

THE REACTION OF CYANATE ION WITH ORGANIC ISOCYANATES.
A NEW GENERAL SYNTHESIS OF DI- AND TRISUBSTITUTED ISOCYANURATES.

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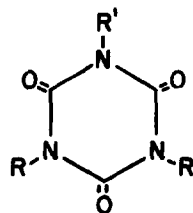
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Certain isocyanurates (I), in view of their polarity, symmetry, thermal stability and polyfunctionality, should be particularly suited for exploitation in polymer synthesis (1,2). Unfortunately, the attention this class of compounds has received in this connection is not

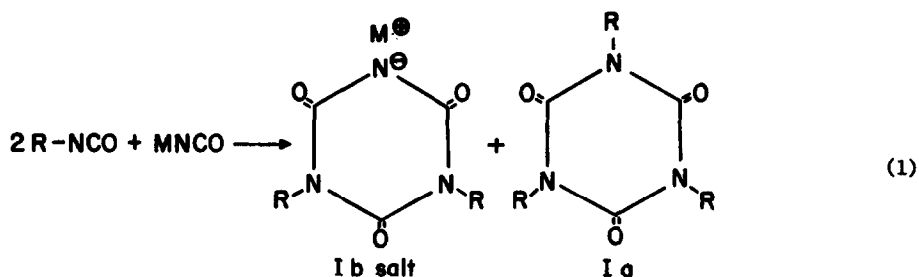


- I
a, R = R' = alkyl or aryl
b, R = alkyl or aryl, R' = H
c, R = alkyl or aryl, R' = alkyl¹

commensurate with their indicated potential. A paucity of suitable routes to all but one class of isocyanurates has been the principal impediment in the growth of isocyanurate chemistry. Thus, symmetrically trisubstituted isocyanurates (Ia) are readily obtained from the base catalyzed trimerization of the corresponding isocyanates (3), but no satisfactory methods (4) are available for the synthesis of the more versatile di- and unsymmetrically trisubstituted isocyanurates (Ib and Ic respectively).

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We wish to report a new approach to the synthesis of isocyanurates which has resulted in selective and convenient routes to the elusive isocyanurates, Ib and Ic. Alkali metal cyanates (MNCO), in contrast to other basic salts which catalyze trimerization, react with organic isocyanates (R-NCO) to give the salt of Ib in addition to the anticipated trimer, Ia (Eq. 1).



Under optimum conditions, yields of the salt in excess of 80% are common. Either the salt or the acid form of Ib is easily isolated uncontaminated by the trimer. The following example serves to illustrate the facility with which disubstituted isocyanurates can now be prepared.



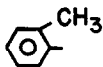
A solution of 35.7 g (0.30 mole) of phenyl isocyanate in 100 ml of dimethylformamide (DMF) was added dropwise over one hour to a slurry¹ of 13.0 g (0.16 mole) of potassium cyanate in 200 ml DMF at 75°. Removal of DMF (50° at 1 mm Hg) provided a white solid which, on trituration with 200 ml of H₂O gave 3.7 g of triphenyl isocyanurate (H₂O insoluble). At this point, the aqueous filtrate may be evaporated in vacuo to yield potassium diphenyl isocyanurate or acidified with aqueous HCl to give 38.5 g of diphenyl isocyanurate (m. 281° from ethanol), yield, 91%.

As illustrated in Table I, this technique is applicable to a wide variety of isocyanates. The selectivity to Ib appears to parallel the reactivity of the isocyanates toward nucleophiles, e.g., alcohols (5).

¹The solubility of KNCN in DMF is limited ($\sim 2.2 \times 10^{-2}$ mole/liter).

TABLE I

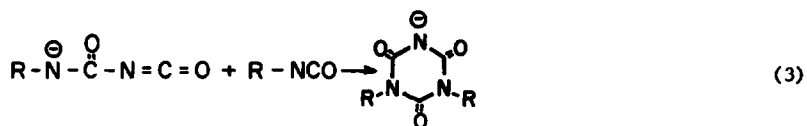
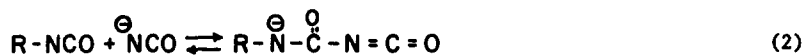
Effect Of Structure On The Reaction Of R-NCO With KNCO In DMF At 75° For One Hr

<u>R</u>	<u>Selectivity^a to Ib</u>	<u>R-NCO Conversion, %</u>
n-C ₄ H ₉ ^b -	0.333	60.0
 -CH ₂ -	0.595	84.4
CH ₂ =CH-CH ₂ -	0.639	76.7
	0.930	98.2
	0.867	87.5

^aMole fraction of R-NCO converted appearing in Ib; Ia was the singular by-product in all cases.

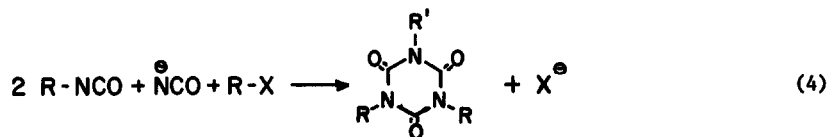
^b100° for 24 Hr.

On the basis of preliminary kinetic data, the following mechanism accounts for the formation of Ib anion.



Dipolar aprotic solvents [e.g., DMF, dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidinone (NMP)] are preferred for high selectivities to Ib.

This synthesis can be readily adapted to the preparation of unsymmetrically trisubstituted isocyanurates, Ic, by carrying out the reaction in the presence of a suitable (non-aryl) organic halide. To illustrate, phenyl isocyanate was reacted with KNCO in the presence of a stoichiometric amount of allyl chloride to give an 86% yield of allyl diphenyl isocyanurate, m. 149-50° (from ethanol).



A recent announcement (6) that the isocyanurate ring dramatically increases flame retardancy in polyurethane foams should stimulate added interest in the general area of isocyanurate-based polymers.

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