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

Condensed Cyclobutane Aromatic Compounds. XV.[1] The Conversion of 5-Halobenzo[a]biphenylenes to 1,2,5,6-Dibenzopentalene Derivatives

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Mild oxidation of 5-bromobenzo[a]biphenylene and its 5-iodo analog give the corresponding 3,8-dioxo-6-halo-1,2,4,5-dibenzocycloocta-1,4,6-trienes. The latter products undergo both acid- and base-catalyzed transannular ring closure to derivatives of 3,3a,4,6a-tetrahydro-1,2,5,6-dibenzopentalene.

The oxidation of the yellow compound, now known to be 5-bromobenzo[a]biphenylene[1a] (I), was first studied by Finkelstein.[2,3] He found that vigorous chromic acid oxidation of I gave the dilactone of benzophenone-2,2′-dicarboxylic acid (II). By mild chromic acid oxidation, a colorless, crystalline substance, presumably an intermediate in the oxidation of I to II, was isolated. This compound, which was contaminated with an iodine-containing impurity, decomposed about 116–125° and had an analysis corresponding most closely to the composition $C_{15}H_9BrO_2$.

In this paper, evidence is presented that the latter compound and its iodo analog, prepared by mild oxidation of 5-iodobenzo[a]biphenylene (III)[4] are actually C_{16} compounds and have the structures of 3,8-dioxo-6-bromo-1,2,4,5-dibenzocycloocta-1,4,-6-triene (IV) and the corresponding 6-iodo derivative (V). These products are those which would result simply by oxidative fission of the cyclobutadienoid double bond of the benzobiphenylene system of I and III.

Compounds IV and V were obtained in good yield [70–80%] by oxidation of I and III with sodium dichromate and acetic acid; compound IV was formed also in 55% yield by neutral permanganate oxidation of I. Both IV and V were colorless, crystalline, neutral materials melting with decomposition at 110–120°. Both showed strong carbonyl absorption in the infrared at 5.97 μ; they absorbed strongly in the ultraviolet in the 220–310-mμ range, but no maxima were observed. The bromide IV gave consistently erratic analytical results, but the iodide V analyzed well for $C_{16}H_9IO_2$. The supposition of Finkelstein that IV was an intermediate in the oxidation of I to II was confirmed by the direct chromic acid oxidation of IV and V to the dilactone II.

Both IV and V reacted readily with methanolic potassium hydroxide at room temperature to give, in high yield, a halogen-free transformation product $C_{18}H_{16}O_4$ (VI). The formulation of VI as a hydroxy ketone was supported by its infrared spectrum which showed hydroxyl and carbonyl bands. The ultraviolet spectrum (see Experimental) was very similar to that of 3-phenylindanone.[5] The dimethyl ketal function present in VI was hydrolyzed quantitatively by recrystallization of VI from ethanol containing a small amount of hydrochloric acid. The resulting hydroxy diketone VII showed ultraviolet absorption almost identical to that of the known 3,3a,4,6a-tetrahydro-3,4-dioxo-1,2,5,6-dibenzopentalene (VIII)[5] (See Experimental). Indeed, VII could be reduced to diketone VIII by hydriodic acid and red phosphorus.

The mechanism of the conversion of IV and V to the ketal VI most certainly involves, at the initial stage, addition of methoxide ion to the β-position of the α,β-unsaturated carbonyl system of IV or V. The anion which forms may then undergo transannular addition to the C-3 carbonyl group. Solvolysis of the resulting α-halo ether would give the observed ketal VI. Alternatively, elimination of iodide ion from the initially formed anion could give 3,8-dioxo-6-methoxy-1,2,4,5-dibenzocycloocta-1,4,6-triene; attack of this species by methoxide ion, followed by transannular addition at C-3, would also lead to ketal VI. This alternate explanation seems less attractive, since molecular models show IV and V to be highly crowded structures in which C-7 is very close to C-3. Under these circumstances addition of a C-7 anion to the C-3 carbonyl in the first phase of the reaction would seem most likely.

A similar transannular ring closure of the iodocyclooctatriene V to the hydroxy diketone VII could be effected directly under acidic conditions, using hydrochloric acid and acetic acid. In this reaction protonation of the C-3 carbonyl group of V probably initiates the observed transformation. The acid-catalyzed conversion of V to VII and the hydriodic acid reduction of VII to the diketone VIII could be combined in one operation. Reduction of V with hot hydriodic acid and phosphorus gave VIII in 65% yield.

(1) For XVI of this series see M. P. Cava and M. J. Mitchell, *J. Org. Chem.*, **27**, 631 (1962).

(1a) M. P. Cava and J. F. Stucker, *J. Am. Chem. Soc.*, **79**, 1706 (1957).

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

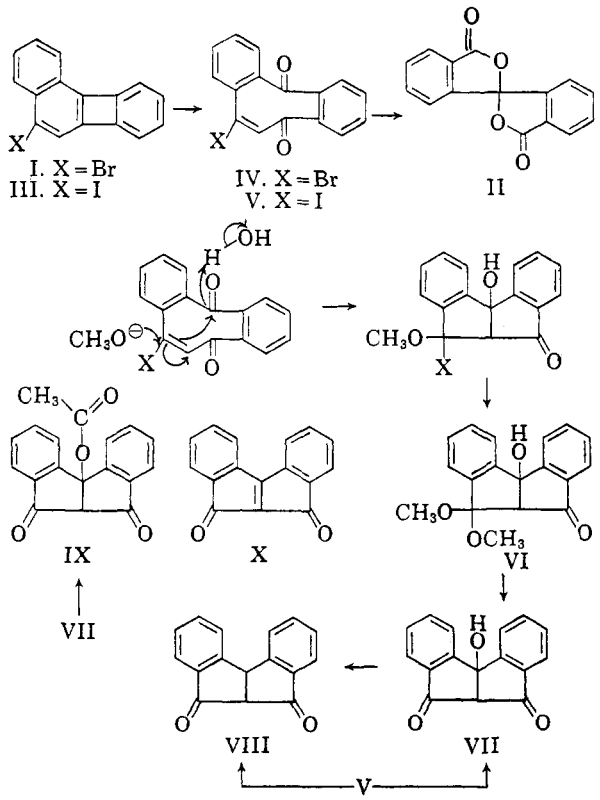
(3) H. Finkelstein, *Chem. Ber.*, **92**, XXXVII (1959).

(4) M. P. Cava, K. W. Ratts, and J. F. Stucker, *J. Org. Chem.*, **25**, 1101 (1960).

(5) W. Baker, J. F. W. McOmie, S. D. Parfitt, and D. A. M. Watkins, *J. Chem. Soc.*, 4026 (1957).

The stability of the hydroxy diketone VII towards dehydration deserves some comment. The hydroxyl group in this compound, although *cis* to the α-hydrogen, is not only β to the ketonic carbonyl, but is also in a tertiary benzylic position. Diketone VII, however, is stable to hot hydrochloric acid and acetic acid as mentioned previously. Reaction of VII with 2,4-dinitrophenylhydrazine gives a mono-2,4-dinitrophenylhydrazone in which dehydration has not occurred.[6] Dehydration of VII would, of course, be impossible if the β-dicarbonyl system in this compound existed in the monoenolic form. Ample evidence has been presented, however,[5] that the closely related diketone VIII exists essentially completely in the diketo form.

Conversion of compound VII to its acetate IX was effected by hot acetic anhydride and zinc chloride. On heating, acetate IX becomes yellow slowly above 150°. A similar color change occurs on heating the hydroxy diketone VII above 230°. Preparative pyrolysis of either VII or IX afforded an orange crystalline compound, melting at 332–337°. This substance does not appear to be the expected dibenzopentalenequione (X), but rather a dimeric material of as yet undetermined constitution.



EXPERIMENTAL[7]

Oxidation of 5-iodobenzo[a]biphenylene (III). A hot solution of 5-iodobenzo[a]biphenylene[4] (5.00 g.) in glacial acetic acid (80 ml.) was added to a boiling solution of sodium dichromate dihydrate (15.0 g.) in acetic acid (60 ml.). The hot solution was allowed to stand 2 min. and then water (300 ml.) was added. Upon cooling light tan needles separated which were filtered and dried to give crude V (4.46 g., 81.3%), m.p. 110–120° dec. Recrystallization from acetone–water gave pure 3,8-dioxo-6-iodo-1,2,4,5-dibenzocycloocta-1,4,6-triene (V) as colorless needles.

Anal. Calcd. for $C_{16}H_9IO_2$: C, 53.35; H, 2.52; I, 35.24. Found: C, 53.06; H, 2.90; I, 34.78.

The ultraviolet spectrum (ethanol) showed continuously decreasing absorption between 220 and 320 mμ [shoulder at 280 mμ].

Oxidation of 5-bromobenzo[a]biphenylene (I). A. *Oxidation with sodium dichromate.* A hot solution of 5-bromobenzo[a] biphenylene (0.281 g.) in glacial acetic acid (5 ml.) was added to a boiling solution of sodium dichromate dihydrate (0.900 g.) in acetic acid (4 ml.). The hot solution was allowed to stand 2 min. and an excess of water was added. Upon standing, a light tan precipitate separated which was filtered and dried to give crude IV (0.240 g., 76.6%). Recrystallization from acetone–water gave 3.8-dioxo-6-bromo-1,2,4,5-dibenzocycloocta-1,4,6-triene (IV) as colorless needles, m.p. 110–120° dec.

A number of attempts to obtain reproducible analytical results for this compound met with failure.

B. *Oxidation with potassium permanganate.* 5-Bromobenzo-[a]biphenylene (1.00 g.) was dissolved in acetone (120 ml.) containing water (14 ml.) and magnesium sulfate (2.0 g.). Potassium permanganate (1.52 g.) in acetone (150 ml.) was added at room temperature with stirring over a 2-hr. period. The stirring was continued 1–2 hr. and the mixture let stand in the refrigerator overnight. The mixture was filtered through Filter Cel and the filtrate evaporated to dryness on the steam bath under a stream of air. The pale yellow solution crystallized upon addition of water. Recrystallization from acetone–water gave diketone IV as small colorless needles (0.61 g., 55%), m.p. 110–120° dec. The infrared spectrum of the product was identical to that obtained in part A above.

The 3,8-dioxo-6-halo-1,2,4,5-dibenzocycloocta-1,4,6-trienes are insoluble in sodium bicarbonate solution. Cold concd. sulfuric acid dissolves the compounds with the formation of a deep red color.

Oxidation of 3,8-dioxo-6-halo-1,2,4,5-dibenzocycloocta-1,4,6-trienes. The halocyclooctatriene was dissolved in glacial acetic acid (10 ml.), and a solution of chromium trioxide (0.390 g.) in glacial acetic acid (20 ml.) was added. The solution was heated 1 hr. on the steam bath, and the acetic acid then evaporated on the steam bath under a stream of air. Concd. hydrochloric acid (25 ml.) was added and the solution boiled for 5 min. Water (5 ml.) was added and the solution cooled in an ice bath several hours. The white precipitate was filtered off, washed with water, and dried. The filtrate was evaporated to dryness, and water (4–5 ml.) was added. An additional amount of the dilactone of benzophenone-2,2′-dicarboxylic acid was filtered from this, washed with water, and dried.

	Bromocyclo-octatriene	Iodocyclo-octatriene
Weight of sample	0.094 g.	0.120 g.
Weight of product	0.042 g.	0.059 g.
Percentage yield	55%	70%

The compounds obtained in both of the above runs were identical to an authentic sample of the dilactone of benzophenone-2,2′-dicarboxylic acid (II) in melting point and infrared spectrum.

Reaction of 3,8-dioxo-6-halo-1,2,4,5-dibenzocycloocta-1,4,6-

(6) The related diketone VIII was found to react with only one equivalent of 2,4-dinitrophenylhydrazone; see ref. 5.

(7) Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn., and by Schwarzkopf Laboratories, Woodside, N. Y. All melting points are uncorrected.

trienes with methanolic potassium hydroxide. A. *Reaction of the bromocyclooctatriene* (IV). The bromocyclooctatriene (0.094 g.) was dissolved in a methanolic potassium hydroxide solution (0.225 g. in 7.5 ml.) and allowed to stand at room temperature under nitrogen for 17 hr.[8] Water (40 ml.) was added, and the solution was neutralized with acetic acid. The solution was extracted with ether (150 ml.) and the ether layer washed with water (100 ml.), 7% sodium bicarbonate (60 ml.), and finally with water (100 ml.). Evaporation of the dried ether solution gave crystalline 3,3a,4,6a-tetrahydro-3-oxo-4,4-dimethoxy-6a-hydroxy-1,2,5,6-dibenzopentalene (VI) (0.075 g., 85%), m.p. 210–213° after crystallization from methanol.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.74; H, 5.46.

The infrared spectrum (potassium bromide) showed high intensity bands at 2.90, 5.91, 8.19, 8.85, 9.11, 9.56, 9.68, and 12.98 μ.

The ultraviolet spectrum (ethanol) showed a strong similarity to that of 3-phenylindanone[5]:

3-Phenylindanone	3,3a,4,6a-Tetrahydro-3-oxo-4,4-dimethoxy-6a-hydroxy-1,2,5,6-dibenzopentalene
244 mμ (log ϵ 4.08)	245 mμ (log ϵ 4.01)
293 mμ (log ϵ 3.41)	293 mμ (log ϵ 3.13)

B. *Reaction of the iodocyclooctatriene* (V). The iodocyclooctatriene (0.120 g.) was treated in the same manner as IV to yield the identical ketal VI (0.095 g., 96%) as colorless crystals, m.p. 210–213°.

3,3a,4,6a-Tetrahydro-3,4-dioxo-6a-hydroxy-1,2,5,6-dibenzopentalene (VII). A. *By acid treatment of 3,8-dioxo-6-iodo-1,2,4,5-dibenzocyclooctatriene.* The iodocyclooctatriene V (0.120 g.) was added to a solution of concd. hydrochloric acid (2.0 ml.) in glacial acetic acid (2.0 ml.). The solution was heated on the steam bath 4 hr., then poured into water (100 ml.) and extracted with benzene (100 ml.). The benzene layer was washed with 10% sodium sulfite (100 ml.), water (100 ml.), and dried over magnesium sulfate. Evaporation of the benzene gave tan crystals, of 3,3a,4,6a-tetrahydro-3,4-dioxo-6α-hydroxy-1,2,5,6-dibenzopentalene (VII), (0.030 g., 36%). Recrystallization from ethanol gave colorless needles. The compound exhibits no sharp melting point, turning yellow at 230°, and finally melting at about 280°.

Anal. Calcd. for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03; mol. wt., 250. Found: C, 76.64; H, 4.02; mol. wt. (Rast), 244.

The infrared spectrum (potassium bromide) showed high intensity bands at 2.92, 5.78, 5.91, 6.22, 7.98, 8.14, 9.42, 9.55, 12.63, and 13.09 mμ.

The ultraviolet spectrum (ethanol) showed the following maxima in comparison to the known 3,3a,4,6a-tetrahydro-3,4-dioxo-1,2,5,6-dibenzopentalene[5]:

3,3a,4,6a-Tetrahydro-3,4-dioxo-1,2,5,6-dibenzopentalene	3,3a,4,6a-Tetrahydro-3,4-dioxo-6a-hydroxy-1,2,5,6-dibenzopentalene
247 mμ (log ϵ 4.25)	246 mμ (log ϵ 4.28)
286 mμ (log ϵ 3.52)	285 mμ (log ϵ 3.29)

The 2,4-dinitrophenylhydrazone was prepared in 80% yield and formed red needles, m.p. 268–269°.

Anal. Calcd. for $C_{22}H_{14}O_6N_4$: N, 13.02. Found: N, 13.08.

B. *By acid hydrolysis of ketal* VI. Recrystallization of ketal VI from ethanol containing a few drops of 10% hydrochloric acid gave, in quantitative yield, colorless needles of hydroxydiketone VII, identical in infrared spectrum with the product described above.

Reduction of 3,8-dioxo-6-iodo-1,2,4,5-dibenzocycloocta-1,4,6-with phosphorus and hydrogen iodide. The iodocyclooctatriene V (0.360 g.) was dissolved in glacial acetic acid (6.0 ml.) to which was added 47% hydriodic acid (6.0 ml.) and a small amount of red phosphorus. The mixture was heated on the steam bath for 4 hr. with intermittent shaking. The phosphorus was filtered from the hot solution and washed well with ether. The acid-ether filtrate was concentrated, then poured into water (300 ml.), and extracted with three portions (100 ml.) of ether. The ether was evaporated, water (100 ml.) was added, and the mixture was extracted with benzene (100 ml.). The benzene layer was washed with 10% sodium sulfite (100 ml.), water (100 ml.), then dried and evaporated to give tan crystals (0.220 g., 65.3%). Recrystallization from benzene gave 3,3a,4,6a-tetrahydro-3,4-dioxo-1,2,5,6-dibenzopentalene (VIII) as colorless needles m.p. 260–263° (reported[5] 259°). The infrared spectrum was identical to that of an authentic sample.[5]

Reduction of 3,3a,4,6a-tetrahydro-3,4-dioxo-6a-hydroxy-1,2,-5,6-dibenzopentalene with phosphorus and hydrogen iodide. Hydroxy diketone VII (0.050 g.) was added to glacial acetic acid (1.0 ml.) containing 47% hydriodic acid (1.0 ml.) and a small amount of red phosphorus. The mixture was heated on the steam bath for 4 hr. The mixture was filtered and the phosphorus washed well with benzene. Water (50 ml.) was added to the benzene-acid filtrate, which was then extracted with benzene (100 ml.). Work-up in the usual manner gave 3,3a,4,6a-tetrahydro-3,4-dioxo-1,2,5,6-dibenzopentalene (VIII) as colorless crystals (0.027 g., 58%), m.p. 260–263°. The product was identical with an authentic sample.

Acetate of 3,3a,4,6a-tetrahydro-3,4-dioxo-6a-hydroxy-1,2-5,6-dibenzopentalene (IX). Hydroxy diketone VII (0.250 g.) was added to hot acetic anhydride (20 ml.) containing a small amount of anhydrous zinc chloride. The solution was heated for 10 min., and then poured into ice water (200 ml.). The mixture was stirred vigorously until only one liquid phase was observed. The precipitate (0.251 g., 84%) was filtered, washed with water, and crystallized from methanol to give colorless needles of IX. Acetate IX has no true melting point, but becomes yellow at 150°, and melts completely over 300°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.96; H, 4.14; mol. wt., 292. Found: C, 74.10; H, 4.15; mol. wt. (Rast), 284.

Pyrolysis of 3,3a,4,6a-tetrahydro-3,4-dioxo-6a-hydroxy-1,2,5,6-dibenzopentalene. Hydroxy diketone VII (1.000 g.) was heated in a small flask with a small flame until the crystals melted and darkened. The dark orange residue was then sublimed at 1.2 mm. while hearing with an open flame. The yellow sublimate was washed from the cold finger with acetone. Evaporation of the acetone left an orange residue which was refluxed with absolute methanol for 10 min. The methanol-insoluble residue was dissolved in a minimum amount of hot methylene chloride and benzene was added slowly until crystals just began to form. Bright orange plates (0.543 g.), m.p. 332–337°, separated on standing. Recrystallization from methylene chloride–benzene yielded the analytical sample.

Anal. Calcd. for $C_{32}H_{18}O_5$: C, 79.66; H, 3.76; mol. wt., 482. Found: C, 80.01; H, 3.67; mol. wt. (Rast), 450.

The infrared spectrum (potassium bromide) showed high intensity bands at 5.79, 5.84, 6.24, and 13.19 μ.

The ultraviolet spectrum (ethanol) showed one maximum at 251 mμ (log ϵ 4.65).

Pyrolysis of acetate IX was carried out in the manner described above. The same orange product, m.p. 332–337°, was obtained.

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(8) Several preparations have been made in which the solution was allowed to stand only one hour with no appreciable lowering of the yield.