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Reaction of Organic Tin(II) Compounds with Ethyl Isocyanate

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The reaction of Sn–OC bond-containing tin(II) compounds with ethyl isocyanate was investigated. From the ν_{NCO} absorption bands, it is recognized that the reactivity, in terms of tin(II) compounds, decreases in the order: bis[2-(dimethylamino)ethoxo]tin(II) > bis[*o*-(ethoxycarbonyl)phenolato]tin(II) > di(phenolato)tin(II) > bis(ethoxycarbonylacetonato)tin(II) > bis(3-ethoxycarbonyl-2-pentanoato)tin(II) > bis(1-phenylbutane-1,3-dionato)tin(II) > bis(dibenzoylmethanato)tin(II). Bis[2-(dimethylamino)ethoxo]tin(II), bis[*o*-(ethoxycarbonyl)phenolato]tin(II), and di(phenolato)tin(II) yielded triethyl isocyanurate as a main product from reactions with ethyl isocyanate, while bis(ethoxycarbonylacetonato)tin(II), bis(3-ethoxycarbonyl-2-pentanoato)tin(II), bis(1-phenylbutane-1,3-dionato)tin(II), and bis(dibenzoylmethanato)tin(II) gave mixtures of the isocyanurate and 6-ethylimino-1,3,5-triethylhexahydro-1,3,5-triazine-2,4-dione. The mechanism for the formation of these products is discussed.

Certain kinds of organic tin(II) compounds are widely used as catalysts for the synthesis of polyurethanes and as curing agents for silicones. Recently, many kinds of organic tin(II) compounds[1—10] have been prepared, and the reactivities of some have been investigated. Previously, the present authors reported that the reaction of bis(acetylacetonato)tin(II) with ethyl isocyanate resulted in 6-ethylimino-1,3,5-triethylhexahydro-1,3,5-triazine-2,4-dione in an excellent yield.[11] In the present paper, the reaction of several organic tin(II) compounds with ethy isocyanate will be described.

Results and Discussion

Reaction of Tin(II) Dialkoxide with Ethyl Isocyanate. Ethyl isocyanate was added to a solution of bis[2-(dimethylamino)ethoxo]tin(II) (**1**), bis[*o*-(ethoxycarbonyl)phenolato]tin(II) (**2**), and di(phenolato)tin(II) (**3**) in benzene at room temperature and then heated for several hours (as indicated in Table 1). The reaction mixtures were hydrolyzed to isolate the products. There results are shown in Table 1.

In the reaction of tin(II) compound **1** with ethyl isocyanate at 20—24 °C, IR spectroscopy demonstrated the absence of the characteristic absorption band of the ν_{NCO} group within 1 h. When the reaction mixture was further refluxed for 3 h, the yield of triethyl isocyanurate was much higher compared with that of the reaction without heating (runs 1 and 2). This indicates that the reaction proceeds through the intermolecular reaction of the intermediate, as described in a previous paper.[13] Judging from the time required for the disappearance of the ν_{NCO} absorption band observed in ethyl isocyanate, it was found that tin(II) compounds **2** and **3** were less reactive than tin(II) compound **1**, and that the reactivity of tin(II) compound **3** was inferior to that of tin(II) compound **2**. These facts indicate that the reduction in the electron density on the oxygen atom of the Sn–OC bond due to the M-effect of the R group results in a decrease in the nucleophilicity of the oxygen atom toward ethyl isocyanate and that the low solubility[6] of tin(II) compound **3** reduced the reaction of that compound **3** toward ethyl isocyanate. In the reaction of tin(II) compound **2**, triethyl isocyanurate was obtained as the main product accompanied by a small amount of the carbamate derivative and tin(II) compound **3** gave triethyl isocyanurate as the only product. This suggests that the Sn–N bond formed by the insertion of ethyl isocyanate into the Sn–OC bond is considerably more active.

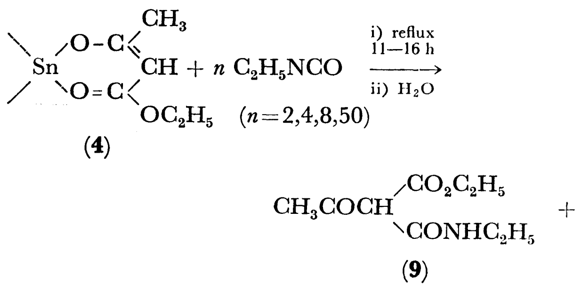
TABLE 1. REACTION OF $Sn(OR)_2$ WITH ETHYL ISOCYANATE IN BENZENE[a]

Run	$Sn(OR)_2$	Reaction time (h)	Yield (%) of products[b]	
			$C_2H_5NHCO_2R$	$(C_2H_5NCO)_3$
1	**1**	3[c]	45.4[e]	38.6[g]
2	**1**	3[d]	25.9	56.1
3	**2**	3	4.9[f]	90.2
4	**2**	8		86.3
5	**3**	8		86.9

a) $[Sn(OR)_2] : [C_2H_5NCO] = 1 : 2$ b) Satisfactory analytical and IR or NMR spectroscopic data were obtained for all compounds prepared. c) Reaction temperature 20—24 °C. d) After the disappearance of the ν_{NCO} band, the reaction mixture was heated for 3 h. e) Bp 70—71 °C at 0.3 mmHg. f) Bp 98—100 °C at 0.3 mmHg. g) Mp 94—95 °C (Lit, 95 °C[12]).

Reactions of the β-Keto Ester and the β-Diketone Tin(II) Derivative with Ethyl Isocyanate. These reactions were carried out using a similiar procedure. The results are summarized in Table 2.

The reaction between the bis(β-keto ester)tin(II) derivative and ethyl isocyanate: bis(ethoxycarbonylacetonato)tin(II) (**4**) reacted with ethyl isocyanate in various molar ratios to give mixtures of ethyl α-(ethylcarbamoyl)acetoacetate (**9**), triethyl isocyanurate (**10**), and 6-ethylimino-1,3,5-triethylhexahydro-1,3,5-triazine-2,4-dione (**11**), as shown in Reaction 1.



$$\mathrm{Sn(OC(CH_3){=}CH{-}C(OC_2H_5){=}O)_2} + n\,\mathrm{C_2H_5NCO} \xrightarrow[\text{ii) } H_2O]{\text{i) reflux } 11\text{—}16\ \text{h}} \mathrm{CH_3COCH(CO_2C_2H_5)(CONHC_2H_5)} +$$

(n=2,4,8,50)

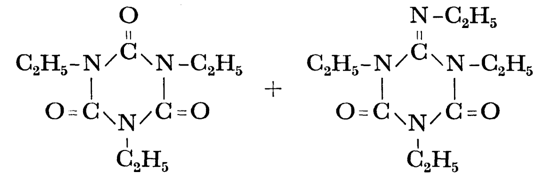
(**4**)

(**9**)

TABLE 2. REACTION OF $Sn(OR)_2$ WITH ETHYL ISOCYANATE IN BENZENE

Run	$Sn(OR)_2$	Molar ratio $RNCO/Sn(OR)_2$	Reaction time (h)	Yield (%) of products **9**[a)]	**10**	**11**[b)]
6	**4**	2	11	79.7		
7	**4**	4	11	60.0	13.9	
8	**4**	8	11	43.0	22.1	9.6
9	**4**	50	16		40.0	27.7
10	**5**	4	15		75.0	trace
11	**5**	50	38		47.7	34.4
12	**6**	4	9		16.1	62.0
13	**6**	50	26		24.5	60.4
14	**7**	2	40		16.7	37.7

a) Bp 80 °C at 0.05 mmHg. b) Bp 84—87 °C at 0.05 mmHg (84—87 °C at 0.05 mmHg[11)]).

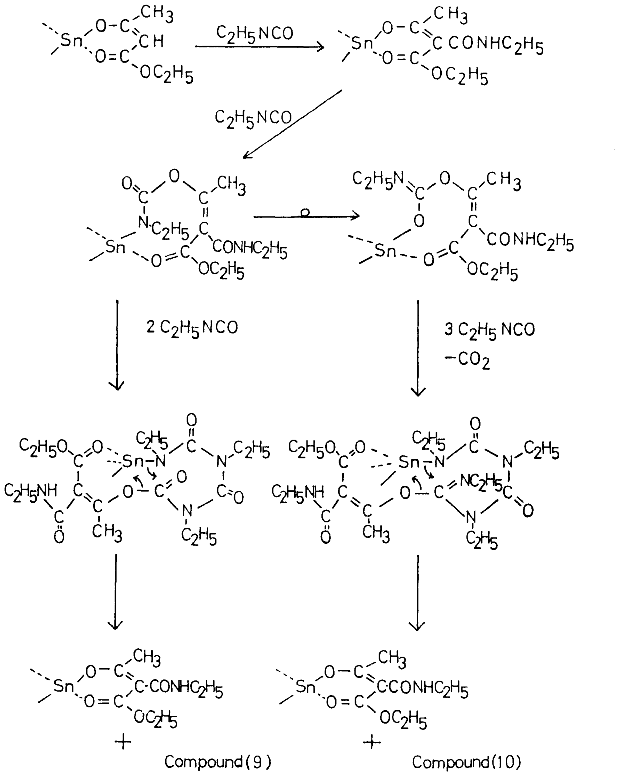


(10) **(11)** (1)

Judging from the reaction time required for the completion of the reaction, β-keto ester tin(II) compounds have been found to be less reactive toward ethyl isocyanate than tin(II) alkoxides. Although all of the reactions between bis(acetylacetonato)tin(II) (**8**) and ethyl isocyanate in various molar ratios gave only compound **11**, the reaction of tin(II) compound **4** with ethyl isocyanate of a molar ratio of 1 : 2 (run 6) yielded compound **9** in a yield of 79.6%. This difference may be related to the lesser nucleophilicity of the oxygen atom of the Sn–OC bond and the preferential reactivity of the methine proton in the chelate ring due to the greater electron-withdrawing force of the ethoxyl group. The reaction of a molar ratio of 1 : 4 (run 7) yielded compound **10** (13.9%) besides the formation of compound **9** (60.0%). In the cases of $n=8$ (run 8) and 50 (run 9), compound **11** was obtained in yields of 9.6 and 27.7%, respectively, together with the formation of compound **10** in 22.1 and 40 % yields, respectively. From these results, it is clear that the yield of compound **11** increases with increasing molar ratio of ethyl isocyanate to tin(II) compound **4**. The reaction of bis(3-ethoxycarbamoyl-2-pentanoato)tin(II) (**5**) with ethyl isocyanate in a molar ratio of 1 : 4 (run 10) gave compound **10** as a main product accompanied by a small amount of compound **11**. When a large amount of ethyl isocyanate ($n=50$, run 11) was treated with tin(II) compound **5**, compounds **10** and **11** were obtained in yields of 47.7 and 34.4 %, respectively. It is worth noting that compound **11** is produced by a reaction with the β-keto ester tin(II) compound, in which the methin proton of the chelate ring is substituted by an ethyl or ethylcarbamoyl group. From these results, the following scheme is given as a plausible reaction path:

TABLE 3. YIELD AND PROPORTION OF PRODUCTS FROM IN THE REACTION OF VARIOUS TIN(II) COMPOUNDS WITH ETHYL ISOCYANATE

$Sn(OC(R){=}CHCOR')_2$	R	R′	Total yield of product (%)	Proportion of products **10**	**11**
8	CH_3	CH_3	89		100
6	C_6H_5	CH_3	85	29	71
7	C_6H_5	C_6H_5	54	31	69
4	CH_3	OC_2H_5	68	59	41



Scheme.

The extent to which N→O migration of the tin atom correlates with the formation of compounds **10** and **11** is considerable.

The Reaction of Bis(β-diketonato)tin(II) Derivatives with Ethyl Isocyanate: When bis(1-phenylbutane-1,3-dionato)tin(II) (**6**) was allowed to react with ethyl isocyanate, compounds **10** and **11** were obtained without the formation of 2-ethylcarbamoyl-1-phenyl-1,3-butanedione. The reaction in a 1 : 4 molar ratio required 4 h for the disappearance of the ν_{NCO} absorption band at about 2270 cm^{-1} and 26 h in a 1 : 50 molar ratio. On the other hand, it was found that the reaction of bis(dibenzoylmethanato)tin(II) (**7**) with ethyl isocyanate was very slow; after heating for 40 h, 96 % of tin(II) compound **7** and 45.6% of ethyl isocyanate were recovered and compounds **10** and **11** were obtained in low yields. Tin(II) compound **8** gave only compound **11** and the other bis(β-diketonato)tin(II) derivatives afforded a mixture of compounds **10** and **11** as reaction products. The bis(β-diketonato)tin(II) derivatives provided compound **11** in higher yields in comparison with the bis(β-keto ester)tin(II) derivatives as described above. It may be assumed that N→O migration of the tin atom occurs more easily in tin(II) compounds **6** and **7** than in tin(II) compounds **4** and **5**.

As can be seen from Table 3, the proportion of products is influenced by the substituent, R′, bonded to the chelate ring; the production of compound **11** increases in the order: $CH_3 > C_6H_5 > OC_2H_5$. Taking account of the $\nu_{C=O}$ absorption band of tin(II) compound **4** ($\nu_{C=O}$ 1600 cm^{-1}),[1] tin(II) compound **6** ($\nu_{C=O}$ 1565 cm^{-1}),[4] tin(II) compound **7** ($\nu_{C=O}$ 1548 cm^{-1}),[4] and tin(II) compound **8** ($\nu_{C=O}$ 1567 cm^{-1}),[1] the strength of co-ordination of the oxygen atom on the R′CO group toward the tin atom appears to play an important role in the formation of compounds **10** and **11**.

Experimental

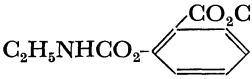
Experiments were carried out in a nitrogen atmosphere dried using liquid nitrogen. The measured melting and boiling points are uncorrected. The IR spectra were recorded with a Hitachi EPI-2S spectrometer and the ^1H-NMR spectra on a Hitachi R-24 (60 MHz) using TMS as an internal standard. The abbreviations s, t, q, br, and m in the NMR spectra denote singlet, triplet, quartet, broad, and multiplet, respectively. Elemental analysis were carried out using a Yanagimoto M-2 CHN corder.

Reagents. Hexane, benzene, and ethanol were dried using the methods given a previous paper.[6] Ethyl acetoacetate, ethyl salicylate, benzoylacetone, phenol, and 2-(dimethylamino)ethanol were dried using an azeotropic distillation method using benzene. Ethyl 3-ethylacetoacetate was prepared by a method given in the litrature.[11] Ethyl isocyanate was obtained commercially and purified by distillation just prior to use. Tin(II) derivatives were prepared by reactions of tin(II) diethoxide with the corresponding alcohol, phenol, ester, or ketone.

General Procedure. Ethyl isocyanate was added dropwise to a benzene (1.4—1.5 ml/$Sn(OR)_2$ mmol) solution of $Sn(OR)_2$ (100 mmol) at 25—30 °C with stirring. After standing at room temperature for 1 h, the solution was heated to 79—81 °C for fixed time intervals and the disappearance of the ν_{NCO} absorption band was observed. After the solution distilled off, the oily residue was hydrolyzed with a water (5—6 ml) and acetone (100 ml) or benzene mixed solution. Removal of the inorganic tin with a centrifugal separator gave a pale yellow solution, which was then concentrated and distilled *in vacuo*. Products **9** and **11** were fractionally distilled under reduced pressure through a 20-cm Widmer fractionating column. The residue (compound **10**) was recrystallized from hexane. In the case of the reaction with tin(II) compound **3**, the unreacted tin(II) compound was filtered off before hydrolysis. The products obtained were identified on the basis of IR, NMR, and mass spectra and elemental analysis. Proof of the structure of compound **11** was also provided by its conversion to triethyl isocyanurate a 2M-HCl alcoholic solution.[11]

$CH_3COCH(CONHC_2H_5)CO_2C_2H_5$ bp 80 °C at 0.05 mmHg, M^+ 201, IR(cm^{-1}); ν_{N-H} 3340, $\nu_{C=O}$ 1730, $\nu_{C=O}$ and $\delta_{O-H\,enol}$ 1650, δ_{N-H} 1550, $\nu_{C=N}$ 1400, $\nu_{C=C}$ 955, 790, NMR (δ); $\mathbf{CH_3}CH_2N$ and $\mathbf{CH_3}CH_2O$ 1.3 district (m), $\mathbf{CH_3}C{=}O$ 2.39(s), $CH_3\mathbf{CH_2}N$ 3.38, $CH_3\mathbf{CH_2}O$ 4.24(q), **NH** 9.23(t), OH 18.69(s). Found: C, 53.61; H, 7.71; N, 7.16%. Calcd for $C_9H_{15}O_4N$: C, 53.72; H, 7.51; N, 6.96%.

$C_2H_5NHCO_2CH_2CH_2N(CH_3)_2$ bp 70—71 °C at 0.3 mmHg, IR(cm^{-1}); ν_{N-H} 3350, $\nu_{C=O}$ 1680, NMR(δ); $CH_3\mathbf{CH_2}N$ 1.11(t), $\mathbf{CH_3}N$ 2.19(s), $\mathbf{CH_2}N$ 2.43(t), $CH_3\mathbf{CH_2}$ 3.12(m), $\mathbf{CH_2}O$ 4.02(t), N–H 5.5(br). Found: 52.46; H, 9.88; N, 17.14%. Calcd for $C_7H_{16}N_2O_2$: C, 52.47; H, 10.07; N, 17.49%.


bp 98—100 °C at 0.3 mmHg, IR(cm^{-1}); ν_{N-H} 3340, $\nu_{C=O}$ 1710, NMR(δ); $\mathbf{CH_3}CH_2$ 1.11(t), $\mathbf{CH_3}CH_2O$ 1.30(t), $CH_3\mathbf{CH_2}N$ 3.23(m), $CH_3\mathbf{CH_2}O$ 4.20(q), N–**H** 5.35(s), phenyl proton 7.20—7.80(m). Found: C, 61.07; H, 6.40; N, 5.80%. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90%.

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