THERMAL REARRANGEMENT OF TRIMETHYLSILYLMETHYL DICHLOROPHOSPHATE

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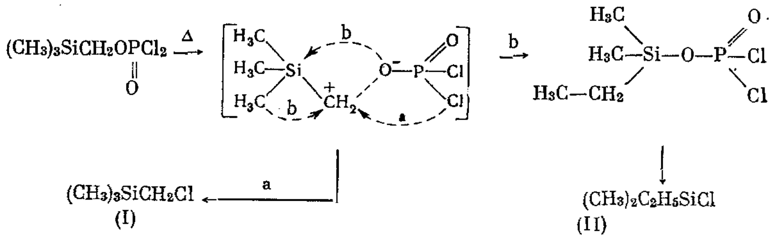
The thermal decomposition of trimethylsilylmethyl dichlorophosphate at 175-200°C leads to the formation of trimethyl(chloromethyl)silane (I), the usual decomposition product of this type of compound, and a substantial amount of dimethylethylchlorosilane (II).

The formation of (II) is apparently associated with the rearrangement of the carbcation portion of the molecule, which consists in the migration of one of the methyl groups to the methylene carbon atom, possibly with the simultaneous nucleophilic attack of the silicon atom by the anion portion of the molecule



It is known that a similar rearrangement can occur by the ionization of trimethyl(chloromethyl)silane when heated in anhydrous $AlCl_3$ [1].

Trimethylsilylmethyl dichlorophosphate (20.0 g) was heated at 200-235° for 3.5 h, and the fraction with bp 83-90° was distilled off through a fractionating column. The temperature of the reaction mixture gradually rose from 175 to 200°. Redistillation of the distillate gave 10.3 g (93%) of product with bp 89-96°, which, based on the NMR* spectral data [(δ, ppm): (I) 2.68 s (CH_2), 0.08 s (CH_3); (II) 0.32 s (CH_3), 0.87 m (CH_2CH_3)] contains 45.6% of (II).

Treatment of an ether solution of the distillate with water gave, along with (I) (2.4 g; 40.7%; bp 97-98°; n_D^{20} 1.4168; cf. [2]) 1.4 g (40%) of tetramethyldiethyldisiloxane, bp 56° (26 mm); n_D^{20} 1.4009; d_4^{20} 0.7974; found: MR 57.98; calculated: MR 58.03, cf. [3]. NMR* spectrum (δ, ppm): 0.03 s (CH_3), 0.51 and 0.95 (A_3B_2 type of multiplet of protons of CH_2 and CH_3 of the ethyl group, respectively), $J_{H_2CCH_3}$ = 7.7 Hz. The parameters of the ethyl group were obtained by processing the spectra on a Nikolet-1080 electronic computer using the iteration program. The multiplet nature of the signals of the ethyl group corresponds to the multiplet nature of the signals that were assigned to the ethyl group of (II) in the spectrum of the pyrolyzate.

LITERATURE CITED

1. F. C. Whitmore, L. H. Sommer, and J. Gold, J. Am. Chem. Soc., 69, 1976 (1947).
2. F. C. Whitmore and L. H. Sommer, ibid., 68, 481 (1946).
3. M. F. Shostakovskii, A. S. Atavin, E. P. Vyalykh, B. A. Trofimov, N. A. Vodbol'skaya, and V. V. Keiko, Izv. Akad. Nauk SSSR, Ser. Khim., 1283 (1966).

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[*] Hexamethyldisiloxane served as the internal standard.

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