

the crude product from water to give bright yellow platelets, m.p. 164–167°.

*Anal.* Calcd. for  $C_{11}H_{14}N_4O_7$ : C, 42.0; H, 4.49; N, 17.8. Found: C, 42.0; H, 4.14; N, 18.1.

**2,6-Diamino-3-nitro-4-pyridinol (VII).**—Fifteen grams of VI was added to 100 ml. of absolute ethanol saturated with potassium hydroxide. The mixture was refluxed on a steam-bath for 3 days. An insoluble red potassium salt was formed as soon as the dicarbamate VI was added to the alcoholic alkali solution but, as the reaction proceeded, the color of the precipitate slowly changed to a yellowish-orange. The cooled mixture was filtered, and the precipitate dissolved in water. On neutralization with concentrated hydrochloric acid, a yellowish-orange precipitate was formed. After filtering and washing with water, the product weighed 5.7 g. A sample recrystallized from water gave fine yellowish-orange platelets which decomposed at 256–258°.

*Anal.* Calcd. for  $C_5H_6N_4O_3$ : C, 35.3; H, 3.55; N, 32.9. Found: C, 35.0; H, 3.70; N, 32.8.

**2,3,6-Triamino-4-pyridinol (VIII).**—2,6-Diamino-3-nitro-4-pyridinol (VII), 0.5 g., was dissolved in 25 ml. of 95% ethanol and shaken for 3 hours with Raney nickel and hydrogen under 50 lb./sq. in. pressure. After the catalyst had been removed, the solvent was evaporated under vacuum to give solid 2,3,6-triamino-4-pyridinol (VIII) which colored rapidly on exposure to air. No attempt was made to analyze the material.

**5-Amino-7-hydroxy-imidazo[b]pyridine (IX).**—To the 2,3,6-triamino-4-pyridinol (VIII) obtained by the above procedure was added 20 ml. of 98% formic acid. The solution was refluxed for 4 hours and then evaporated to dryness on the steam-bath. The solid residue was then heated to 270° for 3 hours at 1 mm. pressure. The residue from this pyrolysis was extracted with boiling water. The solution was decolorized with Darco G-60, filtered and allowed to cool. The 5-amino-7-hydroxy-imidazo[b]pyridine (IX) separated as feathery needles which did not melt below 300°;  $\lambda_{max}$  (in 95% ethanol), 264  $m\mu$ ,  $\log \epsilon$ , 4.15; 282  $m\mu$ ,  $\log \epsilon$ , 4.15. The product was dried at 110° for 4 hours for analysis.

*Anal.* Calcd. for  $C_6H_6N_4O$ : C, 48.0; H, 4.02; N, 37.3. Found: C, 47.6; H, 3.98; N, 37.1.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

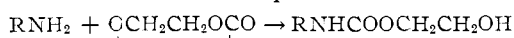
## The Preparation of Polymeric and Cyclic Urethans and Ureas from Ethylene Carbonate and Amines

BY ELIZABETH DYER AND HARVEY SCOTT<sup>1</sup>

RECEIVED AUGUST 13, 1956

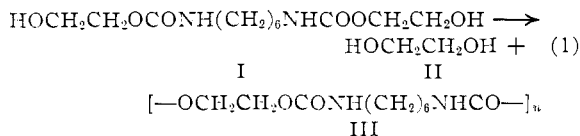
2-(Hydroxyethyl)-carbamates, obtained from primary amines and ethylene carbonate, lose ethylene glycol when subjected to vacuum distillation with an alcohol in the presence of barium oxide or zinc borate as catalysts. The alcohol group may be part of the 2-(hydroxyethyl)-carbamate or of a diol. Polyurethans were obtained from the reaction products of ethylene carbonate with 1,6-hexanediamine, 1,10-aminodecanol and 4-aminomethylbenzyl alcohol and also from the reaction of bis-(2-hydroxyethyl)-1,6-hexanedicarbamate with two high-boiling diols. Cyclic urethans were prepared from the reaction of ethylene carbonate with 2-aminoethanol, the *N*-ethyl- and *N*-butyl-2-aminoethanols, 1,3-aminopropanol and 4-aminobutan-2-ol. A polyurea was obtained from ethylene carbonate and *N*-isobutyl-1,6-hexanediamine. A cyclic urea resulted from ethylene carbonate and *N*-isopropyl-1,3-propanediamine.

In the last few years the preparation of various 2-hydroxyethyl carbamates from ethylene carbonate and amines has been reported<sup>2</sup>



It occurred to the authors that polyurethans might be prepared from 2-(hydroxyethyl)-carbamates by elimination of ethylene glycol as is done in the commercial preparation of polyethylene terephthalate.<sup>3</sup> Such a procedure would avoid the need for chemically sensitive diisocyanates, which are the most common starting materials for the preparation of polyurethans.<sup>4</sup>

The following types of reactions were investigated

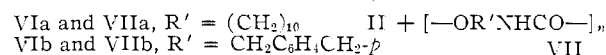
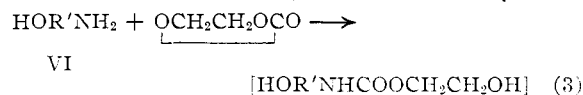
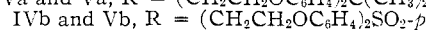
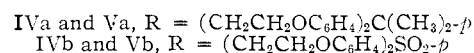


(1) From the Ph.D. Thesis, 1956, of Harvey Scott, Armstrong Cork Co. Research Fellow, 1953–1955.

(2) (a) F. Strain, U. S. Patent 2,441,298 (May 11, 1948); (b) R. Delaby, A. Sekera, P. Chabrier and P. Piganiol, *Bull. soc. chim. France*, 392 (1951); (c) R. Delaby, P. Chabrier and H. Najer, *Compt. rend.*, **234**, 2374 (1952); (d) R. Delaby, P. Chabrier and H. Najer, *ibid.*, **235**, 376 (1952); (e) M. J. Viard, British Patent 689,705 (April 1, 1953); (f) W. Kern and W. Thoma, *Makromol. Chem.*, **11**, 10 (1953).

(3) J. R. Winfield and J. T. Dickson, British Patent 578,079 (June 14, 1946).

(4) (a) O. Bayer, *Angew. Chem.*, **59**, 257 (1947); (b) C. S. Marvel and J. H. Johnson, *THIS JOURNAL*, **72**, 1674 (1950); (c) J. H. Brewster, *ibid.*, **73**, 368 (1951); (d) E. Dyer and G. W. Bartels, *ibid.*, **76**, 591 (1954).



A polyurethan III was obtained readily by subjecting bis-(2-hydroxyethyl)-1,6-hexanedicarbamate<sup>2d</sup> (I), to vacuum distillation at 150° in the presence of a catalytic amount of barium oxide. This polymer was shown by analysis and infrared absorption to have the same composition as the polyurethan obtained by Brewster<sup>4c</sup> from 1,6-hexane diisocyanate and ethylene glycol. Attempts to apply this synthesis to the preparation of *N*-substituted polyurethans, by starting with secondary diamines, were unsuccessful.

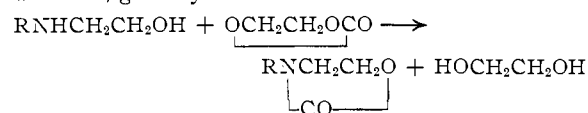
In order to extend this type of reaction to the preparation of polyurethans other than those derived from ethylene glycol, reaction 2 was investigated. Appreciable transesterification was not accomplished by the reaction of I with 1,4-butanediol, *p*-xylylenediol, 1,4-bis-(2-hydroxyethoxy)-benzene or 1,5-bis-(2-hydroxyethoxy)-naphthalene, be-

cause these diols volatilized along with the ethylene glycol and escaped from the reaction. Polyurethans were obtained, however, by treatment of I with either of two high-boiling diols: 2,2-bis-(4- $\beta$ -hydroxyethoxyphenyl)-propane (IVa) and 4,4'-bis-(2-hydroxyethoxy)-phenyl sulfone (IVb). Analyses showed that these polyurethans were not simple representatives of polymer V, but that they could be considered copolymers containing from 5 to 22% by weight of units of type III along with a major quantity of units of type V.

A polyurethan of the exact composition of Va, prepared in the conventional manner from the diol IVa and 1,6-hexane diisocyanate, had approximately the same infrared absorption as the 95-5 copolymer from the diol IVa and I. The former polymer had a slightly higher melting point and greater toughness than the polymer formed by transesterification. Some evidence for the possibility of copolymer formation by alcoholysis is the fact that the homopolymer III was shown to react with the diol IVb with the evolution of ethylene glycol.

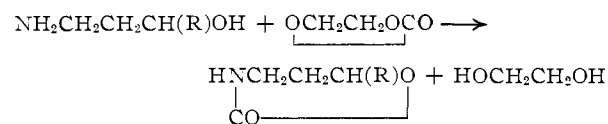
The preparation of polyurethans by method 3 has the advantages of avoiding the formation of copolymers and of thermally unstable ethylene glycol units.<sup>4a</sup> Polyurethans of the expected composition (VII) were obtained by treating 10-amino-1-decanol (VIa) and 4-aminomethylbenzyl alcohol (VIb) with ethylene carbonate and subjecting the products to vacuum distillation in the presence of barium oxide and zinc borate.

Amino alcohols of short chain length, when treated with ethylene carbonate and the product distilled, gave cyclic urethans.



Thus 2-aminoethanol and ethylene carbonate yielded 2-oxazolidone,<sup>5</sup> and the 2-N-ethyl- and 2-N-butylaminoethanol gave the corresponding N-substituted 2-oxazolidones, previously obtained by other methods.<sup>5c,6</sup>

Six-membered cyclic urethans were obtained in over 70% yield from the action of ethylene carbonate on 4-amino-2-butanol and on 3-amino-1-propanol.



This good method of preparing simple 2-pentoxazolidones<sup>7</sup> (tetrahydro-2H-1,3-oxazine-2-ones) is of interest in view of the scarcity of such methods. Neither of the six-membered cyclic urethans could be homopolymerized by heat alone or by heating with potassium carbonate, sodium ethoxide or boron trifluoride.

(5) (a) S. Gabriel, *Ber.*, **21**, 569 (1888); (b) P. Vièles and J. Seguin, *Bull. soc. chim. France*, **287** (1953); (c) A. H. Homeyer, U. S. Patent 2,399,118 (Apr. 23, 1946).

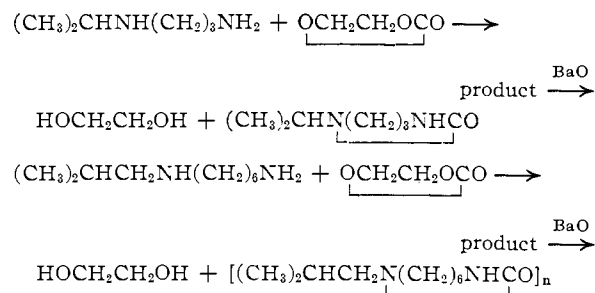
(6) J. R. Caldwell, U. S. Patent 2,658,328 (Oct. 20, 1953).

(7) See G. Y. Leshner and A. R. Surrey, *THIS JOURNAL*, **77**, 636 (1955), for a summary of the literature.

No carbamate products could be obtained from the reaction of ethylene carbonate with N,N'-dimethyl-1,2-ethanediamine or with N,N'-diethyl-1,6-hexanediamine. Carbon dioxide was evolved; this might indicate a hydroxyethylation reaction as was observed with dibutylamine and ethylene carbonate.<sup>8</sup>

The reactions of ethylene carbonate giving either a carbamate (by attack of an amine at a carbonyl group) or a hydroxyethylation product (by attack of an amine at a methylene group) are parallel to the reactions of  $\beta$ -propiolactone with nucleophilic reagents under various conditions.<sup>9</sup> It is probable that attack of an amine at the carbonyl group of ethylene carbonate is made difficult by the low basicity of the amine or by the presence of bulky groups on the nitrogen. The ease of formation of carbamates from ethylene carbonate and piperazine<sup>2e</sup> or morpholine<sup>10</sup> in contrast to the difficulty of formation from N,N'-diethyl-1,6-hexanediamine could be attributed to a more favorable steric arrangement in the case of the former compounds.

The applicability of the glycol elimination reaction to the preparation of cyclic and polymeric ureas was shown by the examples



In both of these preparations, as in most of the other glycol elimination reactions, the effect of the catalyst was pronounced. No significant amount of glycol was formed until a catalytic amount of barium oxide or zinc borate (or both) was added.

### Experimental<sup>11</sup>

**Cyclic Urethans.**—A mixture of 0.3 mole of ethylene carbonate<sup>12</sup> and 0.3 mole of the amino alcohol<sup>13</sup> was treated as indicated in Table I. The product was usually diluted with a suitable solvent and passed through Amberlite IR 120-H to remove unchanged amine. The solvent was stripped from the eluate and the product distilled at 1 mm. before crystallization. The infrared absorption band at 6.5  $\mu$ , which occurs in the spectra of open-chain monosubstituted urethans, is missing or extremely weak in the cyclic urethans.

**Diols and Amino Alcohols.**—Table II shows the preparation of diols and amino alcohols, four of which are new compounds, indicated by analyses. The remaining compounds, except for the last two on the list, were prepared by methods different from those described in the literature.

(8) W. W. Carlson, U. S. Patent 2,448,767 (Sept. 7, 1948).

(9) T. L. Gresham, J. E. Jansen, F. W. Shaver, J. T. Gregory and W. L. Beears, *THIS JOURNAL*, **70**, 1004 (1948).

(10) Technical Bulletin, "Ethylene Carbonate," Jefferson Chemical Co., Inc., New York, N. Y., p. 7.

(11) Melting points are corrected.

(12) Kindly supplied by the Jefferson Chemical Co.

(13) Samples of 2-(N-ethylamino)-ethanol were kindly supplied by Carbide and Carbon Chemicals Corporation, of 4-amino-2-butanol by Sharples Chemicals, Inc., of 3-amino-1-propanol and N-isopropyl-1,3-propanediamine by American Cyanamid Co.

TABLE I  
 CYCLIC URETHANS AND A CYCLIC UREA FROM ETHYLENE CARBONATE AND AMINO COMPOUNDS

Cyclic compounds	Yield, %	M.p. or b.p., °C. (mm.)	Formula	Calculated		Analyses, %		Found	
				C	H	N	C	H	N
2-Oxazolidone <sup>b</sup>	46 <sup>a</sup>	88–89 <sup>b</sup>	C <sub>3</sub> H <sub>5</sub> NO <sub>2</sub>	41.38 <sup>c</sup>	5.79	16.09	41.35	5.82	15.90
3-Ethyl-2-oxazolidone <sup>bc</sup>	61 <sup>d</sup>	95–95.5 (1.1)							
3-Butyl-2-oxazolidone <sup>bc</sup>	67 <sup>d</sup>	98.2–99.3 (0.5)							
Tetrahydro-2H-1,3-oxazin-2-one	73 <sup>e</sup>	80 <sup>f</sup>	C <sub>4</sub> H <sub>7</sub> NO <sub>2</sub>	47.52	6.98	13.85	47.57	7.03	13.86
Tetrahydro-6-methyl-2-H-1,3-oxazin-2-one <sup>e</sup>	76 <sup>h</sup>	100 <sup>f</sup>	C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub>	52.16	7.88	12.17	52.62	7.95	12.06
1-Isopropyl-hexahydro-2-oxo-pyrimidine <sup>i</sup>	62 <sup>j</sup>	150–151	C <sub>7</sub> H <sub>14</sub> N <sub>2</sub> O	59.12	9.92	19.70	59.17	10.10	19.62

<sup>a</sup> From reaction at 45° for 12 hours with 20 ml. of methanol as solvent. <sup>b</sup> Recrystallized from ethylene glycol dimethyl ether or *n*-butyl acetate. <sup>c</sup> Analyzed because F. Strain, U. S. Patent 2,441,298 (May 11, 1948), reported the product to be an open-chain carbamate. <sup>d</sup> Reactants kept for one hour in ice-bath, then for 7 days at room temperature (an essential step), then refluxed for 12 to 24 hours after adding toluene and dioxane as needed to make a homogeneous solution. <sup>e</sup> Reaction mixture heated on steam-bath for 2 days. <sup>f</sup> Recrystallized from 1-nitropropane. <sup>g</sup> Obtained in 46% yield by A. Weickmann, German Patent 858,402 (Dec. 8, 1952), by a different method. <sup>h</sup> After exothermic reaction at room temperature, mixture was heated at 1 mm. to remove material boiling at 55–57°. <sup>i</sup> Obtained from 0.2 mole of ethylene carbonate and 0.2 mole of *N*-isopropyl-1,3-propanediamine. <sup>j</sup> Reaction mixture warmed until homogeneous, allowed to stand 30 minutes at room temperature, treated with 0.01 g. of barium oxide and distilled. The product, b.p. 110° at 2 mm., was recrystallized from 1:1 *n*-butyl acetate–di-*n*-butyl ether.

 TABLE II  
 PREPARATION OF DIOLS AND AMINO ALCOHOLS

Compound	Method <sup>a</sup>	Yield, %	Solvents <sup>b</sup> for Reacn.	Solvents <sup>b</sup> for Recryst.	M.p., °C.
1,4-Bis-(2-hydroxyethoxy)-benzene <sup>c</sup>	A	24	D	T	103–104
1,5-Bis-(2-hydroxyethoxy)-naphthalene <sup>c</sup>	A	39	D	B	179–180
2,2-Bis-(4-β-hydroxyethoxyphenyl)-propane <sup>d</sup>	A	51	D	T <sup>e</sup>	110.5 <sup>d</sup>
4,4'-Bis-(2-hydroxyethoxy)-phenyl sulfone <sup>f</sup>	A	58	G	D	180
4,4'-Bis-(2-hydroxyethoxy)-benzophenone <sup>f</sup>	A	36	G	D	168
10-Amino-1-decanol <sup>h</sup>	C	74	H	T	72
<i>p</i> -Xylylene diol <sup>i,j</sup>	C	59	H	BE, 1:2	116
4-Aminomethylbenzyl alcohol <sup>k</sup>	C	25	D + H	T + M	82–83
Diacetyl derivative <sup>l</sup>				T	94–95
2-Hydroxyethyl ester of 4-hydroxymethylbenzyl carbamate	m	31	None	E	71–72
Bis-(2-hydroxyethyl)-1,6-hexane dicarbamate <sup>n</sup>	B	80	None	MT, 1:4	94–95
Bis-(2-hydroxyethyl)-1,4-piperazine dicarboxylate <sup>p</sup>	B	74	None	N	110

<sup>a</sup> Methods A, B and C are described in the Experimental. <sup>b</sup> D = dioxane, G = diethylene glycol dimethyl ether, T = toluene, B = 1-butanol, H = tetrahydrofuran, M = methanol, N = 1-nitropropane, E = ethyl acetate. <sup>c</sup> J. W. Fisher and J. Lincoln, British Patent 678,264 (Sept. 3, 1952). <sup>d</sup> G. H. Coleman, B. C. Hadler and R. W. Sapp, U. S. Patent 2,359,622 (Oct. 3, 1944), m.p. "approx. 112°." <sup>e</sup> Containing a small amount of ethanol. <sup>f</sup> *Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>6</sub>S: C, 56.79; H, 5.36; S, 9.47. Found: C, 56.51; H, 5.07; S, 9.44. <sup>g</sup> *Anal.* Calcd. for C<sub>17</sub>H<sub>18</sub>O<sub>6</sub>: C, 67.54; H, 6.00. Found: C, 67.46; H, 5.82. <sup>h</sup> Prepared by reduction of 9-cyanononanoic acid. W. S. Bishop, U. S. Patent 2,300,107 (Sept. 21, 1944), using sodium, got a 32% yield. <sup>i</sup> By reduction of dimethyl terephthalate. <sup>j</sup> E. Bourquelot and A. Ludwig, *Compt. rend.*, 159, 213 (1914), and W. Low, *Ann.*, 231, 374 (1885). <sup>k</sup> Prepared by reduction of methyl terephthalamate. <sup>l</sup> *Anal.* Calcd. for C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub>: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.52; H, 6.86; N, 6.17. <sup>m</sup> Prepared by heating 0.149 mole of 4-aminomethylbenzyl alcohol and 0.165 mole of ethylene carbonate at 80° for 24 hours, followed by passage of a methanol solution through a cation exchange resin. *Anal.* Calcd. for C<sub>11</sub>H<sub>15</sub>NO<sub>3</sub>: C, 58.65; H, 6.71; N, 6.22. Found: C, 58.23; H, 6.90; N, 6.16. <sup>n</sup> Reported<sup>2d,i</sup> m.p. 93.5 and 95–97°. <sup>p</sup> Reported<sup>2e</sup> m.p. 103–104°. Attempts to polymerize this di-carbamate by glycol elimination gave only dark, soft resins.

(A) **Hydroxyethylation of Diphenols.**—A mixture of 0.4 mole of the diphenol,<sup>14</sup> 0.8 mole of ethylene carbonate, 3 ml. of a 40% solution of benzyltrimethylammonium hydroxide in methanol and 100–200 ml. of purified dioxane or diethylene glycol dimethyl ether was refluxed during stirring until the evolution of carbon dioxide ceased (usually after 2 days). The product was precipitated by pouring it into a stirred mixture of ice and dilute base, filtered and washed with base, water, acid and then water. After decolorizing with Norit in methanol or mixtures containing tetrahydrofuran, the product was recrystallized.

(B) **Preparation of Bis-(2-hydroxyethyl)-dicarbamates.**—The diamine and ethylene carbonate (1:2 molar ratio) were mixed, cooled to moderate the exothermic reaction, then heated at 90–110° for 12 hours. Purification was effected

by passage of a methanol solution through a cation exchange resin followed by recrystallization.

(C) **Diols and Amino Alcohols by Reduction.**—Reductions were done with a slurry of lithium aluminum hydride in refluxing tetrahydrofuran (Table II). The excess hydride was decomposed with methanol and the alumina dissolved with acid. After adding excess base, the organic product was separated by extraction with 1-butanol, distilled at a pressure of 0.3 to 0.8 mm. and recrystallized.

**Methyl Terephthalamate.**—Crude methyl hydrogen terephthalate was recrystallized from a 1:1 mixture of xylene and methanol containing a small amount of Methyl Carbitol to a melting point of 210–215° (lit.<sup>15</sup> "about 230°"). A mixture of 2 ml. of triethylamine, 100 g. (0.56 mole) of methyl hydrogen terephthalate and 400 g. of distilled

(14) The 4,4'-dihydroxydiphenyl sulfone was kindly supplied by Monsanto Chemical Company and the 4,4'-dihydroxybenzophenone by the Dow Chemical Company.

(15) J. B. Cohen and H. S. Pennington, *J. Chem. Soc.*, 113, 63 (1918).

TABLE III  
 PREPARATION OF POLYURETHANS

Poly- mers <sup>a</sup>	Catalyst <sup>b</sup>	Softening temp., °C.	Sol- vent <sup>c</sup>	Rel. viscos. <sup>d</sup>	Formulas	C	Calcd. H	Analyses, %		Found H	N
								N	C		
III	Ba	164-169 <sup>e</sup>	P	1.19,C	C <sub>10</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>			12.17			12.12
Va <sup>f</sup>	None <sup>g</sup>	90	D	1.22,F	C <sub>27</sub> H <sub>36</sub> N <sub>2</sub> O <sub>8</sub>	66.92	7.45	5.78	66.80	7.54	5.76
Va <sup>h</sup>	Zn	84-93 <sup>i</sup>	P	1.07,F	<sup>j</sup>	66.18	7.47	6.10	66.42	7.17	6.27
Vb <sup>k</sup>	Ba	112-136	P	1.06,F	<sup>l</sup>	55.30	6.40	6.99 <sup>i</sup>	56.90	6.57	7.14
Vb <sup>m</sup>	Ba + Zn	117-135	P		<sup>n</sup>	56.30	6.21	6.36 <sup>n</sup>	57.30	6.60	6.74
VIIa	Ba + Zn	145-147	D	1.21,C	C <sub>11</sub> H <sub>21</sub> NO <sub>2</sub>	66.29	10.62	7.03	66.67	10.67	7.02
VIIb	Ba + Zn	208-215	P	1.12,C	C <sub>9</sub> H <sub>9</sub> NO <sub>2</sub>	66.24	5.56	8.58	65.91	5.80	8.82

<sup>a</sup> Numbers refer to labeled compounds in equations. <sup>b</sup> Ba = barium oxide, Zn = zinc borate. <sup>c</sup> Solvent for the polymer. P = N-methyl-2-pyrrolidone, D = dioxane. <sup>d</sup> Relative viscosity in *m*-cresol (C) or dimethylformamide (F). <sup>e</sup> Reported m.p.<sup>4c</sup> for polyurethan from 1,6-hexanediisocyanate and ethylene glycol, 170°. <sup>f</sup> Prepared from 2,2-bis-[4-β-hydroxyethoxyphenyl]-propane and 1,6-hexanediisocyanate. <sup>g</sup> Bulk polymerization at 170-180°. <sup>h</sup> Prepared from 2,2-bis-(4-β-hydroxyethoxyphenyl)-propane and bis-(2-hydroxyethyl)-1,6-hexanedicarbamate. <sup>i</sup> Increasing time of polymerization from 18 to 50 hours changed m.p. to 88-103°, but did not affect the composition of the polymer. <sup>j</sup> Calcd. for 95% C<sub>27</sub>H<sub>36</sub>N<sub>2</sub>O<sub>8</sub> (Va) and 5% C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub> (III). <sup>k</sup> Polymer prepared by heating 4,4'-bis-(2-hydroxyethoxy)-phenyl sulfone and bis-(2-hydroxyethyl)-1,6-hexanedicarbamate for 8 hours. Calcd. for 22% C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub> and 78% C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>O<sub>8</sub>S. <sup>l</sup> Also calcd. for S, 4.94. Found: S, 4.90. <sup>m</sup> Polymer from same reactants as in note <sup>k</sup>, heated for 30 hours. Calcd. for 12.5% C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub> and 87.5% C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>O<sub>8</sub>S. <sup>n</sup> Also calcd. for S, 5.54. Found: S, 5.86.

thionyl chloride was stirred and refluxed for 3 hours.<sup>16</sup> Then excess thionyl chloride was distilled off, the residue dissolved in a small volume of dioxane and the solution added dropwise to 2 l. of concd. ammonium hydroxide during stirring and cooling. The resulting methyl terephthalamate melted at 204-206° (lit.<sup>17</sup> 201°) after recrystallization from water containing Methyl Carbitol.

**Preparation of Polymers.**—The polymerization chamber was a heat-jacketed, 30 × 2.5 cm. test-tube attached by a ground-glass joint to a plain distillation head. A fine capillary through which nitrogen was admitted, produced a stirring effect. Ethylene glycol was collected in a Dry Ice trap.

A mixture of 0.1 mole of melted monomer, 0.01-0.02 g. of barium oxide and frequently the same amount of zinc borate was heated in the polymerization apparatus under a pressure of 0.5-2 mm. at the lowest temperature at which ethylene glycol would form. Then the temperature was raised in successive stages to about 220°. Unless the material solidified or discolored badly, the heating was continued as long as the glycol was formed (up to 50 hours). The ethylene glycol was obtained in yields of 80-90%. The polymer was purified by pouring a filtered solution of it into a stirred non-solvent. Precipitation was repeated, the product was dried *in vacuo* and ground repeatedly and often extracted in a continuous extractor with a solvent such as methanol before drying for analysis.

(16) The procedure and the ester were kindly furnished by E. I. du Pont de Nemours and Co., Inc.

(17) P. Kattwinkel and R. Wolfenstein, *Ber.*, **37**, 3223 (1904).

Dilute solution viscosities ( $\eta_r$ ) were done in an Ostwald viscosimeter at 25°, using 0.4000 g. of polymer in 100 ml. of dimethylformamide or 1.000 g. of polymer in 100 ml. of *m*-cresol.

Polymers Va and Vb (Table III) formed weak films or fibers; the others were brittle powders. All the polyurethans showed strong infrared absorption at approximately 6.00 and 6.54  $\mu$ .<sup>4d</sup>

**Polyurea from N-Isobutyl-1,6-hexanediamine and Ethylene Carbonate.**—A mixture of 0.2 mole of the diamine and 0.2 mole of ethylene carbonate was heated gently until an exothermic reaction took place. After an interval of cooling and standing, the glycol elimination reaction was carried out in the usual way, using barium oxide. The product, precipitated from N-methyl-2-pyrrolidone with ice, and from methanol with water, softened at 81-96°. Weak fibers could be drawn.

*Anal.* Calcd. for C<sub>11</sub>H<sub>22</sub>N<sub>2</sub>O: C, 66.62; H, 11.18; N, 14.13. Found: C, 65.77; H, 11.16; N, 13.95.

**Acknowledgment.**—The authors are indebted to the Armstrong Cork Company for a fellowship in support of this investigation, to Drs. L. H. Dunlap and F. W. Breuer for helpful discussions, to Dr. H. C. Beachell for infrared absorption measurements and interpretations, to Mr. R. N. Walter for the chemical analyses, and to all the manufacturers who contributed samples of their chemicals.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MARYLAND]

## An Example of a Ring Closure Yielding a 5-Methoxyoxazole in Preference to a Dihydroisoquinoline

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RECEIVED JULY 23, 1956

An example is given of a substituted  $\alpha$ -benzamidohydrocinnamate ester (II) which, on treating with phosphorus oxychloride under the usual Bischler-Napieralski conditions, cyclizes predominately to a 5-methoxyoxazole (III) instead of to a dihydroisoquinoline (I).

The synthesis of 3,4-dihydro-6,7-methylenedioxy-1-(3,4,5-trimethoxyphenyl)-3-isoquinolinecarboxylic acid (free acid of I) was originally undertaken because it has certain structural features of podophyllotoxin, a tumor-damaging agent,<sup>1</sup> and be-

(1) M. G. Kelly and J. L. Hartwell, *J. Nat. Cancer Inst.*, **14**, 967 (1954); J. L. Hartwell and A. W. Schrecker, *THIS JOURNAL*, **73**, 2909 (1951).

cause the corresponding dihydroisoquinoline without the carboxylic acid group has been found to have tumor-damaging properties. The synthesis employed is of interest from the chemical standpoint because one intermediate, methyl 3,4-methylenedioxy- $\alpha$ -(3,4,5-trimethoxybenzamido)-hydrocinnamate (II), can cyclize either *via* the classical Bischler-Napieralski reaction to the de-