

contain 5.1 g. of 3-ethylpentane by vapor phase chromatography.

The above material was purified by shaking with potassium permanganate solution followed by vapor phase chromatography ( $n_D^{20}$  1.3929). Final purification was effected by dissolving it in 10 ml. of acetic acid and adding solution of sodium dichromate and perchloric acid in 90% acetic acid until the orange color persisted. Water was added, the hydrocarbon was taken up in ether, washed with sodium bicarbonate solution and isolated by vapor phase chromatography. The mass spectrum, determined at an ionizing potential of 20 v., indicated the presence of at least 97% of one deuterium (based on the parent peaks).

**Kinetic Method.**—Equal volumes of solutions of the hydrocarbon in glacial acetic acid (purified by distillation under reduced pressure from chromium trioxide) and of sodium dichromate ( $2 \times 10^{-3} M$ ) and perchloric acid (1.333  $M$ ) in 90% acetic acid were placed in the two arms of a U-tube which had been sealed onto a 10-mm. Beckman cell. The solutions were degassed under reduced pressure and

brought to 25.0°. The solutions were mixed and transferred to the Beckman cell by inverting the tube. The rate of disappearance of chromium(VI) was followed by the change in absorbance at 390  $m\mu$ . Plots of  $\log(A - A_\infty)$  against time gave a good linear relationship. The rate constants are given in terms of the natural logarithm.

**Oxidation of *cis*-Decalin.**—Commercial *cis*-decalin was purified by vapor phase chromatography. The hydrocarbon (6 g.) was added to a solution of 50 g. of sodium dichromate, 40 ml. of water and 141 g. of 72% perchloric acid in enough acetic acid to make 1 l. of solution. The oxidation was carried out at 8° for 30 min. The reaction mixture was worked up as described above for the oxidation of 3-methylheptane giving 1.1 g. of material, b.p. 60–70° at 0.5 mm., which was largely *cis*-9-decalol. Recrystallization from aqueous ethanol gave pure *cis*-9-decalol, m.p. 64–65°. <sup>37</sup>

(37) The m.p. of *cis*-9-decalol is 65°, whereas that of the *trans* isomer is 54°; W. G. Dauben, R. C. Tweit and R. L. MacLean, *THIS JOURNAL*, **77**, 48 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO, BUFFALO 14, N. Y.]

## Lithium Aluminum Hydride Reactions in Pyridine Solution. Reductive Cleavage of Ketones<sup>1</sup>

By PETER T. LANSBURY

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Pyridine has been shown to be an excellent solvent for lithium aluminum hydride reactions. A number of ketones have been reduced to alcohols under mild conditions. However, certain tetraaryl pinacolones undergo facile reductive cleavage to triarylmethanes and benzylic alcohols. Evidence is presented which supports the role of pyridine as a Lewis base that coordinates aluminum hydride and allows the participation of unassociated alkoxides in the reaction scheme leading to normal and cleavage products. Semi-quantitative studies of reaction stoichiometry suggest that all four hydride ions are potentially available from each aluminumhydride ion.

The purpose of this report is to bring attention to the usefulness of pyridine as a solvent for lithium aluminum hydride (LAH) reactions. During the past decade, a great volume of literature describing modifications of the reducing action of LAH (as well as other complex metal hydrides) by means of added metal halides or by converting the hydride into alkoxyaluminumhydrides has come forth.<sup>2</sup> Less work has been done in investigating solvents other than ethyl ether and tetrahydrofuran for use with LAH.

The limited solubility of many reducible substrates in diethyl ether, plus the inconveniences incurred in purifying and storing anhydrous tetrahydrofuran, aroused our interest in finding other potentially-useful and easily-accessible solvents. The decision to examine pyridine in this connection was somewhat influenced by the report that fluorenes give appreciable concentrations of carbanions in pyridine solution when treated with Triton B.<sup>3</sup> We have observed, similarly, that fluorene and triphenylmethane both give highly-colored

pyridine solutions when treated with LAH at room temperature, whereas no observable reaction occurs in ether under comparable conditions. The enhanced basicity of LAH in pyridine, as compared with ether, affords a convenient method for generating triphenylmethide and related carbanions<sup>4a</sup> in solvents other than liquid ammonia.<sup>4b</sup> Subsequent reactions of these species, such as carboxylation,<sup>5</sup> can then be carried out.

(4) (a) The extent of carbanion formation is not known with certainty; hydrogen-deuterium exchange studies, aimed at determining this information, are presently underway. However, carboxylation experiments (ref. 5) indicate that substantial metalation occurs. The base-strengthening effect of pyridine may result from its tendency to coordinate strongly with incipient  $AlH_3$ , thus causing  $AlH_4^-$  to release hydride more effectively. Pyridine has a relatively high dipole moment (2.1 D.) which correlates with its unusual coordination ability; relative to other tertiary amines (R. W. Parry and R. N. Keller in "Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p. 128). The



ionizing power of pyridine (ref. 21) may also facilitate heterolysis of the C-H bond in triphenylmethane. The basicity of LAH in tetrahydrofuran toward methylenic hydrogens in fluorene has previously been noted (H. Dahn and U. Solms, *Helv. Chim. Acta*, **34**, 907 (1951)) and this combination also weakly metalates triphenylmethane. By contrast, neither fluorene nor triphenylmethane shows any active hydrogen with LAH in ether at 35° (F. A. Hochstein, *THIS JOURNAL*, **71**, 305 (1949)). (b) C. R. Hauser and co-workers (*J. Org. Chem.*, **20**, 1531 (1955)) observed reversion of sodium and lithium triphenylmethide to triphenylmethane when attempting to replace liquid ammonia as solvent by ethers, toluene or triethylamine.

(5) P. T. Lansbury, to be published. In preliminary experiments, triphenylacetic acid and fluorene-9-carboxylic acid have been isolated in 12 and 13% yields, respectively, by pouring the carbanion solutions onto crushed Dry Ice. Higher yields are anticipated when the carbonation step is refined.

(1) Presented at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960. A portion of this work also was reported in a preliminary communication, P. T. Lansbury, *Chemistry & Industry*, 151 (1960).

(2) See, for example: (a) H. C. Brown and R. F. McFarlin, *THIS JOURNAL*, **80**, 5372 (1958); (b) R. F. Nystrom and C. R. A. Berger, *ibid.*, **80**, 2896 (1958); (c) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956; (d) N. G. Gaylord, *J. Chem. Ed.*, **34**, 367 (1957); (e) G. A. Olah, *THIS JOURNAL*, **81**, 3165 (1959); (f) E. L. Eliel and V. G. Badding, *ibid.*, **81**, 6087 (1959); (g) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 2582 (1956); (h) M. N. Rerick, "The Mixed Hydrides," Metal Hydrides, Inc., Beverly, Mass., Review.

(3) Y. Sprinzak, *THIS JOURNAL*, **80**, 5449 (1958).

Since nuclear reduction of pyridine<sup>6</sup> and other nitrogen heteroaromatics<sup>6,7</sup> to dihydro compounds has only been accomplished under forcing conditions,<sup>8</sup> it appeared that pyridine might be an excellent solvent for LAH reductions under mild conditions.<sup>9</sup> This expectation has been realized, plus the unexpected occurrence of remarkably facile reductive cleavages of certain benzpinacolones of the type which undergo hydrolytic cleavage with alcoholic potassium hydroxide.<sup>10</sup>

In choosing suitable substrates for investigation, early attention was given to reduction of benzpinacolone and several analogs in pyridine, since such ketones have poor ether solubility. The addition of 1–1.5 moles of powdered LAH to benzpinacolone (Ia) and di-*p*-biphenylphenylmethyl phenyl ketone (Ib) in pyridine at room temperature resulted in *immediate* color formation, yielding blood red and deep blue solutions, respectively (see Experimental section for detailed procedures). After three hours, compound Ia had been cleaved to triphenylmethane (IIIa) and benzyl alcohol in 72% yield, whereas hydrolysis of the reaction mixture after ten minutes gave a mixture composed of 25% IIIa and 75% benzpinacolyl alcohol (IIa), indicating that the cleavage occurred slowly and not simultaneously with the normal rapid reduction of the carbonyl group.

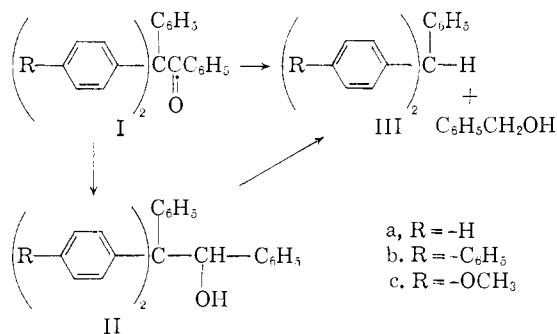


Fig. 1.

In accord with the expectation that the rate of cleavage should be directly related to the stability of the triarylmethide ion which is the leaving group, ketone Ib was quantitatively converted to IIIb and benzyl alcohol *in five minutes at room temperature*.<sup>11</sup> 9-Phenyl-9-benzoylfluorene was reductively cleaved with equal ease. On the other hand, reaction of di-*p*-anisylphenylmethyl phenyl ketone (Ic) with LAH in pyridine gave an immediate red color but even after eighteen hours the product mixture contained no appreciable amount of triarylmethane IIIc, as shown by infrared

(6) F. Bohlmann, *Chem. Ber.*, **85**, 390 (1952).

(7) K. W. Rosenmund, F. Zmalkowski and N. Schwarte, *ibid.*, **87**, 1229 (1954).

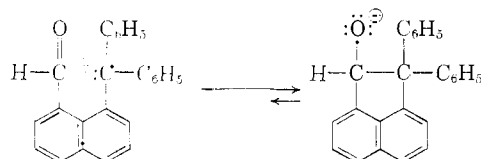
(8) V. M. Micovic and M. L. Milhailovic, *J. Org. Chem.*, **18**, 1190 (1953), reduced *N,N*-diethylnicotinamide to the corresponding amine and aldehyde without any nuclear reduction. Extensive reduction of the pyridine ring has been effected in refluxing di-*n*-butyl ether (P. de Mayo and W. Rigby, *Nature*, **166**, 1075 (1950)).

(9) Pyridine has been used as a solvent for sodium borohydride reductions (O. Mancera, *et al.*, *THIS JOURNAL*, **75**, 1286 (1953)) and is reportedly unaffected by NaBH<sub>4</sub>-AlCl<sub>3</sub> at 25° (ref. 2g).

(10) W. E. Bachmann and R. H. Moser, *ibid.*, **54**, 1127 (1932).

(11) By contrast, this ketone gives no coloration whatsoever in ether with LAH, nor does benzpinacolone.

analysis. Two cyclic tetraarylpinacolones were also subjected to reduction in pyridine. 2,2-Diphenylacenaphthenone gave pure 1,2-diphenylacenaphthylene, after acid-catalyzed dehydration of the reduction product, and no 7,12-dihydro-7-phenylpleiadene,<sup>12</sup> the product resulting from dehydration of any 8-benzhydryl-1-hydroxymethylnaphthalene, which would arise from reductive cleavage. Although the carbanion which would be formed in a cleavage process is more highly resonance-stabilized than triphenylmethide, its rigid proximity to the carbonyl group would be expected to result in rapid recombination with the adjacent electrophilic center.<sup>13</sup> Reduction of 10,10-diphenyl-9-phenanthrone also proceeded with-



out cleavage, yielding only 9,10-diphenylphenanthrene upon dehydration of the reduction product, although in this case the incipient carbanion could become separated from the intermediary aldehyde group by rotation of the biphenyl rings out of coplanarity.

It should be mentioned that carbon-carbon cleavage during LAH reductions is not without precedent. Dornow and Fust<sup>14</sup> reduced a number of *vic*-dinitro compounds to amines, with cleavage of the bond between the carbons bearing the nitro groups. Rona and Feldman<sup>15</sup> reported the cleavage of 9-arylanthracenes; a cleavage of a substituted  $\alpha$ -cyanodesoxybenzoin also has been observed.<sup>16</sup> In the present study, examination of the various factors which influence the cleavage reaction has helped to clarify the mechanism by which normal as well as abnormal reductions (with cleavage) occur in pyridine (*vide infra*).

Table I summarizes the results of the normal reduction of a variety of ketones with LAH in pyridine. The actual yields given are probably not optimum values since infrared examination of the crude reaction mixtures showed that no starting material was present. Apparently, diphenylmethide is not sufficiently stable to act as the leaving group in this reaction, although more vigorous conditions might also effect reductive cleavage of phenyl benzhydryl ketone.

The reduction of hexachloroacetone was of interest in connection with the possibility of generating dichlorocarbene<sup>17</sup> from cleaved trichloromethyl anion. The reaction was carried out in the presence of cyclohexene but no dichloronor-

(12) P. T. Lansbury, *THIS JOURNAL*, **81**, 4325 (1959).

(13) Hot alcoholic potassium hydroxide is an effective reagent for this cleavage, since the carbanion in that case may be irreversibly protonated (W. E. Bachmann and E. Chu, *ibid.*, **58**, 1118 (1936)). The necessity for having active hydrogen compounds present in promoting certain similar cleavages has been discussed by J. L. Greene and H. D. Zook, *ibid.*, **80**, 3629 (1958).

(14) A. Dornow and K. J. Fust, *Chem. Ber.*, **90**, 1774 (1957).

(15) P. Rona and U. Feldman, *J. Chem. Soc.*, 1737 (1958).

(16) P. Reynaud and J. Matti, *Bull. soc. chim. France*, 612 (1951).

(17) W. von E. Doering and A. K. Hofmann, *THIS JOURNAL*, **76**, 6162 (1954).

TABLE I  
REDUCTION OF KETONES TO ALCOHOLS BY LAH IN PYRIDINE  
AT ROOM TEMPERATURE

Ketone	Moles LAH/mole ketone	Product (yield, %)
Benzophenone	0.29-1.0	Benzhydrol (96)
2,4'-Dichlorobenzophenone	2.0	2,4'-Dichlorobenzhydrol (88)
Phenyl benzhydryl ketone	3.0	1,2,2-Triphenylethanol (86)
1,2-Diphenyl-1-propanone	1.0-1.3	1,2-Diphenyl-1-propanol <sup>a</sup> (93)
10,10-Diphenyl-9-phenanthrene	3.0	9,10-Diphenylphenanthrene <sup>b</sup> (80)
2,2-Diphenylacenaphthenone	2.0	1,2-Diphenylacenaphthylene <sup>b</sup> (92)
Phenyl $\alpha$ -ethoxybenzhydryl ketone	2.5	1,2,2-Triphenyl-2-ethoxyethanol (93)
Hexachloroacetone	1.0	Hexachloroisopropyl alcohol (29)

<sup>a</sup> Greater than 75% *erythro*, by infrared analysis. <sup>b</sup> Carbinol dehydrated by *p*-toluenesulfonic acid and acetic acid.

carane was isolated.<sup>18</sup> Similarly, the attempted cleavage of 2,4'-dichlorobenzophenone to benzene<sup>19</sup> did not materialize.

A reasonable scheme for reduction of ketones in pyridine, with or without cleavage of the intermediate alkoxides, which is in accord with the experimental observations, is presented (1-3), using benzpinacolone as the substrate. The relatively

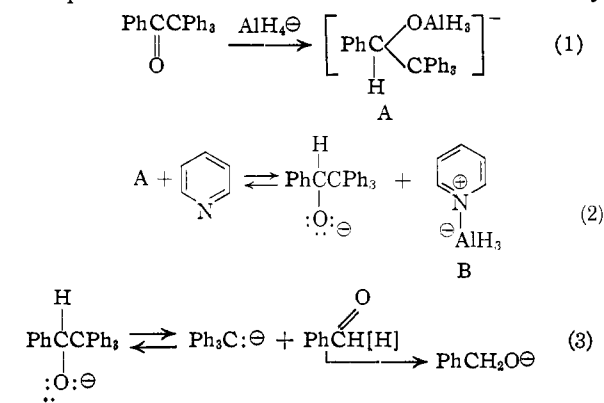


Fig. 2.

slow rate of cleavage as compared with the normal reduction was indicated by the observation that reduction of Ia was essentially complete in ten minutes, but only part of the alkoxide was cleaved. The function of pyridine in promoting the cleavage reaction appears to be coordination of aluminum hydride, which is liberated when the aluminum hydride ion attacks the carbonyl group<sup>20</sup> (A), thus providing an unassociated alkoxide ion, in a good ionizing solvent,<sup>21</sup> which may decompose with the elimination of a resonance-stabilized carbanion. Ether is not sufficiently basic, in this case, to

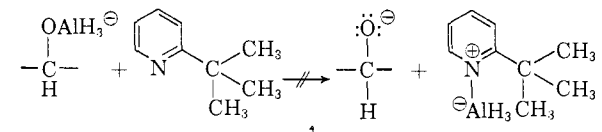
(18) W. E. Parham, in a private communication, reports that hexachloroacetone gives good yields of dichlorocarbene when treated with sodium methoxide, according to the procedure used with ethyl trichloroacetate (*J. Org. Chem.*, **24**, 1733 (1959)).

(19) J. F. Bunnett and B. F. Hrutford, Abstracts of A.C.S. Meeting, Boston, Mass., April, 1959, p. 94-O. These workers cleaved *o*-halobenzophenones with potassium amide in liquid ammonia, yielding aniline *via* benzene.

(20) L. W. Trevo and W. G. Brown, *THIS JOURNAL*, **71**, 1675 (1949).

(21) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 174, and references cited therein.

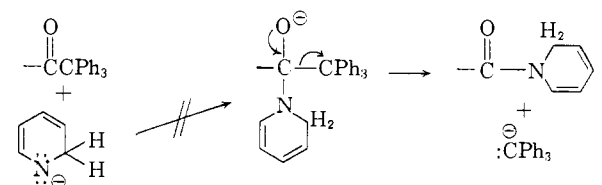
effectively remove  $\text{AlH}_3$  from the intermediate alkoxide, and cleavage is not observed in that solvent. In this connection, it is pertinent to note that Ellison and Kenyon<sup>22</sup> prepared optically active benzpinacolyl alcohol by LAH reduction of the acid phthalate ester in *ether* solution, since attempted saponification (alcoholic potassium hydroxide) resulted in cleavage to triphenylmethane and benzaldehyde, as did the action of alkali on the alcohol itself. Apparently the alkoxide formed in ether is sufficiently covalent (or an undissociated ion pair) to resist cleavage, since benzpinacolyl alcohol (IIa) also was recovered after reaction with excess methyl or ethyl Grignard reagents.<sup>22</sup> On the other hand, we found that IIa is cleaved by LAH in pyridine as easily as in alcoholic base.<sup>23</sup> Evidence supporting the role of pyridine as a donor molecule was gained from the observation that Ia gives only IIa when the sterically-hindered 2-*t*-butylpyridine is used as a solvent, under conditions where complete cleavage occurs in pyridine. Since the steric requirement of aluminum hydride is probably intermediate between those of  $\text{BH}_3$  and trimethylboron, which does not form an addition compound with 2-*t*-butylpyridine,<sup>24</sup> the reduction may proceed without the formation of the ionic alkoxide which is requisite for cleavage.<sup>25</sup> It is not likely that aluminum hydride ion reacts with pyridine to liberate hydride ion prior to attacking



the electrophilic carbonyl group because it has been found that in the LAH reduction of 1,2-diphenyl-1-propanone in pyridine, the *erythro:threo* ratio was identical, within experimental error, with that when reduction was performed in ether,<sup>26</sup>

(22) L. Ellison and J. Kenyon, *J. Chem. Soc.*, 779 (1954).

(23) The facile reductive cleavage of IIa to IIIa rules out the remote possibility that nucleophilic attack by the anion of dihydropyridine is responsible for the reductive cleavage of pinacolones (Haller-Bauer reaction).



However, the possible reducing action of dihydropyridine anion, by a reversal of hydride addition, has not been ruled out. This matter is receiving further attention.

(24) H. C. Brown, *J. Chem. Ed.*, **36**, 424 (1959), and references cited therein.

(25) In his studies of electrophilic substitution at saturated carbon, Cram and co-workers (*THIS JOURNAL*, **81**, 5740 (1959)) found that inversion of configuration is most predominant in solvents of high dielectric constant (proportional to ionizing power) in which partially or wholly dissociated metal alkoxides are involved, and that, other things being equal, the rate of cleavage of metal alkoxides decreases in the order  $\text{K} > \text{Na} > \text{Li}$ , coinciding with decreasing ionic character of the metal-oxygen bond. These results concur with our observations, since cleavage appears to require a highly dissociated alkoxide, preferably in a polar medium, and does not readily occur in the more conventional LAH reactions which utilize a non-ionizing solvent (ether) and proceed *via* associated alkoxides ( $\text{O-Li}$  or  $\text{O-Al}$ ).

(26) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5833 (1932).

thereby implicating the same species, aluminohydride, in both cases.

An indication of the reversible nature of the cleavage reaction was gained from the following experiments. Ketone Ia was allowed to react with slightly more than 0.5 mole of LAH, the quantity needed for reduction of the carbonyl group only (see below for discussion of stoichiometry), and hydrolysis performed by pouring the reaction mixture into 5% hydrochloric acid (instant hydrolysis). Infrared and product isolation studies showed the reaction mixture to be mainly benzpinacolyl alcohol, plus a small amount of IIIa, there being no unreacted benzpinacolone and no benzaldehyde. The reaction was then repeated exactly as before except that hydrolysis was performed at  $-70^{\circ}$  by the slow addition of isopropyl alcohol, whereupon a large amount of benzaldehyde and triphenylmethane was formed, at the expense of IIa. Under these conditions of hydrolysis, isopropyl alcohol preferentially protonates triphenylmethide, the more basic species, removing it from the rapidly equilibrating system and causing a shift to the right (eq. 3) with the predominating formation of cleavage products,<sup>27</sup> as is the case when enough LAH is used in the reduction to remove benzaldehyde by conversion to benzyl alcohol (at least 0.75 mole LAH per mole of benzpinacolone).

Attention has been given to determining how many equivalents of hydride per mole of LAH are available for reduction in pyridine. For this purpose the reductions of benzpinacolone, phenyl benzhydryl ketone and benzophenone were studied, using various molar ratios of substrate to LAH. The results of these semi-quantitative experiments are summarized in Table II.

TABLE II

STOICHIOMETRY OF LITHIUM ALUMINUM HYDRIDE REDUCTIONS IN PYRIDINE

Substrate	Mmoles >C=O	Mmoles LAH	Ratio >C=O/ LAH	Remarks
Benzpinacolone	5	2.9	1.7	Complete redn.
	5	1.7	2.9	1.6 mmoles Ia recovd.
Phenyl benzhydryl ketone	4.6	2.9	1.6	Complete redn.
	4.3	1.6	2.7	1.1 mmole ketone recovd.
Benzophenone	6.0	3.3	1.8	Complete redn.
	10.0	4.0	2.5	Complete redn.
	10.0	2.9	3.5	Complete redn.

In order to completely reduce benzpinacolone and phenyl benzhydryl ketone, the ratio of substrate must not be more than 2:1, implying that bulky, substituted aluminohydride ions, with coordinated alkoxide or pyridine, are too large to attack the sterically-hindered carbonyl group in these compounds. The second hydride ion may be supplied by species such as A and B (Fig. 2), after the initial attack of  $\text{AlH}_4^-$ . However, further reduction by C, D or E, for example, would not be likely because of electronic as well as steric effects. Benzophenone, being an unhindered ke-

(27) P. J. Hamrick, Jr., and C. R. Hauser, *THIS JOURNAL*, **81**, 2096 (1959).

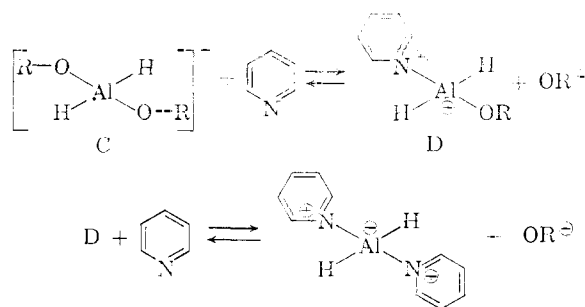


Fig. 3.

tone, underwent complete reduction, even when the amount of LAH was reduced so as to require all four available hydrides. However, it is advisable to use excess LAH in preparative work. The extent of displacement of alkoxides from aluminum by pyridine in the reduction of non-cleavable ketones, such as benzophenone, to give species such as D and E (R = benzhydryl), would be less than in the reduction of ketones Ia and Ib, in which case some driving force for displacement of alkoxide is obtained from consumption of the latter by cleavage (step 3 in the proposed mechanism). Secondly, release of these bulky alkoxides from aluminum relieves considerable steric compression in the case of Ia and Ib particularly. However, participation of the pyridine complexes D and E in the reduction of benzophenone would be negligible since their formation is not greatly facilitated by the two factors discussed above; also, D and E would be more reluctant to part with hydride than C. This line of reasoning, therefore, supports the observation that reduction of benzophenone proceeds *via* intermediates similar to those when ether is solvent (C, for example), in which all four hydrides are utilized.

The use of pyridine as a solvent will further enhance the already widespread utility of lithium aluminum hydride in organic chemistry. In addition to its powerful solvent properties, pyridine advantageously possesses a high boiling point, which essentially eliminates the need for using reflux condensers in smaller scale runs. Hence the technique is operationally simple and time-saving. Certain reductions which are complicated by rearrangements induced by  $\text{AlH}_3$ <sup>28</sup> may be made to proceed without this occurrence in the more basic pyridine. We are continuing our investigations on the use of LAH-pyridine in organic synthesis, especially in the hope of discovering unique applications. Further work on the mechanistic aspects is also in progress.

**Acknowledgment.**—We are grateful to Professors D. J. Cram and H. J. Schaeffer for stimulating discussions and constructive suggestions.

#### Experimental<sup>29</sup>

**General Procedure for Reduction of Ketones by LAH in Pyridine.**—The reductions were generally done on a small

(28) For an example, see A. C. Cope, E. S. Graham and D. J. Marshall, *ibid.*, **76**, 6159 (1954).

(29) Melting points were obtained with a "Mel-temp" capillary apparatus which was checked with known compounds. Infrared spectra were taken in a Perkin-Elmer model 21 spectrometer which was equipped with sodium chloride optics. Oily products were examined without diluent between salt plates, and solids were milled with Nujol.

scale and could therefore be carried out in stoppered erlenmeyer flasks in the absence of stirring and reflux condensers. Reagent grade pyridine was dried over barium oxide prior to use. Lithium aluminum hydride (Metal Hydrides, Inc., 98% pure) was pulverized under aluminum foil before use. In the usual procedure, which is exemplified below, no attempt was made to isolate benzyl alcohol formed when cleavage occurred; however, the alcohol could be obtained from the aqueous layer resulting from hydrolysis by continuous extraction with ether. The alcohol was subsequently characterized as the *p*-nitrobenzoate.

A. Benzpinacolone (1.22 g., 3.5 mmoles) was dissolved in 25 ml. of pyridine in a 50-ml. erlenmeyer flask. Lithium aluminum hydride (0.20 g., 5.3 mmoles) was added in one portion, there being an immediate blood-red color formed and considerable evolution of heat (solutions of LAH in pyridine generally developed a pale orange to green coloration). The flask was then tightly stoppered and allowed to stand at room temperature for 3 hours, with occasional swirling. Hydrolysis was performed by pouring the solution into excess 5% hydrochloric acid and the product extracted with ether. Sometimes the hydrolysis was first affected with methanol. The ether extract was washed with salt solution, 5% sodium bicarbonate, water and then dried over sodium sulfate. Evaporation of the ether left a colorless oil which slowly solidified. The infrared spectrum showed the absence of carbonyl absorption and some hydroxyl absorption. A 0.84-g. portion of the oil was taken up in benzene and chromatographed over 25 g. of alumina, using benzene as eluent. Initially, there was obtained 0.54 g. of IIIa, m.p. 77–81°, which had m.p. and mixed m.p. 90–91° after recrystallization from methanol. Further elution with 3:1 benzene-ethanol afforded 0.30 g. of benzpinacolyl alcohol (IIIa), m.p. 138–143°, melting at 148–150° after recrystallization from methanol. The yields of IIIa and IIa were 72 and 28%, respectively. Similar results were obtained in repeat runs; however, work-up by fractional crystallization was more tedious and less satisfactory than chromatography.

B. Using the same amounts of reactants as in part A, a reduction was carried out for 10 minutes, then poured into 5% hydrochloric acid and worked up as above. The oily product showed no carbonyl absorption in the infrared. Chromatography over alumina, with benzene as eluent, afforded IIIa in 25% yield and 75% of IIa (based on recovered material).

C. Reduction in 2-*t*-butylpyridine: Fifty milligrams of Ia was dissolved in 1.5 ml. of 2-*t*-butylpyridine (kindly furnished by Professor H. C. Brown) and 40 mg. of LAH added. No coloration whatsoever appeared, even on standing overnight. Hydrolysis and work-up afforded pure IIa (80% yield), m.p. 151–151.5° and mixed m.p. 151–152°, as the only product.

D. Reaction with sodium borohydride in pyridine: No color whatsoever appeared when the ketone was kept overnight in pyridine with sodium borohydride.

**Cleavage of Benzpinacolyl Alcohol (IIa).**—The carbinol (0.67 g., 1.9 mmoles) was dissolved in 12 ml. of pyridine and 0.10 g. (2.6 mmoles) of LAH added. The usual exothermic reaction, accompanied by the immediate red coloration, occurred; after 15 minutes at room temperature, the reaction mixture was worked up, yielding 0.35 g. (75% yield) of pure triphenylmethane, m.p. 91.5–93°. Any unreacted carbinol was in the mother liquors.

**Reduction of Di-*p*-anisylphenylmethyl Phenyl Ketone (Ic).**—Five-tenths of a gram of Ic and 0.10 g. of LAH in 8 ml. of pyridine gave an immediate red color. After standing for 20 minutes, the reaction mixture was hydrolyzed and worked up, yielding a viscous oil which refused to crystallize on cooling and scratching, or when various solvents were used. The infrared spectrum of this oil (Nujol mull) showed strong O–H absorption at 2.8–3.0 $\mu$  and no absorption at 882 cm.<sup>-1</sup>, where di-*p*-anisylphenylmethane (IIIc) has a strong band (*vide infra*), indicating that less than 5% of IIIc was present. A second reaction was run, in which Ic was treated with LAH in pyridine overnight, but the infrared spectrum of the oily product was essentially identical to that obtained from the previous run. Neither

Most of the compounds dealt with below are reported in the literature and were prepared by standard procedures. Microanalyses of new compounds were performed by Dr. Alfred Bernhardt, Max Planck Institute, Mulheim, Germany.

a benzoate nor a *p*-nitrobenzoate derivative of the alcohol IIc could be prepared by the standard methods.

Di-*p*-anisylphenylmethane (IIIc) was prepared according to the procedure of Bachmann and Moser<sup>9</sup>; m.p. 98–100° (reported 100–101°). The infrared spectrum (Nujol mull) showed the expected ether and aromatic bands; of importance was the strong, sharp band at 882 cm.<sup>-1</sup> which does not appear in the spectrum of the crude reduction product from Ic.

**Reductive Cleavage of Phenyl-di-*p*-biphenylmethyl Phenyl Ketone (Ib).**—A half gram (1 mmole) of the ketone (kindly furnished by Professor W. A. Mosher) was dissolved in 25 ml. of pyridine and treated with 0.15 g. (4 mmoles) of LAH. A deep blue color developed immediately. After 5 minutes, the reaction mixture was worked up, yielding 0.39 g. (99% yield) of crude IIb, m.p. 149–154°, which when recrystallized from ethanol had m.p. 162.5–163.5° and mixed m.p. 162–163.5°, with the product from the ethanolic potassium hydroxide cleavage of the ketone.<sup>9</sup>

**Reductive Cleavage of 9-Benzoyl-9-phenylfluorene.**—One-tenth of a gram (0.3 mmole) of the ketone was dissolved in 4 ml. of pyridine and 0.05 g. (1.3 mmoles) of LAH added. A bright orange-red color was immediately evident. After 20 minutes at room temperature, the reaction mixture was worked up, yielding 60 mg. (86% yield) of 9-phenylfluorene, m.p. 140–142°. One recrystallization raised the m.p. to 145.5–146° (reported<sup>20</sup> 146°). A sample of this product was recovered unchanged when subjected to the action of hot acetic acid containing *p*-toluenesulfonic acid. Under these conditions the uncleaved carbinol would have dehydrated to 9,10-diphenylphenanthrene.

The reduction of this ketone in ether also proceeds in part by cleavage of the benzoyl group, as evidenced by gradual color formation during a test-tube reaction.

**Reduction of 2,2-Diphenylacacenaphthenone.**—The ketone (0.45 g.) in 8 ml. of pyridine was treated with 0.10 g. of LAH and the resultant pale-green solution allowed to stand for 1 hour. Work-up in the usual manner yielded a colorless oil, which, when treated with acetic acid and *p*-toluenesulfonic acid, gave pure 1,2-diphenylacacenaphthylene (0.39 g. 92% yield) melting at 159–161° (reported<sup>21</sup> 161.3°). This olefin is formed from the normal reduction product.<sup>21</sup>

**Reduction of 10,10-Diphenyl-9-phenanthrone.**—One-half gram (1.4 mmoles) of ketone was dissolved in 8 ml. of pyridine and 0.15 g. (4.0 mmoles) of LAH added. After standing overnight, the pale orange solution was hydrolyzed and worked up to yield an oil, which was dehydrated as above. Cooling the acetic acid solution yielded colorless needles of 9,10-diphenylphenanthrene, m.p. 232–234° and mixed m.p. 233–234°, in 80% yield. No other products were obtained from the mother liquors.

**Reduction of 1,2-Diphenyl-1-propanone. A. In Ether Solution.**—This reduction was run according to the directions of Cram and Abd Elhafez,<sup>25</sup> using 3:1 and 1:1.3 mole ratios of 1,2-diphenyl-1-propanone to LAH. In each case the *erythro*-alcohol predominated (greater than 75% by infrared).

**B. In Pyridine Solution.**—Two reductions were run, using equimolar amounts of hydride and ketone and also 1.3 moles of LAH per mole of ketone. The reaction mixtures were kept at room temperature for 30 minutes, then hydrolyzed in the same manner as the ether reactions. The infrared spectra of the carbinol mixtures, b.p. 136–138° (0.5–1 mm.), were identical with the reduction products using ether solvent (the *erythro* diastereomer was again present in greater than 75% concentration).

A sample of *erythro*-1,2-diphenyl-1-propanol, m.p. 47–49°, was obtained by recrystallization of the mixture of racemates resulting from reduction of the ketone in ether. The *threo* racemate was obtained by saponification of a sample of the *p*-nitrobenzoate furnished by Professor D. J. Cram. Synthetic mixtures of the diastereomers containing 45% and 75% of the *erythro* racemate were prepared and the infrared spectra recorded. By noting the relative intensities of the 782 cm.<sup>-1</sup> band (*erythro*) and the 734 cm.<sup>-1</sup> band (*threo*) it was determined that all alcohol mixtures isolated contained >75% of the *erythro* racemate.

**Reduction of Hexachloroacetone.**—Into a 500-ml. three-neck flask equipped with stirrer, addition funnel and reflux condenser was placed 50 ml. each of cyclohexene

(30) W. E. Bachmann, THIS JOURNAL, 52, 3288 (1930).

(31) R. L. Letsinger and P. T. Lansbury, *ibid.*, 81, 939 (1959).

and pyridine. The flask was swept with nitrogen during the entire experiment. LAH (3.8 g., 0.1 mole) was added to the cold solution (ice-bath) and, while stirring, 26.4 g. (0.1 mole) of hexachloroacetone added dropwise. The addition of ketone required 1.5 hours and became very violent if carried out too rapidly. The viscous orange-brown reaction mixture was allowed to come to room temperature overnight and then stirred on a steam-bath for 2 hours. The mixture was then cooled, diluted with 100 ml. of petroleum pentane and hydrolyzed by the cautious addition of 10 ml. of water followed by 250 ml. of 10% sulfuric acid. The layers were separated from a good deal of tar which had formed. The organic layer was washed with dilute bicarbonate, water, and dried over magnesium sulfate. The solution was slowly distilled through a 1-foot helices-packed column, during which the head temperature did not exceed 67°. This distillate was shown to be mainly cyclohexene, free of cyclohexane, by gas phase chromatography. Distillation of the residue at reduced pressure gave only hexachloroisopropyl alcohol, m.p. 83.5–85° (from ligroin), in 29% yield (7.6 g.). The reported<sup>32</sup> m.p. for hexachloro-2-propanol is 86–87°.

**Reduction of Phenyl Benzhydryl Ketone.**—To 2.72 g. (0.01 mole) of ketone, dissolved in 25 ml. of pyridine, was added 1.14 g. (0.03 mole) of LAH. The pale green solution was kept overnight, then poured into dilute hydrochloric acid and worked up. Trituration of the oily product with 75% acetic acid gave 2.37 g. (86%) of crude 1,2,2-triphenylethanol in two crops, m.p. 77–81° and 75–78°. One recrystallization from 75% acetic acid gave m.p. 85–87° (reported 87°).

**Reduction of Phenyl  $\alpha$ -Ethoxybenzhydryl Ketone.**—The ketone was prepared according to the method of Werner,<sup>33</sup> utilizing phenyl  $\alpha$ -bromobenzhydryl ketone (2.0 g.) and excess absolute ethanol. Cooling and dilution of the reaction mixture with water gave 1.32 g. (73% yield) of crude ketoether, m.p. 75.5–76.5° (reported<sup>33</sup> m.p. 85°). The infrared spectrum of this crystalline material (Nujol mull) showed no O–H absorption at 2.8–3.0 $\mu$  and had a carbonyl band at 1660 cm.<sup>-1</sup>. An analytical sample was prepared from 95% ethanol; m.p. 76.5–77°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>: C, 83.51; H, 6.37. Found: C, 83.50; H, 6.41.

Reduction of 0.64 g. (2 mmoles) of ketone in 10 ml. of pyridine by 0.19 g. (5 mmoles) of LAH was allowed to proceed for 6.5 hours prior to hydrolysis and work-up. A colorless oil (0.60 g., 93%) was obtained, the infrared spectrum showing O–H absorption at 2.8–3.0 $\mu$  and no carbonyl band. After repeated attempts to obtain a crystalline solid, the oil finally gave crystals on prolonged standing in aqueous methanol, m.p. 82.5–83°. Further recrystallization did not change the m.p.

*Anal.* Calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>: C, 83.00; H, 6.93. Found: C, 83.03; H, 6.93.

**Reduction of 2,4'-Dichlorobenzophenone.**—To a stirred slurry of 3.8 g. (0.1 mole) of LAH in 40 ml. of pyridine was added slowly (30 minutes) 12.5 g. (0.05 mole) of 2,4'-dichlorobenzophenone dissolved in 30 ml. of pyridine. The viscous reaction mixture was stirred for several hours under nitrogen and then kept overnight. Subsequent hydrolysis and work-up gave 11.0 g. (88%) of pure 2,4'-dichlorobenzhydrol, b.p. 166–168° (1 mm.) (reported<sup>34</sup> b.p. 180–183° (4 mm.)), which remained a colorless sirup despite numerous attempts to crystallize it. The infrared spectrum of the oil (O–H bands at 2.8 $\mu$  (weak) and 3.0 $\mu$  (strong) and no carbonyl absorption) was identical to that of 2,4'-dichlorobenzhydrol prepared by reduction in ether.

**Stoichiometry Studies: Reduction of Ketones with Less than Molar Equivalents of LAH.** A. Benzpinacolone (Ia).—1. A mixture of 1.75 g. (5 mmoles) of Ia and 0.11 g. (2.9 mmoles) of LAH in 25 ml. of pyridine was allowed to stand for 5 hours, then poured into ice-cold 5% HCl and worked up as usual, giving a colorless oil, whose infrared spectrum (neat) was very similar to that of pure IIa and showed no absorption in the carbonyl region. Tritu-

ration of the oil with ligroin gave 0.86 g. (49%) of IIa, m.p. 147.5–150° and mixed m.p. 148–151°. The filtrate was evaporated to dryness and recrystallized from aqueous methanol, giving 0.05 g. of solid, m.p. 72–97°, which was a mixture of IIa and IIIa and, on further dilution, more impure IIa.

The above reaction was repeated, except that hydrolysis was performed by first cooling the reaction flask in Dry Ice-acetone and slowly adding excess isopropyl alcohol to the viscous red mass. The mixture was allowed to warm to room temperature overnight, then poured into aqueous acid and worked up. The resultant oil smelled strongly of benzaldehyde and its infrared spectrum showed a strong carbonyl band at 5.9 $\mu$  (C<sub>6</sub>H<sub>5</sub>CHO), weaker O–H absorption than the above product from instantaneous hydrolysis, and several bands characteristic of triphenylmethane. No evidence for benzaldehyde was found in previous runs. Only 0.18 g. of IIa, m.p. 145–147°, could be obtained by stirring the oil with ligroin as above.

2. A mixture of 1.75 g. (5 mmoles) of Ia and 0.065 g. (1.7 mmoles) of LAH in 25 ml. of pyridine was kept for 5 hours, then worked up exactly as above. The oily product solidified on scratching, giving 1.54 g. of solid, m.p. 113–125°. The infrared spectrum (Nujol mull) showed O–H absorption at 2.8–3.0 $\mu$  and a strong carbonyl band at 5.98 $\mu$  (unreacted Ia). A portion of the product (0.63 g.) was chromatographed over alumina, using benzene as eluent. A trace of IIIa, m.p. 80–86°, was first eluted, followed by 0.21 g. of unreacted ketone, m.p. 175–178°. The alcohol was subsequently eluted with 3:1 benzene-ethanol. The recovery of Ia corresponds to 1.6 moles, based on total ketone reacted, in agreement with the expected amount, assuming that only two hydrides are available from each aluminohydride ion.

B. Phenyl Benzhydryl Ketone.—1. The reaction of 1.26 g. (4.6 mmoles) of ketone and 0.11 g. (2.9 mmoles) of LAH in 10 ml. of pyridine was run for 4 hours, then hydrolyzed and worked up, giving a viscous oil whose infrared spectrum was identical with that of authentic 1,2,2-triphenylethanol. On standing, the oil solidified; m.p. 81.5–85.5°, wt. 1.16 g. (91%).

2. A mixture of 1.16 g. (4.3 mmoles) of ketone and 0.06 g. (1.6 mmoles) of LAH in 10 ml. of pyridine was allowed to stand for 4 hours, then worked up. The infrared spectrum of the resulting oil showed both hydroxyl (2.85 and 2.95 $\mu$ ) and carbonyl (5.98 $\mu$ ) bands. On the assumption that two hydrides per mole of LAH are available for reduction, the reaction product should contain 26 mole % ketone. A synthetic mixture of ketone and alcohol, containing 27.5 mole % of the former, was melted and its infrared spectrum determined as a melt between salt plates. The two spectra were essentially superimposable, except for several small bands in the fingerprint region. A 0.87-g. portion of the product was chromatographed over alumina, using benzene as eluent, resulting in the isolation of 0.23 g. of pure phenyl benzhydryl ketone, m.p. 134–136°. This corresponds to 26% recovery, as predicted.

C. Benzophenone.<sup>35</sup>—1. After 2 hours reaction time, a solution of 1.09 g. (6.0 mmoles) of benzophenone and 0.24 g. (6.3 mmoles) of LAH in 10 ml. of pyridine was hydrolyzed and worked up, giving an oil which rapidly solidified to crystalline benzhydrol, m.p. 65–66°, wt. 1.06 g. (96%).

2. Repetition of run 1 with only 0.13 g. (3.4 mmoles) of LAH resulted in an 86% yield of benzhydrol, m.p. 65–66°, whose infrared spectrum coincided with that of an authentic specimen.

3. A 2-hour reaction involving 1.82 g. (10 mmoles) of ketone and 0.15 g. (4.0 mmoles) of LAH afforded 1.75 (95%) of benzhydrol, m.p. 64–66°, which was free of starting material (infrared spectrum as a melt).

4. Repetition of run 3 with only 0.11 g. (2.9 mmoles) of LAH afforded 1.78 g. (97%) of benzhydrol, m.p. 64–66°, whose infrared spectrum (Nujol mull) showed no carbonyl absorption. A duplicate run gave a product which contained less than 10% ketone (infrared). Since more than 13% benzophenone would be recovered if only three hydrides per LAH were available, these data indicate that all four hydrides are usable. However, as in LAH reactions in ether, it appears advisable to use excess reducing agent in synthetic work where optimal yields are sought.

(32) M. Geiger, E. Usteri and C. Granacher, *Helv. Chim. Acta*, **34**, 1335 (1951).

(33) A. Werner, *Ber.*, **39**, 1286 (1906).

(34) H. E. Faith, M. E. Bahler and H. J. Florestano, *THIS JOURNAL*, **77**, 543 (1955).

(35) Several of these experiments were performed by Mr. James O. Peterson.