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The Cyclic Trimerization of Isocyanates by Organic Tin(II) Compounds Containing Sn-O-C Bonds

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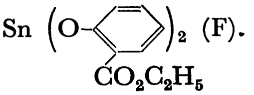
Synopsis. Organic tin(II) compounds containing Sn–O–C bonds were found to be effective catalysts for the cyclic trimerization of phenyl and ethyl isocyanate. The cyclic trimerization mechanism is discussed.

There have been a number of papers[1–3] describing the addition of Sn–O–C bonds of organotin(IV) oxides and alkoxides to compounds containing such activated double bonds as isocyanate, isothiocyanate, and carbodiimide. However, no similar reactions of organic tin(II) compounds have been investigated except for two reports by P. G. Harrison and J. J. Zuckerman on the reaction between phenyl isocyanate and organic tin(II) compounds.[4–5] For the purpose of investigating the reactivity of organic tin(II) compounds containing Sn–O–C bonds towards heterocumulenes, we have examined the reaction of phenyl and ethyl isocyanate with $Sn(OC_2H_4N(CH_3)_2)_2$ (A), $Sn(OC_2H_4OCH_3)_2$ (B), $Sn(OC_2H_5)_2$ (C), $Sn(O\underset{CH_3}{C}{=}CHCOCH_3)_2$ (D), $Sn(O\underset{CH_3}{C}{=}CHCO_2C_2H_5)_2$ (E), and  (F). The above tin(II) compounds showed different degrees of association, that is (A), (D), (E), as well as (F) are monomeric, (B) is dimer or trimer, and (C) is an associated solid.[6]

Results and Discussion

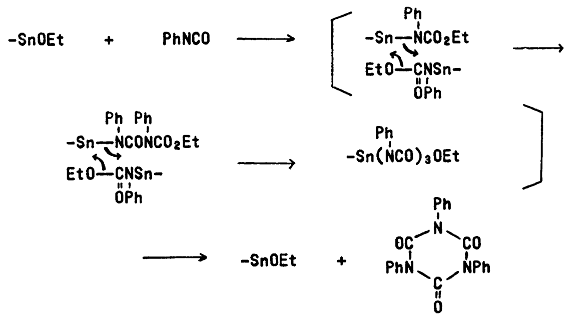
It was found that tin(II) compounds (A—F) were effective catalysts for the cyclic trimerization of phenyl isocyanate (PhNCO) and ethyl isocyanate (EtNCO), with the formation of the corresponding isocyanurates; the catalytic activity of (A) was the best, while that of (F) was least effective (Table 1).

However, similar reactions did not occur between PhNCO and tetravalent tin alkoxide, such as $Sn(OC_4H_9{}^t)_4$ and n-$C_4H_9Sn(OC_4H_9{}^t)_3$, under the same conditions; Rather, they stopped at the stage of the adduct-formation to give simply the corresponding *t*-butyl *N*-phenylcarbamatotin(IV) derivatives.

It may be concluded from these results that: i) the nucleophilicity of the oxygen atom of Sn(II)–OR bonds, which was expected from the I- and M-effects of R and the degree of association of $Sn(OR)_2$, has a marked effect on the catalytic action of Sn(II) compounds; ii) the reactivity of PhNCO toward Sn(II)–OR bonds is less than that of EtNCO; and iii) the divalent tin compounds are far better than the tetravalent tin tetraalkoxide and monoalkyltin trialkoxide as catalysts for the cyclic trimerization of isocyanates.

When a benzene solution of PhNCO and (C) in a molar ratio of 2: 1 was treated at room temperature for 40 min, the IR spectrum of the mixture showed no absorption band assigned to the NCO group. The hydrolysis products were ethyl *N*-phenylcarbamate and triphenyl isocyanurate in yields of 63 and 8% respectively. On the other hand, when the benzene solution was heated at 80—81 °C for 3 hr, the yields of the above hydrolysis products changed to 47 and 40% respectively after the hydrolysis of the reaction mixture.

Although the organotin(IV) compound-catalyzed reaction has been explained by a proposed mechanism[7] involving the successive insertion of three isocyanate units between the tin atom and the heteroatom of the attached group, followed by the elimination of the trimer from 1: 3 adducts, the change in the yields of the hydrolysis products suggests an alternative reaction route involing the four-centered intermolecular co-ordination of the divalent tin intermidiates, as is shown in the following scheme;



(Ph = C_6H_5 , Et = C_2H_5)

Scheme

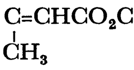
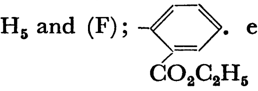
This reaction route was supported by the finding that the nucleophilicity of the nitrogen atom of the *N*-phenyl urethano group in $Sn\left(N\langle{}^{Ph}_{CO_2C_2H_5}\right)_2$ is more depressed than that of the *N*-ethyl urethano group in $Sn\left(N\langle{}^{Et}_{CO_2C_2H_5}\right)_2$; when a mixed solution of (C) (0.1 mol)–PhNCO (0.2 mol) in benzene and (C) (0.1 mol)–EtNCO (0.2 mol) in benzene, neithere of which showed any characteristic infrared absorption band of the NCO group, was heated at 80—81 °C for 3 hr, and then hydrolyzed, ethyl *N*-phenyl-*N'*-ethylallophanate $\left(C_6H_5NHCON\langle{}^{C_2H_5}_{CO_2C_2H_5}\right)$ and *N*-phenyl-*N'*,*N''*-diethyl isocyanurate were obtained in yields of 51 and 6.2% respectively.

Therefore, the four-centered intermolecular co-ordination mechanism may be proposed for the reaction

TABLE 1. YIELDS OF ISOCYANURATE BY THE ACTION WITH $Sn(OR)_2$ ON R′NCO AT 80 °C[a)]

$Sn(OR)_2$[d,e)]	(A)[b)]	(B)	(C)	(D)	(E)	(F)	(C)[b)]
	$R'=C_6H_5$						$R'=C_3H_5$
Yields (%) of $(R'NCO)_3$	100	100	66	33	27	0[c)]	100

a) [R′NCO]: $[Sn(OR)_2]$=50: 1 (3 hrs in benzene) b) IR spectroscopy demonstrated the absence of the characteristic absorption band of NCO group within 2 hr. c) Triphenyl isocyanurate was obtained almost quantitatively by removing benzene under reduced pressure (water pump). d) R: (A); $C_2H_4N(CH_3)_2$ (B); $C_2H_4OCH_3$ (C); C_2H_5, (D);


$\underset{CH_3}{\overset{|}{C}}=CHCOCH_3$, (E);

$\underset{CH_3}{\overset{|}{C}}=CHCO_2C_2H_5$ and (F);

e) Ref. 6.

with organotin(II) compounds containing an Sn–O–C bond, in addition to the conventional view of the successive insertion of isocyanate unites. The mechanism is based on the structural analogy of tin(II) compounds with carbene.

Experimental

Reaction Procedures.[8)] *Reaction of Organic Tin(II) Compounds with PhNCO in a 1: 50 Molar Ratio*: To a suspension of C (0.4 g, 1.8 mmol) in benzene (20 ml), PhNCO (10.1 g, 90 mmol) was added, after which the mixture was heated at 80—81 °C for 3 hr. During the reaction, white crystals precipitated. After cooling, the crystals were filtered off, washed with benzene, and then recrystallized from acetone afford triphenyl isocyanurate; mp 269.2—270 °C. IR: 1710 cm^{-1} ($\nu_{C=O}$). Found: C, 70.58; H, 4.31; N, 11.55%. Calcd for $C_{21}H_{15}N_3O_3$: C, 70.58; H, 4.23; N, 11.76%.

The other organic tin(II) compounds were reacted with PhNCO similarly.

Reaction of C with EtNCO in a 1: 50 Molar Ratio. Ethyl isocyanate (7.8 g, 110 mmol) was added to a suspension of C (4.8 g, 2.3 mmol) in benzene (26 ml), and then the mixture was refluxed for 2 hr. The reaction mixture showed no characteristic absorption band ascribable to the NCO group. After the reaction mixture has been concentrated and then hydrolyzed with aqueous acetone, the insoluble parts of the hydrolyzate were separated centrifugally and concentrated again under reduced pressure. The precipitates were then filtered and recrystallized from *n*-hexane to give 7.6 g (97.4%) of white crystals; mp 94—95 °C. IR: 1680 cm^{-1} ($\nu_{C=O}$). NMR (CCl_4): δ 1.20 (3H, t, CH_3), 3.86 (2H, q, CH_2). Found: C, 50.29; H, 7.16; N, 19.59%. Calcd for $C_9H_{15}N_3O_3$: C, 50.69; H, 7.09; N, 19.71%.

Reaction of $Sn(OC_4H_9{}^t)_4$ with PhNCO in a 1: 50 Molar Ratio. Phenyl isocyanate (27.8 g, 231 mmol) was added, drop by drop, to a solution of $Sn(OC_4H_9{}^t)_4$ (1.9 g, 4.6 mmol) in benzene (55 ml), and then the mixture was refluxed for 3 hr. After the removal of solvent and the unreacted PhNCO *in vacuo*, the residue was recrystallized from benzene to give 3.4 g (83%) of tetrakis(*t*-butyl *N*-phenylcarbamato)tin(IV) as white crystals; mp 151 °C (dec). IR: 1647 cm^{-1}. NMR (C_6H_6): δ 1.45 (s, CH_3). Found: C, 60.11; H, 6.32; N, 6.38; Sn, 12.95%. Mol wt; 850. Calcd for $C_{44}H_{56}N_4O_8Sn$: C, 59.54; H, 6.36; N, 6.31; Sn, 13.37; Mol wt, 888.

The reaction of *n*-$C_4H_9Sn(OC_4H_9{}^t)_3$ with PhNCO was carried out in a similar way. The tin compound thus obtained was identified on the basis of the IR spectrum and its hydrolysis product.

Reaction of C with PhNCO in a 1: 2 Molar Ratio. *Reaction at 80—81 °C*: Phenyl isocyanate (19.8 g, 166 mmol) was added, drop by drop, to a suspension of C (17.2 g, 82.3 mmol) in benzene (69 ml) at 23—25 °C. After the disappearance of the NCO absorption band in their spectrum (40 min), the solution was refluxed for 3 hr. The white crystals thus precipitated were removed by filtration and then recrystallized from benzene to give triphenyl isocyanurate in a yield of 40%. The mother liquor was concentrated and then hydrolyzed with aqueous acetone. After the centrifugal removal of the insoluble parts, the acetone solution of the hydrolyzate was distilled *in vacuo*. *N,N′*-Diphenylurea (mp 234 °C) and ethyl *N*-phenylcarbamate (bp 140.5 °C/10.5 mmHg) were obtained in yields of 12% and 47% respectively.

Reaction at Room Temperature: After the disappearance of the NCO absorption band in the IR spectrum, the reaction mixture was hydrolyzed with aqueous acetone. Triphenyl isocyanurate, *N,N′*-diphenylurea, and ethyl *N*-phenylcarbamate were thus obtained in yields of 8%, 8%, and 63% respectively.

Similarly, the reaction of C with EtNCO in a molar ratio of 1: 2 was carried out.

Reaction of a Solution of C-PhNCO in Benzene with a Solution of C-EtNCO in Benzene. To a solution of C (15.0 g, 72 mmol) and EtNCO (10.2 g, 144 mmol) in benzene (34 ml), a solution of C (15.0 g, 72 mmol) and PhNCO (17.1 g, 144 mmol) in benzene (34 ml) was added, and then the mixture was heated at 80—85 °C for 3 hr. After the distillation of the solvent, the concentrated residue was hydrolyzed with aqueous acetone and the insoluble parts of the hydrolyzate were removed centrifugally. The vacuum distillation of the acetone solution afforded 17.3 g of ethyl *N′*-ethyl-*N*-phenylallophanate [Bp 91 °C/0.25 mmHg. IR: 1691, 1710 (sh), 1725 (sh), 1743 ($\nu_{C=O}$) and 3350 (ν_{N-H}). NMR: δ 1.15 (NCH_2CH_3), 1.20 (OCH_2CH_3), 3.83 (NCH_2), 4.08 (OCH_2), and 6.7—7.13 (C_6H_5). Found: (Calcd for $C_{12}H_{16}N_2O_3$): C, 60.54 (61.00); H, 6.80 (6.82); N, 11.88 (11.86)] and 1.58 g of *N*-phenyl-*N′,N″*-diethyl isocyanurate [Mp 94.5—96.8 °C. IR: 1674 and 1697 ($\nu_{C=O}$). NMR: δ 1.26 (CH_3), 3.97 (CH_2), and 7.1—7.65 (C_6H_5). Found: (Calcd for $C_{13}H_{15}N_3O_3$): C, 59.67 (59.75); H, 5.81 (5.78); N, 16.30% (16.08%)].

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