[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION OF DAINIPPON PRINTING INK MFG. CO., LTD.]

New Reactions of Organic Isocyanates. I. Reaction with Alkylene Carbonates

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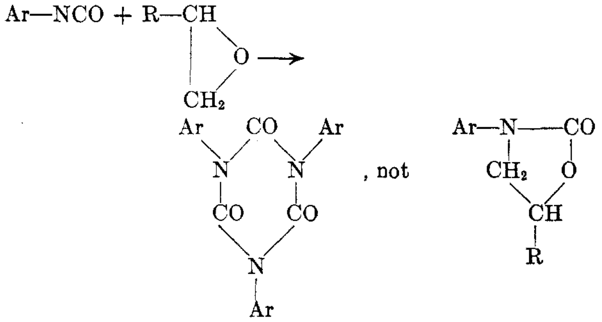
Phenyl isocyanate and ethylene carbonate in the presence of a tertiary amine as catalyst give a crystalline product on heating at 70°. If the reaction is carried out at 130°, 3-phenyloxazolidone-2 is obtained in good yield with elimination of carbon dioxide. A molecular complex of triphenylisocyanurate and ethylene carbonate is proposed for the structure of the former product. Chemical behavior of this complex is discussed in comparison with that of triphenylisocyanurate. Other combinations of various isocyanates and carbonates were also examined.

In recent years, Jones and Savill[1] tried to prepare *N*-substituted oxazolidones by condensation of epoxides with aromatic isocyanates in the presence of basic catalyst, and found that the trimerization of isocyanate alone proceeded smoothly contrary to their expectation.

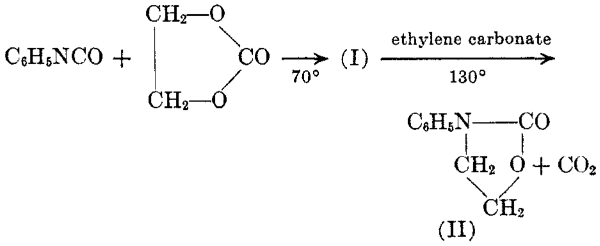


In the course of a study on polyurethane coating material using diisocyanate, we found, independently of Jones's work, that the mixture of tolylene diisocyanate and epichlorohydrine was polymerized at room temperature by adding a small amount of tertiary amine, to produce an insoluble and infusible resinous product. Succeeding experiments have revealed that this polymerization was based on base-catalyzed trimerization of the NCO- group, greatly accelerated in the presence of 1,2-epoxides.

This unexpected phenomenon has led us to extend the research to a wider scope, not only with epoxy compounds but also with other types of reactive cyclic compounds. As a result we have found a series of interesting new reactions of organic isocyanates, and in this paper we report the reaction with alkylene carbonates.

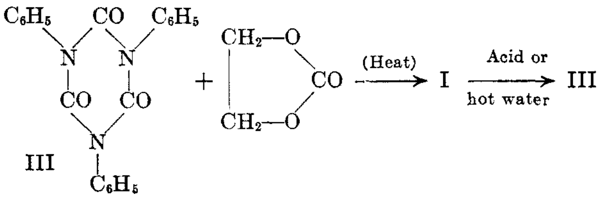
The reaction between isocyanates and alkylene carbonates has not yet been reported in the literature. No change was observed when these two were mixed in the absence of catalyst, but an apparent reaction was observed on adding a trace of tertiary amine. For example, if a few drops of *N*-methylmorpholine was introduced to the mixture of tolylene diisocyanate and ethylene carbonate, the viscosity gradually increased with considerable heat evolution, and finally a transparent, brittle, resinous product was formed, while the addition of catalyst to tolylene diisocyanate without ethylene carbonate did not show any reaction at all under similar conditions. The high polymer thus formed, when heated at 130° or above, began to decompose with a large amount of carbon dioxide evolution and finally a highly viscous substance was left.

In order to investigate this polymer formation and decomposition reaction, we used a model experiment of monofunctional isocyanates. When phenyl isocyanate, ethylene carbonate, and a trace of *N*-methylmorpholine were heated at 70° for a few hours, a crystalline mass was formed and after further heating for about an hour the irritating odor of isocyanate completely disappeared. This crystalline product (I) can be recrystallized from various organic solvents and has a melting point of 222°. I, when heated above 130°, preferably in the presence of excess carbonate, began to decompose with evolution of carbon dioxide, and 3-phenyloxazolidone-2 (II) was isolated in excellent yield from the residue. The amount of carbon dioxide evolved was also almost quantitative (one mole of carbon dioxide from one mole of phenyl isocyanate). These processes can be shown as follows:



(II)

Analytical data of I agree with the formula $3(C_6H_5NCO)\cdot(C_3H_4O_3)$. If treated with dilute mineral acid or hot water, I gave triphenylisocyanurate (III). On the other hand, on heating III and ethylene carbonate in an inert solvent, a crystalline product was obtained which was shown to be I by its melting point and by its infrared absorption spectrum.



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(1) J. I. Jones and N. G. Savill, *J. Chem. Soc.*, 4392 (1957).

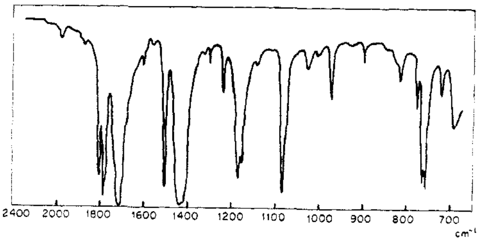
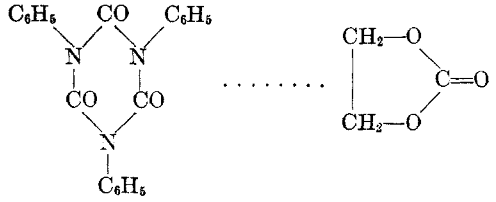


Fig. 1. Infrared spectrum of I (solid in KBr)

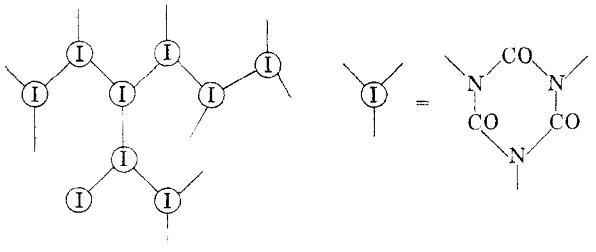
The infrared spectrum of I contains almost all the principal bands of III and ethylene carbonate and no new peak of appreciable strength appears. Molecular weight of I determined by Rast's method was 230, about half the value of that calculated for the formula $3(C_6H_5NCO)\cdot C_3H_4O_3$. I gives a clear x-ray diffraction pattern, which is quite different from those of III and ethylene carbonate. From the facts described above, I is best represented, we think, as an *equimolar molecular complex* of III and ethylene carbonate. The difference between the calculated and observed values of molecular weight might be explained by complete dissociation of the complex to the separate parts under the conditions of the molecular weight determination.



Direct evidence is not presented in this paper to the effect that I is really a molecular complex. Interaction forces between the components and effects of substituents will be discussed later.

From these model experiments it is clear that the base-catalyzed trimerization of the NCO- group is exceedingly accelerated by the presence of ethylene carbonate, and the trimer formed a molecular complex with ethylene carbonate.

In the case of diisocyanate a three-dimensional polymer is thus formed, which has a network structure knotted by an isocyanurate ring. We think these polymers should be called "Polyisocyanurate."



An isocyanate trimer, unlike its dimer, is known to be very stable toward various reagents.[2] To our surprise, I reacted with certain reagents ineffective with the corresponding isocyanate trimer. For instance, heating with aniline at 160° converted I to diphenylurea in good yield, whereas trimer was recovered unchanged under the same conditions. Lower alcohols did not attack I at refluxing temperature, but a higher one, for example octanol, gave its carbanilate almost quantitatively on heating at 170°. In this case also, carbanilate formation did not proceed at all with trimer alone.

$$I + 3\ C_6H_5NH_2 \longrightarrow 3\ C_6H_5NHCONHC_6H_5$$

$$I + 3\ C_8H_{17}OH \longrightarrow 3\ C_6H_5NHCOOC_8H_{17}$$

Aliphatic isocyanates reacted with alkylene carbonates in a similar way, but more slowly, to produce corresponding trimers, and here the formation of oxazolidone with elimination of carbon dioxide seemed rather difficult. Hexamethylene diisocyanate, for example, after heating at 120° for one and a half hours gave a light-colored, transparent resin, which was difficult to decompose at higher temperatures. When the mixture of *n*-butylisocyanate and ethylene carbonate was heated in the presence of catalyst at 120–130°, isocyanate was entirely consumed after a few hours, and two oily layers separated on cooling. They were recognized to be tri-*n*-butylisocyanurate and ethylene carbonate, respectively. Isolation of a molecular complex of the type described above was unsuccessful in this case.

Various *para*-substituted phenyl isocyanates and some alkylene carbonates were also examined. Results are listed in Table I.

In case of dichloroethylene carbonate and vinylene carbonate, side reactions (decomposition and polymerization of carbonate) proceeded predominantly to produce dark substances, and neither complex nor oxazolidone could be obtained.

EXPERIMENTAL

Nacconate-65 (National Aniline Division, Allied Chemical Corp.) was used as tolylene diisocyanate, with distillation before use. Various monoisocyanates were prepared from the corresponding amines by phosgenation in the usual way. Their boiling points were: phenyl, 64–65° (23 mm.); *p*-chlorophenyl, 96° (21 mm.); *p*-tolyl, 79–81° (20 mm.); *p*-ethoxyphenyl, 124° (21 mm.); *n*-butyl, 114–116°, respectively. Triarylisocyanurates were obtained from the corresponding monomers by standing overnight with about an equal amount of epoxide, for example epichlorohydrine, and a small amount of tertiary amine. They usually separated almost quantitatively as big crystals. After filtering and washing, they were pure enough for most purposes.

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(2) R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Revs.*, **57**, 47 (1956).

(3) M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, **77**, 3789 (1955).

TABLE I

REACTION PRODUCTS FROM ISOCYANATES AND ALKYLENE CARBONATES

Isocyanate	M.P. of Trimer, °C.	Carbonate	Complex		Oxazolidone	
			M.P., °C.	Yield, %	M.P., °C.	Yield, %
Phenyl-	273	Ethylene-	220–222	98	117–119	92
p-Cl-Phenyl-	322	Ethylene-	240 (dec.)	59	116–117	70
p-CH_3-Phenyl-	263	Ethylene-	Not isolated		90	63
p-C_2H_5O-Phenyl-	246	Ethylene-	Not isolated		95–96	78
2,4-Tolylenedi-	350<	Ethylene-	Resin		Not isolated	
n-Butyl-	b_2:148–149	Ethylene-	Not isolated		—	—
Hexamethylenedi-	350<	Ethylene-	Resin		—	—
Phenyl-	273	Propylene-[a]	*ca.* 140 (dec.)[b]	55	81–82	94[c]
Phenyl-	273	Chloroethylene-	*ca.* 155 (dec.)[b]	75	Not isolated[d]	

[a] Five-membered methyl ethylene carbonate. [b] Showed indistinct decomposition points. [c] 3-Phenyl-5-methyl-oxazolidone-2 was obtained. [d] On heating, violent gas evolution was observed, and a dark, resinous substance was left.

Chloroethylene carbonate was synthesized by chlorinating ethylene carbonate by Newman's method,[3] b.p. 115–116° (16.5 mm.).

Reaction of tolylenediisocyanate with ethylene carbonate. To a mixture of tolylenediisocyanate, 17.4 g., and ethylene carbonate, 35.2 g., was added a few drops of *N*-methylmorpholine. The temperature began to rise within a few minutes and the viscosity also increased gradually. After about an hour it could not be poured and finally a light yellow, transparent resin was formed. If too much catalyst is present, the reaction proceeds so violently that the resin is often partly charred. The polymer thus formed, when heated over 130°, began to melt again with the evolution of a large amount of carbon dioxide. The final product, after complete gas generation, was highly viscous. Isolation of the corresponding bisoxazolidone was unsuccessful. If the resin was finely powdered and was subjected to decomposition at 160°, 1 hr. was enough for complete degradation.

Reaction of phenylisocyanate with ethylene carbonate to form I. A 12.0-g. sample of phenyl isocyanate, 13.2 g. of ethylene carbonate, and a few drops of *N*-methylmorpholine were heated at 70° for several hours. A crystalline mass was formed, suddenly in most cases, and after further heating for about an hour the irritating odor of phenyl isocyanate completely disappeared, and then the reaction was complete. After cooling, the product was filtered and washed with cold benzene two or three times to remove excess carbonate. Crude I, m.p. 215–218°, weighed 14.5 g. (98% yield). By recrystallization from dry benzene, the melting point was raised to 220–222°.

Anal. Calcd. for $C_{24}H_{19}O_6N_3$ (445): C, 64.71%; H, 4.30%; N, 9.43%. Found: C, 64.73%; H, 4.55%; N, 9.64%. Mol. wt. (Rast), 225 and 235 (average 230).

Reaction of phenylisocyanate dimer with ethylene carbonate. Dimer was obtained from monomer and pyridine by Blair's method.[4] A 1.2-g. sample of dimer (m.p., 175°) and 0.9 g. of ethylene carbonate in dry benzene were heated to reflux with a trace of *N*-methylmorpholine. On cooling the clear solution I separated as white needles, m.p. 220°.

Formation of I *from triphenylisocyanurate and ethylene carbonate.* A 3.0-g. sample of triphenylisocyanurate and 1.0 g. of ethylene carbonate were heated in 10 cc. of dry benzene. Triphenylisocyanurate gradually dissolved, and after distilling the solvent and recrystallizing from benzene there was obtained 2.6 g. of I, which was identified by melting point and infrared spectrum.

3-Phenyloxazolidone-2. A 14.8-g. sample of I, 12.0 g. of ethylene carbonate, and a few drops of *N*-methylmorpholine were heated at 160°. Gas evolution was observed immediately, and the reaction was complete after a few hours. The mixture solidified on cooling, and on washing with cold mixture of petroleum ether–ethyl acetate (1:1) there was obtained 15.0 g. (92% yield) of crude I product. Repeated recrystallization from ethanol raised the melting point to 117–119°. It was shown to be 3-phenyloxazolidone-2 by comparing infrared spectrum with an authentic sample. Similar results were also obtained when phenyl isocyanate and ethylene carbonate were heated at 160° from the beginning.

Reaction of I *with aniline.* A 4.5-g. sample of I and 8.0 g. of aniline were heated at 160° with a small amount of *N*-methylmorpholine. After about 3 hr. fine needles separated, which was shown to be *N,N'*-diphenylurea, m.p. 234–235°, yield 5.1 g. (80%). In the case of aniline and triphenylisocyanurate (III) instead of I, most of the starting material was recovered unchanged after a longer heating period.

Reaction of I *with 2-ethylhexanol.* A mixture of 5.0 g. of I, 20 g. of 2-ethylhexanol [b.p. 84–86° (15 mm.)], and a small amount of *N*-methylmorpholine was heated at 170–180° for 7 hr. After about 0.5 hr. I was completely dissolved. After distilling the excess alcohol, 8.3 g. (99%) of a colorless liquid was obtained, b.p. 160–175° (5 mm.). After rectification it was shown to be 2-ethylhexyl carbanilate, from a comparison of the infrared spectrum with an authentic sample, b.p. 157–159° (3 mm.). On heating triphenylisocyanurate (III), 2-ethylhexanol, and a trace of *N*-methylmorpholine under the same condition, (III) was recovered entirely unchanged.

Reaction of n-butylisocyanate and ethylene carbonate. A 29.7-g. sample of *n*-butylisocyanate and 26.4 g. of ethylene carbonate were heated with 0.5 g. of *N*-methylmorpholine at 120–130° for 5 hr. The isocyanate was then completely consumed and two oily layers separated on cooling. In the case where ethylene carbonate was not present, most of the isocyanate was recovered unchanged after refluxing for 36 hr. in a bath of 140°. Distillation of the reaction mixture under reduced pressure gave 24 g. of a colorless liquid, b.p. 149–152° (1.5 mm.). It was identified as tri-*n*-butylisocyanurate, by comparing infrared spectrum with an authentic sample. The authentic sample was prepared from *n*-butylisocyanate by the action of sodium methylate, b.p. 149–150° (2 mm.).

Anal. Calcd. for $C_{15}H_{27}O_3N_3$: N, 14.13%. Found: N, 14.40%. Mol. wt., calcd. for $C_{15}H_{27}O_3N_3$, 297. Found (cryoscopic method, nitrobenzene), 304 (average of two determinations.

Various isocyanates and carbonates. From mixtures of isocyanates and carbonates other than those described above, were obtained the corresponding complexes and oxazolidones which are listed in Table I. They were identified by melting point, analysis, and infrared spectra.

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(4) J. S. Blair and G. E. Smith, *J. Am. Chem. Soc.*, **56**, 907 (1934).

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[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

Maleamic and Citraconamic Acids, Methyl Esters, and Imides

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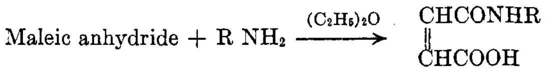
A series of maleamic and citraconamic acids has been made by the reaction of primary and secondary aliphatic and heterocyclic amines with maleic and citraconic anhydrides. Methyl esters have been prepared from several of these acids. It has been found possible to prepare *N*-alkylmaleimides and citraconimides by cyclization of the *N*-alkylmaleamic and citraconamic acids under much milder reaction conditions than had formerly been used.

The preparation of numerous maleamic and citraconamic acids, their methyl esters, and their imides was undertaken because these substances were needed as intermediates for various other projects. Except for a few primary amines[1–4] the reaction of aliphatic amines with maleic anhydride had not been investigated. A few maleamic acids have been mentioned but not well characterized in recent patents.[5,6] The reaction of amines with citraconic anhydride has not been reported. Although considerable work has been described both in the literature and in patents on *N*-arylmaleamic acids and imides,[7] little investigation has been devoted to the synthesis of *N*-alkylmaleimides and citraconimides. Only the *N*-methyl- and *N*-ethylmaleimides[2,8,9] have been reported in the early literature. One or two other *N*-alkylmaleimides have been referred to in some recent patents, but no descriptions of the method of preparation or characterization of the products was given. *N*-Phenylcitraconimide has been reported by Reissert.[10]

The presentation of the material of the current work has been subdivided, for convenience, according to the types of compounds involved.

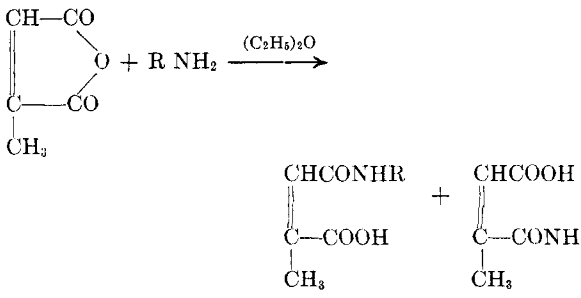
I. *Maleamic and citraconamic acids.* A. *Maleamic acids* (Table I A). Maleic anhydride reacted with a variety of primary and secondary aliphatic and heterocyclic amines, equimolar amounts of the reactants being used in cold dilute ether solution.



$$\text{Maleic anhydride} + \text{R NH}_2 \xrightarrow{(C_2H_5)_2O} \begin{array}{l}\text{CHCONHR}\\ \|\\ \text{CHCOOH}\end{array}$$

Excellent yields of the crystalline maleamic acids resulted in most cases. In a few instances, as with some of the heterocyclic amines, the yields of the maleamic acids were poorer. The amine salt of the maleamic acid was obtained as a side product in some of these runs. A few of these have been isolated and characterized (see Experimental section).

B. *Citraconamic acids* (Table I B). Several representative amines reacted with citraconic anhydride under conditions similar to those described above. In these reactions primary amines invariably gave a mixture of two *isomeric* amide



acids in excellent yields. These mixtures of isomers could usually be separated by their differential solubilities in suitable solvents. When secondary amines were used in this reaction only a single product was isolated. The latter result is consistent

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(1) R. Anschütz, *Ber.*, **20**, 3214 (1887).

(2) A. Piutti and E. Giustiniani, *Gazz. chim. ital.*, **26 I** 431 (1896).

(3) Y. Liwschitz, Y. Edlitz-Pfeffermann, and Y. Lapidoth, *J. Am. Chem. Soc.*, **78**, 307 (1956).

(4) L. E. Coleman, Jr., J. F. Bork, and H. Dunn, Jr., *J. Org. Chem.*, **24**, 135 (1959).

(5) J. M. Weiss and R. P. Weiss, U. S. Patent **2,306,918**, Dec. 29, 1942.

(6) J. J. Giammaria, U. S. Patent **2,727,862**, Dec. 20, 1955.

(7) N. E. Searle, U. S. Patent **2,444,536**, July 6, 1948. This single patent is cited, since it is directly related to the current work.

(8) E. Giustiniani, *Gazz. chim. ital.*, **22 I**, 169 (1892).

(9) A. Piutti, *Gazz. chim. ital.*, **18**, 483 (1888).

(10) A. Reissert and F. Tiemann, *Ber.*, **19**, 623 (1886).