equations of Wynne-Jones and Bjerrum are not applicable to this case.

Since this paper was submitted, R. M. Garrels and F. T. Gucker have published a valuable study of aqueous lead chloride solutions [*Chem. Rev.*, **44**, 117 (1949)]. These authors give considerable additional evidence for incomplete dissociation in such solutions, and derive values for K of about 0.03 from e.m.f. and conductance data.

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RECEIVED JANUARY 31, 1949

The Liberation of Diazotizable Amine from Pteroylglutamic Acid[1]

BY B. KOFT AND M. G. SEVAG

During a study of the possible role of pteroylglutamic acid (PGA)[2] and *p*-aminobenzoic acid (*p*-ABA) on the inhibition by sulfonamides of the growth of *Lactobacillus arabinosus* strain 17-5 and other bacteria, certain inconsistancies have been observed by us. These inconsistencies suggested the possibility that pteroylglutamic acid was undergoing decomposition in the sterile medium. Certainly, if this were so, it would have considerable bearing on the interpretations of the results of physiological experiments with pteroylglutamic acid.

TABLE I

RATE OF THE DECOMPOSITION OF PTEROYLGLUTAMIC ACID (PGA)

Pteroylglutamic acid solutions[a]	μg *p*-ABA/1000 μg of PGA[c] 0 hr.	20 hr.	40 hr.	64 hr.	120 hr.	168 hr.
1 Distilled water brought to *p*H 7.0	1.62	3.00	3.91	6.36	9.09	11.82
2 *M*/30 phosphate buffer *p*H 7.3	1.72	2.73	4.27	6.36	9.54	12.36
3 *M*/30 Na_2HPO_4, *p*H 9.18	1.36	2.55	4.27	11.36	13.63	81.82
4 *M*/30 KH_2PO_4 *p*H 4.5[b]	1.36	2.18	2.72	3.36	4.32	5.45
5 Growth medium (*p*H 7.0) (used for *L. arabinosus*[3])	2.50	3.82	6.18	14.54	18.86	45.44
6 Medium as in (5) without PGA	0	0	0	0	0	0
7 1 μg *p*-ABA/ml. of *M*/30 phosphate buffer of *p*H 7.3	1	1	1	1	1	1

[a] All solutions were autoclaved for ten minutes at 10 lb. pressure. Systems 1 to 5 contained 500 μg of PGA/ml. The solutions were then kept in a constant temperature incubator at 30°. [b] Pteroylglutamic acid dissolves on autoclaving and a precipitate forms on cooling; determinations for *p*-ABA were made on uniform suspensions. [c] *p*-ABA content of the various systems were determined according to Bratton and Marshall[4] using Klett-Summerson photoelectric colorimeter with filter No. 54, 1 μg of *p*-ABA/10 ml. reaction system gives a colorimetric reading of 22.

(1) This investigation was supported, in part, by a research grant from the Division of Research Grants and Fellowships of the National Institute of Health, U. S. Public Health Service.

(2) The authors are indebted to Dr. C. W. Waller, Lederle Laboratories, Pearl River, New York, for a freshly recrystallized sample of PGA. It contained 1 μg of *p*-ABA/1000 μg of PGA.

(3) T. D. Luckey, G. M. Briggs, Jr., and C. A. Elvehjem, *J. Biol. Chem.*, **152**, 157 (1944).

(4) A. C. Bratton and E. K. Marshall, Jr., *ibid.*, **128**, 537 (1939).

The data presented in Table I pertain to this observation.

It can be seen from the table that PGA decomposes at a regular rate on incubation at 30°. A very great rate of decomposition occurs in the sterile medium which has been generally used for the growth of *Lactobacillus arabinosus* 17-5. In this medium, 6.18 to 14.54 μg. of diazotizable amine calculated as *p*-ABA per 1000 μg. of PGA are liberated during an incubation period of from forty to sixty-four hours. The diazotizable component liberated in this medium is significantly greater than the amounts liberated in either aqueous or neutral phosphate buffer solutions of PGA. These results indicate that certain substances in the sterile medium accelerate the decomposition of PGA. The nature of these substances is under investigation.

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RECEIVED MAY 16, 1949

Lithium Borohydride as a Reducing Agent

BY ROBERT F. NYSTROM, SAUL W. CHAIKIN AND WELDON G. BROWN

Lithium borohydride shares with lithium aluminum hydride the property of solubility in ether and other organic solvents. In ether solution it is a more powerful reducing agent than sodium borohydride (in water or alcohol solution) but is milder than lithium aluminum hydride. This combination of properties, together with the prospect of early commercial availability, suggests useful applications for lithium borohydride particularly in the execution of selective reductions.

Solid lithium borohydride has been known to flash on exposure to humid air, some samples being more prone than others, and for this reason transfers of the solid should be conducted in a dry atmosphere. However, solutions of lithium borohydride are relatively insensitive to moisture and in the experiments to be described no special precautions were taken to exclude moisture. Otherwise the procedures followed in lithium borohydride reductions were generally similar to those employed in reductions by lithium aluminum hydride. Tetrahydrofuran proved advantageous as a solvent, since more concentrated solutions of the hydride could be used, *viz.*, 3.5 *M* as compared with 0.5 *M* in diethyl ether.

The aldehydes and ketones (*cf.* Table I) were reduced rapidly at room temperature in exothermic reactions whereas the esters reacted slowly and the mixtures were heated to reflux for periods up to six hours. In the selective reduction of the ketone groups of the keto-esters, and of *m*-nitroacetophenone, ice-bath cooling was employed to enhance selectivity. The attempted selective reduction of ethyl acetoacetate gave rise to a borate complex from which the reduction product could not be

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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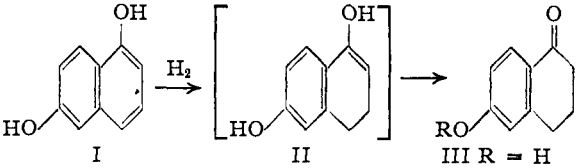
RECEIVED MAY 21, 1949

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 cata ytic 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

(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.