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REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS IX
ADDITION AND SUBSEQUENT β-ELIMINATION REACTIONS OF TRIMETHYLSILYL- AND STANNYLAMINES WITH CHLORAL

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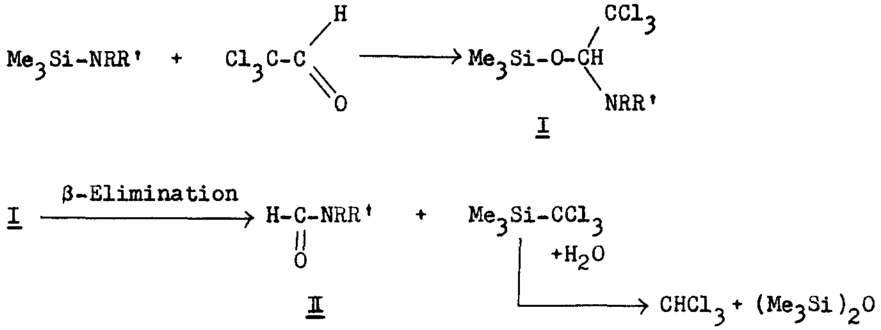
Simple insertion reactions of group IV organometallics have been investigated for various unsaturated systems[1]. When insertion products were unstable, subsequent β-elimination from them were predicted for the reaction of chloral with Sn-O[2] or Pb-O[3] compounds and for that of C=S compounds with N-methylhexamethyldimetallazane[4,5]. In this publication which takes chloral as an addendum, steric requirement on nitrogen atom in trimethylsilyldialkylamine is found to influence predominantly the stability of the insertion products. However, β-elimination products were only obtained for trimethylstannyldimethyl- and diethylamine in the analogous way as Sn-O or Pb-O compounds.

When chloral (10 millimoles) were added to the same molar amounts of trimethylsilyldimethylamine at 0°, exothermic reaction took place. Distillation of above reaction mixture(b.p.$_{0.6}$ 71°) gave exclusively α-dimethylamino-β,β,β-trichloroethoxytrimethylsilane $\underline{I_a}$, in 75% yield. Isolated insertion product $\underline{I_a}$ was identified as follows; Anal. Calcd. for $C_7H_{10}ClNOSi$ Cl 40.19, Found 40.09, nmr; τ 9.80(9H) for $C\underline{H}_3$-Si, τ 7.51(6H) for $C\underline{H}_3$-N, and τ 5.51(1H) for C-$\underline{H}$.

However, distillate for seven other trimethylsilyldialkylamines was the mixture of similar insertion products as $\underline{I_a}$ and N,N-dialkylformamide $\underline{II}_{b-h}$. Formation of $\underline{II}$ and trimethylsilyltrichloromethide, which was identified by comparison its infra-red and nmr spectra with authentic material[6] and by the formation of chloroform (100% based on formed II) and hexamethyldisiloxane (91%) through hydrolysis of reaction mixture, suggests the folowing pathway.



$$\mathrm{Me_3Si{-}NRR'} + \mathrm{Cl_3C{-}CH{=}O} \longrightarrow \mathrm{Me_3Si{-}O{-}CH(CCl_3)(NRR')}\ \ \underline{\mathrm{I}}$$

$$\underline{\mathrm{I}} \xrightarrow{\beta\text{-Elimination}} \underset{\underline{\mathrm{II}}}{\mathrm{H{-}C({=}O){-}NRR'}} + \mathrm{Me_3Si{-}CCl_3} \xrightarrow{+H_2O} \mathrm{CHCl_3} + \mathrm{(Me_3Si)_2O}$$

Relative amounts of II and I were estimated with peak areas of characteristic proton signals around τ 2.0 for II and τ 5.5 for I. Results were summarized in Table I.

As shown in Table I, stability of the insertion product I did not show any relationship with the basicity of corresponding secondary amines. Above order of the ratio II/I suggests that steric requirement of adduct I played dominant role. Although basicity of N-trimethylsilylpiperidine and -morpholine would presumed to differ considerably, the ratios II/I observed were nearly equal. Therefore, "1,3-interaction" favored β-elimination to a large extent compared with less hindered trimethylsilyldiethylamine or N-trimethylsilylpyrrolidine.

When trimethylstannyldimethyl or -diethylamine were treated with chloral instead of corresponding Si-N compounds in the same conditions, simple insertion adducts similar to I were not detected at all for both Sn-N compounds. Sole products were N,N-dimethylformamide (64%) or N,N-diethylformamide (80%) and trimethyltin trichloromethide. The latter was identified with trimethyltin proton signal at 9.52 (lit. 9.50[7] and 9.52[8]), and the wellknown formation of 7,7-dichloronorcarane[7] (46% for Me and 39% for Et) as well as trimethyltin chloride (60% for Me and 78% for Et) by treating above reaction mixtures with cyclohexene at 150° for 24 hours.

Preferential β-elimination for Sn-N compounds seems analogous for Sn-O[2], or Pb-O[3] compounds, however, insertion products for the latter two cases were stable at room temperature. Since σ^+ values[9] for $-NMe_2$ (-1.70) is smaller than for

TABLE I

Relative Ratio of α-Dialkylamino-β,β,β-trichloroethoxytrimethylsilane (I) and N,N-Dialkylformamide(II) for the Reaction of $Me_3Si-NRR'$ with Chloral[a]

Run	R	R'	α-Dialkylamino-β,β,β-trichloro ethoxytrimethylsilane (I)			N,N-Dialkyl- formamide(II)		II/I	pK$_a$ of RR'NH
			Yield (%)	Chemical Shift (τ) $(C\underline{H}_3)_3Si$	Chemical Shift (τ) C-$\underline{H}$	Yield (%)	Chem. Shift (τ) $\underline{H}$-CO-		
a	Me	Me	66.3	9.80	5.51	0	-	0.00	10.87
b	Et	Et	43.8	9.78	5.44	39.5	2.11	0.90	10.98
c	nPr	nPr	23.0	9.78	5.45	69.9	2.10	3.04	11.00
d	$-(CH_2)_4-$		37.4	9.80	5.30	25.0	1.94	0.67	11.29
e	$-(CH_2)_5-$		33.0	9.79	5.59	39.5	2.16	1.19	11.22
f	$-CH_2CH_2-O-CH_2CH_2-$		44.3	9.75	5.62	51.8	2.09	1.17	8.36
g	Me	Cyclohexyl	23.8	9.77	5.40	70.6	2.14,2.21	2.97	-
h	Et	Cyclohexyl	17.4	9.77	5.35	60.5	2.11,2.14	3.47	-

[a] Reactions were carried out by treating 10.0 millimoles of chloral with 10.0 millimoles of trimethylsilyldialkylamine at 0°, and agitating at 78±2° for 20 hours in a sealed tube, then distilling below 100°/ 0.1 mmHg.

-OMe(-0.78), larger mesomeric effect of dialkylamino group would favor elimination of trichloromethide group. Stability of insertion product for Sn-N compounds was therefore depressed compared with that of Sn-O compounds.

Extremely large stability of Si-O bond due to $(p\rightarrow d)_{\pi}$ overlap in the insertion product **I** from the reaction of Si-N compounds with chloral made β-elimination more difficult.

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