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New Reactions of Organic Isocyanates. II. Reaction of Aromatic Isocyanates with β-Propiolactone

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Phenyl isocyanate and β-propiolactone react exothermically with each other in the presence of tertiary amines under mild conditions affording carbon dioxide , *N,N'*-diphenylurea, acrylic anhydride and acrylanilide. A possible mechanism is proposed to explain the process. A plastic foam can be made using polyester and diisocyanate as basic ingredients.

In the previous paper,[1] we explained that organic diisocyanates were easily polymerized at room temperature in the presence of cyclic ethylene carbonate and a tertiary amine to produce a transparent, brittle resin, and that the polymer thus formed was decomposed at elevated temperature releasing carbon dioxide. The mechanism of this polymerization and decomposition was also elucidated by a model experiment of monofunctional phenyl isocyanate. Formerly it was known that a reaction occurs between isocyanates and epoxides either to yield oxazolidones[3,4] or to cause trimerization of isocyanate used.[1,2] From these facts, we presumed the possibility for some other reactive cyclic compounds to react with isocyanate accompanying opening of the ring structure. In this paper, we present an interesting reaction between aromatic isocyanate and β-propiolactone hitherto unseen in the literature.

The method of synthesizing β-propiolactone from ketene and formaldehyde was first discovered by Küng,[5] and since then considerable attention has been paid to this reagent (β-propiolactone) as a useful synthetic chemical. An extensive study was made by Gresham[6,7] on the reactivity of this compound with various reagents, including water, amines, alcohols, mercaptans, phenols, carboxylic acids, etc. When added to β-propiolactone, the reagents caused ring opening and in result β-substituted propionic acids or their derivatives were obtained as primary products. Apart from the above, the reaction in our case involves a proton transfer and yields acrylic acid derivatives.

In a clean vessel attached with a drying tube to prevent moisture were placed 2,4-tolylene diisocyanate and β-propiolactone. Then a trace of tertiary amine was added and within a few minutes the mixture started to release a gas and this reaction became more vigorous with the increase in temperature and viscosity. The gas was identified as carbon dioxide from the familiar milky deposit formed in the aqueous solution of lime. The residue after completion of reaction, was a brittle plastic foam easily crushable into powder. The polymer thus formed was infusible and insoluble in all common solvents and was considered to have a network structure. The reaction proceeded exothermically, all the reaction being carried out without external heating. In the absence of catalyst, the reaction does not proceed at all, even at an elevated temperature. In order to elucidate the mechanism of the reaction, we performed a model experiment using monofunctional phenyl isocyanate. The reaction was carried out in an inert solvent to prevent side reactions due to overheating. When the mixture of an equimolar amount of phenyl isocyanate and β-propiolactone was heated at 50° in dry benzene with *N*-methylmorpholine as catalyst, carbon dioxide was soon released and simultaneously white crystals began to precipitate. When gas release almost ceased, the mixture was refluxed for a couple of hours to complete the reaction. The crystal was filtered after cooling and was identified as *N,N'*-diphenylurea. The yield was about 60%. Neither longer heating nor use of a larger quantity of each component (molar ratio of isocyanate to β-propiolactone, $^1/_2$–$^2/_1$) caused any appreciable increase in the yield. After removing the solvent and residual volatile starting material from the filtrate, there remained a viscous oily liquid. This oily liquid was distilled under vacuum to give a colorless liquid, boiling at 65–75° at 18 mm. It had an unpleasant and irritating odor like acetic anhydride, and did not mix with cold water. But, after shaking for a short time in a warm water bath, it dissolved into a clear aqueous

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(1) R. Tsuzuki, K. Ichikawa, and M. Kase, *J. Org. Chem.* **25**, 1009 (1960).

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

(3) K. Gulbins and K. Hamann, *Angew. Chem.*, **70**, 705 (1958).

(4) G. P. Speranza and W. J. Peppel, *J. Org. Chem.*, **23** 1922 (1958).

(5) F. E. Küng, U. S. Patent **2,356,459** (1944).

(6) T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Am. Chem. Soc.*, **70**, 998 (1948); *J. Am. Chem. Soc.*, **71**, 661 (1949); *J. Am. Chem. Soc.*, **71**, 2807 (1949); *J. Am. Chem. Soc.*, **72**, 72 (1950); *J. Am. Chem. Soc.*, **73**, 2345 (1951); *J. Am. Chem. Soc.*, **74**, 1323 (1952).

(7) T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert and F. T. Fiedorek, *J. Am. Chem. Soc.*, **73**, 3168 (1951).

solution which was acidic to litmus. If methanol was added, the distillate soon began to give an unpleasant odor peculiar to methyl acrylate and this compound was further identified after separation as methyl acrylate by infrared spectrum. From these results, the colorless liquid collected as above was concluded to be acrylic anhydride. The yield was about 33% and our attempts to obtain a better yield of the pure product, comparable to that of diphenylurea, were unsuccessful, presumably due to its highly polymerizing trend. The residue, from which acrylic anhydride was recovered, was again distilled under higher vacuum and yielded a white solid, b.p. 140–155° (3 mm.). This solid, after recrystallizing from methanol-water, was identified as acrylanilide from the analytical and spectral data. The yield of the crude product was about 25%. From these experimental observations a probable mechanism of the reaction was proposed as follows:

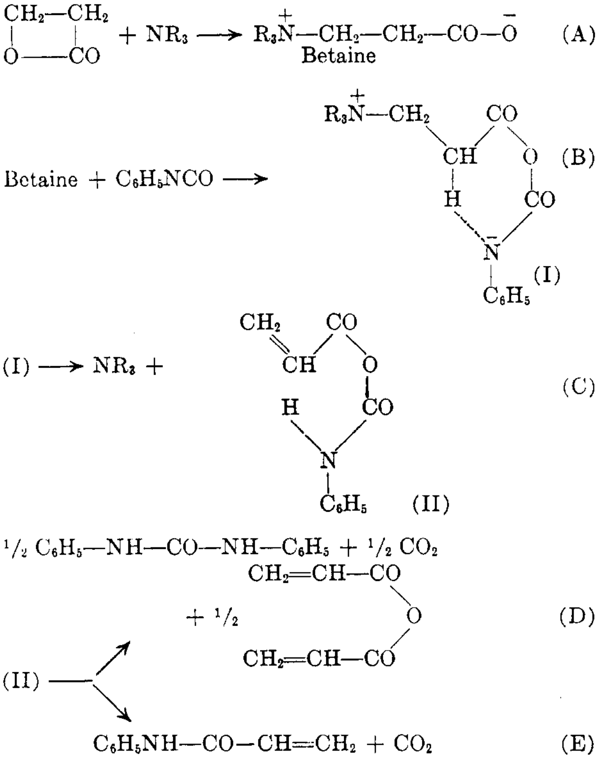

Chart 1

It is shown by Gresham[7] that betaines are formed from β-propiolactone and various tertiary amines. Hence it is not unreasonable to assume that betaine formation is the first step of the reaction (A). The electrophilic attack of the carbonyl of the NCO-group on the carboxyl anion of the betaine follows as the second step (B), to yield an intermediate "Zwitterion" (I). This intermediate, by proton transfer and cyclic rearrangement and by the succeeding elimination of NR_3 and double bond formation, changes to the mixed anhydride (II) of acrylic acid and phenylcarbamic acid (C). (II) is unstable and soon decomposes with carbon dioxide generation by the well known dual path (D and E). Path D yields *N,N'*-diphenylurea and acrylic anhydride, while path E results in formation of acrylanilide.

The reaction does not proceed, as indicated above, in the absence of tertiary amine and the role played by this catalyst seems to be somewhat more important than a mere accelerating action. To find out an evidence for the above, we attempted to isolate betaine from β-propiolactone and *N*-methylmorpholine and to have it react with phenyl isocyanate in an inert solvent. Betaine and phenyl isocyanate were mixed in dry benzene in about equimolar quantities in a moisture free vessel and the suspension was allowed to stand in a warm bath. In a few minutes carbon dioxide began to evolve and this reaction proceeded with considerable ease. After standing overnight the precipitate was filtered and was found to be diphenylurea. Acrylic anhydride and anilide were recovered from the filtrate, the yield of each product being almost the same as the case of the reaction between isocyanate and lactone. The betaine was so hygroscopic that the complete exclusion of moisture from the system could not be expected. It is believed, however, that a considerable yield of diphenylurea recovered in the above experiment is mostly the result of interaction of phenyl isocyanate with betaine, not with moisture absorbed from the air, since, if the latter were the case, acrylanilide and anhydride should not have been formed. Our attempt to isolate the betaines from β-propiolactone with triethylamine and pyridine ended unsuccessfully, because of their strong trend to polymerize the β-lactone; hence the direct reaction between phenyl isocyanate and betaine was confirmed only in the case of *N*-methylmorpholine. However, addition of triethylamine or pyridine was also found greatly to accelerate the reaction between isocyanate and β-propiolactone, controlling polymerization of the lactone to a minor extent. Dimethylaniline proved an ineffective catalyst among those tested. When we used this catalyst, no gas was released nor was any solid precipitated even after three hours' refluxing in benzene. In Gresham's reports,[7] there is not to be found any example where *N,N*-dialkylaniline is treated with β-propiolactone. In our experiment, dimethylaniline proves to be far less effective towards the lactone in betaine formation as well as in polymerization. These results present further evidence that betaine formation is the first step of this reaction.

The yield of the products and the volume of carbon dioxide released in this reaction vary considerably according to the kind of catalyst and solvent used; for example, when we used triethyl-

TABLE I

REACTION PRODUCTS FROM PHENYL ISOCYANATE AND β-PROPIOLACTONE

Moles of Material		Catalyst,		Yield of Product, %			Moles of CO_2
C_6H_5NCO	BPL[a]	G.	Solvent	Urea[b]	Anilide[c]	Trimer[d]	Evolved
0.20	0.20	M,[e] 1.5	Benzene	58	26	0	—
0.20	0.20	M, 1.5	Benzene	58	25	0	—
0.010	0.010	M, 0.04	Benzene	60	—	0	0.0063
0.010	0.010	M, 0.04	Benzene	56	—	0	0.0063
0.020	0.010	M, 0.04	Benzene	40	—	0	0.0073
0.010	0.020	M, 0.04	Benzene	65	—	0	0.0070
0.20	0.20	M, 1.5	Acetonitrile	0	35	46	—
0.010	0.010	M, 0.04	Acetonitrile	—	—	—	0.0049
0.20	0.20	P, 1.5	Benzene	Trace	27	57	—
0.010	0.010	P, 0.04	Benzene	—	—	—	0.0055
0.010	0.010	P, 0.04	Benzene	—	—	—	0.0058
0.10	0.10	T, 0.75	Benzene	Trace	71	0	—
0.010	0.010	T, 0.04	Benzene	0	—	0	0.0093
0.010	0.010	T, 0.04	Benzene	0	—	0	0.0095
0.010	0.010	T, 0.04	Acetonitrile	0	—	40	0.0047

[a] β-Propiolactone. [b] *N,N′*-Diphenylurea. [c] Acrylanilide. [d] Phenyl isocyanate trimer. [e] M; *N*-Methylmorpholine, P; Pyridine, T; Triethylamine.

amine as catalyst and benzene as solvent, the volume of carbon dioxide released was found to be the largest. The solid product isolated was almost exclusively acrylanilide, about 70% in yield. The amount of carbon dioxide released corresponds to 0.95 mole out of one mole of the starting material. This shows that the reaction proceeds principally along path E. On the other hand, in the case of *N*-methylmorpholine, as described before, about 60% yield of diphenylurea (and 25% of acrylic anhydride) is recovered and carbon dioxide collected is about two thirds of the above. This agrees with the case where 20% of II decomposes along path D and the residue goes along E. When pyridine is used as catalyst, the trimer of phenyl isocyanate (triphenyl isocyanurate) is also produced along with acrylanilide, the volume of carbon dioxide being the least. The effect of solvent towards the mode of decomposition is also to be noted, although only two (benzene and acetonitrile) were examined. Trimerization of phenyl isocyanate is also observed in the latter. Results are listed in Table I.

With respect to the mixed anhydrides of various carboxylic acids and carbamic acids, especially their mode of decomposition, several results of experiments have been reported.[8-10] However, very little is known about the mixed anhydride of acrylic acid and carbamic acids; the only example is found in the report by Iwakura,[11] who isolated the adduct between tetramethylene diisocyanate and acrylic acid and studied its behavior on heating. Therefore, we studied the adduct between phenyl isocyanate and acrylic acid and its mode of decomposition with or without tertiary amine, and compared the results with those described above. The mixed anhydride of acrylic acid and phenylcarbamic acid is unstable at room temperature, and our trial to isolate the adduct from the reaction mixture proved unsuccessful. Hence, an equimolar quantity of phenyl isocyanate and acrylic acid were mixed and the adduct formed was left to decompose *in situ*. Carbon dioxide released and the products formed were measured and the predominant path taken by the reaction was investigated as before. As a result of the several experiments, it was shown that the effect of catalyst and solvent on the mode of decomposition was not so marked, and no phenyl isocyanate trimer was formed. Results are illustrated in Table II.

Yields in the tables represent the solid products actually collected but not the amounts formed. There is lack of consistency to some extent between the results shown in Table I and Table II and this seems to suggest some complexity involved in the reaction between isocyanate and lactone. It is also difficult to predict the correct mode of decomposition from the quantity of carbon dioxide released because of the disturbance by side reactions such as formation of isocyanate trimer and polymerization of lactone, both of which are not always negligible. But, we believe that the reaction can be explained largely by the mechanism as shown in Chart 1.

In Table II, no phenyl isocyanate trimer is formed, while in the presence of β-propiolactone, as in Table I, it sometimes occurs, especially when pyridine (catalyst) and/or acetonitrile (solvent) are used. Pyridine is well known as an effective catalyst

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(8) J. H. Saunders and R. J. Slocombe, *Chem. Revs.*, **43**, 203 (1948).

(9)(a) C. Naegeli and A. Tyabji, *Helv. Chim. Acta.* **17**, 931 (1934). (*b*) *Helv. Chim. Acta.* **18**, 142 (1935).

(10) S. Petersen, *Ann.*, **562**, 205 (1949).

(11) Y. Iwakura and K. Yonesima, *J. Chem. Soc. Japan* **70**, 151 (1949).

TABLE II

REACTION PRODUCTS FROM PHENYL ISOCYANATE AND ACRYLIC ACID

Moles of Material		Catalyst,		Yield of product, %			Moles of
C_6H_5NCO	A.A.[f]	g.	Solvent	Urea[b]	Anilide[c]	Trimer[d]	CO_2 evolved
0.10	0.10	M,[e] 0.75	Benzene	73	22	0	—
0.010	0.010	M, 0.04	Benzene	69	—	0	0.0058
0.10	0.10	M, 0.75	Acetonitrile	63	18	0	—
0.010	0.010	P,[e] 0.04	Benzene	62	—	0	0.0067
0.010	0.010	T,[e] 0.04	Benzene	56	—	0	0.0069
0.10	0.10	—	Benzene	70	4	0	—

[a] β-Propiolactone. [b] *N,N'*-Diphenylurea. [c] Acrylanilide. [d] Phenyl isocyanate trimer. [e] M; *N*-Methylmorpholine, P; Pyridine, T; Triethylamine. [f] Acrylic acid.

for polymerizing aromatic isocyanate to its dimer (diaryl uretedion), but not to trimer.[12] But in recent years, it has been revealed[1,2] that trimerization occurs almost exclusively with great ease in the presence of some cyclic compounds (e.g. epoxides and carbonates) by the action of tertiary amines including pyridine. It is supposed that cyclic β-propiolactone also serves as trimerizing agent, and that trimerization of phenyl isocyanate proceeds in the above cases at a comparable rate to that of the principal path shown in Chart 1. In the case of *N*-methylmorpholine and triethylamine, on the contrary, the process leading to elimination of carbon dioxide seems to proceed too fast to allow side reaction (trimerization of isocyanate). Further work is in progress at our laboratory on the effect of polar solvents including acetonitrile, and the result will be reported later.

Figs. 1 and 2 show the curves plotting the quantity of carbon dioxide released against the reaction time, from which an approximate trend of catalyst effectiveness may be seen.

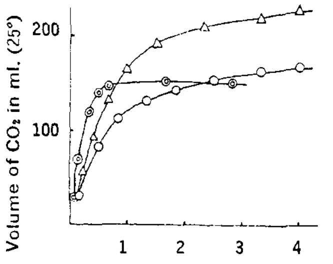

Fig. 1. Gas evolution in the reaction of phenyl isocyanate and β-propiolactone in benzene at 100°.
Catalyst: ○ *N*-Methylmorpholine; △ Triethylamine; ◎ Pyridine

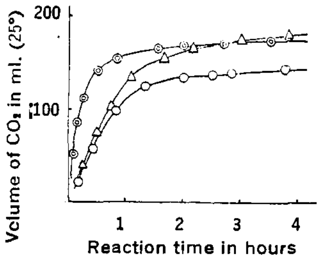

Fig. 2. Gas evolution in the reaction of phenyl isocyanate and acrylic acid in benzene at 100°.
Catalyst: ○ *N*-Methylmorpholine; △ Triethylamine; ◎ Pyridine

EXPERIMENTAL

All melting points and boiling points are uncorrected. Infrared spectra were determined by Koken IR-S Infrared Spectrophotometer.

Materials. β-Propiolactone, commercially available from Celanese Corporation of America, was used after vacuum distillation, b.p. 61.9° (21 mm.). Phenyl isocyanate was prepared from aniline by phosgenation in the usual way, b.p. 59° (18 mm.). Tolylene diisocyanate used was Nacconate 65 (National Aniline Division, Allied Chemical & Dye Corp.), 65/35 mixture of 2,4- and 2,6-isomers. The tertiary amines used as catalyst were dried over potassium hydroxide and then rectified through a good column; *N*-methylmorpholine, b.p. 113-114°; pyridine, b.p. 115.5°; triethylamine, b.p. 89°; dimethylaniline, b.p. 85° (20 mm.). Acrylic acid was synthesized by the acidolysis of methyl acrylate with formic acid, b.p. 49-51° (23 mm.).(C. E. Rehberg. *Org. Syntheses*, **Coll. Vol. III**, 33 (1955)). In the foaming formulation was used Polylite #8651 (Polyester from Japan Reichhold Chemicals, Inc.), acid number 1.8 and hydroxyl number 52.5, as a basic ingredient.

Reaction of phenyl isocyanate with β-propiolactone. A mixture of 14.4 g. (0.2 mole) of β-propiolactone, 23.8 g. (0.2 mole) of phenyl isocyanate and a small amount of *N*-methylmorpholine in 40 ml. of absolutely dry benzene was heated at 50° with exclusion of moisture. The reaction immediately started with the evolution of carbon dioxide and after a short time white needles began to separate. Towards the end of the reaction, the mixture was heated under reflux with occasional shaking. Several hours were enough for the completion of the reaction. After cooling, the precipitate was collected and washed with a small quantity of benzene to give 12.3 g. (58.1% yield) of *N,N'*-diphenylurea, m.p. 234-235°, which was identified by its melting point and infrared spectrum. Recrystallization from glacial acetic acid raised the melting point to 239°. The filtrate obtained by the above-mentioned operations was subjected to a distillation under reduced pressure. After removal of the solvent, acrylic anhydride was collected as a fraction boiling at 65-75° (18 mm.) (lit.[13] b.p. 55-56° (6 mm.), lit.[14] b.p. 97° (35 mm.) and weighed 4.1 g. (32.5% yield). It was identified by comparing its infrared spectrum with that of an authentic sample. Principal bands observed were 1790 cm.$^{-1}$, 1730 cm.$^{-1}$ (C=O), 1630 cm.$^{-1}$, 1400 cm.$^{-1}$, 1005 cm.$^{-1}$, 985 cm.$^{-1}$ (—CH=CH$_2$). Other peaks of remarkable

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

(13) I. A. Arbuzova, S. A. Plotkina, and V. N. Efremova, *Chem. Abstr.*, **50**, 16667 (1956).

(14) Beilsteins Handbuch der Organishen Chemie, Band 2, p. 400.

strength were found at 1172 cm.$^{-1}$, 1100 cm.$^{-1}$ and 1055 cm.$^{-1}$, some of which may be referred to C—O vibration.

The authentic sample was synthesized by the anhydride exchange reaction between acrylic acid and acetic anhydride.[13] Acrylic anhydride obtained as a fraction of vacuum distillation was treated with methanol and further confirmed as methyl acrylate, which was identified by infrared spectrum in the gaseous state after separation by gas chromatography and condensing in a capillary trap dipped in Dry Ice-methanol. The residue, from which acrylic anhydride was recovered, was again distilled under higher vacuum to give 7.3 g. of acrylanilide (25.0% yield), b.p. 140–155° (3 mm.), which solidified by cooling and melted at 93–98°. Recrystallization from methanol-water raised the melting point to 103° (lit. m.p. 105°). It was identified by comparing its melting point and its infrared spectrum with an authentic sample, which was prepared from acrylyl chloride and aniline in benzene. In the infrared spectrum the presence of monosubstituted phenyl (1610 cm.$^{-1}$, 1500 cm.$^{-1}$, 755 cm.$^{-1}$, 685 cm.$^{-1}$), N—H (3360 cm.$^{-1}$, 1550 cm.$^{-1}$), and C═O (1670 cm.$^{-1}$) was found.

Anal. Calcd. for C_9H_9ON: C, 73.45%; H, 6.16%; N, 9.52%. Found: C, 72.30%; H, 6.23%; N, 9.40%.

The last residue was found to be principally polyacrylanilide from the spectral data.

The reaction proceeds in various ways according to the kinds of tertiary amines and solvents used. In the case of a polar solvent especially (acetonitrile) there is a tendency to cause trimerization of phenyl isocyanate as well as polymerization of β-propiolactone. In this case, the volatile solvent was first distilled and then benzene was added, thus separating the phenyl isocyanate trimer (triphenyl isocyanurate) as the crystalline form, which was easily collected by filtration. When trimer was produced along with the diphenylurea, it was possible to separate them by treating with cold chloroform, which is an excellent solvent for the trimer but dissolves the latter to a lesser extent.

4-(2-Carboxyethyl)-N-methylmorpholinium betaine.[7] In a reaction vessel, attached with a drying tube to prevent moisture, was placed 14.4 g. (0.2 mole) of β-propiolactone and 100 ml. of absolutely dry benzene. To the solution was added dropwise 24.2 g. of *N*-methylmorpholine in 20 ml. of benzene in a few minutes under stirring, during which time the temperature was maintained at 20–25°. In a short time the betaine began to precipitate as white crystals, which, after standing overnight, were filtered and washed with benzene as quickly as possible in order to avoid prolonged exposure to atmospheric moisture, and dried; yield 11.5 g. (31.4%), m.p. 111–112° dec. (the material is very hygroscopic). An attempt to obtain a better yield was not tried. The strongest absorption band found in the infrared spectrum was in 1580 cm.$^{-1}$, which is characteristic of ionized carboxyl. The hydrochloride was obtained by treating with hydrochloric acid, m.p. 181–182° (lit.[7] m.p. 179–180°).

Reaction of phenyl isocyanate with 4-(2-carboxyethyl)-N-methylmorpholinium betaine. An 8.0-g. sample (0.044 mole) of the betaine and 5.5 g. (0.046 mole) of phenyl isocyanate were weighed into a flask containing 50 ml. of absolutely dry benzene. In a few minutes the evolution of carbon dioxide was recognized from the surface of suspended powder. As the reaction proceeded, the light powder of suspended betaine gradually disappeared, while white crystals began to separate on the walls. The temperature was raised slowly and toward the end of the reaction the mixture was heated under reflux. Three hours were generally enough for the completion of the reaction, when almost all the betaine was observed to be consumed. On cooling, the crystalline product formed was found to be *N,N'*-diphenylurea, m.p. 232–233°, and weighed 3.2 g. (65.5% yield). From the filtrate was recovered a small amount of acrylic anhydride, b.p. 82° (24 mm.), and 1.3 g. of acrylanilide.

Reaction of phenyl isocyanate with acrylic acid. The mixture of 7.2 g. (0.1 mole) of acrylic acid, 11.9 g. (0.1 mole) of phenyl isocyanate and a catalytic amount of tertiary amine in 20 ml. of dry benzene was heated under reflux for a few hours. *N,N'*-Diphenylurea, acrylic anhydride and acrylanilide were recovered in the similar manner as described above. Results were listed in Table II. In the absence of catalyst, the reaction proceeded in a similar way, but slowly.

Preparation of cellular polyurethane. Polylite #8651, 20 g., 7 ml. of Nacconate-65 and 2 ml. of β-propiolactone were mixed in a paper cup. One milliliter of tertiary amine mixture was then added, and the system was again blended by hand as quickly as possible. It was immediately introduced into another container, where the foaming proceeded to a full rise. An elastic foam with excellent gloss and uniform cell size was obtained, the density being about 0.9. Mechanical properties were found to be appreciably improved by sufficient washing with water after curing. Density as well as mechanical properties of the cellular plastic herein obtained could be varied to a considerable degree according to the formulation and foaming conditions.

Measurement of quantity of carbon dioxide evolved. A five-milliliter, long-necked, round bottomed flask was connected to a gas burette by means of a capillary tube. Halfway along the capillary, a small-sized cooler was inserted to condense the substances less volatile than carbon dioxide. The reaction vessel, containing 0.01 mole of material, 0.04 g. of catalyst and 2 ml. of solvent, was maintained at 100° by immersion into a well controlled bath. Volume of evolved gas was read at intervals until a maximum was reached. Results are shown in Tables I and II, and in Figs. 1 and 2.

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