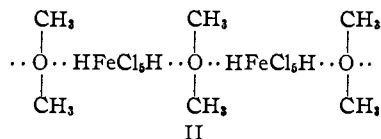is added to the system the composition of each phase remains unaltered, but the relative phase volumes change. Ultimately one of the phases disappears and the system again becomes monovariant at constant temperature and acidity. The three-liquid phase region is indicated by the vertical dotted line of Fig. 5. Systems having average ethereal iron concentrations within this region split into two ether-rich phases of terminal composition. The appearance of a third phase is thus seen to be a consequence of the activity effects which operate in the ether, and is merely an extreme manifestation of the extraction anomaly observed in the two phase region.

The immiscibility gap for the two ether-rich phases of the three phase system has been determined for both the four and five component systems, as shown in Figs. 7 and 8. The effect of $FeCl_2 \cdot 4H_2O$ is to diminish the consolute acid concentration from 7.0 to 4.5 F. Presumably, this is due to an increase in the activity of hydrogen chloride by the addition of chloride ion.

A detailed explanation of the distribution anomaly or the three phase system is not provided by thermodynamics, and would require structural evidence. It is not unreasonable to suppose, however, that the normal extraction is a kind of generalized acid–base reaction in which hydrogen bonding links the chloroferric acid to the ether oxygen to form an "onium" salt (I).

$$
\begin{array}{c}
CH_3 \\
| \\
O \cdots HFeCl_4 \\
| \\
CH_3 \\
\\
I
\end{array}
$$
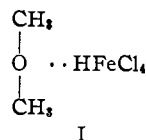
Deviations from normal extraction may be due to polymers, as Swift has suggested. Conceivably, chains might be formed by multiple hydrogen bonding (II).

$$
\begin{array}{ccc}
CH_3 & CH_3 & CH_3 \\
| & | & | \\
\cdots O \cdots HFeCl_5H \cdots O \cdots HFeCl_5H \cdots O \cdots \\
| & | & | \\
CH_3 & CH_3 & CH_3 \\
& II &
\end{array}
$$

Although empirical formulas have been determined for which the $HCl:FeCl_3$ ratio is as large as 4 large deviations from normal extraction occur when the ratio is still unity. It therefore appears that no such well-ordered structures exist as are implied by the term "polymerization," and the deviations from ideal behavior may be due to strong dipole interactions between ether molecules and chloroferric acid which produce "clusters" of indefinite size and structure.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Mr. E. N. Hiebert and of Dr. T. Rosenqvist, who aided in interpretation.

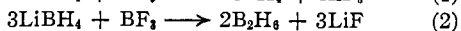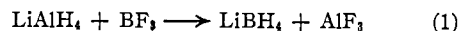[CONTRIBUTION FROM THE CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE TEST STATION]

Preparation of Diborane by the Lithium Aluminum Hydride–Boron Trifluoride Reaction[1]

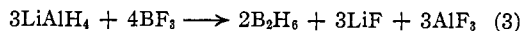BY I. SHAPIRO, H. G. WEISS, M. SCHMICH, SOL SKOLNIK AND G. B. L. SMITH

A study of the preparation of diborane by the reaction of lithium aluminum hydride and boron trifluoride etherate in ether reveals that there are at least two separate reactions involved in the process. First, the reactants in equimolar quantities form lithium borohydride and aluminum fluoride, and then the lithium borohydride reacts with additional boron trifluoride in a 3:1 molar ratio to give diborane and lithium fluoride. Under certain conditions a part of the lithium ends as lithium fluoborate, and the point at which it begins to form assists the interpretation of the whole process.

Of the various methods of producing diborane by the reaction of a boron trihalide with an active hydride,[2,3] one of the most convenient is the one in which solutions of lithium aluminum hydride and boron trifluoride in ether are brought together.[4] However, the yield of diborane is often not so nearly quantitative as might be expected, and the stoichiometry of the other products usually is not simple. As a step toward realizing maximum yields, the chemistry of the reaction has been studied in some detail.

By adding incremental amounts of boron trifluoride to lithium aluminum hydride, one finds that two successive reactions are the main steps in the generation of diborane. These can be expressed by the equations[5]

$$LiAlH_4 + BF_3 \longrightarrow LiBH_4 + AlF_3 \qquad (1)$$
$$3LiBH_4 + BF_3 \longrightarrow 2B_2H_6 + 3LiF \qquad (2)$$

or in sum

$$3LiAlH_4 + 4BF_3 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3 \quad (3)$$

as in the case of boron trichloride.[2] For the reverse order of addition of reactants Eq. 1 and 2 occur concurrently and, consequently, diborane is obtained immediately.

In any actual experiment, however, there usually is found a small proportion of lithium fluoborate, and sometimes a fluoaluminate complex salt, both of which are indicated by X-ray studies of the solid products. It would be reasonable to suppose that lithium fluoborate is formed during the reaction, and acts as a source of boron for the hydridation whenever or wherever the etherate of boron trifluoride is not present in local excess. This idea gains support from an experiment in which a suspension of lithium fluoborate in a solution (in ether) of lithium aluminum hydride was found to yield diborane quite readily.

ported here. For simplicity in writing the equations, the ether formula will be omitted.

(1) Published by permission of the Technical Director, U. S. Naval Ordnance Test Sta.

(2) A. E. Finholt, A. C. Bond and H. I. Schlesinger, THIS JOURNAL, 69, 1199 (1947).

(3) D. T. Hurd, ibid., 71, 20 (1949).

(4) R. C. Lord and E. Nielsen, J. Chem. Phys., 19, 1 (1951); E. Nielsen, unpublished report.

(5) Boron trifluoride is present as the etherate in all reactions re-

Experimental

Material.—Lithium Aluminum Hydride: Solutions of pure lithium aluminum hydride in diethyl ether were prepared[6] by grinding lumps of a commercial sample (*ca.* 95%) in anhydrous ether and decanting the clear liquid. Although lithium aluminum hydride is fairly soluble in ether,[7] a large fraction of the crude material did not dissolve readily in the ether, presumably due to a fine surface coating of oxides on the solid particles. Before each experiment the concentration of lithium aluminum hydride was measured by evaporating to dryness a weighed 10-ml. portion of the solution (to determine the total solids) and analyzing the solid residue for active hydrogen by hydrolysis.[2] Aluminum was determined by precipitation with 8-hydroxyquinoline as a check. *Boron trifluoride etherate:* Commercial boron trifluoride etherate was purified by distillation at ambient temperature under reduced pressure in an all-glass still. Only the middle one-third portion was used in the experiments reported here. Analysis by prescribed procedures[8] indicated that the etherate was substantially free of impurities. The density of the pure boron trifluoride etherate at 25° was measured as 1.125 g./ml. *Ethyl ether:* An analytical reagent-grade anhydrous ether was stored over sodium wire before use. The absence of peroxides in the ether was confirmed by tests with acidified aqueous solutions of potassium iodide. *Lithium carbonate:* C.P. Baker analyzed lithium carbonate powder was used without further purification in the preparation of lithium fluoborate.[9]

Procedure.—Diborane was prepared in conventional-type laboratory apparatus. A known volume of boron trifluoride etherate in a closed-system automatic buret was added in small portions to a solution of lithium aluminum hydride in ether which was contained in a three-neck 2-liter flask. The reaction mixture was agitated continuously by a mercury-sealed stirrer. Predetermined temperatures for the reactions were maintained by a constant temperature bath. Dry nitrogen, introduced slowly into the reaction flask, was used to carry the diborane from the flask through a reflux head (cooled with Dry Ice and acetone) into a condensing trap (cooled with liquid nitrogen). The dry nitrogen flushing was continued for 15 minutes follow-

Fig. 1.—Addition of boron trifluoride to lithium aluminum hydride: I, 24°, initial LiAlH$_4$ concentration of 30 g. in 500 ml. ether; II, 0°, initial LiAlH$_4$ concentration of 16 g. in 300 ml. ether, reflux at 35°.

(6) All preparations and subsequent handling of the hydride solutions were carried out in an inert dry atmosphere (*viz.*, dry nitrogen or high-vacuum systems).

(7) Saturated solutions corresponding to 4.25 *M* lithium aluminum hydride in diethyl ether have been obtained by slow evaporation of ether from dilute hydride solutions. This solubility value is slightly lower than the value reported in ref. 2.

(8) C. F. Swinehart, A. R. Bumblis and H. F. Flisik, *Anal. Chem.*, **19**, 28 (1947).

(9) I. Shapiro and H. G. Weiss, to be published separately.

ing the addition of each portion of the boron trifluoride etherate. The nitrogen gas escaped from the system through mercury-sealed outlets located just beyond the condensing trap. The reflux was used to prevent the bulk of the ether from being carried along with the diborane. The small amount of ether that did pass through the reflux head later was separated from the diborane. The volume and purity of the diborane generated by each addition of boron trifluoride etherate were determined by the usual high-vacuum techniques.

A similar procedure was used for the generation of diborane by the reverse order of addition of reactants.

Purity of Diborane.—The purity of the diborane was determined by vapor pressure measurements (225 mm. at −111.8°). In each case the only impurity found was a trace of ethyl ether which was separated effectively from the diborane by low temperature fractional condensation. McCarty[10] has reported that gaseous boron trifluoride and diborane form a more volatile azeotrope with a composition of 41.6 per cent. B$_2$H$_6$ and 58.4 mole per cent. BF$_3$. Since the present experiments yielded virtually pure diborane from an ethereal solution containing boron trifluoride, it can be presumed that the ether is very effective in preventing the escape of gaseous boron trifluoride from the solution.

Results

Addition of Boron Trifluoride Etherate to Lithium Aluminum Hydride.—The addition of small proportions of boron trifluoride etherate to a solution of lithium aluminum hydride in ether results in a vigorous reaction during which a gelatinous precipitate is formed, but scarcely any diborane is evolved until the mole ratio of BF$_3$ to LiAlH$_4$ approaches 1.00. Thereafter, diborane is evolved in proportion to the amount of boron trifluoride added. The reaction now is far less vigorous and the precipitate takes on a different appearance. These observations suggest that the generation of diborane by the addition of boron trifluoride to lithium aluminum hydride involves at least two distinct steps, such as Eq. 1 and 2. The actual amount of diborane generated as a function of the mole ratio of the reactants at two different temperatures is illustrated graphically by solid lines in Fig. 1.

In the experiment conducted at 24° the excess boron trifluoride in the reaction flask was recovered by separating the solids by filtration, washing with ether, and distilling the combined filtrate and washings. From the quantity of boron trifluoride etherate recovered, it was calculated that the mole ratio of the reactants actually participating in the various reactions was approximately 4.5–5.0 BF$_3$ per 3LiAlH$_4$.

Addition of Lithium Aluminum Hydride to Boron Trifluoride Etherate.—Since the data in Fig. 1 indicate that an excess of boron trifluoride is necessary before the active hydrogen in lithium aluminum hydride appears in the form of diborane, one would expect diborane to be generated as soon as lithium aluminum hydride is added to boron trifluoride. This is true (except for a small solubility effect) as can be seen from Fig. 2, which shows both the theoretical amount and the actual amount of diborane generated as a function of the mole ratio of the reactants.

An inspection of the curves in Fig. 2 reveals three significant features: (1) The sudden break in the slope of each curve occurs at approximately 0.75 mole of lithium aluminum hydride per mole of
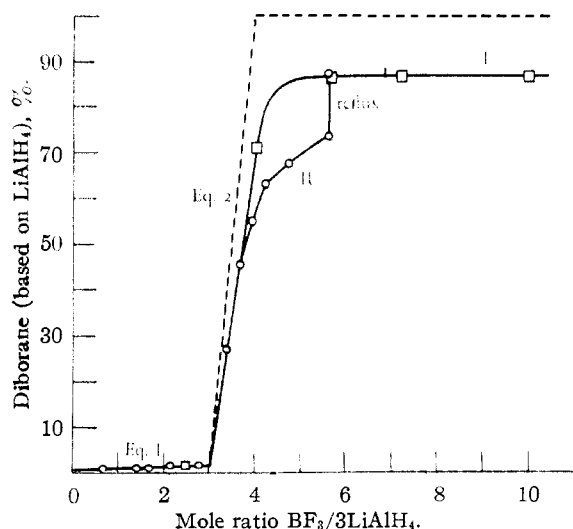
(10) L. V. McCarty, THIS JOURNAL, **71**, 1339 (1949).

boron trifluoride. (2) All curves intersect the abscissa at practically a common point which is removed from the origin (displacement is attributed to some small solubility of diborane). (3) In any one experiment the relative amount of hydride which appears as diborane is approximately constant. This means that the yield of diborane, based upon the increment of lithium aluminum hydride, is nearly constant up to the horizontal part of the curve. Raising the temperature at any earlier point in the process and refluxing at 35° increases this yield; however, raising the temperature after the break in the curve has appeared does not affect the yield of diborane.

A comparison of the two curves for experiments at 0° (Fig. 2) indicates that the yield of diborane is not greatly affected by moderate changes in the starting concentration of the boron trifluoride.

The Latent Hydride.—The hydride which was withheld from appearing as diborane was shown, by pyrolysis and hydrolysis experiments, to have been retained in the precipitate. A portion of the solid obtained at the conclusion of the 0° experiment (curve II, Fig. 2) was pyrolyzed in the vacuum apparatus. Very little effect was noted until the temperature reached about 280°. At this temperature a considerable amount of hydrogen together with a very small amount of a condensible gas (collected in traps at −195°) began to evolve. The characteristic odor of diborane revealed its presence in the condensible gas. The parallelism of these observations with those of Schlesinger and Brown[11] on their pyrolysis of lithium borohydride is noteworthy. These workers found that hydrogen equivalent to about one-half the total hydride was recovered by heating at 280°.
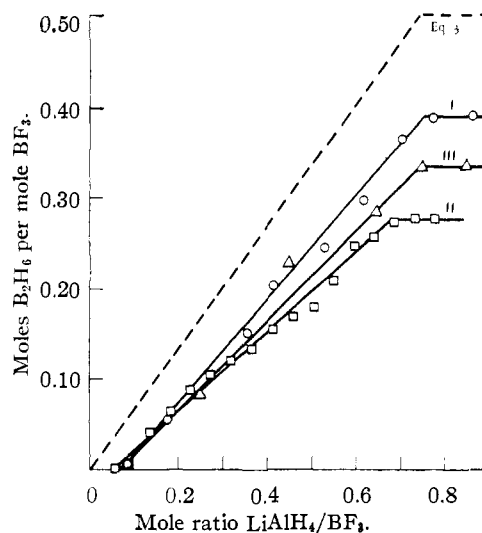

Fig. 2.—Addition of lithium aluminum hydride to boron trifluoride: I, 27.5°, initial boron trifluoride etherate concentration of 47.2 g. in 400 ml. ether, 1.18 M LiAlH$_4$; II, 0°, initial boron trifluoride etherate concentration of 35.2 g. in 350 ml. ether, 1.14 M LiAlH$_4$; III, 0°, initial boron trifluoride etherate concentration of 20.8 g. in 80 ml. ether, 1.47 M LiAlH$_4$.

Hydrolysis of another portion of the above solids indicated that most of the hydride which had escaped conversion to diborane was still active and in the solid residue. Hydrolysis of the ethereal solution revealed very little hydride present in solution even though 0.057 mole of lithium aluminum hydride in excess of that required by Eq. 3 had been added.

The availability of the latent hydride for further reaction with boron trifluoride was shown in another experiment (Table I). Upon addition of small portions of boron trifluoride etherate to a previously prepared reaction mixture, a large quantity of diborane evolved. This indicated some utilization of the hydride which had not been converted to diborane in the early stages of the process. The interpretation of this latter case was that part of the boron trifluoride present in the first stage had been converted to some other compound, and hence was not available for reaction with the hydride.

The Latent Boron Trifluoride.—The apparently excess consumption of boron trifluoride can be inferred also from the curves in Fig. 2. A break in a curve at any value of, or less than, 0.75 LiAlH$_4$/BF$_3$ without complete conversion of hydride to diborane indicates that more boron trifluoride is consumed than would correspond to simple fluoride salts in the end products. This disappearance of boron trifluoride has been attributed to the formation of lithium fluoborate, whose presence has been confirmed by X-ray analysis. Accordingly, it was of interest to determine whether boron trifluoride in that form still is available for reaction with lithium aluminum hydride.

Addition of Lithium Aluminum Hydride to Lithium Fluoborate.—A procedure similar to that described for the boron trifluoride reactions was used for the hydride–fluoborate reaction. The

TABLE I

A. ADDITION OF LITHIUM ALUMINUM HYDRIDE TO BORON TRIFLUORIDE ETHERATE

Temperature 0°; BF$_3$·(C$_2$H$_5$)$_2$O: 20.78 g. in 80 ml. of ether; LiAlH$_4$: 5.57 g. per 100 ml.

Cumulative volume LiAlH$_4$ solution, ml.	Mole ratio LiAlH$_4$/BF$_3$	Cumulative volume, B$_2$H$_6$, cc.[a]	Mole ratio B$_2$H$_6$/BF$_3$
25.0	0.251	272.2	0.083
45.0	.451	751.3	.229
65.0	.652	931.6	.284
75.0	.752	1096.2	.334
85.0	.852	1100.3	.335
Reflux[b]	.852	1104.4	.336

B. SUBSEQUENT ADDITION OF BORON TRIFLUORIDE ETHERATE AT 25° TO REACTION MIXTURE

Volume BF$_3$·(C$_2$H$_5$)$_2$O added, ml.	Mole ratio BF$_3$/3LiAlH$_4$[c]	Cumulative volume, B$_2$H$_6$, cc.[a]	Max. vol. B$_2$H$_6$ expected from LiAlH$_4$,[c] cc.[a]
0.70	1.10	53.91	...
1.80	2.84	72.49	...
2.50	3.94	155.6	...
22.50	35.5	529.6	223.8
Reflux[b]	35.5	595.5	223.8

[a] At 0° and 760 mm. [b] 35°. [c] Excess LiAlH$_4$ as represented by plateau in Fig. 2.

(11) H. I. Schlesinger and H. C. Brown, THIS JOURNAL, 62, 3429 (1940).

lithium fluoborate was formed *in situ* by the addition of boron trifluoride etherate to a slight excess of lithium carbonate (which is inert toward lithium aluminum hydride) in diethyl ether.[9] The reaction mixture was refluxed and flushed with dry nitrogen for several hours before the addition of the lithium aluminum hydride.

The results of the hydride–fluoborate reaction at 0° are given by the curve in Fig. 3. The shape of the curve is very similar to the curves in Fig. 2, *viz.*, essentially a straight line intersecting the abscissa at a mole ratio of *ca.* 0.06 ($LiAlH_4/LiBF_4$). As in the hydride–boron trifluoride reaction, the yield of diborane was increased by heating the reaction mixture to reflux. From an analysis it was found that only an extremely small amount of non-volatile solute was left in solution. The insoluble solids were water-reactive.
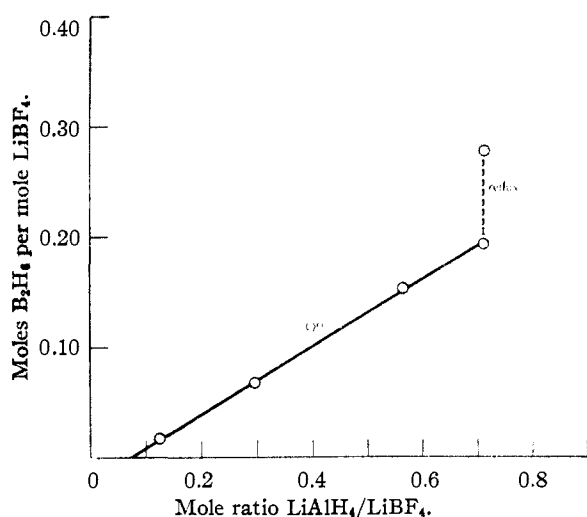

Fig. 3.—Addition of lithium aluminum hydride to lithium fluoborate.

At each point of Fig. 3, the available diborane was removed by the stream of nitrogen, but the yield was less than expected from the amount of added lithium aluminum hydride. However, the lithium aluminum hydride must have been exhausted after each addition, since each new addition at once produced more diborane, in the direct proportion shown by the linear curve. Evidently some of the hydride was inactivated as solid at every stage of the process.

X-Ray Analysis.—Identification of X-ray patterns (powder photographs taken with filtered Cu radiation) of solids formed during the various experiments was made by comparison with patterns of known compounds. These findings corroborated the interpretations presented here for the chemistry of the reactions.

The addition of lithium aluminum hydride to an excess of boron trifluoride etherate at room temperature yielded a solid whose X-ray pattern contained lines of lithium fluoborate as well as unidentified lines which are suspected of belonging to aluminum fluoride. For the case of an excess of lithium aluminum hydride, an air-dried solid gave an X-ray pattern corresponding to that for lithium fluoride, but a sintered specimen gave a pattern containing

lines of lithium fluoaluminate[12] as well as unidentified lines.

The X-ray pattern of an air-dried solid prepared by the addition of lithium aluminum hydride to lithium fluoborate revealed lines of lithium fluoaluminate and unidentified lines. The formation of lithium fluoaluminate at room temperature in this instance is easily understood since both lithium fluoride and aluminum fluoride were precipitated simultaneously. The mere mixing together of the two fluorides at a low (room) temperature is not sufficient to form the complex fluoaluminate.

Discussion

The generation of diborane by the reaction of lithium aluminum hydride and boron trifluoride is a two-stage process, which has been expressed by Eq. 1 and 2. However, these equations are not the only ones which can be postulated to explain the experimental curves in Fig. 1. For example, an equation representing the first stage can be written in which equimolar quantities of lithium aluminum hydride and boron trifluoride give aluminum borohydride and a mixture of lithium fluoride and aluminum fluoride. The second stage can be the reaction of boron trifluoride and aluminum borohydride to give diborane and aluminum fluoride. The over-all reaction, in this case, would be the same as represented by Eq. 3. Attempts to select the proper pair of equations by chemical analysis of the intermediates in the reaction have proven inconclusive; nevertheless, there is sufficient evidence from the experimental data to indicate that Eq. 1 and 2 are to be preferred over those involving aluminum borohydride.

The solid residue containing the latent hydride exhibited physical and chemical characteristics which one would expect if the hydride were lithium borohydride[11] rather than the aluminum borohydride[13] or its etherate. For example, at no time did any of the residues upon exposure or heating in air exhibit the violent reactivity characteristic of aluminum borohydride.

The formation of lithium fluoborate also can be used as a basis for the selection of the proper equations. The postulation of aluminum borohydride as an intermediate would require the formation of lithium fluoborate to occur only during the first stage of the process, whereas if the intermediate is lithium borohydride the fluoborate formation must take place during the second stage. The latter seems to be true, since in Fig. 1 the deviation of the experimental curve from the theoretical curve occurs only during the second stage.

The occurrence of lithium fluoborate can be explained in either of two ways: (1) the direct addition of boron trifluoride to the freshly precipitated lithium fluoride, or (2) as a side product of a series of complex reactions, the sum of which would be Eq. 2. It is still premature to state which factor is the more important until the reaction mechanism has been worked out.

(12) The "known" lithium fluoaluminate sample was prepared according to the procedure of R. H. Carter, *Ind. Eng. Chem.*, **22**, 888 (1930).

(13) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, This Journal, **62**, 3421 (1940).


The Catalytic Dehydrogenation of 5-Substituted 1,2,3,4-Tetrahydronaphthalene Derivatives

BY MELVIN S. NEWMAN AND THEODORE S. BYE[1]

The syntheses of RCOOCH$_3$, RCH$_2$OH, RCH$_2$OCOCH$_3$, RCOCH$_3$, RCH$_2$COCH$_3$ and RCH$_2$CH$_2$COCH$_3$, where R is the 1,2,3,4-tetrahydro-5-naphthyl radical, are described. The products arising from liquid phase catalytic dehydrogenation of these compounds over palladium-on-charcoal are described and the results compared with those previously obtained with 1,2,3,4-tetrahydro-6-naphthyl, 1,2,3,4-tetrahydro-1-naphthyl and 1,2,3,4-tetrahydro-2-naphthyl derivatives.

The work reported herein is a continuation of studies designed to obtain more information concerning the fate of oxygenated functions in hydroaromatic compounds when submitted to liquid phase dehydrogenation over palladium-on-charcoal. The previous reports dealt with 6-substituted 1,2,3,-4-tetrahydronaphthalenes,[2] B, 1-substituted 1,2,-3,4-tetrahydronaphthalenes,[3] C, and 2-substituted 1,2,3,4-tetrahydronaphthalenes,[4] D.

Since the oxygenated functions, OF, of B, C and D differed both in their positions with respect to the point of fusion and in their relative positions with respect to the hydrogen to be removed, it was necessary to study compounds of type A before a complete discussion could be attempted. In this paper, we describe the dehydrogenation of 5-substituted-1,2,3,4-tetrahydronaphthalenes, A, under the above conditions. The results are summarized in Table I.

A   B   C   D
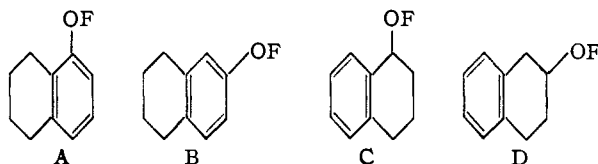
Experimental[5]

1,2,3,4-Tetrahydro-5-naphthoic Acid. A. Hydrogenation of Ethyl α-Naphthoate.[6]—The ester to be hydrogenated was heated for two hours with Raney nickel at 150°. After cooling, the catalyst was filtered and the ester rectified through a column with a one-foot packed section containing glass helices. There was obtained 1920 g. of pure ester.

(1) This work was taken from the dissertation submitted by T. S. Bye to The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, March, 1951.

(2) M. S. Newman and H. V. Zahm, THIS JOURNAL, **65**, 1097 (1943).

(3) M. S. Newman and Fr. T. J. O'Leary, *ibid.*, **68**, 258 (1946).

(4) M. S. Newman and J. R. Mangham, *ibid.*, **71**, 3342 (1949).

(5) All melting points are corrected. Microanalyses marked *ᵇ* by Mrs. E. K. Klotz; *ᶜ* by Clarke Microanalytical Laboratory, Urbana, Illinois.

(6) S. I. Sergievskaya and E. G. Nikhamkina, *J. Gen. Chem. (U. S. S. R.)*, **15**, 988 (1945). We wish to thank the Hooker Electrochemical Company, Niagara Falls, New York, for carrying out the large scale hydrogenation. The following sentences are quoted from a letter: "The hydrogenation was carried out as a 20% ethanol solution and it was found that three separate autoclave runs were required to process the solution. Our Operations Department advises us furthermore, that absorption was rapid and complete after the first hour but that the runs were continued for a total of 5 hours as advised in the reference."

The hydrogenation was carried out as a 20% ethanol solution, using a Raney nickel catalyst, a temperature of 130–150° and a pressure of 50 atmospheres. After removal of the solvent, the mixture of hydrogenated esters was rectified to yield 1532 g. (79.8%) of hydrogenated ester.

B. Preparation of 1,2,3,4-Tetrahydro-5-naphthoic Acid.—This acid was obtained pure from the above mixture of esters in two ways. The last two fractions of ester, 365.7 g., were combined and saponified with alcoholic potassium hydroxide. The acid, after recrystallization from 50% alcohol, weighed 283 g., m.p. 150.7–151.9°. The other fractions were saponified individually to mixtures of 1,2,3,4-tetrahydro-5-naphthoic acid and 1,2,3,4-tetrahydro-1-naphthoic acid. Separation was accomplished by fractional acidification from alkaline solution. Batches of two or three fractions of the mixture of acids were saponified and fractionally acidified according to the principles outlined previously.[7] By this method, there was obtained 261 g. of pure 1,2,3,4-tetrahydro-5-naphthoic acid, m.p. 150.0–151.5°. The total yield of pure acid was 544 g. (32.2% based on the ethyl α-naphthoate).

Methyl 1,2,3,4-Tetrahydro-5-naphthoate (I).—The methyl ester prepared from the above acid in 90% yield formed a colorless liquid, b.p. 93.5–96.5° at 0.5–1.0 mm., n^{25}D 1.5431.

Anal. Calcd. for C$_{12}$H$_{14}$O$_2$: C, 75.8; H, 7.4. Found: C, 75.4, 75.3; H, 7.3, 7.5.

1,2,3,4-Tetrahydro-5-naphthylcarbinol (II).—During two hours, a solution of 110 g. (0.58 mole) of I in 800 ml. of anhydrous ether was dropped into an ethereal solution of 13.5 g. of lithium aluminum hydride.[8] After the reaction mixture had been decomposed with water and dilute sulfuric acid, distillation yielded 91.5 g. (97.7%) of the desired carbinol, II, as a colorless viscous oil, b.p. 105–107° at 0.5–1.0 mm., n^{20}D 1.5682. Its 1-naphthylurethan melted at 136.7–137.7°.

Anal. Calcd. for C$_{11}$H$_{14}$O: 81.5; H, 8.6. Found[ᶜ]: C, 81.7; H, 8.6. Calcd. for C$_{22}$H$_{21}$O$_2$N: C, 79.8; H, 6.3; N, 4.2. Founds: C, 80.5, 80.3; H, 6.0, 6.40 N, 4.3.

The corresponding acetate, III, was formed in 88% yield by heating the carbinol, II, in benzene with acetic anhydride and a trace of p-toluenesulfonic acid. It formed a colorless oil, b.p. 102° at 0.4–0.8 mm., n^{25}D 1.5325.

Anal.[ᶜ] Calcd. for C$_{13}$H$_{16}$O$_2$: C, 76.5; H, 7.9. Found: C, 76.3; H, 8.0.

Methyl 1,2,3,4-Tetrahydro-5-naphthyl Ketone (IV).—Into a solution made from 12.2 g. (1.75 moles) of metallic lithium, 114 g. (0.8 mole) of methyl iodide and 500 ml. of anhydrous ether[9] was slowly added a solution of 20 g. (0.114 mole) of RCOOH in 800 ml. of ether. The mixture was treated with water and the neutral portion distilled to yield 19.5 g. (99%) of the desired ketone, IV, as a colorless oil, b.p. 95.5–99.0° at 0.5–1.0 mm., n^{20}D 1.5550. The semicarbazone melted at 221.5–223.5° with decomposition.

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(8) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 1197 (1947).

(9) D. A. Van Dorp and J. F. Arens, *Rec. trav. chim.*, **65**, 338 (1946).