perature, then refluxed on the steam-bath for two hours. The excess oxalyl chloride was evaporated at reduced pressure, the residue taken up in ether, and added to an ice-cold ethereal solution of diazomethane from 17 g. of nitrosomethylurea. The solution was allowed to stand for three hours, concentrated, and the solid residue refluxed for three hours with a solution of 100 ml. of dioxane, 40 ml. of concentrated ammonium hydroxide and 10 ml. of 10% aqueous silver nitrate solution. After standing overnight, the solution was decolorized, warmed, and diluted with water to the cloud point. After standing two days in the refrigerator, the crystals which had separated were collected and recrystallized from ethyl acetate–petroleum ether, yielding 7.0 g. of **δ-(1-cyclohexenyl)-valeramide**, m.p. 106–107°.

Anal. Calcd. for $C_{11}H_{19}NO$: C, 72.88; H, 10.57; N, 7.73. Found: C, 72.53; H, 10.60; N, 7.90.

δ-(1-Cyclohexenyl)-valeric Acid (IIIf).—A solution of 1.5 g. of IIIe and 4.0 g. of potassium hydroxide in aqueous methanol was refluxed for 24 hours. The methanol was evaporated and the residue diluted with water, then washed with chloroform and acidified with dilute hydrochloric acid. Extraction with chloroform gave, after drying and concentrating the extracts, 1.3 g. of the acid, b.p. 115° (0.02 mm.).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.41; H, 9.96.

δ-(1-Cyclohexenyl)-valeronitrile (IIId).—An intimate mixture of 2.5 g. of pulverized amide IIIe and 5.0 g. of phosphorus pentoxide was distilled *in vacuo*. The distillate was taken up in 25 ml. of ether, washed with 25 ml. of 5% sodium carbonate solution, then dried and evaporated. Vacuum distillation of the residue yielded 1.89 g. of nitrile, which was further purified by chromatography over alumina in ether.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.63; H, 10.25; N, 8.31.

V. Spiro[3,4]octanone-1 Oxime.[46]—The oxime of Ia (1.5 g.) was heated in 15 g. of PPA at 125–130° for 10 minutes and worked up as described before. The crude product was a black tarry mass from which no pure compounds could be isolated.

3-Methylcyclohex-2-enone.—5-Methyl-5-hexenenitrile[47] (2.0 g.) was heated in 70 g. of PPA at 130–135° for 15 minutes and worked up as before. The crude product contained unreacted nitrile in addition to unsaturated ketone, as evidenced by the infrared spectrum, and was converted directly to the 2,4-dinitrophenylhydrazone. After two recrystallizations from chloroform–methanol, this yielded scarlet plates, m.p. 181–182° (lit.[48] m.p. 172.5–173°), with no m.p. depression on admixture with an authentic sample.[49]

N-Propionylcyclohexylamine.—A mixture of 4.2 g. of cyclohexene and 2.8 g. of propionitrile was stirred into 168 g. of PPA, slowly heated to 130°, and maintained at that temperature for 10 minutes. The crude reaction mixture, which showed no ketone bands in the infrared, yielded 3.0 g. of solid, which was recrystallized from ethanol to colorless needles, m.p. 90–91.5°. Sublimation at 90° *in vacuo*, and recrystallization from benzene–petroleum ether, raised the m.p. to 92–92.5° (lit.[50] m.p. 88°), undepressed by admixture with an authentic sample.

Rearrangement of Spiro[cyclopentane-1,2-pseudoindoxyl] Oxime.—The oxime[51] (0.68 g.) was stirred into 20 g. of PPA and kept at 110–115° for 10 minutes. The mixture was poured onto ice and stirred until it became homogeneous, filtered, saturated with salt and extracted with methylene chloride. The extracts were washed with saturated salt solution, dried over sodium sulfate, and evaporated through a short column. The residue was treated with 2,4-dinitrophenylhydrazine reagent to yield 0.53 g. (59%) of **cyclopentanone 2,4-dinitrophenylhydrazone**, m.p. 126–129°. Recrystallization from ethanol raised the m.p. to 139–140°, undepressed by admixture with an authentic sample.

The aqueous solution remaining from the extraction was made strongly alkaline with sodium hydroxide solution and extracted with methylene chloride. The extracts were washed with saturated salt solution, dried and concentrated, yielding 0.29 g. (63%) of pale yellow **anthranilamide**, m.p. 104–105°. Two recrystallizations from benzene afforded colorless leaflets, m.p. 107.5–108.5°, undepressed by admixture with an authentic sample.

PRINCETON, N. J.

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[46] E. Vogel, *Ber.*, **85**, 25 (1952).

[47] Obtained through the courtesy of M. J. Hogsed, E. I. du Pont de Nemours and Co., to whom the authors express their thanks.

[48] C. S. Marvel and C. L. Levesque, THIS JOURNAL, **60**, 280 (1938).

[49] The ketone was prepared by the method of L. I. Smith and G. F. Rouault, *ibid.*, **63**, 631 (1943).

[50] W. Scharvin, *Ber.*, **30**, 2862 (1897).

[51] R. J. S. Beer, L. McGrath and A. Robertson, *J. Chem. Soc.*, 2118 (1950).

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

Condensed Cyclobutane Aromatic Compounds. IX. Benzocyclobutenol and Benzocyclobutenone

BY M. P. CAVA AND K. MUTH

RECEIVED JUNE 12, 1959

Starting from 1-bromobenzocyclobutene, syntheses of benzocyclobutenol and benzocyclobutenone have been achieved. Cleavage of the four-membered ring of both the alcohol and the ketone occurs readily under basic conditions.

Probably the most interesting simple derivatives of benzocyclobutene which have not yet been described are the alcohol and the ketone, benzocyclobutenol (I) and benzocyclobutenone (II). The synthesis of both of these compounds is now reported.

The bromine atom of 1-bromobenzocyclobutene (III)[1,2] was replaced by hydroxyl in an indirect manner under very mild conditions. The reaction of III with silver trifluoroacetate proceeded readily in benzene solution at room temperature to give, in 87% yield, benzocyclobutenyl trifluoroacetate (IV) as a pleasant smelling oil. The hydrolysis of the trifluoroacetate was carried out either by shaking at room temperature with aqueous sodium carbonate, or by ester exchange in refluxing methanol in the presence of an acidic ion exchange catalyst. Benzocyclobutenol (I) was obtained in good yield by either procedure as beautiful colorless needles, m.p. 58°. Preliminary experiments indicate that I is not particularly sensitive to dilute mineral acids, but is surprisingly unstable in the presence of sodium hydroxide. After standing with 0.25 *N* sodium hydroxide for one hour at room temperature the alcohol I was converted in 72% yield to *o*-tolualdehyde. The driving force for this unusual cleavage, which proceeds almost certainly *via* an alkoxide intermediate (Ia), is the

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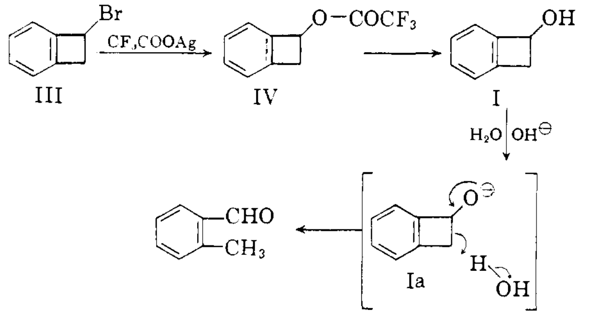
[1] M. P. Cava and D. R. Napier, THIS JOURNAL, **80**, 2255 (1958).

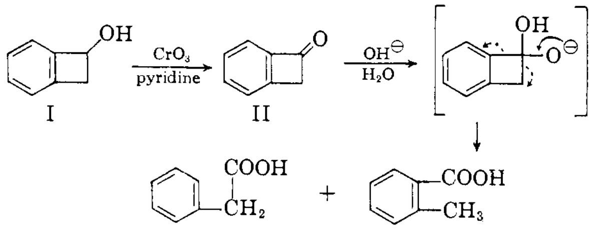
[2] L. Horner, W. Kirmse and K. Muth, *Chem. Ber.*, **91**, 430 (1958).

relief of the strain present in the benzocyclobutene system. Some simple analogs of this reaction are to be found in the facile conversion of cyclopropanol to propionaldehyde,[3–5] and in the base cleavage of 3-hydroxycyclobutanone.[6]



By mild oxidation of I with chromic anhydride in pyridine the simple ketone of the benzocyclobutene series, benzocyclobutenone (II), was obtained in moderate yield as an oil with an odor reminiscent of 1-indanone. The carbonyl absorption band of II in the infrared appeared as a close doublet[7] at 5.640 and 5.695 μ. The short wave lengths observed are very near to the usual value (5.63 μ)[6] for simple cyclobutanones, the small bathochromic shift being the result of conjugation of the carbonyl group with the aromatic ring.

Benzocyclobutenone is quite stable to dilute mineral acids, and reacts rapidly with 2,4-dinitrophenylhydrazine in an acidic medium to give a normal derivative. Aqueous sodium hydroxide, however, slowly destroys the ketone by a ring opening process similar to the base-catalyzed conversion of cyclopropanone hydrate[8] to propionic acid. Rather curiously, the base cleavage of the four-membered ring of II (in contrast to the analogous rupture of I) occurs in an indiscriminate manner at either side of the carbonyl group to give both *o*-toluic acid and phenylacetic acid.



A study of the carbonyl addition of II and the question of its ability to enolize will be discussed in a subsequent paper of this series.

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

Experimental[9]

Benzocyclobutenyl Trifluoroacetate (IV).—A solution of 1-bromobenzocyclobutene[1–2] (III, 4.00 g.) in benzene (25 ml.) was added dropwise over a period of 10 minutes to a stirred and ice-cooled solution of silver trifluoroacetate (5.00 g.) in benzene (40 ml.). Stirring was continued for an additional 3 hours, during which time the temperature of the mixture was allowed to warm up to room temperature. The precipitated silver bromide (3.85 g., theor. 4.05 g.) was removed by filtration and the benzene was evaporated from the filtrate under reduced pressure at 40–50°. Distillation of the residue gave the ester IV (3.85 g., 87%) as an oil, b.p. 68° (3 mm.).

Anal. Calcd. for $C_{10}H_7O_2F_3$: C, 55.55; H, 3.24. Found: C, 55.37; H, 3.23.

Benzocyclobutenol (I). (a) By Basic Hydrolysis.—An emulsion of trifluoroacetate ester IV (3.16 g.) and 5% aqueous sodium carbonate (20 ml.) was stirred rapidly for 9 hours at room temperature. The crystalline precipitate was extracted into ether, and the extract was washed with water, dried (Na_2SO_4) and evaporated. Crystallization of the residue from petroleum ether (30–60°) gave pure benzocyclobutenol (1.40 g. 75%) as white needles, m.p. 58°.

Anal. Calcd. for C_8H_8O: C, 80.00; H, 6.66. Found: C, 79.82; H, 6.55.

(b) By Ester Interchange.—To a solution of trifluoroacetate ester IV (0.80 g.) in 30 ml. of dry methanol was added 4 g. of Amberlite IR-120 (acid phase, washed well with methanol). After refluxing the mixture for three hours, the resin was removed by filtration and the methanolic filtrate was evaporated under reduced pressure. Crystallization of the residue from petroleum ether (30–60°) afforded pure alcohol I (0.42 g., 90%), identical in melting point and infrared spectrum with that obtained by the sodium carbonate hydrolysis method.

Ring Cleavage of Benzocyclobutenol (I).—Aqueous 0.25 *N* sodium hydroxide (2 ml.) and alcohol I (0.050 g.) were allowed to stand at room temperature for one hour. The reaction mixture, which now exhibited a strong aromatic aldehyde odor, was treated directly with an excess of aqueous acidic 2,4-dinitrophenylhydrazine solution. The precipitated derivative was filtered, washed with a little cold alcohol and dried. The product (0.089 g., 72%) showed an infrared spectrum identical to that of authentic *o*-tolualdehyde 2,4-dinitrophenylhydrazone, and its melting point (193°) was not depressed by admixture with the authentic derivative.

In a similar attempt to cleave I (0.050 g.) by 2 *N* hydrochloric acid (2 ml.) for one hour at room temperature, no dinitrophenylhydrazone was obtained; the starting material I (0.035 g., 72%) was recovered unchanged.

Benzocyclobutenone (II).—A solution of benzocyclobutenol (2.0 g.) in pyridine (25 ml.) was added dropwise over a 10-minute period to a well-stirred solution of chromic anhydride (2.0 g.) in pyridine (22 ml.). During the addition, the temperature was held below 8°. After stirring for an additional 3 hours at about 10°, the mixture was allowed to stand overnight at room temperature, then poured into water (200 ml.). The reaction product was extracted into 30–60° petroleum ether (four 50-ml. portions) and the extract washed thoroughly with water (fifteen 50-ml. portions). Evaporation of the dried solvent and distillation of the residue afforded benzocyclobutenone (0.80 g., 42%), b.p. 71–72° (2 mm.), as a colorless oil. The ketonic carbonyl appeared as a doublet (5.640, 5.695 μ) in the infrared.

Anal. Calcd. for C_8H_6O: C, 81.36; H, 5.09. Found: C, 81.44; H, 5.09.

The yellow-orange **benzocyclobutenone 2,4-dinitrophenylhydrazone** (m.p. 204°) formed readily in the cold in the usual manner, and was crystallized from ethanol.

Anal. Calcd. for $C_{14}H_{10}N_4O_4$: C, 56.38; H, 3.36; N, 18.79. Found: C, 56.05; H, 3.40; N, 18.68.

Ring Cleavage of Benzocyclobutenone (II).—The ketone II (0.075 g.) was shaken with 5 *N* aqueous sodium hydroxide (2 ml.) and the emulsion allowed to stand at room temperature. After 4 hours the ketonic odor had vanished and an ethereal extract of the basic solution failed to give a positive reaction with 2,4-dinitrophenylhydrazine reagent. The basic aqueous solution was acidified with hydrochloric acid

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(3) J. K. Magrane and D. L. Cottle, THIS JOURNAL, **64**, 484 (1942).

(4) G. W. Stahl and D. L. Cottle, *ibid.*, **65**, 1782 (1943).

(5) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 3176 (1951).

(6) E. Vogel and K. Hasse, *Ann.*, **615**, 22 (1958).

(7) For an interesting analysis of another case of the splitting of the carbonyl absorption band of a pure monoketone in solution, see P. Yates, N. Yoda, W. Brown and B. Mann, THIS JOURNAL, **80**, 202 (1958).

(8) P. Lipp, J. Buchkremer and H. Seeles, *Ann.*, **499**, 1 (1932).

(9) Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are corrected.

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).

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

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

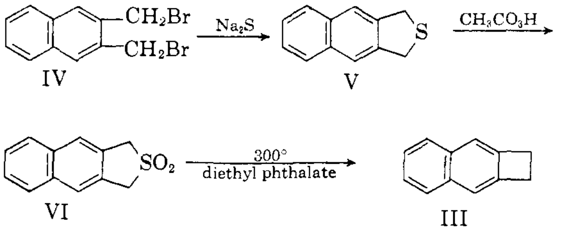
By M. P. Cava and R. L. Shirley

Received July 2, 1959

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.

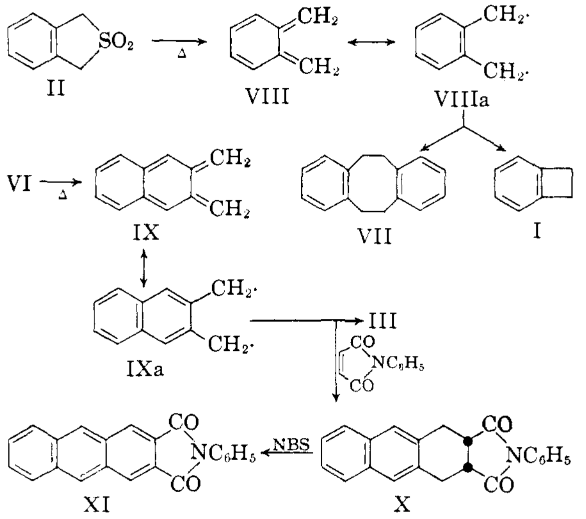
In a recent paper of this series,[1] a fundamentally new synthesis of benzocyclobutene (I) was described by the pyrolytic decomposition of 1,3-dihydroisothianaphthene 2,2-dioxide (II). The extension of this sulfone pyrolysis method to the synthesis of the hitherto unknown naphtho[b]cyclobutene (III) 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-dibenzocyclooöctadiene (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 intermediates VIII and IX. The 2,3-naphthoquinodimethane (IX), which is an analog of the unknown 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

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[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).