The procedure of Rapp and co-workers was normally followed for preparative-scale reactions, and yields of better than 95% were generally noted.[14] In one case, the stainless steel bomb containing chlorotrifluoroethylene was brought rapidly to 300° (whereupon a pressure of 990 p.s.i. was noted). As soon as the pressure fell to 900 p.s.i., the reaction was quenched by immersing the pressure bomb in an ice bath. A yield of only 3% was obtained for this reaction, and gas chromatography was used to measure the product ratio. Pure *cis* adduct was placed in a stainless steel vessel and heated to 350–400° for 3 hr. An infrared spectrum of material which had been treated in this fashion indicated that the starting cyclobutane was at least 95% unchanged. This same experiment was carried out on the pure *trans* adduct with an identical result.

Chlorotrifluoroethylene (5 ml. of liquid) was vacuum transferred into a heavy wall glass tube (12 ml.) which had been cooled to −195°. The tube was sealed under vacuum and heated at 200° for 24 hr. The crude reaction mixture was analyzed by gas chromatography. A second reaction was carried out in a sealed glass ampoule at lower pressures (590 mm.) and higher temperature (340° for 24 hr.). In the latter case, 300 mm. of chlorotrifluoroethylene was admitted to an evacuated ampoule which was then sealed off under vacuum. Upon completion of the reaction, starting material was removed by cooling the mixture to −78° and evacuating (1 mm.) the sample tube for 20 min. The infrared spectrum of the remaining liquid was taken. In both of the preceeding experiments, the *cis–trans* ratio appeared to be the same as was obtained in stainless steel apparatus.

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[14] K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. A. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3642 (1950).

The Isomerization of 7,14-Diketo-1,2,3,4,6,6a,7a,8,8a,9,10,11,13,13a,14a,14b-hexadecahydrodibenz[*a*,*h*]anthracene

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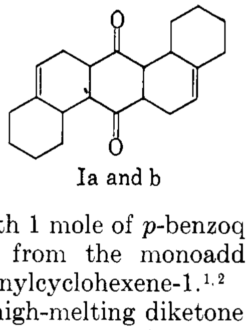
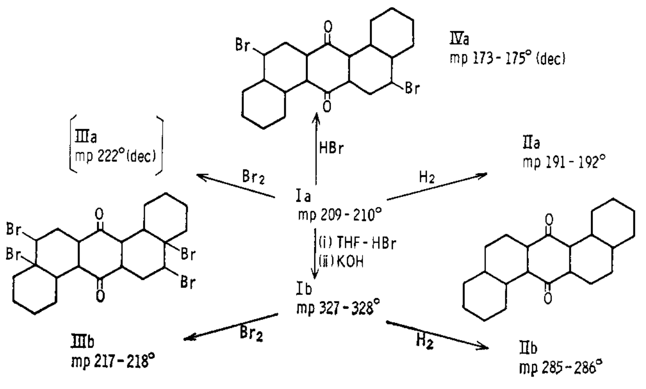
In the course of the development of a new general synthetic scheme for the preparation of various substituted dibenz[*a*,*h*]anthracenes, the title compound, Ia, was prepared by condensation of 2 moles of 1-vinylcyclohexene-1 with 1 mole of *p*-benzoquinone, and also, in higher yield, from the monoadduct of *p*-benzoquinone and 1-vinylcyclohexene-1.[1,2] Ia readily isomerized to a new high-melting diketone (Ib) labeled the "isobisadduct," m.p. 327–328°, by treatment of a solution of Ia in tetrahydrofuran with dry hydrobromic acid gas. The bisadduct Ia can also be converted to Ib by refluxing with methanolic potassium hydroxide. However, it is recovered unchanged when refluxed with acetic anhydride.



Ia and b

The isomerization of Ia to Ib also does not occur when Ia is heated with aqueous hydrobromic acid or with tetrahydrofuran alone or when it is refluxed with 1,4-dibromobutane, which is the product of the reaction between tetrahydrofuran and hydrobromic acid.[3]

Chart I

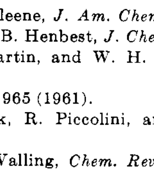


In view of the recent interest in the stereochemistry of the bisadducts of butadiene[4-6] and cyclopentadiene[7] with *p*-benzoquinone, the isomerization observed with the bisadduct of 1-vinylcyclohexene-1 and *p*-benzoquinone are recorded here. The reactions carried out on the two isomers Ia and Ib are summarized in Chart I.

Both Ia and Ib gave the hydrocarbon dibenz[*a*,*h*]anthracene on dehydrogenation with palladium. The isomeric dibenz[*a*,*j*]anthracene could not be detected by paper and thin layer chromatography, thus confirming the structure of the bisadduct as Ia, previously assigned to it.[1,2]

Both isomers Ia and Ib could be catalytically hydrogenated to two different saturated compounds IIa and IIb. The isobisadduct Ib and its catalytic hydrogenation product IIb had notably higher melting points than their isomers Ia and IIa. Bromination of Ia in dioxane gave an unstable bromide. The tetrabromide of the isobisadduct IIIb, on the other hand, was stable. Ia could be converted to a saturated dibromide (IVa) by treatment with hydrobromic acid in chloroform.

Since the hydrobromination was carried out in the presence of a small amount of benzoyl peroxide, the bromide is probably IVa rather than the isomer in which bromine becomes attached to the more highly substituted carbon atom.[8] The monoadduct of 1-vinylcyclohexene-1 and *p*-benzoquinone would be expected, according to the Alder and Stein[9] rule, *i.e.*, *endo* addition in the Diels–Alder reaction, to have the *cis–syn* structure V, since mild conditions are used in the preparation of this monoadduct. The formation of adducts with *cis–anti* configurations under strenuous



V

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[1] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 58 (1938).

[2] H. J. Backer and J. R. van der Bij, *Rec. trav. chim.*, **62**, 561 (1943).

[3] R. Fried and R. D. Kleene, *J. Am. Chem. Soc.*, **62**, 3258 (1940).

[4] N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960).

[5] R. K. Hill, J. G. Martin, and W. H. Stouch, *J. Am. Chem. Soc.*, **83**, 4006 (1961).

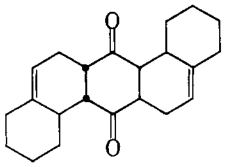
[6] R. L. Clarke, *ibid.*, **83**, 965 (1961).

[7] L. de Vries, R. Heck, R. Piccolini, and S. Winstein, *Chem. Ind.* (London), 1416 (1959).

[8] F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).

[9] K. Alder and G. Stein, *Ann.*, **501**, 247 (1933).

Diels–Alder conditions, recently described,[10] is not expected to apply in the present case. On the basis of the careful work of Hill and co-workers[5] and Crossley and Henbest[4] on the Diels–Alder addition of butadiene to *p*-benzoquinone, the bisadduct obtained in the present study probably has the *cis–anti–cis* structure VI.



VI

Isomerization of the *cis–anti–cis* isomer of the butadiene–*p*-benzoquinone bisadduct with alkali[9] is known to yield the *trans–syn–trans* isomer.[4] It cannot be concluded from this that the isobisadduct Ib of the present study has the same configuration. However, a comparison of the melting points in the hydroanthraquinone and hydrodibenz[*a,h*]anthraquinone series and their hydrogenation products is of interest. The melting points of these compounds are compared in Table I. This comparison suggests that the isobisadduct Ib, obtained by alkali isomerization, is the *trans–syn–trans* isomer.

TABLE I

MELTING POINTS OF DIELS–ALDER ADDUCTS AND THEIR HYDROGENATION PRODUCTS

Configuration	M.p., °C.	Compd. no.	M.p., °C.
Hydroanthraquinones		Hydrodibenz[*a,h*]-anthraquinones	
cis–anti–cis	154–155[a]	Ia	209–210[b]
trans–syn–trans[c]	244–245[a]	Ib[c]	327–328[b]
Saturated Hydroanthraquinones[d]		Saturated Hydrodibenz-[*a,h*]anthraquinones[d]	
cis–anti–cis	183[e]	IIa	191–192[b]
trans–syn–trans	253–256[f]	IIb	285–286[b]

[a] Ref. 4. [b] This study. [c] Obtained from lower melting epimers by alkali isomerization. [d] Obtained by catalytic hydrogenation of corresponding unsaturated isomers. [e] Ref. 5. [f] Ref. 6.

The possibility that the isobisadduct Ib is a double-bond isomer of Ia was also considered. A double-bond isomer of Ia would contain either a tetrasubstituted ethylenic bond or a conjugated double bond. Both Ia and Ib show in their infrared absorption spectra in carbon disulfide solution, peaks in the 800- to 840-cm.$^{-1}$ region. Bands in this region are characteristic for trisubstituted ethylenes.[11] For Ia this band is at 815 cm.$^{-1}$, whereas for Ib there is a band at 816 cm.$^{-1}$ with a shoulder at 825 cm.$^{-1}$. The carbonyl absorption bands for both these compounds are in the regions characteristic for unconjugated carbonyl.

Experimental

All melting points were measured in a Thomas–Hoover silicone bath and are uncorrected.

Condensation of *p*-Benzoquinone and 1-Vinylcyclohexene-1 to Ia.—1-Vinylcyclohexene-1,[1,2] 21.6 g. (0.2 mole), was condensed with 10.8 g. (0.1 mole) of pure *p*-benzoquinone by refluxing in tetralin.[1] The product was crystallized from dioxane to give colorless needles, m.p. 209–210°, 4.5 g., 14% yield (lit. m.p. 200–202°,[1] 202–204°[2], 11% yield[1]). This bisadduct could be prepared in higher over-all yield *via* the monoadduct. The monoadduct, m.p. 92° (lit.[2] m.p. 84.5–85.5°), was prepared as described earlier.[1] Reaction of 1 mole of monoadduct with 1 mole of 1-vinylcyclohexene-1 at room temperature for 7 days gave a 34% yield of bisadduct, m.p. 209–210°.

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.55; H, 8.71. Found: C, 81.87; H, 8.86.

Infrared absorption in potassium bromide pellet was 2970, 2955, 2925, 2905, 2862, 2830 (C—H), 1712 cm.$^{-1}$ (C=O); in carbon disulfide, 815 cm.$^{-1}$ (trisubstituted ethylene).

Bromination of Ia gave a bromide which was recrystallized from dioxane, m.p. 222° dec. This product darkened on standing and did not give satisfactory analytical data.

Hydrobromination of Ia to IVa.—Ia, dissolved in dichloromethane was treated with dry hydrobromic acid gas at 4° in the presence of a small amount of benzoyl peroxide until no more hydrobromic acid was absorbed. The solvent was removed *in vacuo* and the residue crystallized from dioxane to give a 60% yield of straw-colored prisms, m.p. 173–175° dec.

Anal. Calcd. for $C_{22}H_{30}Br_2O_2$: C, 54.37; H, 6.22. Found: C, 54.45; H, 6.32.

Catalytic Hydrogenation Ia to IIa.—Ia, 100 mg., in 10 ml. of dioxane was hydrogenated with 15 mg. of Adams catalyst; 1.83 moles of hydrogen was absorbed. The product was purified by crystallization from dioxane, m.p. 191–192°.

Anal. Calcd. for $C_{22}H_{32}O_2$: C, 80.55; H, 9.83. Found: C, 80.78; H, 9.96.

Infrared absorption in potassium bromide pellet was 2941, 2867 (C—H), 1700 cm.$^{-1}$ (C=O).

Dehydrogenation of Ia.—Ia (100 mg.) was mixed with 100 mg. of palladium black and heated at 300° for 1 hr. The product was extracted with benzene, chromatographed on a Florisil column and the residue was recrystallized from benzene. The colorless plates, m.p. 264–265°, 14 mg. (16.2% yield), gave no depression on admixture with dibenz[*a,h*]anthracene. Paper chromatography[12] of the mother liquors with N,N-dimethylformamide–hexane as solvent on Whatman No. 1 paper did not reveal the presence of dibenz[*a,j*]anthracene.

Isomerization of Ia to Ib. A. With Tetrahydrofuran and Hydrobromic Acid.—The bisadduct (1 g.) suspended in 200 ml. of tetrahydrofuran was treated with dry hydrobromic acid gas with stirring. The adduct went into solution, and a white precipitate gradually settled out from the transitory clear solution. The white crystalline product, 0.68 g. (yield 68%), was filtered off, m.p. 327–328°. The product was recrystallized from chloroform.

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.55; H, 8.71. Found: C, 81.45; H, 8.63.

Infrared absorption in potassium bromide pellet was 2987, 2965, 2950, 2938, 2920, 2870, 2857, 2835 (C—H), 1709 cm.$^{-1}$ (C=O); in carbon disulfide, 816, 825 (sh) cm.$^{-1}$ (trisubstituted ethylene).

B. With Methanolic Potassium Hydroxide.—Ia (100 mg.) was suspended in 10 ml. of dioxane and refluxed with 5 ml. of 10% methanolic potassium hydroxide in a nitrogen atmosphere for 3 hr. The bisadduct dissolved during the course of heating but the product crystallized out on cooling. The solvent was removed *in vacuo*, the residue was washed several times with water, dried *in vacuo*, and recrystallized twice from dioxane, m.p. 326–327°, undepressed on admixture with Ib. Ia was recovered unchanged when it was refluxed for 1 hr. with acetic anhydride.

Bromination of Ib to IIIb.—Ib (100 mg.) was suspended in dioxane, cooled to 0°, and a cold solution of 200 mg. of bromine in 10 ml. of dioxane was added with stirring. The insoluble starting material gradually disappeared as bromination proceeded. The reaction mixture was allowed to warm and stand at room temperature for 3 hr. in the presence of a slight excess of bromine. The solvent and excess bromine were evaporated under a stream of nitrogen and the residue was crystallized from chloroform–ether to give 120 mg. (yield 60%) of colorless needles, m.p. 217–218° dec.

Anal. Calcd. for $C_{22}H_{28}Br_4O_2$: C, 41.03; H, 4.38; Br, 49.61. Found: C, 40.57; H, 4.25; Br, 49.23.

Catalytic Hydrogenation of Ib.—Ib was hydrogenated as Ia was above. The product was purified by crystallization from ben-

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[10] V. Georgian and J. Lepe M., *J. Org. Chem.*, **29**, 45 (1964).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 51.

[12] B. L. Van Duuren, *J. Natl. Cancer Inst.*, **21**, 1 (1958).

zene followed by vacuum sublimation at 170° (0.05 mm.), m.p. 285–286°.

Anal. Calcd. for $C_{22}H_{32}O_2$: C, 80.55; H, 9.83. Found: C, 80.93; H, 9.56.

Infrared absorption in potassium bromide pellet was 2941, 2882 (C—H), 1715 cm.$^{-1}$ (C═O).

Dehydrogenation of Ib.—A mixture of isobisadduct, 100 mg., and 100 mg. of palladium black were heated at 300° for 1 hr. During the heating process a white solid sublimed on the side of the tube; subsequently the green fluorescence of dibenz[*a,h*]-anthracene appeared. The product was extracted with benzene and chromatographed on activated alumina to give several fractions. Dibenz[*a,h*]anthracene, m.p. 264–265°, was eluted with benzene, 14 mg. (yield 16.2%), melting point undepressed on admixture with an authentic sample.

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A Reinvestigation of the Condensation of Ethyl Tricarballylate with Benzaldehyde

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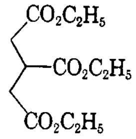
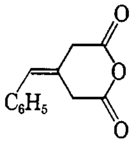
Received March 31, 1964

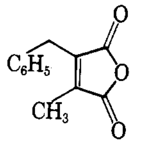
Müller[1] observed that ethyl tricarballylate (1,2,3-tricarboethoxypropane, I), benzaldehyde, and sodium ethoxide reacted to give a mixture of acidic esters which, upon saponification, followed by acidification and steam distillation, yielded an acid anhydride, $C_{12}H_{10}O_3$, m.p. 44–45°. This compound could not be converted to the free acid as acidification of its salts gave only the anhydride. On the basis of the elemental analysis, the neutralization equivalent and the elimination of several isomeric structures, Müller proposed that the compound was β-benzylideneglutaric anhydride II. In this paper evidence is presented which shows the compound to be benzylmethylmaleic anhydride III.



I



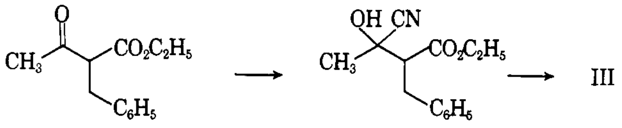
II



III

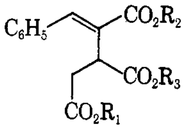
The anhydride was prepared according to Müller's directions,[1] except that the base-catalyzed condensation was effected by sodium hydride in benzene.[2] The product (m.p. 42.5–43.0°), isolated in 2% yield, had the elemental composition reported by Müller. The infrared spectrum showed bands at 1850, 1810, and 1760 cm.$^{-1}$, typical of a maleic anhydride moiety[3]; the ultraviolet spectrum in cyclohexane showed a maximum at 243 mμ (ε 5400); and the nuclear magnetic resonance spectrum consisted of three singlets at τ 2.87, 6.34, and 8.08 of relative areas 5.0:2.0:3.0. These spectra are clearly inconsistent with the structure of β-benzylideneglutaric anhydride and indicate the correct structure is that of benzylmethylmaleic anhydride III.

In order to confirm the structural assignment, benzylmethylmaleic anhydride III was synthesized by an alternate route. Triethylamine-catalyzed addition of hydrogen cyanide to ethyl 2-benzylacetoacetate (IV) afforded a mixture of the diastereomeric cyanohydrins V along with some unreacted keto ester IV. This mixture on being heated at reflux with concentrated hydrochloric acid afforded as neutral products, 4-phenylbutan-2-one (presence inferred from infrared band at 1720 cm.$^{-1}$) and the anhydride III which was separated by fractional crystallization. The latter was shown by mixture melting point determination and comparison of the ultraviolet and infrared spectra to be identical with the anhydride prepared according to Müller's directions.

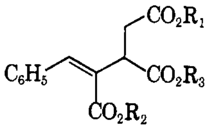


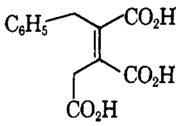
IV V

The reaction sequence which is considered to account best for the formation of III is shown below. Benzaldehyde condenses with ethyl tricarballylate in the manner of the Stobbe condensation[2] to give a mixture of acidic esters VIa and VIIa. Migration of the double bond of VIa or VIIa under the conditions of the condensation (or during the subsequent saponification) gives after saponification the triacid VIII which readily decarboxylates. Loss of water gives the anhydride III. It should be noted that the anhydride is derived from a "normal" Stobbe product (condensation occurring at a *methylene* carbon of ethyl tricarballylate).



VIa, $R_1 = R_2 = C_2H_5$; $R_3 = H$
b, $R_1 = H$; $R_2 = C_2H_5$; $R_3 = H$
c, $R_1 = C_2H_5$; $R_2 = H$; $R_3 = H$
d, $R_1 = H$; $R_2 = C_2H_5$; $R_3 = C_2H_5$





VIII

VIIa, $R_1 = R_2 = C_2H_5$; $R_3 = H$
b, $R_1 = H$; $R_2 = C_2H_5$; $R_3 = H$
c, $R_1 = C_2H_5$; $R_2 = H$; $R_3 = H$
d, $R_1 = H$; $R_2 = C_2H_5$; $R_3 = C_2H_5$

An alternative scheme for the formation of the anhydride III involves the formation of the acidic esters VId and VIId by the intermediacy of a six-membered lactone in the Stobbe condensation. These compounds would be at best only minor products of the condensation because of the known preference for the formation of five rather than six-membered lactonic intermediates

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(1) H. Müller, *Ber.*, **39**, 3590 (1906).

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(3) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 45.