[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

Condensed Cyclobutane Aromatic Compounds. XXVI. Benzocyclobutadienoquinone: Synthesis and Simple Transformations[1]

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RECEIVED FEBRUARY 20, 1963

The synthesis of benzocyclobutadienoquinone (II) has been achieved by several routes. In the first of these, *trans*-1,2-diiodobenzocyclobutene (or the corresponding dibromide) is converted by silver nitrate into a mixture of *cis*-benzocyclobutene-1,2-diol dinitrate and *trans*-benzocyclobutene-1,2-diol dinitrate. Either nitrate is converted by triethylamine into quinone II. A more practical preparation of the quinone from 1,1,2,2-tetrabromobenzocyclobutene and silver trifluoroacetate is also described. Quinone II is stable thermally but behaves chemically as a reactive α-diketone. A number of transformations of II are discussed including oxidation, hydride reduction, alkaline cleavage, and carbonyl additions.

With the exception of certain metallic complexes,[3] no example of an isolable cyclobutadiene or monobenzocyclobutadiene is yet known, despite an intensive search carried out in many laboratories. Several derivatives of cyclobutenedione (I) have been described in recent years, however. These include phenylcyclobutenedione,[4,5] diphenylcyclobutenedione,[6] dihydroxycyclobutenedione[7] and dimethylcyclobutenedione.[8] Cyclobutenediones are of usual interest not only because, like cyclobutadienes, they contain a four-membered ring of only sp^2-hybridized carbon atoms, but also because they may be viewed formally as stable quinones of the unstable cyclobutadienes. In this paper the synthesis, physical properties and some simple reactions of benzocyclobutenedione (II), the quinone of the transient benzocyclobutadiene,[9-11] are described.[1]

Synthesis of Benzocyclobutadienoquinone.—The first synthesis of diketone II was achieved from both *trans*-1,2-benzocyclobutenediol dinitrate (III) and the corresponding *cis*-dinitrate IV. A mixture of the two isomers was obtained by the reaction of silver nitrate with either *trans*-1,2-dibromobenzocyclobutene (V)[9,12] or *trans*-1,2-diiodobenzocyclobutene (VI)[13] in acetonitrile. The higher melting dinitrate, m.p. 110°, obtained in 27–29% yield, was assigned the *cis* configuration IV on the basis of reductive experiments described below; the lower melting dinitrate, m.p. 57–59°, obtained in 35–44% yield, was assigned the *trans* configuration III.

In the infrared spectra of both isomeric nitrates, the asymmetric NO_2 frequency occurred at 6.04 μ; however, the symmetric NO_2 vibration, observed as a single band at 7.9 μ in the *trans* isomer, occurred as a doublet at 7.80 and 7.92 μ in the *cis* isomer. If this splitting occurs as a result of molecular symmetry, examination of the corresponding bands in other rigid *cis*- and *trans*-dinitrate pairs may prove to be of use in distinguishing the stereoisomers.

As a first step in the proof of the stereochemistry of the dinitrates III and IV, the reduction of these esters to the corresponding diols VII and VIII was attempted. Both nitrates reacted with lithium aluminum hydride to give not the desired diols, but phthalyl alcohol (IX), the product of reductive ring cleavage. The two dinitrates were then subjected to reduction by hydrazine in the presence of palladium, a method used successfully for the mild reduction of other nitrate esters to the corresponding alcohols.[14] Although the *trans*-dinitrate III gave only a brown gum by this procedure, the *cis* isomer IV afforded the crystalline *cis*-1,2-benzocyclobutenediol (VIII), m.p. 130–131°. The gross structure of this diol was confirmed by its oxidation to *o*-phthalaldehyde by periodic acid. The *cis* configuration was assigned to diol VIII on the basis of its rate of oxidation by lead tetraacetate. The observed rate constant was greater than 30,000. This may be compared with the rate constants reported for the lead tetraacetate oxidation of several 1,2-*cis*- and *trans*-cyclobutane and cyclobutenediols.[15,16] The *cis*-diols gave constants greater than 10,000 while the corresponding *trans* isomers gave constants of 100 or less. The *cis* configuration of VIII which was arrived at in this manner was consistent with the stereochemical assignment made on the basis of the OH infrared absorption bands of VIII.[17]

It has been known for some time that benzyl nitrate, when treated with alcoholic potassium hydroxide, undergoes elimination of nitrous acid with the formation of benzaldehyde in 70% yield.[18] When either of the dinitrates III or IV was treated with potassium *t*-butoxide in *t*-butyl alcohol, almost two equivalents of nitrate ion were liberated, but the only crystalline product isolated proved to be *t*-butoxyphthalide (X), m.p. 87–88°.[19] A reasonable rationalization of this reaction, consistent with the subsequently discovered base cleavage of II, is shown in Chart I.

The successful conversion of *trans*-1,2-benzocyclobutenediol dinitrate to diketone II was achieved using triethylamine as the base catalyst for the elimination of nitrous acid. The reaction was capricious and highly dependent upon the exact conditions used, although yields as high as 87% were obtained. The *cis*-dinitrate IV proved to be much more stable to elimination, although it was converted to diketone II in poor yield by triethylamine at 70°.[20]

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[1] For a preliminary communication of a portion of this investigation, see M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 3606 (1957).

[2] Fellow of the Alfred P. Sloan Foundation, 1958–1962.

[3] For the most recent example of such a complex, and for further references in this area, see H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194 (1961).

[4] E. J. Smutny and J. D. Roberts, *ibid.*, **77**, 3420 (1955).

[5] E. J. Smutny, M. C. Caserio and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

[6] (a) A. T. Blomquist and E. A. LaLancette, *ibid.*, **83**, 1387 (1961); (b) *ibid.*, **84**, 220 (1962).

[7] S. Cohen, J. R. Lacher and J. D. Park, *ibid.*, **81**, 3480 (1959).

[8] A. T. Blomquist and R. A. Vierling, *Tetrahedron Letters*, 655 (1961).

[9] (a) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956); (b) *ibid.*, **79**, 1701 (1957).

[10] C. D. Nenitzescu, M. Avram and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957).

[11] M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, **81**, 5409 (1959).

[12] H. Finkelstein, *Chem. Ber.*, **92**, xxvii (1959).

[13] F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958).

[14] L. P. Kuhn, *J. Am. Chem. Soc.*, **73**, 1510 (1951).

[15] (a) R. Criegee and K. Knoll, *Ann.*, **627**, 1 (1959); (b) R. Criegee, E. Höger, G. Huber, P. Kruck, F. Marktscheffel and H. Schellenberger, *ibid.*, **599**, 81 (1956).

[16] The rate constant units used by us are identical with those used by Criegee (l./mole/min.).

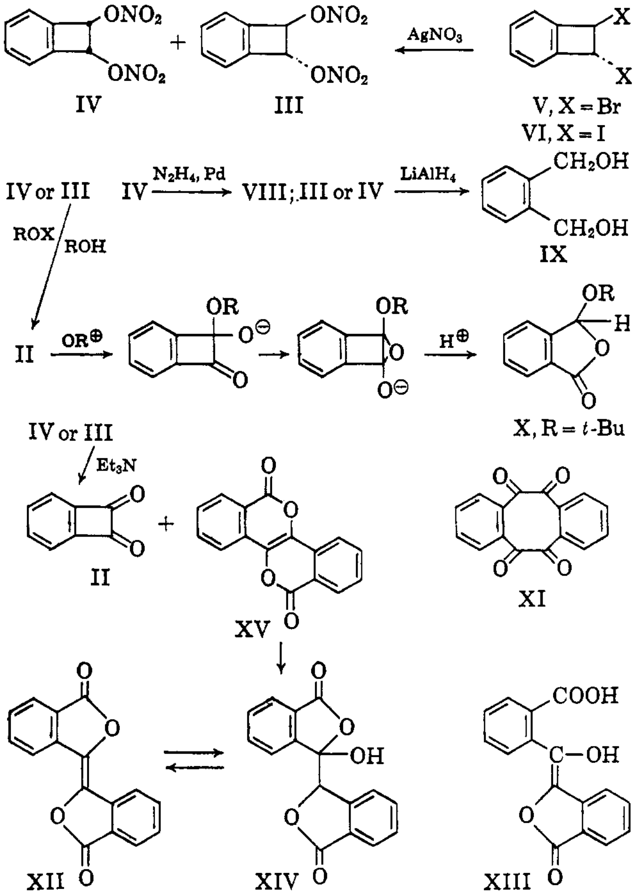
[17] E. J. Moriconi, W. F. O'Connor, L. P. Kuhn, E. A. Keneally and F. Wallenberger, *J. Am. Chem. Soc.*, **81**, 6472 (1959). Since reference to diol VIII is made here only in a table and footnote, it may be stated that the material used was obtained from diketone II by a hydride reduction similar to that described later in this paper (E. J. Moriconi, private communication).

[18] J. U. Nef, *Ann.*, **309**, 175 (1899).

[19] D. Wheeler, D. Young and D. Erley, *J. Org. Chem.*, **22**, 547 (1957). The melting point of XIII reported in this paper is 77–79°, but it was found that the melting point of material prepared as described by these authors could be raised to 87–88° by extensive recrystallization.

CHART I

SYNTHESIS AND REACTIONS OF BENZOCYCLOBUTENEDIOL DINITRATES



In the course of synthesizing II from either of the dinitrates, there was always obtained, in low yield (under 5%), a colorless dimer of II, m.p. 334–336°. The dimer, which showed carbonyl absorption in the infrared at 5.73 μ, failed to give a 2,4-dinitrophenylhydrazone and was not converted into phthalic acid by peracetic acid. This evidence, as well as the lack of yellow color of the compound, eliminated structure XI from further consideration. Although a mixture melting point determination and an infrared comparison proved that the dimer was different from the isomeric biphthalyl (XII), m.p. 352–354°,[21] both compounds on basic hydrolysis gave the known diphthalyllactonic acid, which could be reconverted to biphthalyl by heating to 240°.[22] Structure XIII, originally assigned to diphthalyllactonic acid, has been revised to the dilactone formulation XIV. In accord with the latter assignment, diphthalyllactonic acid shows hydroxyl absorption in the infrared at 2.90 μ, and only a single carbonyl band at 5.70 μ attributable to the γ-lactone function. The dimer of II was therefore assigned the isocoumarin structure XV. Like biphthalyl, structure XV is a dehydration product of benzoin-2,2′-dicarboxylic acid, the hypothetical open form of diphthalyllactonic acid. As expected, the δ-lactone carbonyl of dimer XV absorbs at a longer wave length (5.73 μ) than the corresponding γ-lactone carbonyl of biphthalyl (5.62 μ).[23] The mechanism of formation of dimer XV remains obscure. It has been determined, however, that XV is not a simple thermal transformation product of quinone II. Refluxing a solution of II in xylene for two days afforded none of the dimer.

It was reported recently that the reaction of 1,1,2,2-tetrabromobenzocyclobutene (XVI) with silver trifluoroacetate in benzene gave quinone II in 41% yield.[24] This reaction, employed originally as a structure proof of tetrabromide XVI, has now been modified to afford an excellent preparative synthesis of II. Closer investigation of the reaction of XVI with silver trifluoroacetate in benzene revealed the formation of a colorless by-product melting at 80–85°; its infrared spectrum showed bands at 5.47 and 5.54 μ. This substance was quite unstable and could not be satisfactorily purified for analysis. On refluxing with aqueous methanol, however, it was converted into II. On the basis of the foregoing observations, it was assigned structure XVII. By carrying out the hydrolysis of XVI in aqueous acetonitrile the formation of this by-product was avoided, and quinone II was obtained directly in 89% yield.

An attempt was made to prepare quinone II starting with *trans*-1,2-dihydrophthalic acid.[25] Acid XVIII was converted into the acid chloride with thionyl chloride, and the acid chloride was refluxed with triethylamine in benzene. It was hoped that the bisketene XIX would be generated and would undergo cyclization to quinone II, but this expectation was not realized. It is worthy of note that previous attempts to prepare cyclobutenones and cyclobutadienones *via* ketene intermediates have met with failure.[26,27]

Properties and Simple Reactions of Benzocyclobutadienoquinone.—Benzocyclobutadienoquinone II forms pale yellow prismatic crystals, m.p. 132–135°, which possess a faint but musty quinone-like odor. It appears to be quite stable thermally and sublimes unchanged at 100° under 0.2 mm. pressure. Its ultraviolet spectrum in ethanol (Fig. 1) shows four strong maxima between 220 and 301 mμ and a weaker one at 427 mμ. Its infrared spectrum shows relatively few strong bands, in accord with the symmetry of the molecule. The spectrum was resolved most clearly in potassium bromide (Fig. 2), in which medium the carbonyls absorb as a sharp triplet at 5.53, 5.62, and 5.68 μ.

Quinone II was oxidized rapidly by hydrogen peroxide in acetic acid to give phthalic acid in quantitative yield.

The reduction of II with lithium aluminum hydride afforded the *cis*-diol VIII in 30% yield. No other crystalline product was isolated from the amorphous reduction residues.

The α-diketone system of II was cleaved readily by base. After five hours at room temperature in the presence of 5% sodium hydroxide in aqueous methanol, compound II was converted to *o*-phthalaldehydic acid (XX) in 94% yield. This behavior parallels the alkaline cleavage of acenaphthenequinone to 1,8-naphthaldehydic acid under considerably more vigorous conditions.[28] As has already been pointed out,[6b] both diphenylcyclobutadienoquinone and phenylcyclobu-

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[20] In our preliminary communication (ref. 1) it was stated that the diketone II was obtained in 75% yield from either dinitrate. In subsequent work, the yield of II from the *cis*-dinitrate never exceeded 18% under the original conditions.

[21] F. Ramirez, H. Yamanaka and O. H. Basedow, *J. Org. Chem.*, **24**, 1838 (1959).

[22] C. Graebe and H. Schmalzigang, *Ann.*, **228**, 134 (1885).

[23] The infrared spectra of lactones XII, XIV and XV were determined in KBr mulls. Somewhat shorter wave length carbonyl bands would be expected in solution.

[24] M. P. Cava and K. Muth, *J. Org. Chem.*, **27**, 755 (1962).

[25] We wish to thank Professor W. N. White for a generous gift of this material.

[26] A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **79**, 2021 (1957).

[27] E. F. Silversmith, Y. Kitahara and J. D. Roberts, *ibid.*, **80**, 4088 (1958).

[28] C. Graebe and E. Gfeller, *Ann.*, **273**, 1 (1893).

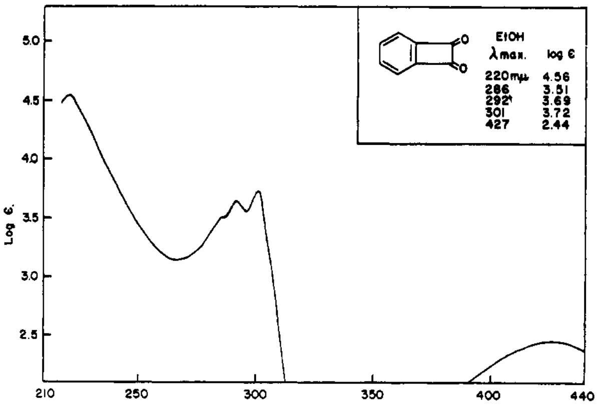
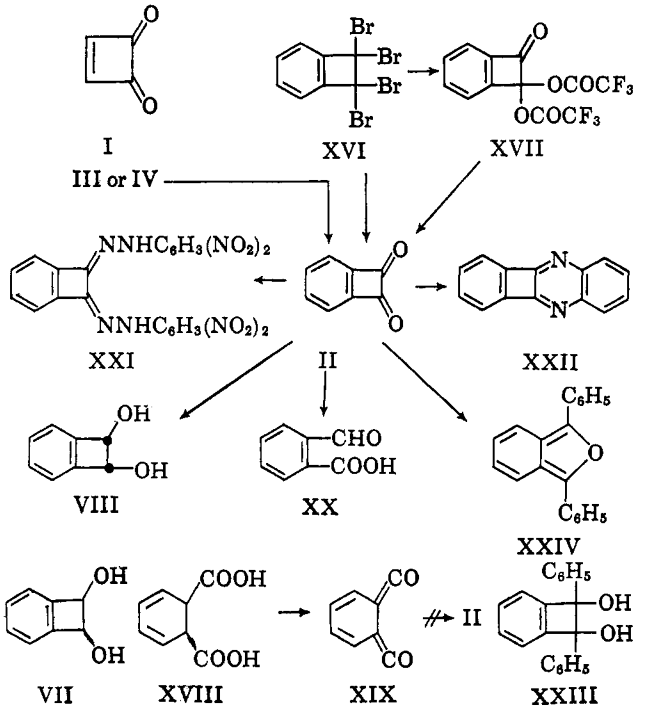


Figure 1.

tadienoquinone react with sodium hydroxide in a different manner, resulting in cleavage of the original cyclobutene double bond.

Chart II

Synthesis and Reactions of Benzocyclobutadienoquinone



The carbonyl groups of II reacted normally with 2,4-dinitrophenylhydrazine to give the bis-2,4-dinitrophenylhydrazone XXI. Quinone II reacted normally also with *o*-phenylenediamine to give 5,10-diazabenzo-[*b*]biphenylene (XXII), m.p. 238–239°, which represents the first example of a heterocyclic analog of a biphenylene system. In contrast, *o*-phenylenediamine reacts with both diphenylcyclobutadienoquinone[6b] and phenylcyclobutadienoquinone[29] to give rearranged quinoxaline derivatives arising by initial Michael addition of an amino group to a cyclobutenone double bond.

The reaction of II with phenylmagnesium bromide was investigated in an attempt to prepare one or both of the isomeric diphenylbenzocyclobutenediols (XXIII). The only product isolated, in 60% yield, was diphenylisobenzofuran (XXIV). It is not clear at this time whether the cleavage of the four-membered ring occurred during the Grignard addition process, or during the work-up of the reaction mixture.

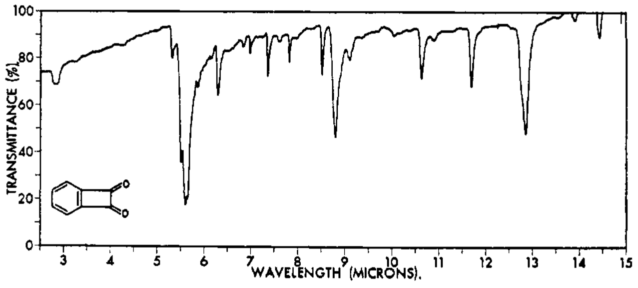


Figure 2.

Experimental[30]

Benzocyclobutadienoquinone (II). A. From *trans*-Dinitrate IV.—To a solution of *trans*-dinitrate IV (4.20 g.) in methylene chloride (8 ml.) was added with stirring a solution of triethylamine (3.87 g.) in methylene chloride (4 ml.). The reaction was exothermic, and was controlled by adding the amine solution at such a rate as to maintain a gentle refluxing of the solution. When the reaction had subsided, the orange mixture was refluxed on the steam-bath for 50 min. The insoluble precipitate of dimer XV (0.17 g.) was filtered off, and the filtrate was evaporated completely to dryness under vacuum at room temperature. The orange residue was dissolved in methylene chloride, and the organic solution was washed with water, dried, and evaporated to dryness under reduced pressure. Sublimation of the residue at 100° and 0.5 mm. gave yellow crystals of diketone II (1.92 g., 81%). The analytical sample, m.p. 132–135°, was obtained by crystallization from methylene chloride–petroleum ether (pale yellow plates), followed by resublimation.

Anal. Calcd. $C_8H_4O_2$: C, 72.73; H, 3.05. Found: C, 72.77; H, 3.08.

The highly insoluble orange bis-2,4-dinitrophenylhydrazone of II, m.p. 268–270° dec., did not require further purification when prepared in ethanol in the absence of excess 2,4-dinitrophenylhydrazine reagent.

Anal. Calcd. $C_{20}H_{12}N_8O_8$: C, 48.78; H, 2.46; N, 22.76. Found: C, 48.73; H, 2.69; N, 22.57.

B. From *cis*-Dinitrate III.—To a stirred solution of urea (0.530 g.) in dimethylacetamide (10 ml.) at 70° was added slowly and simultaneously a solution of *cis*-dinitrate III (1.000 g.) in dimethylacetamide (5 ml.) and a solution of triethylamine (1.4 ml.) in dimethylacetamide (5 ml.). After addition of the reagents was complete, the mixture was maintained at 70° for 2 hr., cooled, and diluted with water (200 ml.). Extraction with methylene chloride and work-up of the extract in the usual manner followed by sublimation and recrystallization afforded diketone II (0.204 g., 35%), identical in its infrared spectrum with the sample prepared from the *trans* isomer.

C. From 1,1,2,2-Tetrabromobenzocyclobutene (XVI).—A mixture of tetrabromide XVI (8.43 g.), silver trifluoroacetate (17.67 g.), water (4 ml.) and acetonitrile (70 ml.) was refluxed with stirring for 12 hr. while protected from light with a shield of metal foil. The precipitated silver bromide was filtered from the cooled solution and washed several times with acetonitrile. The solvent was removed under reduced pressure at 40–50°; the yellow residue was taken up in methylene chloride (15 ml.) and was washed twice with water (10 ml.) and twice with saturated aqueous sodium chloride (10 ml.). Evaporation of the dry methylene chloride solution, followed by sublimation of the residue at 100° (0.5 mm.), afforded diketone II (2.53 g.), m.p. 126–129°. Recrystallization from methylene chloride–petroleum ether (30–60°) gave yellow prisms of pure product (2.46 g., 89%), m.p. 130–131°.

Reaction of *trans*-1,2-Diiodobenzocyclobutene (VI) and *trans*-1,2-Dibromobenzocyclobutene (V) with Silver Nitrate.—To a 500-ml. two-necked flask provided with stirrer and drying tube were added diiodide VI (46.5 g., 0.130 mole) and silver nitrate (47.6 g., 0.280 mole), each dissolved in acetonitrile (150 ml.). The mixture was stirred at room temperature and in the dark for 8 days. At the end of this time the precipitated silver iodide (58 g.) was filtered off and washed with acetonitrile (100 ml.). The filtrate was concentrated under reduced pressure to *ca.* 75 ml. whereupon additional (4 g.) silver iodide (total 62 g., 100%) separated. The light yellow filtrate (150 ml. with washings) was again evaporated under reduced pressure to *ca.* 75 ml., and water (400 ml.) was added. The oil which separated from the aqueous phase was extracted into methylene chloride (250 ml.). After washing with water (400 ml.), the wet methylene chloride solution was dried thoroughly (sodium sulfate) and evaporated under reduced pressure until nearly all the solvent had been

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(29) J. D. Roberts, *Rec. Chem. Progr.*, **17**, 103 (1956).

(30) Analyses were carried out by Schwarzkopf Laboratories, Woodside, N. Y. Melting points are uncorrected.

removed. At this point, crystallization of residue commenced and was essentially complete after cooling at 5° for 0.5 hour. The solid which separated was filtered off, washed with 1:1 methanol–petroleum ether (15 ml.) and recrystallized once from methylene chloride–petroleum ether (30–60°) to yield *cis*-dinitrate IV (8.0 g., 27%) as colorless needles, m.p. 107–109°. Slow crystallization from the same solvents gave IV as colorless rhombs, m.p. 110°.

Anal. Calcd. for $C_8H_6O_6N_2$: C, 42.48; H, 2.67; N, 12.39. Found: C, 42.29, 42.50; H, 2.67, 2.59; N, 12.23, 12.42.

The filtrate was cooled at −5° for 18 hr. during which time the *trans*-dinitrate III crystallized. Recrystallization from methylene chloride–petroleum ether gave colorless crystals of III (13.3 g., 44%), m.p. 51–53°. Further crystallization from the same solvent mixture gave the analytical sample, m.p. 57–59°.

Anal. Calcd. for $C_8H_6O_6N_2$: C, 42.48; H, 2.67; N, 12.39. Found: C, 42.24, 42.21; H, 2.88, 2.60; N, 12.29, 12.31.

From a reaction similar to that described above using *trans*-dibromide V (150 g.) there was obtained *cis*-dinitrate IV (37.3 g., 29%), m.p. 103–105°, and *trans*-dinitrate III (44.7 g., 35%), m.p. 57–59°.

Lithium Aluminum Hydride Reduction of *trans*-Dinitrate III and *cis*-Dinitrate IV.—To a solution of lithium aluminum hydride (3.80 g.) in ether (100 ml.) was added with stirring a solution of *trans*-dinitrate III (2.36 g.) in ether (100 ml.) at a rate sufficiently slow to maintain the exothermic reaction under control. After stirring the mixture at room temperature for an additional 5 hr., excess hydride was destroyed by the slow addition of a 1:1 mixture of 95% ethanol in ether. After filtration of the organic salt, evaporation of the dried ether solution gave an oil which crystallized from methylene chloride at 10° to give 1.28 g. (95%) of phthalyl alcohol IX, m.p. 61.5–62.5°. The identity of the product was established by infrared and mixture melting point comparisons with authentic material.

A similar reduction of *cis*-dinitrate IV (0.80 g.) afforded phthalyl alcohol (0.340 g., 70%), m.p. 61–63°.

***cis*-1,2-Benzocyclobutenediol (VIII). A. By Hydrazine Reduction of Dinitrate IV.**—A solution of *cis*-dinitrate IV (3.07 g.) in methanol was added to 10% palladium-on-charcoal (1.2 g.) under nitrogen. To the stirred suspension was added dropwise a mixture of one part hydrazine hydrate and three parts methanol until the theoretical volume of nitrogen had been evolved. The filtered solution was evaporated to dryness under reduced pressure at 30° to give a white solid (1.05 g., 59%). The pure diol, m.p. 131°, was obtained as small white needles after crystallization from methylene chloride–petroleum ether.

Anal. Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.29; H, 5.94.

B. By Lithium Aluminum Hydride Reduction of Diketone II.—A solution of quinone II (0.296 g.) in dry ether (20 ml.) was added dropwise to an ethereal solution of lithium aluminum hydride (1.5 mmole). Excess hydride was decomposed by the slow addition of saturated aqueous sodium sulfate, the ethereal layer was decanted, and the remaining slurry was extracted four times with 10-ml. portions of 1:3 benzene–ether mixture. Evaporation of the combined organic extracts gave a white solid residue (0.250 g.) which was recrystallized from methylene chloride at −20° to give diol IX (0.091 g., 30%), m.p. 129–130°, as fine white needles. The mother liquors of the *cis*-diol afforded a yellow gum which was not further investigated.

Oxidation of Diketone II.—Diketone II (0.100 g.) was dissolved in a mixture of acetic acid (1 ml.) and 30% hydrogen peroxide (1 ml.). Evaporation of the resulting colorless solution gave phthalic acid (0.121 g., 96%), m.p. 205°. A portion of the product was sublimed to give phthalic anhydride, m.p. 131–132°, identified by infrared comparison with an authentic sample.

Alkaline Cleavage of Diketone II.—To a solution of diketone II (0.100 g.) in methanol (5 ml.) was added 10% aqueous sodium hydroxide (5 ml.). The color of the resulting solution faded slowly after standing at room temperature for 5 hours. Water (5 ml.) and concd. hydrochloric acid (10 ml.) were added to the decolorized solution which was then extracted twice with 150-ml. portions of ether. Evaporation of the dried ether extracts and crystallization of the residual solid from methylene chloride–petroleum ether afforded phthalaldehydic acid (XX, 0.065 g.), m.p. 97.5–98.5°. The identity of the product was confirmed by mixture melting point and infrared determinations. Additional phthalaldehydic acid was isolated as its 2,4-dinitrophenylhydrazone, m.p. 263° (reported[31] 270°), raising the total yield formed in the cleavage reaction to 94%.

5,10-Diazabenzo[*b*]biphenylene (XXII).—The quinoxaline analog XXII was prepared in 63% yield by mixing equimolar solutions (0.001 mole) in 4 ml. of methanol of diketone II and *o*-phenylenediamine followed by the addition of 1 drop of acetic acid. The reaction product, m.p. 238–239°, which separated rapidly in long white needles, was filtered and washed with methanol followed by petroleum ether. The melting point was not raised after recrystallization from methanol and petroleum ether.

Anal. Calcd. for $C_{14}H_8N_2$: C, 82.33; H, 3.95; N, 13.72. Found: C, 82.21; H, 3.84; N, 13.83.

Periodic Acid Cleavage of Diol VIII.—Compound VIII (0.068 g.) was dissolved in warm water (5 ml.) containing methanol (1 ml.) and a solution of metaperiodic acid (0.130 g.) in water (1 ml.) was added. After 10 min. the brown solution was extracted with methylene chloride (20 ml.). Evaporation of the dried extract gave a dark residue which was extracted with boiling 30–60° petroleum ether (*ca.* 30 ml.). The extract was evaporated and the residue sublimed at 100° and 2 mm. to yield crude crystalline *o*-phthalaldehyde. The aldehyde was converted to the known bis-2,4-dinitrophenylhydrazone (reported[32] m.p. 280° dec.). The amorphous derivative (0.247 g., 91%) formed orange-brown crystals, m.p. 282–284° dec. after crystallization from pyridine; its infrared spectrum was identical with that of an authentic sample prepared from *o*-phthalaldehyde.

Reaction of Benzocyclobutenedione (II) with Phenylmagnesium Bromide.—To a solution of phenylmagnesium bromide (0.036 mole) in ether (100 ml.) was added a solution of benzocyclobutenedione (0.92 g., 0.0075 mole) at a rate fast enough to maintain a gentle reflux. After addition was complete, the mixture was stirred at room temperature for 15 minutes. The complex and excess Grignard reagent were hydrolyzed with 0.2 *N* HCl. The ethereal layer was separated, washed with water and dried over sodium sulfate. Removal of solvent under reduced pressure (25°) gave an oil which was recrystallized from methylene chloride–petroleum ether to give 1.17 g. (60%) of diphenylisobenzofuran (XXIV), m.p. 126–130°, raised to 130° after two recrystallizations, and identified by mixture melting point and infrared comparison with an authentic sample.

***t*-Butoxyphthalide (X).**—To a refluxing solution of *cis*-dinitrate IV (1.55 g.) in dry *t*-butyl alcohol (20 ml.) was added cautiously 10 ml. of a 1.7 *N* potassium *t*-butoxide in *t*-butyl alcohol. After the vigorous exothermic reaction had subsided, the solution was evaporated under reduced pressure. The resulting light tan powder was partitioned between 30–60° petroleum ether (200 ml.) and water (50 ml.). Evaporation of the dried hydrocarbon solution and sublimation of the residual material at 100° (0.2 mm.) gave a solid but oily sublimate (0.327 g.). After several recrystallizations (methylene chloride–petroleum ether) and sublimations, pure *t*-butoxyphthalide (0.20 g., 14%), m.p. 87–88°, was obtained; infrared absorption (KBr): 5.63 μ (carbonyl).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.75; H, 6.72.

The aqueous phase from the petroleum ether extraction was diluted to 250 ml. and an aliquot (10 ml.) was added to excess aqueous sodium iodide (25 ml.). After acidification of the acetic acid, the liberated iodine, as determined by titration with standardized sodium thiosulfate, corresponded to 1.92 equivalents of nitrite ion from 1.00 equivalent of the original nitrate ester used.

Comparable yields of lactone XI (10–14%) were obtained in a similar manner from *trans*-dinitrate III.

An authentic sample of *t*-butoxyphthalide was prepared by the method of Wheeler.[19] The material originally obtained, m.p. 79–81°, was recrystallized eight times from methylene chloride–petroleum ether to give the pure lactone X, m.p. 87–88°, identical in infrared and mixture melting point determinations with material obtained from the nitrate esters.

Dimer of Quinone II.—To a solution of *trans*-dinitrate II (4.20 g.) in methylene chloride (8 ml.) was added with stirring a solution of triethylamine (3.87 g.) in an equal volume of methylene chloride at rates sufficient to maintain gentle reflux. After the exothermic reaction had subsided, the orange solution was refluxed an additional 50 min. on the steam-bath, then filtered to yield dimer XV (0.17 g.), m.p. 334–336°. Work-up of the filtrate yielded quinone II in 81% yield.

Anal. Calcd. for $C_{16}H_8O_4$: C, 72.73; H, 3.05. Found: C, 73.12; H, 3.12.

Hydrolysis of Dimer XV.—A mixture of dimer XV (0.50 g.), sodium hydroxide (0.24 g.), water (5 ml.), and methanol (5 ml.) was refluxed for 30 min. The cooled blue solution was poured into a mixture of concentrated hydrochloric acid (5 ml.) and ice (50 g.) and the white precipitate was filtered, washed with water and dried. After crystallization from ethanol, pure di-phthalyllactonic acid (0.48 g., 86%) was obtained.

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Anal. Calcd. for $C_{16}H_{10}O_5$: C, 68.02; H, 3.58. Found: C, 67.68; H, 3.96.

The hydrolysis product was identical by infrared analysis with an authentic sample of diphthalyllactonic acid[22] obtained by the alkaline hydrolysis of biphthalyl[21]; on heating above 240° the colorless product turned yellow and biphthalyl was regenerated,[22] as identified by its infrared spectrum.

Acknowledgment.—This work has supported by a grant from the National Science Foundation and, in part, by a predoctoral fellowship (to R. J. P.) from the Eastman Kodak Company. This aid is gratefully acknowledged.

[Contribution from the Evans Chemical Laboratory of The Ohio State University, Columbus 10, Ohio]

Condensed Cyclobutane Aromatic Compounds. XXVII. 1,2-Dimethylenebenzocyclobutene and Related Substances[1]

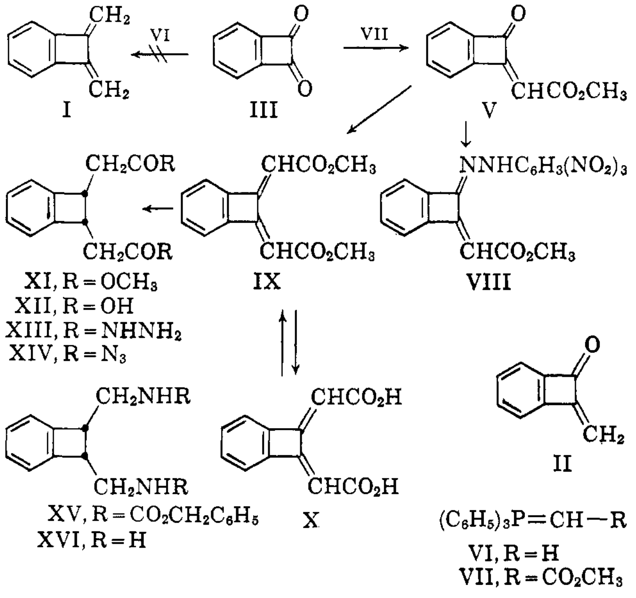
By M. P. Cava,[2] R. J. Pohl and M. J. Mitchell

Received February 20, 1963

Benzocyclobutadienoquinone (III) has been converted into 1-keto-2-carbomethoxymethylenebenzocyclobutene (V), 1,2-dicarbomethoxymethylenebenzocyclobutene (IX), and 1,2-dimethylenebenzocyclobutene (I). Some chemical and physical properties of these compounds are described.

The delocalization energies of a number of methylenecyclobutenes and ketocyclobutenes have been calculated by the molecular orbital method.[3] According to these calculations, 1,2-dimethylenebenzocyclobutene (I) and 1-keto-2-methylenebenzocyclobutene (II) have delocalization energies of 3.15β and 3.17β, respectively. These values are of the same order of magnitude as that (3.13β) predicted for benzocyclobutadienoquinone (benzocyclobutenedione, III), a known compound of considerable stability.[4] We now wish to report in detail the synthesis and properties of 1,2-dimethylenebenzocyclobutene (I) and its 1,2-dicarbomethoxy derivative IX, and of the carbomethoxy derivative (V) of 1-keto-2-methylenebenzocyclobutene (II).

Reaction of Benzocyclobutadienoquinone with Wittig Reagents.—The most direct approach to the synthesis of diene I appears to be the reaction of dione III with triphenylphosphinemethylene (VI).[5] However, the only isolable product of this reaction is triphenylphosphine. After the successful synthesis of diene I by another route (see below), this reaction was repeated and it was shown by gas chromatography that I is not produced, even in trace amounts. When Wittig reagent VI was replaced by the much less nucleophilic triphenylphosphinecarbomethoxymethylene (VII), olefin formation took place cleanly in methylene chloride at room temperature, and the reaction could be controlled to give either the mono- or the diolefinic product. By the slow addition of one equivalent of reagent VII to dione III, 1-keto-2-carbomethoxymethylenebenzocyclobutene (V), m.p. 87–88°, was obtained in 93% yield. The keto ester V exhibits strong bands in the infrared at 5.62, 5.83, and 5.92 μ, characteristic of a carbonyl in a four-membered ring, an ester carbonyl, and the conjugated exocyclic olefin function, respectively. The ultraviolet spectrum showed only one broad maximum in ethanol at 246 mμ (log ε 4.55). The ketonic carbonyl of V reacted with 2,4-dinitrophenylhydrazine to give a normal derivative (VIII), m.p. 235° dec. In addition, it reacted readily with Wittig reagent VII to give 1,2-dicarbomethoxymethylenebenzocyclobutene (IX), m.p. 123–124°, also obtainable directly and in 85% yield from dione III and two equivalents of VII. Diester IX shows ester carbonyl absorbtion at 5.80 μ, as well as a strong band at 6.04 μ attributed to the conjugated diene system. Its ultraviolet spectrum in ethanol is characterized by a very strong broad band (log ε 4.64) centered at 256 mμ and a second, weaker, but broad band at 290.5 mμ (log ε 410). The diene system of IX was quite stable under both basic and acidic conditions as evidenced by the alkaline hydrolysis of IX to the corresponding dicarboxylic acid X, m.p. 313–315°, and the re-esterification of X to IX with methanol containing a drop of sulfuric acid. A number of attempts were made to decarboxylate diacid X to dimethylenebenzocyclobutene by pyrolyzing it in the presence of soda lime, barium oxide, or quinoline containing copper sulfate.[6] In all cases only a trace of volatile material was obtained, although under the latter conditions at 200–210° the theoretical amount of carbon dioxide was evolved during one hour.



Catalytic reduction of diester IX took place readily at room temperature in the presence of palladium-on-charcoal to give *cis*-dicarbomethoxymethylbenzocyclobutene (XI) as an oil which was hydrolyzed by base to the corresponding dicarboxylic acid (XII), m.p. 189–190°. The reduced diester XI was characterized in the ultraviolet by the band triplet (λ_{max} 259, 265, and 271 mμ) typical of the unconjugated benzocyclobutene chromophore.[7] Several attempts were made

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[1] For preliminary communications of portions of this investigation, see M. P. Cava and R. J. Pohl, *J. Am. Chem. Soc.*, **82**, 5242 (1960); M. P. Cava, M. J. Mitchell and R. J. Pohl, *Tetrahedron Letters*, **No. 18**, 825 (1962).

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