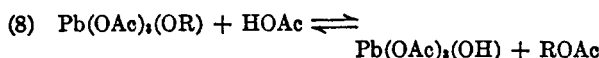


The formulations used for the decomposition of alkoxy lead triacetate result in the development of positive polarity on the hydroxyl oxygen and are, therefore, essentially equal to our previous formulations with positive character on oxygen atoms in alcohol oxidations.²

The high yield of pinacolyl acetate (Run No. 3, Table I) is probably due to the decomposition of the monoester of tetravalent lead, *i.e.* $\text{Pb}(\text{OAc})_3(\text{OR})$, *via* Equation 8.



The resulting tetravalent lead salt equilibrates with the other tetravalent lead compounds or reacts with solvent (acetic acid) to reform lead tetraacetate.

Kharasch, *et al.*¹⁰ have shown that lead tetraacetate reacts, when heated to 120° in acetic acid solution, to give carbon dioxide (42%), methane (30%), acetoxyacetic acid (40%), and methylene diacetate (6%). These workers propose a radical type mechanism involving triacetoxy lead radicals to account for the observed reaction products. Mosher and Kehr⁴ reinvestigated and extended the work of Kharasch, *et al.* to a variety of organic acids in an attempt to elucidate the type of mechanism involved. Mosher and Kehr concluded that the decomposition of lead tetraacetate in acetic and similar organic acids occurred *via* an ionic mechanism even at the high temperature (100–135°) used in their study.

The results of the present oxidation study are also best explained by an ionic mechanism. Any attempt to explain the cleavage products by a free radical mechanism falls short because of the absence of isobutane and hexamethylethane in the product mixture. It is known, for example, that *t*-butyl free radicals, when formed in solution at the same temperature employed in this study disproportionate quantitatively to isobutane and isobutene.¹³ At low temperatures the *t*-butyl free radical is known to dimerize to give hexamethylethane (in the preparation of branched chain carbinols with *t*-butyl Grignard reagents, some hexamethylethane is always found as a by-product). In the oxidation of methyl-*t*-butylcarbinol, neither isobutane nor hexamethylethane was found in the product mixture.

NEWARK, DEL.

(13) H. C. McBay Ph.D. Dissertation, University of Chicago (1945).

[CONTRIBUTION FROM UNION CARBIDE PLASTICS CO., DIVISION OF UNION CARBIDE CORP.]

Aromatic Aldehydes from Benzyl Alcohols *via* Inorganic Hypochlorite Oxidation¹

CAL Y. MEYERS²

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The action of aqueous inorganic hypochlorite on several benzyl alcohols has been studied. Benzaldehyde and *o*-methoxybenzaldehyde were thus obtained in good yield from their respective alcohols. Under the conditions employed there was no evidence of reaction between the hypochlorite and these aldehydes. *o*-Hydroxybenzyl alcohol, under identical conditions, provided no aromatic aldehyde but was chlorinated in the nucleus with a concurrent elimination of formaldehyde. Possible mechanisms are considered.

The potential stock of variously substituted hydroxybenzyl alcohols is apparent from the recent compilations by Martin³ and Megson.⁴

(1) Presented before the Meeting-in-Miniature, North Jersey Section, American Chemical Society, Jan. 28, 1957.

This particular type of benzyl alcohol is simply prepared from the phenol and formaldehyde and

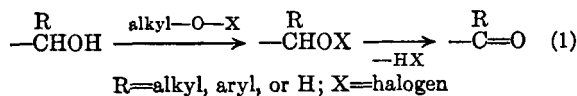
(2) Present address and that to which inquiries should be directed: Istituto di Chimica Industriale, Università di Bologna, Viale Risorgimento, 4, Bologna, Italy.

thus may be a future economical source of many corresponding derivatives. This communication is concerned with the use of aqueous inorganic hypochlorite with benzyl alcohols as a possible simple and economical means of preparing the corresponding aromatic aldehydes.

The transformation of an alcohol to its aldehyde may be regarded as dehydrogenation and usually is initiated by an oxidation process.⁵ The latter, however, may have deleterious effects upon the sensitive nucleus of these phenolic systems: Ring-fission⁶ and polyhydroxylation⁷ are often observed. A variety of oxidation schemes have, on occasion, afforded aldehydes from phenol alcohols.⁸ The success of any one method is very much dependent upon the nature of ring substituents. If the latter is nitro, for example, a strong oxidant like permanganate works well and does not destroy the ring. Weak reagents, such as cupric sulfate, are successful when the phenol alcohol has an additional hydroxyl or methoxyl in the nucleus. Saligenin (*o*-hydroxybenzyl alcohol) in *anhydrous* ether or hexane is transformed into salicylaldehyde by a suspension of manganese dioxide.⁹ Organic agents have been used, but they are expensive and often are difficult to remove from the desired aldehyde. In most instances oxidants tend to react with the sensitive aldehydes formed, yielding acids. To diminish the sensitivity of the ring and that of the resulting aldehyde, it is advisable to block the phenolic hydroxyl group prior to oxidation. Permanganate or dichromate then may be used with general success in obtaining the corresponding blocked aldehydes.⁸

A general method was still desired which would transform phenol alcohols directly into their aldehydes, in good yield. The application of an indirect oxidation approach seemed reasonable. Halogenation-dehydrohalogenation schemes have been generally successful in preparing ketones and some aldehydes from the corresponding alcohols, *tert*-butyl hypochlorite being the most widely reported agent.¹⁰ These reactions probably involve the formation of corresponding hypohalite of the alcohol,

which readily is dehydrohalogenated yielding the desired carbonyl product (Equation 1). However,



organic hypohalites (and, presumably, similar reagents such as *N*-halosuccinimides, -acetamides, etc.) can function as ionic or free radical halogenating agents, depending on the solvent used and the reactions involved.^{11a} Thus, methoxy- and hydroxybenzaldehydes may react promptly with these reagents to form the corresponding ring-halogenated aldehyde (ionic, free radical) or benzoyl halide (free radical).^{11b} With phenol alcohols, then, any advantage of this scheme with these reagents over ordinary oxidation methods seemed defeated.

The haloform reaction¹² as applied to methylalkylcarbinols involves initial transformation to the ketone by inorganic hypohalite,^{12,13} generally in aqueous solutions. The α -methylene functions are then rapidly halogenated, however, through an ionic mechanism.¹³ Under the polar conditions necessarily used with inorganic hypohalites, the latter do not function *via* free radical mechanisms.¹¹ Thus, primary alcohols should yield the corresponding aldehydes; if the latter have no α -hydrogens they should be quite stable to further reaction: ---CHO groups are halogenated by a free radical sequence, not ionic; furthermore, mildly alkaline hypochlorite apparently is no better an oxygen source than is molecular oxygen dissolved in water.¹⁴ The only reactive agent in inorganic hypohalite solutions is the free hypohalous acid, not hypohalite ion; and hypohalous acids are weaker halogenating agents than the corresponding free halogens.^{11a} It seemed quite possible, therefore, that mildly alkaline solutions of these hypohalites, maintained at moderate temperatures, would not attack the nuclei of hydroxy- or methoxybenzaldehydes.

Few accounts could be found describing the preparation of corresponding aldehydes by treatment of alcohols with aqueous halogenating solutions. In one, chlorine-water was utilized.¹⁵ In another, aqueous hypochlorite, sodium hydroxide, and temperatures exceeding 100° were employed.¹⁶ These conditions differed from those hypothesized above as being optimum for the direct preparation of alde-

(11)(a) Ref. 10, pp. 943-953; (b) Ref. 10, Table VI, p. 938.

(12) R. C. Fuson and B. A. Bull, *Chem. Revs.*, **15**, 275 (1934).

(13) E. R. Alexander, *Ionic Organic Reactions*, John Wiley, New York, 1950, pp. 206 ff.

(14) G. Holst, *Chem. Revs.*, **54**, 179 (1954).

(15) F. D. Chattaway and O. G. Backeburg, *J. Chem. Soc.*, 123, 2999 (1923). The intention of this study was to isolate benzyl hypochlorite by treating benzyl alcohol with $\text{Cl}_2\text{---H}_2\text{O}$. Instead, benzaldehyde was identified in the product and the desired hypochlorite was postulated as the isolable intermediate (*cf.* Equation 1).

(3) R. W. Martin, *The Chemistry of Phenolic Resins*, John Wiley, New York, 1956.

(4) N. J. L. Megson, *Phenolic Resin Chemistry*, Academic Press, New York, 1958.

(5) For provocative discussions the following are noted: P. D. Bartlett, *Organic Chemistry*, Vol. III, H. Gilman, ed., John Wiley, New York, 1953, pp. 75-78; and W. A. Waters, *Organic Chemistry*, Vol. IV, H. Gilman, ed., John Wiley, New York, 1953, p. 1207.

(6) C. K. Ingold, *Chemistry of Carbon Compounds*, Vol. IIIA, E. H. Rodd, ed., Elsevier Publishing Co., Princeton, N. J., 1954, p. 78.

(7) H. D. Dakin, *Am. Chem. J.*, **42**, 477 (1909); H. D. Dakin, *Org. Syntheses*, Coll. Vol. I, 149 (1947).

(8) These are reviewed by Martin, Ref. 3, pp. 225 ff.

(9) M. Harfenist, A. Bavley, and W. A. Lazier, *J. Org. Chem.*, **19**, 1608 (1954).

(10) M. Anbar and D. Ginsburg, *Chem. Revs.*, **54**, 925 (1954); note especially Table V, p. 937.

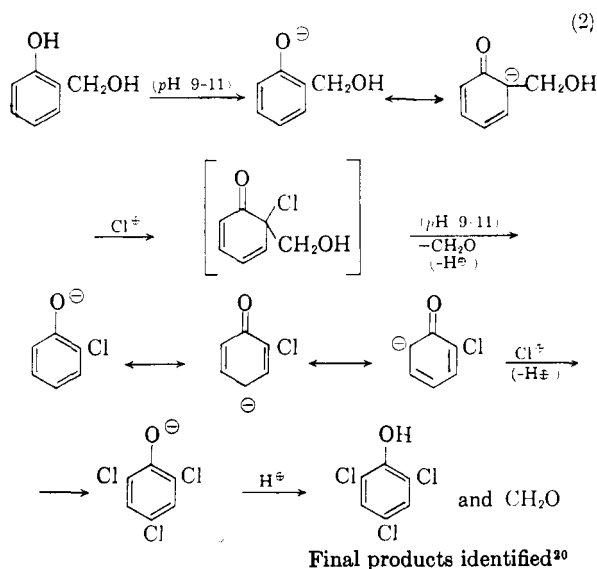
hydes in aqueous media.¹⁷ Moreover, and more important, the effects of these conditions on the sensitive hydroxy- and methoxy- substituted nuclei were not reported.

DISCUSSION

In this study, commercial "bleaching powder" (calcium chloride-calcium hypochlorite mixture) was converted to the more water-soluble potassium hypochlorite. Aqueous solutions of the latter were then standardized and used in all of the reactions studied. The transformation of benzyl alcohol to benzaldehyde was examined first. In the course of several reactions, experimentally optimum conditions of alcohol reaction and aldehyde stability were determined: (1) The use of slightly more than equivalent amounts of hypochlorite. (2) The addition of methanol to aid solution of the benzyl alcohol. (Pure methanol is stable to aqueous hypochlorite solutions.¹⁸) (3) The maintenance of pH 9-11 by adjusting the amount of potassium carbonate in the hypochlorite solution prepared. (4) Mechanical agitation of the reaction mixture at room temperature for at least twelve to fourteen hours. Under such conditions the reactions proceeded smoothly and yields close to eighty per cent of benzaldehyde were realized in single-pass experiments. No benzoic acid or halogenated derivatives were detected in these preparations.

The next reaction studied involved saligenin, the type of alcohol obtained from phenol and formaldehyde.^{3,4} Unlike benzyl alcohol, this phenol alcohol possesses reactive ring positions. Under the mild reaction conditions outlined above, it was hoped that only salicylaldehyde would result; the reactive nucleus and -CHO of the latter, it is recalled, are vulnerable to attack by organic hypochlorites.^{11b} The results, however, were disappointing, but interesting. Not only was the ring chlorinated in the open positions (4- and 6-) but the 2-hydroxymethyl

group was eliminated as formaldehyde and replaced by chlorine, 2,4,6-trichlorophenol being a product isolated. This result may be explained. At pH 9-11 the phenoxy anion would be present as its several resonance forms whose negative centers would be the *primary* targets of the electrophilic positive chlorine of the hypochlorite.¹⁹ When the 2-position is so attacked the resulting system is stabilized (benzenoid formation) by the elimination of formaldehyde, and subsequent ring halogenation may follow (Equation 2).²⁰



Similar displacement of formaldehyde during bromination of such phenols has been previously recognized.²¹ It has been found, in fact, that diazonium coupling reactions on the *ortho*-position of these phenols occur with the preferential displacement of the hydroxymethyl group rather than a hydrogen atom.²² This was originally believed true also in *para* reactions,²³ but the converse was proved in these cases.²² Chelation of the *o*-methylol with the phenolic oxygen has been recognized^{24,25} and may account for the easy displacement of the former. On this basis Equation 2 depicts the hydroxymethyl group being displaced before the 4- and 6-hydrogen atoms. The postulate of a semiquinoid intermediate (following initial chlorination and before loss of

(16) C. O. Benedetti, A. P. Vanselow, and W. Vanselow, U. S. Patent No. 1,405,261, Jan. 31, 1922. This is sparsely detailed but describes an industrial scheme whereby the production of benzaldehyde is made possible by "... the great difference in volatility with steam of benzyl alcohol and benzaldehyde." It is implied that if the aldehyde is not removed "as formed," great amounts of benzoic acid result. However, as the solutions contained free sodium hydroxide and the reaction temperatures exceeded 100°, there is little doubt that these drastic conditions, independent of hypochlorite effect, would readily permit acid formation from the aldehyde by atmospheric oxidation and *via* the Cannizzaro reaction. The present study verifies the stability of such aldehydes to aqueous hypochlorite under more moderate conditions.

(17) Organic hypochlorites are sparingly soluble in water. They are used mainly in chloroform, carbon tetrachloride, acetic acid, etc. In contact with water, moreover, they are readily hydrolyzed into hypochlorous acids, the latter being the actual halogenating agents for substrates in the solution.^{11a}

(18) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 3rd ed., John Wiley, New York, 1948, p. 138.

(19) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N. Y., 1940, pp. 149-150, 204-205.

(20) Formaldehyde was the only aldehyde formed. Trichlorophenol, though in minor amounts, was the only other product isolated. The other chlorophenols, obviously the major products, are much more water soluble and were apparently removed by the too-thorough washing process.

(21) Ref. 3, p. 218.

(22) J. H. Freeman and C. E. Scott, *J. Am. Chem. Soc.*, **77**, 3384 (1955).

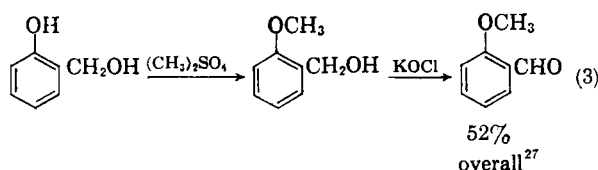
(23) E. Ziegler and G. Zigeuner, *Monatsh.*, **79**, 26, 89 and 158 (1948).

(24) G. R. Sprengling and C. W. Lewis, *J. Am. Chem. Soc.*, **75**, 5709 (1953).

(25) J. H. Freeman and C. W. Lewis, *J. Am. Chem. Soc.*, **76**, 2080 (1954).

formaldehyde) closely parallels that reported in analogous bromodesulfonation studies.²⁶

While anisole is intermediate between benzene and phenoxy ion in nuclear reactivity to electrophilic agents¹⁹ it remained to be determined whether this reactivity would predominate over that of the carbinol group in the reaction of *o*-methoxybenzyl alcohol with this hypochlorite reagent. Under conditions virtually identical with those described above, this alcohol followed the oxidation pattern of benzyl alcohol rather than that of ring chlorination-formaldehyde loss suffered by saligenin. The overall yield²⁷ of *o*-methoxybenzaldehyde, based on the original charge of saligenin, was about fifty-two per cent. The reaction sequence is noted in Equation 3.



Neither formaldehyde nor *o*-methoxybenzoic acid was detected in the final reaction mass. Rather vigorous treatment of this methoxybenzaldehyde with hydriodic acid in acetic acid failed to generate salicylaldehyde.²⁸

CONCLUSION

(1) Nonphenolic aromatic aldehydes may be simply prepared from the parent alcohols by treating the latter essentially with aqueous solutions of "bleaching powder." Methoxy derivatives are included. (2) Phenol alcohols, under these conditions, may lose the alcohol side chain and are ring-halogenated, as indicated by the reactions of saligenin. (3) Aldehyde groups are apparently stable in aqueous hypochlorite solutions of pH 9–11 at room temperature. (4) Aqueous inorganic hypochlorite may be more specific in these aldehyde syntheses, and certainly more economical, than organic hypochlorites. The latter, moreover, necessarily are used in organic solvents.¹⁷

EXPERIMENTAL²⁹

Preparation of hypochlorite solution. Commercial bleaching powder containing 24% "available chlorine" was found satisfactory but "H.T.H." (Monsanto) containing 35% "available chlorine" was preferable. This was treated with aqueous potassium carbonate solution to a final pH 9–11

(26) L. G. Cannell, *Abstracts of Papers*, American Chemical Society, 130th Meeting, Sept., 1956, p. 570.

(27) The use of bisulfite, while affording an excellent purification-isolation scheme for the aldehyde, no doubt reduced its yield considerably.

(28) Methoxy groups in similar structures are also only difficultly removed with this and other hydrolytic agents (L. I. Smith, H. E. Ungnade, J. W. Opie, W. W. Prichard, R. B. Carbin, and E. W. Kaiser, *J. Org. Chem.*, **4**, 323 (1939).

(29) All melting points are uncorrected.

and the precipitated calcium carbonate was removed by filtration. The precipitate was washed thoroughly with water and the combined washings plus original filtrate then diluted so that 100 ml. contained 0.1 mole of potassium hypochlorite. In these experiments 100 g. of "H.T.H." was accordingly treated so that 1000 ml. of final solution was virtually of this concentration.

Benzyl alcohol-hypochlorite reaction. A solution was prepared containing 112 ml. (0.112 mole) of potassium hypochlorite and 10.8 g. (0.1 mole) of distilled benzyl alcohol (b.p. 204–205°) dissolved in 60 ml. of methanol. The solution was diluted with 250 ml. of water and shaken for several minutes. The almond odor of benzaldehyde was detected almost immediately and the reaction temperature rose to 46° during these first minutes. Automatic shaking was continued overnight at room temperature (36–40°, in this laboratory). Finally, the turbid solution (pH remained 9–11) was extracted four times with benzene and the combined extracts were dried over anhydrous sodium sulfate then concentrated under reduced pressure. The slightly yellow oily residue was fractionally distilled, the main cut boiling at 178–180°, which is correct for benzaldehyde. The 2,4-dinitrophenylhydrazone prepared from several drops of distillate melted sharply at 236.5–237°; lit.,³⁰ m.p. 237°. A Tollens test produced a brilliant silver mirror within several minutes in a warm water bath. The 8.4 g. of pure benzaldehyde represents a 77% yield. The alkaline aqueous residue from the benzene extracts was acidified with cold hydrochloric acid but no benzoic acid was detected.

***o*-Hydroxybenzyl alcohol-hypochlorite reaction.** The method used here was virtually identical with that described for benzyl alcohol, but the latter was replaced with 12.4 g. (0.1 mole) of *o*-hydroxybenzyl alcohol (saligenin) melting sharply at 84–85° (recrystallized from toluene). However, in this case the solution darkened immediately and the odor of formaldehyde was detected as quickly. The identity of the latter was confirmed *in situ* by its 2,4-dinitrophenylhydrazone which, when purified, melted at 165–166° (lit. value³⁰ is the same). A mixture of this derivative from pure formaldehyde and from the reaction mass also melted sharply at 165–166°. The dark mixture was adjusted to pH 4 with dilute hydrochloric acid and extracted several times with ether. The combined ethereal solutions were dried over anhydrous sodium sulfate and then concentrated under reduced pressure. There resulted a mass of slightly yellow crystals which, after being washed thoroughly with water and dried (*in vacuo*), melted at 66–68°. 2,4,6-Trichlorophenol melts at 67–68°³⁰ and a mixture of pure sample and isolated crystals also melted at 66–68°.³⁰

Preparation of *o*-methoxybenzyl alcohol. Sodium saligenin monohydrate was prepared by the treatment of saligenin with an equivalent of sodium hydroxide in aqueous solution. The crystalline salt was precipitated from acetone, washed with the latter, and desiccated *in vacuo* at room temperature. The monohydrated salt was identified by its neutralization equivalent (titrated to bromphenol blue), by its water content (Karl Fischer method) and by its weight loss after 2 hr. at 150°.

To 16.4 g. (0.1 mole) of sodium saligenate monohydrate in 100 ml. of dry methanol was added slowly 12.6 g. (0.1 mole) of dimethyl sulfate in 50 ml. of dry methanol. The mixture was agitated vigorously and kept below 35° by the intermittent use of an ice bath. The original orange color slowly disappeared and after being agitated overnight at room temperature the mixture was only slightly yellow and the pH was 6–7. These indicated that the saligenate had been completely utilized. The mixture was diluted with ether and the sodium methyl sulfate was removed by filtration. The filtrate was dried over anhydrous sodium sulfate, the solvents removed *in vacuo*, and the residue fractionally distilled. The

(30) E. H. Huntress and S. A. Mulliken, *Identification of Pure Organic Compounds*, Order I, John Wiley, New York, 1941.

main cut, a colorless oil, was taken at 111–112°/8–10 mm.; lit. value³⁰ for *o*-methoxybenzyl alcohol, b.p. 104°/5 mm.

o-Methoxybenzyl alcohol-hypochlorite reaction. The total pure cut of the above distillate was dissolved in 15 ml. of methanol and this solution was diluted with 100 ml. of water. This solution was then added to 100 ml. (0.1 mole) of potassium hypochlorite solution and then diluted with 100 ml. of water. At this point the solution had pH 11. The system was mechanically shaken overnight at room temperature which was attained shortly after the initial exotherm (to 51°) on mixing the reactants. The organic constituents were then removed by ether extraction (to negative 2,4-dinitrophenylhydrazone test of aqueous residue) and the aldehyde removed from the combined ether portions by extraction with aqueous sodium bisulfite solution (to negative 2,4-dinitrophenylhydrazone test of ethereal layer). These combined

aqueous extracts were acidified to pH 2 with dilute cold hydrochloric acid, then extracted with ether until no aldehyde remained in the aqueous portion (negative 2,4-dinitrophenylhydrazone test). The combined ether extracts were dried over anhydrous sodium sulfate, the ether was removed under reduced pressure, and 7 g. of water-white oil remained. Several drops of the oil were used to make derivatives: 2,4-dinitrophenylhydrazone, dark orange crystals, m.p. 249–252° (lit.³⁰ m.p., 253° for this derivative of *o*-methoxybenzaldehyde); *oxime*, white needles, m.p. 89–91° (lit.³⁰ m.p., 92° for this derivative of *o*-methoxybenzaldehyde). The 7 g. of pure *o*-methoxybenzaldehyde obtained represented a 51.5% yield³¹ (overall reaction, based on sodium saligenate). No methoxybenzoic acid was found.

BOUND BROOK, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

Further Application of the Hypochlorite Method of Chain Shortening in the Carbohydrate Series¹

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D-Arabinose from D-mannonic acid and D-lyxose from D-galactonic acid are prepared in yields of 35.3% and 40.7%, respectively. β -Maltose monohydrate is converted to 3-*O*- α -D-glucopyranosyl- α -D-arabinose in 32.6% yield and α -lactose monohydrate is converted to 3-*O*- β -D-galactopyranosyl- α -D-arabinose in 38.1% yield. This convenient chain shortening procedure is thus, apparently, well suited to oligosaccharides. The glycosylpentoses are obtained in crystalline form and as crystalline osazones. The galactosylarabinose is also obtained as its crystalline anilide.

Recently Whistler and Schweiger² described the preparation of D-arabinose from D-glucose by a two-stage, but single batch, hypochlorite oxidation. D-Arabinose was obtained in 35% crystalline yield. Work is here undertaken to determine the applicability of this convenient chain shortening procedure to two hexoglyconic acids and to two reducing disaccharides.

General usefulness of the oxidation reaction to glyconic acid is indicated by application to D-mannonic acid and D-galactonic acid with the production of D-arabinose and D-lyxose in crystalline yields of 35.3% and 40.7%, respectively. The yields thus approximate those obtained through use of the Ruff degradation.³

A very useful extension of the procedure appears to be to the reducing oligosaccharides where other chain shortening procedures are cumbersome or lead to low over-all yields. The hypochlorite procedure when applied to β -maltose monohydrate produces 3-*O*- α -D-glucopyranosyl- α -D-arabinose in a yield of 32.6%, and when applied to α -lactose mono-

hydrate produces 3-*O*- β -D-galactopyranosyl- α -D-arabinose in 38.1% yield. Both disaccharides are obtained crystalline and as the crystalline phenylosazones. The second disaccharide is also obtained as the crystalline anilide, *N*-phenyl-(3-*O*- β -D-galactopyranosyl) - D - arabinosylamine monohydrate.

EXPERIMENTAL

Oxidation of maltose. Ten grams of β -maltose monohydrate were dissolved in 200 ml. of water and the pH was adjusted to 11 with sodium hydroxide. To this was added 500 ml. of 0.334*N* sodium hypochlorite (3 moles of oxidant per mole of maltose) which was adjusted to pH 11 with sodium hydroxide and sodium carbonate. The mixture was kept at 25° in the dark and the pH was frequently checked and corrected by addition of sodium hydroxide solution. In 22 hr. when about 2.4 moles of sodium hypochlorite per mole of maltose were consumed, the solution was brought to pH 5.0 by the addition of hydrochloric acid. To this was added 300 ml. of 0.266*N* sodium hypochlorite: 1.4 moles per mole of original maltose. The mixture was kept at 25° in the dark and the pH was maintained at pH 4.5–5.0 by the addition of sodium hydroxide solution. After 12 hr. when the oxidant was consumed, the solution was neutralized and concentrated under reduced pressure until sodium chloride crystallized in large amounts. After addition of three volumes of methanol, the salt crystals were removed by filtration. The filtrate was then further desalted by passage through Amberlite IR-120(H) and IR-45(OH) exchange resins.⁴ The solution was filtered through a thin layer of activated carbon⁵ and concentrated to a sirup under reduced pressure.

(4) Products of Rohm & Haas, Philadelphia.

(5) Darco G-60, a product of the Matheson Company, Inc., East Rutherford, N. J.

(1) This is paper No. 8 in a series concerning "Action of Oxidants on Carbohydrates." The previous paper is R. L. Whistler and A. M. Belfort, *TAPPI*, in press. Journal Paper No. 1640 of the Purdue Agricultural Experiment Station, Lafayette, Ind.

(2) R. L. Whistler and R. Schweiger, *J. Am. Chem. Soc.*, **81**, 5190 (1959).

(3) See: H. G. Fletcher, Jr., H. W. Diehl, and C. S. Hudson, *J. Am. Chem. Soc.*, **72**, 4546 (1950).