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The Isocyanurates. III. The Formation of Tributyl Isocyanurates from Butyl Bromides in the Presence of 1-Butanol

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The reaction of *n*-butyl or *s*-butyl bromide with potassium cyanate in dimethylformamide was carried out at 100°C for 3 hr. to give tri-*n*-butyl or tri-*s*-butyl isocyanurate. In this process, the presence of unpolymerized *n*-butyl or *s*-butyl isocyanate in the reaction mixture was detected by treating the mixture with benzylamine, thus forming 1-*n*-butyl- or 1-*s*-butyl-3-benzyl urea. The presence of 1-butanol in the reaction system resulted in an increase in the yield of the corresponding isocyanurates. This tendency was remarkable when *s*-butyl bromide was used as a starting material. The addition of *n*-butyl *N*-*n*-butyl- or *n*-butyl *N*-*s*-butylcarbamate to the reaction system strongly accelerated the formation of isocyanurates. The acceleration due to the addition of 1-butanol described above was, therefore, attributed to the effect of carbamates formed in the reaction system. An attempt to trimerize *n*-butyl or *s*-butyl isocyanate in the presence of carbamates and dimethylthylformamide, or in the presence of carbamates and potassium cyanate, resulted in failure. Therefore, carbamates acted as strong accelerators for the trimerization of butyl isocyanates, in cooperation with basic alkali metal salts, such as potassium cyanate, in dimethylformamide.

Previous papers[1] have described how trialkyl or trialkenyl isocyanurates were prepared by the reaction of alkyl or alkenyl halides with alkali cyanates in an aprotic solvent, such as dimethylformamide or dimethylsulfoxide. In this process, the formation of 1, 3-dialkyl urea was often observed when the reaction mixture was poured into water immediately after the desired reaction time. This fact supported indirectly the idea that the reaction between alkyl halides and alkali cyanates generated alkyl isocyanates at the first step,[2] and that those were subsequently polymerized to trialkyl isocyanurates by the catalysis of alkaline compounds (e. g., alkali cyanate)[3] present in the reaction mixture. Therefore, the presence of the unpolymerized alkyl isocyanate in the reaction mixture caused a depression in the yield of trialkyl isocyanurate.

In order to promote the trimerization of isocyanates, an isocyanate-polymerizing catalyst,[4] such as potassium carbonate, sodium benzoate, pyridine or triethylamine, was added to the reaction system. However, all such attempts resulted in failure in the reaction system containing alkyl halides.

On the other hand, some compounds bearing a hydroxyl or an imino group were found to be effective in the trimerization of an initially-formed alkyl isocyanate, even in the presence of alkyl halides.

In the present work, the effects of the addition of 1-butanol, *n*-butyl *N*-*n*-butyl- or *n*-butyl *N*-*s*-butylcarbamate on the reaction of *n*-butyl or *s*-butyl bromide with potassium cyanate in dimethylformamide were studied. The reaction mixture was treated by the following two methods: (I) the reaction mixture was allowed to stand for 24 hr. and then distilled to obtained isocyanurates, and (II) the reaction mixture was quenched at the end of the reaction period and mixed with benzylamine, thus converting the remaining isocyanate into 1-butyl-3-benzyl urea.

A previous paper[1] described how the reaction 1 between *n*-butyl bromide and potassium cyanate, together with water, afforded 1, 3-di-*n*-butyl urea in an 80 to 87% yield (based on the water added) and how the yield of tri-*n*-butyl isocyanurate decreased with the amount of the water added. In this reaction, the decomposition of potassium cyanate proceeded easily in the presence of more than 0.6 mol. of water per mole of the cyanate.

$$n\text{-C}_4\text{H}_9\text{Br} + \text{KNCO} + \text{H}_2\text{O} \xrightarrow{\text{DMF}} (n\text{-C}_4\text{H}_9\text{NH})_2\text{CO} + (n\text{-C}_4\text{H}_9\text{NCO})_3 \qquad (1)$$

In the reaction 2 of *n*-butyl bromide with potassium cyanate in the presence of 1-butanol, the use of an equimolar amount of butanol to butyl bromide resulted in the yield of *n*-butyl *N*-*n*-butylcarbamate being limited to 47%, while that of tri-*n*-butyl

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[1] K. Fukui and H. Kitano, Japanese Pat. 282402 (1961); K. Fukui, F. Tanimoto and H. Kitano, This Bulletin, **33**, 1586 (1965).

[2] K. Fukui and H. Kitano, Japanese Pat. 282468 (1961).

[3] T. Yamabe, A. Nagasawa, H. Kitano and K. Fukui, *J. Chem. Soc., Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **66**, 821 (1963).

[4] A. W. Hofmann, *Ber.*, **18**, 764 (1885); W. J. Balon, U. S. Pat. 2353518 (1958); A. W. Hofmann, *Jahresber. Fortschritte Chem.*, **1862**, 335.

Table I. The reaction of *n*-butyl or *s*-butyl bromide and potassium cyanate with or without 1-butanol

Reactant (mole)	Method* employed	Yield of the product, %		
		$C_4H_9NHCONHCH_2C_6H_5$	$(C_4H_9NCO)_3$	$C_4H_9NHCO_2C_4H_9$-*n*
n-C_4H_9Br (0.2) KNCO (0.3)	I	0	83	—
	II	51	27	—
n-C_4H_9Br (0.4) KNCO (0.6) *n*-C_4H_9OH (0.4)	I	0	36	47
	II	0	35	47
s-C_4H_9Br (0.2) KNCO (0.3)	I	0	73	—
	II	40	31	—
s-C_4H_9Br (0.6) KNCO (0.9) *n*-C_4H_9OH (0.6)	I	0	63	12
	II	0	62	11

* Method I: Distillation of the reaction mixture;
Method II: The addition of benzylamine to the reaction mixture.

isocyanurate reached 36%, much higher than in the case of the addition of water (13%). Moreover, when *s*-butyl bromide was used in place of *n*-butyl bromide, this trend became remarkable and a 63% yield of tri-*s*-butyl isocyanurate was obtained (Eq. 3):

$$n\text{-}C_4H_9Br + KNCO + n\text{-}C_4H_9OH \xrightarrow{\text{DMF}} n\text{-}C_4H_9NHCO_2C_4H_9\text{-}n + (n\text{-}C_4H_9NCO)_3 \quad (2)$$

$$s\text{-}C_4H_9Br + KNCO + n\text{-}C_4H_9OH \xrightarrow{\text{DMF}} s\text{-}C_4H_9NHCO_2C_4H_9\text{-}n + (s\text{-}C_4H_9NCO)_3 + CH_3CH{=}CHCH_3 \quad (3)$$

The two methods, I and II, were adopted for the reaction with and without the use of 1-butanol. Table I indicates the results.

The clear difference between the results from I and II observed in the absence of 1-butanol implies that considerable amounts of isocyanates remained unpolymerized for several hours in the reaction mixture (Eq. 4), while, in the presence of 1-butanol, I and II were not appreciably different, indicating the absence of free isocyanates in the reaction mixture.

$$C_4H_9Br + KNCO \begin{cases} \xrightarrow{\text{Method I}} (C_4H_9NCO)_3 \\ \xrightarrow[C_6H_5CH_2NH_2]{\text{Method II}} C_4H_9NHCONHCH_2C_6H_5 + (C_4H_9NCO)_3 \end{cases} \quad (4)$$

Table I also apparently illustrates that the addition of 1-butanol to the reaction system 4 served to increase the yield of tributyl isocyanurates.

On the basis of our observations that the addition of water to the reaction system 4 did not increase the yield of the isocyanurate,¹⁾ we assumed that the trimerization of butyl isocyanates was accelerated neither by water, nor by urea, nor by 1-butanol, but by *n*-butyl *N*-butylcarbamates derived from the reaction with 1-butanol. In this regard, it may be recollected that Kogon⁵⁾ carried out the trimerization of phenyl isocyanate in the presence of ethyl carbanilate and *N*-methyl morpholine.

The effect of the addition of half a more of *n*-butyl *N*-*n*-butyl- or *n*-butyl *N*-*s*-butylcarbamate per mole of *n*-butyl or *s*-butyl bromide on the reaction of butyl bromides with potassium cyanate in dimethylformamide was examined in order to confirm that *N*-monosubstituted carbamates may be expected to promote the trimerization of aliphatic isocyanates. In this reaction 5, the yields of tributyl isocyanurates were about 80% and there was no butyl isocyanate remaining in the reaction mixture which was detectable by the benzylamine method II described above.

$$C_4H_9Br + KNCO \xrightarrow[C_4H_9NHCO_2C_4H_9]{\text{DMF}} (C_4H_9NCO)_3 \quad (5)$$

Furthermore, the trimerization 6 of *n*-butyl or *s*-butyl isocyanate with a *n*-butyl *N*-*n*-butylcarbamate-dimethylformamide mixture led to the recovery of the isocyanates in about a 90% yield, while the reaction 7 of the isocyanates in the presence of potassium cyanate and the carbamate in toluene resulted in the recovery of the isocyanates in almost a quantitative yield:

$$C_4H_9NCO \not\xrightarrow[n\text{-}C_4H_9NHCO_2C_4H_9\text{-}n,\ \text{DMF}]{} (C_4H_9NCO)_3 \quad (6)$$

$$C_4H_9NCO \not\xrightarrow[n\text{-}C_4H_9NHCO_2C_4H_9\text{-}n,\ \text{KNCO}]{} (C_4H_9NCO)_3 \quad (7)$$

The trimerization 8 of the isocyanates with the carbamate and potassium cyanate in dimethylformamide gave isocyanurates in twice the yield of the reaction 8 in the absence of the carbamate:

$$C_4H_9NCO \xrightarrow[n\text{-}C_4H_9NHCO_2C_4H_9\text{-}n,\ \text{KNCO, DMF}]{} (C_4H_9NCO)_3 \quad (8)$$

Consequently, it was concluded that *n*-butyl *N*-butyl-carbamates exhibited a strong accelerating ability in the trimerization of butyl isocyanates

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5) I. C. Kogon, *J. Am. Chem. Soc.*, **78**, 4911 (1956).

in cooperation with basic alkali metal salts, such as potassium cyanate, in dimethylformamide, in spite of the presence of butyl bromides, which reduced the isocyanate-trimerizing property of some basic compounds described in the preliminary experiment; this information will be useful for the syntheses of isosyanurates from aliphatic halides and alkali cyanates.

Experimental

Materials.—*n*-Butyl and *s*-butyl bromides were prepared from the corresponding alcohols by the usual methods.[6,7] We described the purity of potassium cyanate[8] and dimethylformamide in a previous paper[1]. *n*-Butyl and *s*-butyl isocyanates were prepared by the phosgenation[9] of anhydrous *n*-butyl or *s*-butylamine hydrochloride in tetralin and were purified by treating them with calcium oxide and molecular sieves, followed by fractional distillation. The specimens used had the following physical properties: *n*-butyl; b. p. 115°C, n_D^{20} 1.4058 (Ref.[10] b. p. 113—116°C, n_D^{20} 1.4060) and *s*-butyl; b. p. 102°C, n_D^{20} 1.3995 (Ref.[10] b. p. 99—101°C, n_D^{20} 1.3989). *n*-Butyl *N*-*n*-butylcarbamate (b. p. 102°C/4 mmHg, n_D^{20} 1.4359) and *n*-butyl *N*-*s*-butylcarbamate (b. p. 91—92°C/4 mmHg, n_D^{15} 1.4429) were prepared by the reaction of an excess of pure *n*-butanol with butyl isocyanates (the specimens described above) and were purified by distillation under reduced pressure. These carbamates were identified with the authentic samples prepared by Curry's method.[11]

The Reaction of *n*-Butyl or *s*-Butyl Bromide with Potassium Cyanate.—*(A) Method I (The Distillation of the Reaction Mixture)*.—In a three-necked flask fitted with a reflux condenser, a thermometer, and a mercury-sealed mechanical stirrer, there was placed a mixture of 27.4 g. (0.2 mole) of *n*-butyl or *s*-butyl bromide, 24.3 g. (0.3 mole) of potassium cyanate, and 100 g. (1.4 mole) of dimethylformamide. The mixture was well stirred and then kept at 100±1°C for 3 hr. After the reaction mixture had then been allowed to stand for 24 hr. at room temperature, it was filtered to removed inorganic salts. The filtrate was distilled under reduced pressure to give dimethylformamide and tri-*n*-butyl isocyanurate (b. p. 160—162°C/4 mmHg, n_D^{20} 1.4720[1]) or tri-*s*-butyl isocyanurate (b. p. 138—140°C/4 mmHg, n_D^{15} 1.4600[1]). The yields of the isocyanurates are shown in Table I.

(B) Method II (The Addition of Benzylamine to the Reaction Mixture).—The reaction of *n*-butyl bromide with potassium cyanate was carried out as in the case of Method I. After 3 hr., the reaction mixture was quickly quenched with ice water; the inorganic precipitates were filtered off, and the filtrate was at once mixed with 26.8 g. (0.25 mole) of benzylamine. The resulting mixture was allowed to stand for 24 hr. at room temperature and then poured into cold water to afford a white crystalline mass. The mass was collected by filtration, washed with water and *n*-butyl ether, and recrystallized from a methyl ethyl ketone-ligroin mixture (1 : 1) to give 1-*n*-butyl-3-benzyl urea, m. p. 101°C.

Found: N, 13.5%. Calcd. for $C_{12}H_{18}ON_2$: N, 13.6%.

The filtrate was poured into a saturated sodium chloride solution and extracted with benzene. The extract was dried over anhydrous magnesium sulfate overnight and distilled under reduced pressure to give tri-*n*-butyl isocyanurate.

When *s*-butyl bromide instead of *n*-butyl bromide was used in this experiment, 1-*s*-butyl-3-benzyl urea, m. p. 102.5°C, tri-*s*-butyl isocyanurate and butene-2 were obtained.

Found: N, 13.4% Calcd. for $C_{12}H_{18}ON_2$: N, 13.6%.

These results are summarized in Table I.

The Reaction of *n*-Butyl Bromide with Potassium Cyanate in the Presence of 1-Butanol.—A mixture of 54.8 g. (0.4 mole) of *n*-butyl bromide, 48.6 g. (0.6 mole) of potassium cyanate, 200 g. (2.8 mole) of dimethylformamide and 29.6 g. (0.4 mole) of 1-butanol was kept at 100±1°C for 3 hr. with stirring. The reaction mixture was then treated by the two methods, I and II, to give *n*-butyl *N*-*n*-butylcarbamate (b. p. 97—98°C/3 mmHg, n_D^{20} 1.4726) and tri-*n*-butyl isocyanurate (b. p. 158—160°C/3 mmHg). The results are shown in Table I. The yields of the above products which depend upon the amount of 1-butanol added are listed in Table II.

TABLE II. THE REACTION OF *n*-BUTYL BROMIDE WITH POTASSIUM CYANATE IN THE PRESENCE OF 1-BUTANOL

n-C_4H_9OH / n-C_4H_9Br mole/mole	Yield (A) of n-$C_4H_9NHCO_2$-C_4H_9-n %	Yield (B) of $(n$-$C_4H_9NCO)_3$ %	Total yield (A+B) %
0.5	35	47	82
1.0	47	36	83
1.5	56	28	84
2.0	61	22	83
4.0	83	—	83

The Reaction of *s*-Butyl Bromide with Potassium Cyanate in the Pressence of 1-Butanol.—In both methods, I and II, the top of the reflux condenser was connected with a trap chilled by a dry ice-methanol bath. A mixture of 83.2 g. (0.6 mole) of *s*-butyl bromide, 72.9 g. (0.9 mole) of potassium cyanate, 300 g. (4.2 mole) of dimethylformamide, and 42.6 g. (0.6 mole) of 1-butanol was maintained at 100±1°C for 5 hr. with stirring. The reaction mixture, when then treated by the above methods, yielded *n*-butyl *N*-*s*-butylcarbamate (b. p. 90—91°C/4 mmHg, n_D^{15} 1.4428) and tri-*s*-butyl isocyanurate (b. p. 137—139°C/4 mmHg). The results are shown in Table I, while the effects of the amount of 1-butanol added on the yields of the carbamate and the isocyanurate are summarized in Table III. In this table, the yield of butene-2 was determined from the bromine number of the distillate in the trap.

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6) O. Kamm and C. S. Marvel, "Org. Syntheses," Coll. Vol. I, 28 (1956).

7) C. R. Noller and R. Dinsmore, ibid., Coll. Vol. II, 359 (1948).

8) A. Scattergood, "Inorg. Syntheses," **2**, 87 (1953).

9) M. W. Farlow, "Org. Syntheses," **31**, 62 (1951).

10) R. J. Slocombe, E. E. Hardy, J. H. Saunders and R. L. Jenkins, *J. Am. Chem. Soc.*, **72**, 1888 (1950).

11) H. H. Curry and J. P. Mason, *J. Am. Chem. Soc.*, **73**, 5043 (1951).

TABLE III. THE REACTION OF s-BUTYL BROMIDE WITH POTASSIUM CYANATE IN THE PRESENCE OF 1-BUTANOL

n-C_4H_9OH / s-C_4H_9Br mole/mole	Yield (A) of s-$C_4H_9NHCO_2C_4H_9$-s %	Yield (B) of (s-$C_4H_9NCO)_3$ %	Yield (C) of $CH_3CH{=}CHCH_3$ %	Total yield (A+B+C) %
0.5	30	42	6	78
1.0	11	62	4	77
1.5	15	58	3	76
2.0	16	57	1	74
4.0	17	54	0.5	72

The Reaction of n-Butyl or s-Butyl Bromide with Potassium Cyanate in the Presence of n-Butyl N-Butylcarbamates.—A mixture of 27.4 g. (0.2 mole) of n-butyl or s-butyl bromide, 24.3 g. (0.3 mole) of potassium cyanate, 100 g. (1.4 mole) of dimethylformamide, and 17.3 g. (0.1 mole) of n-butyl N-n-butyl or n-butyl N-s-butylcarbamate specimens, was heated at 100±1°C for 3 hr. The reaction mixture was then treated by Methods I and II to give tri-n-butyl and tri-s-butyl isocaynurate respectively. The yields of the isocyanurates by the two methods, are shown in Table IV. The carbamate added was recovered in a quantitative yield.

TABLE IV. THE REACTION OF n-BUTYL OR s-BUTYL BROMIDE WITH POTASSIUM CYANATE IN THE PRESENCE OF n-BUTYL N-BUTYLCARBAMATES

Reactant	Carbamate	Method*	Yield of isocyanurate, %
n-C_4H_9Br	n-$C_4H_9NHCO_2C_4H_9$-n	I	83
		II	81
s-C_4H_9Br	s-$C_4H_9NHCO_2C_4H_9$-s	I	73
		II	72

* Method I: Distillation of the reaction mixture;
Method II: The addition of benzylamine to the reaction mixture.

Attempted Trimerizations of n-Butyl and s-Butyl Isocyanates.—After a mixture listed in Table V was heated at 100±1°C for 3 hr. while being stirred, the resultant mixture was quenched with ice water and 5 ml. of the mixture was pipetted out. The sample was then mixed with 20 ml. of a 0.5 N di-n-butylamine-dioxane solution and allowed to stand for 2 hr. at room temperature. The residual isocyanate content in the sample was determined by titrating the excess of di-n-butylamine with a 0.1 N hydrochloric acid - ethanol solution, using bromocresol purple as the indicator.3) The results are shown in Table V.

TABLE V. THE ATTEMPTED TRIMERIZATION OF n-BUTYL AND s-BUTYL ISOCYANATES

Components of the reaction mixture*	Recovered C_4H_9NCO %
n-C_4H_9NCO, $CH_3C_6H_5$	99.5
n-C_4H_9NCO, n-$C_4H_9NHCO_2C_4H_9$-n, KCNO, $CH_3C_6H_5$	99.4
n-C_4H_9NCO, $HCON(CH_3)_2$	90.9
n-C_4H_9NCO, n-$C_4H_9NHCO_2C_4H_9$-n, $HCON(CH_3)_2$	91.0
n-C_4H_9NCO, KCNO, $HCON(CH_3)_2$	83.5
n-C_4H_9NCO, n-$C_4H_9NHCO_2C_4H_9$-n, $HCON(CH_3)_2$, KCNO	65.4
s-C_4H_9NCO, $CH_3C_6H_5$	99.4
s-C_4H_9NCO, n-$C_4H_9NHCO_2C_4H_9$-n, $CH_3C_6H_5$, KCNO	99.6
s-C_4H_9NCO, $HCON(CH_3)_2$	89.2
s-C_4H_9NCO, n-$C_4H_9NHCO_2C_4H_9$-n, $HCON(CH_3)_2$	89.4
s-C_4H_9NCO, KCNO, $HCON(CH_3)_2$	81.5
s-C_4H_9NCO, n-$C_4H_9NHCO_2C_4H_9$-n, $HCON(CH_3)_2$, KCNO	61.6

* C_4H_9NCO: 0.01 mole, n-$C_4H_9NHCO_2C_4H_9$-n: 0.005 mole, KCNO: 2.5×10^{-5} mole, $CH_3C_6H_5$: 10 ml., $HCON(CH_3)_2$: 10 ml.

With regard to Table V, toluene was used as a diluent of the isocyanates in order to obtain accurate results from the analysis of the reaction mixture in the absence of dimethylformamide, because toluene itself did not influence the polymerization of the isocyanates.