REACTION OF BIS(TRIMETHYLSILYL) SULFATE WITH PHOSPHORUS ACID CHLORIDES

A. N. Pudovik, G. V. Romanov, and T. Ya. Stepanova

UDC 542.91:547.1'118

Trimethylchlorosilane and SO_2 are evolved and P(V) derivatives are formed when bis(trimethylsilyl) sulfate (I) is heated with P(III) acid chlorides. Thus, for example, the reaction of phenyldichlorophosphine with (I) leads mainly to bis(trimethylsilyl) phenylphosphonate ($\delta^{31}P$ = 0 ppm [1]). Judging by the ^{31}P NMR spectra, the reaction of diphenylchlorophosphine with (I) leads to oxidation products, and specifically diphenylphosphinic chloride ($\delta^{31}P$ = —44 ppm [1]) and tetraphenyldiphosphine dioxide ($\delta^{31}P$ = —28 ppm [2]). The reaction of diethyl chlorophosphite with (I) gave tetraethyl pyrophosphate ($\delta^{31}P$ = +14 ppm [1]) in 57% yield. In a special experiment tributylphosphine oxide and hexamethyldisiloxane were isolated by heating tributylphosphine with (I):

$$Bu_3P + (Me_3SiO)_2SO_2 \rightarrow Bu_3PO + (Me_3Si)_2O$$

This fact and the literature data that (I) functions as an oxidizing agent [3] make it possible to assume that diphenylchlorophosphine reacts with (I) by the following scheme:

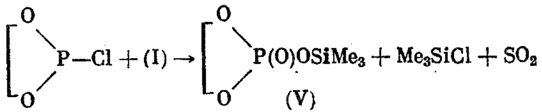
$$Ph_2PCl + (I) \rightarrow Ph_2P(O)Cl + (Me_3Si)_2O + SO_2$$
$$Ph_2P(O)Cl + (Me_3Si)_2O \rightarrow Ph_2P(O)OSiMe_3 + Me_3SiCl$$
$$Ph_2P(O)OSiMe_3 + Ph_2PCl \rightarrow Ph_2P(O)P(O)Ph_2 + Me_3SiCl$$

The following scheme can be proposed for the reaction of diethyl chlorophosphite with (I):

$$(EtO)_2PCl + (I) \rightarrow \underset{(II)}{(EtO)_2P(O)Cl} + (Me_3Si)_2O + SO_2\uparrow$$
$$(EtO)_2P(O)Cl + (Me_3Si)_2O \rightarrow \underset{(III)}{(EtO)_2P(O)OSiMe_3} + Me_3SiCl$$
$$(EtO)_2P(O)OSiMe_3 + (EtO)_2P(O)Cl \rightarrow \underset{(IV)}{(EtO)_2P(O)OP(O)(OEt)_2} + Me_3SiCl$$

The intermediate formation of (II) and (III) is confirmed by the presence of the corresponding weak signals in the ^{31}P NMR spectra of the reaction mixture and separate fractions ($\delta^{31}P$ = —3 ppm (II) and +4 ppm (III) [2]). Judging by the ^{31}P NMR spectra, the reaction of diethyl chlorophosphate with (I) gives tetraethyl pyrophosphate ($\delta^{31}P$ +14 ppm [2]) and various products of substituting ethyl groups on the trimethylsilyl group ($\delta^{31}P$ +19, +28, +32 ppm [2]). The presence of side products is apparently explained by the fact that, in contrast to the reaction with diethyl chlorophosphite, in the given case it is not the easily removed SO_2 that is formed, but instead SO_3, which is capable of binding the liberated trimethylchlorosilane in a complex [4] that probably functions subsequently as a silylating agent.

The acid chloride of ethylene glycol phosphorus acid reacts with (I) to give mainly trimethylsilyl ethylene glycol phosphate (V):



Together with (V) is also recorded the formation of trimethylsilyl ethylene glycol phosphite (δ ^{31}P —123 ppm [2]). In general, the formation of these products is found to be in agreement with the above stated postulation that P(III) derivatives are initially oxidized by silyl sulfate (I).

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2644-2645, November, 1979. Original article submitted April 2, 1979.

0568-5230/79/2811-2461$07.50

EXPERIMENTAL

The ^{31}P NMR spectra were recorded on a KGU-4 NMR instrument at a frequency of 10.2 MHz relative to 85% H_3PO_4, the IR spectra were recorded on a UR-20 instrument, and the PMR spectra were recorded on a Varian T-60 spectrometer (60 MHz), using benzene as the internal standard.

Reaction of (I) with Phenyldichlorophosphine. A mixture of 5.6 g (0.02 mole) of (I) and 2.7 g (0.01 mole) of phenyldichlorophosphine was heated for 2 h at 140°C until the liberation of Me_3SiCl (yield 46%, bp 57°, n_D^{20} 1.3880) ceased. Vacuum-distillation gave 2.0 g (44%) of bis(trimethylsilyl)phenylphosphonate [1] with bp 75° (0.08 mm); δ_{31P} 0 ppm. Infrared spectrum (ν, cm^{-1}): 1260 (P=O), 773, 835, 1260 ($SiMe_3$). Found: P 10.00; Si 18.12%. $C_{12}H_{23}O_3PSi_2$. Calculated: P 10.26; Si 18.54%.

Reaction of (I) with Tributylphosphine. A mixture of 2.3 g (0.01 mole) of (I) and 2 g (0.01 mole) of tributylphosphine was heated at 150° until the liberation of HMDS (yield 70%, bp 105°, n_D^{20}1.3780; cf. [5]) ceased. Vacuum-distillation gave 1.4 g (67%) of tributylphosphine oxide [6] with bp 92° (0.07 mm); $\delta^{31}P$ –42 ppm. Infrared spectrum (ν, cm^{-1}): 1160 (P=O). Found: P 13.83%. $C_{12}H_{27}OP$. Calculated: P 14.22%.

Reaction of (I) with Diethyl Chlorophosphite. A mixture of 15 g (0.09 mole) of diethyl chlorophosphite and 11.6 g (0.045 mole) of (I) was heated for 2 h at 120° until the liberation of trimethylchlorosilane (yield 60%, bp 57°, n_D^{20} 1.3850) ceased. The evolution of SO_2 was observed, which decolorized iodine in starch solution. Vacuum-distillation gave 8 g (57%) of tetraethyl pyrophosphate [7] with bp 124° (0.03 mm); n_D^{20} 1.4190; $\delta^{31}P$ + 14 ppm. Infrared spectrum (ν, cm^{-1}): 1298 (P=O), 1040 (P–O–C), 950, 985, 765 (P–O–P). PMR spectrum in benzene (δ, ppm): 3.54 m (CH_2), 1.18 t (CH_3). Found: P 20.98%. $C_8H_{20}O_7P_2$. Calculated: P 21.37%.

Reaction of (I) with Acid Chloride of Ethylene Glycol Phosphorus Acid. A mixture of 14.0 g (0.05 mole) of (I) and 14.5 g (0.1 mole) of the acid chloride of ethylene glycol phosphorus acid was heated at 120° for 2 h until the liberation of trimethylchlorosilane (yield 40%, bp 57°, n_D^{20} 1.3880) ceased. Vacuum-distillation gave 4.5 g (38%) of the trimethylsilyl ester of ethylene glycol phosphoric acid with bp 132° (1 mm), $\delta^{31}P$ +18 ppm. Infrared spectrum (ν, cm^{-1}): 1280 (P=O), 1055 (P–O–C), 870, 770, 1270 ($SiMe_3$). PMR spectrum in benzene (δ, ppm): 0.34 ($SiMe_3$). Found: P 15.19; Si 13.71%. $C_5H_{13}O_4PSi$. Calculated: P 15.82; Si 14.28%.

CONCLUSIONS

Bis(trimethylsilyl) sulfate when reacted with trivalent phosphorus acid chlorides oxidizes them to the P(V) derivatives, whose structure is determined by the nature of the starting acid chloride.

LITERATURE CITED

1. O. A. Varnavskaya-Samarina, É. A. Ishmaeva, G. V. Romanov, R. Ya. Nazmutdinov, A. B. Remizov, and A. N. Pudovik, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 363.
2. V. Mark, C. Duncan, M. Crutchfield, and J. van Wazer, Topics in Phosphorus Chemistry, Vol. 5, New York (1967).
3. N. Duffaut, R. Calas, and J. Dunogues, Bull. Soc. Chim. France, 1963, 512.
4. M. Schmidt and H. Schmidbaur, Ber., 95, 47 (1962).
5. M. G. Voronkov, V. K. Roman, and E. A. Maletina, Chemistry of Heteroorganic Compounds [in Russian], Nauka, Leningrad (1976), p. 52.
6. R. A. Y. Jones and A. R. Katritzky, Angew. Chem., 1, 32 (1962).
7. A. E. Arbuzov and B. A. Arbuzov, Zh. Obshch. Khim., 2, 348 (1932).