## REACTION OF $\alpha$ -ETHOXYACROLEIN WITH BIS(TRIMETHYLSILYL) HYPOPHOSPHITE

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The reactivity of  $\alpha$ -ethoxyacrolein was studied previously [1]. In order to obtain some new biologically active phosphorus-containing compounds we reacted it with bis(trimethylsilyl) hypophosphite. The existing data on the addition of bis(trimethylsilyl) hypophosphite (I) [2] to carbonyl-containing compounds [3-6] made it possible to expect that when (I) is reacted with  $\alpha$ -ethoxyacrolein (II) at low temperatures the carbonyl group will take part with the formation of either trimethylsilyl ( $\alpha$ -trimethylsiloxy- $\beta$ -ethoxy)- $\beta$ , $\gamma$ propenylphosphonite (III) or trimethylsilyl ( $\beta$ -ethoxy)- $\beta$ , $\gamma$ -propenyl phosphite (IV).



The possibility of forming 2,2-bis (trimethylsiloxy)-4-ethoxy- $\Delta^4$ -oxa-phospholene (V) [7] can also not be excluded.



However, the experimental data obtained by us revealed that even at low temperatures, in an inert atmosphere, hypophosphite (I) reacts with (II) without the formation of stable adducts. When the reaction mixture was distilled we isolated ethyl trimethylsilyl phosphite  $(CH_3)_3SiO(C_2H_5O)P(O)H$  (VI), bis (trimethylsilyl) phosphite  $[(CH_3)_3SiO]_2P(O)H$  (VII), and a polymer (VIII) of composition  $C_6H_{13}O_5P_1$ . The structure of compounds (VI) and (VII) was proved by <sup>1</sup>H NMR and <sup>31</sup>P NMR spectroscopy. In addition, HMDS, ethanol, and  $(C_2H_5)_2O$  were detected among the low-boiling-point reaction products, which were identified by GLC and NMR.

A study of the reaction mixtures of (I) and (II) in toluene or  $CCl_4$ , in the range from -20 to  $35^{\circ}C$ , by NMR also revealed that (VI)-(VIII) are reaction products. The functional groups of the starting (II) (H<sub>2</sub>C =, -CHO) are absent in all of the products, except the polymeric products. Based on the elemental analysis data, the obtained polymer contains a substantial amount of phosphorus. Based on the IR spectral data, it contains the C=O group, and based on the NMR data, it contains the ethoxy group. As a result, the polymeric product is a copolymer of (II) with phosphorus-containing unstable adducts [for example, of the (III) type], the decomposition of which probably yields ethyl trimethylsilyl phosphite (VI). The instability of the  $\alpha$ -trimethylsiloxy derivatives of tetracoordinated phosphorus is known [8]. However, the formation of the starting compounds was not observed in the given case.

The formation of phosphite (VII) in high yield is probably due to the oxidation of hypophosphite (I) via reaction with (II).

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## EXPERIMENTAL METHOD

The NMR spectra were taken on a Tesla BS 487B spectrometer, while the <sup>31</sup> P NMR spectra were taken on a Varian XL-100/12 instrument. Cyclohexane and 85% H<sub>3</sub>PO<sub>4</sub> were used as the standards. The chromatograms were obtained on a CL-6 chromatograph, using a column packed with DNP deposited on silanized Celite 545, helium as the carrier gas, and a temperature of 140°.

A solution of (I), obtained by reacting ammonium hypothosphite with trimethylsilane in toluene medium, was filtered through a porous glass plate into an evacuated Claisen flask that was equipped with an Arbuzov receiver. Distillation gave 13.4 g (0.067 mole) of (I) with bp 50° (8 mm). All of the hypophosphite was added in drops to the cooled evacuated receiver, which contained 5.16 g (0.0515 mole) of (II). An exothermic effect was observed here. The mixture was kept at 4° in vacuo for 3.5 h. after which it was stirred and left to stand for 12 h at ~20° in a dry oxygen-free nitrogen atmosphere. Distillation in a nitrogen atmosphere gave 6.0 g of an azeotropic mixture of compounds (VI) and (VII) with bp 44° (2 mm);  $nD^{20}$ 1.4123;  $d_4^{20}$  0.9718. Found: C 32.69; H 8.10; Si 11.72; P 19.12%. Based on the NMR data, the (VI) : (VII) ratio =1:2.7. Calculated for a mixture of (CH<sub>3</sub>)<sub>3</sub>SiOP(O)H(OC<sub>2</sub>H<sub>5</sub>) and [(CH<sub>3</sub>)<sub>3</sub>SiO]<sub>2</sub>P(O)H (1:2.7:C 35.6; H 9.30; Si 14.50; P 15.60%. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>):2430 (P-H), 1260 (P=O), 1020-1070 (P-O-C). NMR spectrum ( $\tau$ , ppm): 9.70 s [(CH<sub>3</sub>)<sub>3</sub>, (VI) and (VII)], 8.76 t CH<sub>3</sub>C, (VI)], 6.04 d. q (CH<sub>2</sub>OP, (VI), <sup>3</sup>JPOCH = 8 Hz) 3.29 d (P-H, (VI), <sup>4</sup>JPH=692 Hz), 3.31 d (P-H, [VII], <sup>4</sup>JPH=687 Hz). <sup>34</sup>P NMR spectrum ( $\delta$ , ppm): P(VI) +3.3, P(VII) +13.2.

In addition, we obtained 3.5 g of a low-boiling-point fraction with by 40-65° (6 mm), which, based on the GLC data, contains 1.3 g (37.3%) of toluene, 1.42 g (0.0082 mole) of HMDS, 0.23 g (0.005 mole) of ethanol, and 0.18 g (0.0024 mole) of  $(C_2H_5)_2O$ . The distillation flask contained 7.8 g of tarry residue, which is soluble in CCl<sub>4</sub>, ethyl cellosolve, or acetone and is slightly soluble in ether or benzene. The polymer fraction, which was reprecipitated from CCl<sub>4</sub> solution with hexane, contains: P 13.02, Si 0.54, C 37.36, and H 6.47%. The IR spectrum has absorption bands at 1060 (P-O-C), 1260 (P=O), and 1730 cm<sup>-1</sup> (C=O).

## CONCLUSIONS

The reaction of bis(trimethylsilyl) hypophosphite with  $\alpha$ -ethoxyacrolein leads to the formation of an unstable adduct, the decomposition products of which are ethyl trimethylsilyl phosphite, hexamethyldisil-oxane, and a noncombustible polymer.

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