E. A. CHERNYSHEV, E. F. BUGERENKO, N. A. NIKOLAEVA,

Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

1962

SovietRxiv

Abstract

Full Text

CHEMISTRY

E. A. CHERNYSHEV, E. F. BUGERENKO, N. A. NIKOLAEVA, Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

INTERACTION OF DIETHYL PHENYLPHOSPHINITE WITH α-, β-, AND γ-CHLOROALKYLALKYLALKOXYS

Continuing our investigations in the field of the synthesis of compounds containing phosphorus and silicon ([1,2]), we studied the interaction of diethyl phenylphosphinite $C_6H_5P(OC_2H_5)_2$ (I) with various α-, β-, and γ-chloroalkylalkylalkoxysilanes:

$$R_n(C_2H_5O)_{3-n}Si(CH_2)_{kCl} + C_6H_5P(OC_2H_5)_2 \rightarrow R_n(C_2H_5O)_{3-n}Si(CH_2)_{kP}(=O)(C_6H_5)(OC_2H_5) + C_2H_5Cl$$

$$n = 0, 1, 2, 3; \quad k = 1, 2, 3; \quad R = CH_3,\ C_2H_5,\ C_6H_5,\ CH_2{=}CHCH_2.$$

A. E. Arbuzov showed ([3]) that the interaction of compound I with haloalkyls proceeds at a higher rate than the reaction, under analogous conditions, of triethyl phosphite with the same compounds. The same regularity is also observed in the interaction of I and triethyl phosphite with haloalkylalkylalkoxysilanes. Thus, even with the least active trimethylchloromethylsilane, I reacts almost completely (yield of reaction product 80.3%) in 10 hr, whereas triethyl phosphite with this same haloalkylsilane gives a 25% yield of reaction product on boiling the reaction mixture for 120 hr ([4]). From comparison of experiments Nos. 1-4 (see Table 1) it is evident that replacement at the silicon atom of a methyl group by an ethoxy group sharply decreases the duration of the interaction of chloromethylmethylethoxysilanes with compound I. The same regularity was noted by us in studying the Arbuzov rearrangement of triethyl phosphite with chloroalkylalkylalkoxysilanes ([1]). For example, with chloromethyldimethylethoxysilane (experiment No. 2) the interaction with I is practically completed in 45 min; chloromethylmethyldiethoxysilane reacts with I in 15 min (experiment No. 3), and chloromethyltriethoxysilane (experiment No. 4) in less than 10 min, the reaction proceeding so vigorously that it is necessary to reduce the heating in order to avoid overheating and ejection of the reaction mixture from the flask.

The properties of the compounds obtained are given in Table 2.

Table 1

Experiment No.	Haloalkylsilane	Amount, g (mol)	Amount of $C_6H_5P(OC_2H_5)_2$, g (mol)	Temperature interval, °C	Reaction time, min	Yield, g (%)
1	$(CH_3)_3SiCH_2Cl$	14.4(0.15)	14.9(0.075)	109–128	600	15.4(80.3)
2	$C_2H_5O(CH_3)_2SiCH_2Cl$	15.3(0.11)	22(0.11)	110–145	45	24.7(78.5)
3	$CH_3(C_2H_5O)_2SiCH_2Cl$	16.6(0.11)	15.5(0.18)	110–155	15	51(89.5)
4	$(C_2H_5O)_3SiCH_2Cl$	18.3(0.11)	15.5(0.078)	110–170	10	19.7(73)
5	$C_6H_5(CH_3)_2SiCH_2Cl$	18.5(0.11)	14.9(0.075)	120–240	15	22(92.4)
6	$CH_2{=}CH(CH_3)_2SiCH_2Cl$	13.5(0.1)	9.9(0.05)	120–225	30	7.7(56.1)
7	$(C_2H_5O)_3SiCH_2Cl$	22.7(0.11)	9.9(0.05)	183–212	180	6.9(38.4)
8	$CH_3(C_2H_5O)_2SiCH_2Cl$	18.3(0.11)	14.9(0.075)	120–223	45	10.1(67.5)
9	$C_2H_5(C_2H_5O)_2SiCH_2Cl$	22.5(0.13)	9.9(0.05)	115–221	40	11.6(64.5)
10	$(C_2H_5O)_3SiCH_2Cl$	36.6(0.15)	14.9(0.075)	110–224	35	19.6(69.7)

Table 2

No.	Compound	b.p., °C (mm)	n_D^{20}	d_4^{20}	Found, % C	Found, % H	Found, % P + Si	Calculated, % C	Calculated, % H	Calculated, % P + Si
I	$(CH_3)_3SiCH_2P(O)(OC_2H_5)(C_6H_5)$	194 (1)	1.5039	1.1288	56.1	8.03	23.3	56.3	8.21	23.1
II	$C_2H_5O(CH_3)_2SiCH_2P(O)(OC_2H_5)(C_6H_5)$	123 (2)	1.4964	1.0558	54.0	8.03	22.4	54.5	8.03	20.6
III	$CH_3(C_2H_5O)_2SiCH_2P(O)(OC_2H_5)(C_6H_5)$	129 (2)	1.4863	1.0748	54.7	7.90	20.3	53.15	7.90	18.7
IV	$(C_2H_5O)_3SiCH_2P(O)(OC_2H_5)(C_6H_5)$	153 (3)	1.4796	1.0675	52.8	8.05	18.7	52.0	7.79	17.0
V	$C_6H_5(CH_3)_2SiCH_2P(O)(OC_2H_5)(C_6H_5)$	154 (3)	1.5508	1.0888	64.6	7.57	16.8	64.15	7.24	18.5
VI	$CH_2ClCH_2(CH_3)_2SiCH_2P(O)(OC_2H_5)(C_6H_5)$	117 (1.5)	1.5053	1.0927	58.6	7.49	16.8	59.6	8.15	20.9
VII	$(C_2H_5O)_3SiCH_2P(O)(OC_2H_5)(C_6H_5)$	167 (3)	1.4740	1.0783	53.3	7.89	18.3	53.4	8.06	16.4

No.	Compound	b.p., °C (mm)	n_D^{20}	d_4^{20}	Found, % C	Found, % H	Found, % P + Si	Calculated, % C	Calculated, % H	Calculated, % P + Si
VIII	$CH_3(C_2H_5O)_2SiCH_2CH_2P(O)(OC_2H_5)(C_6H_5)$	171 (2.5)	1.4866	1.0582	55.4	8.47	16.9	55.8	8.43	17.15
IX	$C_2H_5(C_2H_5O)_2SiCH_2CH_2P(O)(OC_2H_5)(C_6H_5)$	188 (3)	1.4800	1.0275	57.9	8.85	16.2	57.0	8.67	16.5
X	$(C_2H_5O)_3SiCH_2CH_2P(O)(OC_2H_5)(C_6H_5)$	186 (2.5)	1.4792	1.0730	56.7	8.02	15.7	54.5	8.29	15.8

Experimental Part

The properties of the chloroalkylalkylalkoxysilanes used have been described by us in earlier papers ([1,2]). Trimethylchloromethylsilane was prepared by the Grignard reaction from chloromethyldimethylchlorosilane and methylmagnesium bromide and had properties coinciding with the literature data ([5]). Similarly, allyldimethylchloromethylsilane was obtained from chloromethyldimethylchlorosilane and allylmagnesium bromide; it had b.p. 146–148°, n_D^{20} 1.4492, d_4^{20} 0.9123. Compound I was obtained by ethoxylation of phenyldichlorophosphine with absolute ethyl alcohol in the presence of pyridine and had the following properties: b.p. (99–100°/4 mm), n_D^{20} 1.5118, d_4^{20} 1.0243 (literature data ([6]): b.p. 235–237°, n_D^{20} 1.5120, d_0^{20} 1.0247).

Preparation of ethyl esters of alkylalkoxysilyl-substituted alkylphenylphosphinous acids. The reaction of compound I with haloalkylalkylalkoxysilanes was carried out in a two-necked flask fitted with a thermometer immersed in the reaction mixture and a reflux condenser connected through an outlet to a Tishchenko bottle containing concentrated H_2SO_4. The reaction was continued until the evolution of ethyl chloride bubbles in the Tishchenko bottle ceased. The conditions of the experiments and the yields of the reaction products are presented in Table 2.

Received
18 VII 1962

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

References Cited

1. E. F. Bugerenko, E. A. Chernyshev, A. D. Petrov, DAN, **143**, No. 4 (1962).

2. E. A. Chernyshev, E. F. Bugerenko et al., Izv. AN SSSR, OKhN, 1962, No. 6.

3. A. E. Arbuzov, Doctoral dissertation in selected works, Izd. AN SSSR, 1952.

4. A. E. Satan and C. Eaborn, J. Chem. Soc., 1959, 3751.

5. F. C. Whitmore, L. H. Sommer, J. Am. Chem. Soc., **68**, 481 (1946).

6. B. A. Arbuzov, V. S. Vinogradova, Izv. AN SSSR, OKhN, 1947, 459.

Note: Figure translations are in progress. See original paper for figures.