3-Benzal-4,5,6,7-tetrachlorophthalide.—The procedure of Weiss[13] for benzalphthalide was used. Phenylacetic acid (136 g., 1.0 mole), tetrachlorophthalic anhydride (238 g., 0.84 mole) and 3 g. of sodium acetate were heated at 230 to 260° for several hours using a short column and downward condenser to remove the water formed. The molten residue was then poured out and recrystallized from five liters of xylene. The product, 173 g. (53%) melted at 300°.

Anal. Calcd. for $C_{15}H_6O_2Cl_4$: C, 50.0; H, 1.67; Cl, 39.5. Found: C, 50.6; H, 2.26; Cl, 39.40.

Ethyl Phthalideneacetate.—Phthalideneacetic acid[14] (170 g., 0.9 mole) and 225 cc. of thionyl chloride were refluxed for four hours and the excess thionyl chloride was evaporated under water-pump vacuum. The resultant crystalline solid was broken up and treated with 300 cc. of cold absolute ethanol. After stirring for several hours the yellow solid was filtered and recrystallized from a mixture of benzene and hexane to give 90 g. (46%) of yellow crystals, m. p. 131–133°. The analytical sample after two more recrystallizations melted at 134–135°.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62; sapn. no., 218. Found: C, 66.33; H, 4.62; sapn. no., 212.

Earlier attempts to esterify phthalideneacetic acid directly with an excess of ethanol using sulfuric acid as a catalyst gave a good yield of ethyl *o*-acetylbenzoate, b. p. 112–115° (2 mm.), n^{25}_{D} 1.5122.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.8; H, 6.32; sapn. no., 192. Found: C, 68.92; H, 6.55; sapn. no., 199.

Saponification of a small sample with alcoholic potassium hydroxide gave *o*-acetylbenzoic acid,[15] m. p. 115°. In one esterification run the crude distilled product having n^{25}_{D} 1.5238 was thought to contain some methylenephthalide since the material polymerized to an insoluble incompatible mass on standing at room temperature for several days.

Methyl Phthalideneacetate.—Treatment of phthalideneacetyl chloride with methanol at 5–10° in a similar fashion gave a 61% yield of the methyl ester, yellow crystals, m. p. 171–172° cor., after recrystallization from a mixture of benzene and hexane.

Anal. Calcd. for $C_{11}H_8O_4$: C, 64.7; H, 3.92. Found: C, 64.78; H, 4.12.

***n*-Hexyl Phthalideneacetate.**—Seventy grams of crude phthalideneacetyl chloride was treated with 250 cc. of *n*-hexanol at room temperature and warmed to 60° with stirring. The resultant oil was distilled twice to give 54 g. (59%) of a pale yellow oil, b. p. 208–210° (3 mm.).

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.2; H, 6.58. Found: C, 69.92; H, 6.96.

Summary

The preparation of 3-ethylidenephthalide from phthalic anhydride and propionic anhydride in the presence of sodium acetate has been studied and 2-methyl-1,3-indanedione has been isolated as a by-product. The formation of a second by-product, 3-ethyl-3-propionoxyphthalide, is inferred since an analogous compound has been isolated from a similar reaction using tetrachlorophthalic anhydride. 3-Propylidenephthalide, 3-*n*-hexylidenephthalide, 3-ethylidenethiophthalide, 3-ethylidene- and 3-benzal-4,5,6,7-tetrachlorophthalides, and the methyl, ethyl and hexyl esters of phthalideneacetic acid have been prepared and characterized.

DAYTON, OHIO RECEIVED AUGUST 5, 1948

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[13] Weiss, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 61.

[14] Gabriel and Newman, *Ber.*, **26**, 951 (1893).

[15] Karslake and Huston, THIS JOURNAL, **31**, 479 (1909).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Reduction of Aldehydes, Ketones and Acid Chlorides by Sodium Borohydride

BY SAUL W. CHAIKIN AND WELDON G. BROWN

The successful use of lithium aluminum hydride as a reducing agent for organic compounds[1] has prompted the investigation of the reducing properties of other complex hydrides. The borohydrides of aluminum,[2] gallium,[3] beryllium,[4] lithium[5] and sodium[6] have been described. Of these, the sodium compound appeared to be of the greatest practical interest because it is potentially a cheaper material than lithium aluminum hydride and because a convenient preparative method is available.[6]

The reduction of various inorganic substrates by sodium trimethoxyborohydride, $NaBH(OCH_3)_3$, in aqueous solution has been studied by Sheft,[7] who also effected the reduction of carbon dioxide to formate. Previous studies on sodium borohydride, $NaBH_4$, as a reducing agent by Schlesinger, Schaeffer and collaborators[8] have been concerned with applications in the fields of inorganic and analytical chemistry, but have nevertheless served to indicate the potential value of the reagent in organic synthesis.

We find that the reduction of aldehydes and ketones by sodium borohydride follows the same pattern as with lithium aluminum hydride. The reactions occur rapidly at room temperature in most cases, although occasionally heating is required, and the corresponding alcohols are formed in comparable yields. Unsaturated aldehydes and ketones, in three examples studied, furnish the unsaturated alcohols.

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[1] Nystrom and Brown, THIS JOURNAL, **69**, 1197, 2548 (1947).

[2] Schlesinger, Sanderson and Burg, *ibid.*, **62**, 3421 (1940).

[3] Schlesinger, H. C. Brown and Schaeffer, *ibid.*, **65**, 1786 (1943).

[4] Burg and Schlesinger, *ibid.*, **62**, 3425 (1940).

[5] Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

[6] (a) Albert E. Finholt, Ph.D. Dissertation, The University of Chicago, June, 1946; (b) Schlesinger, "Final Report on Contract W.3434-SC-174," Official Publications Board, PB 6331, Department of Commerce, Washington, 1946.

[7] Irving Sheft, M.S. Dissertation, The University of Chicago, March, 1944.

[8] (a) Henry R. Hoekstra, Ph.D. Dissertation, The University of Chicago, August, 1946; (b) Albert C. Stewart, M.S. Dissertation, The University of Chicago, March, 1948; (c) Schaeffer and Frank, unpublished work.

The experimental techniques are quite different, for whereas lithium aluminum hydride must be used in non-hydroxylic solvents and must be rigorously protected from moisture, the reductions with sodium borohydride may be carried out in water or methanol solution. This represents a gain in convenience and economy, and suggests a possible further advantage in the reduction of ether-insoluble compounds, such as the sugars, for which lithium aluminum hydride is unsuitable.

However, a limitation is imposed by the difficultly hydrolyzable nature of the intermediate alkyl borates in certain cases. The *n*-alkyl borates are very rapidly hydrolyzed and thus, where the reduction of an aliphatic aldehyde is carried out in an aqueous solution of sodium borohydride, hydrolysis of the intermediate boron ester takes place concurrently. Other types undergo hydrolysis less readily,[9] and in the reduction of aromatic aldehydes and some of the ketones studied subsequent heating with alkali was necessary in order to liberate the alcohols. Stable complexes with boric acid are formed by α-hydroxy-acids[10] and by many polyhydroxy compounds[11] and the isolation of such products presents a problem which has not been satisfactorily solved. Thus pyruvic acid and glucose, although evidently reduced by sodium borohydride, form complexes from which boron-free reduction products could not be isolated.

The reduction of the carboxylate group of acids by sodium borohydride does not occur to any appreciable extent under the conditions described above for the reduction of carbonyl groups. Moreover, these conditions are not appropriate, because of the alkaline medium, for the reduction of easily hydrolyzable derivatives of carboxylic acids. Acid chlorides may be successfully reduced however by employing a suspension of sodium borohydride in dioxane or other inert solvent. The reaction is vigorous with aliphatic acid chlorides but aromatic acid chlorides require heating. Simple acid chlorides are converted to the alcohols in good yields but the results for unsaturated and other polyfunctional acid chlorides are less clean-cut.

Crotonyl chloride and cinnamoyl chloride evidently undergo reaction at the carbon–carbon double bonds as is shown by the isolation, in the latter case, of some hydrocinnamyl alcohol, and by the fact that in neither case was it possible to isolate any of the unsaturated alcohol. Analogous reactions of lithium aluminum hydride are known[1,12] and on the basis of this analogy it is assumed that the borohydride adds to the double bond forming a carbon–boron bond with the β-carbon atom. This bond, in contrast with the analogous aluminum compounds, is evidently highly resistant to hydrolytic fission. It is noteworthy that the reduction of cinnamaldehyde by sodium borohydride in methanol solution could not be forced beyond the cinnamyl alcohol state.

Under conditions favorable for the reduction of acid chlorides, sodium borohydride is without action on the esters and nitriles tested. Acids and acid anhydrides show only slight reduction on prolonged heating of the mixtures. It is with respect to these types that the milder reducing action of sodium borohydride, as compared with lithium aluminum hydride, is most clearly evident.

The lower reactivity of the borohydride is advantageous in permitting the selective reduction of acid chloride or carbonyl groups in the presence of other functional groups which, with lithium aluminum hydride, would also be reduced. This special application is perhaps most strikingly illustrated in the present work by the selective reduction at the carbonyl groups in levulinic acid, ω-bromoacetophenone[13] and *m*-nitrobenzaldehyde.

Although precise determinations of the stoichiometrical relationships have not been carried out the end-point in the strongly exothermic reaction of most aldehydes and ketones with sodium borohydride is easily recognizable. Semi-quantitative observations of this kind leave no doubt that four moles of the aldehyde or ketone react with one of the borohydride and the course of the reactions may be formulated as

$$4R_2CO + NaBH_4 = NaB(OCHR_2)_4 \quad (1)$$

$$NaB(OCHR_2)_4 + 2NaOH + H_2O = Na_3BO_3 + 4R_2CHOH \quad (2)$$

Experimental

Sodium Borohydride.—The sodium borohydride used in this work was supplied to us through the kindness of Professor H. I. Schlesinger. Analysis, by measurement of the hydrogen gas evolved upon acidification of an aqueous solution, showed 90% sodium borohydride. It was kept in a screw-cap bottle which was opened intermittently with no special precautions to prevent access of atmospheric moisture; the rate of deterioration was less than 2% per year. Aqueous or methanolic solutions were prepared for immediate use by dissolving the required quantity to make a 10–15% solution. Aqueous solutions, stabilized by the addition of sodium hydroxide (0.2 *N*), showed less than 5% loss of activity in two weeks. A solution 6 *N* in sodium hydroxide showed only slight decomposition at 100°.

Reduction of Aldehydes and Ketones.—The order in which the reactants were combined was largely arbitrary except where special considerations indicated a preference. Alkali-sensitive compounds, *e. g.*, crotonaldehyde, were reduced by addition of the compound, dissolved in water or methanol, to a solution of the hydride in order to avoid prolonged contact of unreduced compound with alkali. Compounds of very low solubility, *e. g.*, benzil and dicyclohexyl ketone, were more conveniently reduced by adding a solution of the hydride to a suspension of the compound in methanol; in such cases the reaction mixtures became homogeneous as the reactions proceeded.

Two ketones, mesityl oxide and dicyclohexyl ketone, required heating to 60–70° to initiate reaction. More com-

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[9] Scattergood, Miller and Gammon, THIS JOURNAL, **67**, 2150 (1945), have reported qualitative observations on the ease of hydrolysis of alkyl borates and have noted that a wide variation exists, secondary alkyl borates hydrolyzing less rapidly than primary with pronounced chain-branching effects in both types.

[10] Kolthoff, *Rec. trav. chim.*, **45**, 607 (1926).

[11] Hermans, *Z. anorg. Chem.*, **142**, 83 (1925).

[12] Hochstein and Brown, THIS JOURNAL, **70**, 3484 (1948).

[13] This compound is reduced to methylphenylcarbinol by lithium aluminum hydride (unpublished work by Mr. Lloyd Trevoy).

monly, cooling was necessary to moderate the reactions and to maintain the temperature in the range 20–30°.

In order to avoid the acid-catalyzed decomposition of hydride which would otherwise be caused by the free acidic groups, the solutions of levulinic acid and of *m*-hydroxybenzaldehyde were neutralized by the addition of sodium hydroxide prior to reduction.

When necessary, to establish completeness of reaction, the presence of excess sodium borohydride was detected by adding one drop of the reaction mixture to 1 ml. of dilute acid, the immediate evolution of hydrogen constituting a positive test.

Striking color phenomena were observed during the course of the reduction of benzil. A reddish-purple color appeared on the first addition of hydride solution and persisted until about one third of the required amount of hydride had been added. Thereafter, until nearly the end of the addition of hydride, the color was discharged on each fresh addition of hydride, leaving the yellow color of benzil, and then slowly returned. After all of the hydride solution had been added the color was still yellow; on warming the mixture to 60° it became colorless. The crude product from this reduction melted over the range 124–131° and was evidently a mixture of *meso*- and *dl*-hydrobenzoin. By multiple recrystallizations from carbon tetrachloride and from mixtures of carbon tetrachloride and chloroform, following the procedure of Böeseken and Elsen,[14] ***meso***-hydrobenzoin, m. p. 137°, was isolated in 56% yield.

TABLE I

REDUCTION OF ALDEHYDES AND KETONES

Compound	Product	Yield, %	n_D or m. p.,[a] °C.
A. Reductions in Aqueous Solution			
Acetonylacetone	Hexanediol-2,5	86	1.4453
***n*-Butyraldehyde (C)**[b]	*n*-Butanol	85	1.3977
Chloral hydrate	2,2,2-Trichloroethanol	61	
Crotonaldehyde (C)	Crotyl alcohol	85	1.4249
Cyclopentanone	Cyclopentanol	90	1.4520
Diacetyl	Butanediol-2,3	62	1.4336
Levulinic acid	γ-Valerolactone	81	1.4319
Mesityl oxide (C)[c]	4-Methyl-3-pentenol-2[d]	77	1.4310
Methyl ethyl ketone	*s*-Butanol	87	1.3956
B. Reductions in Methanol Solution			
Anisaldehyde (C)	Anisyl alcohol	96	24
Benzil	Hydrobenzoin[e]	89	124–131
ω-Bromoacetophenone	Styrene bromohydrin	71	1.5751
Cinnamaldehyde	Cinnamyl alcohol	97	32.5
Dicyclohexyl ketone	Dicyclohexylcarbinol	88	62
***p*-Dimethylaminobenzaldehyde (C)**	*p*-Dimethylaminobenzyl alcohol	96	1.5775
***m*-Hydroxybenzaldehyde (C)**	*m*-Hydroxybenzyl alcohol	93	64
***m*-Nitrobenzaldehyde**	*m*-Nitrobenzyl alcohol[f]	82	30.5

[a] Melting points are given for solid products, refractive indices (at 25°) for liquid products. Other data pertaining to characterization are omitted except in special cases noted below. [b] The letter "C" designates the order of addition to be: compound added to solution of the borohydride, except where thus designated the order of addition was the opposite. [c] Mesityl oxide was purified by the procedure of Stross, Monger and de V. Finch [THIS JOURNAL, 69, 1627 (1947)]; b. p. 128.8–129°, n^{24}_D 1.4435. The reduction was carried out in a 2:1 water-methanol mixture. [d] B. p. 138–140°. Doeuvre [*Bull. soc. chim.*, 10, 371 (1943)] who prepared this compound in 25% yield by the Meerwein–Ponndorf reduction of mesityl oxide, reported b. p. 138–140°, n^{15}_D 1.4377. The 63% yield, given by Wilds ["Organic Reactions," Vol. II, Wiley & Sons, New York, N. Y., 1944, p. 209], is incorrectly quoted from earlier literature. [e] The stated yield pertains to a mixture of isomers (*cf.* text). [f] The compound was observed in two allotropic modifications, one melting at 15° and a stable form melting at 30.5°. The literature melting point is 27° [Staedel, *Ber.*, 27, 2112 (1894)].

In the reduction of diacetyl no comparable color phenomena were observed. The yellow color of diacetyl disappeared when a quantity of hydride had been added which was sufficient to reduce one carbonyl group.

Our results for aldehydes and ketones are summarized in Table I.

Reduction of Acid Chlorides.—Dioxane, used in the reduction of acid chlorides, was purified by refluxing for twenty-four hours over calcium hydride followed by distillation, rejecting the forerun until a 1-ml. test sample showed no gas evolution when treated with a few milligrams of sodium borohydride. Diethyl carbitol was used instead of dioxane in those cases where the boiling point of the reduction product is near that of dioxane. The diethylcarbitol was a technical grade, purified by distillation.

The reduction of aliphatic acid chlorides was carried out by the regulated addition of the acid chloride, dissolved in dioxane if necessary, to a cooled suspension of sodium borohydride, in excess, in dioxane. The mixtures were heated on the steam-bath for a short time following the addition and then, after cooling, water was added. The addition of water invariably resulted in a vigorous exothermic reaction accompanied by the evolution of hydrogen gas in the amount of approximately four moles per mole of acid chloride taken. The evolution of hydrogen was probably caused by the acid, liberated in the hydrolysis of the intermediate complexes, acting upon the excess sodium borohydride. Isolation of the reduction products was accomplished by appropriate methods with the results shown in Table II.

TABLE II

REDUCTION OF ACID CHLORIDES

Compound	Product	Yield, %	n_D or m. p.[a] °C.
Benzoyl chloride	Benzyl alcohol	76	1.5371
n-Butyryl chloride	*n*-Butanol	81	1.3979
Cinnamoyl chloride	Hydrocinnamyl alcohol[b]	12	1.5248
Monoethyl succinate acid chloride	Butyrolactone[c]	40	
Palmitoyl chloride	Cetyl alcohol[d]	87	47.5–49
o-Phthalyl chloride	Phthalide[e]	49	72
	Phthalyl alcohol[e]	15	59

[a] See footnote (*a*), Table I. [b] Identified through the 3,5-dinitrobenzoate, m. p. 91°. A major portion of the product consisted of an organic material containing boron not decomposed by hot alkali. [c] B. p. 87–87.5° (12 mm.). Chromic acid oxidation furnished succinic acid, m. p. 183–184.5°. [d] Reaction product hydrolyzed in hot dilute acid. [e] Identity of products verified by mixed melting points with authentic specimens.

In the case of aromatic acid chlorides, which were found not to react at room temperature, a modified procedure was followed in which the mixtures were heated on the steam-bath for one to two hours, and then were cooled in an ice-bath before adding water. Some difficulty with foaming during the first addition of water was experienced.

Miscellaneous Experiments.—The following compounds, heated with a dioxane or diethylcarbitol suspension of sodium borohydride for one hour, showed no evidence of reduction: ethyl butyrate, ethyl phenylacetate, benzyl cyanide, maleic acid. Partial reduction was observed under similar conditions with butyric acid, phthalic anhydride and succinic anhydride. Cinnamyl alcohol, refluxed for one hour with an alkaline methanol solution of sodium borohydride, was recovered unchanged.

The isolation of boron-free products was unsuccessful, although reduction obviously occurred, with pyruvic acid,

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(14) Böeseken and Elsen, *Rec. trav. chim.*, **47**, 694 (1928).

glucose, anthraquinone and crotonyl chloride. Acetylacetone evidently suffered cleavage prior to or during the reduction; isopropyl alcohol was isolated in 63% yield.

Solutions of benzene diazonium chloride exhibited a rapid and strongly exothermic reaction with sodium borohydride. Benzene, aniline and phenylhydrazine were isolated in relatively small yields. The course of the reaction was qualitatively similar in neutral and in strongly alkaline solutions.

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Summary

Sodium borohydride, in water or methanol solution, is an effective reagent for the conversion of aldehydes and ketones to the corresponding alcohols. Its properties are compared with those of lithium aluminum hydride and it is shown to be superior in selective reductions. Acid chlorides are reduced to primary alcohols in non-aqueous media, but carboxylic acids, anhydrides, esters and nitriles are practically unaffected.

CHICAGO, ILLINOIS RECEIVED JUNE 14, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Crystalline Derivatives of Isomaltose[1,2]

BY M. L. WOLFROM, L. W. GEORGES[3] AND I. L. MILLER[4]

In the course of our studies on the structure of starch it became desirable to have a reference compound made up of two D-glucose residues combined by a 6-α-D-glucosyl linkage. Musculus,[5] Grimaux and Lefèvre[6] and Gautier[7] had prepared weakly reducing non-fermentable sirupy disaccharides by condensing D-glucose in the presence of acids. E. Fischer[8] in attempts to synthesize maltose, obtained a similar material which he called "isomaltose" and characterized as its phenylosazone (m. p. 158°). Georg and Pictet[9] prepared isomaltose according to the procedure of Fischer as modified by Friedrichs[10] and obtained a sirup which produced an amorphous acetate upon hot acetylation with acetic anhydride and sodium acetate. By means of a fractional precipitation procedure from ethanol the crude acetate was separated into three fractions: octaacetylgentiobiose, m. p. 190–195°; β-octaacetylisomaltose, amorphous, fusing at 72–77° and showing a rotation of $[\alpha]^{20}\mathrm{D}$ $+93.7°$ (c 4.8); a small amount of a third fraction, amorphous and fusing at 115–123°. The β-octaacetylisomaltose was converted into amorphous α-octaacetylisomaltose by heating with acetic anhydride and zinc chloride, $[\alpha]^{19}\mathrm{D}$ $+115.5°$ (c 4.2). The free sugar exhibited a rotation of $[\alpha]^{23}\mathrm{D}$ $+104.6°$ (ten minutes), $+99.7°$ (twenty-four hours) (c 5.1, water), and produced a phenylosazone which melted at 160° and had a rotatory value of $[\alpha]^{23}\mathrm{D}$ $+23.1°$ (c 1.2, methanol). Upon methylation of the free sugar with subsequent hydrolysis, Georg[11] obtained 2,3,4-trimethyl-D-glucose and 2,3,4,6-tetramethyl-D-glucose indicating a 6-D-glucopyranosyl structure. Myrbäck[12] prepared "isomaltose" as a reversion product of D-glucose by the action of hydrochloric acid and by methylation studies confirmed Georg's observation that it is 6-α-D-glucosyl-D-glucose. Berlin[13] has been able to isolate gentiobiose octaacetate from the "isomaltose" of Fischer. He believes that this preparation is a gross mixture containing gentiobiose. His observation is supported by Isaiev.[14] By acid hydrolysis and by Taka diastase treatment, Ahlborg and Myrbäck[15] obtained from corn starch a sirupy disaccharide which on methylation and hydrolysis yielded 2,3,4,6-tetramethyl-D-glucose and 2,3,4-trimethyl-D-glucose. It was thus established as an "isomaltose" derivative. Following the publication of our preliminary notice,[1] Montgomery, Weakley and Hilbert[16] hydrolyzed amylopectin (waxy corn starch) with a Taka diastase type of enzyme and isolated a disaccharide characterized by a crystalline octa-p-nitrobenzoate and by two isomeric crystalline octaacetates. One of the latter was shown to be identical with the product described herein by a direct comparison involving mixed melting point and comparative X-ray powder diffraction diagrams.

For a source of this disaccharide we turned to the synthetic polysaccharide dextran which is made from sucrose by the action of *Leuconstoc dextranicum*. Methylation studies[17,18] have shown that

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[1] A preliminary communication by the present authors describing the crystalline octaacetate of 6-α-D-glucosyl-β-D-glucose appeared in THIS JOURNAL, **69**, 473 (1947).

[2] In the present communication we will employ provisionally the term isomaltose to designate 6-α-D-glucopyranosyl-D-glucose.

[3] Corn Industries Research Foundation Associate of The Ohio State University Research Foundation (Project 203).

[4] Corn Industries Research Foundation Fellow of The Ohio State University Research Foundation (Project 203).

[5] Musculus, *Bull. soc. chim. France*, [2] **18**, 66 (1872).

[6] E. Grimaux and L. Lefèvre, *Compt. rend.*, **103**, 146 (1886).

[7] A. Gautier, *Bull. soc. chim. France*, [2] **22**, 145 (1874).

[8] E. Fischer, *Ber.*, **23**, 3687 (1890); **28**, 3024 (1895).

[9] A. Georg and A. Pictet, *Helv. Chim. Acta*, **9**, 612 (1926).

[10] O. v. Friedrichs, *Arkiv Kemi Mineral. Geol.*, **5**, No. 4, 1 (1913); *Chem. Centr.*, **85**, I, 763 (1914).

[11] A. Georg, *Compt. rend. soc. phys. hist. nat. Genève*, **47**, 94 (1930).

[12] K. Myrbäck, *Svensk Kem. Tid.*, **53**, 67 (1941); **53**, 264 (1941).

[13] H. Berlin, THIS JOURNAL, **48**, 1107 (1926).

[14] B. J. Isaiev, *Chem. Listy*, **20**, 251 (1926); *C. A.*, **20**, 3159 (1926).

[15] K. Ahlborg and K. Myrbäck, *Biochem. Z.*, **308**, 187 (1941).

[16] Edna M. Montgomery, F. B. Weakley and G. E. Hilbert, THIS JOURNAL, **69**, 2249 (1947).

[17] E. C. Fairhead, M. J. Hunter and H. Hibbert, *Can. J. Research*, **B16**, 151 (1938).

[18] S. Peat, E. Schlüchterer and M. Stacey, *J. Chem. Soc.*, 581 (1939).