The Synthesis of Isocyanurates on the Trimerization of Isocyanates under High Pressure

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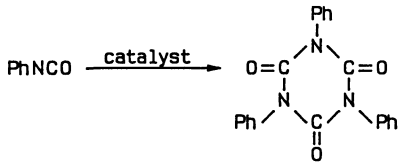
The trimerization of phenyl isocyanate in the presence of triethylamine was accelerated under high pressure to give triphenyl isocyanurate almost quantitatively. The reaction in benzene was remarkably accelerated by compression. The effects of pressure, temperature, catalysts, and solvents were examined on the trimerization of phenyl isocyanate. Aryl and normal alkyl isocyanates trimerized under high pressure to give the corresponding isocyanurates in good yields, whereas isocyanates having bulky alkyl groups such as *t*-butyl and cyclohexyl did not trimerize even under 800 MPa.

Isocyanurates have high thermal stability and have potential applications in the development of polymers or in the modification of polyurethanes.[1,2] The most common procedure for preparing isocyanurates is the trimerization of isocyanates by the action of various catalysts.[1,2] A number of reports have been published particularly on the trimerization of phenyl isocyanate as a model compound.[3]



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On the other hand, high pressure accelerates many organic reactions[4,5] including the trimerization of nitriles,[6] but there has been no report on the trimerization of isocyanates under high pressure.

In this paper, we report that the trimerization of phenyl isocyanate in the presence of triethylamine is accelerated under high pressure to give triphenyl isocyanurate nearly quantitatively. The effects of pressure, temperature, catalysts, and solvents on the trimerization of phenyl isocyanate have been investigated. The trimerization of various isocyanates under high pressure was also examined.

Results and Discussion

Phenyl isocyanate in a sealed tube at 100 °C in the presence of triethylamine catalyst did not trimerize (Table 1; Run 4), but trimerized nearly quantitatively when the reaction was carried out under 800 MPa (Run 6). At 500 MPa, the rate of the trimerization was enhanced satisfactorily even at 40 °C (Run 2).

Table 2 shows the effects of various catalysts on the trimerization of phenyl isocyanate. *N,N*-Dimethylethylamine, triethylamine, tributylamine, *N*-methylmorpholine, and *N,N*-dimethylaniline were good catalysts under 800 MPa. Lithium chloride and tetraethylammonium bromide are widely used as catalysts of the reactions of heterocumulenes.[7,8] Lithium chloride also catalyzed the trimerization (Run 10), but tetraethylammonium bromide had no catalytic activity (Run 9). When pyridine was used as a catalyst, a small amount of the trimer of phenyl isocyanate was obtained (Run 8), while a considerable amount of dimer was produced. This result agrees with the report of the dimerization by pyridine catalyst at ordinary pressure.[9] Lewis acid such as

Table 1. Trimerization of Phenyl Isocyanate[a]

Run	Press.	Temp	Et_3N	Trimer[b]
	MPa	°C	mmol	%
1	0.1[c]	40	0.50	0
2	500	40	0.50	75
3	800	40	0.50	78
4	0.1[c]	100	0.05	0
5	800	70	0.05	65
6	800	100	0.05	100

a) PhNCO 5 mmol, benzene 3 ml, catalyst Et_3N, reaction time 20 h. b) Determined by GLC. c) In a sealed glass tube.

Table 2. Effect of Catalyst on the Trimerization of Phenyl Isocyanate[a]

Run	Catalyst	1	Solvent	Trimer[b]
		mmol		%
1	None		Benzene	0
2	$Me_2(Et)N$	0.05	Benzene	77
3	Et_3N	0.05	Benzene	100
4	Bu_3N	0.05	Benzene	83
5	*N*-Methylmorpholine	0.06	Benzene	86
6	*N,N*-Dimethylaniline	0.07	Benzene	64
7	Pyridine	0.06	Benzene	22
8	$BF_3 \cdot Et_2O$	0.06	Benzene	0
9	Et_4NBr	0.06	CH_3CN	0
10	LiCl	0.12	THF	79

a) PhNCO 5 mmol, solvent 3 ml, pressure 800 MPa, reaction time 20 h, reaction temperature 100 °C. b) Determined by GLC.

$BF_3 \cdot Et_2O$ did not catalyze the trimerization (Run 8).

Figure 1 shows that the rate of trimerization of phenyl isocyanate is proportional to the amount of triethylamine catalyst when a limited amount of triethylamine is used.

Table 3 shows the effect of solvents. Under 800 MPa, triphenyl isocyanurate was obtained at high yields in most of the solvents. However, 25% of phenyl isocyanate was recovered in hexane, and many by-products were detected in acetone and ethyl methyl ketone by GLC analysis (Run 10 and 11).

Figure 2 shows the effect of pressure on the trimerization of phenyl isocyanate in hexane, benzene, and acetonitrile. In acetonitrile, 57% of isocyanurate was formed in a sealed glass tube at 70 °C. However, only few percent of isocyanurate was obtained even under 200 MPa in benzene or hexane. This result indicates that the rate of the trimerization depends much upon the kind of solvents at low pressure. The trimerization rate of phenyl isocyanate decreased in the order: in acetonitrile>in benzene>in hexane. This order is in agreement with the order of their polarity.

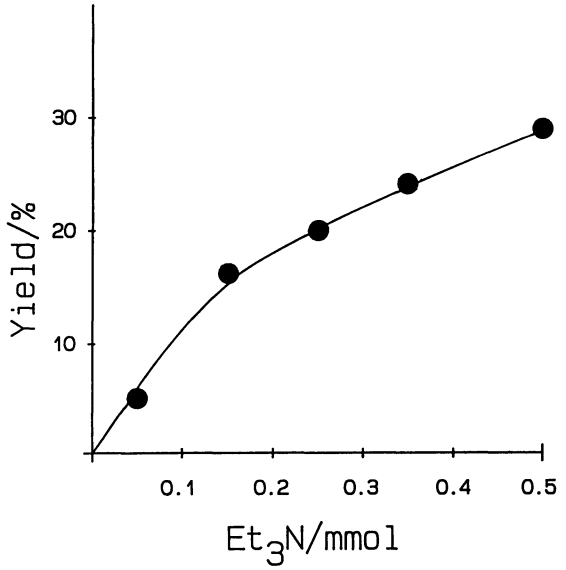
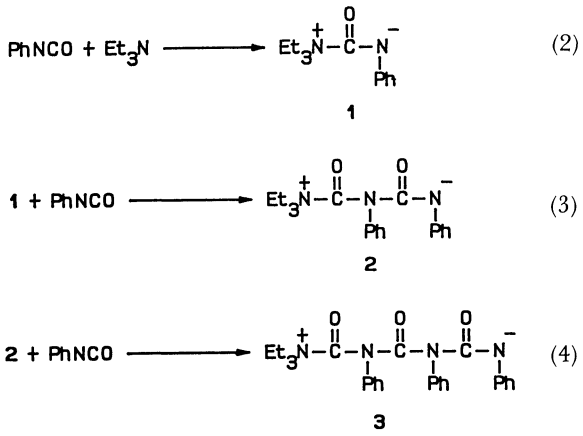


Fig. 1. Effect of amount of Et_3N on the trimerization of phenyl isocyanate: PhNCO 5 mmol, hexane 3 ml, reaction temperature 40 °C, reaction time 20 h, pressure 800 MPa. The yield of triphenyl isocyanurate was determined by GLC.

Table 3. Solvent Effect on the Trimerization of Phenyl Isocyanate[a)]

Run	Solvent	Trimer[b)] %
1	Hexane	65
2	Cyclohexane	74
3	Benzene	92
4	Diisopropyl ether	75
5	CH_2Cl_2	100
6	$CHCl_3$	88
7	CCl_4	77
8	THF[c)]	85
9	CS_2	72
10	Acetone	54
11	Ethyl methyl ketone[c)]	61
12	CH_3CN	99
13	DMF	84

a) PhNCO 5 mmol, solvent 3 ml, Et_3N 0.5 mmol, pressure 800 MPa, reaction time 20 h, reaction temperature 70 °C. b) Determined by GLC. c) Reaction temperature 100 °C.



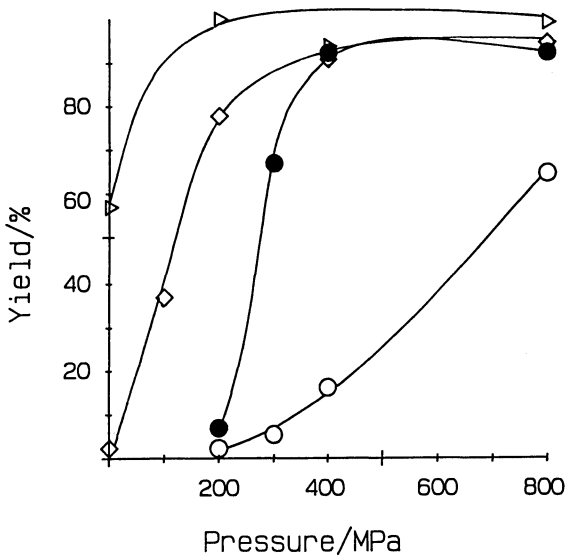
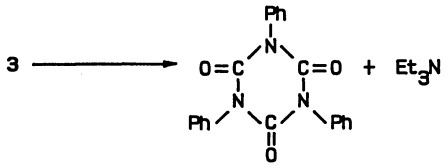


Fig. 2. Efeect of pressure on the trimerization of phenyl isocyanate: PhNCO 5 mmol, solvent 3 ml, reaction time 20 h. The yield of triphenyl isocyanurate was determined by GLC.
—●—: Solvent benzene, Et_3N 0.5 mmol, reaction temperature 70 °C.
—○—: Solvent hexane, Et_3N 0.5 mmol, reaction temperature 70 °C.
—▷—: Solvent CH_3CN, Et_3N 0.5 mmol, reaction temperature 70 °C.
—◇—: Solvent CH_3CN, Et_3N 0.05 mmol, reaction temperature 40 °C.



(5)

The trimerization of phenyl isocyanate in the presence of triethylamine seems to proceed successively with the first step of adduct **1** from phenyl isocyanate and triethylamine (Eq. 2), then stepwise addition of phenyl isocyanate yielding **2** and **3** (Eq. 3 and 4), and ring closing of **3** (Eq. 5). This mechanism has been reported on the trimerization of isocyanates at ordinary pressure.[10,11]

Table 4 shows the yields of the trimerization of aryl isocyanates under 800 MPa. The IR and ^{1}H NMR data of these products agreed with those of the compounds obtained by the known method.[12]

On the other hand, the trimerization of ethyl isocyanate did not occur when Kogon's method[12] was used. However, 56% of triethyl isocyanurate was obtained at 100 °C under 800 MPa in benzene (Table 5; Run 4). Table 5 shows the yields of the trimerization of ethyl isocyanate under high pressure. As a result, the trimerization of ethyl isocyanate seems to need higher pressure and temperature than that of phenyl isocyanate (Table 1 and Fig. 2), and ethyl isocyanate was little trimerized in hexane even under 800 MPa at 100 °C (compare with Run 1 in Table 3).

Table 4. Trimerization of Aryl Isocyanates under High Pressure[a]

Run	Isocyanate	Trimer[b] %
1	*p*-Chlorophenyl isocyanate	86
2	*m*-Chlorophenyl isocyanate	66
3	*o*-Chlorophenyl isocyanate	62
4	1-Naphthyl isocyanate	85

a) Isocyanates 5 mmol, benzene 3 ml, Et_3N 0.5 mmol, reaction temperature 100 °C, pressure 800 MPa, reaction time 20 h. b) Yield after recrystallization from EtOH-$CHCl_3$.

Table 5. Pressure Effect on the Trimerization of Ethyl Isocyanate[a]

Run	Solvent	Press. MPa	Temp °C	Trimer %
1	CH_3CN	400	40	0
2	Benzene	400	100	Trace
3	Benzene	600	100	5
4	Benzene	800	100	56
5	Hexane	800	100	Trace
6	CH_3CN	800	100	69
7	DMF	800	100	62

a) Ethyl isocyanate 5 mmol, solvent 3 ml, Et_3N 0.5 mmol, reaction time 20 h.

Table 6. Trimerization of Alkyl Isocyanates under High Pressure[a]

Run	Isocyanate	Solvent	Temp °C	Trimer %
1	Methyl isocyanate	Benzene	100	60[b]
2	Ethyl isocyanate	Benzene	100	56[c]
3	Propyl isocyanate	Benzene	70	53[c]
4	Propyl isocyanate	CH_3CN	100	47[c]
5	Butyl isocyanate	Benzene	70	72[c]
6	Butyl isocyanate	CH_3CN	100	50[c]
7	*t*-Butyl isocyanate	Benzene	70	Trace
8	Cyclohexyl isocyanate	Benzene	70	Trace

a) Isocyanates 5 mmol, solvent 3 ml, Et_3N 0.5 mmol, pressure 800 MPa, reaction time 20 h. b) Yield after recrystallization from CH_3CN. c) Yield after distillation.

Table 6 shows the yields of the trimerization of alkyl isocyanates under 800 MPa. Normal alkyl isocyanates were trimerized under high pressure to give the corresponding isocyanurates in good yields, whereas isocyanates having bulky alkyl groups such as *t*-butyl and cyclohexyl were not trimerized.

These results and our previous reports[7,13,14] suggest that heterocumulenes such as carbon disulfide and isocyanates are hopeful reagents for the high-pressure synthesis, and that the chemistry of heterocumulenes under high pressure is an attractive field.

Experimental

Apparatus. The apparatus used for the high pressure reaction was the same as that described previously.[15]

Measurement. GLC was carried out by a JEOL 20KF chromatograph with 20% SE-30 columns and Shimadzu GC-14A chromatograph with capillary column (Shimadzu CBP-M-25-025). ^{1}H NMR spectra were measured in $CDCl_3$ by a Hitachi R-40 (90 MHz) spectrometer. Mass spectra were measured by a JEOL DX-303 GC-MS spectrometer. IR spectra were obtained by a JASCO A-302 spectrophotometer.

Triaryl Isocyanurates. Phenyl, *p*-chlorophenyl, *m*-chlorophenyl, *o*-chlorophenyl, and 1-naphthyl isocyanates were trimerized according to the procedure of Kogon.[12] Isocyanurates thus obtained were used as standards for the identification.

Trimerization of Aryl Isocyanates under High Pressure. A typical procedure is as follows: A homogeneous mixture of phenyl isocyanate (5 mmol), triethylamine (0.5 mmol), and benzene (3 ml) in a sealed teflon tube was compressed to 800 MPa, heated at 70 °C, and maintained for 20 h in a high-pressure equipment. The GLC analysis using hexadecane as a standard showed that 65% of triphenyl isocyanurate was obtained.

p-Chlorophenyl, *m*-chlorophenyl, *o*-chlorophenyl, and 1-naphthyl isocyanates were trimerized in a similar manner to phenyl isocyanate. Unreacted isocyanate was distilled in vacuo from the resulting mixture, and the residue was recrystallized from EtOH-$CHCl_3$ to give isocyanurate. The spectral data of these trimers agreed with those of

standard samples.

Trimerization of Alkyl Isocyanates under High Pressure. A typical procedure is as follows: A homogeneous mixture of ethyl isocyanate (5 mmol), triethylamine (0.5 mmol), and benzene (3 ml) in a sealed teflon tube was compressed to 800 MPa, heated at 100 °C, and maintained for 20 h in a high-pressure equipment. The resulting mixture was subjected to evaporation and the residue was purified by distillation with Kugelrohr to give 0.20 g (56%) of triethyl isocyanurate. IR 1683, 1453 cm^{-1}; ^1H NMR δ=1.24 (t, 9H, $3CH_3$), 3.96 (q, 6H, $3CH_3$); MS *m/z* 213 (M^+).

Found: *m/z* 213.1140. Calcd for $C_9H_{15}N_3O_3$: M, 213.1103.

Methyl, propyl, butyl, *t*-butyl, and cyclohexyl isocyanates were trimerized in a similar manner to ethyl isocyanate. The spectral data of these trimers are as follows:

Trimethyl Isocyanurate. IR 1669, 1475 cm^{-1}; ^1H NMR δ=3.33 (s, 9H, $3CH_3$); MS *m/z* 171 (M^+).

Found: *m/z* 171.0621. Calcd for $C_6H_9N_3O_3$: M, 171.0644.

Tripropyl Isocyanurate. IR 1684, 1466 cm^{-1}; ^1H NMR δ=0.93 (t, 9H, $3CH_3$), 1.30—1.90 (m, 6H, $3CH_2$), 3.83 (t, 6H, $3NCH_2$); MS *m/z* 255 (M^+).

Found: *m/z* 255.1586. Calcd for $C_{12}H_{21}N_3O_3$: M, 255.1583.

Tributyl Isocyanurate. IR 1685, 1462 cm^{-1}; ^1H NMR δ=0.93 (t, 9H, $3CH_3$), 1.10—1.85 (m, 12H, $6CH_2$), 3.87 (t, 6H, $3NCH_2$); MS *m/z* 297 (M^+).

Found: *m/z* 297.2019. Calcd for $C_{15}H_{27}N_3O_3$: M, 297.2052.

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