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Carbodiimides. I. Conversion of Isocyanates to Carbodiimides with Phospholine Oxide Catalyst

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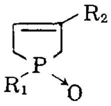
Aromatic and aliphatic isocyanates are converted in high yield to carbodiimides under mild conditions using a phospholene oxide catalyst.

Carbodiimides as a class of compounds have not been studied extensively, probably because of the rather involved methods of synthesis and the tendency of the compounds to polymerize on standing. Methods of preparation used have included desulfurization of thioureas by metal oxides[2a,b] by sodium hypochlorite,[3] or by ethyl chloroformate in the presence of a tertiary amine[4]; halogenation of ureas and thioureas followed by dehydrohalogenation of the N,N′-disubstituted carbamic chloride,[5] and by dehydration of disubstituted ureas using *p*-toluenesulfonyl chloride and pyridine.[6] Khorana has reviewed the early methods of synthesis[7]; the processes are in general multi-step with, in many cases, difficult purification procedures.

It has now been found that isocyanates can be converted to carbodiimides in high yields under mild conditions using a phospholene oxide catalyst[8] (I) according to the equation

$$2\mathrm{RNCO} \longrightarrow \mathrm{RN{=}C{=}NR} + \mathrm{CO_2} \qquad (1)$$

The most active catalyst used was 3-methyl-1-ethyl-3-phospholene-1-oxide. The corresponding phenyl derivative



a, $R_1 = C_2H_5$; $R_2 = CH_3$
b, $R_1 = C_6H_5$; $R_2 = CH_3$

Ib was also used and, although somewhat less reactive, has the advantage of being more readily accessible.[9]

Experimentally, the carbodiimides are prepared by treating the isocyanate, either in bulk or in solution, with approximately 0.1% by weight of the catalyst at room temperature or slightly above. Results with some representative isocyanates are shown in Table I, which includes comparative yields obtained by other methods of preparation. The yields, in most cases, deviate from 100% only because of losses in handling or traces of impurities in the isocyanates. The quantitative nature of the reaction is indicated by the fact that high molecular weight condensation polymers can be produced from diisocyanates.[10] If the reaction were not quantitative, chain termination would occur with production of low polymers.

TABLE I

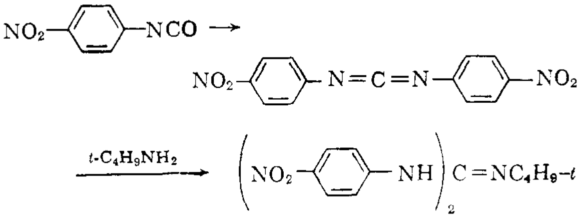
$$2\mathrm{RNCO} \longrightarrow \mathrm{RNCNR} + \mathrm{CO_2}$$

R	Yield, %	Yield,[a] lit., %	Calculated, % C	Calculated, % H	Calculated, % N	Found, % C	Found, % H	Found, % N
C_6H_5	94	53[1]	80.4	5.2	14.4	80.5	5.3	14.4
o-$CH_3C_6H_4$	87		81.0	6.3	12.7	81.3	6.3	12.6
m-$CH_3C_6H_4$	98	81[1]	81.0	6.3	12.7	80.7	6.3	12.4
p-$CH_3C_6H_4$	88	96[1]	81.0	6.3	12.7	80.8	6.2	12.4
o-$CH_3OC_6H_4$	92		70.8	5.5	..	70.8	5.8	..
p-$CH_3OC_6H_4$	99	81[1]	...	...	11.1	..	..	11.1
m-ClC_6H_4	99	80[1]	59.2	3.0	..	59.3	3.1	..
p-ClC_6H_4	91	83[1]	59.2	3.0	..	59.3	3.1	..
o-$NO_2C_6H_4$	95	..	54.9	2.8	..	54.8	3.0	..
m-$NO_2C_6H_4$	91	30[1]	54.9	2.8	..	54.7	2.9	..
p-$NO_2C_6H_4$	52	..	54.9	2.8	19.7	54.8	2.9	19.9
α-$C_{10}H_7$	99	50[8]	..	..	9.5	..	..	9.8
n-C_4H_9	60	90[7]	..	..	18.2	..	..	18.0
2-C_8H_7	89	..	..	..	..	..	..	..

[a] Yields based on final step of conventional synthesis, *i.e.*, oxidation of thiourea to carbodiimide.

The structure of the isocyanate has a strong influence on the ease of formation of the carbodiimide. With aromatic isocyanates, electron-withdrawing groups increase the rate of reaction markedly. For example, molten *p*-nitrophenyl isocyanate at 60° reacted almost explosively. Conversely, electron-donating groups decrease the reaction rate with the most pronounced effect being found in the *o*-substituted derivatives.

The carbodiimides so produced may advantageously be used in solution without isolation, particularly highly reactive species. Thus, for example, *p*-nitrophenyl isocyanate was converted to bis-(*p*-nitrophenyl)-*t*-butylguanidine in excellent over-all yield without isolation of the intermediate carbodiimide.



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(1) To whom inquiries should be addressed.

(2) (a) S. Hunig, H. Lehmann and G. Grinner, *Ann.*, **579**, 77 (1953); (b) E. Schmidt and F. Moosmuller, *ibid.*, **597**, 235 (1955).

(3) E. Schmidt, M. Seefelder, R. G. Jennen, W. Striewsky and H. V. Martius, *ibid.*, **571**, 83 (1951).

(4) R. F. Coles and H. A. Levine, U. S. Patent 2,942,025 (1960); *C. A.*, **54**, 24464 (1960).

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(6) G. Amiard and R. Heymes, *Bull. soc. chim. France*, 1360 (1956).

(7) A. G. Khorana, *Chem. Revs.*, **53**, 145 (1953).

(8) W. B. McCormack, U. S. Patent 2,663,737; *C. A.*, **49**, 7601p (1955).

(9) W. B. McCormack, *Org. Syntheses*, in press.

(10) T. W. Campbell, *J. Am. Chem. Soc.*, **84**, in press (1962); U. S. Patent 2,941,966 (6/21/60) to du Pont.

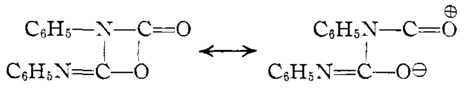
Aliphatic isocyanates react more slowly with the phospholene oxide catalysts. For example, *n*-butyl isocyanate gave only a 17% yield of product when refluxed for 20 hr. with 1.4% by weight of catalyst Ia. However, use of a high boiling solvent raised the yield to 60% with a much shorter reaction time. With a higher boiling isocyanate, the reaction was rapid; 2-octyl isocyanate gave an 89% yield of carbodiimide in two hours at 140–160°.

Although the cyclic phosphine oxides are by far the most active catalysts, other phosphine oxides and phosphine derivatives and certain amine and stibine oxides also show appreciable catalytic activity.[11]

In the course of this work, the reaction of phenyl isocyanate in the absence of any catalyst was also investigated. Stalle[12] reported the formation of diphenylcarbodiimide in unspecified yield by heating phenyl isocyanate in a sealed tube at 180° for 24 hr. It has now been found that refluxing phenyl isocyanate for 46.5 hr. gives no carbodiimide with 97% recovery of the isocyanate. However, repetition of the experiment with slow passage of a stream of nitrogen through the system gave 56% of the theoretical amount of carbon dioxide. Distillation of the reaction mixture yielded diphenylcarbodiimide in fair yield. Evidently, an equilibrium is established which lies far on the side of unchanged phenyl isocyanate

$$2\ C_6H_5NCO \rightleftharpoons C_6H_5N{=}C{=}NC_6H_5 + CO_2$$

The nitrogen apparently removes carbon dioxide and shifts the equilibrium toward carbodiimide formation. Although there is no evidence for the intermediate, one is forced to the conclusion that a structure such as



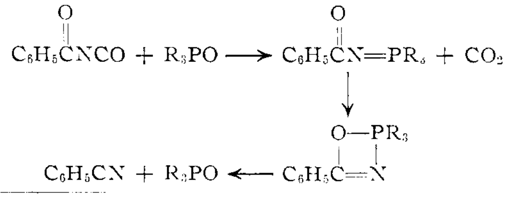
is probably involved.

The mechanism proposed for the catalyzed reaction[13] involves the intermediate formation of a phosphinimide with subsequent reaction of the imide with a second molecule of isocyanate with all species capable of equilibration

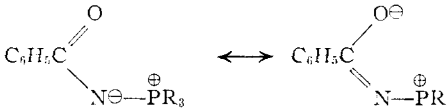
$$R_3PO + R'NCO \rightleftharpoons R_3P{=}NR' + CO_2 \quad (2)$$

$$R_3P{=}NR' + R'NCO \rightleftharpoons R'N{=}C{=}NR' + R_3PO \quad (3)$$

In connection with this proposed mechanism, it was interesting to speculate on the reaction of related compounds with the phospholene oxides. With benzoyl isocyanate, it would be predicted that the first step would be the production of the postulated phosphinimide followed by an internal reaction of the imide group with the adjacent carbonyl group to yield benzonitrile



A moderate yield of benzonitrile was obtained from this reaction; however, the reaction path is not clear. On addition of catalyst to benzoyl isocyanate, a copious crystalline precipitate is formed, with evolution of carbon dioxide. This crystalline product appears to have the empirical structure $C_{22}H_{15}N_3O_2$, and decomposes on further heating to carbon dioxide, benzonitrile and unidentified products. Its structure is not presently known, but it may arise from a 1,4-dipolar reaction of the intermediate



With phenyl isothiocyanate, the reaction was not clean cut. After refluxing in xylene for 20 hr. with catalyst Ia, no carbodiimide bands were found in the infrared spectrum of the reaction mixture. However, a small yield of a carbodiimide fraction was obtained after prolonged heating of neat phenyl isothiocyanate with 4% of catalyst. Infrared analysis showed that this fraction was predominantly diphenylcarbodiimide contaminated with isocyanate and isothiocyanate.

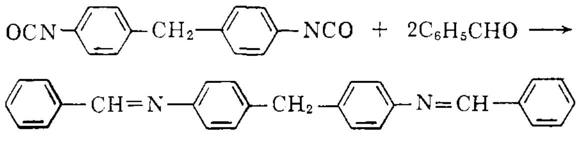
The fact that phenyl isothiocyanate can be converted to carbodiimide suggested that this, too, probably involved an equilibrium such as

$$R'NCS + R_3PO \rightleftharpoons R'\overset{-}{N}\text{-}\overset{+}{P}R_3 + COS$$

$$R'\overset{-}{N}\text{-}\overset{+}{P}R_3 + R'NCS \rightleftharpoons R'NCNR' + R_3PS$$

This would imply that phospholene sulfides are good catalysts, which they are.

In connection with a study of solvents for carrying out the polymerization of diisocyanates to polycarbodiimides,[10] it was found that benzaldehyde reacted with methylene bis-(4-phenyl isocyanate) in the presence of catalyst to give a Schiff base[14]



The catalyst is necessary, since in its absence only undefined substances could be isolated.

Experimental

All melting points were taken on a Kofler hot-stage with a polarizing microscope.

Preparation of 1-Ethyl-3-methyl-3-phospholene-1-oxide.[8]—A 2-l. 4-necked flask was fitted with a spiral condenser topped with a Dry Ice condenser, thermometer, 1-l. dropping funnel with pressure equalizing side arm and a magnetic stirrer. To this flask was added 1 g. of copper stearate, 780 g. (5.96 moles) of dichloroethylphosphine[15] and from the dropping funnel 447 g. (6.56 moles) of freshly distilled isoprene. The reaction mixture was stirred and refluxed under nitrogen for 42 hr., cooled and allowed to stand for 2 days and then refluxed without stirring for 5 days. Excess isoprene was distilled from the mixture and 850 ml. of water was added dropwise with stirring to the reaction flask, which was cooled in an ice-bath. The dark brown aqueous solution was transferred to a 5-l. flask and 1250 ml. of 30% sodium hydroxide solution was added gradually to make the

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[11] J. J. Monagle, *J. Am. Chem. Soc.*, **84**, in press (1962).

[12] R. Stalle, *Ber.*, **41**, 1125 (1908).

[13] J. J. Monagle, T. W. Campbell and H. F. McShane, Jr., *J. Am. Chem. Soc.*, **84**, in press (1962).

[14] H. Staudinger, *Ber.*, **50**, 1042 (1917).

[15] M. S. Kharasch, E. V. Jensen and S. Weinhouse, *J. Org. Chem.*, **14**, 429 (1949).

solution slightly alkaline (*p*H 8). The mixture was filtered and the aqueous solution was extracted continuously with chloroform for 12 days. The chloroform was distilled and the residue was vacuum distilled through a 25-cm. Vigreux column to give 435 g. (51%) of water-white liquid with a slight odor of phosphine. The product was further purified by oxidation at 50° with excess 3% hydrogen peroxide for 6 hr. The aqueous mixture was extracted continuously with benzene and the oxide was recovered by distillation, b.p. 115–119° (1.2–1.3 mm.), $n^{25}\mathrm{D}$ 1.5050. *Anal.* Calcd. for $C_7H_{13}OP$: C, 58.4; H, 9.0; P, 21.5. Found: C, 58.3; H, 8.8; P, 21.6.

Preparation of Diphenylcarbodiimide.[16]—Fifty milliliters (54 g., 0.45 mole) of phenyl isocyanate was pipetted into 50 ml. of dry benzene under nitrogen. Catalyst (0.25 mole, 0.2 g.) was added and the solution was heated to 50° with stirring. Evolution of carbon dioxide was vigorous. Heating and stirring were continued for 2.5 hr. at which point gas evolution was very slow. Solvent was removed under reduced pressure and the residue was vacuum distilled to yield 41.1 g. (94%) of an oil, b.p. 119–121° (0.40–0.45 mm.), $n^{25}\mathrm{D}$ 1.6372. *Anal.* Calcd. for $C_{13}H_{10}N_2$: C, 80.4; H, 5.2; N, 14.4. Found: C, 80.5; H, 5.3; N, 14.4.

In an attempt to prepare diphenylcarbodiimide from phenyl isothiocyanate, a mixture of 25 g. of the isothiocyanate and 25 ml. of xylene was refluxed with 0.3 g. of the preferred phospholene oxide catalyst. After refluxing for 20 hr., an examination of infrared spectrum showed that no chemical change had occurred in the solution.

In a second experiment, 2.3 g. (0.016 mole) of catalyst was added to phenyl isothiocyanate (56.2 g., 50 ml., 0.42 mole). The solution was stirred and heated slowly. At 60–70°, a moderate evolution of gas, which gave a precipitate with calcium hydroxide solution, was observed. The reaction mixture was then heated at 177–185° for 13.5 hr. Distillation yielded 44.9 g. of phenyl isothiocyanate, b.p. 108–109° (23 mm.), an intermediate fraction, 6.4 g., b.p. 109–126° (23 mm.), and high boiling fraction, 3.9 g., b.p 142–144° (2.8–3.4 mm.). An infrared spectrum showed the presence of diphenylcarbodiimide along with isothiocyanate and isocyanate contaminants.

Preparation of 4,4′-Ditolylcarbodiimide.[1,16]—One hundred grams (0.75 mole) of unpurified *p*-tolyl isocyanate was diluted with 150 ml. of xylene and refluxed. Catalyst was added and the mixture was refluxed for 4 hours. Carbon dioxide was evolved in copious quantities during this period. The reaction mixture was distilled. After removal of xylene, the boiling point rose abruptly to 165° (2.4 mm.) at which temperature 73 g. (88%) of ditolylcarbodiimide melting at 56.6–57.5° was obtained. *Anal.* Calcd. for $C_{15}H_{14}N_2$: C, 81.1; H, 6.31; N, 12.61. Found: C, 80.8, 80.9; H, 6.18, 6.22; N, 12.42, 12.46.

Preparation of 3,3′-Ditolylcarbodiimide.[1,17]—A mixture of 25.3 g. (0.19 mole) of *m*-tolyl isocyanate and 0.06 g. (0.0004 mole) of catalyst was maintained at room temperature *in vacuo* (10 mm.) for 16 hr. The next day, infrared examination of the mixture showed that essentially no isocyanate remained and the product was essentially pure carbodiimide. The yield of product was 20.6 g. (98%). Without further purification, it was analyzed. *Anal.* Calcd. for $C_{15}H_{14}N_2$: C, 81.1; H, 6.3; N, 12.6. Found: C, 80.7, 80.7; H, 6.27, 6.28; N, 12.4, 12.5. The product boiled at 151° (1.1 mm.).

Preparation of Di-*o*-tolylcarbodiimide.—A mixture of 25 ml. (25.5 g., 0.2 mole) of *o*-tolyl isocyanate and 0.25 g. (0.0017 mole) of catalyst was heated at 50–55° for 9.5 hr. The reaction mixture was distilled through a Claisen head to yield 19.3 g. (87%) of di-*o*-tolylcarbodiimide, b.p. 118–122° (0.15–0.10 mm.), $n^{25}\mathrm{D}$ 1.6230. *Anal.* Calcd. for $C_{15}H_{14}N_2$: C, 81.0; H, 6.3; N, 12.6. Found: C, 81.4, 81.3; H, 6.3, 6.3; N, 12.6, 12.6.

Preparation of Bis-*p*-methoxyphenyl)-carbodiimide.[4]—One hundred grams (0.671 mole) of *p*-methoxyphenyl isocyanate diluted with 100 ml. of xylene was converted to carbodiimide by refluxing with a trace of catalyst for 4 hr. The product boiled at 193–194° (1.3 mm.). It was a pale yellow oil obtained in virtually quantitative yield (84.2 g., 99%) which crystallized on standing. The product without further purification melted at 52–53°. *Anal.* Calcd. for $C_{15}H_{14}O_2N_2$: N, 11.1. Found: N, 11.1, 11.0.

Preparation of Bis-(*o*-methoxyphenyl)-carbodiimide.—A mixture of 26.7 g. (0.18 mole) of *o*-methoxyphenyl isocyanate and 0.06 g. (0.0004 mole) of catalyst was allowed to stand at room temperature in a moderate vacuum for 16 hr. Next day, the mixture had crystallized partially. Infrared spectra showed that the mixture consisted of approximately 65% carbodiimide and 35% isocyanate. The reaction was completed by warming at 100° for 1 hour. The hot residue was diluted with equal volume of cyclohexane and the mixture was allowed to cool to room temperature. The crystalline product was filtered, washed with a small amount of cold cyclohexane and dried. The product (19.4 g., 85%) melted at 73.5–74.5°. The combined filtrates were evaporated to approximately one-fourth of their volume to give an additional 2.1 g. of crystals melting at 68–73°. Complete evaporation of the solvent gave approximately 0.3 g. of non-crystallizable oil. The second crop of crystals was recrystallized a second time from cyclohexane to give an additional 1.5 g. of pure product, m.p. 73.5–74°. The total yield of pure bis-(*o*-methoxyphenyl)-carbodiimide was thus 20.9 g. (92%). *Anal.* Calcd. for $C_{15}H_4O_2N_2$: C, 70.8; H, 5.51. Found: C, 70.7, 70.9; H, 5.78, 5.81.

Preparation of Bis-(*p*-chlorophenyl)-carbodiimide.[1,18]—A mixture of 50 g. (0.32 mole) of *p*-chlorophenyl isocyanate and 0.06 g. of the catalyst was allowed to stand at room temperature in a vacuum desiccator for about 2 hr. The evolution of carbon dioxide was brisk and the liquid soon turned to a mass of crystals. Without further purification, this material (42.3 g., 99%) melted at 54–56°, leaving a trace of high-melting crystalline residue. For purification, 2.0 g. of the as-formed product was dissolved in isoöctane and filtered free of insoluble matter. The filtrate was evaporated to dryness to give 1.83 g. (91%) recovery of a crystalline product which melted sharply at 56–57°. *Anal.* Calcd. for $C_{13}H_8N_2Cl_2$: C, 59.2; H, 3.04. Found: C, 59.3, 59.4; H, 3.09, 3.19.

Bis-(*m*-chlorophenyl)-carbodiimide[1] was prepared in essentially the same manner as that described for the *p*-chloro compound. A 99% yield of unpurified product which melted sharply at 42–43° was obtained. *Anal.* Calcd. for $C_{13}H_8N_2Cl_2$: C, 59.2; H, 3.04. Found: C, 59.3, 59.2; H, 3.16, 3.08.

Preparation of Bis-(*p*-nitrophenyl)-carbodiimide.—A solution of 69.6 g. (0.424 mole) of pure *p*-nitrophenyl isocyanate, m.p. 56–57°, in 1 liter of carbon tetrachloride was placed in a three-neck flask fitted with reflux condenser, nitrogen inlet, magnetic stirrer and a rubber septum. The flask was swept with a stream of dry nitrogen; catalyst, 0.348 g., diluted with 5 ml. of carbon tetrachloride was added from a hypodermic. An exothermic reaction took place with the vigorous evolution of carbon dioxide. The temperature of the reaction was slowly raised over 2 hours to 62° and held at this temperature for 2 additional hours. In this length of time, 9.04 g. (0.21 mole) of carbon dioxide was evolved and trapped in Ascarite-filled weighing tubes. During the evolution of the carbon dioxide, a yellow crystalline solid formed and precipitated. The reaction mixture was cooled to room temperature and the solid filtered to give 57.5 g. (95%) of N,N′-di-*p*-nitrophenylcarbodiimide, m.p. 166–167°.

In a second experiment, *p*-nitrophenyl isocyanate (21.0 g., 0.128 mole) was melted and treated with 0.03 g. of catalyst at about 60°. Carbon dioxide was evolved almost explosively, and in a matter of 1–2 min. the mixture had set to a crystalline mass. The last traces of carbon dioxide were removed *in vacuo* and 18 g. of a yellow crystalline solid melting at 165–170° was obtained. The solid was dissolved in chloroform at room temperature and the solution treated with decolorizing carbon and filtered. Bis-(*p*-nitrophenyl)-carbodiimide was precipitated as fine pale yellow needles by addition of petroleum ether to the chloroform solution. The product melted at 166°, with subsequent recrystallization on the slide to orange leaflets melting in the range 335–350°. *Anal.* Calcd. for $C_{13}H_8N_4O_4$: C, 54.9; H, 2.81; N, 19.7. Found: C, 54.8, 54.7; H, 2.88, 3.02; N, 19.9, 20.0.

Preparation of Bis-(*m*-nitrophenyl)-carbodiimide.[1]—*m*-Nitrophenyl isocyanate (41 g., 0.25 mole) was melted and treated with 0.06 g. of catalyst. The mixture evolved

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(16) F. Zetsche, *et al.*, *Ber.*, **71B**, 1512 (1938); **73B**, 467 (1940).

(17) L. C. Raiford and W. T. Daddow, *J. Am. Chem. Soc.*, **53**, 1552 (1931).

(18) C. K. Ingold, *J. Chem. Soc.*, **122**, 100 (1921).

carbon dioxide copiously and in a few minutes set to a pale yellow mass of crystals. These melted sharply at about 160° without unmelted residue. The yield of unpurified crystalline product was 35 g. (98%). For purification, 3 g. of the solid was dissolved in a mixture of 50 ml. of xylene and 50 ml. of cyclohexane. The product (2.8 g., 93% recovery) crystallized as fine yellow needles, m.p. 157–159°. *Anal.* Calcd. for $C_{13}H_8N_4O_4$: C, 54.9; H, 2.81. Found: C, 54.6, 54.9; H, 2.87, 3.08.

Preparation of Bis-(*o*-nitrophenyl)-carbodiimide.—A solution of 3.0 g. (0.018 mole) of *o*-nitrophenyl isocyanate in 25 ml. of cyclohexane at about 50° was filtered free of some insoluble matter. Catalyst (0.03 g.) was added and a rapid evolution of carbon dioxide was noticed. After a few minutes, a copious crystalline precipitate was obtained. In 15 min., the yellow-orange solid was filtered and dried. The yield was 2.45 g. (96%), melting at 93–96° but leaving a trace of high-melting crystalline residue. *Anal.* Calcd. for $C_{13}H_8N_4O_4$: N, 19.7. Found: N, 19.2.

A sample (1.0 g.) was recrystallized from 25 ml. of cyclohexane. The solution was filtered to remove a quantity of orange gum which was insoluble in the cyclohexane. The product (0.72 g.) recrystallized on cooling as fine, pale yellow needles, m.p. 97–98.5°. Some decomposition or polymerization occurred at the melting point since the melt on cooling recrystallized to a product which remelted in the range 91–95°. *Anal.* Calcd. for $C_{13}H_8N_4O_4$: C, 54.9; H, 2.81. Found: C, 54.8, 54.8; H, 2.99, 3.05.

Preparation of (Di-α-naphthyl)-carbodiimide.[19]—A mixture of 25 g. (0.148 mole) of α-naphthyl isocyanate, 25 ml. of xylene and 0.1 g. of catalyst was refluxed for 4 hours. The solution was then evaporated to dryness to give a crystalline product which melted mostly in the range 91–92° but left some unmelted crystalline particles. The solid was dissolved in benzene, treated with decolorizing carbon and filtered. The yield of product melting sharply at 91–91.5° was 21.4 g. (99%). *Anal.* Calcd. for $C_{21}H_{14}N_2$: N, 9.52. Found: N, 9.72, 9.95.

Preparation of (Di-*n*-butyl)-carbodiimide.[20,21]—Fifty grams (0.5 mole) of butyl isocyanate was maintained at the boiling point in the presence of 0.7 g. of catalyst for 15 hr. The reaction mixture was then distilled to give a yield of 6.2 g. of pure di-*n*-butylcarbodiimide, b.p. 82° (8 mm.) after a large forecut of unchanged *n*-butyl isocyanate. *Anal.* Calcd. for $C_9H_{18}N_2$: N, 18.2. Found: N, 18.0, 18.1.

Increasing temperature and catalyst concentration gave higher conversion of isocyanate to carbodiimide. Thus, a yield of about 4.6 g. of carbodiimide (60%) was obtained when a mixture of 10 g. (0.1 mole) of *n*-butyl isocyanate and 90 ml. of decahydronaphthalene was refluxed with 1.5 g. of catalyst for 15 min.

Conversion of 2-Octyl Isocyanate to Carbodiimide.—Catalyst I (2.8 g., 0.019 mole) was added to 21.5 g. (0.14 mole) of 2-octyl isocyanate (b.p. 114–116° (100 mm.)) and the solution was stirred and heated slowly. At 135°, a moderate evolution of carbon dioxide began. The solution was heated at 140–145° for 0.5 hr. and at 150–160° for 1.5 hr. Distillation of the reaction mixture yielded 1.8 g. of 2-octyl isocyanate, b.p. 33–89° (10–50 mm.), and 16.5 g. of colorless oil, b.p. 108–109° (1.5 mm.). The infrared spectrum indicated that the sample was carbodiimide contaminated with a small amount of isocyanate.

The Effect of Heat on Di-*p*-tolylcarbodiimide.—Five grams of ditolylcarbodiimide dissolved in 50 ml. of xylene was refluxed for 24 hr. An examination of the infrared spectrum indicated that little, if any, change had occurred. The solution was evaporated and heated *in vacuo* overnight on the steam-bath. Considerable carbodiimide (m.p. 56°) sublimed to the top of the flask where it crystallized. However, a substantial residue remained which was solid at steam-bath temperature. This was submitted for infrared examination. This new product, probably a cyclic trimer, showed a strong band at 6.02 μ, presumably due to the presence of a C=N group.

Preparation of Ditolyl-*t*-butylguanidine.—Three grams of ditolyl carbodiimide in 25 ml. of benzene was refluxed for 24 hr. with 15 ml. of *t*-butylamine. The benzene was then evaporated under nitrogen on the steam-bath and the non-volatile residue was recrystallized two times from ethanol. The product melted at 126–126.5° and showed a strong band at 6.10 μ in the infrared which is presumed to be due to the guanidine grouping. *Anal.* Calcd. for $C_{19}H_{24}N_3$: C, 77.39; H, 8.48; N, 14.20. Found: C, 77.4, 77.2; H, 8.03, 8.04; N, 13.7, 13.9.

An aqueous suspension of ditolyl-*t*-butylguanidine was treated with an excess of sulfuric acid on the steam-bath. A homogeneous solution resulted which crystallized on cooling. The product melted at 183–186° and showed again the band characteristic of the guanidine grouping at 6.10 μ. *Anal.* Calcd. for $C_{19}H_{24}N_3 \cdot H_2SO_4$: C, 58.0; H, 6.9; N, 10.6. Found: C, 58.0, 58.1; H, 6.6, 6.5; N, 10.2, 10.4.

Synthesis of Bis-(*p*-nitrophenyl)-*t*-butylguanidine.—A solution of 0.92 g. of *p*-nitrophenyl isocyanate in 50 ml. of benzene was heated to the boiling point and 1 drop of the phospholene oxide catalyst was added. The mixture was refluxed for 10 min., cooled to about 50° and treated with an excess of *t*-butylamine. The mixture was evaporated to dryness and the yellow solid was recrystallized from absolute alcohol. The yield of shiny orange leaflets melting at 208–209.5° was 0.81 g. (74%). *Anal.* Calcd. for $C_{17}H_{19}N_5O_4$: C, 57.1; H, 5.3. Found: C, 56.8, 56.7; H, 5.3, 5.5.

Synthesis of Bis-(*p*-chlorophenyl)-*t*-butylguanidine.—The preceding experiment was repeated substituting 1.0 g. of *p*-chlorophenyl isocyanate. The product was recrystallized from aqueous alcohol and dried. The yield was 0.78 g. (71%) and the melting point was 140–142°. *Anal.* Calcd. for $C_{17}H_{19}N_3Cl_2$: C, 60.7; H, 5.66. Found: C, 60.4, 60.5; H, 5.4, 5.6.

Uncatalyzed Conversion of Phenyl Isocyanate to Diphenylcarbodiimide.—Phenyl isocyanate (54.1 g., 0.45 mole) was refluxed for 46.5 hr. (161°). At the end of this period, distillation yielded 52.5 g. of phenyl isocyanate (97%) with a cloudy liquid residue of 0.6 g.

In a second experiment, a slow stream of nitrogen was passed through refluxing phenyl isocyanate (100 g.) and the evolved carbon dioxide was trapped in an Ascarite tube and weighed. After 48 hr., the carbon dioxide amounted to 56% of the theoretical. The residue was distilled to give 42 g. of unchanged isocyanate, and 41 g. (50%) of diphenylcarbodiimide, b.p. 121° (0.5 mm.).

Conversion of Phenyl Isothiocyanate to Diphenylcarbodiimide.—A mixture of 27 g. (0.2 mole) of phenyl isothiocyanate and 1.08 g. (4% by weight) of phospholine oxide catalyst was heated at 120° for 13.5 hr. Distillation of the resulting mixture yielded 3.1 g. (16%) of a fraction, b.p. 117–119° (0.4 mm.). Infrared analysis of this product showed it to be predominantly diphenylcarbodiimide contaminated with isocyanate and isothiocyanate.

Reaction of Methylene-bis-(4-phenyl Isocyanate) with Benzaldehyde.—(a) Seven grams of methylene-bis-(4-phenyl isocyanate) was mixed with 50 ml. of purified benzaldehyde and one drop of phospholine oxide catalyst. This mixture was heated at reflux for 4 hr. and poured into 400 ml. of petroleum ether to give a crystalline precipitate. This product was collected and recrystallized three times from absolute ethanol to give 2.25 g. (20%) of a product, m.p. 130.5–131.5°. The infrared spectrum confirmed the expected structure N,N'-bis-(benzylidene)-4,4'-diaminodiphenylmethane, and showed the complete absence of isocyanate and carbonyl bands. *Anal.* Calcd. for $C_{27}H_{22}N_2$: C, 86.6; H, 5.9; N, 7.5. Found: C, 86.3; H, 5.7; N, 7.6.

(b) Seven grams of methylene-bis-(4-phenyl isocyanate) was dissolved in 50 ml. of purified benzaldehyde and heated at reflux for 4 hr. This dark solution was poured into 400 ml. of petroleum ether to give a small precipitate of dark gum. No crystalline product could be isolated.

Reaction of Benzoyl Isocyanate in Presence of the Phospholine Oxide Catalyst.—Benzoyl isocyanate was prepared by the method of Hill and Degnan[22] using dry carbon tetrachloride as reaction medium; b.p. 94–96° (38 mm.) (lit.[1] 88–91° (20 mm.)).

A solution of 4.52 g. of isocyanate in 50 ml. of dry (over CaH_2) toluene was mixed with 2 drops of the phospholine oxide catalyst, and the flask was warmed to 45° in an oil-

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bath. Carbon dioxide evolution started immediately, and in about 15 minutes a precipitate began to form. After 1 hour, the precipitate was collected, the filtrate was evaporated to dryness, and both solids were dried over P_2O_5 in high vacuum. The product, 3.3 g., was recrystallized from chloroform–hexane. On standing, the compound developed a distinct odor, reminiscent of benzaldehyde or benzonitrile. *Anal.* Calcd. for $C_{22}H_{15}N_3O_2$: C, 74.6; H, 4.3; N, 11.9; O, 9.1. Found: C, 74.6, 74.1; H, 4.5, 4.4; N, 11.64, 11.78; O, 8.6, 8.9.

Decomposition of the unknown compound at 220° gave a 20% yield of a distillate identified as crude benzonitrile, and an unidentified solid residue (nitrile trimer ?) in addition to an undetermined amount of CO_2.

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Hexacyanoethane

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The synthesis of hexacyanoethane, the first percyanoalkane, is described.

Percyanoalkynes[1,2] and a percyanoalkene[3] are known, but no percyanoalkane has been reported. We have now prepared hexacyanoethane, the first percyanoalkane, by treating sodium pentacyanoethanide[4] with cyanogen chloride.

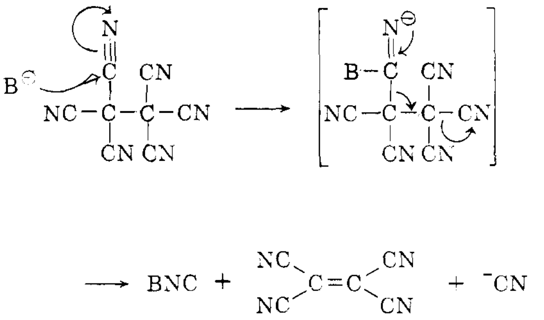
$$(NC)_3CC(CN)_2Na + ClCN \longrightarrow (NC)_3CC(CN)_3 + NaCl$$

In contrast to the usual cyanations of this type, the success of the reaction depends on the absence of a solvent for hexacyanoethane except for excess cyanogen chloride. Best results are obtained in the presence of aluminum chloride.

Careful sublimation of the crude product gave hexacyanoethane contaminated by tetracyanoethylene. The latter was removed by washing with benzene, in which hexacyanoethane is insoluble. The low yield of pure hexacyanoethane (17%) is caused by decomposition during isolation, for the infrared spectrum of the crude product is essentially that of hexacyanoethane.

Hexacyanoethane is a colorless solid that decomposes in a sealed tube above 150°. Its most striking property is its instability. It can be sublimed at 75° (2 mm.), but some decomposition to tetracyanoethylene and, presumably, cyanogen occurs during sublimation. At room temperature it soon decomposes to tetracyanoethylene and polymeric materials, but it has been stored at −80° for long periods without change. Hexacyanoethane dissolved at room temperature in ethyl acetate, tetrahydrofuran or dimethoxyethane decomposes completely overnight; this decomposition is accelerated greatly by base, moderately by acid.

On several occasions when crude hexacyanoethane was heated at reduced pressure it decomposed rather violently with the formation of tetracyanoethylene. This is reminiscent of the decomposition of isosteric hexabromoethane to the corresponding ethylene.[5] In view of the extreme sensitivity of hexacyanoethane toward base, we propose the following autocatalytic base-induced mechanism for this decomposition.



Hexacyanoethane is assigned its structure on the basis of its composition, mode of formation, decomposition to tetracyanoethylene, and infrared and mass spectra. Its infrared spectrum has only four peaks, which is consistent with a highly symmetrical structure. A single peak at 4.40 μ indicates the presence of just one kind of nitrile group, and that unconjugated. The mass spectrum shows no parent peak, but there is a large peak due to the tricyanomethyl fragment, and lesser ones corresponding to tetracyanoethylene and dicyanoacetylene.

Hexacyanoethane might be expected, like dicyanoacetylene,[6] cyanogen[6] and tetracyanoethylene,[7] to have an exceptionally high flame temperature. That this is true is indicated by a calculation like those of Kirshenbaum and von Grosse[6] based on an observed heat of combustion of about 990 kcal./mole at 25°[8]; this suggests a flame temperature in the range 4000–4600°K. Hexacyanoethane has a high endothermic heat of formation, estimated from the heat of combustion to be 240 kcal./mole at 25°; this is in fair agreement with a value of 195 kcal./mole calculated from Pauling's[9] bond energies.

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