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THE REACTION OF ORGANOSILICON HYDRIDES WITH ETHYL AZIDOFORMATE. FORMATION OF ORGANOSILYL ISOCYANATES AND ALKOXIDES FROM ETHYL N-ORGANOSILYLCARBAMATES

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Reaction of organosilicon hydrides with ethyl azidoformate was investigated. The products, ethyl N-silylcarbamates which were formed in 30-80% yields, are shown to be thermally unstable and to give organosilyl isocyanates and alkoxides by heating.

In previous papers we have reported the insertion reaction of carbenes, methoxycarbonylcarbene$^{1)}$ and trimethylsiloxyphenylcarbene$^{2,3)}$ into the Si-H bond of various organosilicon hydrides. As an extension of our continuing study on the reaction of such active intermediates with hydrosilanes, we have examined the thermal decomposition of ethyl azidoformate in the presence of organosilicon hydrides expecting to obtain ethyl N-silylcarbamates which have one hydrogen on nitrogen in the molecule. In fact, N-organosilylcarbamates of this type are rather difficult to obtain, although the reaction of a silyl azide$^{4)}$ and phenyl azide$^{5)}$ with organosilicon hydrides is known to give the corresponding organosilylamines. Only a single report on the formation of trimethylsilyl N-trimethylsilylcarbamate has appeared.$^{6)}$

Thus, we have found that the present insertion reaction of ethoxycarbonylnitrene generated from the azidoformate into the Si-H bond proceeds smoothly to form the expected products in good yields. However, the resulting carbamates are rather unstable and thermally decompose easily into silyl isocyanates and alkoxides, the mode of decomposition of this type of compounds being different from that of N-alkyl and N-aryl substituted N-organosilylcarbamates.$^{7)}$

The typical method to afford the final products is as follows: 1) heating of a hydrosilane with ethyl azidoformate followed by subsequent heating of the resulting crude N-silylcarbamate at higher temperature; 2) heating of a mixture of a hydrosilane and ethyl azidoformate at an elevated temperature during a prolonged period of time.

$$\underset{\text{(I)}}{R_1R_2R_3Si\text{-}H} + \underset{\text{(II)}}{N_3CO_2Et} \xrightarrow{\Delta} \underset{\text{(III)}}{[\ R_1R_2R_3SiNHCO_2Et\ ]} + N_2$$

$$\text{III} \xrightarrow{\Delta} \underset{\text{(IV)}}{R_1R_2R_3SiNCO} + \underset{\text{(V)}}{R_1R_2R_3SiOEt}$$

Ia; IIIa-Va: $R_1=R_2=R_3=Et$

Ib; IIIb-Vb: $R_1=R_2=n\text{-}Bu$; $R_3=H$

Ic; IIIc-Vc: $R_1=R_2=Me$; $R_3=Ph$

In a small flask fitted with a reflux condenser, which had previously been flushed with dry nitrogen, Ia (1.349 g, 11.6 mmol) and II (0.606 g, 7.3 mmol) were placed and refluxed for 4.5 h under dry nitrogen at 100-110°C (oil bath). The reaction mixture was evaporated in vacuo to give a crude product of IIIa (0.79 g, 79%). The product purity was checked by GLC analysis (1m × 4mm Teflon column, 20% silicone SF-96 on Celite 545; column temp. 150°C) which disclosed the sample to be ca. 95% in purity. The spectral analyses by means of NMR and IR showed that the product was pure enough to assign its structure to IIIa.8)

In a similar reaction, on heating a mixture of Ia (8.5 mmol) and II (5.6 mmol) at 105-115°C for 4 h gave another crude product of IIIa (0.763 g, after evaporation) which was heated in a sealed tube at 195-200°C for 20 h. The resulting mixture was subjected to GLC analysis with the same column as one described above and shown to contain IVa and Va as the final products. The products isolated by preparative GLC were identified by the usual manner (NMR, IR,9) and elemental analysis). Based on the amount of the azidoformate used, the combined yield of the final products was 4.5 mmol; 80% (IVa:Va=49:51) (Run 2).

In a reaction of the method 2 as above, when a mixture of Ia (0.801 g, 6.9 mmol) and II (0.535 g, 4.6 mmol) was heated at 180-190°C for 20 h in a flask under nitrogen and analyzed, the bombined yield of the final products was 2.0 mmol; 43% (IVa:Va=55:45) (Run 4).

It is worthwhile to note that the reaction between dibutylsilane and ethyl azido-

$$\underset{\text{(VI)}}{Bu_2Si(OEt)NCO}$$

Table 1

Reaction of Organosilicon Hydrides with Ethyl Azidoformate and Decomposition of Intermediate N-Silylcarbamates (III)

Run	Reaction of I with II to form III					Decomposition of III		Final reaction products			
	Reactants			Conditions		Conditions		Yield[a,b]	Distribution		
	Hydrosilane I	(mmol)	II (mmol)	Temp. (°C)	Time (h)	Temp. (°C)	Time (h)	(mmol; %)	IV	V	VI
1	Ia	4.1	3.9	100-110	5	140-150; 170-180	20 11	1.5; 38	59	41	
2	"	8.5	5.6	105-115	4	195-200[c]	20	4.5; 80	49	51	
3	"	9.0	5.0	95-105	4.5	195-200	15	2.5; 50	54	46	
4[d]	"	6.9	4.6	180-190	20	..	..	2.0; 43	55	45	
5	Ib	2.9	2.7	120-130	4	150-160	13	1.4; 52	30	46	24
6	"	9.9	5.7	100-105	4	130-135	36	4.2; 74	33	53	14
7[d]	"	10.1	5.0	170-180	12	..	..	1.6; 32	30	70	e
8	Ic	5.4	4.6	100-110	3.5	150-160	15	2.5; 54	32	68	
9	"	7.5	4.9	100-110	4	180-205	18	3.6; 73	31	69	
10[d]	"	10.0	5.0	170-190	22	..	..	3.5; 70	43	57	

[a] Based on ethyl azidoformate used. [b] Overall combined yield of the final products by GLC; thermal conductivity correction with an internal standard (high boiling alkane) was made. [c] In a sealed tube (see the text). [d] Method 2) (see the text). [e] Yield was not determined, but very low.

formate gave, in addition to IVb and Vb, dibutylethoxysilyl isocyanate (VI) which has both the -NCO and -OEt groups on silicon was obtained as one of the final reaction products (Run 5-7). The mechanism by which VI was formed is not clear at the present time.

Although a few reports of the formation of silyl isocyanates from other types of N-silyl compounds have appeared,$^{10,11)}$ the present method of preparing silyl isocyanates via the N-silylcarbamate intermediates is of interest, since the reaction can be easily carried out with readily available reagents under rather mild conditions. Further, the formation of the ethyl N-organosilylcarbamates and the decomposition into the corresponding silyl isocyanates and alkoxides are also mechanistically of interest.

A detailed investigation of the reaction and the mechanism is now underway.

References and notes

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8) The purity could not be improved further because of contamination by a small amount of IVa and Va derived from partial decomposition of IIIa during the purification by vacuum distillation or GLC separation. The spectral data of III are shown below: NMR δ, ppm (CCl_4; TMS internal standard) IIIa: 4.13(broad, NH), 4.06(q, $OC\underline{H}_2CH_3$), 1.23(t, $OCH_2C\underline{H}_3$), 1.4-0.4(m, SiEt); IIIb: 4.54(m, SiH), 4.27(broad, NH), 4.08(q, $OC\underline{H}_2CH_3$), 1.70-0.30(m, $OCH_2C\underline{H}_3$ and n-Bu); IIIc: 7.70-7.15(m, Ph), 4.58(NH), 4.01(q, $OC\underline{H}_2CH_3$), 1.17(t, $OCH_2C\underline{H}_3$), 0.47(s, SiMe) and IR cm^{-1} (neat, sandwich) IIIa: 3280 (m, NH); 1730(s), 1305(s)(CO); 1240(m, SiEt); IIIb: 3310(m, NH); 2120(s, SiH); 1720 (s), 1300(s)(CO); IIIc: 3310(m, NH); 1715(vs), 1310(s)(CO); 1430(s), 1120(s)(SiPh).

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