curred upon treatment with water, so the organic material was extracted with ether, washed and dried. The ether was evaporated, the residue taken up in *n*-hexane, and the solution chromatographed on alumina. An oil came down in the earlier fractions; the more polar, unchanged ketone was eluted layer. The oil gave crystals from hexane. Upon recrystallization from alcohol the expected product was not immediately obtained. However, the crystals were seen to become pasty upon a week's standing; the infrared spectrum now showed a great similarity to that of II. This material, recrystallized twice from alcohol, gave an 11% yield of pure II.

This same method was used in an attempt to prepare 2,2-bis(*p*-tolyl)-1,1,1-trichloroethane. Although several minor variations were made, only the dienone could be recovered; there was no infrared evidence for formation of the desired product.

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Reaction of D-Glucopyranosylamine with Phosgene

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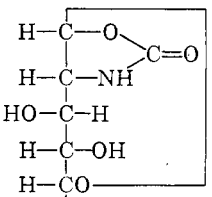
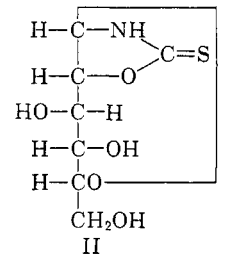
Zemplén *et al.*[1] prepared a "μ-thioglucoxazoline" by a reaction of D-glucose with potassum thiocyanate. Oxidation of the compound with hydrogen peroxide gave the corresponding "μ-hydroxyglucoxazoline" to which they assigned the structure I.



I

Bromund and Herbst[2] failed to prove unequivocally the structure of Zemplén's compound by hydrolysis. They also attempted unsuccessfully to cyclize amorphous *N*-carbethoxy and *N*-carbomethoxy derivatives of D-glucopyranosylamine to the corresponding oxazolidone.

Edward and Martlew[3] identified D-glucopyranosylamine and di-D-glucosylamine, but no D-glucosamine, among the acid hydrolysis products of Zemplén's "μ-thiolglucoxazoline". Therefore, structure II was proposed for it.

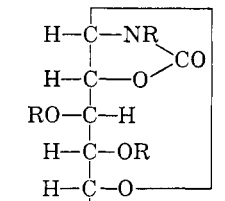


II

On the basis of periodic acid oxidation Schwarz[4] proposed for Zemplén's compound the furanose rather than the pyranose structure.

No reactions of phosgene with sugar amines seem to have been reported to date. It was expected that a reaction of phosgene with 1-D-glucopyranosylamine might give the known 1,3-bis(1-D-glucopyranosyl)urea.

Contrary to expectations, reactions of phosgene with aqueous solutions of D-glucopyranosylamine in the presence of sodium hydroxide, sodium carbonate, triethylamine, or pyridine gave a product for which formula III is proposed.



III. R = H
IV. R = Ac

Compound III consumed one molar equivalent of periodic acid without formation of either formic acid or formaldehyde. It gave a tetraacetyl derivative IV.

Both III and IV are different from the corresponding compounds made by Zemplén and coworkers,[1] as can be seen from Table I.

TABLE I

COMPARISON OF MELTING POINTS AND OPTICAL ROTATIONS

	M.P.	$[\alpha]_D$
Zemplén's μ-hydroxyglucoxazoline I	—	+6.79[a]
I tetraacetate	95	+104.8[b]
Oxazolidone III	220–222	+56.0[a]
Tetraacetate IV	150–151	+12.14[b]

[a] In H_2O. [b] In $CHCl_3$.

As oxazolidone III was made from D-glucopyranosylamine of established structure, it is safe to assume that the nitrogen atom is attached to carbon 1 of D-glucose. The results of periodic acid oxidation indicate that the compound has the pyranose ring. A furanose would yield formaldehyde on periodate oxidation, and an open chain com-

(1) G. Zemplén, A. Gerecs, and M. Rados, *Ber.*, 69, 748 (1936).

(2) W. H. Bromund and R. M. Herbst, *J. Org. Chem.*, 10, 267 (1945).

(3) J. T. Edward and E. F. Martlew, *Chem. & Ind. (London)*, 1034 (1952).

(4) G. C. P. Schwarz, *J. Chem. Soc.*, 2644 (1954).

pound would also give formic acid. The change of the specific optical rotation from $[\alpha]_D$ + 18.9° in D-glucopyranosylamine to +56.0° in compound III may be interpreted as being brought about by inversion of the amino group from the β- to the α-form incidental to the cyclization reaction.

Compound III is most likely the oxazolidone which Bromund and Herbst[2] attempted to prepare unsuccessfully.

EXPERIMENTAL[5]

Reaction of D-glucopyranosylamine with phosgene. Into a solution of 12.0 g. (0.067 mole) of D-glucopyranosylamine in 80 ml. of 1*N* sodium carbonate (0.08 mole) was slowly introduced 6.0 g. (0.061 mole) of phosgene at −5° to 0°. The solution was stirred for 2 hr. at 0° and then kept for 18 hr. at 5°. A solid material was recovered by filtration; yield 3.3 g. (24%). It was recrystallized twice from 50 ml. of 70% aqueous methanol and melted at 220–222° (dec.); $[\alpha]_D^{25}$ +56.0° (c, 2.2, H_2O). Infrared absorption at 1738 cm.$^{-1}$ (oxazolidone carbonyl), compared with 1720 cm.$^{-1}$ for authentic 2-oxazolidone. For periodic acid oxidation, the sample was dissolved in 1,2-dimethoxyethane.

Anal. Calcd. for $C_7H_{11}NO_6$: C, 40.99; H, 5.41; N, 6.83. Found: C, 41.16; H, 5.11; N, 6.72.

In other experiments compound III was obtained in yields varying from 6% to 30%.

Acetylation of III. The oxazolidone III (0.85 g., 0.0041 mole), dissolved in 16 ml. of pyridine, was treated with 6.3 g. (0.062 mole) of acetic anhydride added dropwise with stirring at room temperature. The solution was kept for 20 hr. at room temperature, and the product was precipitated by pouring on crushed ice; yield 1.2 g. (88%). Recrystallized twice from methanol-water, it melted at 150–151°; $[\alpha]_D^{24}$ +12.14° (c 0.8, $CHCl_3$).

Anal. Calcd. for $C_{15}H_{19}NO_{10}$: C, 48.26; H, 5.13; N, 3.76. Found: C, 48.62; H, 4.70; N, 3.94.

Acknowledgment. The author thanks Dr. Mack C. Harvey for measuring the infrared absorption spectra of compound III and of 2-oxazolidone and Dr. G. L. Braude and J. A. Cogliano for preparing large batches of D-glucopyranosylamine by pressure reactions of D-glucose with liquid ammonia.

Professor M. L. Wolfrom of the Ohio State University gave valuable assistance in preparing the manuscript.

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(5) All melting points are uncorrected. The elemental analyses were done by Clark Microanalytical Laboratory, Urbana, Ill.

Syntheses of 2,5,5-Trimethyl-3-hexanone, 2,5,5-Trimethyl-2-hexanol, 2,3-Epoxyheptane, 2,3-Heptanediol, and 4,4-Dimethyl-1,2-pentanediol

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Derivatives of 2,2,5-trimethylhexane with substituents in the 4-position provide the simplest structure for study of elimination reactions in which hydrogen atoms on a highly hindered secondary and an unhindered tertiary carbon atom react competitively with a base. Although syntheses of 2,5,5-trimethyl-3-hexanone and 2,5,5-trimethyl-3-hexanol can be effected by reaction of isopropylmagnesium halides with esters or acid halides[4] of *t*-butylacetic acid, or presumably with 3,3-dimethylbutanal, no convenient method for preparing any of these on a large scale has been reported. The chromic acid oxidation of 3,3-dimethyl-1-butanol (neohexyl alcohol) has been used for the preparation of *t*-butylacetaldehyde and *t*-butylacetic acid.[5]

Yields of 0–15% of neohexyl alcohol have been reported for the reaction of ethylene oxide with *t*-butylmagnesium chloride.[6] Repetition and modification using diethylene glycol dimethyl ether as a higher boiling solvent were unsuccessful as was an attempt to oxidize neohexyllithium, formed by addition of *t*-butyllithium to ethylene.[7] After several attempts to synthesize the aldehyde directly were abandoned (see below), a convenient route to the alcohol was discovered. The preparation of neohexyl chloride by addition of *t*-butyl chloride to ethylene[8] was employed; then the halide was converted to the Grignard reagent and oxidized by air. The reaction of neohexylmagnesium chloride with acetone led to the previously unreported 2,5,5-trimethyl-2-hexanol. The synthesis of 2,5,5-trimethyl-3-hexanone was effected through oxidation of neohexyl alcohol to *t*-butylacetic acid by potassium permanganate, preparation of the acid chloride with thionyl chloride, esterification with methanol, and reaction of the ester with isopropylmagnesium bromide. The semicarbazone was prepared and hydrogenated, but no amine was found.

Attempts to prepare *t*-butylacetaldehyde more directly met with limited success. Allyl chloride and *t*-butylmagnesium chloride were used for the preparation of 4,4-dimethyl-1-pentene, which reacted with performic acid to form 4,4-dimethyl-1,2-pentanediol (previously unknown). This was cleaved with lead tetraacetate to give *t*-butylacetaldehyde. However, the yields were low in all three steps (38%, 21%, and 53%, respectively). The

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(3) From a thesis presented by Garson P. Shulman in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Syracuse University, 1959.

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