after recrystallization from methanol, had the m.p. 61–62°, alone or when mixed with authentic hydrazone I.

Reaction of Ethyl Pyruvate 2,6-Dimethylphenylhydrazone (I) with Zinc Chloride in the Presence of Excess Maleic Anhydride.—A mixture of 38 g. of freshly distilled I, 57 g. of powdered anhydrous zinc chloride, 240 g. of maleic anhydride and 400 ml. of nitrobenzene was beaten with a Hershberg stirrer while it was heated at 135° for 0.5 hr. Steam distillation of the reaction mixture removed the nitrobenzene and left 22 g. of a black, water-insoluble residue which was extracted with ether in a Soxhlet apparatus until only 4.9 g. of black, ether-insoluble material remained. The ether extract was shaken with 180 ml. of 10% aqueous sodium hydroxide, and when the alkaline solution was acidified, 3.29 g. of a tan, amorphous powder separated. Sublimation of this powder at 140° (1 μ) produced about 50 mg. of a pale yellow solid. A solution of this material in ether–petroleum ether deposited 10 mg. of a yellow, crystalline solid, m.p. 110–111°.

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.52; H, 6.02; N, 11.96. Found: C, 61.14; H, 6.02; N, 12.32.

Following the extraction with sodium hydroxide, the ether solution was shaken with 180 ml. of 10% aqueous hydrochloric acid and then with water. The dried (Drierite) ether solution yielded 4.5 g. of a brown powder when the ether was removed. Sublimation of this powder at 110–120° (10 μ) gave 2.2 g. of a solid, m.p. 119–131°. Recrystallization from *n*-heptane following charcoal treatment afforded 1.25 g. of pale yellow crystals, m.p. 130–135°. Saponification of this sample of II with sodium hydroxide in accordance with directions previously described gave a sample of the corresponding carboxylic acid, m.p. 198–200°. Re-esterification with ethanol containing sulfuric acid yielded a new sample of II, m.p. 136–137°. The infrared absorption spectrum showed the sample of m.p. 130–135° to be II, with very little contamination.

Infrared absorption spectra were measured by means of a Perkin–Elmer infrared spectrophotometer model 21, equipped with sodium chloride optics. The spectra of the isomeric samples of ethylpyruvate 2,5-dimethylphenylhydrazones were measured in 3% solutions in chloroform; all others were measured in 2% solutions in carbon disulfide. The legend used throughout this section: i = intense (>70% absorption), m = medium (40–70% absorption), w = weak (<40% absorption), s = shoulder (band not resolved).

Acknowledgment.—The authors are grateful to Dr. R. A. Friedel of the U. S. Bureau of Mines, Bruceton, Pa., who determined some of the infrared spectra reported in this paper.

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Condensation of Bisurethans and the Formation of New Polymers

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Bisurethans of the type $C_2H_5OC(=O)-NH-(CH_2)_n-NH-C(=O)OC_2H_5$ condense with themselves at elevated temperatures in the presence of an alkaline catalyst to yield polymers possessing urea units and dimerized and trimerized isocyanate units. When n = 3, trimethyleneurea is formed, along with the polymer. Structures have been assigned to these condensation products.

The condensations of bisurethans with bifunctional compounds, such as glycols, dimercaptans and amino-alcohols, have been the subject matter of numerous patents.[1] However, a study of the self-condensation of bisurethans had not been reported until after the present work was completed.[2] Since an extended study of the condensation of biscarbonates has been made in these Laboratories,[3] it seemed of value to investigate the analogous bisurethans.

The biscarbonates have been shown to condense to yield polycarbonates, with the elimination of diethyl carbonate, according to the reaction

$$C_2H_5OC(=O)O(CH_2)_nOC(=O)OC_2H_5 \longrightarrow (O(CH_2)_nOC(=O)O(CH_2)_nOC(=O)-)_x + (CH_2H_5)_2CO_3 \quad (1)$$

Therefore, one might expect the bisurethans to yield polyureas as

$$C_2H_5OC(=O)NH(CH_2)_nNHC(=O)OC_2H_5 \longrightarrow (N(CH_2)_nNHC(=O)NH(CH_2)_nNHC(=O)-)_x + (C_2H_5)_2CO_3 \quad (2)$$

(I → II)

Indeed, this does take place, but it is accompanied by a more predominant reaction. The purpose of this paper is to discuss the results of a study where compounds of type (I), where n = 2, 3, 4, 6 and 10, were condensed with themselves at elevated temperatures in the presence of alkaline catalysts.

Experimental

Bisurethans.—The bisurethans (N,N'-bis-carbethoxy-1,*n*-diamines) were prepared by the reaction of the appropriate diamine with ethyl chlorocarbonate in the presence of sodium hydroxide. One mole of the diamine in 250 ml. of water was added to 250 ml. of benzene. A solution of 2 moles of sodium hydroxide in 300 ml. of water was cooled to 10°. The diamine was allowed to react stepwise with 2 moles of ethyl chlorocarbonate as follows: The amine solution was stirred and kept at 10° by external cooling while one mole of ethyl chlorocarbonate was added slowly with stirring. Then 1 mole, *i.e.*, one-half of the sodium hydroxide solution, was added. Next, one-half mole of ethyl chlorocarbonate was added slowly, followed by one-half mole of sodium hydroxide. This stepwise process was continued until all of the reagents had been added. The reaction mixture was stirred for an additional hour. The white crystalline product was separated and recrystallized from ethanol. The products are listed in Table I.

(1) U. S. Patents 2,343,808, P. Schlack, March 7, 1944; 2,568,885, H. Dreyfus, Sept. 25, 1951; 2,623,867, H. Dreyfus, Dec. 30, 1952. British Patent 620,116, H. Dreyfus, Nov. 21, 1949. Belgium Patent 449,106, Zellwolle- und Kunstseide Ring G.m.b.H., Mar., 1943; 449,368, Thüringer Zellwolle A.B., Mar., 1943.

(2) E. Dyer and H. Scott, THIS JOURNAL, **79**, 672 (1957).

(3) Williams, D. D. Reynolds, Dunham and Tinker, *J. Org. Chem.*, in press.

TABLE I

PREPARATION OF BISURETHANS[a]

$$C_2H_5OC(=O)-N(R)(CH_2)_nN(R)-C(=O)OC_2H_5$$

n	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2	61.4	110	47.0	47.5	7.8	8.0	13.7	13.2
3	75	43	49.6	49.6	8.2	8.2	12.8	12.7
4	95	93	51.8	51.7	8.6	8.5	12.0	12.3
6	70	84	55.4	55.7	9.2	9.1	10.8	11.0
10	95	91	60.7	60.7	10.2	10.1	9.2	8.8
6	61	[b]	58.3	58.1	9.7	10.0	9.7	9.4

[a] R = H, except in experiment 6 where it is CH_3. [b] B.p. 138–141° (0.3 mm.).

Condensation Reactions.—The bisurethan was heated under nitrogen to 230–250° (bath temperature). A slow stream of dry nitrogen was passed through the flask. As soon as the bisurethan melted, titanium butoxide catalyst was added. Within a few minutes, a mixture of ethanol and diethyl carbonate began to distil and was collected in a Dry Ice trap.

As the reaction progressed in the cases where R = $(CH_2)_n$ with $n > 3$, the reaction products gradually became more viscous until a point was reached where they cross-linked spontaneously to fill the flask with foamed polymers. These products were infusible and insoluble. Samples for analysis were prepared by leaching in ethanol, mixing with Dry Ice and grinding to 20-mesh. By removing the viscous polymers before cross-linking began, polymers soluble in dimethylformamide were obtained.

When R = $(CH_2)_3$, some polymer was formed but the major portion of the product was trimethyleneurea.

When R = $(CH_2)_2$, the reaction product did not go through a viscous stage. Instead, it separated after a short reaction time as a finely divided, white powder which did not melt at 250°.

When an N-substituted bisurethan was heated under the conditions just described, no reaction took place and the starting material was recovered quantitatively.

Experimental details are given in Table II. Other alkaline catalysts, *e.g.*, sodium methoxide, have been used with comparable results.

TABLE II

CONDENSATION OF BISURETHANS[a]

$$C_2H_5OC(=O)-N(H)(CH_2)_nN(H)-C(=O)OC_2H_5$$

n	Distillate, g.	Molar ratio $C_2H_5OH/(C_2H_5O)_2CO$	Reaction time, min.	Remarks
2	12.7	0.95/1.0	35	White powder (11 g.) soluble in phenol
3	11.1	1.0/2.9	45	Prod. (13.5 g.) is mixt. of trimethyleneurea and poly.
4	7.0	7.3/1.0	240	Insol. foam poly. (16 g.)
6	3.4	15.0/1.0	20	Sol. in dimethylformamide, intrinsic visc. 60 phenol:40 tetrachloroethane
6	4.5	16.5/1.0	35	Insol. foam poly.
6	7.4	8.2/1.0	120	Insol. foam poly. (17 g.)
10	1.7	5.5/1.0	60	Insol. foam poly. (7.5 g.)

[a] 25.0 g. of bisurethan and 6 drops of titanium butoxide were used in all experiments except 13, in which 10 g. and 3 drops were used.

Condensation of N-Hexylurethan.—Twenty grams of N-hexylurethan was heated for 8 hr. at 250° in the presence of six drops of titanium butoxide. As with the bis compounds, the distillate was collected and analyzed. It contained ethanol and diethyl carbonate in a molar ratio of 70 to 1.

The reaction mixture was cooled overnight during which a crystalline product separated. The whole of the product was dissolved in ethyl ether and chilled. Crystalline 1,3-dihexylurea separated. It melted at 75–76° and gave no lowering of melting point when mixed with an authentic sample. Moreover, its infrared curve was identical with that of a known sample.

The oil which was obtained from the ether filtrate was fractionally distilled. The distillable portion was shown to be unreacted starting material. It had a refractive index of 1.4353 at 25°. The original N-hexylurethan had a refractive index of 1.4350 at 25°. The undistillable residue had analytical values corresponding to those of trimeric *n*-hexyl isocyanate. *Anal.* Calcd. for $(C_6H_{13}NCO)_3$: C, 66.1; H, 10.2; N, 11.0; mol. wt., 381. Found: C, 66.5; H, 10.6; N, 11.1; mol. wt., 396.

Trimerization of Hexyl Isocyanate.—*n*-Hexyl isocyanate was prepared by the reaction of phosgene with *n*-hexylamine hydrochloride. It was distilled at 162.5–164°. A 10-g. sample of the isocyanate was mixed with two drops of titanium butoxide and left at room temperature for ten days. The product was freed of volatiles up to 163° at about 1 mm.

1,3-Dihexylurea.—1,3-Dihexylurea was prepared by the reaction of equimolar quantities of *n*-hexyl isocyanate and *n*-hexylamine in ether. The product which separated was recrystallized three times from ether; m.p. 76°. *Anal.* Calcd. for $C_{13}H_{28}N_2$: C, 68.2; H, 12.2; N, 12.2. Found: C, 67.8; H, 12.3; N, 12.3.

Discussion

In order to determine the nature of the reactions which occurred and also to elucidate the structures of the reaction products, the following analytical data were obtained: (1) composition of distillate by mass spectroscopy; (2) carbon, hydrogen and nitrogen determinations; and (3) infrared curves of starting materials and final products.

Reactions Involved.—In all cases, the distillate consisted of a mixture of ethanol and diethyl carbonate. When $n = 2$, the molar quantities were about equal. When $n = 3$, the molar quantity of diethyl carbonate predominated and when $n > 3$, the molar amount of ethanol was the greater. Details are shown in Table II.

When $n > 3$, the diethyl carbonate resulted from the intermolecular reaction shown in equation 2.

When $n = 3$, the diethyl carbonate was formed predominantly by an intramolecular reaction which yielded trimethylene urea. A smaller portion of the diethyl carbonate resulted from an intermolecular reaction.

When $n = 2$, one might expect the intramolecular reaction to predominate since the product would be ethyleneurea. This five-membered ring is known to form by a reaction of diethyl carbonate and ethylenediamine. However, under the experimental conditions, no ethyleneurea was isolated from the reaction product. This indicates that the diethyl carbonate which was formed resulted from an intermolecular reaction. An alternative explanation is that it was formed by intramolecular reaction accompanied by the formation of ethyleneurea and that the ethyleneurea polymerized under the reaction condition. There is no experimental evidence for the latter possibility.

In all cases, the ethanol resulted from a reaction involving the pyrolysis of the urethan to form an isocyanate, as

$$C_2H_5OC(=O)-N(H)(CH_2)_nN(H)-C(=O)OC_2H \longrightarrow C_2H_5OC(=O)-N(H)(CH_2)_nN=C=O + C_2H_5OH \quad (3)$$

This reaction may take place on both ends of the monomer to give a diisocyanate, or it may take place on one or both ends of the polymer chains formed during the condensation. Supporting evidence for this reaction is given by Schweitzer[4] who has patented a method for the preparation of isocyanates by heating N-substituted carbamates at temperatures ranging from 135 to 500°. It is reasonable to believe that isocyanates are intermediates in the work described recently by Dyer and Scott.[2]

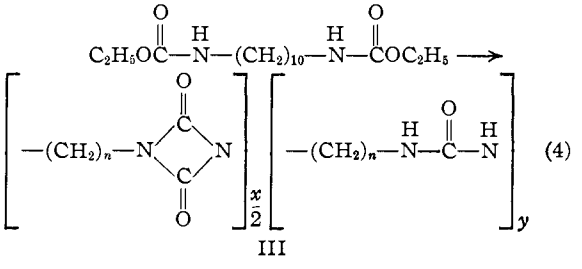
It was of interest to observe that no reactions took place when the N-substituted urethans were heated under the reaction condition used herein. Of course, this would not permit the formation of isocyanate, and evidently the active hydrogen is involved in the catalysis for the elimination of diethyl carbonate.

Assignment of Structural Units.—On the basis of the two reactions (equations 2 and 3), structural units have been assigned to the polymers. The crystalline product formed when R = $(CH_2)_3$ was shown to be trimethyleneurea by analysis for carbon, hydrogen and nitrogen and by the fact that it gave no lowering of melting point when mixed with an authentic sample.

As already mentioned, the elimination of diethyl carbonate was accompanied by the formation of urea linkages (II). Since it is well known[5] that isocyanates dimerize readily to form four-membered rings, it is reasonable to believe that isocyanate units which were formed by the elimination of ethanol reacted with each other to form polymeric chains having the dimeric structure III.

Since isocyanates trimerize, the cross-linking which occurred is explained readily by the formation of three-dimensional polymers by trimerization through the isocyanate units. Such trimerization may take place by the reaction of isocyanate end groups with preformed dimeric units.

On the basis of the above reactions, the formation and general structure of the soluble polymers are represented as



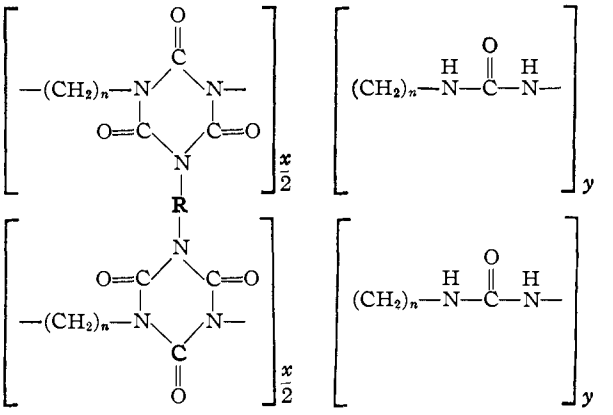
(4)

III

where x is equivalent to the number of moles of ethanol eliminated and y equals the molar quantity of diethyl carbonate formed.

The cross-linked polymers possess the following type of structure, where R is a chain which may vary from $-(CH_2)_n-$ to the length of the polymer chain formed.

Support of Postulated Structural Units.—These postulated units are supported by (1) a comparison of the theoretical and found values for carbon, hydrogen and nitrogen; (2) the isolation and determination of structures of the analogous products formed by the condensation of monofunctional urethans; and (3) infrared studies.

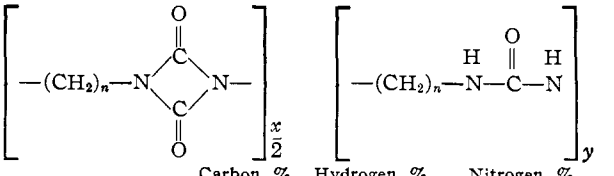


By using the assigned units, along with the found molar ratios of ethanol to diethyl carbonate (Table II), the theoretical values for carbon, hydrogen and nitrogen readily can be calculated. According to the reactions which have been indicated, the following is representative of the general type of calculations which can be made. Since the cross-linking units have compositions similar to the polymer chains, they need not be considered. When the reaction (equation 4), where n = 10, was carried out experimentally, the collected distillate was found to contain 68 weight % of ethanol and 32 weight % of diethyl carbonate. This is equivalent to a molar ratio of ethanol to diethyl carbonate of 5.5 to 1, *i.e.*, x/y = 5.5/1. Substituting these values in the structural formula and calculating the theoretical values for carbon, hydrogen and nitrogen, one obtains: Calcd.: C, 65.4; H, 9.6; N, 13.1. Found: C, 65.5; H, 9.6; N, 12.3.

In like fashion, based on the analysis of the distillates, one may calculate the theoretical values for carbon, hydrogen and nitrogen for other members of the series. Such calculations have been made and are shown, along with the found values, in Table III. Considering the fact that the materials are polymeric, all values are within the limits of experimental error. The consistently low values for the found-nitrogen values may be ex-

TABLE III

COMPARISON OF CALCULATED AND FOUND VALUES OF C, H AND N



			Carbon, %		Hydrogen, %		Nitrogen, %	
n	x	y	Calcd.	Found	Calcd.	Found	Calcd.	Found
2	0.95	1.0	42.3	42.5	5.6	5.3	29.6	28.1
2	0.94	1.0	42.3	42.0	5.6	5.3	29.6	28.9
4	7.3	1.0	52.2	52.1	6.3	7.0	21.0	18.6
6	15.0	1.0	57.2	56.7	7.5	8.3	16.9	15.3
6	16.5	1.0	57.6	56.3	7.5	7.5	16.9	15.7
6	8.2	1.0	57.4	57.2	7.7	8.3	17.2	16.2
10	5.5	1.0	65.4	65.5	9.6	9.6	13.1	12.3

(4) C. E. Schweitzer, U. S. Patent 2,409,712, Oct. 22, 1946.

(5) V. Saunders and R. Slocombe, *Chem. Revs.*, **43**, 203 (1948); C. J. Bowen, *J. Chem. Soc.*, 2931 (1955).

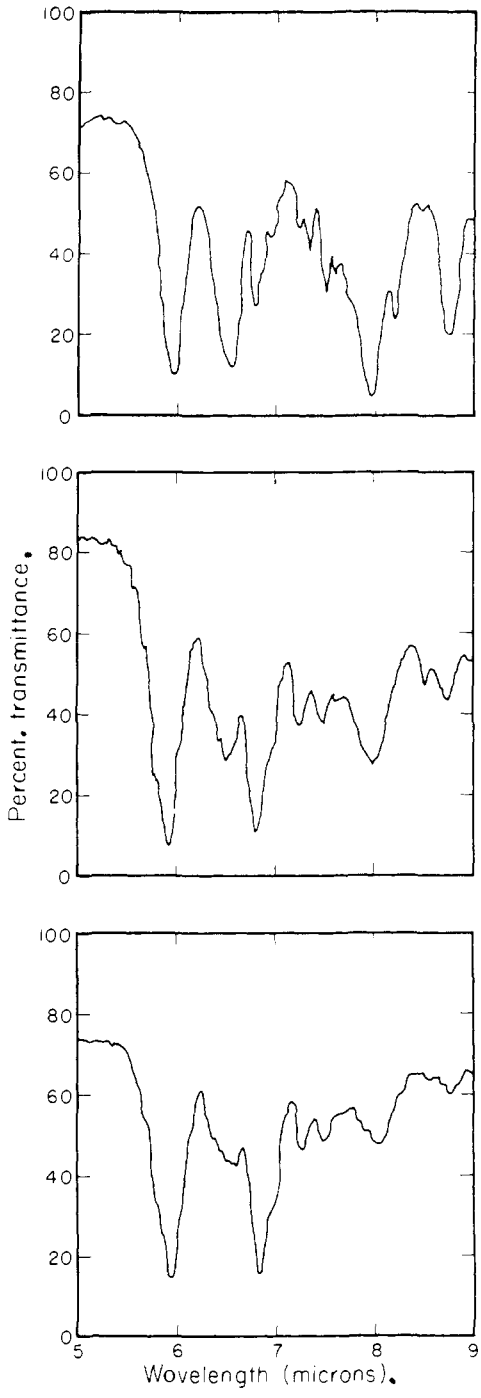
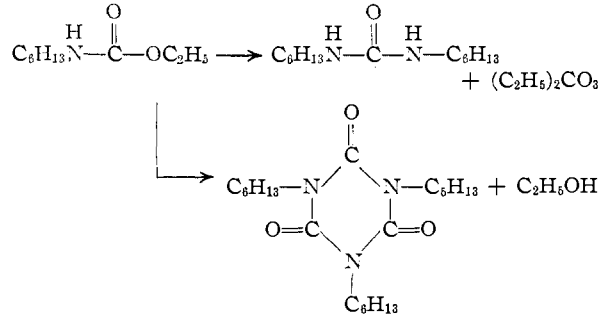


Fig. 1.—Infrared curves showing disappearance of amide II bond and O—C bond during self-condensation of N,N'-bis-(carbethoxy)-hexamethylenediamine.

plained by the urethan end-groups, evidence for which is shown in the infrared curves. These data support the postulated structures.

Analogy cannot be used as proof of structure, but it can lend supporting evidence. On this basis, N-hexylurethan was prepared and heated under conditions comparable to those for the bisurethans. The use of a monofunctional compound offers the advantage that the reaction products can be isolated and identified. Identification of the products showed that these two reactions had taken place



This corresponds exactly with the postulated reactions for polymer formation. The structure of 1,3-dihexylurea was proved by carbon, hydrogen and nitrogen analysis and by comparing its melting point and its infrared spectra with those of an authentic sample prepared by the reaction of phosgene with *n*-hexylamine and also by the reaction of *n*-hexyl isocyanate with *n*-hexylamine. The structure of the trimeric hexyl isocyanate was substantiated by carbon, hydrogen and nitrogen analysis, by molecular weight determination and by infrared analysis.

N-Ethylurethan and N-hexylurethan were prepared as reference compounds. A comparison of their infrared spectra with those of the bisurethans shows excellent agreement. Characteristic absorption bands are 5.9 μ (urethan carbonyl), 6.5 μ (amide II) and 8.0 μ (O–C bond).

On the basis of the structures which have been assigned to the polymers, one would expect four definite changes in the absorption characteristics to take place during their preparation, namely: (1) a decrease in the amide II bond and (2) a disappearance of the O–C bond absorption at approximately 8.0 μ, (3) a decrease in the strong urethan carbonyl and (4) the appearance of a urea carbonyl at 6.0. The first two changes are readily seen by comparing the curve (Fig. 1) for N,N'-bis-(carbethoxy)-hexamethylenediamine with those obtained for its condensation products. Preparation of the polymers differed only in reaction time. The disappearance of the urethan carbonyl at 5.9 is masked by the simultaneous appearance of the very strong band at 5.9 produced by the cyclic isocyanate units. The urea carbonyl is not evident, probably because of the cyclic isocyanate band. However, other supporting evidence leaves little doubt of its presence. Similar effects were observed in all cases except where $n = 2$, in which case early solidification resulted in a low degree of reaction.

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