

### Trimerization of isocyanates by organozinc amines and alkoxides: an example of homogeneous coordination catalysis involving a template effect\*

We have observed that organozinc amines  $RZnNR'_2$  and alkoxides  $RZnOR'^1$  are efficient catalysts for the trimerization of isocyanates. Recently other types of organometallic compounds, notably organotin alkoxides and oxides<sup>2</sup> and trialkyl-antimony and -arsenic oxides<sup>3</sup> have been reported to catalyse this reaction, and a mechanism involving successive insertion of three isocyanate units between the tin atom and the hetero atom of the attached group followed by elimination of the trimer from the 1:3 adduct has been proposed for the organotin-catalyzed reactions<sup>2</sup>. The reactivity of the Zn-O and Zn-N bond towards isocyanates<sup>1</sup> suggested that a similar mechanism might operate in the organozinc-catalyzed trimerizations, but we find this is not the case, and we present our views on the actual mechanism.

Trimerization of alkyl isocyanates  $RNCO$  ( $R = \text{Me, Et, Hex}$ ) catalyzed by  $\text{EtZnNPh}_2$  (benzene solution) followed by hydrolysis affords  $(RNCO)_3$  quantitatively together with  $\text{RNH}\cdot\text{CO}\cdot\text{NPh}_2$  in a quantity equivalent to the amount of catalyst used. This suggests that the primary 1:1 adduct of  $\text{EtZnNPh}_2$  and  $RNCO$  ( $\text{EtZnNR}\cdot\text{CO}\cdot\text{NPh}_2$ \*\* , an organozinc urea) rather than  $\text{EtZnNPh}_2$  itself is the actual catalytic species. The 1:1 adduct of  $\text{EtZnNPh}_2$  and  $\text{PhNCO}$ <sup>†</sup> equals  $\text{EtZnNPh}_2$  in catalytic activity. Trimerization of  $\text{MeNCO}$  using  $\text{EtZnNPh}\cdot\text{CO}\cdot\text{NPh}_2$  as a catalyst yields  $(\text{MeNCO})_3$  as the sole trimer formed. Hydrolysis of the mother liquor (benzene solution) affords  $\text{PhNH}\cdot\text{CO}\cdot\text{NPh}_2$  quantitatively, which rules out an insertion-elimination mechanism.

We have succeeded in isolating crystalline 1:1 adducts "A" of the catalyst ethylzinc triphenylurea with alkyl isocyanates.



Hydrolysis of "A" ( $R = \text{Et, Hex}$ ) affords  $(RNCO)_3$  and  $\text{PhNH}\cdot\text{CO}\cdot\text{NPh}_2$  (both in nearly quantitative yield), which excludes the possibility that in (1) insertion of  $RNCO$  has occurred either into the Zn-N bond (a biuret  $\text{RNH}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NPh}_2$  would have been isolated) or into the Zn-C bond (a propionamide  $\text{RNH}\cdot\text{CO}\cdot\text{Et}$  would have been isolated\*\*\*). If in "A" the  $\text{N}=\text{C}=\text{O}$ -function were intact, hydrolysis would have afforded a dialkylurea  $\text{RNH}\cdot\text{CO}\cdot\text{NHR}$ . Isolation of  $(RNCO)_3$  suggests that this entity is somehow part of "A". Organozinc urea derivatives are trimeric in dilute solution in benzene<sup>4</sup> (e.g.  $\text{EtZnNPh}\cdot\text{CO}\cdot\text{NPh}_2$ : ebull. mol. wt. 1135,  $n = 3.02$ ). Thus, "A" might conceivably be a coordination complex of trimeric  $\text{EtZnNPh}\cdot\text{CO}\cdot\text{NPh}_2$  and  $(RNCO)_3$ . This is supported by the nearly quantitative isolation of  $(RNCO)_3$  after adding the strongly complexing agent ethylenebis(dimethylamine) to a solution of "A" ( $R = \text{Et, Hex}$ ):



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\*\* Arguments for the presence of a Zn-N bond will be presented in the full paper<sup>4</sup>.

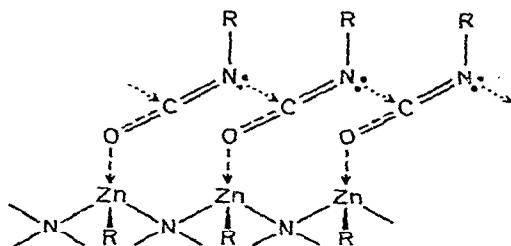
\*\*\*  $\text{PhNCO}$  does react with formation of  $\text{Et}\cdot\text{CO}\cdot\text{NPh}\cdot\text{Zn}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NPh}_2$ .

Moreover, ebulliometric mol.wt. determinations (e.g. "A", R = Hex: 1310,  $n = 2.85$ ) as well as IR data (to be reported in the full paper) are in agreement.

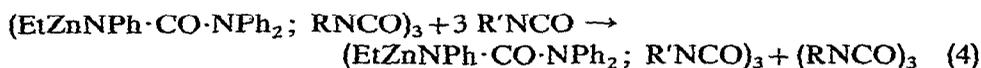
However, since the isocyanurate molecule is flat, and the non-bonding electron pairs of the oxygen atoms are in the plane of the ring, "A" cannot be a complex of the organozinc urea and the isocyanurate  $(\text{RNCO})_3$  proper. Indeed we have been unable to obtain "A" (R = Et, Hex) according to (3) under a variety of conditions and have confirmed the lack of interaction by ebulliometry and IR spectroscopy. Thus, any dissociation of "A" is irreversible.



The following mechanism is proposed for the  $\text{EtZnNPh}_2$ -catalyzed trimerizations. One mole of  $\text{RNCO}$  is inserted into the  $\text{Zn-N}$  bond of the catalyst. The resulting trimeric organozinc urea  $\text{EtZnNR}\cdot\text{CO}\cdot\text{NPh}_2$  forms a complex having three molecules of  $\text{RNCO}$  with oxygen coordinated to zinc (adduct "A"). In this complex strong interaction exists between the electrophilic carbon and the nucleophilic nitrogen of different  $\text{RNCO}$  molecules. Actually, a "pre-trimer" is present, the important point being that the trimeric organozinc urea acts as a template for its formation as schematically shown below. Displacement of the "pre-trimer" by excess of  $\text{RNCO}$



(with regeneration of "A"; cf. the effect of EBDA) and bond rearrangement affords the isocyanurate  $(\text{RNCO})_3$ . The outcome of (4) (R = Et or Hex; R' = Hex or Et) supports this view:



Actually, a mixture of products is observed because of the unequal reactivity of  $\text{R}'\text{NCO}$  towards "A" (R = Et) and "A" (R = Hex).

We have found that the 1:1 adduct<sup>1</sup>  $\text{EtZn}\cdot\text{NR}\cdot\text{CO}\cdot\text{OMe}$  is the actual catalytic species in the  $\text{EtZnOMe}$ -catalyzed trimerization of  $\text{RNCO}$ . Since organozinc carbamates are trimeric in benzene<sup>4</sup> (e.g.  $\text{EtZnNPh}\cdot\text{CO}\cdot\text{OMe}$ : ebull. mol.wt. 695,  $n = 2.85$ ) the catalytic activity of organozinc alkoxides  $\text{RZnOR}'$  may be explained along the same lines by accepting a coordination mechanism involving a template effect of the trimeric organozinc carbamate species.

The reality of the template effect postulated for the trimeric organozinc urea and carbamate derivatives is supported by the observation that the thio-analogs  $\text{EtZnNPh}\cdot\text{CS}\cdot\text{NPh}_2$  and  $\text{EtZnNPh}\cdot\text{CS}\cdot\text{OMe}$  which are both dimeric<sup>4</sup> fail to display catalytic activity. The same is true for  $\text{EtZnNPh}\cdot\text{CO}\cdot\text{H}$  ( $n > 5$ ),  $\text{EtZnNPh}\cdot\text{CO}\cdot\text{Me}$  (tetrameric) and  $\text{EtZnNPh}\cdot\text{CS}\cdot\text{Me}$  (dimeric) (Ref. 4).

We believe that the proposed mechanism has not been encountered before in

organometallic catalysis. The main characteristic is that a *poly-metallic* complex through a coordination template-effect, forces a defined number of monomer molecules into a specific configuration (both sterically and electronically). Covalent bonds between the activated monomeric species are established upon breaking the initial coordinative bonds with the catalyst.

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*Institute for Organic Chemistry TNO  
Utrecht (The Netherlands)  
Laboratory for Organic Chemistry,  
State University, Utrecht (The Netherlands)*

J. G. NOLTES

J. BOERSMA

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