isolated. Similar difficulties have been encountered in the reduction of keto-acids by sodium borohydride.[1]

TABLE I

REDUCTIONS BY LITHIUM BOROHYDRIDE

Compound	Product	Yield, %
n-Heptaldehyde	*n*-Heptanol	83
Benzaldehyde	Benzyl alcohol	91
Crotonaldehyde	Crotyl alcohol	70
Methyl ethyl ketone	*s*-Butanol	77
Benzophenone	Benzhydrol	81
n-Butyl palmitate	*n*-Hexadecanol	95
Ethyl benzoate	Benzyl alcohol	62
Ethyl sebacate	Decamethylene glycol	60
β-Benzoylpropionic acid	γ-Phenylbutyrolactone	78
Ethyl levulinate	γ-Valerolactone	44
m-Nitroacetophenone	α-(*m*-Nitrophenyl)-ethanol[a]	93

[a] This product was obtained in an unstable crystalline modification, m. p. 25°, reverting on melting to the stable form, m. p. 61.5°; reported [Lund, *Ber.*, **70**, 1520 (1937)] m. p. 62.5°.

The action of lithium borohydride on carboxylic acids is complex. Benzoic acid caused decomposition of the hydride with the evolution of some diborane, but the benzoic acid was recovered unchanged. Butyric acid, after one half hour, was reduced to butyl alcohol to the extent of 8% and 75% of the acid was recovered. Crotonic acid, refluxed two hours, was recovered to the extent of 45%, the only isolable products being butyl alcohol (4%) and butyric acid (10%).

Nitrobenzene, after refluxing for eighteen hours with excess lithium borohydride in an ether–tetrahydrofuran mixture, furnished 22% aniline, 30% of an intractable dark red oil, and 30% unchanged nitrobenzene.

As the examples given in Table I show, neither the nitro group (*m*-nitroacetophenone) nor the free carboxyl group (β-benzoylpropionic acid) seriously interferes in the reduction of carbonyl groups.

[1] Chaikin and Brown, THIS JOURNAL, **71**, 122 (1949).

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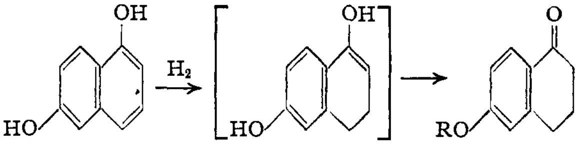
6-Methoxy-1-tetralone

BY DOMENICK PAPA

The selective hydrogenation of β-naphthol and β-naphthyl methyl ether[1] to the corresponding aryl-tetrahydro derivatives has been the most favored approach to the synthesis of 6-methoxy-1-tetralone[2] (IV). In addition, ring closure of γ-arylbutyric acids[2,3] and alkali fusion of tetralin-6-sulfonic acid[4] have given intermediates for the synthesis of IV.

Recently it has been reported[5] from these laboratories that 1,6-dihydroxynaphthalene (I) on treatment with Raney nickel–aluminum alloy in aqueous alkaline solution affords good yields of 6-hydroxy-1-tetralone (III). This reaction may be assumed to proceed either through the intermediate dihydro compound II, which rearranges to the tetralone III, or through the formation of 1,6-dihydroxytetralin (V) and subsequent dehydrogenation of V to III.[6]



I II III R = H
IV R = CH_3

The failure of the alloy procedure to reduce III even after prolonged treatment with large excesses of nickel–aluminum alloy suggested that mild catalytic hydrogenation of I would yield III. Hydrogenation of I in 2% aqueous sodium hydroxide solution with Raney nickel catalyst at room temperature and a pressure of 2–3 atmospheres gave an uptake of one mole of hydrogen within one to one and one-half hours. The crude tetralone III was converted to IV with dimethyl sulfate in an over-all yield of 72%.

Preliminary experiments indicate that the noble metal catalysts give better yields of IV, as the semicarbazone, from I in acidic than in neutral or alkaline medium. As yet, we have not succeeded in isolating (IV) in pure form from the catalytic reduction with the noble metals. We are continuing our studies of the reduction of I and 6-methoxy-1-naphthol by catalytic and chemical methods.

Experimental

Hydrogenation with Raney Nickel.—To a solution of 16.0 g. (0.1 mole) of 1,6-dihydroxynaphthalene[7] (m. p. 137–138°) in 300 cc. of 2% sodium hydroxide, there was added 5 cc. of Raney nickel catalyst.[8] The hydrogenation was carried out in the conventional Parr apparatus at room temperature at an initial pressure of 35–40 lb. After one and one-half hours[9] the hydrogen absorption ceased

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[1] Stork, THIS JOURNAL, **69**, 576 (1947).

[2] Thomas and Nathan, *ibid.*, **70**, 331 (1948); refs. 1–6.

[3] Johnson and Glenn, *ibid.*, **71**, 1092 (1949).

[4] Burnop, Elliot and Linstead, *J. Chem. Soc.*, 727 (1940).

[5] (a) Papa, Schwenk and Breiger, *J. Org. Chem.*, **14**, 366 (1949); (b) Papa and Schwenk, U. S. Patent 2,475,781, July 12, 1949.

[6] Compare Schwenk, Papa, Whitman and Ginsberg, *J. Org. Chem.*, **9**, 1 (1944). Although this sequence of reactions is not very probable, the action of Raney nickel–aluminum alloy on V is being studied.

[7] Generous samples of 1,6-dihydroxynaphthalene have been obtained from National Aniline Division of Allied Chemical and Dye Corporation through the courtesy of Mr. B. M. Helfaer of the Buffalo plant.

[8] The Raney nickel catalyst was prepared at 50° essentially as described by Mozingo, Wolf, Harris and Folkers, THIS JOURNAL, **65**, 1015 (1943), and was washed once with distilled water after decanting off the alkaline solution.

[9] In one instance the hydrogenation was quite sluggish, possibly due to the poisoning of the catalyst. In this case the nickel catalyst was filtered off and a fresh sample added. The hydrogenation then proceeded normally.

and corresponded to one mole of hydrogen. The alkaline solution was filtered to remove the nickel catalyst, diluted to 500 cc. with 25% sodium hydroxide solution. To this solution there was added 50 cc. of dimethyl sulfate and the methylation was carried out as usual. The alkaline solution was then extracted with two 100-cc. portions of ether and the combined ether extracts washed and dried. After removing the ether, the residue was distilled; yield 12.7 g. (72%), b. p. 135–139° (1 mm.), m. p. 75–77°. The semicarbazone, prepared in the usual manner, melted at 235.5–236.5° after recrystallization from aqueous alcohol.

Anal. Calcd. for $C_{12}H_{15}O_2N_3$: N, 18.01. Found: N, 18.06.

Reduction with Platinum Oxide Catalyst.—To 16.0 g. (0.1 mole) of 1,6-dihydroxynaphthalene in 150 cc. of acetic acid, there was added 200 mg. of Adams platinum oxide catalyst. The hydrogenation was carried out as described for the nickel catalyst and at the end of approximately three hours one mole of hydrogen had been absorbed. After filtering the platinum catalyst, the acetic acid was removed *in vacuo* and the residue dissolved in 300 cc. of 10% sodium hydroxide. Methylation of the crude hydroxy tetralone and isolation of the methylated product was carried out as described above. In this case, distillation yielded 6.8 g. of a pale yellow liquid, b. p. 130–144° (1 mm.) from which no crystalline material could be isolated. One gram of the distilled product was treated with semicarbazide hydrochloride and 0.16 g. of semicarbazone was isolated. The semicarbazone, after recrystallization from aqueous alcohol, melted at 230–232° and showed no depression on admixture with the product obtained by the nickel catalyst reduction. We are continuing our studies of this reduction procedure in order to establish the nature of the non-ketonic material.

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Sulfanilamido-quinoxalines

BY BERTIE C. PLATT AND THOMAS M. SHARP

A paper by Wolf, Pfister, Beutel, Wilson, Robinson and Stevens[1] has appeared almost simultaneously with one by us[2] on sulfonamides derived from substituted quinoxalines. It is possible by inspection of the melting points quoted by Wolf,[1] *et al.*, to identify some of the compounds which were not fully identified by them.

In Table III[1] two 2-amino-6(or 7)-methylquinoxalines are described (a) m. p. 178–180° and (b) m. p. 171–173°. The former must be 2-amino-6-methylquinoxaline since it was prepared from 2-chloro-6-methyl-quinoxaline identified by Platt[3] by an unambiguous synthesis of 2-hydroxy-6-methylquinoxaline from 4-nitro-*m*-tolylglycine and conversion to the corresponding chloro and amino derivatives. The compound (b) m. p. 171–173° appears to be a mixture of 2-amino-6-methyl and 2-amino-7-methylquinoxalines since it was prepared from an impure 2-chloro-7-methylquinoxaline m. p. 56–57°. Pure 2-chloro-7-methylquinoxaline has m. p. 76° (Platt[3]). Platt[3] found 2-amino-6-methylquinoxaline, prepared by a method which could yield only one isomer, to have m. p. 181–182°, and 2-amino-7-methylquinoxaline, prepared in a similar manner to have m. p. 178–180°. A mixture of the two in approximately equal proportions had m. p. 172–174°. It is well known that mixtures of isomers in the quinoxaline series are very difficult to separate.

2-Chloro-5(or 8)-methylquinoxaline, m. p. 92–93°, of Table II[1] is identified as 2-chloro-5-methylquinoxaline which we[3] have synthesized rationally (m. p. 95°) and converted to 2-amino-5-methylquinoxaline (m. p. 201–2°). 2-Amino-5(or 8)-methylquinoxaline (m. p. 202–3°) of Table III[1] is therefore the 5-methyl isomer. (The isomeric 2-amino-8-methylquinoxaline we find to melt at 129°). The corresponding N^4-acetylsulfanilamide, m. p. 228–229°, and the N^1-sulfanilamide, m. p. 205–206° (Tables IV and V[1]) accordingly have the methyl groups in the 5-positions.

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LONDON, N. W. 1, ENGLAND
RECEIVED APRIL 26, 1949

[1] Wolf, Pfister, Beutel, Wilson, Robinson and Stevens, THIS JOURNAL, **71**, 6 (1949).

[2] *J. Chem. Soc.*, 2129 (1948).

[3] Platt, *ibid.*, 1310 (1948). This was recognized by Wolf, *et al.*, but by an unfortunate misprint they say ambiguous instead of unambiguous.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,[1] PHILADELPHIA 18, PENNSYLVANIA]

2-(2-Chloroethoxy)-ethyl Acetate and 2-Chloroethyl Vinyl Ether

BY C. E. REHBERG

Dioxane is the principal impurity in the crude 2-chloroethyl vinyl ether prepared by the method of Cretcher.[2] Cretcher considered that the two formed an azeotrope which boiled at 107°. This azeotrope appeared remarkable in that its boiling point was between those of the two components of the azeotropic mixture.

In the work reported here, chloroethyl vinyl ether was prepared in 60% yield by Cretcher's method. When the crude product was distilled through a column having 60 theoretical plates, dioxane was obtained at 101–102°, a mixture of dioxane and ether at 102–108°, and finally, pure ether at 108°. Since both pure dioxane and pure ether were distilled from the mixture, it is evident that no azeotrope was formed.

The ether was also distilled at reduced pressure (120 mm.). Dioxane distilled at 52–53°, and chloroethyl vinyl ether at 59°; a mixture of variable composition was obtained between the pure components.

The following properties were observed with chloroethyl vinyl ether[3]: b. p., 108°, 59° (120 mm.); $n^{20}\mathrm{D}$ 1.4378; $d^{20}{}_4$ 1.0475.

(2-Chloroethoxy)-ethyl Acetate.—An effort was made to produce chloroethyl vinyl ether by

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] Cretcher, Koch and Pittenger, THIS JOURNAL, **47**, 1173 (1925).

[3] Cretcher reported b. p., 109° (740 mm.); $d^{15}{}_{15}$ 1.0525; W. Chalmers reported b. p. 108°, $n^{20}\mathrm{D}$ 1.4362; $d^{20}{}_4$ 1.044 (*Can. J. Research*, **7**, 464 (1932)).