five grams of barium benzoate was added and the mixture stirred until nearly all of the benzoate was dissolved. Thirty-one cc. of bromine was added and the flask shaken until all the bromine was in solution. The flask was set aside in a dark place for twenty-four hours. The precipitated benzoic acid was removed by filtration, the excess bromine by a stream of air and the barium by sulfuric acid. After filtration the solution was heated and treated with 140 g. of lead carbonate in aqueous suspension. After cooling and filtering the remaining bromide was removed with silver carbonate and the excess lead and silver precipitated with hydrogen sulfide. The insoluble sulfides were removed, the filtrate was heated with decolorizing carbon and evaporated under reduced pressure to 400 cc. The benzoic acid which had separated from solution was filtered off and that in solution was extracted with chloroform. Evaporation *in vacuo* was continued until the lactone suddenly precipitated in a solid crystalline mass. Enough 95% alcohol was added to dissolve all the lactone (hot). On cooling, the product crystallized. After filtering and drying it melted at 138–141°.

It was recrystallized from alcohol. Thirty-six grams of γ-mannonic lactone melting at 151° was obtained; $[\alpha]_D^{25}$ +51.3°. The physical constants of this substance as determined by Nef[8] are: m. p. 151° and $[\alpha]_D^{20}$ +51.8°. On concentration of the combined mother liquors an additional 4 g. of pure lactone was recovered.

Summary

The method of oxidation of aldehyde sugars recently described by Hudson and Isbell applied to mannose has made possible the preparation of γ-*d*-mannonic lactone in improved yield.

Pittsburgh, Pennsylvania

[Contribution from the Chemical Laboratory of Iowa State College]

FURTHER OBSERVATIONS ON THE INTERFERENCE OF NITRO GROUPS ON THE ZEREWITINOFF METHOD FOR THE QUANTITATIVE ESTIMATION OF ACTIVE HYDROGEN

By Henry Gilman, R. E. Fothergill and E. B. Towne

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Introduction

Where there is no hydrogen there can be no active hydrogen.

Recently, Gilman and Fothergill[1] showed that nitro, nitroso and azo groups interfered with the Zerewitinoff method for the quantitative estimation of active hydrogen. Long years ago attention was directed by Hibbert and Sudborough[2] to abnormal results given by some nitro substituted compounds. They obtained slightly more than the calculated volume of gas (based on the one hydroxyl group) when *o*-nitrophenol was treated at room temperature with an amyl ether solution of methylmagnesium iodide. The volume of gas increased when the mixture was allowed to stand for an additional eight hours at room temperature.

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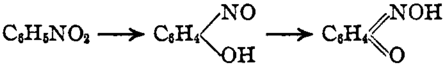
[8] Nef, *Ann.*, **403**, 316 (1914).

[1] Gilman and Fothergill, This Journal, **49**, 2815 (1927); **50**, 867 (1928).

[2] Hibbert and Sudborough, *J. Chem. Soc.*, **85**, 933 (1904).

Heating for twenty minutes at 115–120° caused the evolution of more gas, so that the total gas given off was almost twice that calculated for one active hydrogen.

They very correctly stated that "the high results obtained with *o*-nitrophenol appear to be due to the presence of the nitro group, as other nitro derivatives not containing hydroxyl groups, for example, *m*-dinitrobenzene, evolve a gas when mixed with methylmagnesium iodide, and the volume of gas is considerably increased when the mixture is heated." They suggested that this may be due to the nitro compound reacting as the tautomeric nitrosophenol or quinone-oxime, as follows



$$C_6H_5NO_2 \longrightarrow C_6H_4\left\langle\begin{matrix}NO\\OH\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}NOH\\O\end{matrix}\right. \qquad \text{(I)}$$

This appears to be an altogether reasonable conjecture, and it has the merit of postulating two tautomeric forms each of which has an active hydrogen, namely, a hydrogen atom attached to oxygen. However, our studies on nitro[3] and nitroso[4] compounds have led us to the view that the interference of these groups is a property inherent in the nitro and nitroso groups, respectively. One way of finding a definite answer to this question is to determine the effect of a nitro group contained in a molecule free of hydrogen. This we have done. In the present study we have shown that tetranitromethane, $C(NO_2)_4$, and pentabromo-nitrobenzene, $C_6Br_5NO_2$, evolve considerable gas when treated with alkylmagnesium halides after the Zerewitinoff method for the quantitative estimation of active hydrogen. This proves that a phenolic or oximic or other active hydrogen grouping[5] is not necessary for the evolution of gas by a nitro compound. It does not prove, of course, that the tautomeric forms postulated in Reaction (I) are incorrect. However, our results do show that if the tautomeric phenolic and oximic forms of (I) are to have any claims to correctness they would rest on a more secure foundation on evidence other than that given by the reaction with alkylmagnesium halides.

Experimental Part

The several determinations were carried out in accordance with the procedure used by Gilman and Fothergill[1] in their earlier studies on nitro compounds. Methylmagnesium iodide was used with all compounds. The solvent, both for the Grignard reagent and the nitro compound, was *n*-butyl ether, excepting that the Grignard reagent for the tetranitromethane experiment was prepared in *iso*-amyl ether.

In a typical determination, 0.2497 g. of tetranitromethane when heated at 70°

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[3] Gilman and McCracken, This Journal, **51**, 821 (1929).

[4] Gilman and McCracken, *ibid.*, **49**, 1052 (1927).

[5] By active hydrogen we mean here, in general, hydrogen attached to any element other than carbon, and in certain compounds of the latter class where, for example, the hydrogen is attached to a trebly bonded carbon of the acetylenic series.

for fifteen minutes gave 40.7 cc. of gas (measured under standard conditions). This is equivalent to 1.43 so-called "active hydrogens."

With pentabromo-nitrobenzene, 0.2552 g. of the compound when heated with methylmagnesium iodide at 70° for one and one-half hours gave 10.95 cc. of gas[6] (measured under standard conditions). This is equivalent to 0.99 so-called "active hydrogens." By way of reference, mention should be made of an experiment with pentabromobenzene, C_6HBr_5. When 0.2763 g. of this compound was heated at 70° for one-half hour, 0.35 cc. of gas was evolved. This is equivalent to 0.027 so-called "active hydrogens," and is within experimental error.

The pentabromo-nitrobenzene was prepared by the following reactions. First, *p*-nitro-aniline was brominated to 2,6-dibromo-4-nitro-aniline.[7] This was then diazotized and the amino group replaced by hydrogen to give 3,5-dibromonitrobenzene,[7] which was then reduced to 3,5-dibromo-aniline.[8] Bromination of the 3,5-dibromoaniline gave the pentabromo-aniline,[9] from which the amino group was replaced by hydrogen by means of the diazo reaction to give pentabromobenzene.[10] The pentabromobenzene when nitrated gave the desired pentabromo-nitrobenzene, which melted at 230°. The melting point of our pentabromobenzene was 158–159°.

Summary

The interference of the nitro group in the Zerewitinoff method for the quantitative estimation of active hydrogen is an inherent property of the nitro group because gas is evolved from compounds such as tetranitromethane and pentabromo-nitrobenzene which contain no hydrogen.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IRREVERSIBLE OXIDATION OF ORGANIC COMPOUNDS. IV.[1] THE OXIDATION OF ALDEHYDES

BY J. B. CONANT, J. G. ASTON AND C. O. TONGBERG

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The first two papers of this series[2] were concerned with the rate of oxidation of phenols and enols by strictly reversible oxidizing agents such as potassium ferricyanide. It was found that the speed of these irreversible oxidations was a function of the oxidation potential of the reagent and that the results could be formulated in terms of "apparent oxidation potentials."

In attempting to extend our methods to the study of the oxidation of aldehydes, we encountered surprising complications. A qualitative study[1]

[6] Some halogen-nitro compounds like bromopicrin, when treated with methylmagnesium iodide evolve a mixture of gases, a part of which is methyl bromide.

[7] Meyer, Meyer and Taeger, *Ber.*, **53**, 2041 (1920).

[8] Holleman, *Rec. trav. chim.*, **25**, 194 (1906).

[9] Hantzsch and Smythe, *Ber.*, **33**, 520 (1900).

[10] Jacobson and Loeb, *ibid.*, **33**, 703 (1900).

[1] The third paper of this series was published in THIS JOURNAL, **50**, 2783 (1928), under the title "Certain New Oxidation Reactions of Aldehydes."

[2] Conant and Pratt, *ibid.*, **48**, 3178, 3220 (1926).