CONCLUSIONS

A simple method was proposed for the synthesis of 8Z-1-dodecenyl acetate and 9Z-1-tetradecenal from 1,1,9-trichloro-1-nonene.

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ACID AND ALKALINE CATALYSIS IN EXCHANGE REACTIONS OF PHOSPHOROUS THIOESTERS

O. G. Sinyashin, É. S. Batyeva, A. N. Pudovik, and E. N. Ofitserov UDC 541.128:541.515:547.1'118

Previously it was shown [1] that the heating (120°C, 3 days) of the trimethyl and tributyl trithiophosphites in the presence of traces of HCl leads to an equilibrium mixture of four thiophosphites.

$$(MeS)_{3}P + (BuS)_{3}P \rightleftharpoons (MeS)_{2}PSBu + (BuS)_{2}PSMe$$

In order to ascertain the effect of various catalysts on the rate of exchange reactions in the series of P(III) acid thioesters we used the 31 P NMR method to study the reaction between the trimethyl and triethyl trithiophosphites in the presence of acid (Et₃N·HCl, CH₃COOH) and alkaline (CH₃SNa, EtSNa, EtSNa, EtONa) catalysts.

In Fig. 1 are shown the ³¹ P NMR spectra of the reaction mixtures in the presence of alkaline (b) and acid (c, d) catalysts, which were recorded at definite time intervals at various temperatures. From these data it can be seen that in the case of CH_3SNa the exchange products are recorded within 1 h after mixing the reactants at ~ 20° (spectrum 1b), while in the presence of acid catalysts the exchange products of the thio-alkyl groups are recorded only after 1 h at 60° (spectrum 2c, d). When CH_3SNa is used the reaction reaches equilibrium in 4 days at ~ 20° (3b), whereas in the presence of acid catalysts the exchange rate is much slower (3c, d). Trialkyl trithiophosphites, specially freed of acid and alkaline impurities, in general do not enter into the exchange reaction under these conditions (spectra 1-3a).

The obtained experimental results on the catalytic effect of acid catalysts on the exchange reaction in the series of trialkyl trithiophosphites, in combination with the data obtained by us when studying the reaction of P(III) acid thioesters with mineral [2] and carboxylic [3] acids, permits postulating the following scheme for the formation of the exchange products in the presence of acid catalysts.

$$(\mathrm{RS})_{\mathfrak{z}}\mathrm{P} + (\mathrm{R}'\mathrm{S})_{\mathfrak{z}}\mathrm{P} + 2\mathrm{HX} \rightleftharpoons (\mathrm{R}'\mathrm{S})_{\mathfrak{z}}\mathrm{PX} + \frac{\mathrm{RSH}}{\mathrm{R}'\mathrm{SH}} \rightleftharpoons (\mathrm{RS})_{\mathfrak{z}}\mathrm{PSR}' + \mathrm{RSP}(\mathrm{SR}')_{\mathfrak{z}} + 2\mathrm{HX}$$

The reaction of trimethyl trithiophosphite with EtSNa leads to an equilibrium mixture of four thiophosphites

$$(MeS)_{3}P + 3EtSNa \rightleftharpoons (MeS)_{2}PSEt + MeSP (SEt)_{2} + (EtS)_{3}P$$

In contrast to this, the reaction of triethyl trithiophosphite with EtONa gives only triethyl phosphite and EtSNa. The absence of mixed thiophosphites in this reaction is apparently related to the fact that the reverse

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. 9, pp. 2133-2134, September, 1981. Original article submitted December 18, 1980.



Fig. 1. ³¹P NMR spectra of reaction mixture $(MeS)_3P + (EtS)_3P$, freed of acid and basic impurities (a), and in presence of MeSNa (b), $Et_3N \cdot HCl$ (c), MeCOOH (d). The spectra were recorded: 1) 1 hafter mixing the reactants at ~20°; 2) after heating at 60° for 1 h; 3) after 4 days.

reaction of triethyl phosphite with EtSNa does not go even at $100-120^{\circ}$ (4 h), whereas the reaction of trimethyl trithiophosphite with EtSNa is reversible. The data obtained by us explain the results given in [1], where it was shown that exchange between trialkyl trithiophosphites and the full esters of phosphorous acids is not realized in the presence of either alkaline or acid catalysts.

According to the obtained data, the reaction of a trialkyl trithiophosphite with AlkSNa proceeds by the following scheme:

$$(\mathrm{RS})_{\mathbf{3}}\mathrm{P} + \mathrm{R'SNa} \rightleftharpoons (\mathrm{RS})_{2}\mathrm{PSR'} + \mathrm{RSNa} \rightleftharpoons (\mathrm{R'S})_{2}\mathrm{PSR} + \mathrm{RSNa} \rightleftharpoons (\mathrm{R'S})_{\mathbf{3}}\mathrm{P} + \mathrm{RSNa}$$

Evidently, the reaction of phosphorous acid thioesters with a sodium alcoholate also proceeds in a similar manner.

EXPERIMENTAL

The ³¹P NMR spectra were obtained on a KGU-4 NMR instrument at an operating frequency of 10.2 MHz, and using 85% H₃PO₄ as the external standard. To a solution of 0.14 mole of EtONa (from 3.22 g of Na and 40 ml of alcohol) was added 0.046 mole of (EtS)₃P, the mixture was refluxed for 2 h, and then kept for 5 h at 0.02 torr. From the trap, cooled with liquid nitrogen, was isolated a solution of (EtO)₃P in ethanol. The alcohol was removed, and the residue was fractionally distilled to give 3.3 g (42%) of triethyl phosphite with bp 45-46° (10 mm), nD²⁰ 1.4129, δ P 139 m.d. (cf. [4]), and 1.2 g of diethylphosphorous acid with bp 74° (10 mm), nD²⁰ 1.4095, δ P 9 m.d., J_{PH} = 686 Hz, which corresponds to the data given in [4].

CONCLUSIONS

The exchange of thioalkyl radicals in the series of trialkyl trithiophosphites is catalyzed by either acids or bases, in which connection the exchange rate increases when going from acid to basic catalysts.

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