tillate showed that the product corresponded roughly to heptaallyl sucrose: $n^{20}D$ 1.4912; d^{20}_4 1.1071; viscosity at 25°, 792.5 centipoises; $[\alpha]^{26}D$ +50.5°; molecular refraction, 163.01 (calcd. for heptaallyl sucrose, 164.79); allyl, 44.3% (calcd. for $C_{33}H_{50}O_{11}$, 46.2%).

Acknowledgment.—The assistance of Esther M. Terry, who made the free-hydroxyl and unsaturation determinations, and of A. N. Wrigley, who helped to prepare some of the compounds, is gratefully acknowledged.

Summary

1. Allyl ethers of D-mannitol, D-sorbitol, glycerol, ethylene glycol, 1,3-butylene glycol, dipropylene glycol, pentaerythritol, inositol and sucrose have been prepared and their polymerization has been studied.

2. A possible mechanism of oxidation of allyl ethers of polyhydric alcohols is discussed.

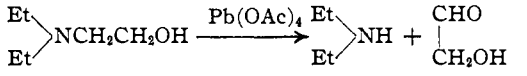
PHILADELPHIA, PA. RECEIVED SEPTEMBER 29, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Lead Tetraacetate Oxidation of Aminoalcohols

BY NELSON J. LEONARD AND MELVIN A. REBENSTORF

Apparently there has been no study of the oxidative cleavage of aliphatic tertiary hydroxyamines beyond the observation by Nicolet and Shinn[1] that periodic acid at room temperature will oxidize a secondary hydroxyamine (diethanolamine) but not a tertiary hydroxyamine (2-diethylaminoethanol). Oxidation of tertiary hydroxyamines now has been effected by lead tetraacetate in glacial acetic acid at 60°. It was found



that these compounds were not oxidized by periodic acid even under more strenuous conditions.

The oxidation of 2-diethylaminoethanol, 1-diethylamino-2-propanol and 1-diethylamino-2-methyl-2-propanol, as measured by the disappearance of lead tetraacetate, was complete within twelve hours. There was little qualitative change in the speed of oxidation of these 1,2-aminoalcohols when the alcohol function was varied from primary to secondary or tertiary. Diethylamine, isolated in good yield as the picrolonate, was identified as one of the products of the lead tetraacetate oxidation of each of these aminoalcohols. Piperidine was isolated and identified as the picrolonate from the oxidation of 2-(1-piperidino)-ethanol under the same conditions.

3-Diethylamino-1-propanol and 4-diethylamino-1-butanol were oxidized by lead tetraacetate in glacial acetic acid at 60° within about four days; diethylamine was isolated in small yield from the oxidation of both of these aminoalcohols. Neither was oxidized as rapidly as any of the 1,2-aminoalcohols studied, but evidently lead tetraacetate under the conditions employed exhibits no real specificity for the 1,2-compounds.

Blanks were run concurrently with the above oxidations. In control oxidations under identical conditions with 1-propanol, 2-propanol, and trimethylene glycol, respectively, as substrates, no appreciable consumption of lead tetraacetate was observed. Triethylamine was attacked only very slowly by the lead tetraacetate; less than one-half mole equivalent of lead tetraacetate was consumed after five days at 60°. A mixture of triethylamine and 1-propanol, which would correspond roughly to an aminoalcohol with functional groups separated by a very great number of carbon atoms, was found to be oxidized less rapidly than the 1,3- and 1,4-aminoalcohols, but more rapidly than triethylamine alone. A mole equivalent of lead tetraacetate was consumed in this case after about five days at 60°, and diethylamine was isolated in small yield from the reaction mixture.

Isolation of a non-nitrogenous product from the lead tetraacetate oxidation of the aminoalcohols has been successful with two starting compounds: 2-diethylaminoethanol and 2-(1-piperidino)-ethanol. Following lead tetraacetate oxidation of these compounds, the acetic acid solution was diluted with water and treated with *p*-nitrophenylhydrazine. Glyoxal *p*-nitrophenylosazone was isolated and identified in both cases.

It is obvious from the production of secondary amines in all cases and glyoxal in the above two cases that the aminoalcohol molecule must have undergone cleavage of the carbon–nitrogen bond, either in the reaction with lead tetraacetate or during the subsequent isolation procedure. Therefore, the lead tetraacetate oxidation of tertiary hydroxyamines at 60° is a *different reaction* from the lead tetraacetate oxidation of glycols or primary and secondary hydroxyamines at room temperature. In the former oxidation reaction, only the carbon–nitrogen bond undergoes cleavage; in the latter, the carbon–carbon bond undergoes cleavage.[2,3] There are already in the literature other examples of the accelerated speed and the altered capacity of reaction due to elevated temperatures, with both lead tetraacetate and periodic acid, as well as examples where these oxidizing agents have followed different courses of reaction with the same substrate.[4,5]

(1) Nicolet and Shinn, THIS JOURNAL, **61**, 1615 (1939).

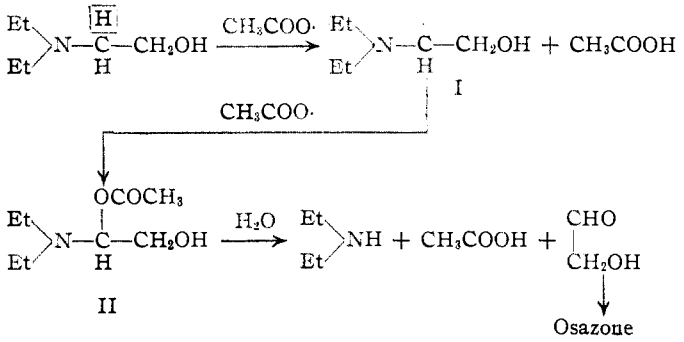
(2) Criegee, *Z. angew. Chem.*, **50**, 153 (1937).

(3) Price and Kroll, THIS JOURNAL, **60**, 2726 (1938); Price and Knell, *ibid.*, **64**, 552 (1942).

(4) Criegee, *Z. angew. Chem.*, **53**, 321 (1940).

(5) Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 341.

While more complete data are desirable, it is possible to explain the facts known at present in the following manner. Evidently the attack of lead tetraacetate at 60° upon the amine molecule is enhanced by the presence of a hydroxyl group. This is indicated by the fact that triethylamine is attacked more rapidly by lead tetraacetate when 1-propanol is present. It is also indicated by the fact that among the tertiary hydroxyamines, those in which the hydroxyl and amine functions are on contiguous carbons are most rapidly oxidized. It is known that lead tetraacetate in hot glacial acetic acid solution furnishes the acetoxy free radical.[6] The reaction of lead tetraacetate with 2-diethylaminoethanol may involve the removal by this radical of a hydrogen atom from the carbon attached to the diethylamino group to form acetic acid and a free radical (I). Reaction of another acetoxy free radical with I may follow, leading to the formation of 1-diethylamino-2-hydroxyethyl acetate (II). The formation of compound II would account for the consumption of one mole equivalent of lead tetraacetate. This compound would be expected to undergo hydrolysis readily in the presence of water to diethylamine and glycolaldehyde. Treatment of glycolaldehyde with *p*-nitrophenylhydrazine would of course result in the formation of glyoxal *p*-nitrophenylosazone, which compound was isolated and identified in addition to the diethylamine. These reactions are in accord with the known behavior of the compounds involved and provide a means of explaining the limited data on hand at the present time.



Experimental

Aminoalcohols.—The aminoalcohols required in this investigation were known previously and were well characterized. They were prepared in the usual manner from the secondary amine with the appropriate chlorohydrin or epoxy compound and finally purified by fractional distillation.

Attempted Oxidation of 2-Diethylaminoethanol with Periodic Acid.—Solutions containing 1.00 ml. of 2-diethylaminoethanol and 80 ml. of 0.1 *M* periodic acid in water, together with blanks containing only aqueous periodic acid, were heated at 60° during twenty-four hours and finally at the reflux temperature. Aliquot portions were withdrawn at regular intervals and added to acidified potassium iodide solution; the liberated iodine was titrated with sodium thiosulfate to the disappearance of the iodine color. The titration values of the solutions remained identical with those of the blanks even under the strenuous conditions applied.

Oxidation of 2-Diethylaminoethanol with Lead Tetraacetate.—Solutions containing 0.50 ml. of 2-diethylaminoethanol and 80 ml. of 0.05 *M* lead tetraacetate in glacial acetic acid, together with blanks containing only lead tetraacetate, were heated at 60 ± 10°. The course of the reaction was followed by the withdrawal of 1.00-ml. aliquot portions which were added to 10 ml. of a solution containing 2.5% potassium iodide and 20% sodium acetate. The liberated iodine was titrated with 0.01 *M* sodium thiosulfate solution to the starch end-point. A mole equivalent of lead tetraacetate was consumed by the 2-diethylaminoethanol solution within twelve hours, while the titration value of the blank remained constant. The oxidized aminoalcohol solution was made alkaline with dilute aqueous sodium hydroxide and extracted several times with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and then filtered free of the drying agent. Addition of a saturated solution of picrolonic acid in ether to the dried ether extract resulted in the precipitation of fine yellow crystals. After three recrystallizations from absolute ethanol, the yellow prisms melted with decomposition at 260–261° (uncor.).

Anal. Calcd. for $C_{14}H_{19}N_5O_5$: C, 49.84; H, 5.68. Found: C, 49.80; H, 5.56.

The melting-decomposition points of this picrolonate, of an authentic sample of diethylamine picrolonate and of mixtures of the two were identical.

A second sample of the oxidized 2-diethylaminoethanol solution was diluted with an equal volume of water and treated with *p*-nitrophenylhydrazine in aqueous acetic acid. The clear solution was heated on the steam-bath for four hours, during which time a copious red precipitate formed. The mixture was cooled and the solid was collected on a filter. After three recrystallizations from pyridine, the red elongated prisms melted with decomposition at 309–310° (uncor.).

Anal. Calcd. for $C_{14}H_{12}N_6O_4$: C, 51.22; H, 3.52. Found: C, 51.05; H, 3.63.

The melting-decomposition points of this compound, of an authentic sample of glyoxal *p*-nitrophenylosazone and of mixtures of the two were identical.

Lead tetraacetate oxidations of the other aminoalcohols were carried out in duplicate in the same manner, as indicated in the accompanying table. Diethylamine, isolated as the picrolonate, was obtained in approximately 80% yield from the oxidation of each of the following: 2-diethylaminoethanol, 1-diethylamino-2-propanol and 1-diethylamino-2-methyl-2-propanol. The oxidation of 2-(1-

TABLE I

OXIDATION WITH 0.05 *M* LEAD TETRAACETATE IN GLACIAL ACETIC ACID AT 60 ± 10°

Compound	Mole equivalents of $Pb(OAc)_4$ consumed	Time,[a] hr.	Oxidation product identified
2-Diethylaminoethanol	*ca.* 1	12	Diethylamine
1-Diethylamino-2-propanol	1	12	Diethylamine
1-Diethylamino-2-methyl-2-propanol	1	12	Diethylamine
2-(1-Piperidino)-ethanol	1	24	Piperidine
3-Diethylamino-1-propanol	1	84	Diethylamine[b]
4-Diethylamino-1-butanol	1	96	Diethylamine[b]

(6) Kharasch, Friedlander and Urry, Abstracts of Papers, 107th Meeting Am. Chem. Soc., Cleveland, Ohio, April, 1944, p. 4M.

TABLE I (*Concluded*)

Compound	Mole equivalents of $Pb(OAc)_4$ consumed	Time,[a] hr.	Oxidation product identified
Blank determinations			
1-Propanol	0	168	
2-Propanol	0	168	
Trimethylene glycol	0	72	
Triethylamine	0.5	120	
Triethylamine + 1-propanol	*ca.* 1	120	Diethylamine[b]

[a] Time is approximate since titrations were run at six-hour intervals. [b] Isolated in small yield.

piperidino)-ethanol resulted in the production of piperidine in similar yield. The base was likewise isolated and identified as the picrolonate which melted, with decomposition, at 245-246° (uncor.) and gave no depression of melting-decomposition point when mixed with an authentic sample of piperidine picrolonate. Glyoxal *p*-nitrophenylosazone was also isolated after treatment of the oxidized solution with *p*-nitrophenylhydrazine, just as in the case with 2-diethylaminoethanol. From the oxidation of both 3-diethylamino-1-propanol and 4-diethylamino-1-butanol, diethylamine—as the picrolonate—was obtained in small yield, as it was from the oxidation of a mixture of triethylamine and 1-propanol.

Summary

1. Aminoalcohols containing contiguous hydroxyl and tertiary amino groups have been found to undergo oxidative cleavage with lead tetraacetate in glacial acetic acid at 60°, with one mole of aminoalcohol requiring approximately one mole of lead tetraacetate.

2. Diethylamine has been isolated and identified as one of the products of lead tetraacetate oxidation of 2-diethylaminoethanol, 1-diethylamino-2-propanol and 1-diethylamino-2-methyl-2-propanol. Piperidine has been isolated from the oxidative cleavage of 2-(1-piperidino)-ethanol. The formation, in the degradation of the two aminoethanols, of glyoxal *p*-nitrophenylosazone indicates that the other product of cleavage of these two compounds is glycolaldehyde.

3. Lead tetraacetate in glacial acetic acid at 60° is evidently not specific for the 1,2-aminoalcohols, since 3-diethylamino-1-propanol, 4-diethylamino-1-butanol and a mixture of triethylamine and 1-propanol were oxidized, although more slowly.

4. A possible mechanism for the oxidation of the tertiary 1,2-hydroxyamines has been proposed on the basis of the products isolated.

URBANA, ILLINOIS RECEIVED OCTOBER 2, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Changes in Autoclaved Glucose

BY D. T. ENGLIS AND DONALD J. HANAHAN

As one phase of a study of the causes of discoloration of corn sirup, attention was directed to certain changes which take place upon the heating of pure glucose in the presence of small amounts of other substances. Among the factors which are said to be responsible for the discoloration of commercial glucose, or corn sirup, are[1,2,3] the presence of inorganic salts, nitrogenous and other non-sugar substances, as well as the changes in the carbohydrates themselves as a result of heat treatment and *p*H effects. It is possible, too, that oxidation[4] may contribute to the degree of discoloration.

In studying the browning of autoclaved milk Kass and Palmer[5] observed that when lactose solutions were heated with various buffers the discoloration was accompanied by a development of acidity, pronounced fall of optical activity, comparatively slight loss of copper reducing ability and an appreciable, but constant, conversion of lactose to ketoses, or substances not oxidized by sodium hypoiodite. In following the changes taking place, these investigators employed the reduction in optical rotation as the principal index of the degree of transformation of the lactose, although in a few cases this was supplemented with the estimation of aldoses by iodometric method. The loss of optical activity and production of discoloration was found to be a complex function of the buffer concentration and duration of heating and was directly proportional to the initial concentration of lactose. Increased conversion of lactose was observed with increase in the concentration of a phosphate buffer at approximately constant *p*H.

In the usual commercial processing of corn sirup, the *p*H of the material is always on the acid side. Furthermore, the salt content is very low and conditions are generally favorable to stability of the sirup. However, traces of phosphate are present and it is possible that some of the reactions which are characteristic of the constituents in a sirup mixture of higher salt concentration may take place at a slower rate and to a lesser degree upon processing and aging. Since glucose, the simplest and perhaps the most active sugar constituent in the corn sirup, is an aldose sugar, it is to be expected that it will show the same general

(1) Kröner and Kothe, *Z. Spiritusind.*, **60**, 191, 199, 207 (1937); *Chem. Abs.*, **33**, 2361 (1939); *ibid.*, **62**, 191, 197, 205, 245, 253; *ibid.*, **34**, 3941, 3942 (1940); *ibid.*, *Vorratspflege u. Lebensmittelforsch*, **2**, 299 (1939); *Chem. Abs.*, **35**, 3843 (1941).

(2) Kröner, *Forschungdienst*, **9**, 538 (1940); *Chem. Abs.*, **36**, 5377 (1942).

(3) Porst, Orig. Comm. 8th Int. Cong. Appl. Chem., **13**, 205-212 (1912).

(4) Frankenhoff, *Ind. Eng. Chem.*, **34**, 987 (1942).

(5) Kass and Palmer, *Ind. Eng. Chem.*, **32**, 1360 (1940).