

10. G. H. Posner and C. M. Lentz, *Tetrahedron Lett.*, **1977**, 3215.
 11. J. A. Miller, G. M. Stevenson, and B. C. Williams, *J. Chem. Soc., C* **1971**, 2714.

REACTION OF TRIALKYL PHOSPHITES
 WITH 1,1,1-TRIFLUOROACETONE

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The reactions of trialkyl phosphites with aliphatic aldehydes at 20°C [1], and also with chloral [2] and pentafluorobenzaldehyde [3] at low temperatures, give the corresponding 2,2,2-trialkoxy-1,4,2-dioxaphospholane derivatives, in which connection the 2,2,2-trialkoxy-3,5-bis(pentafluorophenyl)-1,4,2-dioxaphospholane when heated is converted to the 2,2,2-trialkoxy-4,5-bis(pentafluorophenyl)-1,3,2-dioxaphospholane [3]. According to [3], the formation of the 1,4,2-dioxaphospholanes is characteristic for aldehydes, while ketones, activated by electron-acceptor substituents, when reacted with trialkyl phosphites, give only the 1,3,2-dioxaphospholanes.

To obtain more detailed information on the mechanism of the reactions of activated carbonyl compounds with trialkyl phosphites we studied the reaction of the latter with 1,1,1-trifluoroacetone by the ^{31}P NMR method. In the ^{31}P NMR spectrum of a mixture of $(\text{EtO})_3\text{P}$ and MeCOCF_3 (1:2) at 20° are observed the appearance, and then a decrease in the signal with δ 37 ppm of the corresponding 2,2,2-triethoxy-3,5-dimethyl-3,5-bis(trifluoromethyl)-1,4,2-dioxaphospholane. We recently isolated a similar dioxaphospholane in the pure state from the reaction of ethyl ethylene phosphite with MeCOCF_3 [4]. Later in the spectrum appears and increases the signal with δ 75 ppm of the end reaction product, namely triethoxy- α -trifluoromethyl- α -(1-methyl-2,2-difluorovinyl)oxy)ethoxyfluorophosphorane. For phosphoranes with a close structure, containing a P-F bond, δ 75 ppm [5]. A gradual decrease in the signal of the starting $(\text{EtO})_3\text{P}$ (-138 ppm) is observed during reaction. The process is accompanied by the formation of a small amount of a phosphate with δ 3 ppm. The reaction is completed in 216 h (Fig. 1). The analogous reaction of $(\text{MeO})_3\text{P}$ with MeCOCF_3 is completed in 168 h. Here, besides trimethoxy- α -trifluoromethyl- α -(1-methyl-2,2-difluorovinyl)oxy)ethoxyfluorophosphorane (δ 75 ppm) and the phosphate (δ 3 ppm), is formed a small amount of dimethyl methylphosphonate (δ -32 ppm) (Fig. 2a). It was found that the product with δ 3 ppm (Fig. 2b) could be removed by distillation of the reaction mixture. The PMR spectrum of the residual mixture has the signals (δ ppm, J, Hz): 1.35 (MeP, $J_{\text{HP}}=18$) and 3.65 (MeOP, $J_{\text{HP}}=11$), which coincide with those observed for the authentic $\text{MePO}(\text{OMe})_2$.

The structure of trimethoxy- α -trifluoromethyl- α -(1-methyl-2,2-difluorovinyl)oxy)ethoxyfluorophosphorane was confirmed by the ^{19}F NMR spectrum (δ , ppm, J, Hz): 1.55 (CF_3 , $J_{\text{FP}}=7$), 5.48 (CF_2^-), -2.44 (FP, $J_{\text{FP}}=1115$). For fluorophosphoranes of analogous structure, $J_{\text{FP}}=822$ Hz [5]. The ratio of the integral intensity of the CF_3 , $=\text{CF}_2$, and F signals is equal to 3:2:1. The IR spectrum has a very weak band at 1680 cm^{-1} ($\nu\text{C}=\text{C}$), which has a medium intensity in the Raman spectrum.

The mass spectrum of the reaction products was obtained at 50 eV, m/e (relative intensity, % of total ionic current down to m/e 29, $\% \Sigma_{29}$): 333(0.23), 329(0.02), 319(0.04), 318(0.09), 317(1.3), 303(0.04), 302(0.32), 297(0.05), 295(0.14), 287(0.08), 282(0.091), 279(0.23), 272(0.14), 263(0.09), 262(0.18), 233(0.68), 223(0.23), 222(0.18), 221(0.13), 193(0.41), 185(0.319), 183(0.73), 171(0.52), 169(1.71), 153(0.64), 151(0.50), 149(0.32), 141(2.0), 140(0.41), 139(0.50), 127(2.7), 124(1.8), 121(0.82), 120(0.27), 110(0.32), 117(0.18), 113(5.9), 110(4.1), 109(5.9), 103(0.55), 97(0.39), 96(0.41), 95(2.7), 94(7.7), 93(4.1), 91(0.68), 90(0.41), 89(0.41), 85(0.23), 83(0.23), 82(0.32), 81(0.55), 80(0.55), 79(8.7), 78(0.23), 77(1.2), 76(0.23), 75(0.41), 69(1.7), 65(0.82), 64(0.32), 63(2.2), 59(0.91), 58(0.36), 57(0.36), 55(0.32), 53(0.18), 51(0.60), 50(0.18), 49(0.27), 48(0.36), 47(2.37), 46(0.23), 45(1.23), 44(2.0), 43(4.57), 42(0.41), 41(0.59), 40(2.3), 39(0.68), 33(0.55), 31(5.5), 30(1.7), 29(4.6). The peak with m/e 124 corresponds to the molecular ion $\text{MePO}(\text{OMe})_2$, whose mass spectrum is known only at 70 eV [6]. We obtained the mass spectrum of this compound at 50 eV, m/e ($\% \Sigma_{29}$): 124(6.9), 109(9.6), 94(24.4), 93(9.9), 79(26), 63(4.7), 47(7.2), 45(1.1), 31(4.6), 29(5.4).

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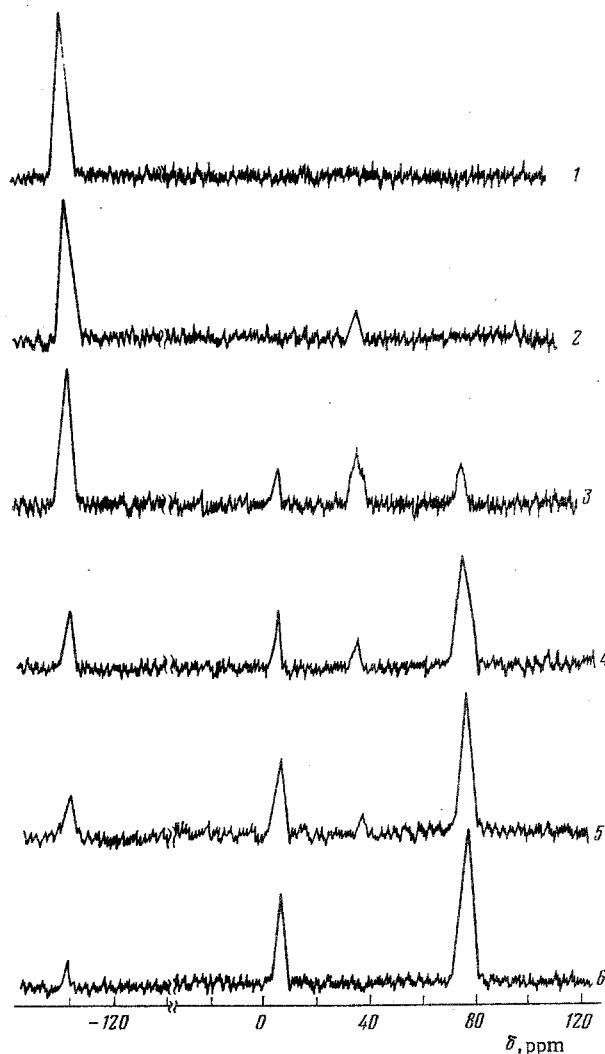


Fig. 1. ^{31}P NMR spectra of reaction mixture during reaction of triethyl phosphite with 1,1,1-trifluoroacetone at 20° : 1) immediately after mixing; 2) after 1 h; 3) 22 h; 4) 166 h; 5) 168 h; 6) 216 h after mixing.

A comparison of the mass spectra of the mixture of products and $\text{MePO}(\text{OMe})_2$ testifies to a slight superimposition of the peaks with m/e 124, 94, and 79 of the phosphorane and $\text{MePO}(\text{OMe})_2$. The ratio of the intensities of the peak with m/e 124 and m/e 94 and 79 in the mass spectrum of the mixture is close to their ratio in the mass spectrum of the pure $\text{MePO}(\text{OMe})_2$. We will mention that the metastable peaks with m/e 71.3, 57.3, and 66.4 of the decomposition reactions $124 \rightarrow 94$, $109 \rightarrow 79$, $94 \rightarrow 79$ in the mass spectrum of the mixture and $\text{MePO}(\text{OMe})_2$ coincide with those given in [6]. On the assumption that the peak with m/e 124 is caused only by $\text{MePO}(\text{OMe})_2$, we calculated the mass spectrum of the pure phosphorane, m/e ($\% \Sigma_{29}$): 333(0.31), 329(0.02), 329(0.02), 319(0.06), 318(0.12), 317(1.8), 303(0.06), 302(0.43), 297(0.07), 295(0.20), 287(0.12), 282(0.12), 279(0.31), 272(0.20), 263(0.12), 262(0.25), 233(0.93), 223(0.31), 222(0.25), 221(0.20), 193(0.56), 185(0.43), 183(0.99), 171(0.71), 169(2.4), 153(0.86), 151(0.68), 149(0.43), 141(2.7), 140(0.56), 139(0.68), 127(3.7), 121(1.1), 120(0.37), 119(0.43), 117(0.25), 113(8.0), 110(5.6), 109(4.7), 103(0.74), 97(0.52), 96(0.56), 95(3.7), 94(0.94), 93(2.1), 91(0.93), 90(0.56), 89(0.56), 85(0.31), 83(0.31), 82(0.43), 81(0.74), 80(0.74), 79(2.6), 78(0.31), 77(1.6), 76(0.31), 75(0.56), 69(2.3), 65(1.1), 64(0.43), 63(1.4), 62(0.50), 59(1.2), 58(0.50), 57(0.50), 55(0.43), 53(0.25), 51(0.80), 50(0.25), 49(0.37), 48(0.50), 47(0.70), 46(0.31), 45(1.3), 44(2.5), 43(6.2), 42(0.56), 41(0.80), 40(3.1), 39(0.93), 33(0.74), 31(5.8), 30(2.2), 29(4.3). The absence of the $\text{M}^{+\bullet}$ peak is full explainable by the properties of this class of compounds [5]. Usually in the mass spectra of branched compounds, which have methyl groups, the $(\text{M}-\text{Me})^+$ ion proves to be most heavy. The peak with m/e 333 corresponds to the $(\text{M}-\text{Me})^+$ ion, while the peak with m/e 329 corresponds to the $(\text{M}-\text{F})^+$ ion. The presence of a CF_3 group in the molecule is confirmed by the peaks with m/e 279 $(\text{M}-\text{CF}_3)^+$ and m/e 69 $(\text{CF}_3)^+$. In the mass spectra of phosphorus esters the intense peaks corre-

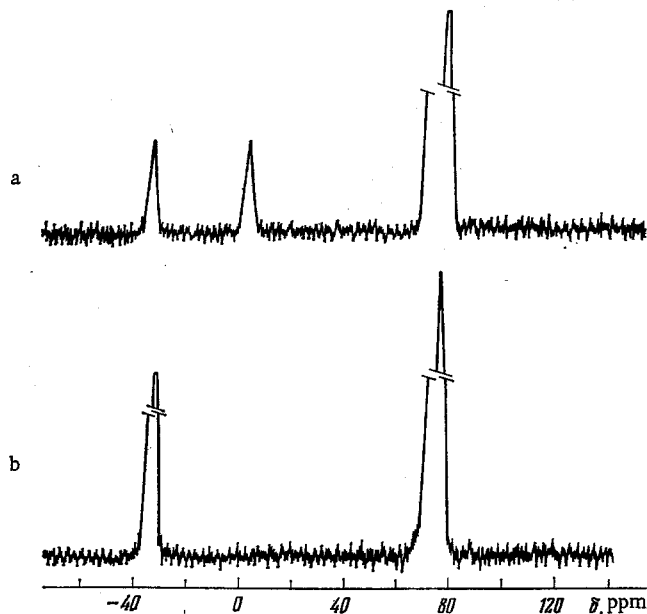
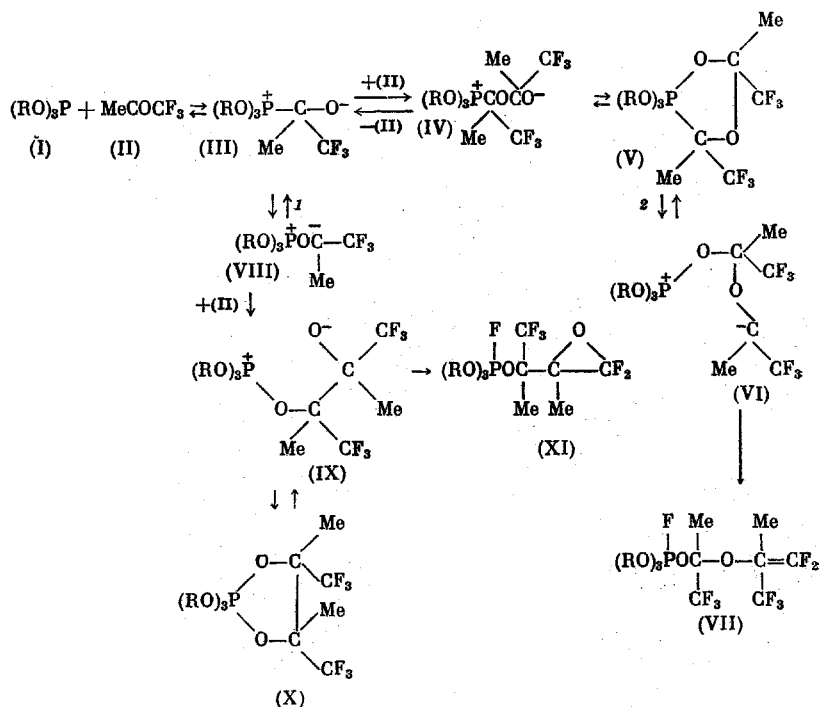


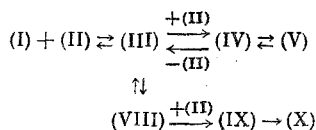
Fig. 2. ^{31}P NMR spectrum of mixture of trimethoxy- α -trifluoromethyl- α -(1-methyl-2,2-difluorovinyl-oxo)ethoxyfluorophosphorane and products with $\delta^{31}\text{P}$ 3 and 32 ppm (a), and with dimethyl methylphosphonate (b).

respond to the $(\text{M} - \text{OR})^+$ ions [7]. In the spectrum of the studied phosphorane the peak with m/e 317 $(\text{M} - \text{MeO})^+$ proves to be the most intense in the region of heavy ions. The peaks of the ions $[\text{M} - \text{MeO} + \text{Me}]^+$ and $[\text{M} - (\text{MeO} + \text{Me} + \text{CH}_2\text{O})]^+$, with m/e 302 and 272 respectively, are also present.

As a result, the refluxing mixture contains, besides $\text{MePO}(\text{OMe})_2$, also a pentavalent P compound with mol. wt. 348, which contains a P-F bond. The formation of such phosphoranes can be explained by one of the directions in the depicted scheme.



As was shown by us, ethyl ethylene phosphite reacts with MeCOCF_3 by the following scheme:



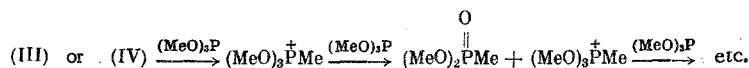
Here a fluorophosphorane of the (XI) type [4] is not formed. Isomerization of the type (X) \rightarrow (IX) \rightarrow (XI) was also not observed for the 2,2,2-trialkoxy-4,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholane [8, 9]. Based on the ^{31}P NMR (see Figs. 1 and 2), the reaction products of trialkyl phosphites with MeCOCF_3 do not contain the 2,2,2-trialkoxy-4,5-dimethyl-4,5-bis(trifluoromethyl)-1,3,2-dioxaphospholane, whose formation could be expected if direction 1 is realized, and consequently this direction must be considered improbable. The possibility of reaction along direction 2, $(I) + (II) \rightleftharpoons (III) \xrightleftharpoons[+(II)]{-(II)} (IV) \rightleftharpoons (V) \rightleftharpoons (VI) \rightleftharpoons (VII)$, does not evoke doubt.

Examples of cleaving the endocyclic P-C bond are described in [10].

As a result, trialkyl phosphites react with MeCOCF_3 to give mainly the 2,2,2-trialkoxy-3,5-dimethyl-3,5-bis(trifluoromethyl)-1,4,2-dioxaphospholane, which slowly isomerizes to the trialkoxy- α -trifluoromethyl- α -(1-methyl-2,2-difluorovinyl)oxyethoxyfluorophosphorane.

The reversibility of a process of type $(I) + (II) \rightleftharpoons (III) \xrightleftharpoons[+(II)]{-(II)} (IV) \rightleftharpoons (V)$, which was discussed by us in detail in [4, 11], stipulates the simultaneous existence of the starting phosphite and bipolar ions (III) and (IV) in the reaction mixture; i.e., all of the conditions are present for the dealkylation of the quasiphosphonium compounds (III) and (IV) by the phosphite by the mechanism proposed in [12] and experimentally confirmed in [13].

As a result, the formation of dimethyl methylphosphonate in the reaction of $(\text{MeO})_3\text{P}$ with MeCOCF_3 can be explained by the following scheme:



Due to the smaller steric hindrance, phosphites with less bulky radicals should dealkylate quasiphosphonium compounds more easily and preferably lead the reaction in this direction. Consequently, it is obvious that diethyl ethylphosphonate is not formed in the reaction of $(\text{EtO})_3\text{P}$ with MeCOCF_3 .

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrometer in the 400-3600 cm^{-1} region as a liquid film, while the Raman spectra were obtained on a Coderg PHO-82 spectrometer equipped with an LG-38 helium-neon laser. The ^1H and ^{19}F NMR spectra were recorded on a Tesla 487-C spectrometer at 80 MHz, and respectively using TMS and CF_3COOH as the internal standards. The ^{31}P chemical shifts were measured on RYa-2305 and KGU-4 instruments at 10 MHz relative to 85% H_3PO_4 . The mass spectra were obtained on an MI-1305 mass spectrometer, equipped with a glass admission system, at an admission temperature of 80° and an energy of 50 eV for the ionizing electrons.

Reaction of Trimethyl Phosphite with 1,1,1-Trifluoroacetone. With stirring and cooling with water, to 75.4 g of 1,1,1-trifluoroacetone was added 41.7 g of $(\text{MeO})_3\text{P}$ in 1 h (ratio of reactants 1:2). The mixture was kept for 168 h at 20° and then the volatile compounds were distilled off at 20° in vacuo (10 mm). Vacuum-distillation of the residue gave 64.6 g of crude trimethoxy- α -trifluoromethyl- α -(1-methyl-2,2-difluorovinyl)oxyethoxyfluorophosphorane with bp 63-71° (10 mm). Repeated distillation of this product in a Perkin-Elmer-251 apparatus in a 1° range [reflux ratio 200, distillation rate 1 drop/sec, bp 65° (10 mm)] gave 15.2 g of a mixture of the dimethyl phosphonate and trimethoxy- α -trifluoromethyl- α -(1-methyl-2,2-difluorovinyl)oxyethoxyfluorophosphorane.

CONCLUSIONS

Trialkyl phosphites react with 1,1,1-trifluoroacetone to give 2,2,2-trialkoxy-3,5-dimethyl-3,5-bis(trifluoromethyl)-1,4,2-dioxaphospholanes, which slowly isomerize to trialkoxy- α -trifluoromethyl- α -(1-methyl-2,2-difluorovinyl)oxyethoxyfluorophosphoranes.

LITERATURE CITED

1. F. Ramirez, A. V. Patvardhan, and S. R. Heller, *J. Am. Chem. Soc.*, **86**, 514 (1964).
2. T. Kh. Gazizov, Yu. I. Sudarev, and A. N. Pudovik, *Zh. Obshch. Khim.*, **46**, 924 (1976).
3. F. Ramirez, *Acc. Chem. Res.*, **1**, 168 (1968).
4. A. M. Kibardin, T. Kh. Gazizov, P. I. Gryaznov, and A. N. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1979**, 1391.
5. I. L. Knunyants, U. Utebaev, E. M. Rokhlin, E. P. Lur'e, and E. I. Mysov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 876.
6. D. A. Bufus, E. J. Gallegos, and R. F. Kiser, *J. Phys. Chem.*, **70**, 2618 (1966).
7. J. L. Occolowitz and G. L. White, *Anal. Chem.*, **35**, 1179 (1963).
8. E. M. Rokhlin, Yu. V. Zeifman, Yu. A. Cheburkov, N. P. Gambaryan, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **161**, 1356 (1965).
9. F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patvardhan, *Tetrahedron Lett.*, **1966**, 2151.
10. V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963).
11. A. M. Kibardin, T. Kh. Gazizov, and A. N. Pudovik, *Zh. Obshch. Khim.*, **45**, 1982 (1975).
12. P. Rumpf, *Bull. Soc. Chim. France*, **1951**, 128 C.
13. L. V. Nesterov and A. Ya. Kessel, *Zh. Obshch. Khim.*, **37**, 728 (1967).

REACTIONS OF KETOALCOHOLS WITH ORGANOPHOSPHORUS
COMPOUNDS9. FORMATION OF 2-SUBSTITUTED OXA-3-PHOSPHOLANOLS
FROM AMIDOPHOSPHITES AND DIACETONE ALCOHOL

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Phosphorous acid amides enter into substitution reactions with alcohols, in which connection the coordination number of the phosphorus atom is retained here [1]. As a continuation of studying the reactions of ketoalcohols with various phosphorus-containing compounds we used the alcoholysis reaction of amidophosphites for the purpose of adding β -ketoalcohol moieties to the P^{III} phosphorus atom. Here it was of especial interest to substitute two amide groups in view of the fact that the anticipated bis(γ -ketoalkyl) phosphites were postulated as being intermediates in the synthesis of 2-substituted oxa-3-phospholanols from P^{III} acid dichlorides and diacetone alcohol [2].

Initially the alcoholysis was run by heating the reactants up to a temperature where the liberated amine distilled off. It proved that under these conditions (120–200°C) diacetone (DAA), β -acetoethyl, and β -acetoisopropyl alcohols give a complex mixture of products with hexaethyltriamidophosphite (HETP), ethyl tetraethylamidophosphite (ETEDP), tetraethyldiamidophenylphosphonite, tetraethyldiamidoethylphosphonite, tetramethyldiamidophenylphosphonite, and tetramethyldiamidoethylphosphonite. Based on the ³¹P NMR data, in all of the experiments with DAA the reaction mixture prior to distillation contained at least eight phosphorus-containing compounds, which could not be isolated pure. Dark brown tarry masses are formed in the experiments with either β -acetoisopropyl or β -acetoethyl alcohol. The stepwise substitution of the amido groups when heated by ketoalcohol radicals is probably complicated by the decomposition of the obtained products into unsaturated ketone and phosphorus acid [3]. The formed new compounds are capable of reacting both with the starting reactants and with each other, and also of disproportionating, which leads to the observed complex picture.

It is known that proton-donor reagents facilitate the alcoholysis of amidophosphites [4], and consequently it was decided to change the experimental conditions and study the reactions of β -ketoalcohols with amidophosphites in the presence of AcOH. Such reaction with DAA is exothermic and gives compounds that, based on the

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