

**Saponification of X: 5-Methylbicyclo[2,2,2]oct-2-ene-5-carboxamide (XIII).**—When 15 g. of X was saponified by the procedure employed for III, there was obtained 12 g. of the carboxamide, m.p. 121–122° after several recrystallizations from hexane. In spite of the sharp melting point and a satisfactory elementary analysis, this material was shown subsequently (*vide infra*) to consist of a mixture of the stereoisomeric carboxamides.

**Ureidomethyl Derivatives. General Procedure.**—One to 2 g. of the bicyclic carboxamide or nitrile in absolute ether solution was added to a suspension of a 50% molar excess of lithium aluminum hydride<sup>32</sup> in absolute ether and the mixture was refluxed for 2–8 hours. Carboxamides which were only slightly soluble in ether, *i.e.*, II and its stereoisomer, were reduced by the Soxhlet technique. The reaction mixture was then cooled in ice and the complex was decomposed with a minimum volume of water and the same volume of 50% aqueous sodium hydroxide solution. The inorganic salts generally separated as a pasty solid from which the almost anhydrous solution of the amine could be decanted readily. The amine was precipitated with gaseous hydrogen chloride from the ether solution. The amine hydrochloride then was dissolved in aqueous alcohol containing an equimolar amount of sodium hydroxide and nitrourea.<sup>33</sup> The solution was warmed at 70–75° for 1–2 hours and allowed to cool. The ureidomethyl derivative which separated upon cooling or concentrating the solution was recrystallized from water or from aqueous ethanol.

When Ia was reduced with lithium aluminum hydride and the product was treated with nitrourea, 5-*endou*reidomethyl-2-norbornene (m.p. 120–121°) was obtained after several recrystallizations from water. This compound also was obtained directly in a high state of purity from 2-norbornene-5-*endocarboxamide*; infrared absorption maxima: 10.77(w), 11.05(w), 11.96(w), 12.11(w), 12.85(w), 13.88(m) and 14.16(m)  $\mu$ .

*Anal.* Calcd. for  $C_9H_{14}N_2O$ : C, 65.03; H, 8.49; N, 16.85. Found: C, 65.12; H, 8.32; N, 16.66.

5-*exo*Ureidomethyl-2-norbornene (m.p. 129–130°) was obtained as the sole product of the reaction from either Ib or II; infrared absorption maxima: 11.00(w), 11.11(w), 11.60(w), 12.09(w), 12.70(w), 12.85(w), 13.22(w), 14.13(m) and 14.28(s)  $\mu$ .

*Anal.* Found: C, 65.00; H, 8.54; N, 17.05.

5-*exo*Methyl-5-*endou*reidomethyl-2-norbornene, m.p. 163–164°, was obtained as the sole reaction product from

(32) V. M. Mićović and M. L. Mihailović, "Lithium Aluminum Hydride in Organic Chemistry," Serbian Academy of Sciences, Belgrade, 1955.

(33) T. L. Davis and K. C. Blanchard, *THIS JOURNAL*, **51**, 1790 (1929).

IV; infrared absorption maxima: 11.17(m), 11.46(m), 11.93(m), 12.20(m), 12.90(m), 13.52(s), 13.87(s), 14.15(m) and 15.07(m)  $\mu$ .

*Anal.* Calcd. for  $C_{10}H_{16}N_2O$ : C, 66.63; H, 8.95; N, 15.54. Found: C, 66.90; H, 9.06; N, 15.55.

5-*endo*Methyl-5-*exou*reidomethyl-2-norbornene, m.p. 134–135°, was obtained from 5-*endomethyl*-2-norbornene-5-*exocarboxamide* as the sole product of the reaction; infrared absorption maxima: 11.11(s), 11.45(m), 11.87(m), 11.97(m), 12.19(s), 12.91(s), 13.78(s), 14.00(s) and 14.21(s)  $\mu$ .

*Anal.* Found: C, 66.72; H, 8.92; N, 15.45.

**Ureidomethyl Derivatives of XIIIa and XIIIb.**—To a solution of 4 g. of lithium aluminum hydride in 200 ml. of absolute ether was added with stirring a solution of 11 g. of XIII, the saponification product of 5-cyano-5-methylbicyclo[2,2,2]oct-2-ene (X), in 500 ml. of absolute ether. The mixture was refluxed for 6 hours and the complex was decomposed. Distillation of the extracts gave 8.1 g. of an amine, b.p. 98–100° (20 mm.). The amine was suspended in 250 ml. of 20% ethanol and treated with 12 g. of nitrourea. Upon standing overnight, the solution deposited 12.3 g. of 5-*exomethyl*-5-*endou*reidomethylbicyclo[2,2,2]oct-2-ene (XVa) which melted at 188–189° when recrystallized several times from ethyl acetate; infrared absorption maxima: 10.96(m), 11.14(w), 12.33(w), 12.94(w), 13.72(m), 14.30(s) and 14.95(m)  $\mu$ .

*Anal.* Calcd. for  $C_{11}H_{18}N_2O$ : C, 68.00; H, 9.34; N, 14.42. Found: C, 68.23; H, 9.33; N, 14.60.

The aqueous alcoholic filtrates above were evaporated to dryness under reduced pressure. The residue of 4.3 g. of 5-*endomethyl*-5-*exou*reidomethylbicyclo[2,2,2]oct-2-ene (XVb) melted at 146–147° after several recrystallizations from ether; infrared maxima: 10.86(m), 11.12(m), 11.35(m), 11.90(m), 12.30(m), 12.96(s), 13.79(s), 14.45(s) and 15.10(s)  $\mu$ .

*Anal.* Found: C, 68.11; H, 9.46; N, 14.21.

Hydrogenation of either XVa or XVb in ethanol solution at 45 lb. pressure in the presence of palladium catalyst gave fine plates of 2-methyl-2-ureidomethylbicyclo[2,2,2]octane, m.p. 159–160°.

*Anal.* Calcd. for  $C_{11}H_{20}N_2O$ : C, 67.30; H, 10.27; N, 14.27. Found: C, 67.29; H, 10.24; N, 14.50.

Conversion of XIIIb to the ureidomethyl derivative gave XVb (m.p. 145–146°) as the main product together with some higher melting material which could not be purified. When pure XIIIa was employed as the starting material in the above reaction sequence, XVa (m.p. 188–189°) was obtained as the sole product of the reaction.

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

## Thermal Degradation of Carbamates of Methylenebis-(4-phenyl Isocyanate)<sup>1</sup>

BY ELIZABETH DYER AND G. EARL NEWBORN, JR.<sup>2</sup>

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The products of pyrolysis at 300° of the biscarbamates prepared from methylenebis-(4-phenyl isocyanate) and 1-butanol, 2,2-dimethyl-1-propanol and benzyl alcohol, and of the polycarbamate from methylenebis-(4-phenyl isocyanate) and 1,6-hexanediol have been determined quantitatively. In all cases carbon dioxide and the parent alcohol or diol were formed. The benzyl biscarbamate and the polycarbamate yielded amine residues, which contained 4,4'-diaminodiphenylmethane. Polymeric carbodiimides were isolated from degradation of the *n*-butyl and neopentyl biscarbamates and were shown to be possible intermediates in pyrolysis of the benzyl biscarbamate and the polycarbamate.

The literature contains little work on the purely thermal degradation of biscarbamates or of polycarbamates. Monomeric carbamates of the type RNHCOOR' are known to be degraded above 200° to the isocyanate and the alcohol,<sup>3</sup> and there are

scattered references to the formation of other products, such as carbon dioxide,<sup>4,5</sup> ureas<sup>4,5</sup> and olefins.<sup>4</sup> Studies of thermal degradation of carbamates in the presence of amines and organic acids have been conducted recently by Mukaiyama and

(1) From the Ph.D. dissertation of G. Earl Newborn, Jr., University of Delaware, 1958.

(2) Armstrong Cork Co., Research Fellow, 1955–1957.

(3) M. Métayer, *Bull. soc. chim. France*, 802 (1951).

(4) A. F. McKay and G. R. Vavasour, *Can. J. Chem.*, **31**, 688 (1953).

(5) M. A. Fletcher, M. W. Lakin and S. G. P. Plant, *J. Chem. Soc.*, 3898 (1953).

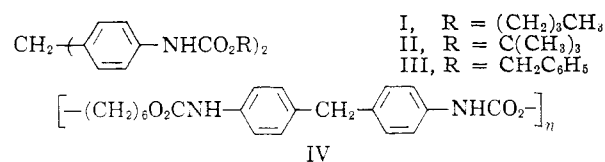
TABLE I

PYROLYSES AT 300°							
Products from carbamates of MDI <sup>a</sup>							
Carbamate	Time, min.	CO <sub>2</sub> , % <sup>c</sup>	Alc., % <sup>d</sup>	Other <sup>d</sup> volatiles	Total <sup>e</sup> base, %	Non-acet. <sup>f</sup> base, %	Wt. % re-covd., %
I <i>n</i> -Butyl <sup>b</sup>	45	55.3 ± 1.9	76.5 ± 2.3	1-Butene, tr.	.....	.....	92.7 ± 0.6
II Neopentyl <sup>b</sup>	75-120	44.8 ± 1.2	89.5 ± 3.0	.....	.....	.....	98.5 ± .9
III Benzyl <sup>b</sup>	60-90	84.0 ± 1.9	25.4 ± 2.5	Toluene <sup>h</sup>	72.2 <sup>i</sup> ± 0.2	17.6 ± 0.5	98.4 ± .4
IV Hexamethylene <sup>i</sup>	230-270	73.6 ± 4.3	Small amts.	1-Hexene-6-ol <sup>o</sup>	70.5 ± 4.5	12.6 ± 1.6	99.2 ± .1
Products from heating polycarbodiimide with an alcohol							
With benzyl alc.	90	76 <sup>k</sup>	40 <sup>l</sup>	Toluene, 5	68 <sup>j</sup>	12	99.6
With 1,6-hexanediol	210	74 <sup>k</sup>	Tr. <sup>m</sup>	1-Hexene-6-ol, 43	70 <sup>j</sup>	12	98.8 <sup>n</sup>

<sup>a</sup> Methylenebis-(4-phenyl isocyanate). <sup>b</sup> Averages of data from 5 to 7 runs. <sup>c</sup> Calcd. as mole % of the carbonyl of the sample. <sup>d</sup> Calcd. as mole % of the alcohol moiety. <sup>e</sup> Calcd. as mole % of the nitrogen. <sup>f</sup> Non-acetyltable base. <sup>g</sup> Weight % of the sample recovered as CO<sub>2</sub>, distillate and residue. <sup>h</sup> 5.2 ± 0.1; in addition, 1.0 ± 0.3 mole % of benzaldehyde. <sup>i</sup> Calculations of products based on the repeating unit  $[-(\text{CH}_2)_6\text{O}_2\text{CNHC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NHCO}_2-]$ ; data from 3 runs. <sup>j</sup> Contains 4,4'-diaminodiphenylmethane. <sup>k</sup> Includes CO<sub>2</sub> from formation of polycarbodiimide as well as CO<sub>2</sub> from reaction of polymer with the alcohol. <sup>l</sup> Benzyl alcohol. <sup>m</sup> 1,6-Hexanediol. <sup>n</sup> Data from two runs. <sup>o</sup> 31.8 ± 1.1.

co-workers,<sup>6</sup> and the effect of heat on bisurethans in the presence of titanium butoxide<sup>7</sup> or strontium<sup>8</sup> has been reported by Laakso and Reynolds.

In the present work three biscarbamates, I, II, III, and one polycarbamate, IV, were prepared by the action of methylenebis-(4-phenyl isocyanate) on 1-butanol, 2,2-dimethyl-1-propanol, benzyl alcohol and 1,6-hexanediol, respectively.



Thermal degradation of these carbamates was done at atmospheric pressure under dry nitrogen, at a temperature of 300°, the lowest temperature at which an appreciable rate of decomposition occurred. Heating at this temperature was continued until the reactions were approximately complete. Under these conditions all the carbamates yielded carbon dioxide, a distillate fraction consisting of the parent alcohol or diol and in certain cases its dehydration products and a non-volatile residue. The distribution of these products is shown in Table I.

The data in Table I show that the amounts and nature of the degradation products differed with the boiling point of the alcohol portion of the carbamate. In the case of the *n*-butyl and neopentyl biscarbamates, derived from relatively low-boiling alcohols, the yields of carbon dioxide were lower and of the corresponding alcohol were higher than in the case of the benzyl biscarbamate and hexamethylene polycarbamate, derived from relatively high-boiling alcohols. Moreover, the residues from the *n*-butyl and neopentyl biscarbamates were infusible polymers, while those from the benzyl biscarbamate and the hexamethylene polycarbamate were low-melting, basic solids.

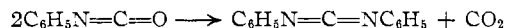
The mixtures of bases were shown by non-aqueous titration to contain more than 70 mole % of the original nitrogen of the carbamate. One of

the bases was 4,4'-diaminodiphenylmethane, isolated in yields of 17 and 8 mole % of degradation of the benzyl and hexamethylene carbamates, respectively. Efforts to separate other amines, including the basic material which was not acetylated by acetic anhydride, were unsuccessful.

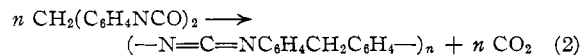
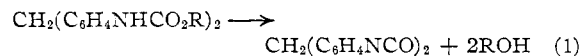
The polymeric residues from degradation of the *n*-butyl and neopentyl biscarbamates were intractable solids, unaffected by heat at 300° and insoluble in common polymer solvents, with the exception of benzyl alcohol, in which solution occurred after long refluxing. The infrared spectra of the two intractable residues showed absorption at 4.7-4.8 μ, a location which is characteristic<sup>9</sup> of the carbodiimide group. The basic residues from the other two carbamates, however, showed no absorption at this wave length.

Heating methylenebis-(4-phenyl isocyanate) at 300° under dry nitrogen at atmospheric pressure for 45 minutes gave a 92% yield of carbon dioxide and a residue having the same properties as those from the degradation of the *n*-butyl and neopentyl biscarbamates, including the strong carbodiimide absorption at 4.7-4.8 μ.

Stollé<sup>10</sup> showed that phenyl isocyanate, when heated at 300° in a sealed tube, formed diphenyl carbodiimide and carbon dioxide in nearly quantitative yield



The behavior of methylenebis-(4-phenyl isocyanate) at 300°, shown by the current work to be analogous to that of phenyl isocyanate, suggests that, in the thermal degradation of the *n*-butyl and neopentyl biscarbamates, the alcohol and isocyanate were produced first and that on further heating the isocyanate reacted to give a polymeric carbodiimide of methylenebis-(4-phenyl isocyanate)



The intractable nature of the polycarbodiimide residues could be due to partial cross-linking, since it is known<sup>9</sup> that aromatic carbodiimide groups polymerize readily.

(6) T. Mukaiyama and Y. Hoshino, *THIS JOURNAL*, **78**, 1946 (1956); T. Mukaiyama and M. Iwanami, *ibid.*, **79**, 73 (1957).

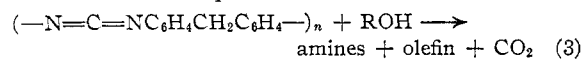
(7) T. M. Laakso and D. D. Reynolds, *ibid.*, **79**, 5517 (1957).

(8) D. D. Reynolds and T. M. Laakso, U. S. Patent 2,784,163, March 5, 1957.

(9) H. G. Khorana, *Chem. Revs.*, **53**, 145 (1953).

(10) R. Stollé, *Ber.*, **41**, 1125 (1908).

Evidence for the intermediate formation of the isocyanate was obtained by heating the biscarbamates under reduced pressure. At 300° and 3 mm. pressure the *n*-butyl biscarbamate gave a 20% yield of the parent diisocyanate (MDI). Under these conditions the benzyl biscarbamate distilled unchanged, but at 300° and 50–60 mm. benzyl alcohol was produced in an 80% yield. Moreover, a residue was obtained having the same properties as the residues from the degradation of the neopentyl and *n*-butyl biscarbamates. These findings suggest that reactions 1 and 2 occurred in the atmospheric pressure degradations of the benzyl and hexamethylene carbamates, as well as in the case of the carbamates of the lower-boiling alcohols (butyl and neopentyl). Subsequent reaction of the polymeric carbodiimide with the alcohol present could furnish the other products observed



To test the possibility that the basic and olefinic products originated from the polymeric carbodiimide as indicated in reaction 3, samples of the carbodiimide residue from degradation of the neopentyl biscarbamate were heated with benzyl alcohol and with hexamethylene glycol, respectively, at 300° and atmospheric pressure (under dry nitrogen). The products (shown in the second part of Table I) consisted of carbon dioxide, the parent alcohol or its dehydration product, and basic materials containing 4,4'-diaminodiphenylmethane and unidentified amines. The similarity in the nature and quantities of the products from the degradation of the carbamates and from heating the carbodiimide with each alcohol indicates that the carbodiimide is a possible intermediate in the atmospheric pressure degradations of the benzyl and hexamethylene carbamates at 300°. The details of the mechanism of these conversions are not yet elucidated.

The fact that the degradation of the hexamethylene polycarbamate gave 32% of the olefinic alcohol, 1-hexene-6-ol, whereas only a trace of butene was obtained from the *n*-butyl biscarbamate could be explained by the very rapid distillation of the butanol at 300° and atmospheric pressure, giving insufficient time for reaction with the polycarbodiimide.

The total evidence has shown that reactions 1, 2 and 3 are a feasible route to the degradation products (at 300° and atmospheric pressure) of the biscarbamates and the polymeric carbamate studied. However, since a polycarbodiimide actually was isolated only in the cases of the butyl and neopentyl biscarbamates, the possibility that the degradation products might arise from breakdown of the carbamate without formation of a carbodiimide cannot be totally eliminated. Fletcher, Lakin and Plant<sup>5</sup> found that carbamates of carbazole, which cannot form carbodiimides, decomposed at elevated temperatures to give the amine, carbon dioxide and an olefin. Similar products, with minor formation of carbodiimide, have been obtained by Wright<sup>11</sup> from thermal degradation of simple carbamates of the structure ArNHCOOR.

(11) G. C. Wright, Ph.D. dissertation, University of Delaware, 1958.

**Acknowledgment.**—The authors are indebted to the Armstrong Cork Co. for a fellowship in support of this investigation and to Drs. L. H. Dunlap and J. A. Parker for helpful discussions.

### Experimental

**Materials.**—Freshly distilled methylenebis-(4-phenyl isocyanate)<sup>12</sup> boiled at 182–183° at 3 mm. and had a purity of at least 99.5%, as determined by the piperidine method.<sup>13</sup> Alcohols and solvents were dried and redistilled.

**Preparation of Biscarbamates.**—The procedure of Gaylord and O'Brien<sup>14</sup> was used. The white, gelatinous product was washed with *n*-hexane, recrystallized to constant melting point from an appropriate solvent, and dried for about 12 hours at 100° and a pressure of 3 mm. The new biscarbamates and their recrystallization solvents were: I, *n*-butyl, ethanol; II, neopentyl, methanol (95%); III, benzyl, acetone. Their properties are given in Table II.

**Preparation of the Polycarbamate of Methylenebis-(4-phenyl Isocyanate) and Hexamethylene Glycol.**—The general procedure of Marvel and Johnson<sup>15</sup> was used. The diol (0.0316 mole) was dissolved in 100 ml. of an 80:20 (by volume) mixture of chlorobenzene-*o*-dichlorobenzene. Methylenebis-(4-phenyl isocyanate) (0.0315 mole) was dissolved in 100 ml. of the same solvent. The white reaction product was dissolved in dimethylformamide, the solution filtered, and the polycarbamate reprecipitated by dropwise addition of the filtrate to methanol with rapid stirring. The precipitated carbamate was pulverized in a mortar, and dried for 24 hours at room temperature and 10 mm. pressure. The pure polycarbamate IV was a white solid which formed tough fibers and films.

**Infrared spectra** of the four carbamates and their degradation residues were obtained, using a Baird Associates, Inc., infrared recording spectrophotometer, model B. The potassium bromide pellet technique was used.

All of the residues from the thermal degradation of the four carbamates showed negligible absorption at 5.9  $\mu$ , indicating loss of the carbamate carbonyl group, and poorly defined absorption in the 2.9–3.6  $\mu$  and 6.1–6.9  $\mu$  regions. The residues from degradation of methylenebis-(4-phenyl isocyanate), the *n*-butyl biscarbamate and the neopentyl biscarbamate showed a sharp absorption peak at 4.7–4.8  $\mu$ .

**Non-aqueous Titrations.**—Residues from thermal degradation of the benzyl biscarbamate and the hexamethylene polycarbamate were dissolved in nitrobenzene. Aliquots (10 ml.) were titrated potentiometrically with 0.1 *N* perchloric acid in acetic acid<sup>16</sup> for total base and for non-acetyltable base after the addition of acetic anhydride. The same titrations were performed on the residues from interaction of the polycarbodiimide with benzyl alcohol and with hexamethylene glycol.

**Gas Chromatography.**—Distillates from thermal degradation of the carbamates were analyzed with a recording Aerograph, model A-100, using helium as a carrier gas. In the quantitative analysis of the distillate from the thermal degradation of the benzyl biscarbamate the internal normalization technique<sup>17</sup> was used.

**Thermal Degradation of Carbamates.**—Samples weighing 2.5–4.5 g. were heated at 300° and 1 atmosphere under nitrogen. The train included the nitrogen tank, drying tower filled with a mixture of phosphorus pentoxide and shredded asbestos, 50-ml. distilling flask containing the carbamate, tared distillate receiver, Ascarite tube and bubble counter.

The system was flushed for 90 min. with nitrogen. A tared Ascarite tube was then inserted in the train between the distillate receiver and the original ascarite tube, the distillate receiver was partially immersed in a Dewar flask

(12) Kindly furnished by National Aniline Division of Allied Chemical and Dye Corporation.

(13) E. Dyer, H. A. Taylor, S. J. Mason and J. Samson, *THIS JOURNAL*, **71**, 4107 (1949).

(14) N. G. Gaylord and J. J. O'Brien, *Rec. trav. chim.*, **74**, 218 (1955).

(15) C. S. Marvel and J. H. Johnson, *THIS JOURNAL*, **78**, 3207 (1956).

(16) J. S. Fritz, *Anal. Chem.*, **22**, 1028 (1950).

(17) C. Phillips, "Gas Chromatography," Butterworth's Scientific Publications, London, 1950, pp. 63–64.

TABLE II  
 PROPERTIES OF CARBAMATES

Compound	Yield, %	M.p., °C.	Solv. <sup>a</sup>	Carbon, <sup>b</sup> %		Hydrogen, %		Nitrogen, <sup>c</sup> %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
I	81	119	A, B, C, D, E, F	69.31	69.03	7.59	7.46	7.03	7.03
II	48	128	A, C, D, E, F, H, I, J	70.41	70.84	8.04	8.01	6.57	6.50
III	75	198-199	C, G	74.66	75.16	5.62	5.65	6.01	5.83
IV	81	229-231 d.	K, L, M, N	80.30	80.48	4.96	5.37	13.05	13.01

<sup>a</sup> A, ethanol; B, carbon tetrachloride; C, acetone; D, ethyl acetate; E, methanol; F, dioxane; G, benzyl alcohol; H, chloroform; I, ether; J, cyclohexane; K, dimethylformamide; L, *m*-cresol; M, dimethyl sulfoxide; N, *N*-methyl-2-pyrrolidone. <sup>b</sup> Analyses for carbon and hydrogen by Geller Microanalytical Laboratories. <sup>c</sup> Analyses for nitrogen by semi-micro Kjeldahl.

containing a mixture of acetone and Dry Ice, and the nitrogen flow rate was decreased to about 25 ml./min.

The flask containing the carbamate sample then was lowered into a salt-bath, the temperature of which was maintained at  $300 \pm 5^\circ$ . In all experiments, heating was continued until degradation appeared to be complete.

**A. *n*-Butyl Biscarbamate.**—The gas which boiled from the distillate at room temperature was passed into bromine in carbon tetrachloride solution. Removal of solvent gave a trace of slightly impure 1,2-dibromobutane, semi-micro b.p.,  $163^\circ$ . The degradation distillate, after volatilization of the butene, was identified as pure *n*-butyl alcohol, b.p.  $117^\circ$  and  $n_D^{20}$  1.391. Methylenebis-(4-phenyl isocyanate) from the reduced pressure pyrolysis was identified as the benzyl biscarbamate, m.p.  $198-199^\circ$ , which did not depress the melting point of an authentic sample.

**B. Neopentyl Biscarbamate.**—The degradation distillate was pure neopentyl alcohol, b.p.  $112-114^\circ$ . The absence of other volatile compounds was shown by a negative test with bromine in carbon tetrachloride and by gas chromatography.

The solid residue from pyrolysis of neopentyl biscarbamate (or from *n*-butyl biscarbamate) was a brown, brittle solid, which showed infrared absorption at 6.1, 6.3 and 6.7  $\mu$ , with an intense, sharp peak at 4.75  $\mu$ . It was insoluble in dioxane, acetone, dimethylformamide, formic acid, acetic acid, *m*-cresol, dimethyl sulfoxide, pyridine, sodium hydroxide or hydrochloric acid. It dissolved in benzyl alcohol after lengthy refluxing and in hot concentrated nitric or sulfuric acids. Analytical data indicate that the polymer was not pure, but purification was impossible because of the insolubility of the product.

*Anal.* Calcd. for  $C_{14}H_{16}N_2$ : C, 81.53; H, 4.89; N, 13.59. Found: C, 80.48; H, 5.37; N, 13.01.

**C. Benzyl Biscarbamate.**—The degradation distillate was a mixture of toluene, benzaldehyde and benzyl alcohol, as shown by gas chromatography. Benzyl alcohol also was identified by formation of benzyl *N*-phenylcarbamate, m.p.  $78^\circ$ , which gave no depression of the melting point of an authentic sample. Benzaldehyde also was identified by formation of its 2,4-dinitrophenylhydrazone, m.p.  $237^\circ$ . The distillate from the reaction at  $300^\circ$  of benzyl alcohol and the polycarbodiimide (from the degradation of the neopentyl carbamate) was a mixture of toluene, benzaldehyde and benzyl alcohol, as shown by gas chromatography. The non-volatile residue yielded, by reduced pressure distillation, 4,4'-diaminodiphenylmethane, m.p.  $94-95^\circ$ , which

did not depress the melting point of an authentic sample. Other amines, indicated to be present by the non-aqueous titrations, were not separable, although separation could be effected with known mixtures of the above amine with the expected secondary and tertiary amines, 4,4'-bis-(benzyl-amino)-diphenylmethane and 4,4'-bis-(dibenzylamino)-diphenylmethane.

**D. Hexamethylene Polycarbamate.**—Fractional distillation of the degradation distillate gave a volatile fraction of slightly impure 1-hexene-6-ol and a residual fraction containing hexamethylene glycol. The volatile fraction was identified by comparison of its constants with those of a specimen of 1-hexene-6-ol synthesized by the method of Golmov,<sup>18</sup> b.p.  $163^\circ$  (semi-micro) and  $n_D^{20}$  1.4359, and by a mixed melting point of the 1-naphthyl carbamate, m.p.  $65^\circ$ . Hexamethylene glycol was identified by reaction with phenyl isocyanate to form the biscarbamate, m.p.  $173^\circ$ , which showed no depression in a mixed melting point with an authentic sample.

**Heating Polycarbodiimide with Alcohols.**—Samples of 1.2 to 1.6 g. of the polycarbodiimide from the neopentyl biscarbamate containing 0.006 to 0.008 mole of ( $-N=C=NC_6H_4CH_2C_6H_4-$ ) were heated at  $300^\circ$  with two equivalents of benzyl alcohol and with one equivalent of 1,6-hexanediol, respectively, using the same techniques as for the degradation of the carbamates.

**4,4'-Bis-(dibenzylamino)-diphenylmethane.**—This reference compound was obtained by heating a mixture of 10.0 g. of 4,4'-bis-(benzylamino)-diphenylmethane, prepared as by Sprinzak,<sup>19</sup> 6.7 g. of benzyl chloride and 4.2 g. of potassium hydroxide for 5 hours at a temperature of  $140^\circ$ . The crude product was washed with water, recrystallized twice from a 1:20 water-acetone mixture, and the crystals triturated with boiling ethanol to give the new diamine, m.p.  $130^\circ$ , in 62% yield.

*Anal.* Calcd. for  $C_{41}H_{38}N_2$ : C, 88.13; H, 6.86; N, 5.02. Found: C, 87.50; H, 6.90; N, 4.93.

The diamine was soluble in acetone, benzene, chlorobenzene, chloroform, benzyl alcohol and nitrobenzene and insoluble in ethanol, diethyl ether, *n*-hexane, acetic acid and 5% hydrochloric acid solution.

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(18) V. P. Golmov, *J. Gen. Chem. U.S.S.R.*, **22**, 2187 (1952).

(19) Y. Sprinzak, *This Journal*, **78**, 3207 (1956).