Experimental Section

Nmr spectra were recorded on a Varian A-60 using tetramethylsilane as the internal standard and carbon tetrachloride or deuteriochloroform as the solvent. Infrared spectra were recorded on a Perkin-Elmer 257 in CCl_4 and CS_2 as solvents. All melting points were taken on a Mel-Temp apparatus and are uncorrected.

10-Ethyl-10-phenylanthrone.—To a stirred solution of 38 g (0.148 mol) of 10-ethyl-10-chloroanthrone[3] and 140 ml of dried benzene maintained between 45–50° was slowly added (2.5 hr) 20.0 g (0.150 mol) of aluminum chloride. After all of the aluminum chloride was added, the solution was hydrolyzed by pouring onto a mixture of ice and concentrated hydrochloric acid. The mixture was separated, and the aqueous portion was extracted once with ether. The combined organic extracts were washed successively with 1% NaOH and saturated NaCl solution and then dried over Na_2SO_4. The solvent was evaporated to a volume of 100 ml; 200 ml of ligroin was added; and the solution was allowed to cool to give 38.5 g (0.126 mol, 85% yield) of 10-phenyl-10-ethylanthrone, mp 151–152° (analytical). The ir spectrum has characteristic bands at 1670 (s), 1600 (s), 1320 (s), 1300 (s), 930 (s) and 695 (s) cm^{-1}. The nmr spectrum has peaks centered at τ 1.7 (multiplet, 2 H), 2.6–3.2 (multiplet, 11 H), 7.5 (quartet, $J = 7$ cps, 2 H), and 9.7 (triplet, $J = 7$ cps, 3 H).

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.60; H, 6.18.

10-Phenyl-10-ethyl-9-methylene-9,10-dihydroanthracene.—A solution of methylmagnesium iodide was prepared from 1 g (0.04 g-atom) of magnesium and 5.7 g (0.040 mol) of methyl iodide in 40 ml of dry ether, and to it was added dropwise a solution of 10 g (0.034 mol) of 10-phenyl-10-ethylanthrone dissolved in 150 ml of dry ether and 15 ml of dry THF. The mixture was stirred for 7 hr at room temperature and then hydrolyzed with an NH_4Cl solution. The ether layer was separated, washed with saturated NaCl solution, dried (Na_2SO_4), and evaporated to dryness.

The 10 g of crude solid product (9-phenyl-9-ethyl-10-methyl-10-hydroxy-9,10-dihydroanthracene) and 0.5 g of *p*-toluenesulfonic acid in 200 ml of dry benzene were heated under reflux for 2 hr. The solution was allowed to remain at room temperature overnight, and then the benzene was removed under vacuum. The 10 g of crude product was column chromatographed on 400 g of activated alumina. The olefin was eluted with 95:5 mixture of pentane and benzene to give a total weight of 5.8 g (0.196 mol, 62% yield) of an oil which was crystallized from acetonitrile, mp 97–99°.

The infrared spectrum had characteristic bands at 1620 (s), 880 (s), and 690 (s) cm^{-1}. The nmr spectrum has peaks centered at τ 2.4 (multiplet, 2.2 H), 2.8–3.5 (multiplet, 11 H), 4.4 (singlet, 2 H), 7.7 (quartet, $J = 7$ cps, 2 H), and 9.45 (triplet, $J = 7$ cps, 3 H).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.11; H, 6.81.

9-Methyl-10-ethyltriptycene.—To 0.150 g of 9-phenyl-9-ethyl-10-methylene-9,10-dihydroanthracene was added 9 ml of polyphosphoric acid. The flask was kept under N_2, heated to 110°, and stirred for 40 hr. During this time the solution changed from deep maroon to brown-yellow to a dark orange-yellow. The flask was cooled, and water was added. The solid was filtered, and preparative thin layer chromatography of this solid on silica gel PF with 7.3 pentane-benzene afforded a band which weighed 0.152 g. The compound was recrystallized from acetonitrile–ethanol, mp 182.5–184°.

The infrared spectrum had strong bands at 1450 (s), 745 (s), and 740 (s) cm^{-1}. The nmr spectrum had a slightly unsymmetrical A_2B_2 between τ 2.7 and 3.4 (12 H), 7.1 (quartet, $J = 7$ cps, 2 H), 7.8 (singlet, 3 H), and 8.4 (triplet, $J = 7$ cps, 3 H); λ_{max}^{EtOH} 263 mμ (sh), 270 (log ϵ 3.45) and 278 (log ϵ 3.55).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.19; H, 6.90.

To 0.2 g of crude 9-phenyl-10-methyl-10-hydroxy-9,10-dihydroanthracene was added 10 ml of polyphosphoric acid, and the mixture was heated to 95° and stirred for 72 hr under nitrogen. Hydrolysis yielded a crude solid which was analyzed by vpc (SE-52 column at 260°) and shown to be 9-methyl-10-ethyltriptycene (80% yield, based on peak areas) by comparison with an authentic sample.

Registry No.—I, 17398-80-0; II, 17407-18-0; 10-phenyl-10-ethylanthrone, 17407-19-1.

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[3] P. L. Julian, W. Cole, and T. F. Wood, *J. Amer. Chem. Soc.*, **57**, 2508 (1935).

The Hydroboration of 10-Benzylidene-9-anthrones

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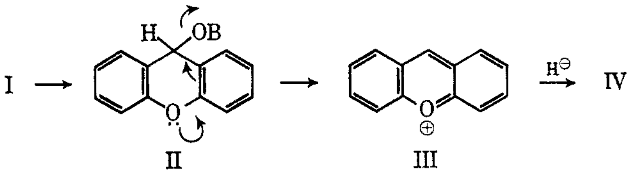
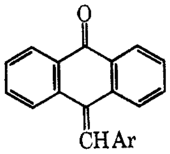
Whereas diaryl ketones are reduced by diborane to the corresponding diarylcarbinols, Wechter[1] has shown that xanthone (I), thioxanthone, and acridone are converted by hydroboration into the methylene compounds [*e.g.*, xanthone (I) yields xanthene (IV)]. This difference may be ascribed to the ability of these three ketones to give fully aromatic positive ions, *e.g.*, the case of xanthone (I) to give positive ion III (*via* II).

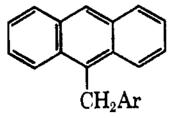


The reduction of the ion III to IV requires a hydride ion, supplied by the diborane. It should be borne in mind that a zwitterionic form of I contributes significantly to the ground state of the xanthone molecule, as indicated by its dipole moment[2] and its infrared frequency (1660 cm^{-1});[3] this makes I a good substrate for the hydroboration reaction.

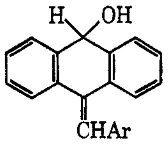
The interesting observation has now been made that 10-arylmethylene-9-anthrones (V) are reduced by diborane to 9-arylmethylanthracenes (VI) (see Table I for details), while lithium aluminium hydride yields the normal reduction products of the carbonyl group VII. The carbonyl group in V is highly polar (for Ar = C_6H_5, $\nu_{C=O}$ 1658 cm^{-1}), so that here too some zwitterionic contribution to the ground state exists.



V



VI



VII

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[1] W. J. Wechter, *J. Org. Chem.*, **28**, 2935 (1963).

[2] See, *e.g.*, E. D. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1318 (1936).

[3] E. D. Bergmann and S. Pinchas, *J. Chim. Phys.*, **49**, 537 (1952).

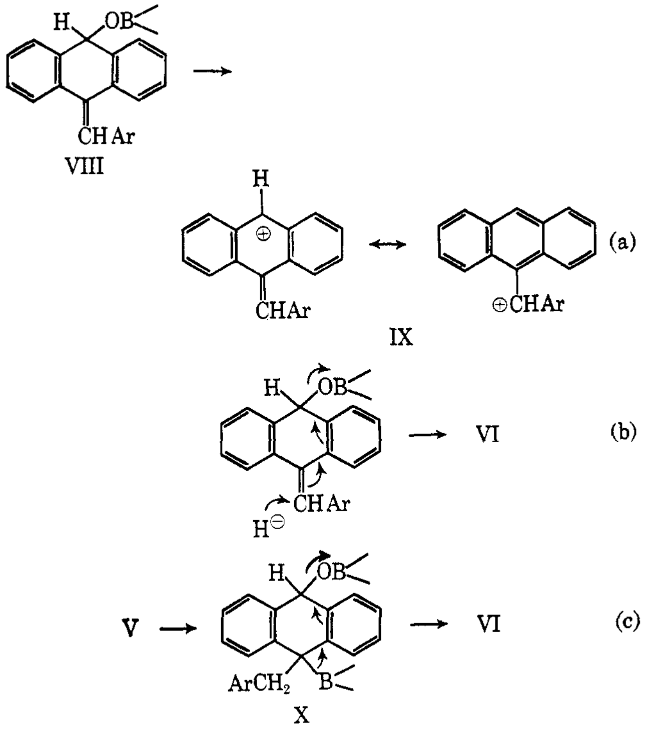
TABLE I

DIBORANE REDUCTION OF 10-BENZYLIDENE-9-ANTHRONES (V)

		9-Benzylanthracenes (VI)								
						Analysis, %				
Registry no.	Ar	Formula	Yield, %	Mp, °C	Recryst from	C, calcd	C, found	H, calcd	H, found	Remarks
VIa, 1498-71-1	C_6H_5	$C_{21}H_{16}$	65	133-134	EtOH	94.0	94.2	6.0	5.7	*a*, *b*
VIb, 1498-79-9	$4\text{-}CH_3C_6H_4$	$C_{22}H_{18}$	70	151	*n*-PrOH	93.6	93.3	6.4	6.1	
VIc, 17407-22-6	$4\text{-}ClC_6H_4$	$C_{21}H_{15}Cl$	63	129	C_6H_6-C_6H_{14}	83.4	83.1	4.9	4.9	*c*
VId, 17407-23-7	$2\text{-}ClC_6H_4$	$C_{21}H_{15}Cl$	60	121	EtOH	83.4	83.2	4.9	4.7	
VIe, 17407-24-8	$4\text{-}CH_3OC_6H_4$	$C_{22}H_{18}O$	65	130	*n*-PrOH	88.6	88.8	6.0	5.8	

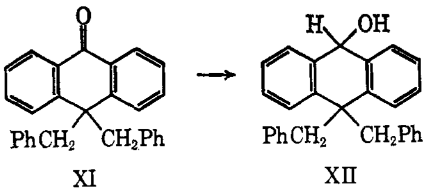
[a] λ_{max}^{EtOH} 220 mμ (log ε 4.32), 257 (5.15), 320 (3.60), 333 (3.52), 349 (3.83), 368 (4.00), 389 (4.00). The other benzylanthracenes had practically identical uv spectra.[b] [b] Described by E. de B. Barnett, J. W. Cook, and T. E. Ellison, *J. Chem. Soc.*, 885 (1928): mp 134°; mmp 134°. [c] Described by E. de B. Barnett and J. L. Wiltshire, *Ber.*, **62**, 3072 (1929), mp 129°.

Three mechanisms can be considered to explain the results of this reaction. (a) An intermediate carbonium ion IX is formed by the ionization of the borate VIII; this carbonium ion can abstract a hydride ion from diborane. (b) An attack of a hydride ion is on the exocyclic carbon with concerted elimination of a borate ion from VIII, to give directly VI. (c) An addition of borane to the exocyclic double bond occurs, so that the boron atom is linked to the carbon in the cyclic system (this manner of addition is favored by the directive effect of the oxygen).[4] The formed boron-borate X undergoes a 1,4 elimination to give VI. The fact that lithium aluminium hydride does give the normal reduction product of the carbonyl VII seems to rule out mechanisms a and b and thus to favor mechanism c.



The result of hydroboration was identical, whether the reaction mixture was decomposed with water, aqueous alkali, or alkaline hydrogen peroxide solution.

10,10-Dibenzyl-9-anthrone (XI), in contrast to V, is reduced by diborane to 10,10-dibenzyl-9,10-dihydro-9-anthrol (XII). This shows that cyclic ketones without an activating group like a double bond or a heteroatom react with diborane in a similar manner to the open-chain diaryl ketones—a normal hydride reduction.



Experimental Section

The experiments were carried out in the manner described previously[5] with 2 g of the compounds V. The starting materials were prepared according to the literature;[6-8] 10,10-dibenzyl-9-anthrone (XI) was prepared according to Hallgarten.[9]

10,10-Dibenzyl-9-anthrone (XI) and Diborane.—The reaction was carried out in the same manner as for the benzylidene-anthrones (VI). The product was recrystallized from *n*-propyl alcohol: mp 180°; 75% yield. The ir spectrum showed the presence of a hydroxyl group so that the compound was 10,10-dibenzyl-9,10-dihydro-9-anthrol (XII).

Anal. Calcd for $C_{28}H_{24}O$: C, 89.3; H, 6.3. Found: C, 89.2; H, 6.6.

10-Benzylidene-9,10-dihydro-10-anthrol (VII, Ar = C_6H_5) (from V, Ar = C_6H_5, and Lithium Aluminum Hydride).—Lithium aluminum hydride (0.6 g) was added under an inert atmosphere to 4 g of 10-benzylidene-9-anthrone in 50 ml of dry ether. After refluxing for 2 hr 50 ml of tetrahydrofuran was added, and reflux was continued for another 3 hr. The usual work-up yielded 3 g of an oil which upon trituration with methanol precipitated as white crystals, mp 120°. The ir spectrum showed the presence of a hydroxyl group (ν 3300 cm^{-1}). The molecular ion appeared at *m/e* 284 and the base peak at 261 (M − OH). The product turned into the yellow starting material at room temperature.

10-(*p*-Chloro)benzylidene-9,10-dihydro-10-anthrol (VII, Ar = $4\text{-}ClC_6H_4$) (from V, Ar = $4\text{-}ClC_6H_4$, and Lithium Aluminum Hydride).—The reduction was carried out according to the above described procedure. The result was an unstable white crystalline product, mp 110°. The ir spectrum showed the presence of a hydroxyl group, and the molecular ion appeared at *m/e* 318; ratio M:M + 2 = 3:1; strong peaks appeared at *m/e* 301, 283, 281.

Registry No.—VII (Ar = C_6H_5), 17407-25-9; VIII (Ar = $4\text{-}ClC_6H_4$), 17407-26-0; XII, 17407-27-1.

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[4] J. Klein and E. Dunkelblum, *Tetrahedron Lett.*, 6047 (1966).

[5] M. Rabinovitz, G. Salemnik, and E. D. Bergmann, *ibid.*, 3271 (1967).

[6] J. W. Cook, *J. Chem. Soc.*, 2160 (1926).

[7] A. Haller and R. Padova, *C. R. Acad. Sci., Paris*, **141**, 857 (1905).

[8] E. D. Bergmann, M. Rabinovitz, and S. Glily, *Tetrahedron*, **8**, 141 (1966).

[9] F. Hallgarten, *Ber.*, **21**, 2508 (1888).