water increased the colloidal surface of highly swollen cellulose by at least 20%, but the increase for unswollen samples was perhaps thirty fold. These data threw fresh light upon the significance of the "mercerization" or "reactivity" ratio of cellulose, which is usually given as about 1.5.

5. The surfaces of two of the swollen cellulose samples were estimated by a standard method involving the determination of the nitrogen adsorption isotherm at −195.8° but the correlation of this method with the thallous ethylate technique requires further study.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Diacetone Xylitol (2,3,4,5-Di-isopropylidene-D,L-xylitol)

BY RAYMOND M. HANN, A. T. NESS AND C. S. HUDSON

Tipson and Cretcher[1] have recently prepared a crystalline diacetone xylitol by condensing the components under suitable conditions. The substance contains one free hydroxyl group and they prepared its crystalline monotosyl derivative and subjected this substance to the action of a solution of sodium iodide in acetone at 100° for two hours, conditions which have been recommended by Oldham and Rutherford[2] for use in their method of distinguishing primary and secondary hydroxyl groups in the case of the aldohexosides, where it appears to be a general rule that a tosyl group is replaced by iodine only when it is attached at the primary hydroxyl of carbon atom 6. Tipson and Cretcher found that tosyl diacetone xylitol reacts with sodium iodide, as is shown by their isolation of sodium tosylate in nearly quantitative yield; it is not mentioned whether the isolation of the expected iodo diacetone xylitol was attempted. They found on the other hand, that all four tosyl groups of tetratosyl-erythritol are removable as sodium tosylate by the acetone solution of sodium iodide under the same conditions and that the erythritol moiety undergoes extensive change to volatile products, a component of which appears to be butadiene, as shown by a test for conjugated double bonds. They concluded therefore that "Oldham and Rutherford's rule apparently does not apply to tosyl esters of the sugar alcohols." Drawing this conclusion, the position of the free hydroxyl group in diacetone xylitol was left undecided.

We have used the Oldham–Freudenberg technique for the preparation of iodo derivatives of the sugar alcohols on numerous occasions. In all but two cases, the tosyl groups of the substances which we studied were attached only to primary hydroxyl groups; these tosyl groups were replaceable by iodine in conformity with the Oldham–Rutherford rule. However, in these cases the general question of the applicability of the Oldham–Rutherford rule did not arise, because we determined the position of the iodine atom in the iodo derivative by an independent and conclusive method, namely, the replacement of the iodine by hydrogen to yield a desoxy compound, the structure of which was then determined through oxidation by per-iodic acid or lead tetraacetate and the estimation of the resulting acetaldehyde. In one of the excepted cases,[3] the 1,4-ditosyl derivative of 2,3,5,6-di-isopropylidene-D,L-galactitol has been shown to give a nearly quantitative yield of a mono-iodo monotosyl derivative, a result which agrees with the Oldham–Rutherford rule in an appropriate test case. In the second excepted case,[4] it has been shown that the substance which has the structure 1,6-ditosyl-2,3,4,5-dimethylene-D-mannitol (as proved conclusively by per-iodic acid oxidation of an appropriate derivative and the estimation of acetaldehyde) reacts with sodium iodide according to the Oldham–Rutherford directions to give the expected 1,6-di-iodo-2,3,4,5-dimethylene-D-mannitol in 98% yield. A second substance which is also a di-tosyl-dimethylene-D-mannitol, was found to be entirely unreactive toward sodium iodide even under more drastic conditions; it seems highly improbable that this second closely similar substance can have either of its tosyl groups at a primary position. We assumed from their lack of reactivity, as contrasted with the proved reactivity of the 1,6-tosyl groups in the isomer, that they are attached to secondary hydroxyl groups; our interpretation of this case is that it follows the Oldham–Rutherford rule.

In the course of studies on methylene acetals of sugar alcohols we have obtained a dimethylene-L-xylitol (m. p. 215–217° (cor.), $[\alpha]^{20}D$ −25.3° in water) and a crystalline desoxy-dimethylene-D,L-xylitol (m. p. 155–156°), which will be described further in later publications; it became important in the study of these substances that the desoxy-xylitol which would be expected to be obtainable from Tipson and Cretcher's diacetone xylitol, be prepared. Our results confirm their work in the preparation of the diacetone xylitol and its tosyl derivative. The replacement of the tosyl group by iodine was accomplished

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[1] Tipson and Cretcher, *J. Org. Chem.*, **8**, 95 (1943).

[2] Oldham and Rutherford, THIS JOURNAL, **54**, 366 (1932); *cf.* Oldham, *J. Chem. Soc.*, **127**, 2840 (1925); Freudenberg and Raschig, *Ber.*, **60**, 1633 (1927).

[3] Hann, Maclay and Hudson, THIS JOURNAL, **61**, 2440 (1939).

[4] Haskins, Hann and Hudson, *ibid.*, **65**, 67 (1943).

by a modification of the Oldham–Freudenberg technique which has been suggested by Murray and Purves,[5] namely, the use of acetonylacetone in place of acetone as the solvent of the sodium iodide. On allowing the reaction to proceed at 60° for nineteen hours the tosyl-di-isopropylidene-xylitol was converted in a yield of 88% to a crystalline iodo-di-isopropylidene-xylitol. This iodo derivative was transformed in alkaline solution by hydrogen and Raney nickel to a desoxy-di-isopropylidene-xylitol, which is a colorless, mobile and somewhat volatile liquid which could be purified by distillation (b. p. 88–90° at 6–7 mm.); its analysis for carbon and hydrogen gave correct percentages. Mild acid hydrolysis removed its acetone groups and there resulted a desoxy-xylitol, which is a colorless viscid odorless sirup, of correct carbon and hydrogen analysis. The oxidation of the desoxy-di-isopropylidene-xylitol by per-iodic acid showed that a reaction was complete in five hours at room temperature, with the consumption of 3.06 molecular equivalents of oxidant; evidently the substance is easily hydrolyzed in the acid solution to acetone and desoxy-xylitol and the latter is then oxidized according to the following equation, which represents the only course that is compatible with the consumption of three moles of the oxidant

$$CH_3(CHOH)_3CH_2OH + 3HIO_4 = CH_3CHO + 2HCOOH + HCHO + 3HIO_3 + H_2O$$

The equation limits the desoxy group to a terminal position. This inference was confirmed by the oxidation of the desoxy-xylitol with sodium periodate; each mole consumed 2.88 moles of oxidant and generated 1.96 moles of acid, 3.00 and 2.00 moles, respectively, being the theoretical values. Finally, desoxy-xylitol was oxidized by per-iodic acid and the resulting acetaldehyde was determined by the procedure of Nicolet and Shinn[6] for the estimation of acetaldehyde in the presence of formaldehyde. Each mole of desoxy-xylitol produced 0.91 mole of acetaldehyde. These quantitative results, and especially the acetaldehyde measurement, prove conclusively that the desoxy-xylitol has the terminal CH_3 in its structure, from which it follows that the free hydroxyl group of diacetone xylitol is a primary one. The acetone groups must be attached to the remaining four carbon atoms; the arrangement of these groups is left undecided. Owing to the *meso* configuration of xylitol, the desoxy-xylitol must consist of equal amounts of two enantiomorphs and the substance is to be named 1-desoxy-D,L-xylitol. This relationship would not hold for a terminal desoxy-D-arabitol because 1-desoxy- and 5-desoxy-D-arabitol are different substances. The tosyl derivative is 1-tosyl-2,3,4,5-di-isopropylidene-D,L-xylitol, the iodo derivative is 1-iodo-2,3,4,5-di-isopropylidene-D,L-xylitol and the product from its reduction is 1-desoxy-2,3,4,5-di-isopropylidene-D,L-xylitol. The question of whether any of the crystalline members of this series of racemic mixtures is a true racemate has not been investigated.

It is apparent from the foregoing that the Oldham–Rutherford rule should not be regarded as inapplicable to sugar alcohols in general. We believe that its apparent failure to hold in the case of tetratosyl-erythritol, where Tipson and Cretcher find that all four tosyl radicals are removed by sodium iodide in acetone, only discloses a special structural influence that has not been noticed in previous applications of the rule. In tetratosyl-erythritol, the tosyl groups that are on secondary hydroxyl positions are contiguous to tosyl groups on primary ones. Except for tritosyl-glycerol[7] and tetratosyl-erythritol, we are not aware that there has been any previous test of a 1,2-ditosyl derivative in considering the applicability of the Oldham–Rutherford rule. However, some evidence on the subject can be supplied at present.[8] Upon heating the known 5,6-ditosyl-1,2,3,4-dibenzylidene-D-sorbitol[9] with sodium iodide and acetone at 100° for four hours, there were formed two molecular equivalents of sodium tosylate and a crystalline compound (m. p. 187–188°; $[\alpha]^{20}_D$ $+19.0°$ in chloroform) which decolorizes bromine in carbon tetrachloride and shows a correct analysis for 1,2,3,4-dibenzylidene-D-sorbitoleen; the latter substance was reduced by hydrogen and Raney nickel to what is presumably 1,2,3,4-dibenzylidene-5,6-di-desoxy-D-sorbitol (m. p. 184–185°; $[\alpha]^{20}_D$ $+39.4°$ in chloroform. Calculated for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.84; H, 6.78). It appears, therefore, that contiguous tosyl groups, one of which is attached at a primary hydroxyl position and the other at a secondary, are both removed by treatment with sodium iodide in acetone with the ultimate production of a double bond. The behavior which Tipson and Cretcher have described falls in this category. The behavior of tritosyl-glycerol may be analogous. This method of forming a double bond in a 1,2-position opens many possibilities, particularly in the study of sugar alcohols. According to the idea which underlies the Oldham–Rutherford rule, a 1-iodo-2-tosyl derivative is to be expected as the first step in the ultimate formation of a double bond.

We express our appreciation to Dr. B. H. Nicolet and Mr. L. A. Shinn, of the Bureau of Dairy Industry, U. S. Department of Agriculture, for assistance in the acetaldehyde determinations.

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[5] Murray and Purves, THIS JOURNAL, **62**, 3195 (1940).

[6] Nicolet and Shinn, *J. Biol. Chem.*, **138**, 91 (1941); THIS JOURNAL, **63**, 1456 (1941).

[7] Levene and Mehltretter, *Enzymologia*, **4** (II), 232 (1937).

[8] Unpublished results obtained by Dr. John K. Wolfe in this Laboratory in a research which is temporarily suspended. We thank Dr. Wolfe for permission to quote the data.

[9] Wolfe, Hann and Hudson, THIS JOURNAL, **64**, 1495 (1942).

Experimental

2,3,4,5-Di-isopropylidene-D,L-xylitol.—Xylitol and acetone were condensed by the method which Levene and Tipson[10] used for the condensation of uridine and acetone. A mixture of 10.0 g. of crystalline xylitol,[11] 200 cc. of acetone, 20.0 g. of anhydrous copper sulfate and 0.2 cc. of concentrated sulfuric acid was agitated on a shaking machine for forty-eight hours at 25°; the copper sulfate was separated by filtration and the filtrate was shaken with 10 g. of powdery calcium hydroxide for one hour to neutralize the acid; the solids were removed by filtration and the solvent by distillation *in vacuo* at 50°. The sirupy residue, weighing 14.8 g. (97%) seems to be essentially 2,3,4,5-di-isopropylidene-D,L-xylitol. It is sufficiently pure for the preparation of derivatives, but if the crystalline substance be desired, seed crystals of it may be obtained by dissolving the sirupy product in hexane and cooling the solution in dry-ice. If seed crystals are available, the crystallization of the substance from hexane solution progresses satisfactorily at ice-box temperatures. The crystalline diacetone xylitol melted at 33–34° in agreement with the melting point of 34–34.5° reported by Tipson and Cretcher.

1-Acetyl-2,3,4,5-di-isopropylidene-D,L-xylitol.—A solution of 6.9 g. of 2,3,4,5-di-isopropylidene-D,L-xylitol in a mixture of 50 cc. of pyridine and 50 cc. of acetic anhydride was kept at 25° for eighteen hours and then poured into 500 cc. of ice-water. The acetic acid was neutralized with potassium carbonate and the solution was extracted with five 50-cc. portions of chloroform. The chloroform extracts were combined, washed successively with ice-cold 2% hydrochloric acid, 2% sodium bicarbonate solution and water, and dried over anhydrous sodium sulfate. The chloroform was removed by concentration *in vacuo* and the thin sirup which remained was brought to crystallization by dissolving it in a small amount of alcohol and cooling the solution in dry-ice. The acetyl derivative was recrystallized from 10 parts of 50% alcohol and it formed prisms which melted at 45–46°. The substance is soluble in acetone, chloroform, ether, methyl alcohol and hot water and relatively insoluble in cold water. The yield was nearly quantitative.

Anal. Calcd. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08; CH_3CO, 15.7. Found: C, 56.90; H, 8.10; CH_3CO, 15.5.

1-Benzoyl-2,3,4,5-di-isopropylidene-D,L-xylitol.—This compound was obtained in quantitative yield (10.0 g.) by the benzoylation of 2,3,4,5-di-isopropylidene-D,L-xylitol (6.9 g.) in pyridine solution with benzoyl chloride. It was recrystallized from 5 parts of alcohol and obtained in the form of stout needles which melted at 61–62°. The substance is soluble in warm methyl and ethyl alcohols, acetone and chloroform, relatively insoluble in cold alcohol, and insoluble in water.

Anal. Calcd. for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19; C_6H_5CO, 31.2. Found: C, 64.47; H, 7.31; C_6H_5CO, 31.0.

1-Tosyl-2,3,4,5-di-isopropylidene-D,L-xylitol.—A solution of 14.3 g. of 2,3,4,5-di-isopropylidene-D,L-xylitol in 71.5 cc. of pyridine was cooled in ice and 14.3 g. of *p*-toluenesulfonyl chloride was added. After standing for forty-eight hours at 25° the reaction mixture was poured into 500 cc. of ice water and the precipitated tosyl derivative (21.6 g.; 91%) was separated by filtration and recrystallized from 3 parts of alcohol. The once recrystallized compound melted at 77–78° and further recrystallization did not alter this melting point; Tipson and Cretcher record 70–71°. The substance is relatively unstable which may account for the difference in melting point; it decomposed spontaneously on standing a few days at room temperature. It is readily soluble in acetone, methyl and ethyl alcohols, chloroform and ethyl acetate and insoluble in water.

Anal. Calcd. for $C_{18}H_{26}O_7S$: C, 55.94; H, 6.78; S, 8.30. Found: C, 55.82; H, 6.81; S, 8.26.

1-Iodo-2,3,4,5-di-isopropylidene-D,L-xylitol.—A solution of 15.5 g. of recrystallized 1-tosyl-2,3,4,5-di-isopropylidene-D,L-xylitol and 15.0 g. (2.5 molecular equivalents) of sodium iodide in 60 cc. of acetonylacetone,[5] was heated at 60° for nineteen hours; the cooled reaction mixture was poured into 1 liter of ice water and after standing at 5° overnight the precipitated 1-iodo-2,3,4,5-di-isopropylidene-D,L-xylitol (12.1 g.; m. p. 55–57°; 88%) was separated by filtration and recrystallized by solution in 2 parts of alcohol and the addition of 1 part of water; it was obtained in the form of thin rectangular plates which melted at 57–59°. The substance is soluble in acetone, chloroform, methyl and ethyl alcohols and dioxane and insoluble in water.

Anal. Calcd. for $C_{11}H_{19}O_4I$: C, 38.61; H, 5.60; I, 37.09. Found: C, 38.66; H, 5.72; I, 37.19.

1-Desoxy-2,3,4,5-di-isopropylidene-D,L-xylitol.—The suspension of 2.0 g. of Raney nickel in 25 cc. of absolute methyl alcohol was saturated with hydrogen at a temperature of 27° and a pressure of 5 cm. of mercury and then 2.5 g. of 1-iodo-2,3,4,5-di-isopropylidene-D,L-xylitol and 4.5 cc. of 1.8 *N* barium methylate[12] (0.55 molecular equivalent) were added and the reaction mixture was agitated in a glass bottle under a slight positive pressure of hydrogen. In thirty minutes the calculated amount of hydrogen (181 cc. at 27° and 756 mm.) was taken up and no further absorption occurred in an additional thirty minutes. The catalyst was separated by filtration and the filtrate was concentrated *in vacuo* to a thick slurry; this residue was extracted with ether and the extract, upon evaporation of the solvent, yielded a colorless liquid. The product is volatile and care must be exercised in the last stages of the evaporation to prevent loss. A sample of 4.3 g. of this sirup was distilled *in vacuo* and a 3.1 g. fraction boiling at 83–89° at 7 to 8 mm. was collected; this fraction was redistilled *in vacuo* and the major portion (2.8 g.), which distilled at 88–90° at 6 to 7 mm., was analyzed and found to agree in composition with desoxy-di-isopropylidene-xylitol. The clear mobile liquid, which had a mild and slightly pungent but rather agreeable odor, showed a refractive index $n^{21}\text{D}$ of 1.4308.

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found: C, 61.15; H, 9.32.

Per-iodic Acid Oxidation of 1-Desoxy-2,3,4,5-di-isopropylidene-D,L-xylitol.—To a solution of 0.2236 g. of 1-desoxy-2,3,4,5-di-isopropylidene-D,L-xylitol in 25 cc. of water at 25° was added 5 cc. of 0.675 *M* per-iodic acid (3.26 molecular equivalents) and the volume was adjusted to 50 cc. with water. Analysis of 5-cc. subsamples at the expiration of one, two and one-half, five and twenty-two hours showed that 2.48, 3.00, 3.06 and 3.18 molecular equivalents of oxidant had been consumed. This experimental result indicated that the diacetal was readily hydrolyzed by the per-iodic acid under the experimental conditions, and that the resulting 1-desoxy-xylitol was then oxidized in accordance with the expected reaction course, the equation for which has been given.

1-Desoxy-D,L-xylitol.—A solution of 1.6 g. of 1-desoxy-2,3,4,5-di-isopropylidene-D,L-xylitol in 25 cc. of 20% aqueous acetic acid was refluxed for four hours and the solvent then removed by concentration *in vacuo*. The sirupy reaction product was dried by the successive addition and evaporation *in vacuo* of two 25-cc. portions of absolute alcohol. The final product was a viscid odorless sirup showing $n^{21}\text{D}$ 1.4706. The yield was 0.8 g. (quantitative).

Anal. Calcd. for $C_5H_{12}O_4$: C, 44.11; H, 8.88. Found: C, 44.12; H, 8.66.

Sodium Periodate Oxidation of 1-Desoxy-D,L-xylitol.—To an ice-cold solution of 0.1255 g. of 1-desoxy-D,L-xylitol in 35 cc. of water 8.54 cc. of 0.432 *M* sodium periodate (4.00 molecular equivalents) was added and the solution was allowed to warm to 25°; the volume was then adjusted to 50 cc. with water. Analysis of 5-cc. aliquots at the expiration of one, six and twenty-four hours indicated that 2.85, 2.88 and 2.88 molecular equivalents of oxidant had

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[10] Levene and Tipson, *J. Biol. Chem.*, **106**, 115 (1934).

[11] Wolfrom and Kohn, THIS JOURNAL, **64**, 1739 (1942).

[12] Levene and Compton, *J. Biol. Chem.*, **111**, 326 (1935); *cf.* Haskins, Hann and Hudson, THIS JOURNAL, **65**, 1419 (1943).

been consumed. At the expiration of twenty-four hours the titration of a 10-cc. subsample required 3.60 cc. of 0.1 *N* sodium hydroxide (using methyl red as indicator), equivalent to 1.96 molecular equivalents of formic acid. As previously mentioned, the oxidation of 1-desoxy-xylitol should consume three molecular equivalents of sodium periodate and produce two molecular equivalents of formic acid.

Determination of the Acetaldehyde Produced in the Oxidation of 1-Desoxy-D,L-xylitol by Per-iodic Acid.—A 5-cc. aliquot (0.0737 millimole) of a solution of 0.1003 g. of 1-desoxy-D,L-xylitol in 50 cc. of water was oxidized by per-iodic acid and the acetaldehyde produced was determined by the procedures described by Nicolet and Shinn.[6] The consumption of 0.02 *N* iodine (6.68 cc.) corresponded to 0.0668 millimole of acetaldehyde, equivalent to 0.91 mole of acetaldehyde per mole of 1-desoxy-xylitol. As previously indicated, the expected production of acetaldehyde was one molecular equivalent.

Summary

Proof of the structure of the diacetone xylitol of Tipson and Cretcher is presented. Its tosyl derivative reacts with sodium iodide in acetonylacetone solution to form a crystalline iododiacetonexylitol, which is reduced by hydrogen and Raney nickel to a liquid desoxydiacetonexylitol. The latter substance, upon mild acid hydrolysis, yields a sirupy desoxyxylitol, which must be a 1-desoxy derivative because it is oxidized by per-iodic acid or sodium periodate with the consumption of three moles of oxidant and the production of one mole of acetaldehyde. Owing to the meso configuration of xylitol the substances are racemic mixtures. Their structures may now be described by the following names: 2,3,4,5-di-isopropylidene-D,L-xylitol, 1-tosyl - 2,3,4,5 - di - isopropylidene - D,L - xylitol, 1 - iodo - 2,3,4,5 - di - isopropylidene - D,L - xylitol, 1 - desoxy - 2,3,4,5 - di - isopropylidene - D,L - xylitol, 1-desoxy-D,L-xylitol. The arrangement of the acetal linkages among the 2,3,4,5-positions remains undecided.

The applicability of the Oldham–Rutherford rule to sugar alcohols is discussed.

BETHESDA, MARYLAND RECEIVED SEPTEMBER 3, 1943

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 291]

The Formation of Anhydro Derivatives by the Action of Alkali upon Some Mononitrate-acetates of Glucose and Methylglucoside

BY E. K. GLADDING[1] AND C. B. PURVES

The recognition that the organic esters of sulfonic acids not only are cleaved by alkaline reagents in the sense $R_1R_2R_3C{-}O \vdots SO_2R$, but also in the sense $R_1R_2R_3C \vdots O{-}SO_2R$, explains the frequency with which the course of the reaction resembles the hydrolysis of the corresponding alkyl chloride, $R_1R_2R_3C \vdots Cl$.[2] Walden inversions often occur in both cases[3,4] and today are attributed to the formation of a charged, asymmetric carbonium ion, $R_1R_2R_3C^+$, whose rearrangement to an electrically neutral molecule is associated with the expulsion of a proton. The final molecule may contain a double bond, an anhydro ring, or be combined with a negative group, such as alkoxyl, derived from the environment. These ideas have been very successfully used to explain the chemical behavior of sugar sulfonates in alkaline media[5,6,7] and there is evidence that *p*-toluenesulfonic esters of cellulose react in a similar way.[8]

The mechanism underlying the reaction between alkali and the esters of nitric acid has not been studied extensively and most of the published work is restricted to the identification of the products.[9] Guncotton, for example, suffers rapid oxidative degradation when immersed in aqueous caustic soda, and carbon dioxide and sodium nitrite are formed.[9] Degradation in presence of diphenylamine and traces of copper salts produces oxidized and nitrated derivatives of the base.[10,11] Degradation is marked in ammonia at 65°[12] and we have found that such a weak base as pure, dry pyridine causes a vigorous decomposition of dissolved, stabilized guncotton at steam-bath temperature. Nitrogen dioxide is evolved in this decomposition as a volatile pyridine addition complex that readily crystallizes when cooled. Nef,[13] however, has emphasized that simple, aliphatic nitrates, sulfates

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(1) Du Pont Cellulose Fellow, 1942–1943. Present address, Magnolia Petroleum Co., Field Research Department, Dallas, Texas.

(2) Ferns and Lapworth, *J. Chem. Soc.*, 273 (1912).

(3) Phillips, *ibid.*, 44 (1923).

(4) Kenyon, Phillips and Turley, *ibid.*, 399 (1925). See also Day and Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941), who reviewed the hydrolysis of carboxylic esters.

(5) Hirst and Peat, *Ann. Repts. Chem. Soc.*, **31**, 173 (1934); **32**, 280 (1935).

(6) Peat, *ibid.*, **36**, 258 (1939).

(7) Isbell, *Ann. Rev. Biochem.*, **9**, 65 (1940).

(8) Gardner and Purves, THIS JOURNAL, **65**, 444 (1943).

(9) Kenyon and H. LeB. Gray, *ibid.*, **58**, 1422 (1936), referred to many results concerning the decomposition of low-molecular nitrates by alkali.

(10) Maraour, *Bull. soc. chim.*, [5] **3**, 2240 (1936).

(11) Becker and Hunold, *Z. ges. Schiess- u. Sprengstoffw.*, **33**, 213, 244 (1938). Literature reviews included.

(12) Chernitskaya, Kargin and Gutenmakker, *J. Applied Chem.*, U. S. S. R., **13**, 1159 (1940); *Chem. Abs.*, **35**, 2322 (1941).

(13) Nef, *Ann.*, **309**, 126 (1899).