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The Synthesis of Heterocyclic Compounds by the Reaction of Tin(II) Bis(acetylacetonate) with Isocyanates

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It was found that phenyl isocyanate reacted with tin(II) bis(acetylacetonate) to yield triphenyl isocyanurate, 5-acetyl-6-methyl-2-oxo-3-phenyl-4-phenylimino-3,4-dihydro-2*H*-1,3-oxazine, and *N*,*N'*-diphenylurea, while ethyl isocyanate reacted with tin(II) bis(acetylaceonate) to afford only 2,4-dioxo-6-ethylimino-1,3,5-triethylhexahydro-1,3,5-triazine.

It has recently been reported that some monomeric tin(II) compounds containing Sn–OC bonds reacted smoothly with *n*-alkyl iodides to give the oxidative addition compounds.[1-2] While there have already been reports on the reaction of tin(II) compounds containing Sn–OC bonds with some isocyanate,[3-5] the reaction with metal acetylacetonate has not yet been studied. It is of interest to investigate the behavior of tin(II) bis(acetylacetonate) toward compounds containing activated double bonds such as isocyanate. In this paper, we will describe the synthesis of heterocyclic compounds by the reaction of tin(II) bis(acetylacetonate) with phenyl and ethyl isocyanates.

From the reaction of phenyl isocyanate (PhNCO) with a catalytic amount of tin(II) bis(acetylacetonate), Sn(acac)$_2$, triphenyl isocyanurate was obtained in a yield of 33%. The product was identified on the basis of the elemental analyses and its IR spectrum. In order to obtain further information on the behavior of Sn(acac)$_2$ toward PhNCO, the reaction was carried out while varying the molar ratio of PhNCO to Sn(acac)$_2$ from 1: 1 to 4: 1.

The reaction in a molar ratio of 1: 1 gave two colorless compounds which were found to be $C_{19}H_{16}N_2O_3$ (I) and $C_{13}H_{12}N_2O$ (II). The infrared spectrum of (I) showed bands ascribable to $\nu_{C=O}$ at 1723, and 1689, to $\nu_{C=C}$ at 1660, to $\nu_{C=N}$ at 1419, to ν_{C-N} at 1345, to δ_{s-CH_3} at 1435, and to δ_{as-CH_3} at 1365 cm^{-1}. Its NMR spectrum in CDCl$_3$ displayed bands at 2.56 (3H, $CH_3C=$) and 2.03 (3H, CH$_3$CO) ppm, besides the aromatic proton (10H). From these data, (I) was found to be 5-acetyl-6-methyl-2-oxo-3-phenyl-4-phenylimino-3,4-dihydro-2*H*-1,3-oxazine. This assingment was also supported by the mass spectral data—*i.e.*, the peaks of M$^+$, M$^+$—1, CH$_3$CO, and C$_6$H$_5$ at *m/e* 320, 319, 43, and 77 respectively. There were also observed fragment ions resulting from the loss of a methyl or carbonyl group from the molecular ion. Compound (II) could also be assinged to *N*,*N'*-diphenylurea by a comparison of the melting point with that of an authentic sample.

The reaction of Sn(acac)$_2$ with PhNCO in a molar ratio from 1: 2 to 1: 4 yielded (I) and (II) in equal amounts, which increased with the ratio of PhNCO to Sn(acac)$_2$ (Table 1).

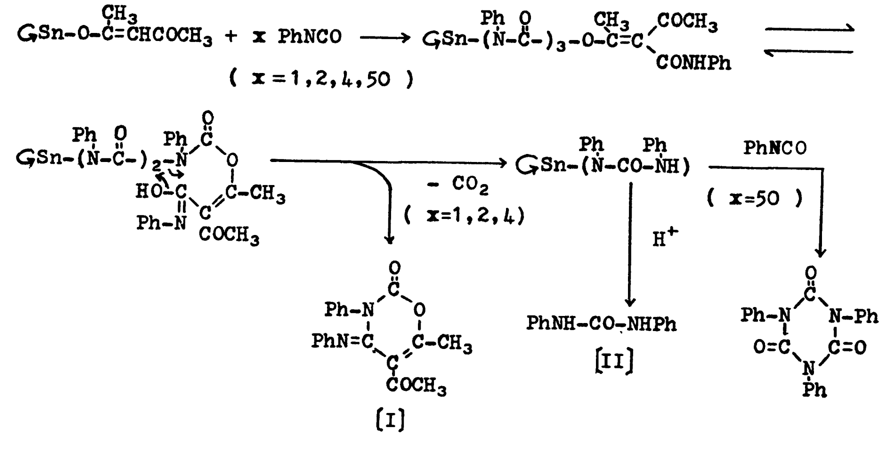
Table 1. Results of the reaction of Sn (acac)$_2$ (0.1 mol) with PhNCO in various molar ratios

Molar ratio PhNCO/Sn(acac)$_2$	Yields (mol)	
	(I)	(II)
1	0.0062	0.0060
2	0.0363	0.0334
4	0.0801[a]	0.0721

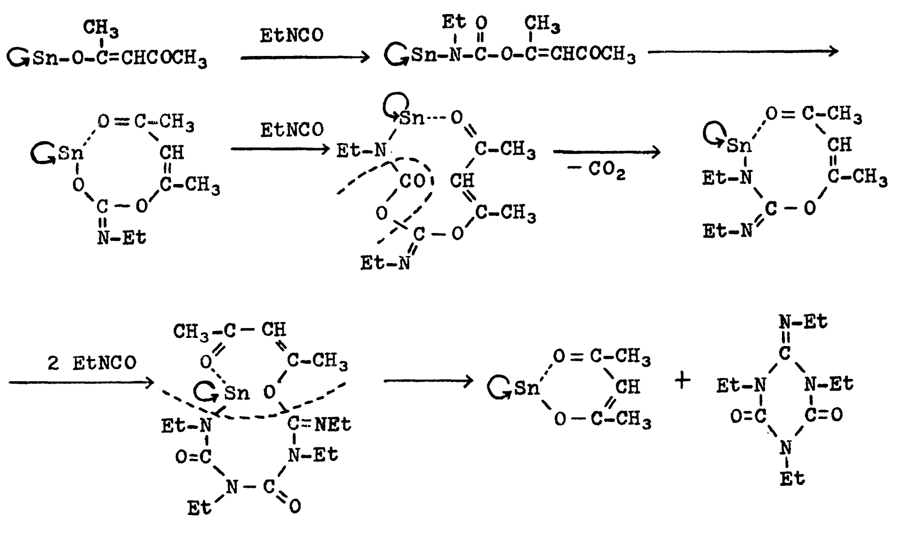
a) Triphenyl isocyanurate was detected in a small quantity.

Therefore, as for the formation of (I), (II), and triphenyl isocyanurate, we tentative propose the process depicted in Scheme 1.

Contrary to the reaction with PhNCO, Sn(acac)$_2$ reacted easily with various molar ratios of ethyl isocyanate (EtNCO) at 67—72 °C to give only 6-ethyl-



Scheme 1



Scheme 2.

imino-1,3,5-triethylhexahydro-1,3,5-triazine in a high yield, with the quantitative recovery of $Sn(acac)_2$. The structure was confirmed by the IR and NMR spectra, by elemental analyses, and by a molecular-weight determination. The IR spectrum exhibited a band at 1672 cm^{-1} which can be ascribed to the carbonyl group. The NMR spectrum showed triplets at 1.18 (9H, $-\overset{|}{N}-CH_2C\underline{H}_3$) and 1.25 (3H, $\rangle C{=}N-CH_2C\underline{H}_3$) ppm, and quartets at 3.35 (2H, $\rangle C{=}N-CH_2-$), 3.85 (2H, $\begin{smallmatrix}-CO\\-CO\end{smallmatrix}\rangle N-C\underline{H}_2-$), and 3.89 (4H, $\begin{smallmatrix}-CN\\-CO\end{smallmatrix}\rangle N-C\underline{H}_2-$) ppm. A further proof of the structure was provided by its conversion into triethyl isocyanurate by hydrolysis with alcoholic hydrochloric acid. The IR spectrum was identical with that of an authentic sample prepared by the trimerization of EtNCO with a catalytic amount of $Sn(OC_2H_5)_2$. The formation of 6-ethylimino-1,3,5-triethylhexahydro-1,3,5-triazine seems to involve the processes shown in Scheme 2.

Although a detailed explanation cannot be offered for the remarkable difference between the reaction of PhNCO and that of EtNCO with $Sn(acac)_2$, it is clearly possible that the reaction between PhNCO and the methine proton on the C-3 of the Chelate ring leads to the formation of the 1,3-oxazine derivative.

Experimental

The experiments were carried out under a dry nitrogen atmosphere. The IR spectra were recorded on a Hitachi EPI-S2 infrared spectrometer as KBr disks or liquid films. The NMR spectra were determined by means of a Hitachi R-24 spectrometer (60 MHz) in CCl_4 or $CDCl_3$, using TMS as the internal standard. The chemical shifts are expressed in δ values. The mass spectra were measured on a Hitachi RMU-7 model double-focusing spectrometer. The elemental analyses were carried out with a Yanagimoto CHN analyzer, Model MT-2.

Materials. Tin(II) bis(acatylacetonate) was prepared in accordance with the method of a previous paper.[6] The other were commercially available.

Reaction Procedures. *The Reaction of PhNCO in the Presence of a Catalytic Amount of $Sn(acac)_2$:* A solution of PhNCO (46 g, 0.386 mol) and $Sn(acac)_2$ (2.9 g, 9.15 mmol) in benzene (92 ml) was stirred at 80—81 °C for 3 hr. The solids thus precipitated were filtered off and recrystallized from ethanol. Triphenyl isocyanurate was obtained in a 33% yield; mp 269—270 °C (lit, 275 °C[7]). IR (KBr) $\nu_{C=O}$ 1710 cm^{-1}.

The Reaction of PhNCO with $Sn(acac)_2$ in a Molar Ratio of 1: 1—4: 1: Phenyl isocyanate was added, drop by drop, to a *n*-hexane of solution of $Sn(acac)_2$ (0.1 mol) at 26—27 °C, and then the solution was heated with stirring in an oil bath for 3 hr. An evolution of carbon dioxide was observed throughout the reaction. The precipitated yellow solids were isolated by filtration, treated with 2M-HCl at room temperature and extracted with benzene using a Soxhlet extractor. The subsequent evaporation of the benzene from the extract left a solid residue. The recrystallization of the residue from methanol and then acetone gave a product (I) as white crystals; mp 213—213.3 °C (Found: C, 71.54; H, 4.97; N, 8.60%. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.04; N, 8.75%). IR (KBr): 1723, 1689, 1660, 1435, 1419, 1365, and 1345 (cm^{-1}). NMR ($CDCl_3$): 2.03, 2.56, and 7.0—7.67 ppm. Mass spectra: *m/e* 320 (M^+), 319, 77, and 43. The yellow powders remaining in the Soxhlet extractor were recrystallized from acetone. White needles (II) were thus obtained as the product; mp 234—235 °C (lit, 235 °C[8]. *m/e*: 212 (M^+). IR: 3310 and 1648 cm^{-1}.

On the other hand, $Sn(acac)_2$ was recovered by distilling the evaporation residue of the filtrate in a vacuum.

The Reaction of EtNCO with $Sn(acac)_2$: A mixture of $Sn(acac)_2$ (0.1 mol) and EtNCO (0.2, 0.4, 0.8, and 5.0 mol) in benzene (150 ml) was refluxed for 3 hr at 64—72 °C with stirring in an oil bath. An evolution of carbone dioxide was observed throughout the reaction. After the removal of the solvent in a vacuum, the residue was distilled, giving a mixture of triazine and $Sn(acac)_2$ in a quantitative yield. The mixture was then treated with 1—2 ml of water in acetone (30 ml), and the resulting white solids were separated centrifugally. The acetone solution was distilled *in vacuo* to give a light yellow viscous liquid in an 82—89% yield; bp 84—87 °C/0.5 mmHg (Found: C, 54.52; H, 8.40; N, 21.04%. Mol wt 228 (cryoscopically in benzene). Calcd for $C_{11}H_{20}N_4O_2$: C, 54.99; h, 8.38; N, 21.04%, Mol wt 240). IR (liquid films): 1672 cm^{-1}. NMR (CCl_4): 1.18, 1.23, 1.25, 3.35, 3.85, and 3.89 ppm.

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