Carbodiimides. IV.
High Polymers Containing the Carbodiimide Repeat Unit

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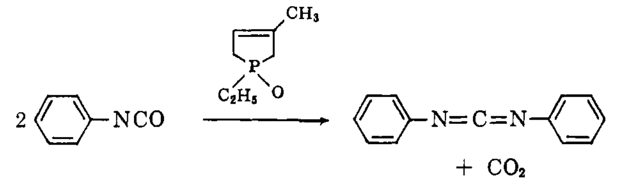
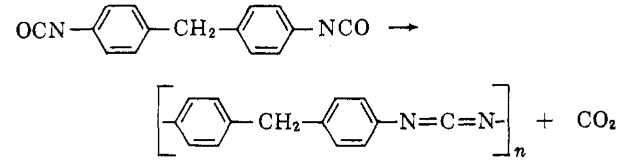
High molecular weight polymers containing the carbodiimide repeat unit have been synthesized by the catalytic action of 1-ethyl-3-methyl-3-phospholene oxide on diisocyanates in inert solvents. These polymers are tough, flexible, and can be molded into clear, tough films and other objects. Chemically they are quite inert when in the solid state. When swollen or in solution, however, they react with active hydrogen compounds to give new classes of polymers: for example, high molecular weight polyguanidines.

The number of chemical linkages which have been used to build high molecular weight condensation polymers is quite small, since there are very few condensation reactions which proceed in the near-quantitative yield necessary for achieving high molecular weight. Thus, polyesters, polyamides, polyethers, and polyurethanes are the major types now available. A recent discovery[1] of the catalytic activity of certain phospholenes and phospholene oxides, notably 1-ethyl-3-methyl-3-phospholene oxide, in converting isocyanates to carbodiimides prompted investigation of this catalyst for preparation of polymers containing carbodiimide linkages in the repeat unit.





The reaction proceeded quite well with a variety of diisocyanates, and the structurally very unusual polymeric carbodiimides were obtained, usually in quantitative yield. These polymers were unusual in that they were of quite high molecular weights, could be molded into *tough, clear, nylon-like films*, which in some cases were crystalline and orientable, and exhibited quite good tensile and electrical properties (Tables I and II).

Table I

Properties of Films of Poly(3,3′-dimethoxy-4,4′-biphenylene Carbodiimide). Film Molded at 300°, and Drawn 4.5 Times at 115°

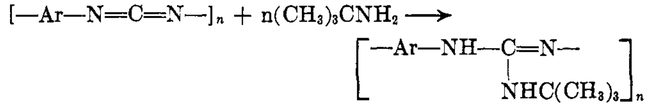
Initial modulus (p.s.i.)	1,183,500
% Elongation	6.2
Tenacity (p.s.i.)	39,800
Dielectric constant	3.4 (25°)
(10^2–10^5 c.p.s.)	3.8 (170°)
Dissipation factor	0.002–0.003 (25°)
(10^2–10^5) c.p.s.)	0.006–0.02 (170°)
Volume resistivity	>1 × 10^{14} (25°)
	2.2 × 10^{11} (200°)

Table II

Physical Test Data on Poly(toluene Carbodiimide) Film Strips

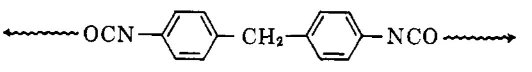
Temp. °C.	Tenacity, g.p.d.	Elongation, %	Initial modulus, g.p.d.	Denier
25	3.2	52	38	467
110	0.3	121	0.19	449

The products were identified as polymeric carbodiimides by (1) method of preparation, (2) very characteristic infrared spectrum, (3) ultimate analyses, and (4) conversion to derivatives, such as polymeric guanidines. In the absence of solvents for the polymers, the polymers (in the form of thin films) were inert to boiling acid and alkali as well as to certain organic reagents. This is very surprising in view of the high degree of reactivity of the —N=C=N— linkage[2,3] in monomeric compounds. This probably reflects a lack of penetration of the reagent, rather than a lack of reactivity of the group, since addition of amines to metastable solutions such as are described brought about the rapid conversion of the carbodiimide linkages to guanidine groups.



$$[\text{—Ar—N=C=N—}]_n + n(CH_3)_3CNH_2 \longrightarrow \left[\text{—Ar—NH—}\underset{\displaystyle NHC(CH_3)_3}{\underset{|}{C}}\text{=N—}\right]_n$$

Polymerization occurs by growth in both directions simultaneously and the products are of very high molecular weight, since a pure diisocyanate has a perfect material balance.



The end groups of the polymer chain must always be isocyanates, since no side reaction except that between isocyanate and carbodiimide can be visualized. Exchange of this type does occur, although no effect on molecular weight is possible, since such an exchange does not alter the number or nature of either the connecting links or the end groups.[4]

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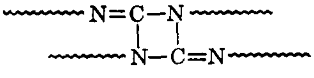
[1] T. W. Campbell, J. J. Monagle, and V. S. Foldi, *J. Am. Chem. Soc.*, **84**, 3673 (1962).

(2) Monomeric carbodiimides have a reactivity similar to that of isocyanates towards organic reagents. Among the many examples of high reactivity, one of the most striking is the ability of diphenyl carbodiimide to dehydrate aromatic sulfonic acids to the corresponding sulfonic anhydride, $ArSO_2OSO_2Ar$ [H. G. Khorana, *Can. J. Chem.*, **31**, 585 (1953)].

(3) The reactions of carbodiimides are reviewed in a paper by H. G. Khorana, *Chem. Rev.*, **53**, 145 (1953).

(4) The very high molecular weight and intractable nature of the polymers may also reflect the presence of a few cross links of the following type.



$$\begin{array}{l} \sim\sim N=C-N\sim\sim \\ \qquad\;\; | \quad\; | \\ \;\sim\sim N-C=N\sim\sim \end{array}$$

If such cross links are present, they are not present in very high concentration, since they are not detectable in the infrared. See also ref. 7

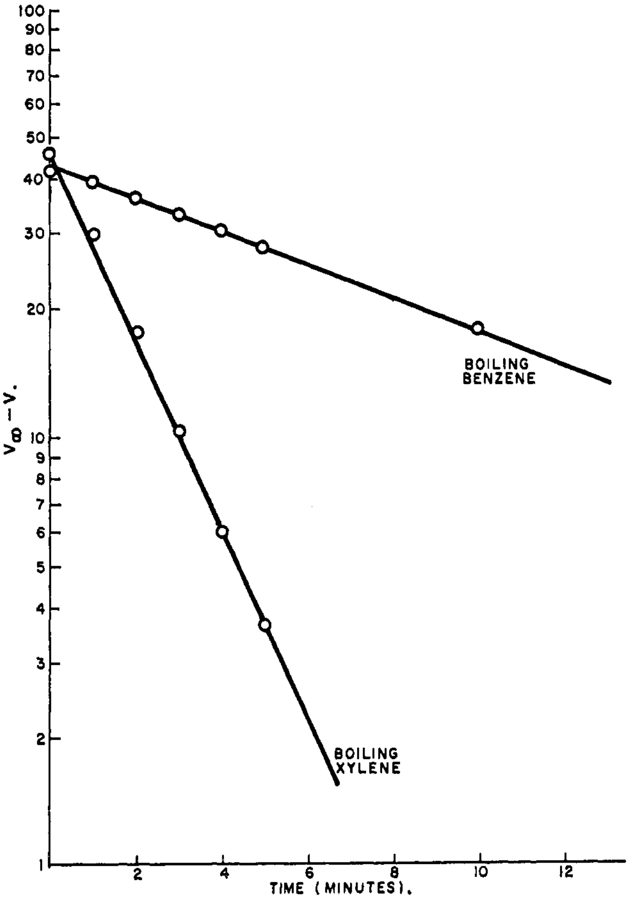
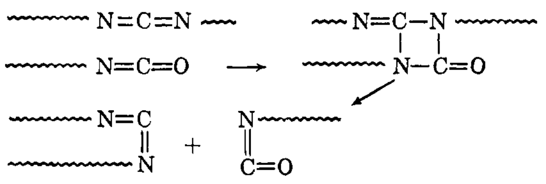
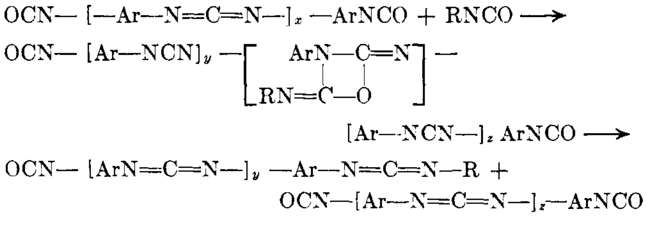


Figure 1

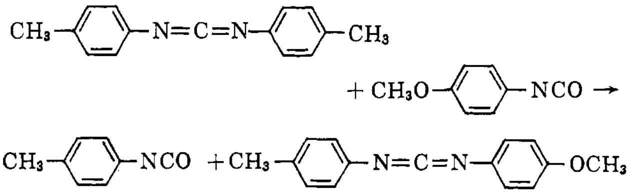


Proof that such an exchange occurs[5] can be found in two observations. Addition of a monoisocyanate to a viscous polycarbodiimide solution caused the viscosity to drop, indicating that reaction of the entering monoisocyanate was not exclusively with the end groups, but also took place randomly along the chain with cleavage at the point of attack. This could only occur if isocyanates and carbodiimides could exchange as suggested above, and as indicated in the following equation.



$$\mathrm{OCN—[—Ar—N{=}C{=}N—]_x—ArNCO + RNCO} \longrightarrow$$
$$\mathrm{OCN—[Ar—NCN]_y—}\left[\begin{array}{c}\mathrm{ArN—C{=}N} \\ \mathrm{|\quad\ \ |} \\ \mathrm{RN{=}C—O}\end{array}\right]\mathrm{—}$$
$$\mathrm{[Ar—NCN—]_z\,ArNCO} \longrightarrow$$
$$\mathrm{OCN—[ArN{=}C{=}N—]_y—Ar—N{=}C{=}N—R +}$$
$$\mathrm{OCN—[Ar—N{=}C{=}N—]_z—ArNCO}$$

Existence of this exchange reaction was confirmed by heating a mixture of ditolyl carbodiimide and *p*-methoxyphenyl isocyanate.



The production of tolyl isocyanate was shown unequivocally by gas phase chromatography.

Scope of Polymerization.—A wide range of available diisocyanates was studied and a number of polymerization variables was examined. The results are summarized in the Experimental section. From the data, the following conclusions can be drawn.

1. **Types of Monomers Which Will Polymerize.**—Since all diisocyanates examined could be polymerized, the reaction seems to be completely general. Aliphatic diisocyanates are slower than the aromatic derivatives, and the polymers obtained were in general of poorer quality. Steric hindrance in aromatic diisocyanates also slows the reaction; however, the resulting polymers are still attractively tough, although they may be slightly discolored by excessive reaction time.

2. **Nature of the Polymers.**—In general, the polymers separate from the polymerization medium as swollen lumps, which appear to be of extremely high molecular weight. In some cases, the polymer precipitates as a fine white powder with a high degree of crystallinity. With rare exceptions, it has not been possible to prepare a polymer, by the methods described in this paper, which could be redissolved in any solvent.[7] The polymers do not melt on the Dennis hot bar until about 350–400°, where they begin to leave a trail which is accompanied by decomposition. Certain of the polymers are crystalline (Fig. 3). Poly(3,3′-dimethoxy-4,4′-biphenylenecarbodiimide) showed a crystalline melting point of about 200°, although the melting point on the bar was in the 300–400° range, indicative of very high molecular weight. The polymeric carbodiimides were pressed at 250–300° to clear, usually somewhat yellowish film, again with difficulty because of high melt viscosity. These films, notably ones from poly(2,4-tolylenecarbodiimide), are characterized by their great toughness. The tensile properties of a few films decrease rapidly with increasing temperature. Thus, poly(2,4-tolylenecarbodiimide), which is quite stiff, and cold drawable at room temperature, becomes elastomeric at 100° (Table II).

3. **Stability.**—These polymers can be melt pressed in a Carver press at 250–300° repeatedly without change in properties. However, various samples maintained thirty minutes at 350° blackened and became brittle. Samples of finely divided polymer were refluxed for four hours with 10% sulfuric acid, 10% sodium hydroxide, 10% aqueous ethanol-amine, and distilled water. About 50% of the carbodiimide bonds were altered. However, poly(2,4-tolylenecarbodiimide) in film form (1-mil thickness) proved to be completely unaffected by the same series of reagents, after four hours' boiling. This would indicate that these polymers are not very permeable to the reagents used.

4. **Polymerization Conditions.**—Polymers are prepared from solutions containing 10–20% of monomer in refluxing solvent (hydrocarbon) with traces of cata-

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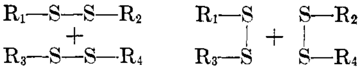
[5] Similar exchanges between polymer chains have been demonstrated for polysulfides.

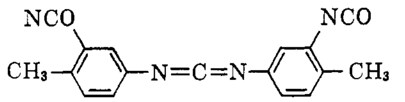


$$\begin{array}{c}\mathrm{R_1—S—S—R_2} \\ + \\ \mathrm{R_3—S—S—R_4}\end{array} \qquad \begin{array}{ccc}\mathrm{R_1—S} & & \mathrm{S—R_2} \\ | & + & | \\ \mathrm{R_3—S} & & \mathrm{S—R_4}\end{array}$$

M. D. Stern and A. V. Tobolsky, *J. Chem. Phys.*, **14**, 93 (1946); M. Mochulsky and A. V. Tobolsky, *Ind. Eng. Chem.*, **40**, 2155 (1948).

lyst. Polymerizations have been carried out at temperatures from 25° to 265°. The preferred range is 140° (boiling xylene) to 200° (boiling decahydronaphthalene). Yields of polymer were high, being best with more dilute solution, where they were essentially quantitative.[6]

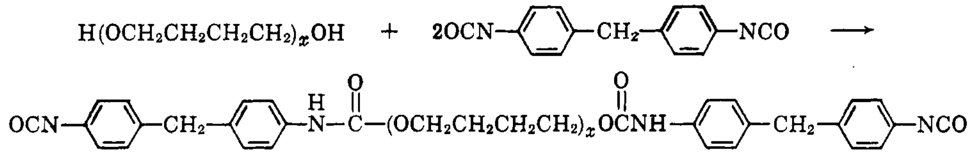
Rate of Polymerization.—It has been shown[6] that the conversion of monoisocyanates to carbodiimides is first order in isocyanate, and that the rate is affected by substituents and steric factors. Diisocyanates behave in the same fashion. The rate of evolution of carbon dioxide from some selected diisocyanates has been measured, and pseudo first-order rate constants have been calculated (Fig. 1 and Fig. 2 and Table V). In the case of toluene 2,4-diisocyanate, there are two nonequivalent isocyanate groups, so the *k* calculated from the half life is a weighted average. Examination of Fig. 2 indicates the difference in reactivity of the two isocyanate groups in toluene 2,4-diisocyanate. This difference in reactivity has made it possible to synthesize the unusual intermediate



by treating toluene 2,4-diisocyanate with catalyst under mild conditions.

Molecular Weight Control.—In most cases the polymers were insoluble in the usual polymer solvents and were of such high molecular weight as to prevent ready fabrication into films and fibers. Several methods for obviating the solubility and molecular weight problems were investigated. Promising results were obtained with all techniques.

In the first method, the carbodiimide linkages were separated by long polymeric segments. The most suitable monomer for doing this was a macro diisocyanate obtained by capping a hydroxyl-ended polytetramethylene ether of 1000 to 2000 molecular weight with a diisocyanate such as methylene bis(4-phenylisocyanate).



The macro diisocyanate was dissolved in xylene and polymerized at the boiling point. Very viscous solutions eventually were obtained. Precipitation of the polymer with alcohol gave an elastomer, which could be processed on a rubber mill to a tough rubbery slab. Elastomers of a similar type have been described in the literature[7]; however, the chain-extending step has ordinarily been the reaction of the macrodiisocyanate with water.

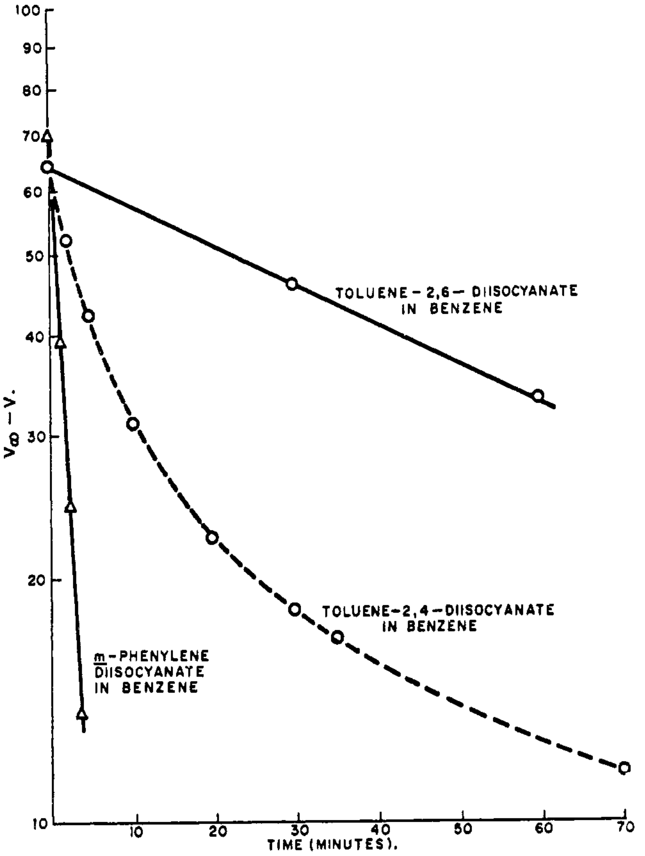
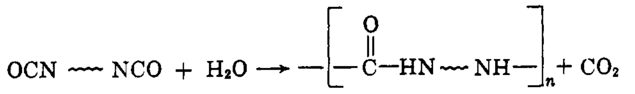
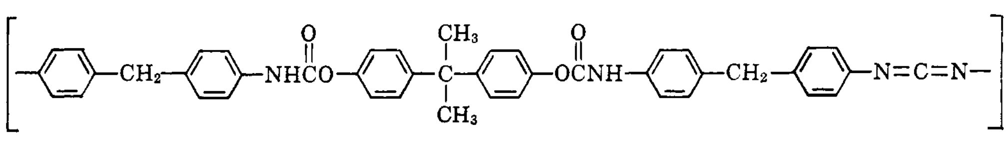


Figure 2

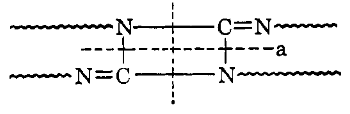


$$\mathrm{OCN} \sim \mathrm{NCO} + \mathrm{H_2O} \longrightarrow -\left[-\overset{\overset{\displaystyle O}{\|}}{C}-\mathrm{HN} \sim \mathrm{NH}-\right]_n + \mathrm{CO_2}$$

Other segments which were capped with isocyanates and polymerized included a hydroxyl-ended polyester, a polyethylene glycol, and diphenylolpropane. The latter polymer was not soluble in the usual solvents and had the following average structure.



The second method used for obtaining solutions involved the use of mixed solvents for the preparation of metastable solutions. As discussed previously, the carbodiimide groups are considered to interact strongly,[8]



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[6] A study of the kinetics and mechanism of catalytic carbodiimide formation from isocyanates has confirmed the quantitative nature of the reaction; see J. J. Monagle, T. W. Campbell, and H. F. McShane, *J. Am. Chem. Soc.*, **84**, 4288 (1962).

[7] R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Rev.*, **57**, 1 (1957). See p. 68 for references. See also E. O. Langerak, U. S. Patents 2,692,873–4, assigned to Du Pont.

[8] Interaction of carbodiimide groups in this way is substantiated by the fact that mesitylene diisocyanate (with hindrance around the functional groups) gives a soluble polymer which is lower melting and can be molded easily.

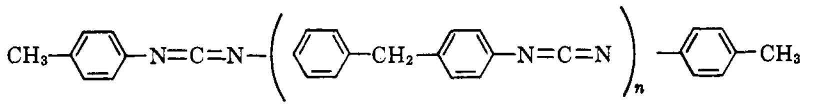
with a possible minor degree of cross linking through four-membered ring formation (p. 2071, bottom col. 2).

Reversion of the four-membered ring can take place by cleavage either *via* course a or b as indicated by the dotted lines. It was felt that, if this were so, addition of highly polar solvents to the polymerizing mixture would help maintain the polymer in solution, since they would be expected to associate with the —N=C=N— linkages, and shield them from interactions such as suggested previously.

The best solutions of carbodiimides obtained were metastable solutions prepared in mixtures of aromatic hydrocarbons with 10–20% of dimethyl sulfoxide, acetonitrile, or dimethylformamide. Most work was done with toluene 2,4-diisocyanate, methylenebis(4-phenyl isocyanate), and 3,3′-dimethoxy-4,4′-biphenylene diisocyanate as monomers. These metastable solutions could be cast to clear, colorless, tough films.

The third method used for molecular weight control was the incorporation of a chain-terminating species. The most promising agents were monomeric isocyanates, and hindered alcohols, such as isopropyl alcohol, which served as chain terminators for both ends of the growing polymer chain.

Since the rates of reaction of isocyanates vary depending upon substituents, it was necessary to take this into account. Thus when polymerizing methylenebis(4-phenyl isocyanate), a monoisocyanate such as *p*-tolyl was used.



A more reactive isocyanate would react preferentially with itself and be used up before it had performed its function. A less reactive isocyanate would react too slowly to act as an efficient terminator.

With alcohols, it was possible to obtain quite low molecular weight products, ranging from molecular weights of 600–700 on up. These products would have the following structure.

The nitrogen flow was started through one of the inlet tubes and 0.4 ml. of 3-methyl-1-ethyl-3-phospholine 1-oxide was introduced into the reaction mixture from a hypodermic syringe at room temperature. The carbon dioxide began to evolve immediately. The amount which evolved was checked periodically by the increase in weight of the Ascarite towers. After 10 min. of reaction, a white solid precipitated from solution. During further reaction, the precipitate became so great that the extra nitrogen inlet tubes were used; otherwise, trouble was encountered with partial plugging of the end of the tube by the fine precipitate.

After 1 hr., 22 g. (0.5 mole) of carbon dioxide was evolved. At this point, 100 ml. of dry chloroform was added to the reaction mixture and the reaction was allowed to continue for 10 min. more. During this time, a small amount of carbon dioxide was evolved giving a total of 23.7 g. Boron trifluoride etherate (0.8 ml.) was introduced into the reaction mixture to inactivate the catalyst, and the mixture was stirred for an additional 15 min. during which time no more carbon dioxide was evolved. The mixture was then cooled in a Dry Ice–acetone cold bath. The mixture was filtered rapidly with the aid of vacuum.

The yellow colored residue was recrystallized from *n*-hexane giving a white powdery solid. At this stage, the product (53% yield) had a m.p. 54–101 with 21.4% NCO.

In order to obtain a purer product, the white solids were recrystallized three successive times from *o*-dichlorobenzene. During each recrystallization, the solution was allowed to cool slowly to room temperature and then filtered without further cooling.

In this way, approximately 7 g. of a white crystalline product was obtained with a m.p. of 113–115° and a isocyanate content of 26.7% or a purity of 97% (theoretical NCO, 27.6%).

Anal. Calcd. for $C_{17}H_{12}N_4O_2$: C, 67.1; H, 3.95; N, 18.4; mol. wt., 304. Found: C, 67.1; H, 3.85; N, 18.8; mol. wt., 276.

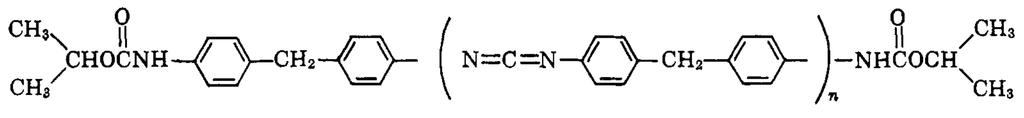
The infrared spectra of a Nujol mull showed only the bands for isocyanate and carbodiimide.

In the isolation of toluene 2,4-diisocyanate-carbodiimide, it was found necessary to pump off absorbed solvents by vacuum in order to get a dry product. Toluene 2,4-diisocyanate-carbodiimide has a great tendency to hold on to solvents, especially hydrocarbons.

Bisethylurethane.—When toluene 2,4-diisocyanate-carbodiimide was refluxed for 2 hr. with a large excess of absolute ethanol, a white crystalline compound was obtained whose melting point was 125–132°.

Anal. Calcd. for $C_{21}H_{24}N_4O_4$: C, 63.6; H, 6.1; N, 14.1. Found: C, 63.9; H, 6.0; N, 14.8.

The infrared spectra of a Nujol mull showed a peak at 3.07 μ (NH), a strong band at 4.7 μ (—N=C=N—), and a band at 5.82 μ (urethane, >C=O).



Experimental Part

The Catalyst.—Among the catalysts used, the most potent was 1-ethyl-3-methyl-3-phospholene oxide. It was used almost exclusively in our work, although occasionally the corresponding phospholene was used. These catalysts were prepared according to the method of McCormack.[9-11]

Synthesis of 4,4′-Ditolylcarbodiimide 3,3′-Diisocyanate.—Pure toluene 2,4-diisocyanate (1.0 mole) was added to 400 ml. of petroleum ether in a 1-l., seven-neck, round-bottom flask fitted with a stirrer, thermometer, four sintered glass nitrogen inlet (whose outlets were below the surface of the mixture) tubes and a spiral type condenser. The top of the condenser was connected to a Dry Ice–acetone cold trap which in turn was connected to a series of Ascarite towers set on a balance enclosed in a box with a movable plastic front.

Polymerization of 2,4-Toluene Diisocyanate.—2,4-Toluene diisocyanate was distilled through a spinning band column. After a small forecut, distillation proceeded smoothly at 81° (1.3 mm.). Polymerization of a 10% solution in boiling decahydronaphthalene was carried out with catalytic quantities of 1-ethyl-3-methyl-3-phospholene oxide. The reaction was complete in less than an hour, and the polymer was obtained in small fluffy particles very reminiscent of puffed cereal in appearance and texture. These little particles were white and gave very tough, clear, nearly colorless film when pressed at 275°. Strips of this film could be cold drawn; however, the film strips relaxed in boiling water and exhibited no crystallinity and extremely low X-ray orientation.

Anal. Calcd. for $(C_8H_6N_2)_x$: C, 73.8; H, 4.61; N, 21.4. Found: C, 73.4, 73.5; H, 4.4, 4.2; N, 21.0, 21.0.

Polymerization of Methylenebis(4-phenyl Isocyanate).—In a three-neck, 500-ml. flask equipped with stirrer, condenser, and nitrogen inlet was placed 150 ml. of xylene, 20 g. of diisocyanate, and 0.03 g. of 1-ethyl-3-methyl-3-phospholene, and the mixture was heated to reflux. First the solution became milky, then a second liquid phase began to separate. This liquid phase became

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[9] W. McCormack, U. S. Patents 2,663,736 to 2,663,739, assigned to Du Pont.

[10] Other catalysts have been studied. See J. Monagle, in press.

[11] The P-phenyl derivative is also effective. See W. McCormack, *Org. Syn.*, in press.

more and more viscous and eventually yielded high molecular weight fibrous material. The fibrous nature of the product resulted from the shearing action of the stirrer blade on the rapidly thickening prepolymer which separated initially. After the polymer had been separated and air dried, these short filaments could be separated manually from the bulk of the polymer and could be cold drawn. The drawn filaments were slightly cream colored and quite tough. Physical test data[12] were obtained on various of these filaments. The average values for T/E/M were 3.9/20/35 with a filament denier ranging from 51 to 630. It should be noted that these values are minimum values since the shape of these filaments was nonuniform, being rather that of a highly elongated, truncated cone. X-ray examination of the boiled fibers showed approximately 30% lateral crystallinity, and 5% longitudinal crystallinity, coupled with a high degree of orientation (Fig. 3).

Anal. Calcd. for $(C_{14}H_{10}N_2)_x$: C, 81.52; H, 4.89; N, 13.6. Found: C, 81.71, 81.86; H, 4.86, 5.04; N, 13.0, 13.2.

Preparation of Poly(3,3′-dimethoxy-4,4′-biphenylenecarbodiimide).—Ten grams of diisocyanate was dissolved in 100 ml. of hot xylene. The solution was filtered free of a small amount of undissolved foreign matter and polymerized with 0.04 g. of 1-ethyl-3-methyl-3-phospholene oxide in a three-necked flask with refluxing and stirring. After 5 hr. the white, finely divided polymer was filtered, washed with benzene, and dried. The yield was 8.5 g. It had a high X-ray crystallinity. It could be melt-pressed at 250° to a film with a slight yellow color. The film, cut in strips, could be stretched 3–4 times at 160°. The film exhibited typical necking phenomena on stretching, characteristic of high polymers such as nylon 6–6, polyethylene, etc., and showed strong birefringence when examined with a polarizing microscope. The birefringence disappeared at about 190°. X-ray examination of the drawn polymeric material indicated that the product was crystalline with good longitudinal order and a fairly high degree of orientation.

Anal. Calcd. for $C_{15}H_{12}N_2O_2$: C, 71.4; H, 4.76; N, 11.1. Found: C, 71.0, 70.6; H, 4.6, 4.6; N, 10.7, 10.8.

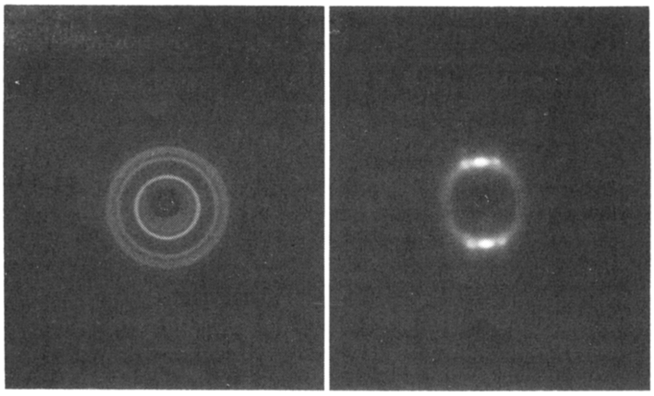
Polymerization of 3,3′-Dimethyl-4,4′-biphenylene Diisocyanate.—A sample of this diisocyanate weighing 20 g. was dissolved in 200 ml. of hot xylene. The solution was filtered free of insoluble matter and was polymerized with 1 drop of 1-ethyl-3-methyl-3-phospholene oxide at the boiling point of xylene. Carbon dioxide was evolved rapidly. The mixture was allowed to stir and reflux overnight. Next day the polymer had precipitated and had been sheared by the reaction of the stirrer blade to short filaments which were quite tough. Film could be pressed from the polymer at 250–275° and held at that temperature for 0.5 hr. without signs of decomposition. Short hand-drawn fibrils were quite tough but showed essentially no crystallinity and only a modest degree of orientation.

Polymerization of Propane-2,2-bis(4-phenyl Isocyanate).—A solution of 10 g. of diisocyanate in 75 ml. of hot xylene was filtered free of a trace of insoluble matter. One drop of the preferred phospholene oxide catalyst was then added and the mixture was allowed to polymerize in the usual way at the reflux temperature. Contrary to the usual polycarbodiimide formation, the solution thickened without immediate precipitation of the polymer. The viscous solution was poured into a hypodermic syringe and wet spun into hexane. The fibers so obtained could be cold-drawn and showed moderate toughness. This polymer showed the best as-prepared solubility in pure xylene of any polycarbodiimide studied.

In another experiment, the same diisocyanate was polymerized in the presence of a chain terminator. A mixture of 7.5 g. of isocyanate, 45 ml. of toluene, 5 ml. of tetrachloroethane, 0.04 g. of *p*-chlorophenyl isocyanate, and 1 drop of catalyst was refluxed. After about 3 hr., the mixture became quite viscous and some polymer precipitated around the edges. Contrary to any previous observation, this precipitated polymer returned to solution on stirring. A portion of this viscous solution was cast to a tough film. The remainder of the polymer was precipitated with acetone and could be pressed into clear film at 200°. The precipitated polymer was dried in a high vacuum at 100° for 3 hr. before pressing.

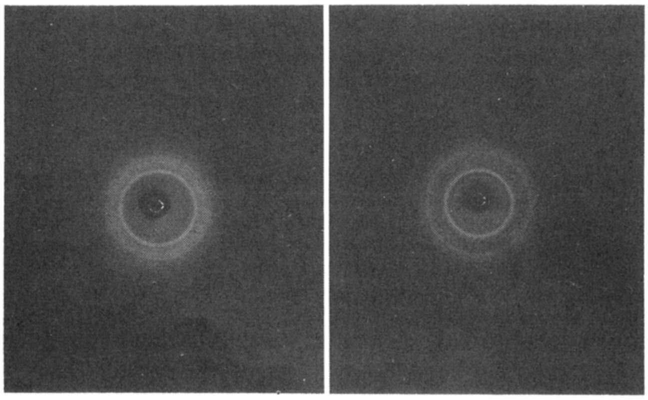
Polymerization of *m*-Phenylene Diisocyanate.—Eight grams of monomer was dissolved in 75 ml. of xylene, and the mixture was heated to reflux, and 0.03 g. of the preferred phospholene oxide catalyst was added. The polymerization was carried out at the boiling point for about 3 hr. The resulting polymer, which was obtained in the form of very tough lumps, was washed with benzene and dried in a vacuum. The yield was about 6.5 g., with considerable loss occurring because of the tendency of the polymer to adhere to the glass flask. The polymer was amorphous and could be pressed at about 250° into clear, colorless, very tough film. A combustion analysis of the dried polymer showed the following results.

Anal. Calcd. for $(C_7H_4N_2)_x$: C, 72.4; H, 3.45; N, 24.1. Found: C, 72.2, 72.4; H, 3.4, 3.5; N, 23.1, 23.3.



Poly(1,5-naphthalene-
carbodiimide)
as formed

Poly[methylene-
bis(*p*-phenylene)-
carbodiimide]
stretched filaments



Poly(4,4′-biphenylene-
carbodiimide)
as formed

Poly(3,3′-dimethoxy-
4,4′-biphenylene-
carbodiimide)
as formed

Fig. 3.—X-ray patterns of polycarbodiimides.

Polymerization of 4,4′-Biphenylene Diisocyanate.—A 15-g. sample of the diisocyanate was dissolved in 150 ml. of xylene, and the mixture was heated to the boiling point. The preferred phospholene oxide catalyst (0.03 g.) was added, and the mixture was refluxed for 4 hr. The polymer was isolated as a finite white powder by filtration. It had a high degree of crystallinity as formed (Fig. 3) and a crystalline melting point above 300°. It could be molded to very stiff, tough film at temperatures over 300°.

Polymerization of Mesitylene Diisocyanate.—Fifteen grams of mesitylene diisocyanate was dissolved in 150 ml. of xylene, and 0.15 g. of the preferred phospholene oxide catalyst was added to the refluxing solution. After 24 hr., a moderately viscous solution resulted from which could be obtained a tough film by evaporation of the solvent. The polymer was precipitated by the addition of isopropyl alcohol and then was dried. The polymer had a melting point of 130°. A clear, tough film was easily melt pressed at 100°. This film could be stretched 8 times at 100°. X-Ray examination of the stretched polymer showed a low degree of crystallinity and orientation.

Polymerization of Hexamethylene Diisocyanate.—Fifteen grams of the diisocyanate was mixed with 25 ml. of xylene and held at 140° in the presence of 0.15 g. of the phospholene oxide catalyst for 6 hr. The polymer precipitated as a lump of gel

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[12] R. G. Beaman and F. B. Cramer, *J. Polymer Sci.*, **21**, 223 (1956).

which was cut up in a Waring Blendor in acetone. The resulting polymer could be pressed to rather weak film. The infrared spectrum of the polymer films showed conclusively that the material contained no isocyanate and the calculated amount of carbodiimide linkages.

Polymerization of a Triisocyanate.—2,4,4′-Triisocyanatodiphenyl ether was prepared according to the literature.[13] A solution of 10 g. of this triisocyanate in 68 ml. of xylene was treated with 0.03 g. of 1-ethyl-3-methyl-3-phospholene-1-oxide. After about 2 hr. at the reflux temperature, the hard cream-colored solid which had precipitated was filtered and extracted with benzene. The polymeric product was completely infusible and insoluble and could not be molded to a film. These properties are those of a typical three-dimensional polymer.

Preparation of an Elastomer Based on a Polyester Glycol.—A polyester with hydroxyl end groups and a molecular weight of about 2000 was prepared by heating sebacic acid with excess 2,2-diethylpropanediol. Water and excess glycol were removed at reduced pressure. A mixture of 23 g. of this polyester was heated for 1.5 hr. on a steam bath with 5.8 g. of methylenebis(4-phenyl isocyanate). The reaction mixture was then diluted with 100 ml. of xylene containing 0.1 g. of the catalyst. After about 1 hr. at reflux, a very viscous solution resulted which could be converted into a sheet of tough elastomeric material similar to that in the following experiment.

Preparation of an Elastomer Based on Polytetramethylene Ether Glycol.—A mixture of 33.7 g. of polytetramethylene ether glycol having an average molecular weight of about 2000 was heated on a steam bath for 90 min. with 8.7 g. of methylenebis-(*p*-phenyl isocyanate). The reaction product was diluted with 200 ml. of xylene containing 0.1 g. of the preferred phospholene oxide catalyst. The mixture was refluxed for 1 hr. to give a very viscous solution. This viscous solution was cast onto a glass plate, and the solvent was evaporated. A clear, very tough, snappy sheet of an elastomer was obtained. This material could be elongated 600% and showed good recovery.

In a similar experiment, 145 g. of polytetramethylene ether glycol with an average molecular weight of 3400 was heated on the steam bath for 2 hr. with 171 g. of 2,4-toluene diisocyanate. The cooled product was transferred to a Werner–Pfleiderer mixer, where the mass was blended at 80–100° for 4 hr. with 0.8 g. of the phospholene oxide catalyst. The tough, rubbery mass which resulted was milled on a rubber roll mill to give a rough sheet, a portion of which was molded under pressure for 1 hr. at 232°. This slab of elastomer had the following properties at room temperature: tensile strength, 2400 p.s.i.; elongation, 500%; modulus at 300% elongation, 486 p.s.i.

Preparation of an Elastomer from Polyethylene Glycol.—A mixture of 50 g. of polyethylene glycol of a molecular weight about 1000 and 26.1 g. of toluene 2,4-diisocyanate was heated at 90–95° for about 1 hr. To the polyether now bearing isocyanate end groups was added 0.1 g. of the preferred phospholene oxide catalyst. The mixture was mixed in a Werner–Pfleiderer mixer at 70–100° for 2 hr. During this period, carbon dioxide was evolved, and the mass became quite thick. After 2 hr., the mixture was milled on a rubber mold for 1 hr. at 70° and then for 0.5 hr. at 100°. The resulting product was molded under pressure at 120° to give a clear slab of synthetic elastomer which had good snap and elasticity.

Polymerization of the Reaction Product from 4,4′-Isopropylidenediphenol and Methylenebis(4-phenyl Isocyanate).—A mixture of 11.4 g. of 4,4′-isopropylidenediphenol and 25 g. of methylene bis(4-phenyl isocyanate) was refluxed with 85 ml. of xylene for 2 hr. to yield a diurethane with terminal isocyanate groups. Three-tenths gram of the preferred phospholene oxide catalyst was then added and refluxing was continued for about 30 min. Polymerization occurred rapidly with the production of an insoluble, very tough polymer.

Anal. Calcd. for $(C_{44}H_{36}N_4O_4)_x$: C, 77.2; H, 5.3; N, 8.2. Found: C, 77.5; H, 5.2; N, 7.6.

Polymerization of Toluene Diisocyanate in Mixtures Containing Dimethyl Sulfoxide.—A mixture of 40 ml. of xylene and 10 ml. of dimethyl sulfoxide was heated to boiling and 10 ml. of toluene diisocyanate was added, followed by 1 drop of the preferred phospholene oxide catalyst. Evolution of carbon dioxide was brisk. After about 1.5 hr., the polymer was still in solution. Continued heating eventually caused the solution to gel. The polymer was isolated in a Waring Blendor, washed repeatedly with acetone, and pressed to film. This film stuck to a Dennis hot bar at 340° and could be pulled out to long filaments.

TABLE III

EQUIVALENTS N=C=N PER MOLE FOR POLYCARBODIIMIDES DERIVED FROM TOLUENE 2,4-DIISOCYANATE

Alcohol used	Total wt. CO_2, g.	Mol. wt. calcd. from CO_2 data	Equiv. N=C=N/mole
Ethanol	7.3	902	4.89
Ethanol	6.7	670	3.11
Isopropyl alcohol	7.0	794	3.85
Isopropyl alcohol	7.8	1334	8.00
Benzyl alcohol	6.9	855	3.58
Ethanol	8.2	2114	14.22
Ethanol	7.3	1332	4.87[a]

[a] Polycarbodiimide derived from methylenebis(4-phenyl isocyanate).

TABLE IV

COMPARISON OF MOLECULAR WEIGHT FOR STABILIZED POLYCARBODIIMIDES USING TITRATION DATA AND CO_2 DATA

Diisocyanate used	Alcohol used	Total wt., CO_2, g.	Mol. wt. calcd. from CO_2 data	Mol. wt. from titration data
2,4–TDI[a]	Ethanol	6.7	670	664
2,4–TDI	Isopropyl alcohol	7.0	794	803
MDI[b]	Ethanol	7.3	1332	3700
2,6–TDI[c]	Ethanol	6.6	642	1176
MDI	Ethanol	8.1	2752	2771

[a] Toluene 2,4-diisocyanate. [b] Methylenebis(4-phenyl isocyanate). [c] Toluene 2,6-diisocyanate.

In another experiment, polymerization was carried out in a mixture of 45 ml. of xylene and 5 ml. of dimethyl sulfoxide. Again, the mixture became quite viscous but the polymer did not precipitate out of solution. The solution was cast after about 1.5 hr. to a film which was dried at 110° for 3 hr. in a forced draft oven. The film was quite tough and stiff. Strips of this film could be drawn 5 times at 100°. However, the film strips could not be heat-set. The film strips proved to be elastomeric above 110°.

Use of Phenyl Isocyanate as a Chain Terminator.—Three identical polymerizing mixtures were prepared by mixing 47 ml. of xylene, 3 ml. of dimethyl sulfoxide, 10 ml. of toluene diisocyanate, and 1 drop of catalyst at the boiling point. To one was added 0.1 g. of phenyl isocyanate, to the second 0.2 g., and to the third 0.5 g. Qualitatively, the rate at which the solutions thickened decreases with increasing phenyl isocyanate. When an appropriate viscosity was reached, each solution was cast on a plate and dried. Qualitatively, the toughness decreased with increasing phenyl isocyanate content.

Polymerization of 2,4-Toluene Diisocyanate in the Presence of *p*-Chlorophenyl Isocyanate.—A stock solution of *p*-chlorophenyl isocyanate was prepared by diluting 1.0 g. of isocyanate to 50 ml. with xylene. Two polymerizations then were carried out. In the first, 90 ml. of xylene, 10 ml. of dimethyl sulfoxide, 10 ml. of toluene diisocyanate, and 1 drop of the phospholene oxide catalyst were mixed and refluxed until the mixture began to get viscous. At this point, 5 ml (0.1 g.) of the stock solution (0.1 g. *p*-chlorophenyl isocyanate) was added. The viscosity of the solution dropped rapidly, indicating that depolymerization was taking place. In the second experiment, the *p*-chlorophenyl isocyanate (0.18 g.) was added before the catalyst. Polymerization of this mixture gave a solution which attained only a moderate viscosity. The polymer was precipitated with acetone and converted into a tough film at 250°. The precipitated, washed, polymer contained 0.4% by weight of chlorine, indicating that all of the capping agent had been incorporated.

Preparation of the Polycarbodiimide Derived from Toluene 2,4-Diisocyanate and Chain Terminated with Ethanol.—A 500-ml., four-necked, round-bottom flask was fitted with a stirrer, thermometer, a sintered glass tipped nitrogen inlet tube, and a spiral type condenser which was connected at the top to a Dry

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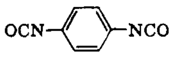
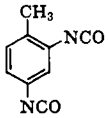
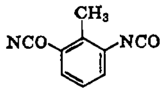
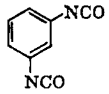
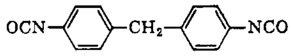
[13] Werth and Krahler, U. S. Patents 2,765,341 and 2,786,864, to Du Pont.

TABLE V

EVOLUTION OF CO_2 FROM SELECTED DIISOCYANATES IN AN OPEN SYSTEM CALCULATION OF PSEUDO FIRST-ORDER CONSTANTS

Diisocyanate	$t_{1/2}$ (80°), sec.	$t_{1/2}$ (110°), sec.	$t_{1/2}$ (140°), sec.	k (80°)	k (110°)	k (140°)
	204	—	—	3.4×10^{-3}	—	—
	570	168	—	1.2×10^{-3}	4.1×10^{-3}	—
	4080	—	552	1.7×10^{-4}	—	1.3×10^{-3}
	150	65	—	4.6×10^{-3}	9.4×10^{-2}	—
	480	—	84	1.4×10^{-3}	—	8.3×10^{-3}

Ice–acetone cold trap and then to an Ascarite tower fitted on a balance inside a box containing a movable plastic front panel. To the flask was added 34.8 g. of toluene 2,4-diisocyanate (0.2 mole) and 200 ml. of dry benzene. This mixture was heated in an oil bath to 50 ± 1° under a stream of dry nitrogen bubbling through the solution. To the heated mixture was added 0.2 ml. of 3-methyl-1-ethyl-3-phospholene 1-oxide from a calibrated hypodermic syringe.

Carbon dioxide evolution measurements were taken periodically by the increase in weight of the Ascarite tower. During 37 min., 6.0 g. (0.136 mole) of carbon dioxide had evolved; 12 ml. (0.2 mole) of absolute ethanol was introduced into the reaction mixture. During the next 23 min., a total of 6.7 g. (0.152 mole) of carbon dioxide was measured. The reaction mixture was then heated for an additional 45 min. during which time no more carbon dioxide had evolved.

The benzene and excess alcohol were distilled from the reaction mixture using high vacuum and a bath temperature of 40–50°.

The product was a light yellow solid which was soluble in chloroform, benzene, and tetrahydrofuran. The infrared spectra of an evaporated film from chloroform solution showed an —NH band at 3.02 μ, an —N=C=N— band at 4.70 μ, and a band at 5.77 μ for the urethane, $>$C=O. All other urethane-terminated polycarbodiimides were prepared in a similar fashion.

The equivalents of carbodiimide groups per mole for a number of polycarbodiimides derived from toluene 2,4-diisocyanates are given in Table III.

Another series of polymers was prepared in similar manner, and the molecular weights checked by a titration method. This method consists of the reaction of excess ethylamine with the carbodiimide, elimination of the excess amine, and titration of the guanidine with 0.1 N hydrochloric acid. This procedure was found to be applicable to stabilize polycarbodiimides as well as to the simple compounds.

The per cent —N=C=N— present in the molecule is calculated as follows

$$\% \text{ N=C=N} = \frac{\text{ml. HCl} \times N \text{ of HCl} \times 4.0}{\text{weight of sample}}$$

where 4.0 is the equivalent weight of N=C=N × 100/1000. The data are shown in Table IV.

Hydrolytic Stability of Polycarbodiimides.—Both poly(3,3-dimethoxy-4,4-biphenylenecarbodiimide) and poly(4,4-biphenylenecarbodiimide) were boiled as fine powders with 10% sulfuric acid, 10% sodium hydroxide, distilled water, and 10% aqueous aminoethanol. After 24 hr. approximately half of the carbodiimide bonds had been altered, as shown by infrared measurements. These figures could not be obtained accurately since potassium bromide pellet formation for infrared analyses was poor.

In another experiment, five samples of poly(2,4-toluenecarbodiimide) film of 1-mil thickness were prepared. These samples were boiled with, respectively, 10% sulfuric acid, 3 N sodium hydroxide, water, and 10% ethanolamine. The fifth sample was retained as a control. No change could be detected in the spectra of the various film samples indicating that no chemical reaction had taken place between the polymer and the hydrolyzing medium.

Infrared Study of Carbodiimide Formation.—The infrared spectrum of a polymerizing mixture of 50 g. of methylenebis(4-phenyl isocyanate) in 200 ml. of boiling xylene was taken several times during the polymerization. The appearance of the carbodiimide band was matched quite closely by the disappearance of the isocyanate band. After about half an hour, the isocyanate band intensity had dropped to about one-half of its original intensity, and the carbodiimide band had built up to about one-half of its final intensity. After 3 hr., no isocyanate could be detected, only carbodiimide with a band at about 4.76 μ.[14] The intensity of the band was such that within the limits of accuracy of the infrared measurements, all of the isocyanate could be accounted for as carbodiimide.

Reaction of *p*-Methoxyphenyl Isocyanate with Ditolylcarbodiimide.—A mixture of approximately equal weights of ditolylcarbodiimide and *p*-methoxyphenyl isocyanate and a trace of phospholene oxide catalyst was heated at 150° for 5 min. and then swept out with a stream of argon gas. The effluent gases were run through a gas chromatographic column which gave a clear, well defined band indicative of the presence of substantial quantities of tolyl isocyanate.

Kinetic Measurements.—Rates of evolution of carbon dioxide were measured exactly as in paper II of this series.[6] Data are shown in Fig. 1 and 2 and Table V.

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[14] (a) G. D. Meakins and R. J. Moss, *J. Chem. Soc.*, 993 (1957); (b) H. G. Khorana, unpublished work quoted in ref. 3.