

chloride with 2-bromoethylamine hydrobromide according to the procedure of Leffler and Adams.⁸ It melted at 142–144° after two recrystallizations from benzene and one recrystallization from ether in which the compound is sparingly soluble. Yield of crude product was 94%.

Method B. *N*-2-Bromoethyl-*p*-ethoxybenzamide was prepared in 96% yield by addition of 315 mg. of *N*-*p*-ethoxybenzoyl ethylenimine with stirring to 5 ml. of cold 48% hydrobromic acid. Recrystallization from benzene gave a product melting 142–144°. A mixed melting point with the material produced by Method A was 141–144° and the infrared spectra of the products by Methods A and B were identical.

2-*p*-Ethoxyphenyl-2-oxazoline. This compound was prepared by a previously described method² for making 2-*p*-chlorophenyl-2-oxazoline. It involved the alkaline methanolysis of *N*-2-bromoethyl-*p*-ethoxybenzamide. The oxazoline melted at 105–107° (from aqueous ethanol).

Anal. Calcd. for C₁₁H₁₃NO₂: N, 7.32. Found: N, 7.45.

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DEPARTMENT OF CHEMISTRY
BUCKNELL UNIVERSITY
LEWISBURG, PA.

(8) M. T. Leffler and R. Adams, *J. Am. Chem. Soc.*, **59**, 2252 (1937).

Nitrogen-Containing Polymers Arising from 1,2:5,6-Dianhydro-3,4-*O*-isopropylidene-*D*- mannitol¹

M. L. WOLFROM, J. O. WEHRMÜLLER, E. P. SWAN,
AND A. CHANEY

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The preparation of polymers containing carbohydrate repeating units has been of considerable interest in recent years.² The preparation of a polyamine containing carbohydrate units by Wiggins,³ who condensed 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-*D*-mannitol (I) with 1,6-diamino-1,6-dideoxy-2,3,4,5-*di-O*-methylene-*D*-mannitol, suggested a route that would afford interesting nitrogen-containing carbohydrate polymers.

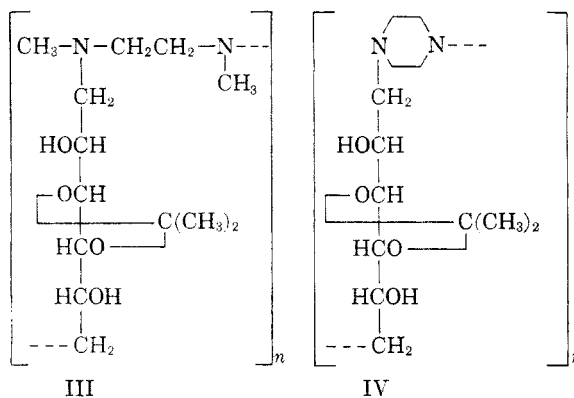
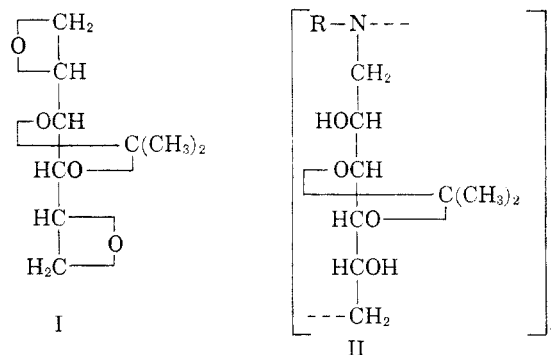
Our initial studies quickly showed that ethylenediamine, hydrazine, and ammonia condensed readily with equimolar quantities of the diepoxide I.

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(2) P. L. Nichols, Jr., and E. Yanovsky, *J. Am. Chem. Soc.*, **66**, 1625 (1944); C. L. Mehlretter and R. L. Mellies, *J. Am. Chem. Soc.*, **77**, 427 (1955); W. N. Haworth, (Mrs.) H. Gregory, and L. F. Wiggins, *J. Chem. Soc.*, 488 (1946); W. N. Haworth, R. L. Heath, and L. F. Wiggins, *J. Chem. Soc.*, 155 (1944); W. G. Overend, F. Shafizadeh, and M. Stacey, *J. Chem. Soc.*, 994 (1951).

(3) L. F. Wiggins, *J. Chem. Soc.*, 384 (1946).

However, the polymeric products obtained were insoluble materials which were not amenable to purification. It appeared that all of the amino hydrogens were reacting to some extent to produce intractable cross-linked polymers.



Attention was therefore directed to the condensation of the diepoxide I with bis-secondary and simple primary amines: piperazine, *N,N'*-dimethylethylenediamine, methylamine, 2-aminoethanol, and 2-amino-2-(hydroxymethyl)-1,3-propanediol. Although the opening of the diepoxide rings of I with sodium alkoxides has been carried out at relatively high temperatures for extended periods,⁴ the amines reacted readily at room temperature. Diluents were necessary to avoid excessive heating and decomposition.

The polymers obtained (II to IV) were soluble in chloroform and alcohols; the polymer (II, R = C(CH₂OH)₃) from 2-amino-2-(hydroxymethyl)-1,3-propanediol was water-soluble. The reduced viscosities (Nsp/c) of the polymers were 0.06 to 0.16 deciliter/g., indicating that the chain lengths were not very great. Attempts to increase the relative viscosities by alteration of the reaction conditions either had no effect or afforded partially insoluble products with the viscosity of the chloroform-soluble fractions unchanged.

The soluble polymers could be de-acetonated with refluxing aqueous hydrochloric acid. A variety of nitration techniques were applied to the de-aceto-

(4) G. P. McSweeney, L. F. Wiggins, and D. J. C. Wood, *J. Chem. Soc.*, 37 (1952); L. Anderson, A. J. Lueptow, and H. A. Lardy, *J. Am. Chem. Soc.*, **73**, 5002 (1951).

nated polymers. In most cases low yields were obtained and in all cases the nitrate ester derivatives obtained decomposed after isolation with the evolution of nitrogen oxides. This instability of the nitrated polymers may be analogous to the reported⁵ instability of the structurally related nitrate ester-nitrate salt derivatives of the mono-, di-, and tri-ethanolamines. The acetate derivatives could be prepared in stable form.

The details of the polymer preparation techniques are illustrated in the experimental section together with examples of the derivatives prepared.

EXPERIMENTAL

Materials. The amines employed were either commercial products or were prepared following syntheses given in the literature. Following the method of Siwoloff,⁶ 1,6-dichloro-1,6-dideoxy-D-mannitol was prepared and converted to 1,2:5,6-dianhydro-3,4-O-isopropylidene-D-mannitol (I) by the procedure of Wiggins.³

Condensation of piperazine with 1,2:5,6-dianhydro-3,4-O-isopropylidene-D-mannitol. Piperazine (0.7 g., 8.1 mmol.) dissolved in 5 ml. of chloroform was added to 5 ml. of chloroform solution containing 1.5 g. (8.1 mmol.) of the diepoxide I. The reaction was allowed to proceed for 24 hr. at room temperature whereupon the solution was poured with stirring into 40 ml. of dry ether. The resulting gummy mass hardened after trituration with additional ether. The white product was soluble in methanol, ethanol, and chloroform; evaporation of such solutions deposited clear, brittle films. No definite melting point was observed but the polymer was liquid at 160°. A solution of the polymer (IV) in chloroform had a reduced viscosity (N_{sp}/c) of 0.16 deciliter/g. (c 0.5, 25°), as measured with an Ostwald viscometer.

Anal. Calcd. for $(C_{12}H_{20}O_4N_2)_n$: C, 57.33; H, 8.88; N, 10.27. Found: C, 56.92; H, 8.68; N, 10.21.

No increase in the viscosity of the polymers obtained resulted when the reaction was carried out at room temperature in pyridine, in methanol containing triethylamine, or in refluxing chloroform. The product obtained by refluxing the polymer in methanol with fresh diepoxide was only partially soluble in chloroform and the viscosity of the soluble fraction had not changed.

The isopropylidene groups were removed by treating the polymer (0.425 g.) with *N* hydrochloric acid (20 ml.) on the steam bath for 18 hr. The polymer dissolved, and after reaction the solution was treated with Amberlite IRA-400⁷ exchange resin until the solution was neutral. The resin was removed by filtration and washed with water. The filtrate was lyophilized to yield a nearly white powder; yield 0.28 g. This product was nitrated by suspending it in acetic anhydride (5 ml.) at 0° and slowly adding a cold solution of absolute nitric acid (4 ml.) in acetic anhydride (10 ml.). After standing for 2 hr., the reactants were poured into ice and water to give a low yield of a white powdery product which was recovered by centrifugation. The product decomposed into water- and ethanol-soluble products and could not be isolated in a pure state.

Condensation of 2-amino-2(hydroxymethyl)-1,3-propanediol with 1,2:5,6-dianhydro-3,4-O-isopropylidene-D-mannitol. 2-Amino-2(hydroxymethyl)-1,3-propanediol (2.8 g., 23.3 mmol.) was dissolved in 20 ml. of refluxing chloroform and 4.9 g. (25.8 mmol.) of 1,2:5,6-dianhydro-3,4-O-isopropylidene-D-mannitol dissolved in 10 ml. of chloroform was added in 4 equal parts during 6 hr. After 8 hr. of refluxing, the solvent was distilled and the residual orange gum was dissolved in warm water. Addition of acetone (3 vol.) caused the formation of some precipitate which was discarded. After evaporation of the acetone from the solution, hydrochloric acid was added to the aqueous residue and the polymer was de-acetonated as described above to afford a yellow powder; yield 5.8 g. A sample of the polymer (II) isolated from its aqueous solution by freeze-drying prior to treatment with acid, had a reduced viscosity of 0.06 deciliter/g. (c 3, 25°, water).

A portion of the de-acetonated polymer was nitrated as above with similar results. Another portion of the polymer was nitrated with dinitrogen pentoxide in chloroform following the method of Caesar and Goldfrank.⁸ At the end of the nitration (14 hr. at 0°), the reaction mixture was concentrated under reduced pressure and the residual solid was washed with ethanol and dried. Although a higher yield was obtained, the nitrate soon decomposed with the evolution of nitrogen oxides.

Another portion (1.0 g.) of the de-acetonated polymer was dissolved in a mixture of pyridine and acetic anhydride (20 ml. each). After 24 hr. at room temperature, the mixture was poured into water. The precipitate was washed with water, ethanol, and petroleum ether to afford 1.29 g. of white powder after drying.

Anal. Calcd. for $(C_{24}H_{38}O_{14}N)_n$: C, 51.34; H, 6.24; N, 2.50. Found: C, 51.19; H, 6.36; N, 2.44.

Condensation of other amines with 1,2:5,6-dianhydro-3,4-O-isopropylidene-D-mannitol. The diepoxide also condensed with hydrazine, ethylenediamine, and ammonia to give yellow to brown colored brittle materials which were insoluble in solvents and whose isopropylidene groups were, in general, difficult to remove. The polymers obtained by condensation of the diepoxide with methylamine, 2-aminoethanol, or *N,N'*-dimethylethylenediamine III were yellow or orange in color but did dissolve in chloroform.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

(8) G. V. Caesar and M. Goldfrank, *J. Am. Chem. Soc.*, **63**, 372 (1946).

Reaction of *t*-Butylmagnesium Chloride with a Number of Alkyl Aryl Ketones

GUS A. ROPP,¹ ROBT. W. KENNEDY,^{2a} B. F. LANDRUM,^{2b}
AND CHAS. T. LESTER³

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This paper reports a further extension of the investigation of the reactions of 17 alkyl aryl ketones with various reagents.⁴ Each of the ketones reacted with *t*-butylmagnesium chloride under conditions as nearly like those previously reported as possible.^{4b} The reactions were designed to measure

(1) Oak Ridge National Laboratory.

(2) Taken in part from (a) the M.S. thesis of R. W. Kennedy, Emory University, 1954, and (b) the Ph.D. Dissertation of B. F. Landrum, Emory University, 1950.

(3) To whom inquiries should be directed.

(4) (a) M. J. Craft, B. F. Landrum, E. C. Suratt, and C. T. Lester, *J. Am. Chem. Soc.*, **73**, 4462 (1951). (b) B. F. Landrum and C. T. Lester, *J. Am. Chem. Soc.*, **74**, 4954, (1952); *J. Am. Chem. Soc.*, **76**, 5797 (1954).

(5) J. Barbière, *Bull. soc. chim. France*, [5], **11**, 470 (1944); Aubry, *Mem. poudres*, **25**, 189 (1932).

(6) A. Siwoloff, *Ann.*, **233**, 368 (1886).

(7) A product of the Rohm & Haas Co., Philadelphia, Pa.