ethanol gave 18.5 g (43%) of **3**, mp 130–132.5° (lit.[8] mp 131°). The ir spectrum was identical with a reference scan.

Hydrolysis of 2 (X = Cl).—A mixture of 9 g (0.025 mol) of **2** (X = Cl) was suspended in 100 ml of concentrated hydrochloric acid and was heated at reflux with stirring for 7 hr. Complete solution did not occur. After cooling at room temperature overnight the solid was collected, washed thoroughly with water, and air dried to give a 5-g (56%) recovery of the starting material, mp 210.5–212.5°, whose ir spectrum was unchanged.

The filtrate was evaporated *in vacuo* at 50–60° to give 1.5 g of residue, which, upon recrystallization from 4:1 ethanol–water gave 0.8 g of ethylenediamine dihydrochloride, mp 325–327° dec (lit.[1] mp 327° dec). Based on a 4-g loss of **2** (X = Cl) this represents a 62% recovery of dihydrochloride.

1,2-Bis(trichloroacetamido)propane.—Using procedure A, 88 g (1.2 mol) of propylenediamine in 450 ml of ethanol was allowed to react with 426 g (2.4 mol) of methyl trichloroacetate in 450 ml of ethanol to give 361 g (82%) of product: mp 201–202° (lit.[1] mp 196–197°); $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 3.02, 6.53 (NH), 5.91 (C=O), 12.15 μ (CCl_3).

Anal. Calcd for $C_7H_8Cl_6N_2O_2$: C, 23.04; H, 2.21. Found: C, 22.89; H, 2.34.

Using procedure A the following amides were prepared.

1,2-Bis(tribromoacetamido)propane.—Propylenediamine (0.02 mol) and 0.04 mol of ethyl tribromoacetate in 16 ml of ethanol gave 1.5 g (11.9%) of product: mp 201.5–203° (isopropyl alcohol); $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 2.99, 6.65 (NH), 5.95 (CO), 16.6 μ (CBr_3).

Anal. Calcd for $C_7H_8Br_6N_2O_2$: C, 13.31; H, 1.26; N, 4.44. Found: C, 13.90; H, 1.18; H, 4.61.

Bromoform was shown to be present in the ethanol filtrate from the crude amide by glpc analysis.

1,2-Bis(trifluoroacetamido)propane.—Propylenediamine (0.05 mol) and ethyl trifluoroacetate (0.1 mol) in 18 ml of ethanol gave 5 g (38%) of product: mp 146–148°; $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 3.0, 6.38 (NH), 5.79, 5.87 (CO), 8.26, 8.37, 8.67 μ (CF_3).

Anal. Calcd for $C_7H_8F_6N_2O_2$: N, 10.53. Found: N, 10.98.

1,2-Bis(chlorodifluoroacetamido)propane.—Propylenediamine (0.05 mol) and methyl chlorodifluoroacetate (0.1 mol) gave 3 g (20%) of product: mp 132–136° (isopropyl ether–hexane); $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 3.06 6.43 (NH), 5.93 (CO), 8.5, 8.8 (CF), 13.6, 14.5 μ (CCl).

Anal. Calcd for $C_7H_8Cl_2F_4N_2O_2$: N, 9.37; Found: N, 9.27.

1,2-Bis(dichlorofluoroacetamido)propane.—Propylenediamine (0.045 mol) and 0.09 mol of methyl dichlorofluoroacetate in 20 ml of ethanol gave 4.5 g (26%) of product: mp 171–173° (ethanol); $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 3.02, 6.45 (NH), 5.87 (CO), 9.23 (CF), 11.6, 15.15 μ (CCl).

Anal. Calcd for $C_7H_8Cl_4F_2N_2O_2$: N, 8.44. Found: N, 8.66.

Registry No.—Ethylenediamine, 107-15-3; propylenediamine, 78-90-0; **2** (X = Cl), 17408-50-3; **3**, 120-93-4; 1,2-bis(trichloroacetamido)propane, 17408-51-4; 1,2-bis(tribromoacetamido)propane, 17408-52-5; 1,2-bis(trifluoroacetamido)propane, 17408-53-6; 1,2-bis(chlorodifluoroacetamido)propane, 17408-54-7; 1,2-bis(dichlorofluoroacetamido)propane, 17408-55-8.

(8) E. Fischer and A. Koch, *Ann.*, **232**, 277 (1886).

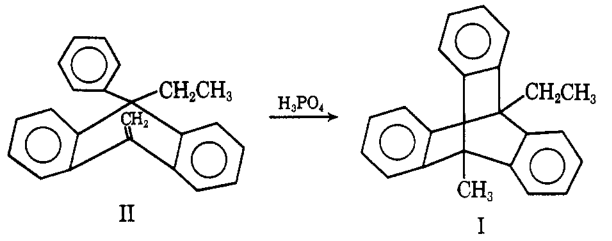
A New Synthesis of Triptycene Systems[1]

H. M. Walborsky and T. Bohnert

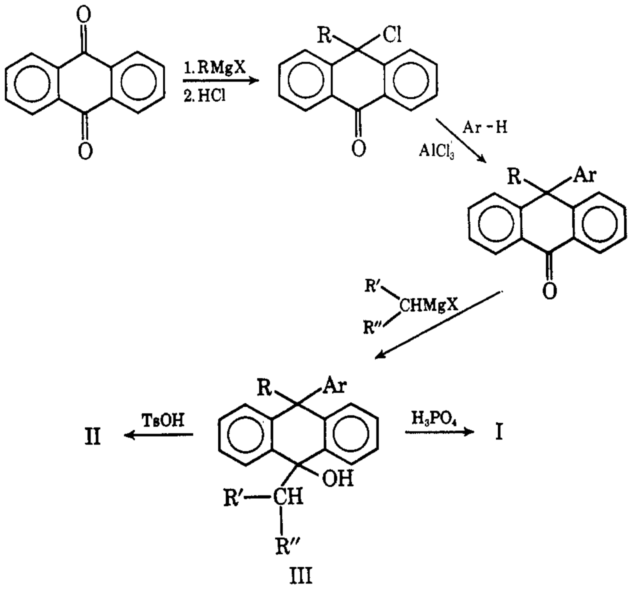
Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Received May 20, 1968

Syntheses of triptycene and substituted triptycenes have been limited to the use of Diels–Alder-type condensations using benzyne intermediates or quinones as the dienophile and anthracenes as the diene. There have also been some limited studies to prepare substituted triptycenes by carrying out electrophilic substitutions on triptycene itself.[2] A serendipitous observation in our laboratory has led to a synthesis of triptycene which has the potential for the preparation of a wide variety of triptycene derivatives. The discovery that 9-ethyl-10-methyltriptycene (I) is formed in excellent yield when 9-phenyl-9-ethyl-10-methylene-9,10-dihydroanthracene (II) is placed in polyphosphoric acid is the basis of this new synthesis. This reaction is not surprising in view of the required boat conformation of the 9,10-dihydroanthacene system and the resulting close proximity of the diaxial positions of C-9 and C-10.



The synthesis of the starting material (II) is straightforward and proceeds in good yield starting from anthraquinone. Moreover, it is not necessary to use II since its precursor (*i.e.*, III, R′ = R″ = H) gives identical results.



The variability of substitution patterns and the different types of substituents that can be employed is readily apparent. Furthermore, in the Friedel–Crafts step one could use substituted aromatics or even polynuclear aromatics which would lead to even more diverse substitution patterns as well as to entirely different types of systems.

No further experimental work to utilize this type of triptycene synthesis is planned. However, many different aspects of the chemistry of II are under active investigation.

---

(1) This work was supported by Public Service Research Grant No. CA 04065-10 from the National Cancer Institute.

(2) C. Paget and A. Burgar, *J. Org. Chem.*, **30**, 1329 (1965), and references cited therein.

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.

---

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

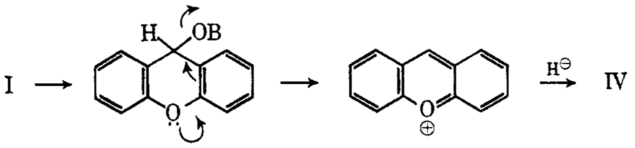
The Hydroboration of 10-Benzylidene-9-anthrones

MORDECAI RABINOVITZ AND GAD SALEMNIK

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Received May 2, 1968

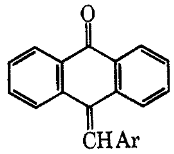
Whereas diaryl ketones are reduced by diborane to the corresponding diarylcarbinols, Wechter[1] has shown that xanthone (I), thioxanthone, and acridone are converted by hydroboration into the methylene compounds [*e.g.*, xanthone (I) yields xanthene (IV)]. This difference may be ascribed to the ability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



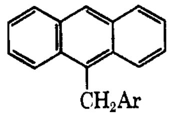
II III

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.

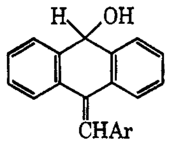
The interesting observation has now been made that 10-arylmethylene-9-anthrones (V) are reduced by diborane to 9-arylmethylanthracenes (VI) (see Table I for details), while lithium aluminium hydride yields the normal reduction products of the carbonyl group VII. The carbonyl group in V is highly polar (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

---

[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).