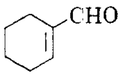
bersome. It has recently been reported that cyclohexenyltrichloromethylcarbinol (II) decomposes under the influence of alkali to (I) and cyclohexenylglycolic acid (III) in yields of 35 and 30%, respectively.[5,6] Since (II) is easily accessible from chloral and cyclohexene in the presence of aluminum chloride[6] (yield 82%), this sequence of reaction appeared to provide an easy, even if not very lucrative, method for the preparation of I.

We have found that II, when heated with 4 moles of 20% sodium hydroxide solution, gives reproducibly a 25% yield of III, but that the yield of I is variable, much polymeric material being formed. Equally, all experiments failed to pyrolyze II in the presence of potassium hydroxide, potassium carbonate or copper powder, or to split it by means of concentrated sulfuric acid or lead tetraacetate.

An indirect method, however, led to the desired result. In accordance with the data of Weizmann, Bergmann, and Sulzbacher,[7] treatment of II with 5 moles of sodium hydroxide, dissolved in methanol or propanol, gave cyclohexenyl-α-methoxy- and -α-propoxy-acetic acid (IV) in 54% and 73% yield, respectively. Pyrolysis of these acids in the presence of copper powder[8] led to I in 34% and 82% yield, so that the over-all yield, calculated on cyclohexene, was 15 and 49%, respectively.

Treatment of II with 2 moles of methanolic sodium methoxide gave in 90% yield a neutral liquid which, according to its analysis and properties, was the glycolide (V). Sodium hydroxide (1 mole) converted V into III, sodium methoxide (1 mole) into IV ($R = CH_3$); in both cases the yields were nearly quantitative.



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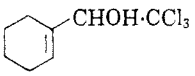

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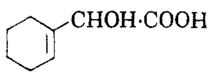

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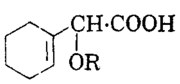

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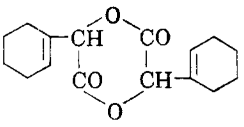

V

EXPERIMENTAL

Cyclohexenyltrichloromethylcarbinol (II) was prepared in 82% yield from 1 mole of chloral, 2 moles of cyclohexene, and 14 g. of aluminum chloride. B.p. 150° (15 mm.).

Dicyclohexenylglycolide (V). A solution of 1 mole of II and 2 moles of sodium methoxide in 500 ml. of methanol was refluxed for 3 hr. The methanol was distilled off and the remaining solid filtered and washed with 100 ml. of ether. To the filtrate and washings, water and 200 ml. of ether were added, and the ethereal liquid was dried over magnesium sulfate and distilled. B.p. 140° (20 mm.). Yield, 124 g. (90%).

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 70.6; H, 7.2. Found: C, 70.3; H, 6.9.

Cyclohexenylglycolic acid (III). (*a*) A mixture of 57 g. (0.25 mole) of II and 50 g. (1.25 moles) of sodium hydroxide in 100 ml. of water was refluxed for 1 hr. and the solution cooled, extracted with ether, and acidified with 10% hydrochloric acid. Renewed extraction with ether gave 10 g. (25%) of III. B.p. 155° (30 mm.), m.p. 125°.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.5; H, 7.8. Found: C, 61.2; H, 8.1.

(*b*) When 27.6 g. of (V) was refluxed for 3 hr. with 8 g. of sodium hydroxide in 100 ml. of water, 30 g. (96%) of III was obtained, which solidified spontaneously and melted at 125° without further purification.

Cyclohexenylmethoxyacetic acid (IV, $R = CH_3$). (*a*) To a solution of 50 g. of sodium hydroxide in 200 ml. of methanol and a little water, 57 g. of II was added slowly. When the exothermic reaction had subsided, the mixture was refluxed for 1 hr. and the alcohol removed *in vacuo*. Addition of water, extraction with ether, and acidification of the aqueous layer gave the desired acid, which was extracted with ether and distilled. B.p. 124° (0.1 mm). Yield, 23 g. (54%).

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.5; H, 8.4. Found: C, 63.7; H, 8.5.

(*b*) The same result was obtained when instead of sodium hydroxide sodium methoxide was used.

(*c*) A mixture of 27.6 g. of the glycolide (V), 18 g. of sodium methoxide, and 100 ml. of alcohol was refluxed for 2 hr. Water was added and the mixture acidified and extracted with ether. Thus, 31 g. (97%) of IV ($R = CH_3$) was obtained; b.p. 124° (0.1 mm.).

Cyclohexenylpropoxyacetic acid (IV, $R = C_3H_7$). To a solution of 50 g. of sodium hydroxide in 300 ml. of propanol, 57 g. of II was added slowly. When the reaction had subsided, the mixture was refluxed for 1 hr. and worked up as above; b.p. 156° (25 mm.). Yield, 36 g. (73%).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.7, H, 9.1. Found: C, 66.9; H, 9.4.

Cyclohexen-1-aldehyde (I). (*a*) A mixture of 17 g. of cyclohexenylmethoxyacetic acid (IV, $R = CH_3$) and 1 g. of copper powder was heated in a distillation flask at 200° for 2 hr. The distillate was fractionated; b.p. 61° (1 mm.). Yield, 3.7 g. (34%).

(*b*) A mixture of 10 g. of cyclohexenylpropoxyacetic acid (IV, $R = C_3H_7$) and 1 g. of copper powder was heated at 200° for 2 hr. and worked up as above. Yield, 4.5 g. (82%).

The *2,4-dinitrophenylhydrazone*, after recrystallization from butanol, melted at 212°.

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[5] J. Colonge and A. Perrot, *Compt. rend.*, **239**, 541 (1954).

[6] J. Colonge and A. Perrot, *Bull. soc. chim. France*, 658 (1957).

[7] Ch. Weizmann, E. D. Bergmann, and M. Sulzbacher, *J. Am. Chem. Soc.*, **70**, 1153 (1948). *Cf.* E. D. Bergmann, D. Ginsburg, and D. Lavie, *J. Am. Chem. Soc.*, **72**, 5012 (1950), and H. Gilman and G. R. Wilder, *J. Am. Chem. Soc.*, **77**, 6644, 6659 (1955).

[8] G. Darzens, *Compt. rend.*, **196**, 348, 489 (1933).

Isomerization of *N-p*-Ethoxybenzoylethylenimine

HAROLD W. HEINE AND ZOE PROCTOR

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Our earlier interest in ethylenimine and its derivatives[1] and oxazolines[2] has prompted the current

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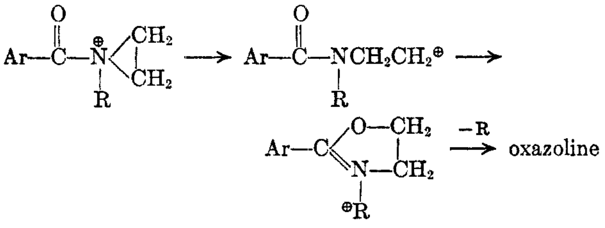
[1] H. W. Heine and B. L. Kapur, *J. Am. Chem. Soc.*, **77**, 4892 (1955); H. W. Heine, B. L. Kapur, and C. S. Mitch, *J. Am. Chem. Soc.*, **76**, 1173 (1954).

study of the isomerization of *N*-*p*-ethoxybenzoylethylenimine into 2-*p*-ethoxyphenyl-2-oxazoline.

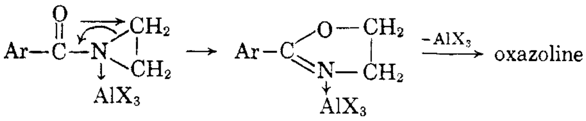
In 1895 Gabriel and Stelzner[3] prepared impure *N*-benzoylethylenimine by benzoylation of ethylenimine. Attempts to purify the compound by distillation resulted in the formation of 2-phenyl-2-oxazoline in unspecified yield and a viscous, tarry residue. Many years later Goldberg and Kelley[4] distilled as rapidly as possible a crude product obtained from benzoylating ethylenimine at 0°. The distillate could not be induced to crystallize but based on its behavior toward cold dilute hydrochloric acid was estimated to contain 70% oxazoline and 30% *N*-benzoylethylenimine. The *N*-benzoylethylenimine reacts immediately with cold dilute hydrochloric acid while 2-phenyl-2-oxazoline is stable towards this reagent. More recently Fanta and Deutsch[5] reported that 1-acetyl-2,2-dimethylethylenimine undergoes pyrolysis to *N*-(β-methallyl)acetamide in high yield. The latter compound was isomerized in 50% yield to 2,5,5-trimethyl-2-oxazoline by treatment with concentrated sulfuric acid. It was concluded that the rearrangement of the *N*-acylethylenimine to the *N*-(β-methallyl)-acetamide must be purely pyrolytic and not acid-catalyzed.

In the present work *N*-*p*-ethoxybenzoylethylenimine was easily isomerized to give 2-*p*-ethoxyphenyl-2-oxazoline in 97% yield. The isomerization was carried out in refluxing heptane in the presence of small quantities of aluminum bromide or aluminum chloride or 2-bromoethylamine hydrobromide. Control runs in refluxing heptane for 40 hr. in the absence of these catalysts resulted in recovering the *N*-aroylethylenimine unchanged. No transformation was observed even when dodecane was used as a solvent and the reaction mixture heated to 170–180° for several hours. The mechanism for the isomerization may be pictured as the addition of a proton or aluminum halide to the unshared electrons of the amido nitrogen to form I, followed by the formation of the carbonium ion (II), subsequent cyclization by the oxygen to form the oxazolinium salt (III), and finally regeneration of the catalyst.



Ia, R = H II, R = H, AlX_3^- III
Ib, R = AlX_3^-

However, it is conceivable that a solvent with a low dielectric constant (*i.e.* heptane) would not favor the generation of charge in the transition state (Ia) nor even an intermediate with charge separation (Ib). An alternate and more likely representation for the isomerization is as follows:



A similar transition state has been proposed to account for the reaction of ethylenimines with benzoic acids in dioxane.[6]

EXPERIMENTAL

N-0-Ethoxybenzoylethylenimine. Two hundred grams of ice, 200 g. C_6H_6, 6.5 g. NaOH, and 7.5 g. of ethylenimine were placed in a Waring blender. To this mixture was added portionwise over 0.5 hr. 30 g. of *p*-ethoxybenzoyl chloride. After an additional 1.5 hr. with the occasional addition of ice the reaction mixture was poured into a separatory funnel and the benzene layer separated. The aqueous layer was extracted twice with ether, the ethereal extracts pooled with the benzene layer, dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. The crude material melted at 59–61° and weighed 24.7 g. and was recrystallized from petroleum ether, b.p. 60–100° to give 22 g. of *N*-*p*-ethoxybenzoylethylenimine melting at 60–62°. This material gave an infrared spectrum consistent with the proposed structure,[7] *i.e.* a carbonyl peak at 5.97 μ. As described below it reacted immediately with cold 48% hydrobromic acid to give *N*-2-bromoethyl-*p*-ethoxybenzamide.

Anal. Calcd. for $C_{11}H_{13}NO_2$: N, 7.32. Found: N, 7.38.

Isomerization of N-p-ethoxybenzoylethylenimine. Into a 100-ml. round bottomed flask were placed 40 ml. of heptane, 7.8 mg. of $AlBr_3$, and 382 mg. of *N*-*p*-ethoxybenzoylethylenimine. A reflux condenser equipped with a drying tube was attached to the flask and the mixture refluxed for 47 hr. The hot solution was decanted and the solvent removed at room temperature to give 355 mg. (93%) of 2-*p*-ethoxyphenyl-2-oxazoline, m. 102–106°. A mixed melting point with an authentic sample of 2-*p*-ethoxyphenyl-2-oxazoline melted at 103–106°. An infrared spectrum of the reaction product was identical with that of 2-*p*-ethoxyphenyl-2-oxazoline prepared by the alkaline solvolysis of *N*-2-bromoethyl-*p*-ethoxybenzamide described below.

An analogous experiment with 40 ml. of heptane, 17 mg. of $AlBr_3$, and 382 mg. of *N*-*p*-ethoxybenzoylethylenimine gave after 17 hr. refluxing 370 mg. (97%) of the oxazoline. Another experiment involved 40 ml. heptane, 7.7 mg. of 2-bromoethylamine hydrobromide, and 400 mg. of the *N*-aroylethylenimine and a reflux period of 40 hr. A 93% yield of the oxazoline was observed. Analogously 40 ml. of heptane, 7.9 mg. $AlCl_3$, 200 mg. *N*-aroylethylenimine gave a 93% yield of oxazoline. To check the possibility that the rearrangement was due to thermal conditions 382 mg. of the *N*-aroylethylenimine and 40 ml. of heptane were refluxed 40 hr. and the solvent removed. The starting material was recovered unchanged as evidenced by melting point, mixed melting points, and infrared spectrum.

N-2-Bromoethyl-p-ethoxybenzamide. Method A. This compound was prepared by the reaction of *p*-ethoxybenzoyl

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(2) H. W. Heine, *J. Am. Chem. Soc.*, **78**, 3708(1956); H. W. Heine, *J. Am. Chem. Soc.*, **79**, 907 (1957).

(3) S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895).

(4) A. A. Goldberg and W. Kelley, *J. Chem. Soc.*, 1919 (1948).

(5) P. E. Fanta and A. S. Deutsch, *J. Org. Chem.*, **23**, 72 (1958).

(6) D. H. Powers, V. B. Schatz, and L. B. Clapp, *J. Am. Chem. Soc.*, **78**, 907 (1956).

(7) The authors wish to acknowledge the help of Kenneth Bradley of the Dow Chemical Co., Midland, Mich. for an infrared analysis.

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*-ethoxybenzoylethylenimine 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 method[2] 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 $C_{11}H_{13}NO_2$: N, 7.32. Found: N, 7.45.

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[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-mannitol[1]

M. L. Wolfrom, J. O. Wehrmüller, E. P. Swan, and A. Chaney

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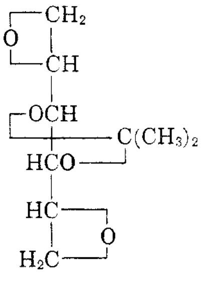
The preparation of polymers containing carbohydrate repeating units has been of considerable interest in recent years.[2] The preparation of a polyamine containing carbohydrate units by Wiggins,[3] who condensed 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol (I) with 1,6-diamino-1,6-dideoxy-2,3,4,5-di-*O*-methylene-D-mannitol,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



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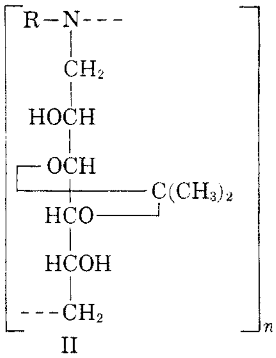

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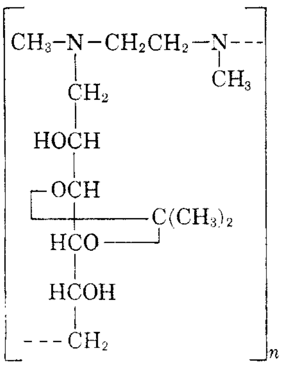

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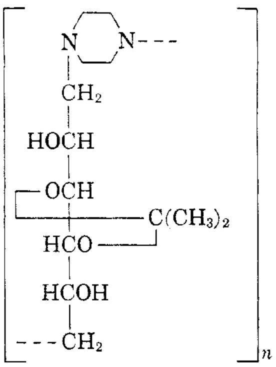

IV

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 = $C(CH_2OH)_3$) 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-

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[1] This work was carried out under contract between the Ordnance Corps (DA-33-019-ord-2025) and The Ohio State University Research Foundation (Project 675). The support of the supervising agency, the Ballistic Research Laboratories of Aberdeen Proving Ground, Md., and the inspiration of Dr. L. P. Kuhn are gratefully acknowledged.

[2] P. L. Nichols, Jr., and E. Yanovsky, *J. Am. Chem. Soc.*, **66**, 1625 (1944); C. L. Mehltretter 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).

[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).