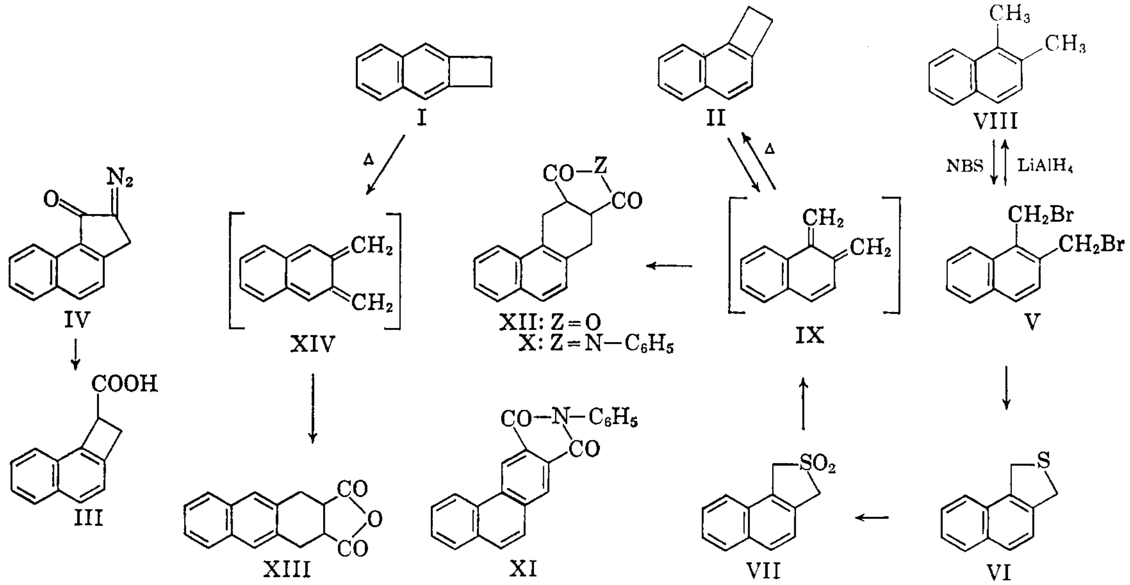
The only derivative of naphtho[*a*]cyclobutene described previously is the carboxylic acid (III), obtained in 7% yield by the ultraviolet irradiation of the diazoketone (IV) in aqueous tetrahydrofuran.[3]

The reaction of aqueous alcoholic sodium sulfide with 1,2-bis(bromomethyl)naphthalene[4] (V) afforded, in satisfactory yield, 1,3-dihydronaphtho[1,2-*c*]thiophene (VI), m.p. 78.5–79.5°. Peracetic oxidation of sulfide VI gave the corresponding sulfone, 1,3-dihydronaphtho[1,2-*c*]thiophene 2,2-dioxide (VII), m.p. 170.5–171.0°. Pyrolysis of sulfone VII in boiling ethyl phthalate yielded neither hydrocarbon II nor a crystalline dimer of this substance. Naphtho[*a*]cyclobutene was obtained, however, as a colorless oil in 51% yield by pyrolysis of VII in the vapor phase at low pressure at about 500°. The spectral properties of II were compared with those of 1,2-dimethylnaphthalene (VIII). As commercial samples of VIII were not completely free of other isomers,[5] a pure sample of VIII was prepared by reduction of the crystalline dibromide V with lithium aluminum hydride.

The infrared spectrum of naphtho[*a*]cyclobutene (II) differed from that of 1,2-dimethylnaphthalene (VIII) mainly in the 12–14-μ region. A strong absorption band at 13.08 μ in the spectrum of VIII appeared as a doublet at 13.00 and 13.20 μ in the spectrum of II. In addition two intense absorption bands of VIII, observed at 12.50 and 13.69 μ, were displaced to 12.42 and 13.79 μ in the spectrum of II.

A comparison of the ultraviolet absorption spectra of hydrocarbons II and VIII (Fig. 1) shows the greatest differences in the region beyond 300 mμ. The strained hydrocarbon II shows considerably more intense absorption in this region and the more clearly resolved absorption bands appear at longer wave lengths than the corresponding bands of VIII.

In analogy to the pyrolysis of other previously studied related sulfones,[1,6] pyrolysis of sulfone VII in the presence of maleic anhydride or *N*-



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[1] M. P. Cava and R. L. Shirley, *J. Am. Chem. Soc.*, **82**, 654 (1960).

[2] M. P. Cava and R. L. Shirley, *J. Org. Chem.*, **26**, 2216 (1961).

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

[4] W. Ried and H. Boden, *Ber.*, **89**, 708 (1956).

[5] Unpublished experiments of L. Friedman.

[6] M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4226 (1959).

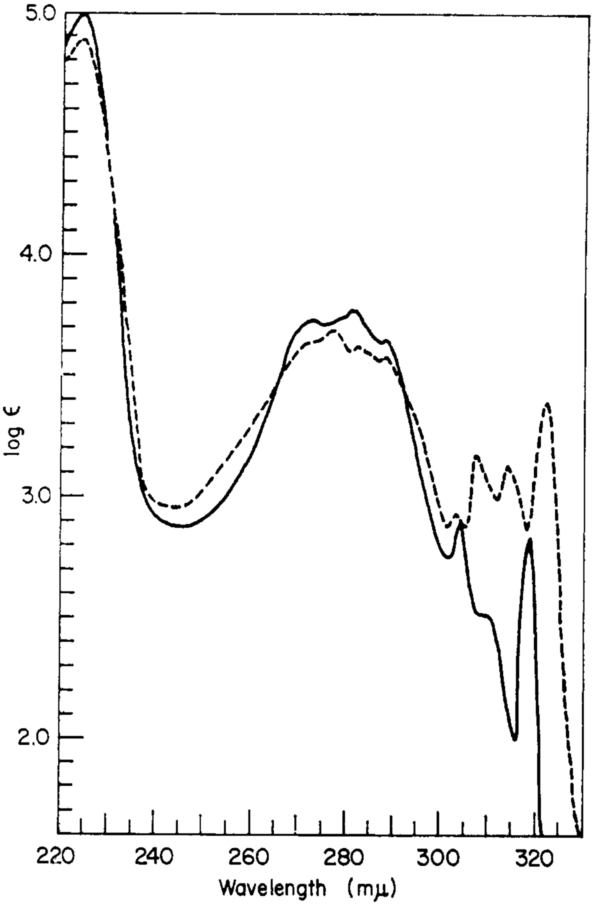

Fig. 1. Ultraviolet absorption spectra of: ——— 1,2-dimethylnaphthalene; - - - - naphtho[*a*]cyclobutene

phenylmaleimide led to the formation of Diels-Alder adducts of the initially generated 1,2-naphthoquinodimethane (IX). The *N*-phenylmaleimide adduct (X) was dehydrogenated by palladium at 360° to *N*-phenyl-2,3-phenanthrenedicarboximide (XI).

Although naphtho[*a*]cyclobutene is formed by the intramolecular cyclization of the quinomethane intermediate IX, the reversal of this reaction was detected by heating the hydrocarbon II with maleic anhydride for one hour at 200°, when the adduct (XII) of the quinomethane IX with maleic anhydride was formed in 53% yield. Under the same conditions, naphtho[*b*]cyclobutene gave the maleic anhydride adduct (XIII) of 2,3-naphthoquinodimethane (XIV) in only 2% yield. Rupture of the four-membered ring of naphtho[*b*]cyclobutene was much more rapid at 250°, however, and adduct XIII was obtained in 61% yield after one hour. These experiments confirm the expectation that the completely nonbenzenoid linear quinomethane XIV should be a species of higher energy than its partially benzenoid 1,2-isomer IX.

EXPERIMENTAL[7]

1,3-Dihydronaphtho[1,2-c]thiophene (VI). A mixture of 1,2-bis(bromomethyl)naphthalene (V, 20.5 g.), sodium sulfide nonahydrate (60 g.), and 95% ethanol (450 ml.) was stirred under reflux for 3 hr. The hot solution was filtered, diluted with water (150 ml.), and cooled in the refrigerator. The crude sulfide VI separated as yellow leaflets (7.0 g., 58%), m.p. 70–78°, of sufficient purity for oxidation to the corresponding sulfone. Analytically pure sulfide, m.p. 78.5–79.5°, was obtained after several crystallizations from ethanol.

Anal. Calcd. for $C_{12}H_{10}S$: C, 77.40; H, 5.41; S, 17.19. Found: C, 77.47; H, 5.66; S, 17.33.

1,3-Dihydronaphtho[1,2-c]thiophene 2,2-dioxide (VII). A mixture of commercial [Becco] 40% peracetic acid (25 ml.) and acetic acid (25 ml.) was added slowly to a stirred suspension of sulfide VI (5.8 g.) in acetic acid (50 ml), the temperature of the reaction mixture being maintained at 15–20° by external cooling during the addition. The yellow solution was kept in a refrigerator for two days, after which the crystalline sulfone VII (4.5 g., 68%) was removed by filtration. Recrystallization from chloroform gave the pure sulfone as small white needles, m.p. 165–166° or m.p. 170.5–171.0°. The two melting points characterized two dimorphic forms, which had different infrared spectra in a solid mull (KBr) but identical spectra in chloroform solution. When the lower melting dimorph was fused and then allowed to resolidify, it melted at 170–171°.

Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 66.05; H, 4.62; S, 14.67. Found: C, 65.85; H, 4.80; S, 14.88.

Naphtho[a]cyclobutene (II). A mixture of sulfone VII (1.0 g.) and copper powder (0.2 g.) was subjected to gas phase pyrolysis over a hot nichrome coil in the apparatus used previously[6] to prepare benzocyclobutene. The coil temperature was ca. 500° (dull red heat), and the sulfone sublimation required 3 hr. at 5 mm. (bath temperature 180–200°). The pyrolysate, which was collected on a cold finger cooled to −78°, was extracted with petroleum ether (b.p. 30–60°). Evaporation of the solvent and distillation of the residue gave 0.361 g. (51%) of naphtho[*a*]cyclobutene, b.p. 98° [1–2 mm.], n_D^{20} 1.6384. The ultraviolet spectrum (ethanol) showed the following maxima: λ_{max} 224 (log ε 4.89), 277 (3.68), 282 (3.61), 288 (3.58), 303 (2.93), 307 (3.16), 314 (3.11), 322 (3.39); shoulder at 272 mμ.

Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.25; H, 6.55.

The 2,4,7-trinitrofluorenone complex of II, m.p. 145–147.5° [sealed capillary], crystallized in orange-red needles from acetic acid.

Anal. Calcd. for $C_{25}H_{15}O_7N_3$: C, 63.97; H, 3.22; N, 8.95. Found: C, 63.88; H, 3.41; N, 8.70.

1,2-Dimethylnaphthalene (VIII). A solution of pure dibromide V (6.28 g.) in tetrahydrofuran (70 ml.) was added slowly to a stirred suspension of lithium aluminum hydride (0.76 g.) in tetrahydrofuran (20 ml.). The mixture was refluxed for 1 hr., then the excess hydride was decomposed by water, and the product worked up in the usual way to yield 1,2-dimethylnaphthalene (1.39 g., 44%), b.p. 134–135° (13–14 mm.), n_D^{20} 1.6165 (reported[8] n_D^{20} 1.6135). The ultraviolet spectrum (ethanol) showed the following maxima: λ_{max} 224 (log ε 4.99), 272 (3.72), 281 (3.77), 288 (3.64), 304 (2.91), 319 (2.83); shoulders at 277 and 308 mμ.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92,10; H, 7.68.

The 2,4,7-trinitrofluorenone complex of VIII, m.p. 144.5–146.5° (sealed capillary), separated from acetic acid as a yellow-orange microcrystalline powder.

Anal. Calcd. for $C_{25}H_{16}O_7N_3$: C, 63.69; H, 3.64; N, 8.91, Found: C, 63.61; H, 3.89; N, 9.10.

1,2,3,4-Tetrahydro-cis-2,3-phenanthrenedicarboxylic acid anhydride (XII). A. A mixture of sulfone VII (0.218 g.), maleic anhydride (0.125 g.) and diethyl phthalate (1 ml.) was refluxed until the evolution of sulfur dioxide ceased. The liquid

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[7] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Schwarzkopf Laboratories, Woodside, N. Y. Melting points are uncorrected.

[8] O. Kruber and W. Schade, *Ber.*, 68, 11 (1935).

deposited large white crystals of XII on cooling in the refrigerator. After washing well with petroleum ether, the crude product (0.246 g., 94%), m.p. 207–208°, was recrystallized from benzene to give the analytical sample, m.p. 208–209°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.45; H, 5.05.

B. A mixture of naphtho[*a*]cyclobutene (0.026 g.), maleic anhydride (0.021 g.), and diethyl phthalate (0.2 g.) was heated for one hour at 200°. The cooled mixture was diluted with ether and the crystals which separated were washed well with ether to yield pure XII (0.023 g., 53%), m.p. 208–209°.

1,2,3,4-Tetrahydro-cis-2,3-anthracenedicarboxylic acid anhydride (XIII). A. Naphtho[*b*]cyclobutene (I, 0.100 g.) maleic anhydride (0.068 g.) and diethyl phthalate (1 ml.) were heated (250°) in a test tube for 1 hr. The cooled reaction mixture was washed and rubbed well with ether, then dried to give anhydride (0.101 g., 61%), m.p. 306–308°. Repetition of this experiment at 200° afforded the same product in only 2% yield. The adduct was recrystallized from acetic anhydride for analysis.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.85; H, 4.70.

B. A mixture of 1,2-dihydronaphtho[2,3-*c*]thiophene 2,2-dioxide[1] (0.50 g.) and maleic anhydride (2.22 g.) was refluxed gently for 1 hr. The cooled reaction product was washed three times with benzene to remove unchanged maleic anhydride. Crystallization of the residue from acetic anhydride gave anhydride XII (0.31 g.), identical in melting point and infrared spectrum with the product obtained in Section A.

N-Phenyl-1,2,3,4-tetrahydro-cis-2,3-phenanthrenedicarboximide (X). A mixture of sulfone VII (1.00 g.) and *N*-phenylmaleimide (1.00 g.) was heated in an open flask. At about 220° evolution of sulfur dioxide was observed. When no further sulfur dioxide was evolved, the melt was cooled and taken up in absolute ethanol. An insoluble amorphous residue was removed by filtration, and the filtrate was concentrated and cooled to give white needles of imide X (1.05 g., 70%), m.p. 149.5–150.0°.

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.73; H, 4.20; N, 4.28. Found: C, 80.55; H, 4.98; N, 4.30.

The ultraviolet spectrum (ethanol) showed the following maxima: λ_{max} 227 (log ϵ 4.91), 273 (3.71), 283 (3.76), 291 (3.61), 312 (2.66), 320 (2.62), and shoulders at 264 and 304 mμ.

N-Phenyl-2,3-phenanthrenedicarboximide (XI). Imide X and 10% palladium-on-carbon (0.025 g.) were mixed and heated slowly to 360° under nitrogen (atmospheric pressure). After thirty minutes at 360°, the melt was cooled to 275° and the product sublimed out at 2 mm. pressure onto a cold finger. Two crystallizations from acetic acid afforded pale yellow needles (0.080 g., 80%), m.p. 259–260°. The ultraviolet spectrum in ethanol showed only one maxima: λ_{max} 288 mμ (log ϵ 4.64).

Anal. Calcd. for $C_{22}H_{13}O_2N$: C, 81.72; H, 4.05; N, 4.33. Found: C, 81.72; H, 4.26; N, 4.22.

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Condensed Cyclobutane Aromatic Compounds. XVIII. Synthesis of the Remaining α-Brominated Benzocyclobutenes

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Bromination of 1-bromobenzocyclobutene with *N*-bromosuccinimide gave 1,1-dibromobenzocyclobutene. The same reagent converted either *cis*- or *trans*-1,2-dibromobenzocyclobutene into 1,1,2-tribromobenzocyclobutene and eventually into 1,1,2,2-tetrabromobenzocyclobutene, thus completing the synthesis of all of the possible α-brominated benzocyclobutenes.

Of the six possible bromo derivatives of benzocyclobutene having one or more bromine substituents on the four-membered ring, three already have been described. These compounds are 1-bromobenzocyclobutene (I),[1,2] *trans*-1,2-dibromobenzocyclobutene (II),[3,4] and *cis*-1,2-dibromobenzocyclobutene (III).[5] This paper describes the synthesis of the remaining three bromides (IV, V and VI) and offers evidence for the structures assigned to them.

Although it was reported previously[1,2a] that attempted further bromination of monobromide I with *N*-bromosuccinimide failed, it has been found now that introduction of a second bromine is possible by using pure starting materials and a reaction time of several hours. The only product isolated, aside from starting material and a polymeric residue, was the liquid 1,1-dibromobenzocyclobutene (IV). The structure of IV was confirmed by hydrolysis with 5% sulfuric acid to benzocyclobutenone (VII), isolated in good yield as the known 2,4-dinitrophenylhydrazone.[6] The

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(1) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958).

(2) (a) E. Winkelmann, dissertation, University of Mainz, (1958); (b) L. Horner, W. Kirmse, and K. Muth, *Chem. Ber.*, **91**, 430 (1958).

(3) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957).

(4) H. Finkelstein, *Chem. Ber.*, **92**, XXXVII (1959).

(5) F. R. Jensen and W. E. Coleman, American Chemical Society Meeting, April 1958. Abstract of Papers, p. 79 N. The *cis*-dibromide III was obtained as a minor product of the reaction of either *cis*- or *trans*-1,2-diiodobenzocyclobutene with bromine.

(6) M. P. Cava and K. Muth, *J. Am. Chem. Soc.*, **82**, 652 (1960).