Summary

1. Results have been given to show that hydrogen is highly efficient as a carrier gas for the dehydrogenation of borneol vapor over reduced copper, particularly in respect to catalyst life and purity of product.

2. Optimum conditions with respect to temperature and time have been established for the reaction thus conducted.

3. Results have been given to show that carbon dioxide is in most respects inferior to hydrogen as a carrier.

4. Preliminary experiments have been reported which indicate that reduced cobalt and nickel are excellent catalysts for the dehydrogenation of borneol when used in the presence of hydrogen.

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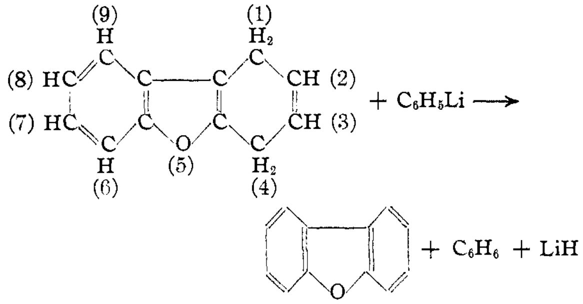
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dehydrogenation by Organometallic Compounds

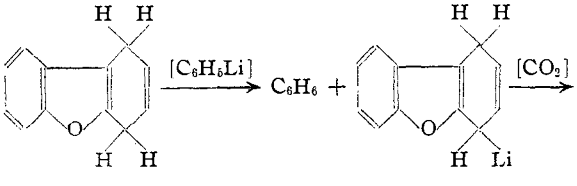
BY HENRY GILMAN AND CHESTER W. BRADLEY

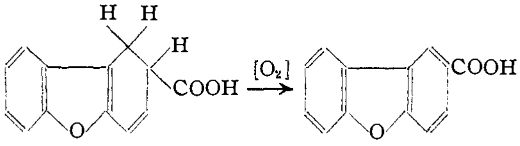
Introduction

In attempting to metalate 1,4-dihydrodibenzofuran in ether solution by means of phenyllithium, dibenzofuran instead of the expected metalation product was the chief compound isolated. The brown color produced at the inception of reaction indicated the formation of a metalation product. This color slowly disappeared on refluxing and a white precipitate, subsequently shown to be lithium hydride, formed. The isolation of dibenzofuran, lithium hydride and benzene indicated that the following transformation had taken place.



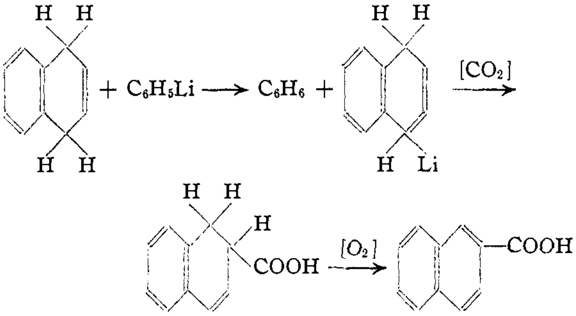
The intermediate metalation product was characterized subsequently (after allowing the reaction to proceed for a shorter time and at a lower temperature) by carbonation, to yield 1,2-dihydrodibenzofuran-2-carboxylic acid. The position of the carboxyl group was established by oxidizing the dihydro acid to the known dibenzofuran-2-carboxylic acid.





Dehydrogenation of 1,4-dihydrodibenzofuran also was effected by *n*-butyllithium and *n*-butylsodium. It was shown subsequently that the related 1,4-dihydrodibenzothiophene is dehydrogenated to dibenzothiophene by organolithium and organopotassium compounds.[1]

A related series of reactions was then observed with 1,4-dihydronaphthalene. Here, also, moderate conditions made it possible to characterize the intermediate metalation compound.



Carbonation of the intermediate organometallic compounds derived from 1,4-dihydrodibenzofuran, 1,4-dihydrodibenzothiophene and 1,4-dihydronaphthalene probably involves an allylic rearrangement. An illustration of a related rearrangement with organosodium compounds is the work of Schlenk and Bergmann.[2] These authors obtained the same acid by carbonating the organosodium compounds obtained from the

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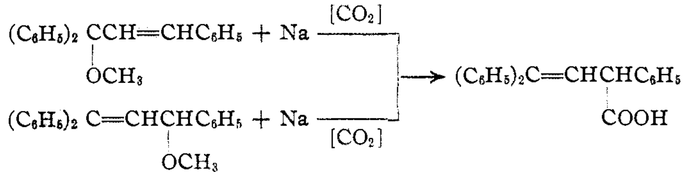
(1) Gilman and Jacoby, *J. Org. Chem.*, **3**, in press (1938).

(2) Schlenk and Bergmann, *Ann.*, **479**, 78 (1930).

methyl ethers of diphenylstyrylcarbinol and β,β-diphenylvinylphenylcarbinol, respectively.



$$(C_6H_5)_2\underset{OCH_3}{C}CH{=}CHC_6H_5 + Na \xrightarrow{[CO_2]} (C_6H_5)_2C{=}CH\underset{COOH}{C}HC_6H_5$$

$$(C_6H_5)_2C{=}CH\underset{OCH_3}{C}HC_6H_5 + Na \xrightarrow{[CO_2]} (C_6H_5)_2C{=}CH\underset{COOH}{C}HC_6H_5$$

The illustrations just given are of lateral types. Related allylic rearrangements also take place with lateral-nuclear types as in 2-furylmethylsodium[3a] and benzyllithium.[3b] Rearrangements of these kinds now appear to be reactions common to practically all types of reactive and moderately reactive organometallic compounds,[4] but they have been most closely examined with organomagnesium compounds.[5]

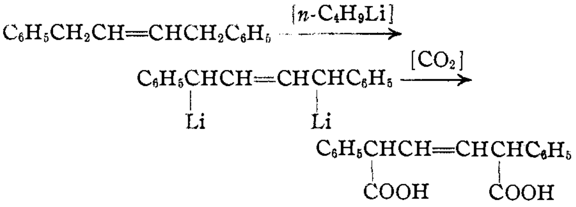
If an allylic rearrangement is the correct interpretation for the mechanism of reaction, it is interesting to inquire why the carboxyl group in the dihydrodibenzofuran- and dihydrodibenzothiophenecarboxylic acids is attached to the 2-position and not to the 3-position. Both dihydro types have active methylene groups in the 1- and in the 4-positions. Replacement of hydrogen in the 1-methylene group followed by rearrangement should give a 3-carboxylic acid, whereas replacement in the 4-methylene group should give the 2-carboxylic acid. It may be significant that metalation of the parent types, dibenzofuran and dibenzothiophene, by organoalkali compounds invariably involves the 4-position. Furthermore, metalations of ethers (like anisole and diphenyl ether) invariably involves the position ortho to the ether linkage.

Dehydrogenation by organometallic compounds is not restricted to cyclic compounds. It has been shown that *n*-butyllithium dehydrogenates 1,4-diphenylbutene-2 to give 1,4-diphenylbutadiene-1,3.

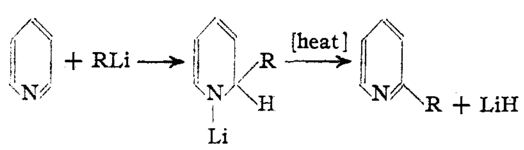
$$C_6H_5CH_2CH{=}CHCH_2C_6H_5 + n\text{-}C_4H_9Li \longrightarrow C_6H_5CH{=}CHCH{=}CHC_6H_5$$

Carbonation of the reaction mixture also yielded 1,4-diphenyl-2-butene-1,4-dicarboxylic acid. This dibasic acid probably was formed as a consequence of dimetalation of the reactive methylene groups in 1,4-diphenylbutene-2.

The loss of alkali hydrides from organometallic compounds at temperatures not exceeding the boiling point of ether rarely has been observed. However, the N-lithium derivatives of some reduced nitrogen heterocycles, formed by addition and not substitution reactions, lose lithium hydride at temperatures as low as 70–100°. The following reaction illustrates a transformation described by Ziegler and Zeiser.[6]



$$C_6H_5CH_2CH{=}CHCH_2C_6H_5 \xrightarrow{[n\text{-}C_4H_9Li]} C_6H_5\underset{Li}{C}HCH{=}CH\underset{Li}{C}HC_6H_5 \xrightarrow{[CO_2]} C_6H_5\underset{COOH}{C}HCH{=}CH\underset{COOH}{C}HC_6H_5$$



A related reaction takes place with other nitrogen heterocycles, but generally at more elevated temperatures. Also, ethylsodium decomposes slowly at room temperature and quite rapidly at 100° to give sodium hydride, ethane and ethylene.[7] Pyrolysis of ethylmagnesium bromide at 175° gives magnesium hydride and ethylene.[8]

Experimental Part

1,4-Dihydrodibenzofuran.—To a solution of 12.0 g. (0.54 g. atom) of sodium in 400 cc. of liquid ammonia was added 30 g. (0.18 mole) of *finely divided* dibenzofuran over a period of twenty to thirty minutes and the stirring continued for thirty minutes.

Ammonium chloride was then added slowly in slight excess, and the product was finally distilled under reduced pressure (b. p. 110° (5 mm.)). The yield was 82%, after recrystallization from methanol and petroleum ether (b. p. 60–68°), m. p. 42°.

Anal. Calcd. for $C_{12}H_{10}O$: C, 84.65; H, 5.93. Found: C, 84.40; H, 5.87.

Dehydrogenation of 1,4-Dihydrodibenzofuran by Phenyllithium.—A filtered ether solution of phenyllithium (0.125 mole) was run into an ether solution of 17 g. (0.01 mole) of 1,4-dihydrodibenzofuran. The mixture immediately turned brownish and the color intensified slowly. In about two hours a white precipitate became noticeable, and at the end of fifteen hours of refluxing all of the brown color disappeared and there was a considerable accumulation of white precipitate.

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[3] (a) Gilman and Breuer, THIS JOURNAL, **56**, 1123 (1934); (b) Gilman and Breuer, *ibid.*, **56**, 1127 (1934).

[4] Studies by Joseph F. Nelson.

[5] General references are contained in the following articles: Gilman and Kirby, THIS JOURNAL, **54**, 345 (1932), and Austin and Johnson, *ibid.*, **54**, 647 (1932).

[6] Ziegler and Zeiser, *Ber.*, **63**, 1847 (1930); *Ann.*, **485**, 174 (1931). See also Bergstrom, THIS JOURNAL, **52**, 2845 (1930).

[7] Carothers and Coffman, *ibid.*, **51**, 588 (1929).

[8] Jolibois, *Compt. rend.*, **155**, 353 (1912); Clapp and Woodward, THIS JOURNAL, **60**, 1019 (1938).

The ether solution was filtered from the precipitate, and the filtrate distilled to yield 1.5 g. (19%) of benzene (identified as the *m*-dinitrobenzene derivative). Distillation of the residue gave dibenzofuran; 88% yield of crude material or 70% yield of compound highly purified by crystallization.

The white precipitate was analyzed by decomposing with water and measuring the hydrogen evolved and also titrating the lithium hydroxide formed. The hydrogen and lithium hydroxide were formed in equivalent quantities from a sample. The hydrogen was analyzed by combustion methods.

In another experiment in which refluxing was continued for only one and one-quarter hours before carbonation, some brownish colored material was present at the end of that time. However, the quantity of intermediate metalation product must have been small for the yield of dibenzofuran was 86% and only a trace of acidic material was isolated.

Apropos the ready loss of lithium hydride, it was noted that refluxing and extended time of reaction are not necessary. From an experiment allowed to run but ten minutes and with no refluxing, the yield of dibenzofuran was 70% and the yield of dihydrodibenzofurancarboxylic acid was 27%.

In another experiment in which an excess of phenyllithium was used there was obtained a 66% yield of dibenzofuran and a 5% yield of dibenzofuran-4-carboxylic acid. This acid undoubtedly was due to metalation of the dibenzofuran by the excess of phenyllithium.

Metalation of 1,4-Dihydrodibenzofuran.—Five-hundredths mole of dihydrodibenzofuran and an equivalent quantity of phenyllithium were allowed to react for thirty-five minutes at −15°, after which time carbonation was effected by an ether–solid carbon dioxide mixture. From the ether extract there was recovered a 59% yield of the dihydrodibenzofuran. No dibenzofuran was isolated.

Acidification of the alkali extract yielded 3.6 g. (34%) of dihydrodibenzofurancarboxylic acid which melted at 278–279° after recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_{10}O_3$; C, 72.75; H, 4.70; neut. equiv., 217. Found: C, 72.58; H, 4.84; neut. equiv., 220.

The dihydrodibenzofurancarboxylic acid was oxidized by two different procedures to dibenzofuran-2-carboxylic acid. First, the dihydro acid was heated with an equal weight of sulfur at 250° for three-fourths of an hour to give a 66% yield of dibenzofuran-2-carboxylic acid. Second, a glacial acetic acid solution of the dihydro acid and an equivalent quantity of bromine were refluxed for fifteen minutes to give a 90% yield of dibenzofuran-2-carboxylic acid. The acid obtained by these two oxidation procedures was identified by (1) direct comparison with an authentic specimen and (2) conversion to methyl dibenzofuran-2-carboxylate which was also compared with an authentic specimen.

Dehydrogenation of 1,4-Dihydrodibenzofuran by *n*-Butylsodium and *n*-Butyllithium.—*n*-Butylsodium was prepared by adding 2.5 g. (0.11 g. atom) of sodium to 8.5 g. (0.0271 mole) of di-*n*-butylmercury in 200 cc. of petroleum ether (b. p. 60–68°). The reaction was allowed to proceed for one hour and then 9.2 g. (0.054 mole) of dihydrodibenzofuran in 25 cc. of petroleum ether was added. Slight warming was observed, and a muddy brown suspension appeared immediately. After three hours of refluxing, the mixture became gray in color.

The supernatant liquid was decanted through a filter, and the residue washed once with petroleum ether. From the petroleum ether was obtained 3.7 g. of dibenzofuran.

The solid residue was suspended in petroleum ether and carbonated. Extraction with 5% sodium hydroxide followed by acidification of the extract yielded 2.5 g. (21.5%) of dibenzofuran-4-carboxylic acid. The petroleum ether fraction yielded an additional 2.4 g. of dibenzofuran which made the total yield of this product 66%.

From a reaction between dihydrodibenzofuran and *n*-butyllithium there was obtained an 84% yield of dibenzofuran.

Dehydrogenation of 1,4-Dihydronaphthalene.—The 1,4-dihydronaphthalene was prepared in accordance with the directions of Bamberger and Lodter[9] and purified by the method of Sand.[10]

Dehydrogenation was carried out with phenyllithium in a manner identical with that used with dihydrodibenzofuran. Reaction was slower, as evidenced by the slow development of the brown color and the noticeable formation of a precipitate in about four hours. After sixteen hours of refluxing the brown color had faded considerably and much white precipitate was present. The reaction mixture was then carbonated and the products worked up. Starting with 4 g. of dihydronaphthalene, the yield of naphthalene was 85%.

In another experiment, the precipitate was filtered before carbonation and shown to be lithium hydride.

Metalation of 1,4-Dihydronaphthalene.—Five grams of 1,4-dihydronaphthalene was metalated at −15° with an equivalent amount of *n*-butyllithium. After stirring for seven hours the reaction mixture was carbonated.

The products isolated were a 64% recovery of dihydronaphthalene and 1.7 g. or a 26% yield of 1,2-dihydro-2-naphthoic acid melting at 105–106°. This dihydro acid was oxidized to β-naphthoic acid in accordance with the procedure of Baeyer.[11] Identification was completed by the method of mixed melting points.

Dehydrogenation of 1,4-Diphenylbutene-2.—A filtered solution of *n*-butyllithium, prepared from 0.014 mole of *n*-butyl bromide, was added to an ether solution of 2.1 g. (0.01 mole) of 1,4-diphenylbutene-2 (prepared in accordance with the directions of Freund and Immerwahr[12]). The mixture turned yellow at first, then brown in about ten minutes, and brilliant red in thirty minutes. The maximum color intensity seemed to have been reached in about two hours. The solution was refluxed for nine hours and was then filtered into an ether–solid carbon dioxide mixture.

From the ether fraction obtained after carbonation there was isolated a 12% yield of 1,4-diphenylbutadiene-1,3 (mixed melting point). In a check experiment the yield was 15%.

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(9) Bamberger and Lodter, *Ann.*, **288**, 75 (1895).

(10) Sand, *Ber.*, **36**, 3705 (1905).

(11) Baeyer, *Ann.*, **266**, 202 (1891).

(12) Freund and Immerwahr, *Ber.*, **23**, 2857 (1890); see also Straus, *Ann.*, **342**, 253 (1905).

The aqueous solution gave 0.30 g. or a 12% yield of acid melting at 219–220°. This acid was shown to be 1,4-diphenyl-2-butene-1,4-dicarboxylic acid.[13]

Summary

It has been shown that the more reactive organometallic compounds dehydrogenate some partially reduced nuclear and open-chained compounds smoothly and under very mild conditions. Illustrations are the conversion of 1,4-dihydronaphthalene to naphthalene, 1,4-diphenylbutene-2 to 1,4-diphenylbutadiene-1,3, and 1,4-dihydrodibenzofuran to dibenzofuran.

Intermediate compounds have been isolated and a mechanism considered.

AMES, IOWA RECEIVED JULY 14, 1938

[13] Schlenk and Bergmann, *Ann.*, **463**, 100 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Reactivities of Organometallic Compounds. XIX. Hydrogenolysis of RM Compounds

BY HENRY GILMAN, ARTHUR L. JACOBY AND HELEN LUDEMAN

Introduction

The smooth and ready dehydrogenation by organometallic compounds described in the preceding[1] paper suggested that the more reactive organometallic compounds might undergo easy hydrogenolysis. This has been found to be the case. Actually, some of the organoalkali compounds are cleaved by hydrogen under extremely mild conditions: room temperature, atmospheric pressure and in the absence of any catalyst. Apparently there is no report of any other class of organic compounds reacting with hydrogen under such mild conditions. Not only do some organometallic compounds undergo easier reduction than any other type of organic compound, but they also appear to be oxidized at least as readily as any other class.

Relative Rates of Hydrogenolysis of RM Compounds Having Different Metals.—The varying rates of hydrogenolysis of organoalkali and other reactive organometallic compounds suggested the possibility of a correlation with the relative reactivities of organometallic compounds established with other reactants. Earlier studies by others pointed to such a relationship. Ipatieff and Rasuwajeff[2a] showed that under elevated pressures (60 atmospheres), elevated temperatures (225 and 350°) and in the absence of catalysts, the rate of hydrogenolysis of the triphenyl derivatives of phosphorus, arsenic, antimony and bismuth increased in the order: P, As, Sb, Bi. Then Zartman and Adkins,[3] in an examination of the hydrogenation of some more reactive RM compounds, found that the order of increasing ease of hydrogenation of R_3Sb, R_4Pb, R_2Zn and R_2Mg compounds was: Sb, Pb, Zn, Mg. These authors used not only elevated temperatures and pressures but also a nickel catalyst. Two reactions were noted, depending on the kind of RM compound used

$$R_2M + H_2 \longrightarrow R{\cdot}R + M$$
$$R_2M + H_2 \longrightarrow 2RH + MH_2$$

For example, tetraphenyllead gave biphenyl and lead, both a catalyst and hydrogen being necessary, and diphenylmagnesium gave benzene and magnesium hydride. Ipatieff and co-workers[2b] observed the following reaction with tetraalkyl- and tetraaryllead compounds in the absence of a catalyst, but in a glass and not a copper reaction vessel.

$$R_4Pb + 2H_2 \longrightarrow 4RH + Pb$$

We have found that the order of increasing ease of hydrogenolysis of some very reactive organometallic compounds is: Ca, Li, Na, K, Rb, Cs. This order together with the orders established by Ipatieff and by Adkins follows almost exactly the order of increasing chemical reactivity of the organometallic compounds as established in other reactions. It is interesting to note that here, as in the recent study[4] on the relative reactivities of organoalkali compounds, there is only a small difference between the relative reactivities of organopotassium and organorubidium compounds.

The preponderant reaction which takes place with organoalkali compounds is

$$RM + H_2 \longrightarrow RH + MH$$

The rate of hydrogenolysis varies somewhat with the medium, as illustrated in Fig. 1. The

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[1] Gilman and Bradley, THIS JOURNAL, **60**, 2333 (1938).

[2] (a) Ipatieff and Razuwajeff, *Ber.*, **63**, 1110 (1930); (b) Ipatieff, Razuwajeff and Bogdanov, *ibid.*, **63**, 335 (1930).

[3] Zartman and Adkins, THIS JOURNAL, **54**, 3398 (1932).

[4] Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936).