num chloride, and sodium chloride were used on a weight ratio of 1:3:0.4, respectively. The liquid reaction mixtures were analyzed by v.p.c. and infrared spectrophotometry and were shown to be unchanged starting materials.

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Lithium Aluminum Hydride Reduction of 9-Anthraldehyde and Related Compounds

Kurt C. Schreiber and William Emerson

Department of Chemistry, Duquesne University, Pittsburgh, Pennsylvania

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The reduction of 9-anthraldehyde in refluxing tetrahydrofuran leads not to the expected 9-anthrylcarbinol but to the formation of mainly 1,2-di-(9-anthryl)ethane. Further investigation of the reaction indicates that the first step in the reaction is the normal reduction to the carbinol, followed by a coupling step to form 1,2-di(9-anthryl)ethanol, which by a β-elimination process is converted to the 1,2-di(9-anthryl)ethene and finally converted to the corresponding ethane. Cleavage of the ethane by lithium aluminum hydride to 9-methylanthracene is also demonstrated. Other aromatic aldehydes have also been investigated for the coupling reaction.

In connection with another investigation, it was necessary to prepare 9-hydroxymethylanthracene (II). Noting the observation of Romo and Romo de Vivar[1] that 9-anthraldehyde (I) on refluxing with lithium aluminum hydride (LAH) in tetrahydrofuran gives 1,2-di(9-anthryl)ethanol (74%, IV) and 1,2-di(9-anthryl)ethane (11%, III), it was decided to investigate the reduction of I with LAH in more detail.

Like most aldehydes,[2] I is reduced by LAH in ether to the corresponding carbinol in a 60% yield. However, owing to the slight solubility of I in ether the procedure is inconvenient since either the aldehyde has to be added in the solid state or slowly extracted into the lithium aluminum hydride solution by means of Soxhlet extractor. In either case the reaction is quite slow. In addition, the aluminum complex of the reaction product precipitates from the ether solution and is difficult to decompose. The reduction can be carried out conveniently using sodium borohydride in tetrahydrofuran, in which 9-anthraldehyde is readily soluble. The 9-hydroxymethylanthracene (II) is thus obtained in 70% yield.

In repeating the work of Romo and Romo de Vivar[1] in refluxing tetrahydrofuran, a 60% yield of III and no IV was obtained. By lowering the reaction temperature to 25–35°, the results comparable with those previously reported[1] were obtained, 50% of IV and 10% of III being isolated. Decreasing the ratio of LAH to I from 2.8 to 0.75 had little effect on the products obtained, giving 61% of IV and 8% of III.

The reduction at 65° was run for 8 hr. instead of 2.5 hr. in an attempt to improve the yield of 1,2-di(9-anthryl)ethane. The amount of LAH was decreased because of the results obtained at 25–35°. An increase in the yield of ethane from 60 to 70% was observed. In one reduction of I at 65°, III was directly isolated from the reaction mixture by filtration before hydrolysis, thus showing that it is not in the form of a metal complex at the end of reaction. Since carbon–oxygen cleavage seemed to be occurring in the reduction of 1,2-di(9-anthryl)ethanol (IV) to the ethane, a similar cleavage of the intermediate 9-hydroxymethylanthracene could yield 9-methylanthracene (V). Therefore, a careful search for V was made and a 10% yield of it was isolated. Increasing the reflux time to 24 hr. gave a decreased yield of III while the yield of V increased. This seemed to indicate that V could also be formed by the LAH cleavage of III. This was further confirmed by carrying out the reduction for 7 days and also by reducing carefully purified III with LAH. In both cases a 24% yield of V was obtained. Since the cleavage of a carbon–carbon single bond is involved in this step, it is not surprising to find that this reaction is very slow.

From the formation of II in the reduction of I by LAH in ether, it would seem logical to assume that this compound is first formed in all the reductions and that the other products are obtained from further reaction of this initial product. This was substantiated by quenching the reaction mixture of I and LAH in tetrahydrofuran at 25–35° immediately after the addition of the aldehyde solution, obtaining a 56% yield of II. Even under these conditions a 4% yield of III was obtained. Small amounts of III can be isolated owing to the great insolubility of III. After the hydrolysis of the reaction mixture, all other reaction products dissolved in benzene, leaving behind III, which was collected by filtration. From the other experiments, it would seem that III must be formed by way of 1,2-di(9-anthryl)ethanol (IV) and, therefore, some IV should be present in the reaction mixture, but none was obtained since small amounts of IV are very difficult to isolate.

Further confirmation that 9-hydroxymethylanthracene (II) is an intermediate in the formation of III and IV was obtained by reaction of II with LAH under conditions used for I. The results, both at 25–35 and 65°, were comparable.

Finally, the reduction of IV with LAH in tetrahydrofuran at 65° gave 65% of III, thus indicating that IV could be an intermediate in the formation of III.

From these experimental results, the following sequence of steps is suggested. The first step is the normal aldehyde reduction.

$$\text{I} \longrightarrow \text{II} \longrightarrow \text{IV} \longrightarrow \text{III} \longrightarrow \text{9-methylanthracene}$$

The second step represents the coupling of two anthracene units. The evolution of hydrogen gas during the conversion of II to III and of IV to III has

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[1] J. Romo and A. Romo de Vivar, *Bol. inst. quim. Univ. Nal. auton. Mex.*, **8**, 10 (1956).

[2] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

TABLE I

HYDROGEN EVOLUTION IN REDUCTION OF 9-ANTHRYL COMPOUNDS

Reactant (mmoles)	Step in reaction	Vol. of gas, cc. (mmoles of H_2 evolved)[a]	Reaction occurring
V (9.08)[b]	IV added to THF	35 (1.5)	THF contd. about 0.06% H_2O
	V added at 10° for 30 min.	230 (10.3)	Formation of alcohol–Al complex
	After reflux for 18 hr.	179 (8.0)	Conversion of V to III
II (19.5)	IV added to THF	42	THF contd. about 0.06% H_2O
	II added at 10° for 30 min.	473 (21.1)	Formation of alcohol–Al complex
	Standing at 25° for 5 hr.	30 (1.33)	Coupling to V
	After reflux for 18 hr.	151 (6.74)	Conversion of V to III

[a] Volume of gas evolved in the particular step. [b] From the reaction mixture at the end of the experiment, 5.9 mmoles of III was isolated.

TABLE II

LITHIUM ALUMINUM HYDRIDE REDUCTIONS OF 9-ANTHRYL DERIVATIVES

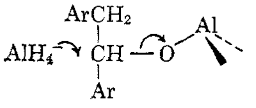
Expt.[a]	Reactant[b]	Time, hr.	Temp. °C.	Mole ratio[c]	$ArCH_2OH$, %	$ArCH_2CHOHAr$, %	$(ArCH_2)_2$, %	$ArCH_3$, %
I C2a	ArCHO	0.5[d]	25–35	0.75	58		4	
I C2b	ArCHO	5	25–35	2.79		50	10	
I C2b	ArCHO	5	25–35	0.75		61	8	
I C1	ArCHO	2.5	65	2.79			60	
I C3	ArCHO	8	65	1.00			70	10
I C3	ArCHO	24	65	1.00			65	14
I C3	ArCHO	168	65	1.00			40	24
II A	ArCOOH	6	65	1.50			64	
II B	$ArCH_2OH$	5	25–35	0.75		75	12	
II C	$ArCH_2OH$	5	65	2.63			59	12
II D	$ArCH_2CHOHAr$	2.5	65	5.26			65	
II E	$ArCH_2CH_2Ar$	168	65	2.00			65 (recovered)	24
II F	$ArCH{=}CHAr$	2.5	65	8.33			78	

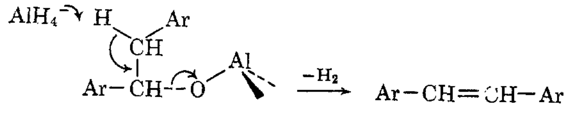
[a] See Experimental Sections. [b] Ar = 9-anthryl. [c] Ratio of moles of LAH to moles of reactant. [d] Time of addition of aldehyde to LAH; all other times after addition was complete.

been studied and the results are summarized in Table I. The data indicate that 1 mole of hydrogen is evolved in the reaction of the aluminum complex of IV to III. In the conversion of II to III, however, little hydrogen was evolved after the formation of the alcohol–aluminum complex during 5 hr. at room temperature. Previous experiments have shown that the coupling takes place under these conditions (see Table II). The small amount of hydrogen evolved can be explained from the further conversion of IV to III, which previous experiments have shown would take place in 8 to 10% yield under these conditions.

The conversion of 1,2-di(9-anthryl)ethanol (IV) to the corresponding ethane (III), is similar to the reduction of 1,2-diphenyl-2-chloropropane[3] with LAH and the reduction of 1,2-diphenyl-2-propanol with dichloro aluminum hydroxide.[3] In the former reaction, a 38% yield of olefin and 62% yield of 1,2-diphenylpropane was obtained, while in the second reaction 61% of olefin and 39% of the hydrocarbon was obtained.

The conversion of IV to III can be pictured either as an SN2 or E2 type of carbon–oxygen cleavage. The direct nucleophilic displacement (shown below) is analogous to the reduction of a toluenesulfonate[4] with LAH or the reductive opening of an epoxide[5] with LAH. The E2 pathway can be formulated as a two-step sequence involving 1,2-di(9-anthryl)ethene as an intermediate, as the product of the initial β-elimination, followed by the hydrogenation of the ethene to form III.





1,2-Di(9-anthryl)ethene, independently obtained by the elimination reaction of IV acetate with potassium hydroxide, is reduced by lithium aluminum hydride in tetrahydrofuran at 65° to 1,2-di(9-anthryl)ethane in 78% yield. In Table I, the hydrogen gas evolution for the reduction of IV to III is given. The amount of hydrogen evolved at 65° corresponds closely to the amount of III and V isolated. Thus, it seems that the ethanol goes through the ethene in reduction to the ethane.

There seems to be little tendency for 9-hydroxymethylanthracene (II) to react further with LAH when the solvent is ether. It was noted before that the aluminum complex of II is quite insoluble in ether and precipitates as it is formed, whereas in tetrahydrofuran the complex remains in solution and further reaction can occur. Probably this difference in solubility in the two solvents is the reason for the difference in the reactions.

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(3) J. H. Brewster, H. O. Bayer, and S. F. Osman, *J. Org. Chem.*, **29**, 110 (1964).

(4) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949).

(5) L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949); R. Fuchs and C. A. Vander Werf, *ibid.*, **74**, 5915 (1952).

Since the reductive coupling of 9-anthraldehyde by LAH in tetrahydrofuran is of unusual character, it was of interest to look for a similar reaction in other aromatic aldehydes. In this study benzaldehyde, mesitaldehyde, 1-naphthaldehyde, 2-naphthoic acid, and 9-phenanthraldehyde were investigated.

Benzaldehyde, refluxed in tetrahydrofuran with 0.7 mole of LAH for 2.5 hr., gave 86% of benzyl alcohol. Benzyl alcohol, treated similarly with 1.5 moles of IV for 18 days and for 50 days, respectively, gave recoveries of benzyl alcohol of 85 and 96%, respectively. Since the work of Brewster[4] has shown that reduction to hydrocarbon is possible in the 1,2-diphenylpropyl system, it must be assumed that the step which is difficult here must be the reductive coupling.

Mesitaldehyde, refluxed 6 hr. with 1.0 mole of LAH, gave mesitylcarbinol (65%) and di(mesitylcarbinyl) ether (20%). The latter compound was probably formed during hydrolysis of the reaction mixture.

1-Naphthaldehyde, refluxed 5 hr. with 2.8 moles of IV, gave 74% of 1-naphthylcarbinol. When 1-naphthaldehyde was refluxed for 22 days with 2.0 moles of LAH, a 41% yield of 1-naphthylcarbinol was obtained by crystallization of the crude product and chromatographing the noncrystalline residue. From the chromatograph two widely separated fractions were obtained (see Experimental Section). The first was an additional small amount of the carbinol. The second was a viscous oil which could not be crystallized. It had a strong –OH band in the infrared and was very likely a mixture probably containing some 1,2-di(1-naphthyl)-ethanol by analogy to the reduction reactions observed with 9-anthraldehyde and 9-phenanthraldehyde (see below).

2-Naphthoic acid, refluxed with 1.5 moles of LAH for 72 hr., gave 70% of 2-naphthylcarbinol, and 12% of the acid was recovered.

9-Phenanthroic acid, refluxed 8 hr. with 2.0 moles of LAH, gave 31% of 9-hydroxymethylphenanthrene. 9-Phenanthraldehyde, treated for 4 days at 65° with 1.0 mole of LAH, gave 58% of 9-hydroxymethylphenthrene and 17% of 1,2-di(9-phenanthryl)ethanol.

From a comparison of these results with those obtained in the reductions of 9-anthraldehyde, an order of reactivity toward reductive coupling might be established as follows: 9-anthryl $\gg$ 9-phenanthryl $\cong$ 1-naphthyl > phenyl. From the single experiment with the 2-naphthyl system it is difficult to place it in this series, but, considering the length of time at reflux (72 hr.) and the yield of normal reduction product (70%), it might be assumed to be somewhere between phenyl and 1-naphthyl. These differences need to be explained in terms of the relative ability of the different aromatic systems to stabilize the transition state intermediate for the conversion of hydroxymethylarene to 1,2-diarylethanol.

Experimental Section

Materials.—Tetrahydrofuran (Matheson Coleman and Bell) was dried by refluxing over sodium metal for 2 days and distilled, collecting the fraction boiling at 64.5–65°. 9-Anthraldehyde was prepared by the method of Campaigne and Archer.[6] The lithium aluminum hydride (LAH) and sodium borohydride were Metal Hydrides grades 95 and 98%+, respectively.

I. Reduction of 9-Anthraldehyde (I). A. With Sodium Borohydride.—To 9.5 g. (0.25 mole) of sodium borohydride in 100 ml. of tetrahydrofuran was added a solution of I (103 g., 0.50 mole) in 500 ml. of tetrahydrofuran over 45 min. After refluxing for 5 hr., 400 ml. of tetrahydrofuran was distilled. The cooled residue was poured with stirring into a mixture of 500 ml. of concentrated hydrochloric acid and 500 g. of finely crushed ice. Stirring was continued for 15 min., and 1 l. of water was added. The product (68.6 g. and 14 g. obtained on concentration of the mother liquor) was washed with water and recrystallized from ethyl acetate yielding 72.8 g. (70%) of 9-hydroxymethylanthracene (II), m.p. 156–158°, lit.[7] m.p. 151–152°.

B. With Lithium Aluminum Hydride (LAH) in Ether.—I (50.0 g., 0.24 mole) was added in portions over 45 min. to 5.0 g. (0.13 mole) of LAH in anhydrous ether. A considerable amount of the yellow aldehyde remained undissolved after addition was complete. The reaction mixture was refluxed with vigorous stirring for 19 hr. during which time the aldehyde went into solution and a greyish white precipitate formed, making the reaction mixture almost solid. The remaining LAH was decomposed by addition of 25 ml. of ether acetate, followed by 500 ml. of water, and the vigorous stirring was continued for 16 hr. to decompose the complex. The reaction mixture was diluted with 1 l. of water; the product was collected by suction filtration and washed with 750 ml. of 4 *M* hydrochloric acid. After several recrystallizations from ethyl acetate, 30.1 g. (60%) of II, m.p. 155–157°, was obtained.

C. With Lithium Aluminum Hydride (LAH) in Tetrahydrofuran.—All of the reactions listed in Table II were carried out by the same general procedure up to the point of isolation of the products. The variables of temperature, time, and ratio of LAH to reactant are indicated in Table I. Thus, a single example, the reduction I with LAH at 65° shown below, describes the general procedure. The isolation of the products will be described for each individual experiment.

1. Reduction of I at 65°.—A solution of I (4.00 g., 0.019 mole) in 50 ml. of tetrahydrofuran was added over 10 min. with stirring to LAH (2.00 g., 0.053 mole) in 50 ml. of tetrahydrofuran. The reaction mixture was refluxed with stirring for 2.5 hr. After cooling, the mixture was decomposed by successively adding 10 ml. of ethyl acetate, 200 ml. of water, and 50 ml. of concentrated hydrochloric acid. The procedure up to this point is general for all the reductions discussed below. The mixture was then poured into 200 ml. of water and stirred for 10 min. The solid product was washed with 400 ml. of water and crystallized from toluene yielding 2.19 g. (60%) of 1,2-di(9-anthryl)-ethane (III), m.p. 314–316°, lit.[8] m.p. 308–313°.

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.34; H, 5.75.

2a. Reduction of I (0.10 Mole) at 25–35°.—After decomposition, the reaction mixture was extracted with 100 ml. of benzene and filtered. Recrystallization of the solid from benzene gave 0.20 g. of III, m.p. 314–316°. The aqueous layer of the reaction mixture was extracted twice more with 100 ml. of benzene. The combined benzene extracts were successively washed with 50-ml. portions of 20% sodium chloride, 10% sodium carbonate, and again 20% sodium chloride and dried over Drierite. Evaporation of the solvent under reduced pressure gave 24.6 g. of partially solidified material, which was recrystallized several times from ethyl acetate, yielding 12.0 g. (58%) of II, m.p. 156–158°, as well as 0.42 g. of additional III. Thus, the total yield of III was 0.72 g. (4%).

2. Reduction of I (0.019 Mole) at 25–35°.—The reaction mixture, after decomposition, was poured into 200 ml. of water and stirred 10 min., and the product was isolated by filtration, washed with water, and recrystallized from ethyl acetate to give 1.92 g. (50%) of 1,2-di(9-anthryl)ethanol (IV), m.p. 203–208°. Several further recrystallizations gave the pure material, m.p. 210–211°.

Anal. Calcd. for $C_{30}H_{22}O$: C, 90.42; H, 5.57. Found: C, 90.13; H, 5.86.

From the residue which did not dissolve in ethyl acetate a 10% yield of II (0.35 g., m.p. 312–15°) was obtained.

This experiment was repeated with a lower LAH to aldehyde ratio, yielding 61% of IV and 8% of III.

IV was identified by preparing the acetate and converting this to the olefin. A solution of 2.00 g. (0.005 mole) of 1,2-di(9-

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[6] E. Campaigne and W. L. Archer, *J. Am. Chem. Soc.*, **75**, 989 (1953).

[7] K. Alder and K. Heimbach, *Ber.*, **86**, 1312 (1953).

[8] I. M. Roitt and W. A. Water, *J. Chem. Soc.*, 2407 (1952).

anthryl)ethanol, 0.9 ml. (0.012 mole) of acetyl chloride, and 0.9 ml. (0.011 mole) of pyridine in 25 ml. of benzene was refluxed for 2 hr., cooled to room temperature, filtered to remove pyridine hydrochloride, and evaporated under reduced pressure on a water aspirator. The crude product was recrystallized from a mixture of 20 ml. of benzene and 175 ml. of cyclohexane, yielding 1.93 g. (88%) of 1,2-di(9-anthryl)ethyl acetate, m.p. 186.5–187.5°.

Anal. Calcd. for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49. Found: C, 87.14; H, 5.59.

A solution of 1.80 g. (0.0041 mole) of the acetate and 8.00 g. (0.14 mole) of potassium hydroxide in a mixture of 18 ml. of 95% ethanol and 18 ml. of benzene was refluxed for 4 hr. After cooling, the product was collected by filtration and recrystallized from benzene, giving 0.50 g. (32%) of 1,2-di(9-anthryl)ethene, m.p. 309–312°.

Anal. Calcd. for $C_{30}H_{30}$: C, 94.70; H, 5.30. Found: C, 94.69; H, 5.50.

3. Reduction of I (0.10 Mole) at 65°.—After decomposition, the reaction mixture was filtered, yielding 14.30 g. of crude product. Recrystallization from a mixture of benzene and toluene gave 12.74 g. of 1,2-di(9-anthryl)ethane (III), m.p. 315–317°. The aqueous layer of the reaction mixture was extracted three times with 200 ml. of benzene; the combined extracts were dried over Drierite and anhydrous sodium carbonate and evaporated under reduced pressure giving 5.10 g. of dark tarry product. This was dissolved in the benzene–toluene mother liquor from the above crystallization and concentrated to 20 ml. An additional quantity (0.66 g., m.p. 313–315°) of III was obtained on cooling, thus giving a 70% total yield of III. The filtrate was concentrated to 10 ml. and chromatographed on a benzene-wetted alumina column (Merck, reagent grade) and eluted with benzene, yielding, after recrystallization from 50 ml. of 95% ethanol, 1.88 g. (10%) of 9-methylanthracene (V), m.p. 80–82°, lit.[9] m.p. 80–81°.

Repeating this experiment but extending the reaction time to 24 and 168 hr., respectively, gave 65 and 40% of III as well as 14 and 24% of V.

4. Reduction of 9-Anthraldehyde at 65° (Product Isolated before Hydrolysis).—The reaction mixture, from 0.02 mole of I and 0.02 mole of LAH, was refluxed for 5 hr., cooled to 0°, and filtered yielding III (2.85 g., 75%).

II. Reduction of Other 9-Substituted Anthracenes with Lithium Aluminum Hydride in Tetrahydrofuran.—The general procedure described in expt. C1 was employed in these experiments, again with the exception of the variables listed in Table I.

A. Reduction of 9-Anthroic Acid at 65°.—Not only the general procedure but also the isolation of product in this experiment was carried out in a manner identical with that described in expt. C1, yielding 64% of III.

B. Reduction of II (0.10 Mole) at 25–35°.—The reaction mixture, after decomposition, was further diluted with 800 ml. of water and stirred for 15 min., and the partially solidified product was isolated by decantation and washed with 500 ml. of water. The product was extracted with 400 ml. of ethyl acetate, leaving a residue, which, on recrystallization from benzene, gave 1.05 g. of III. An additional amount (1.20 g.) of this compound was obtained on concentration of the ethyl acetate solution to 150 ml., thus giving a total yield of 12% of III. The remaining filtrate was evaporated to dryness and the residue was recrystallized several times from a mixture of cyclohexane and benzene, yielding 14.87 g. (75%) of 1,2-di(9-anthryl)ethanol (IV), m.p. 204–209°.

C. Reduction of II (0.076 Mole) at 65°.—After decomposition, the reaction mixture was poured into 800 ml. of 3 *M* hydrochloric acid and stirred 15 min. The solid was recrystallized from benzene, yielding 8.56 (59%) of III. The filtrate was concentrated to 5 ml. and chromatographed on an alumina column previously wetted with benzene. Elution of product with benzene gave material which on recrystallization from 95% ethanol yielded 1.72 g. (12%) of 9-methylanthracene, m.p. 80–82°.

D. Reduction of IV (0.010 Mole) at 65°.—The reaction mixture, after decomposition, was poured into dilute hydrochloric acid and stirred 15 min. The crude product was recrystallized from toluene, giving 2.50 g. (65%) of III.

E. Reduction of III at 65°.—After decomposition, filtration of the reaction mixture from the reduction of 19.25 g. of 1,2-di-(9-anthryl)ethane (III) gave a solid which, after recrystallization from a mixture of benzene and toluene, was identified as unreacted III (12.43 g., m.p. and m.m.p. 315–317°). The filtrate was chromatographed on a benzene-wetted alumina column. Elution was first carried out with benzene, and then with tetrahydrofuran. The tetrahydrofuran eluates on concentration gave a solid which on recrystallization from 95% ethanol gave 1.72 g. of 9-methylanthracene (V), m.p. 80–82°. The benzene eluates yielded on recrystallization 0.14 g. of III, m.p. 313–315°, and the filtrate was rechromatographed. The fractions were eluted with cyclohexane and then with 20% benzene–80% cyclohexane. From this eluate, after recrystallization from 95% ethanol, 2.85 g. of V was obtained. Thus the total yield of V was 4.56 g. (24%) and the recovery of III was 12.57 g. (65%).

F. Reduction of 1,2-Di(anthryl)ethene (0.00032 Mole) at 65°.—After decomposition of the reaction mixture, III (0.094 g., 78%, m.p. and m.m.p. 314–316°) was isolated by suction filtration. The infrared spectrum of the product was identical with that of authentic material.

G. Reduction of 1,2-Di(9-anthryl)ethanol (IV) at 65°.—In this and the following reaction the apparatus was set up to collect the gas evolved during the reaction. A 100-ml. three-necked flask with a condenser and two 25-ml. round-bottom flasks attached by means of rubber stoppers and tubing was used. The top of the condenser was connected with rubber tubing to a water-filled graduated cylinder in a water trough. The two 25-ml. flasks were charged with 0.94 g. (0.0247 mole) of LAH and 3.62 (0.00908 mole) of IV, respectively, and the reaction flask was charged with 60 ml. of tetrahydrofuran. Thus the reactants could be added, and the reaction could be completed in a system closed throughout. The reaction flask was placed in a water bath at 10° resting on a magnetic stirrer.

The reaction was carried out in three steps, the volume of gas evolved being determined at each step. The results are listed in Table I. First, the LAH was added to the tetrahydrofuran and the solution was stirred for 15 min. at 10°. Second, IV was added and the reaction mixture was stirred for 30 min. at 10°. Finally, the reaction mixture was refluxed for 18 hr. and cooled to 10° and the volume was determined. After decomposition, the reaction mixture was extracted with 40 ml. of benzene and filtered, giving III (2.06 g., 61%). The benzene extract was dried over Drierite and anhydrous sodium carbonate, the solvent was removed with a water aspirator, and the residue was sublimed at 160°, yielding 0.61 g. (17%) of V, m.p. 79–81°, m.m.p. 80–82° with an authentic sample.

H. Reduction of II at 65°.—This reaction was run as described in detail in the previous experiment. The volume of gas given off was determined at four stages: (1) after adding the LAH and stirring 15 min. at 10°, (2) after adding II and stirring 30 min. at 10°, (3) after stirring the reaction mixture at 25° for 5 hr., and (4) after refluxing for 18 hr. The reaction mixture 4.06 g. (0.0195 mole) of II and 1.80 g. (0.0474 mole) of LAH was worked up as before yielding 60% of III and 12% of V.

III. Reductions of Other Aromatic Aldehydes, Carbinols, and Acids with Lithium Aluminum Hydride in Tetrahydrofuran at 65°.—The general procedure up to isolation described in expt. I C1 was again used. Table III lists the experiments showing the variables of time and ratio of LAH to reactant.

A. Reduction of Benzaldehyde (0.15 Mole).—The reaction mixture, after decomposition, was extracted three times with 100 ml. of ether; the combined extracts were washed successively with 25 ml. of 10% sodium carbonate and 25 ml. of water and dried over anhydrous magnesium sulfate, and the solvent was removed on the steam bath. The residue was distilled under reduced pressure, yielding 12.40 g. (76%) of benzyl alcohol: b.p. 91.0–91.5° (8 mm.), n^{26}_{D} 1.5385; lit. b.p. 92° (10 mm.),[10a] n^{20}_{D} 1.5395.[10b]

B. Attempted Reduction of Benzyl Alcohol (0.20 Mole).—The reaction mixture after 50 days was worked up as described in expt. III A. Benzyl alcohol was recovered (96%), b.p. 92–93° (10 mm.), n^{26}_{D} 1.5388.[10]

C. Reduction of Mesitaldehyde (0.10 Mole).—After decomposition, the reaction mixture was extracted twice with 200 ml. of benzene, the extracts were dried over Drierite and anhydrous sodium carbonate, and the solvent was removed under reduced pressure with a water aspirator. The residue, on recrystal-

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[9] W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, **60**, 481 (1938).

[10] (a) J. Meisenheimer, *Ber.*, **41**, 1420 (1908); (b) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1953, p. 270.

TABLE III

LITHIUM ALUMINUM HYDRIDE REDUCTIONS OF OTHER AROMATIC SYSTEMS

Expt.[a]	Reactant	Time, hr.	Mole ratio[b]	Products	% yield
III A	C_6H_5HO	2.5	0.70	$C_6H_5CH_2OH$	76
III B	$C_6H_5CH_2OH$	1200	1.12	$C_6H_5CH_2OH$	96
III C	2,4,6-$(CH_3)_3$ C_6H_2CHO	6	1.00	2,4,6-$(CH_3)_3C_6H_2CH_2OH$	65
				Ether of above	20
III D	2-$C_{10}H_7COOH$	72	1.50	2-$C_{10}H_7CH_2OH$	70
				2-$C_{10}H_7COOH$ (recovered)	12
III E	1-$C_{10}H_7CHO$	5	2.72	1-$C_{10}H_7CH_2OH$	74
III F	1-$C_{10}H_7CHO$	528	2.00	1-$C_{10}H_7CH_2OH$	41
				1-$C_{10}H_7CH_2CHOHC_{10}H_7$-1 (?)	20 (crude)[c]
III G	9-$C_{14}H_9CHO$[d]	96	1.00	9-$C_{14}H_9CH_2OH$	58
				$C_{14}H_9CH_2CHOHC_{14}H_9$	16

[a] See Experimental Section. [b] Ratio of moles of LAH to moles of reactant. [c] Not isolated; crude mixture, see Experimental Section. [d] $C_{14}H_9$ = phenanthryl.

lization from 95% ethanol, gave 2.82 g. (20%) of di(mesitylcarbinyl) ether, m.p. 147–148°, lit.[11] b.p. 148°. The infrared spectrum had a strong peak at 1065 cm.$^{-1}$ (C–O–C). From the mother liquors was obtained, after concentration and recrystallization from cyclohexane, 9.72 g. (65%) of mesitylcarbinol, m.p. 86–88°, lit.[12] m.p. 88–89°. The infrared spectrum had an –OH peak at 3275 cm.$^{-1}$.

D. Reduction of 2-Naphthoic Acid (0.10 Mole).—The reaction mixture was extracted with three 100-ml. portions of ether, the extracts were washed with 50 ml. of 10% sodium carbonate and dried over Drierite, and the solvent was removed under reduced pressure. The residue, on recrystallization from petroleum ether (b.p. 60–90°), gave 11.0 g. (70%) of 2-naphthylcarbinol, m.p. 84–85°, lit.[13] m.p. 80–80.5°. 2-Naphthoic acid (2.14 g., 12%) was recovered from the sodium carbonate washings on acidification.

E. Reduction of 1-Naphthaldehyde (0.103 Mole).—The reaction mixture after 5-hr. reflux, was worked up as described for the benzaldehyde experiment (III A), yielding 12.0 g. (74%) of 1-naphthylcarbinol, b.p. 140–144° (10 mm.), m.p. 57–59°, lit.[14] m.p. 59.5–60°.

F. Reduction of 1-Naphthaldehyde (0.10 Mole).—This reaction was carried out at reflux for 22 days. The crude reaction product, 15.4 g., was extracted with 300 ml. of petroleum ether (b.p. 35–60°), the extract was filtered and concentrated to 100 ml., and 50 ml. of benzene was added. On cooling 5.98 g. of 1-naphthylcarbinol, m.p. 61–63°, was obtained. The noncrystalline material was evaporated to dryness. The residue was taken up in 10 ml. of benzene and chromatographed on a benzene-wetted alumina column and eluted first with cyclohexane yielding an additional 0.5 g. of 1-naphthylcarbinol, and, on elution with 75% benzene–25% methanol, 6.14 g. of viscous oil, which could not be crystallized, was obtained. This oil had a strong –OH band at 3425 cm.$^{-1}$ and probably contained 1,2-di-(1-naphthyl)ethanol by analogy to the results obtained with 9-anthraldehyde and 9-phenanthraldehyde. The total yield of 1-naphthylcarbinol was 6.48 g. (41%).

G. Reduction of 9-Phenanthraldehyde (0.005 Mole).—After decomposition, the reaction mixture was extracted twice with 100 ml. of benzene, the combined extracts were dried over Drierite and anhydrous sodium carbonate, and the solvent was removed under reduced pressure. The residue, on recrystallization from benzene, gave 3.68 g. of 9-hydroxymethylphenanthrene, m.p. 154–156°, lit.[15] m.p. 149–149.5°. The filtrate was concentrated to 15 ml. and chromatographed on an aluminum column previously wetted with benzene. The first fraction was eluted with cyclohexane and recrystallized from 50 ml. of cyclohexane, yielding 2.30 g. of 9-hydroxymethylphenanthrene, m.p. 154–156°. Thus the total yield of this product was 58%. The following fractions were eluted with cyclohexane containing increasing amounts of benzene. The second major fraction was obtained on elution with 50% cyclohexane–50% benzene. Concentration of this fraction to 25 ml. and diluting with 25 ml. of petroleum ether deposited 2.32 g. of solid, m.p. 85–95°. Recrystallization of this material from a mixture of benzene–cyclohexane (1:4 ratio) gave a 1.62 g. (16%) of 1,2-di(9-phenanthryl)ethanol, m.p. 97–100°. The infrared spectrum has an –OH peak at 3275 cm.$^{-1}$

Anal. Calcd. for $C_{30}H_{22}O$: C, 90.42; H, 5.57. Found: C, 90.35; H, 5.69.

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