introduction of a second alkyl group. Thus the presence of four alkyl groups activates the double bond to the point where reactivity approaches that of the *cis* olefin.

An alternative argument based on relative ground state stabilities can hardly be used to rationalize the greater reactivity of *cis* olefins relative to *trans* olefins, since it is difficult to envisage the significance of such a factor when the transition state is a cyclic structure with the positive charge primarily on sulfur. It would seem that in such circumstances there would be little lowering of the potential energy barrier due to the relief of *cis* interactions.

Experimental Section

Competitive rate determinations were conducted in the manner of the following example. A volumetric 250-ml *n*-heptane solution containing 3-methyl-1-butene (0.1 mol) and *trans*-2-pentene (0.1 mol), together with 0.05 mol of cyclopentane as an inert internal standard was subjected to three replicate vapor phase chromatographic analyses to determine the area ratio of each olefin to cyclopentane. A 100-ml aliquot was withdrawn, cooled to −70° and a quantity of methanesulfenyl chloride equivalent to 40 mol % of the initial unsaturation added slowly with stirring. After the CH_3SCl was consumed (starch–iodide test) the solution was reanalyzed in triplicate, withdrawing samples at −70, 0, and 25°. The ratio of initial to final concentrations provided sufficient data to utilize the expression

k(3-methyl-1-butene)/k(*trans*-2-pentene) =

$$\log \frac{(\text{methylbutene})_0}{(\text{methylbutene})} \Big/ \log \frac{(\text{pentene})_0}{(\text{pentene})}$$

to calculate the relative reaction of the two olefins.

A second increment of CH_3SCl sufficient for 60% total conversion of the initial unsaturation was then added and the reaction mixture reanalyzed in the same fashion. This procedure was duplicated on a second 100-ml aliquot of the standard solution, thus providing four values for each relative rate. Analytical conditions are tabulated in Table IV, p 873.

Registry No.—Methanesulfenyl chloride, 5813-48-9.

Acknowledgment.—The technical assistance of Mr. J. J. Werner is gratefully acknowledged.

Synthetic Approaches to Dibenzo-1,2,6,7-bisdehydro[10]annulene

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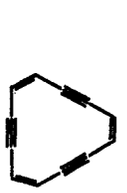
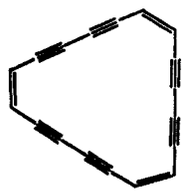
Received October 21, 1968

Several reactions designed to produce 1,5-dibenzo-3,8-bisdehydro[10]annulene were investigated. Evidence is presented for formation of derivatives of this π system as reactive intermediates in the reactions investigated.

By the principle of "ethynylogy" one may slice up [*n*]annulenes, insert *m* triple bonds and reclose to form 2*m*-dehydro[*n* + 2*m*]annulenes.[1] The benzene ethynologs **1** and **2** have been prepared recently.[2-5] The present paper details some work of ours on the dibenzo derivative (**4**) of 1,2,6,7-bisdehydro[10]annulene (**3**).



1



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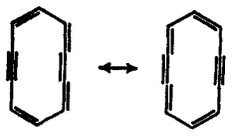
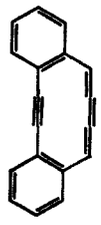


3



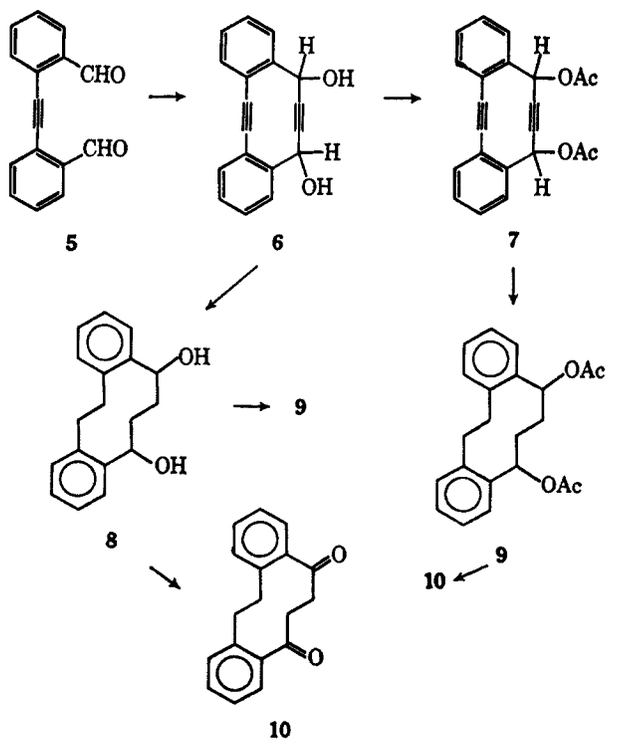
4

(1) T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).
(2) W. H. Okamura and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 5991 (1967).
(3) K. G. Untch and D. C. Wysocki, *ibid.*, **88**, 2608 (1966).
(4) R. Wolovski and F. Sondheimer, *ibid.*, **87**, 5720 (1965).
(5) F. Sondheimer, R. Wolovski, P. J. Garratt, and I. C. Calder, *ibid.*, **88**, 2610 (1966).

Results and Discussion

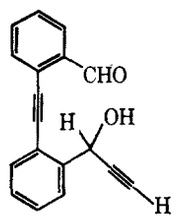
Construction of the ten-membered-ring system related to **4** was accomplished by a novel addition of acetylenedimagnesium bromide to 2,2′-diformyldiphenylacetylene (Scheme I). Reaction of a suspension of

SCHEME I

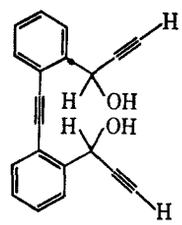


5 **6** **7** **8** **9** **10**

acetylenedimagnesium bromide in tetrahydrofuran[6] with dialdehyde **5** afforded in modest yield a mixture of three identifiable products. Two of them were the normal type of adducts **11** and **12** and were isolated in 4



11



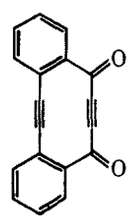
12

and 6% yields, respectively. Their structures rest on elemental analysis and their spectral properties. The bis adduct **12** was presumably a mixture of *meso* and *dl* forms but behaved as a single substance and possessed a reasonably sharp melting point, 122–124°. The third product, **6**, was isolated as a difficultly soluble material by trituration of the crude reaction product. It was isolated in 7% yield and characterized as its diacetate **7**, bis(trideuterio)acetate **7**-d_6, and monoacetate **6a**.

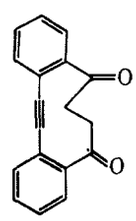
As isolated **7** appeared to be a single stereoisomer since its monoacetate showed a single AX pattern, J_{AX} = 2.2 Hz for the CHOH and CHOAc protons. In the absence of suitable conformationally rigid models of coupling through a triple bond,[7–11] the stereochemistry of **7** and its derivatives remain undefined.

Considerable attention was devoted to demonstrating that **6** did in fact possess a ten-membered ring. While **6** possessed an ultraviolet spectrum consistent with the assigned structure, similar to that of diphenyl acetylene but with loss of vibrational fine structure,[12] and its diacetate **7** was shown to have a molecular weight in the correct region by vapor pressure osmometry, the low yield of **6** coupled with its intractability and the possibility of isomerization accompanying its acetylation made this seem worthwhile. A cyclic series of transformations was carried out on **6** and diacetate **7**. Catalytic hydrogenation of **6** followed by acetylation of the somewhat unstable diol **8** afforded a saturated diacetate (**9**) identical with that prepared by hydrogenation of **7**. Oxidation of the diol **8** with Jones reagent[16] afforded a crystalline diketone (**10**). The same diketone was isolated when saturated diacetate **9** (from **7**) was cleaved by reaction with lithium alumium hydride and the unisolated diol product was oxidized. The available data leave little doubt as to the presence of the ten-membered ring in these compounds.

A number of reagents, whose aim was to effect the over-all elimination of the elements of hydrogen peroxide from **6** merely led to either no reaction or to its complete decomposition.[17–19] Oxidation followed by reduction was more informative. Diol **6** was allowed to stand with chromium trioxide in dimethylformamide[20] at −15°. To the reaction was added acetic anhydride, an excess of sodium borohydride, and controlled amounts of water. Several interesting compounds were isolated from this witches' brew. Diol **6** could be isolated. That it was unreacted starting material and not the reduction product of **13** follows from the deuterium composition (d_0) of its acetate derivative when sodium borodeuteride was used in place of sodium borohydride. The acetylenic diketone **14** was isolated in low yield.



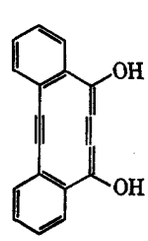
13



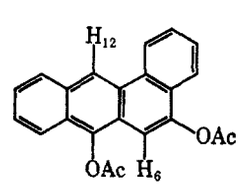
14

The uv spectrum of **14** is of interest in that the four-carbon chain constrains the two aromatic rings to lie in the same plane and the uv spectrum of **14** is very similar to that of the unconstrained dialdehyde **5**.[21]

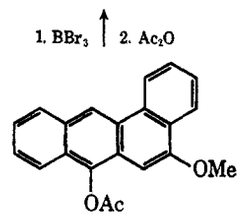
Substitution of sodium borodeuteride for sodium borohydride led to incorporation of 1.95 deuterium atoms into **14** (3% d_0, 16% d_1, 65% d_2, 14% d_3, and 2% d_4); so formation of **14** is most easily rationalized in terms of oxidation of **6** to **13** followed by two consecutive conjugate reductions of **13**. The labeling results are *not* consistent with reduction of **13** on oxygen to produce diol **15** as this should afford ultimately predominantly **14**-d_1.



15



16



The third substance to be isolated was identified as 5,7-diacetoxybenz[*a*]anthracene, **16**, by comparison with a sample synthesized as shown.

The benzanthracene isolated from the sodium borodeuteride contained approximately 1 deuterium per molecule (*e.g.*, 16.4% d_0, 60.2% d_1, and 23.7% d_2) that

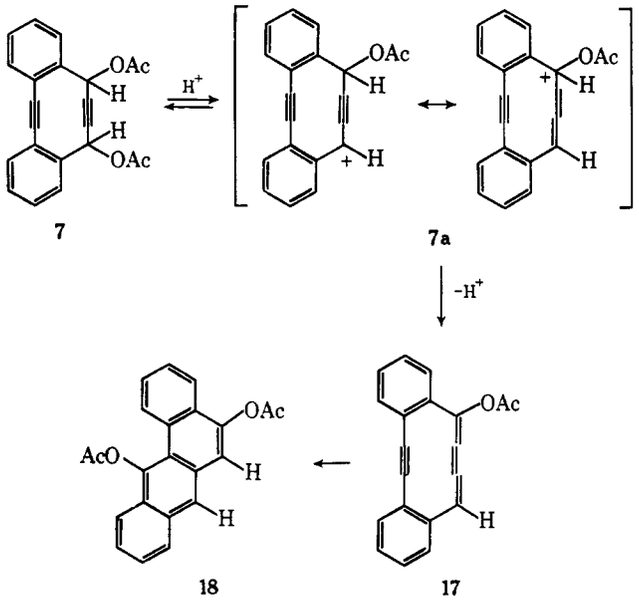
(6) H. H. Inhoffen, O. Isler, G. von der Bey, G. Raspe, P. Zeller, and R. Ahrens, *Ann. Chem.*, **580**, 7 (1953).
(7) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).
(8) B. Braillon, *J. Chim. Phys.*, **58**, 495 (1961).
(9) H. Taniguchi, I. M. Mathai, and S. I. Miller, *Tetrahedron*, **22**, 867 (1966).
(10) J. C. Craig and M. Moyle, *J. Chem. Soc.*, 4402 (1963).
(11) J. H. Van Boom, P. P. Montijn, L. Brandsma, and J. F. Ahrens, *Rec. Trav. Chim.*, **84**, 31 (1965).
(12) A number of other strained systems of this type show the same behavior.[13–15]
(13) F. Toda and M. Nakagawa, *Bull. Soc. Chem. Jap.*, **34**, 862 (1961).
(14) S. Akiyama, M. Nakagawa, and S. Misumi, *ibid.*, **33**, 1293 (1960).
(15) R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, **87**, 5720 (1965).
(16) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).
(17) R. Kuhn and H. Krausch, *Chem. Ber.*, **88**, 309 (1955).
(18) R. Kuhn and J. Jahn, *ibid.*, **86**, 759 (1953).
(19) Conversion of diol **7** into toluenesulfonate and methanesulfonate esters and deoxygenation with zinc in acetic acid were unsuccessful.
(20) G. Snatzke, *Chem. Ber.*, **94**, 729 (1961).
(21) H. Suzuki [*Bull. Chem. Soc. Jap.*, **33**, 389 (1960)] has concluded from MO calculations that the two rings of tolane are coplanar.

was about evenly distributed between H-6 and H-12.[22] The presumed lability of the unacetylated and unisolated diol, coupled with the ability of sodium borohydride to exchange its hydrogens with those of the medium,[25] leaves us unable to interpret this deuterium distribution.

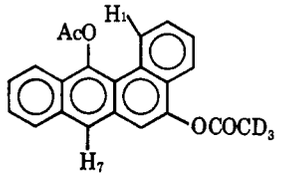
Formation of both **14** and **16** can reasonably be ascribed to the intermediacy of the annulene quinone **13** if one assumes that it is quite susceptible to nucleophilic attack on carbon.

The solvolysis of diacetate **7** was investigated. Our conclusions as to the processes involved are presented in a somewhat speculative form in Scheme II.

SCHEME II

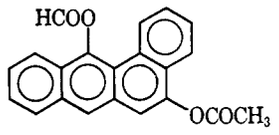


Solvolysis of **7** in acetic acid containing sulfuric acid afforded a single product in good yield whose assigned structure is **18.** The presence of a benz[*a*]anthracene ring system was apparent from comparison of its uv spectrum with that of **16.** The pattern of substitution follows from (1) the absence of the low field singlet at δ 8.7–8.9 assigned to H-12, (2) a singlet at 8.37 assigned[23,24] to H-7, and the presence of a low field multiplet (H-1) at 9.05–9.25, the latter at a somewhat lower field than absorptions due to H-1 in benz[*a*]anthracenes lacking a substituent at C-12. Solvolysis of **7**-d_6 in acetic acid–sulfuric acid afforded, by nmr, a 4:1 mixture of **18**-d_3 and **18**-d_0, **18**-d_3 being *one* (presumably



18-d_3

that shown) of the two isomers possible. Loss of one of the acetoxy groups of **7** to the solvent was confirmed when formolysis of **7** afforded a *single* formate acetate, presumably **19.**



19

The process responsible for formation of a mixture of **16**-d_3 and **16**-d_0 on acetolysis of isotopically pure **7**-d_6 is apparently recapture of the cation **7a** by acetic acid. It was demonstrated the exchange of acetate groups between **16** and acetic acid did *not* occur, but that recovery of **7**-d_6 on part reaction afforded starting material with an appreciably enhanced intensity acetyl CH_3 resonance in its nmr spectrum.

All in all one can reasonably interpret these experimental results in terms of the intermediacy of the acetoxybisdehydro[10]annulene **17.** If this is correct, there is sufficient cross-ring interaction in this type of molecule to render it quite susceptible to nucleophilic and electrophilic attack.

Experimental Section[26]

2,2′-Bis(hydroxymethyl)diphenylacetylene.—The procedure of Letsinger and Nazy[27] was used. Into a stirred solution of 50.09 g (0.149 mol) of 2,2′-dibromodiphenylacetylene in 500 ml of dry ether at 0° under nitrogen was injected 152 ml (0.31 mol) of *n*-butyllithium as a standard solution in heptane. After stirring at 0° for 15 min, the reaction mixture was treated with formaldehyde formed by heating an attached flask containing paraformaldehyde at 190° for 2 hr. Water was then added, the layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with dilute hydrochloric acid and water, dried, and evaporated to afford 49 g of a yellow crystalline material. Recrystallization of this from benzene–hexane afforded 18.5 g (52% yield) of 2,2′-bis(hydroxymethyl)diphenylacetylene, mp 122–126°. The analytical sample was prepared by repeated recrystallization from benzene–hexane: mp 130–131°; λ_{max}^{EtOH} 285 mμ (ϵ 24,800), 294 (18,100), 304 (22,100); δ ($CDCl_3$) 4.17 (2 H, singlet, OH), 4.91 (4 H, CH_2, singlet), 7.7–7.2 (8 H, multiplet ArH).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.83; H, 6.08.

The mother liquors from above were chromatographed on silica gel to afford an additional 3.8 g (11% yield) of the above diol and 3.3 g of 2-hydroxymethyldiphenylacetylene, mp 63–66°. Recrystallization of this from benzene–hexane afforded an analytical sample: mp 67.5–68°; λ_{max}^{EtOH} 278 mμ (ϵ 21,200), 283 (29,900), 292 (21,100), 302 (23,700); δ ($CDCl_3$) 2.44 (1 H, OH, singlet, exchangable with D_2O), 4.87 (2 H, CH_2, singlet), 7.6–7.1 (9 H, ArH, multiplet); *m/e* 208 (parent).

Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.76; H, 5.98.

Acetylation of 2,2′-bis(hydroxymethyl)diphenylacetylene afforded 2,2′-bis(acetoxymethyl)diphenylacetylene: mp 84.5–85.5°; λ_{max}^{EtOH} 285 mμ (ϵ 27,400), 293 (sh, 20,300), 304 (23,200); δ ($CDCl_3$) 2.10 (6 H, CH_3, singlet), 5.37 (4 H, CH_2, singlet), 7.6–7.2 (8 H, ArH, multiplet).

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.63; H, 5.60.

2,2′-Diformyldiphenylacetylene (**5**).—To a stirred solution of

(22) The low field position of H-12[23,24] in the nmr spectrum of **16** allows one to calculate H/D ratio there and the remainder is placed at H-6. The signal associated with H-6 is not separated from those of the remaining aromatic hydrogens.

(23) T. J. Batterham, L. Tsai, and H. Ziffer, *Aust. J. Chem.*, **18**, 1959 (1965).

(24) R. H. Martin, *Tetrahedron*, **20**, 897 (1964), and subsequent papers.

(25) W. L. Jolly and R. E. Masmer, *J. Amer. Chem. Soc.*, **83**, 4470 (1961).

(26) Nmr spectra were determined in the solvent shown and are referenced to internal tetramethylsilane, δ 0 ppm. "Work-up" involves partitioning a reaction mixture between water and ether, washing the ether layer, drying it over anhydrous sodium sulfate, and removing the solvent under reduced pressure. Melting points were determined on a calibrated hot stage.

(27) R. L. Letsinger and J. R. Nazy, *J. Amer. Chem. Soc.*, **81**, 3013 (1959).

12 g of chromium trioxide in 175 ml of pyridine at 10° was added over 30 min a solution of 5.3 g (0.022 mol) 2,2′-bis(hydroxymethyl)diphenylacetylene in 40 ml of pyridine. The mixture was stirred at 0° for 0.5 hr and at 25° for 2.5 hr. After an addition of 2 ml of methanol was added the mixture was diluted with ether (100 ml) and filtered. The filtrate was cooled to 5° and concentrated hydrochloric acid was added slowly with stirring until the mixture was acid to litmus. The layers were separated and the aqueous layer was extracted with three 50 ml-portions of chloroform. The combined organic layers were washed with dilute hydrochloric acid and water, dried, and evaporated. Recrystallization of the residue from ethyl acetate–hexane afforded 3.64 g (70% yield) of dialdehyde **5**, mp 99–104°. The analytical sample was prepared by repeated recrystallization from ethyl acetate–hexane: mp 103–104°; $\lambda_{max}^{CHCl_3}$ 4.5, 5.91 μ; λ_{max}^{EtOH} 239 mμ (ε 24,000), 245 (28,400), 282 (10,400), 291 (11,500), 333 (9200); δ ($CDCl_3$) 10.62 (2 H, **CHO**, singlet), 9.1–7.8 (2 H, Ar**H** *ortho* to CHO, multiplet), 7.7–7.3 (6 H, Ar**H**, multiplet).

Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 81.99; H, 4.39.

2-Formyl-2′-hydroxymethyldiphenylacetylene.—Repetition of the above oxidation at −78°, using a 1.5:1 molar ratio of diol to chromium trioxide afforded, upon chromatography on silica gel, a 56% recovery of starting diol and a 20% yield of the aldehyde alcohol: mp 77–78°; $\lambda_{max}^{CHCl_3}$ 2.76, 2.85, 4.51, 5.90 μ; λ_{max}^{EtOH} 254 mμ (ε 25,400), 278 (16,800), 284 (17,000), 293 (18,000), 328 (7300); δ ($CDCl_3$) 2.72 (1 H, O**H**, exchangeable with D_2O), 4.91 (2 H, CH_2OH, singlet), 7.7–7.2 (7 H, ArH, multiplet), 8.0–7.8 (1 H, ArH *ortho* to CHO, multiplet), 10.48 (H, **CHO**, singlet); *m/e* 236 (parent).

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.87; H, 5.29.

Addition of Acetylenedimagnesium Bromide to 2,2′-Diformyldiphenylacetylene.—Acetylenedimagnesium bromide was prepared by the general procedure of Inhoffen[6] by addition of gaseous acetylene to ethylmagnesium bromide [prepared from 37.1 g (0.34 mol) of ethyl bromide in ether]. The precipitated Grignard reagent was separated, washed with ether, and suspended in 750 ml of dry tetrahydrofuran. The stirred suspension was cooled to −5° under nitrogen and a solution of 11.98 g (0.051 mol) of dialdehyde **5** in 70 ml of dry tetrahydrofuran was added dropwise over 7 min. The reaction mixture was stirred at −5° for 6 hr. A saturated solution of ammonium chloride (50 ml) was added and the layers were separated. The aqueous layer was extracted with ether and the combined organic layers were washed with saturated salt solution, dried over anhydrous sodium sulfate, and evaporated. The resulting dark residue was triturated with methylene chloride (25 ml) and the insoluble material was dissolved in 600 ml of acetone. The acetone solution was decolorized (Norit) and evaporated to afford 0.794 g (5.9% yield) of dibenzo[*a,e*]cyclodeca-1,5-diene-3,8-diyne-7,10-diol (**6**), dec pt 250°, λ_{max}^{EtOH} 285 mμ (ε 21,600), whose structure follows from considerations dealt with below. The methylene chloride soluble material was chromatographed on silica gel to afford the following products in order of elution.

1.—The starting dialdehyde (0.3% yield) was eluted first with 1:9 ethyl acetate–benzene.

2.—An oil, 0.46 g (4% yield), was identified as the uncyclized adduct 2-formyl-2′-(1″-hydroxyprop-2″-ynyl)diphenylacetylene (**11**): δ ($CDCl_3$) 2.65 (1 H, C≡C**H**, doublet, J = 2 Hz), 3.34 (1 H, O**H**, singlet exchangeable with D_2O), 5.94 (1 H, CHOCH≡CH, doublet, J = 2 Hz), 7.2–8.0 (multiplet, 8–9 H, Ar**H**), 10.50 (1 H, **CHO**, singlet). It was characterized as its *p*-nitrophenylhydrazone, mp 201–202°.

Anal. Calcd for $C_{24}H_{17}N_3O_3$: C, 72.90; H, 4.33; H, 10.63. Found: C, 72.90; H, 4.19; N, 10.69.

3.—A solid was eluted third with 15:85 ethyl acetate–benzene (1.94 g). Trituration with methylene chloride afforded 0.92 g (6% yield) of 2,2′-bis(1″-hydroxyprop-2″-ynyl)diphenylacetylene (**12**): mp 98–105°, mp 112–114° (after recrystallization from ethyl acetate–hexane); λ_{max}^{EtOH} 286 mμ (ε 27,200), 304 (22,000); λ_{max}^{KBr} 3.1, 4.71 μ (C≡CH); δ ($CDCl_3$) 2.68 (2 H, C≡C**H**, doublet, J = 2 Hz), 3.20 (2 H, O**H**, exchangeable with D_2O), 5.96 (2 H, CHOHC≡CH, doublet, J = 2 Hz), 7.2–7.9 (8 H, Ar**H**, multiplet).

Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.98; H, 5.02.

4.—A solid, 0.13 g, was identified by its infrared (ir) spectrum as **6**.

7,10-Diacetoxydibenzo[*a,e*]cyclodeca-1,5-diene-3,8-diyne (7).—Acetylation of **6** (94 mg) with an excess of acetic anhydride in pyridine at room temperature for 11 hr afforded on work-up and recrystallization from benzene–hexane 91 mg (76% yield) of the diacetate **7**, dec pt 250°. The analytical sample was prepared by repeated recrystallization from benzene–hexane: dec pt 250°; $\lambda_{max}^{CHCl_3}$ 5.77 μ; λ_{max}^{EtOH} 221 mμ (ε 28,200), 284 (16,600) 307 (15,200); δ ($CDCl_3$) 2.00 (6 H, CH_3CO, singlet), 6.54 (2 H, CHOAC, singlet), 7.1–7.7 (8 H, ArH, multiplet); mol wt (vapor pressure osmometer) 340 (calcd 344). A mass spectrum could not be obtained.

Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.58. Found: C, 76.55; H, 4.66.

Repetition of the acetylation, using acetic anhydride-d_6 afforded the hexadeuteriodiacetate (no detectable signal at δ 2.0) in 70% yield.

Acetylation of 100 mg (0.385 mmol) **6** with 1 molar equiv of acetic anhydride (39 mg) in dry pyridine (3 ml) afforded the following materials: 38 mg of recovered diol, isolated by trituration of the crude product; diacetate **7**, 13 mg (10% yield); and monoacetate **6a**, 43 mg (37% yield), as an oil [$\lambda_{max}^{CHCl_3}$ 2.79, 2.92, 5.79 μ; δ ($CDCl_3$) 2.02 (3 H, $COCH_3$, singlet), 2.55 (1 H, O**H**, broad singlet, exchangeable with D_2O), 5.31 (1 H, C**H**OH, doublet, J = 2.2 Hz), 6.49 (1 H, C**H**OAC, doublet, J = 2.2 Hz), 7.2–7.6 (8 H, Ar**H**, multiplet)], characterized by acetylation to diacetate **7** in 92% yield.

7,10-Diacetoxydibenzo[*a,e*]cyclodeca-1,5-diene (9).—A solution of 68 mg (0.26 mmol) of **6** in 25 ml of dioxane was stirred under 1 atm of hydrogen in the presence of 75 mg of 30% Pd/C. Over 6 hr, 26.3 ml (4 equiv) of hydrogen were absorbed. The solution was filtered and the filtrate was diluted with water and extracted with ether. The combined ether extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated. The semisolid residue was immediately added to a mixture of 1 ml of acetic anhydride and 10 ml of pyridine and allowed to stand for 9 hr at 0° and 2 hr at room temperature. Work-up afforded 99 mg of a yellow-brown solid, mp 147–151° after trituration with ether–hexane. Recrystallization from benzene–hexane afforded a pure sample of **9**, mp 162–164°. Comparison of ir spectra and a mixture melting point with a sample of diacetate from hydrogenation of **7** showed the two samples to be identical.

Hydrogenation of 7,10-Diacetoxydibenzo[*a,e*]cyclodeca-1,5-diene-3,8-diyne.—Stirred with 80 mg of 30% Pd/C in 15 ml of ethyl acetate a 86-mg sample of **7** absorbed 4.1 equiv (26.1 ml) of hydrogen over 4.5 hr. Filtration and evaporation gave, on recrystallization from benzene–hexane, 67 mg (76% yield) of diacetate **9**, mp 157–164°. The analytical sample prepared by repeated recrystallization from benzene–hexane had mp 163–165°; λ_{max}^{KBr} 5.81 μ; λ_{max}^{EtOH} 266 mμ (ε 23,000), 273 (2300); δ (CCl_4) 1.78 (10 H, singlet), 3.20 (4 H, broad singlet), 5.2 (2 H, multiplet), 7.1–7.4 (8 H, Ar**H**, multiplet); mol wt (vapor pressure osmometer) 332 (calcd 352).

Anal. Calcd for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 74.83; H, 7.15.

Dibenzo[*a,e*]cyclodeca-1,5-diene-7,10-dione.—The crude diol from hydrogenation of 140 mg of **6** gave on oxidation with Jones reagent[16] 123 mg of a yellow semisolid. Chromatography on silica gel afforded 79 mg (64% yield) of **10**, mp 125–129°. Repeated recrystallization from benzene–hexane afforded the analytical sample: mp 132–133°; $\lambda_{max}^{CHCl_3}$ 5.93 μ; λ_{max}^{EtOH} 278 mμ (ε 1760), 242 (9700); δ ($CDCl_3$) 3.13 (8 H, CH_2, broad singlet), 7.0–7.2 (8 H, ArH, multiplet); δ (C_6H_6) 2.73 (4 H, CH_2, singlet), 2.99 (4 H, CH_2, singlet); *m/e* 264 (parent).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.67; H, 6.11.

The same diketone, by mixture melting point and ir spectrum, was prepared from hydrogenated diacetate **9** by sequential treatment with lithium aluminum hydride and Jones reagent. The over-all yield for the two steps was 38%.

Oxidation of 7,10-Dihydroxydibenzo[*a,e*]cyclodeca-1,5-diene-3,8-diyne.—The procedure of Snatzke[20] was used. To a stirred solution of 200 mg (0.77 mmol) of **6** in 20 ml of dry dimethylformamide at −13° ± 2° under nitrogen was added in one portion 200 mg (2.0 mmol) of chromium trioxide. One drop of a cold solution of 66 mg of concentrated sulfuric acid in 1 ml of dimethylformamide was immediately added and after stirring at −13° for 5 min the reaction mixture was cooled to −78°. Acetic anhydride (3 ml) was added in one portion followed by 0.227 g

(6 mmol) of sodium borohydride. Water (95 mg, 5.2 mmol) was added and the reaction mixture was allowed to warm to and stand at 0° for 1 hr. Work-up afforded 215 mg of red oil which on trituration with benzene gave 73 mg (37% yield) of insoluble starting diol **6**, identified by its ir spectrum. The benzene-soluble material was adsorbed on 70 g of deactivated silica gel[28] and eluted with 1.5% ethyl acetate in benzene to afford saturated diketone **14**: 3% yield; mp 224–225° (ether–methylene chloride); $\lambda_{max}^{CHCl_3}$ 5.98 μ; λ_{max}^{EtOH} 244 mμ (ε 25,000), 283 (8600), 291 (10,800), 326 (9800); δ ($CDCl_3$) 3.32 (4 H, $COCH_2$, singlet), 7.1–7.8 (6 H, ArH, multiplet), 7.9–8.2 (2 H, ArH, *ortho* to C=O, multiplet); *m/e* 260 (parent).

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.93; H, 4.74.

Dione **14** isolated from the above sequence using sodium borodeuteride in place of sodium borohydride had the following isotope composition: 3% d_0, 16% d_2, 14% d_3, and 2% d_4.

Also isolated was 8 mg (3% yield), 5,7-diacetoxybenz[*a*]anthracene: mp 197–198° (methylene chloride–ether); $\lambda_{max}^{CHCl_3}$ 5.69 μ; identical (ir spectra and mixture melting point) with a sample synthesized below.

5,7-Diacetoxybenz[*a*]anthracene.—The procedure of McOmie and Watts[29] was used. To a stirred solution of 1.0 g (3.16 mmol) of 7-acetoxy-5-methoxybenz[*a*]anthracene[30] in 20 ml of methylene chloride at −5° under nitrogen was added over 20 sec a solution of 1.7 ml (17.6 mmol) of boron tribromide in 5 ml of methylene chloride. After stirring at −5° for 30 min, the red reaction mixture was poured into water and the resulting precipitate was separated by filtration, pressed dry, and immediately dissolved in 20 ml of dry pyridine. To the pyridine solution was added 5 ml of acetic anhydride and the mixture was allowed to stand at room temperature for 12 hr. Water (10 ml) was added followed by addition of solid sodium carbonate until effervescence ceased. The mixture was diluted with ethyl acetate, and hydrochloric acid was added until the aqueous layer was acidic. The layers were separated and the organic layer was washed with dilute hydrochloric acid and water, dried over anhydrous sodium sulfate, and evaporated to afford 0.843 g of a red solid. Two recrystallizations from ethyl acetate afforded 341 mg (32% yield) of 5,7-diacetoxybenz[*a*]anthracene, mp 189–192°. The analytical sample, prepared by repeated recrystallization from benzene–hexane, had mp 196.5–197°; $\lambda_{max}^{CHCl_3}$ 5.69 μ; λ_{max}^{EtOH} 385 mμ (ε 700), 362 (6000), 348 (8500), 334 (7800), 318 (5300), 292 (81,100) 281 (73,300), 272 (42,000), 256 (39,800); δ ($CDCl_3$) 2.46 (3 H, COCH, singlet), 2.57 (3 H, $COCH_3$, singlet), 7.2–8.15 (8 H, ArH, multiplet), 8.70 (1 H, H-1, multiplet), 8.94 (1 H, H-12, singlet); *m/e* 344 (parent).

Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.78; H, 5.08.

Comparison of 5,7-diacetoxybenz[*a*]anthracene prepared as above with material isolated from oxidation–reduction acetylation of **6** showed them to be identical by the criteria of ir spectra and their mixture melting point, 196–197.5°.

Acetolysis of 7,10-Diacetoxydibenzo[*a,e*]cyclodeca-15-diene-3,8-dyne with Formation of 5,12-Diacetoxybenz[*a*]anthracene.—A solution of 50 mg (0.145 mmol) of **7** and 257 mg of sulfuric acid in 50 ml of dry acetic acid was allowed to stand at 25° for 4 hr and then poured into 300 ml of water. The aqueous layer was extracted with benzene and the benzene layers were washed with cold 5% sodium hydroxide solution and water, dried over Norit–anhydrous sodium sulfate, and evaporated to afford 31 mg of a red solid. Recrystallization from ether–methylene chloride gave 18 mg (36% yield) of 5,12-diacetoxybenz[*a*]anthracene, mp 195–199°. The analytical sample was prepared by recrystallization from ether: mp 200–201°; $\lambda_{max}^{CHCl_3}$ 5.76 μ; λ_{max}^{EtOH} 386 mμ (ε 1600), 362 (6800), 350 (8900), 336 (7800), 302 (9300), 288 (74,100), 278 (75,700), 268 (50,000), 260 (43,800); δ ($CDCl_3$) 2.54 (3 H, $CPCH_3$, singlet), 2.64 (3 H, $COCH_3$, singlet), 7.43 (1 H, singlet, H-6), 7.5–7.85 (6 H, ArH, multiplet), 7.9–8.18 (2 H, multiplet, H-4, H-11), 8.37 (1 H, singlet, H-7), 9.05–9.25 (1 H, multiplet, H-1); *m/e* 344 (parent).

Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.77; H, 4.76.

Repetition of this experiment, following its progress by uv spectrometry, showed that the maximum concentration of 5,12-diacetoxybenz[*a*]anthracene (corresponding to a 76% yield) was reached after 3 hr at 25°. After this time the concentration dropped off.

Acetolysis of 7,10-di(trideuterioacetoxy)dibenzo[*a,e*]cyclodeca-1,5-diene-3,8-diyne (**7**-d_6) afforded a 30% yield of a mixture of **16**-d_0 and **16**-d_3: δ ($CDCl_3$) 2.53 (0.75 H, $COCH_3$), 2.64 (3 H, $COCH_3$), 7.43 (1 H, H-6), 7.89–8.2 (2 H, H-4, H-11), 8.37 (1 H, H-4), 9.05–9.25 (1 H, H-1); *m/e* (10 V) 347 (rel intensity 2.2), 344 (rel intensity 1), 305 (rel intensity 4.5), 302 (rel intensity 11).[31] Resubjecting this diacetate to the acetolysis reaction conditions afforded recovery of diacetate with unchanged mass and nmr spectra.

Acetolysis of 30 mg of **7**-d_6 in 30 ml of acetic acid containing 154 mg of sulfuric acid at 25° for 15 min afforded a 65% recovery of **7** whose nmr spectrum showed δ ($CDCl_3$) 2.00 (0.30 H, $COCH_3$, singlet), 6.52 (2 H, CHOAc, singlet), 7.17–7.75 (8 H, ArH, multiplet).

Formolysis of 7,10-Diacetoxydibenzo[*a,e*]cyclodeca-1,5-diene-3,8-diyne with Formation of 5-Acetoxy-12-formyloxybenz[*a*]anthracene.—A solution of 31 mg of **7** in 50 ml of 95% formic acid was allowed to stand at room temperature for 25 min and then poured into water. The resulting precipitate was separated by filtration and dried to give 20 mg of a brown semisolid. Repeated recrystallization from ether gave an analytical sample of **19**: mp 137–138°; λ_{max}^{EtOH} 385 mμ (ε 1400), 361 (5800), 348 (7600), 335 (6500), 301 (9100), 286 (64,200), 276 (67,200), 267 (47,800); δ ($CDCl_3$) 2.54 (3 H, $COCH_3$, singlet), 7.29–7.85 (6 H, ArH, multiplet), 7.94–8.22 (2 H, H-4, H-11, multiplet), 8.37 (1 H, H-7, singlet), 8.43 (1 H, OOCH, singlet), 9.08–9.28 (1 H, H-1, multiplet).

Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.36; H, 4.27. Found: C, 76.16; H, 4.32.

Registry No. — 2,2′-Bis(hydroxymethyl)diphenylacetylene, 18887-49-5; 2′-hydroxymethyldiphenylacetylene, 13141-40-7; 2,2′-bis(acetoxymethyl)diphenylacetylene, 18887-51-9; **5**, 18887-52-0; 2-formyl-2′-hydroxymethyldiphenylacetylene, 18887-53-1; **6**, 18887-54-2; **6a**, 18887-55-3; **7**, 18887-56-4; **9**, 18887-57-5; **10**, 18887-58-6; **11**, 18887-59-7; **11** *p*-nitrophenylhydrazone, 18887-60-0; **12**, 18887-61-1; **14**, 18887-62-2; **16**, 18887-63-3; **18**-d_0, 18887-64-4; **18**-d_3, 18887-65-5; **19**, 18887-66-6.

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(28) A slurry of 300 g of silica gel in 500 cc of water was filtered and dried at 90° for 8 hr.

(29) J. F. W. McOmie, M. L. Watts, and D. E. West, *Tetrahedron*, **24**, 2289 (1968).

(30) L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, **60**, 1893 (1938).

(31) Corrected for natural isotope abundance.