analysis showed that no 2-methyl-2-decanol was formed when the reaction was carried out in the absence of III.

Reaction of Formaldehyde with Cyclohexane.—This reaction was carried out essentially as described, using α,α'-dimethoxy-α,α'-dimethylbibenzyl (III) as the initiator in place of di-*t*-butyl peroxide.[12] The reaction was run at 240–250° in a sealed glass tube. The yield of cyclohexanecarbinol was 24%, determined by vapor phase chromatography and infrared analysis. No product was formed under identical conditions in the absence of III.

The Dehydrochlorination of Allophanoyl Chlorides. A New Synthesis of Isocyanates

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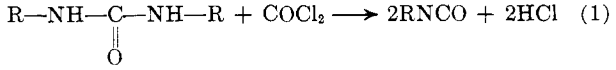
The thermal dehydrochlorination of N,N′-dialkylallophanoyl chlorides afforded isocyanates in high yield. While N,N′-dialkylallophanoyl chlorides are virtually unaffected by base, the cyclic allophanoyl chlorides (2-imidazolidinone-N-carbonyl chlorides) could be dehydrochlorinated to the corresponding diisocyanates at room temperature using a tertiary amine. The influence of various catalysts on the thermal decomposition of allophanoyl chlorides was investigated and the mechanism of the hydrogen chloride elimination reaction is discussed.

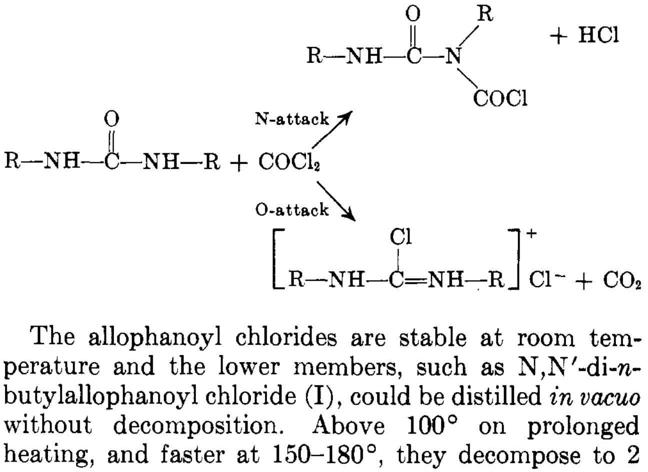
Isocyanates are generally synthesized from primary amines and phosgene. In certain special cases, however, this reaction does not proceed in the desired manner. Thus ethylene, as well as propylene diisocyanate, could not be synthesized from the corresponding diamines and phosgene.[2]

Although both alkylformamides and N-alkylureas have been converted to the corresponding isocyanates by treating the former with sulfuryl chloride[3] and the latter with either boron trifluoride[4] or nitrous acid,[5] the N,N′-dialkylureas have not been utilized in the synthesis of isocyanates. According to eq. 1, N,N′-dialkylureas could react with 1 equiv. of phosgene to afford 2 equiv. of isocyanate and hydrogen chloride. The reaction would have to proceed by N-attack. Since the N-attack intermediates are the chlorides of the hypothetical allophanic acid, we will refer to these compounds from here on as "allophanoyl chlorides."



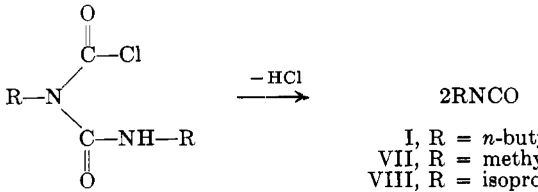
$$\text{R—NH—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—NH—R} + \text{COCl}_2 \longrightarrow 2\text{RNCO} + 2\text{HCl} \quad (1)$$

N,N′-diphenylurea is known[6] to react with phosgene at 150°, where the urea is sufficiently dissociated into phenylisocyanate and aniline,[7] to yield phenyl isocyanate; however, the formation of alkyl isocyanates from N,N′-dialkylureas has never been observed. It has been reported[8] that N,N′-dialkylureas react with phosgene to give the undesired O-attack products, the N,N′-dialkylchloroformamidine hydrochlorides. We have demonstrated recently[9] that allophanoyl chlorides also form; however, this involves the attack of phosgene by the nitrogen of the N,N′-dialkylureas.



The allophanoyl chlorides are stable at room temperature and the lower members, such as N,N′-di-*n*-butylallophanoyl chloride (I), could be distilled *in vacuo* without decomposition. Above 100° on prolonged heating, and faster at 150–180°, they decompose to 2 moles of isocyanate and 1 mole of hydrogen chloride. This thermal decomposition was studied extensively on I and ethyleneallophanoyl chloride (II) as model compounds. Since the straight-chain allophanoyl chlorides differ in many respects from the cyclic, both series will be discussed.

I on refluxing in benzene for several hours was unchanged; however, in refluxing toluene (115°) a slow decomposition with formation of tri-*n*-butyl isocyanurate (III) was observed. In chlorobenzene at 132° a 70% conversion to *n*-butyl isocyanate occurred in 3 hr. The decomposition of I in concentrations of less than 10% in *o*-dichlorobenzene at 180° gave a 91% yield of *n*-butyl isocyanate.



I, R = *n*-butyl
VII, R = methyl
VIII, R = isopropyl
IX, R = *n*-octadecyl
X, R = cyclohexyl

The thermal decomposition without a diluent led to the formation of appreciable amounts of residues with III being the main product. This can be explained by Scheme I outlined below and is perhaps general for the aliphatic series.

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[1] To whom inquiries should be directed.

[2] W. Siefken, *Ann.*, **562**, 75 (1949).

[3] E. Kühle, German Patent 1,090,197 (1960); *Chem. Abstr.*, **55**, 19799 (1961).

[4] F. T. Sowa, U. S. Patent 3,013,045 (1961); *Chem. Abstr.*, **56**, 8632 (1962).

[5] S. Ross, A. Riva, and B. Piantanida, *Chim. Ind.* (Milan), **42**, 1243 (1960); *Chem. Abstr.*, **55**, 25850 (1961).

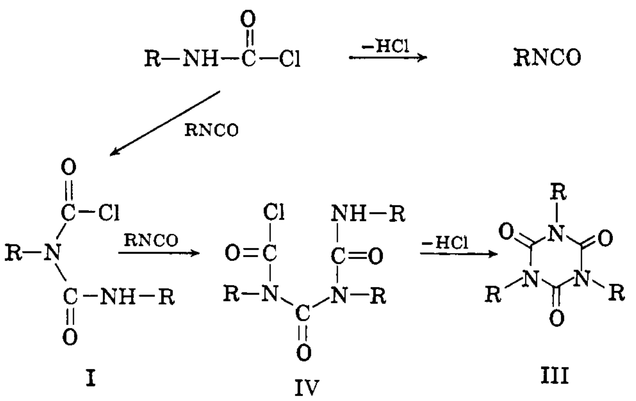
[6] W. Hentschel, *Ber.*, **17**, 1284 (1884); see also Production of Phenyl Isocyanate, O.P.B. Report No. **58**, 913 Frame No. 1082–1087.

[7] H. Eckenroth and M. Wolf, *Ber.*, **26**, 1463 (1893).

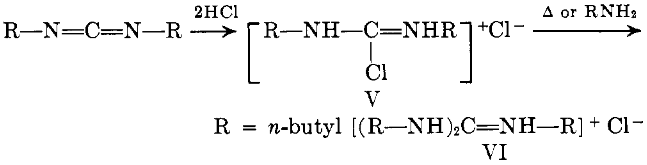
[8] H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960).

[9] (a) H. Ulrich, J. N. Tilley, and A. A. R. Sayigh, *J. Org. Chem.*, **29**, 2401 (1964); (b) J. N. Tilley and A. A. R. Sayigh, *ibid.*, **29**, 3347 (1964).

Scheme I



When a mixture of I and N,N′-di-*n*-butylchloroformamidine hydrochloride (V) is heated in *o*-dichlorobenzene at 180°, in addition to *n*-butyl isocyanate, N,N′,N″-tributylguanidine hydrochloride (VI) is also formed. The latter probably arises by thermal decomposition of V. This is confirmed by the formation of VI from pure V, synthesized from di-*n*-butylcarbodiimide and hydrogen chloride. The structure of VI was established by independent synthesis from V and *n*-butylamine.[9]



$$R{-}N{=}C{=}N{-}R \xrightarrow{2HCl} \underset{V}{\left[R{-}NH{-}\underset{Cl}{\underset{|}{C}}{=}NHR\right]^{+}Cl^{-}} \xrightarrow{\Delta \text{ or } RNH_2}$$

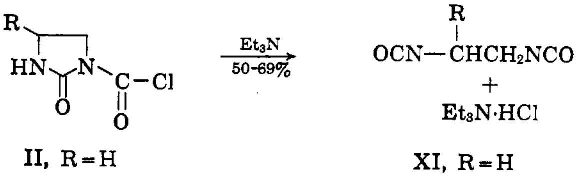
$$R = n\text{-butyl} \quad \underset{VI}{[(R{-}NH)_2C{=}NH{-}R]^{+}\,Cl^{-}}$$

The phosgenation of N,N′-dialkylureas above the decomposition temperature of the allophanoyl chloride resulted in the formation of a mixture of *n*-butyl isocyanate, N,N′,N″-tri-*n*-butylbiuret, VI, and IIIa. The biuret derivative is formed from the generated isocyanate and the starting urea. By contrast the reaction of N,N′-diphenylurea[6] with phosgene under these conditions gives high yields of phenyl isocyanate directly. This clearly demonstrates the different behavior of the aliphatic ureas.

Various catalysts such as triethylamine, collidine, or ferric chloride, which markedly accelerate the decomposition of cyclic ethylene allophanoyl chloride (*vide infra*), appear to have no accelerating influence upon the decomposition of the linear straight-chain allophanoyl chlorides such as I in the temperature range (25–130°) examined.

Analogous to I, the other linear allophanoyl chlorides, N,N′-dimethyl (VII), N,N′-diisopropyl (VIII), N,N′-di-*n*-octadecyl (IX), and N,N′-dicyclohexyl (X), were converted to the corresponding isocyanates in good yield.

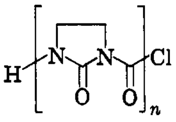
By contrast, the cyclic five-membered ring allophanoyl chlorides II and IIa differ markedly from the linear allophanoyl chlorides in behavior chiefly in these respects. (1) An equivalent of tertiary amine smoothly and rapidly effects dehydrochlorination at 30–40°. (2) Thermal decomposition is very sluggish (5% in 4 hr. at 132°, 25% in 2 hr. at 155°) implying greater thermal stability. (3) Thermal decomposition is markedly accelerated by Lewis acid or base catalysts such as ferric chloride, triethylamine, and collidine as shown in Table I. (4) Polymeric condensation products are extensive if the concentration is above 3–5%.



II, R = H
IIa, R = CH_3

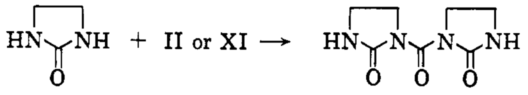
XI, R = H
XIa, R = CH_3

In further contrast, the major by-products formed in the thermal decomposition of II appears to be not triisocyanurate, but rather materials resembling XII.

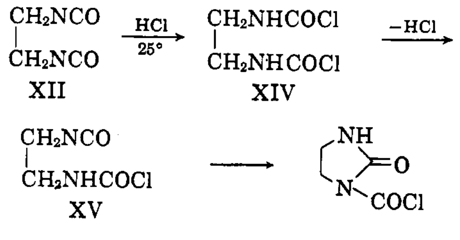


XII ($n \geq 2$)

While actual characterization of materials such as XII ($n \geq 2$) is lacking, several interesting observations infer that these are most reasonable products. Spectra of residues show carbonyl absorptions consistent with II or XII but not triisocyanurates. Ethyleneurea condenses readily with II or XI to give carbonylbisimidazolidinone-2 (XIII). More XI will react with ethyleneurea especially on heating or with tertiary amine, giving glassy polymers. In work reported elsewhere,[9a] the ease of reaction of either II or XI with compounds such as R–X–H, even such as mercaptans, and especially by tertiary amine catalysis is described. Reaction with XI involves a linear intermediate which cyclizes.[9b] Hydrogen chloride reacts with XI to give the dicarbamoyl chloride (XIV) which on heating is converted to II, probably involving similar cyclization of an intermediate XV. Efforts to demonstrate simple interaction of II with XI lead only to the usual pyrolysis of II.



XIII



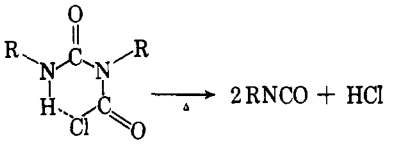
An attractive dehydrochlorination mechanism consistent with the behavior of both the acyclic (I) and cyclic (II) allophanoyl chlorides could involve initial ionization of chloride followed by loss of a proton and scission to the two isocyanate functions. The marked Lewis acid–base catalysis in the reaction of II suggests an ionic process. The greater catalytic sensitivity of II and the lesser thermal stability of I toward dehydrochlorination are largely interpretable from steric con-

TABLE I

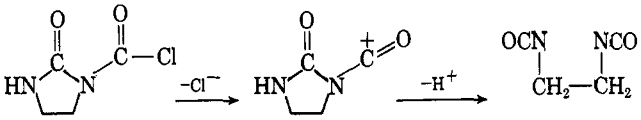
INFLUENCE OF CATALYSTS ON THE DECOMPOSITION OF I AND II[a]

		Isocyanate formed, % yield[c]					
		Reaction time, min.					
Substrate	Catalyst[b]	20	40	60	120	180	300
I	None[d]	12	24	32	57	62	...
I	Collidine[d]	..	..	..	67	73	...
II	None	..	..	..	...	4	7
II	NaI	..	..	24	28	...	28[e]
II	$FeCl_3$	27	40	43	47[e]	...	...
II	Collidine	10	21	37	66	85	95

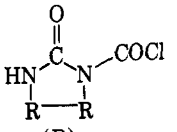
[a] In chlorobenzene at 132°. [b] At 4 to 5% by wt. of the substrate. [c] Taken from smooth plots of experimental points. [d] In refluxing benzene (80°) there was no change without catalyst or even with a molar equivalent of base catalysts. [e] Much white polymer (precipitate) had formed.



I(A)



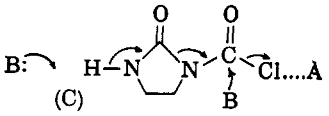
II



(B)

siderations.[10a] A planar conformation (B), representative of II yet energetically unfavorable for I, is much exposed to external polar (catalyst) influence; but a planar structure (A), not possible for II yet energetically favorable for I, would not only better exclude catalysts but might also encourage an internally assisted ionization or even a synchronous Chugaev-type[10b] process—a process not possible in B.

The mode of catalyst interaction, easier in II than in I, can be depicted as in C where base can be involved at the acyl carbon by an SN process[10a-c] in which ionization is still a possibility, or perhaps uniquely with this system a concerted process involving proton abstraction occurs, as suggested by one of the referees.



Other possible mechanisms for the dehydrochlorination involving either Chugaev-like transition states arising from enols or four-membered cyclic transition states arising from intramolecular nucleophilic attack if important are again sterically much better suited to I than to II, and probably electronically poor with II, in view of the behavior of II toward added catalysts.

Experimental[11]

Isocyanates from N,N'-Dialkylallophanoyl Chlorides. General Procedure.—A solution of 0.05 mole of the N,N'-dialkylallophanoyl chloride (prepared from the corresponding N,N'-dialkylurea and phosgene)[9] in dry *o*-dichlorobenzene (5% solution by weight) was refluxed until the rapid evolution of hydrogen chloride ceased (1-2 hr.). It is advantageous to pass nitrogen through the reaction mixture to remove the generated hydrogen chloride. Although the solubility of hydrogen chloride is low in *o*-dichlorobenzene at 180°, a fast removal minimized side reactions. Fractional distillation from the solvent afforded almost quantitative yields of mixtures of the lower alkyl isocyanates and lower alkylcarbamoyl chlorides (from N,N'-dimethyl- and N,N'-diisopropylallophanoyl chloride). From 11.7 g. (0.05 moles) of N,N'-di-*n*-butylallophanoyl chloride (I), 9 g. (91%) of *n*-butyl isocyanate (b.p. 115°) was obtained. In the case of N,N'-di-*n*-octadecylallophanoyl chloride the solvent was removed *in vacuo* and distillation of the residue afforded *n*-octadecyl isocyanate, b.p. 151-160° (0.3 mm.).

Thermal Decomposition of N,N'-Di-*n*-butylallophanoyl Chloride (I). A. Preparative.—An 11.7-g. (0.05-mole) sample of I was heated at 140-150° until the evolution of hydrogen chloride ceased. Fractional distillation afforded 6.3 g. (64%) of *n*-butyl isocyanate, b.p. 112-115°. The infrared spectrum of the residue (3.3 g.) showed a C═O absorption band at 5.9 (tri-*n*-butyl isocyanurate, III) and a band at 6.27 μ due to an unidentified by-product.

B. Comparative Studies with and without Catalyst. (1) **Without Catalyst.**—Di-*n*-butylallophanoyl chloride (2.4 g., 0.01 mole) in 100 ml. of dry chlorobenzene was refluxed for 120 and 200 min., and formation of 1.13 (57%) and 1.23 g. (62%) of *n*-butyl isocyanate, respectively, occurred as indicated by a quantitative infrared study.

(2) **With Collidine.**—To 2.4 g. (0.01 mole) of di-*n*-butylallophanoyl chloride in 100 ml. of chlorobenzene 2 drops of collidine was added. After refluxing for 120 and 180 min., formation of 1.33 (67%) and 1.44 g. (73%) of *n*-butyl isocyanate, respectively, occurred.

(3) **Other.**—When di-*n*-butylallophanoyl chloride (7.6 g., 0.032 mole) was refluxed in 76 ml. of benzene without catalyst and with added amounts of 3.03 g. (0.03 mole) of triethylamine and 200 mg. of $FeCl_3$, respectively, no reaction was observed in all instances.

Thermal Decomposition of N,N'-Di-*n*-butylchloroformamidine Hydrochloride (V).—A solution of 22.7 g. (0.1 mole) of V, obtained from di-*n*-butylcarbodiimide and hydrogen chloride, in 200 ml. of *o*-dichlorobenzene was heated for 2 hr. at 180°. An oily layer separated on top of the solvent on cooling. From the separated oil on treatment with acetone-ether, 5 g. (40%) of N,N',N''-tri-*n*-butylguanidine hydrochloride (VI), m.p. 202-204°, was obtained. A mixture melting point with a sample of VI obtained from V and *n*-butylamine[9] was not depressed and the infrared spectra were identical.

Thermal Decomposition of 2-Imidazolidinone-N-carbonyl Chloride (II). A. General Procedure.—A solution of 0.5 g. (0.00337 mole) of II in 39.5 g. of dry chlorobenzene was immersed in a bath at 150°. Within 5 min. the solution was near reflux at which point in the catalyzed reaction the catalyst was added.

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(10) (a) G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 445-454; (b) D. J. Cram, *ibid.*, p. 308; (c) M. S. Newman, *ibid.*, p. 225; (d) H. K. Hall, Jr., and C. H. Lueck, *J. Org. Chem.*, **28**, 2818 (1963). (e) R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 194.

(11) Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared absorption spectra were made with a Perkin-Elmer Model 21 spectrophotometer.

The reaction mixture was refluxed (132°) and sampled at intervals. The cooled samples were inserted into a 0.1-mm. NaCl infrared cell and scanned in the 4.0–6.0-μ region. The absorbance at λ_{max} 4.45 μ was compared with a plot of absorbance *vs.* concentration determined from spectra of standard solutions of ethylene diisocyanate in chlorobenzene.

B. Codistillation of Ethylene Diisocyanate with the Solvent.—A solution of 1.0 g. (0.0068 mole) of II in either 49 g. of *o*-dichlorobenzene (180° at 760 mm.) or 1-chloronaphthalene (220–230° at 100–200 mm.) was distilled with and without phosgene passing through the distillation apparatus. The yields of ethylene diisocyanate according to the infrared spectra of the distillates were 40 and 50%, respectively.

C. Dehydrochlorination with Triethylamine.—To a suspension of 78 g. (0.525 mole) of II in 1500 ml. of benzene a solution of 50.5 g. (0.50 mole) of triethylamine in 250 ml. of benzene was added at 30–35° over a period of 40 min. After standing for 30 min. at 45–50°, 66.1 g. (96%) of triethylamine hydrochloride was removed by filtration. The filtrate was heated to 70–75° and about 10 g. of phosgene was added. The solution was cooled and filtered (1.3 g. of solids) and after evaporation of the solvent and distillation *in vacuo*, 38.6 g. (69%) of ethylene diisocyanate, b.p. 65–68° (7.5 mm.), b.p. 77–80°, 16 mm.), lit.[2] b.p. 75–76° (14 mm.), n^{23}D 1.4472°, were obtained.

The diethylurethane obtained on treatment with excess ethanol had m.p. 107–108° (lit.[12] m.p. 110°). The mixture melting point with a sample prepared from ethylene diamine and ethyl chloroformate[13] showed no depression.

Carbonylbisimidazolidinone-2 (XIII). A. From Ethyleneurea and II.—A mixture of 1.72 g. (0.02 mole) of ethyleneurea and 2.97 g. (0.02 mole) of II in 60 ml. of ethylene dichloride was refluxed for 5 hr. with nitrogen passing through the reaction mixture to remove the generated hydrogen chloride. Evaporation afforded 3.5 g. (88%) of carbonylbisimidazolidinone-2: m.p. 218–222°; λ_{max}^{KBr} (infrared) 3.11, 5.78, 5.94, 6.72, 7.1, 7.4, 7.95, 8.8, and 9.4 μ.

Anal. Calcd. for $C_7H_{10}N_4O_3$: C, 42.42; H, 5.09; N, 28.27. Found: C, 42.62; H, 5.27; N, 28.32.

B. From Ethyleneurea and Ethylene Diisocyanate.—A mixture of 0.101 g. (0.001175 mole) of ethyleneurea and 5.03 g. (0.0449 mole) of ethylene diisocyanate was heated to 68° (12 mm.) when the formation of a precipitate was observed. Removal of the excess diisocyanate *in vacuo* gave 0.275 g. (calculated, 0.233 g.) of XIII. The infrared spectrum of the residue after trituration with chloroform was identical with that of XIII obtained according to A.

Ethylenedicarbamoyl Chloride (XIV).—To 100 ml. of benzene saturated with hydrogen chloride, 0.574 g. (0.005 mole) of ethylene diisocyanate in 30 ml. of benzene was added dropwise with stirring. An immediate precipitation was observed. The excess hydrogen chloride was removed with nitrogen and filtration afforded 0.611 g. (72%) of ethylenedicarbamoyl chloride XIV: m.p. 95–97° (resolidified above 100° and remelted at 145–150°); $\lambda_{max}^{CHCl_3}$ (infrared) 2.95 (NH) and 5.67 μ (C=O). The infrared spectrum of the resolidified material in chloroform was identical with the infrared spectrum of II.

Anal. Calcd. for $C_4H_6Cl_2N_2O_2$: Cl, 38.20. Found: Cl, 38.69.

Dehydrochlorination of Methyl-2-imidazolidinone-N-carbonyl Chloride (IIa).—To a stirred suspension of 16.3 g. (0.1 mole) of IIa in 350 ml. of benzene there was added dropwise during 10–20 min. 10.0 g. (0.099 mole) of triethylamine. The temperature rose from 31.5 to 35° by the heat of reaction. The mixture was stirred another hour at 35–45° and worked up in the same way as applied to the ethylene diisocyanate preparation. From the 13.3 g. of pale yellow, crude concentrate there was obtained on distillation 8.7 g. (69%) of 1,2-diisocyanatopropane (XIa), b.p. 81° (19 mm.) and 70° (12.5 mm.), n^{24}D 1.4407.

Reaction of 1,2-Diisocyanatopropane with Aniline.—To 2.53 g. (0.02 mole) of 1,2-diisocyanatopropane in 40 ml. of benzene was added a solution of 1.87 g. (0.02 mole) of aniline in 30 ml. of benzene. After reflux for 16 hr. at 80°, 0.109 g. of fine needles, m.p. 235–239°, was filtered off. Evaporation of the solvent afforded 4.265 g. (97%) of methylimidazolidin-2-one-1-carboxanilide, m.p. 120–130°, recrystallized (ethanol) m.p. 145–147°.

Anal. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98; N, 19.17 Found: C, 60.10; H, 5.98; N, 19.15.

The higher melting (235°) material according to its infrared spectrum is believed to be the straight-chain bisurea.

Acknowledgment.—The authors wish to express their gratitude to Mr. B. Tucker and Mr. F. Geremia for valuable assistance in the experiments and in the infrared determinations.

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[12] T. Curtius, *J. prakt. Chem.*, [2] **52**, 210 (1895).

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Some Reactions of Ethylene Diisocyanate

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Ethylene diisocyanate reacts with active hydrogen compounds such as primary and secondary amines, alcohols, and mercaptans to form the novel, cyclic 1:1 adducts, 1-substituted 2-imidazolidinones, in high yield. Even with excess of the active hydrogen compound (ethanol) there is a considerable yield of the 1:1 cyclic adduct as opposed to the expected 1:2 linear adduct, the bisurethan; however, trimethylene diisocyanate appears to have much less tendency to produce the analogous cyclic 1:1 adducts (hexahydropyrimidones).

In the course of our study of the reaction of ethylene diisocyanate (I), we have established that by far the preferred course of reaction of I with an active hydrogen compound (II) is the formation of the cyclic monoadduct (III), a derivative of imidazolidinone, rather than the linear bisadduct (IV). The literature contains brief reference by Naegli and Schroeter[2,3] only to the possibility of the existence of such cyclic compounds. However, there is abundant evidence for the formation of the linear bisadducts[4-6] such as the bisethylurethan (IVa) and the bisphenylurea (IVb) as shown by Curtius and Fischer. Presumably, these cyclic materials, IIIa and IIIb, were overlooked.

Preliminary evidence that the cyclic products have formed came about by the observation during a kinetic study that the infrared spectrum of a reacting mixture of butanol with ethylene diisocyanate exhibited development of a carbonyl triplet, $\lambda_{max}^{dioxane}$ 5.57, 5.69, 5.8 μ, whereas under the same conditions hexamethylene diisocyanate reacted only to form a singlet, $\lambda_{max}^{dioxane}$ 5.79 μ. Species such as IVa or the hexamethylene homolog would be expected to have a single carbonyl, whereas IIIa (and mixtures of IIIa with IVa) would have at least two carbonyl absorptions.

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[1] To whom inquiries should be directed.

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[5] T. Curtius, *J. prakt. Chem.*, **52**, 210 (1895).

[6] T. Curtius and Hechtenberg, *ibid.*, **105**, 285 (1923).