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Abstract

Full Text

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Interaction of Triphenyl Phosphite with ω-Bromoacetophenone

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Earlier we showed (^{1}) that at 160-200° trialkyl phosphites $(RO)_3P$, where R = C_1-C_8, with ω-bromoacetophenone undergo the Arbuzov rearrangement with formation of esters of β-ketophosphinic acids and alkyl halides. The interaction of triaryl phosphites with ω-bromoacetophenone has not been studied at all.

The aim of the present work was to study the interaction of triphenyl phosphite with ω-bromoacetophenone.

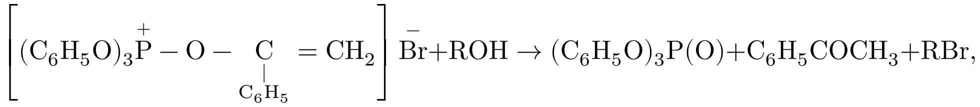
The reaction of triphenyl phosphite with ω-bromoacetophenone under more severe conditions (180-200°, 4 hours) leads to the formation of triphenyl phosphate (79.3%) with resinification of the remaining reaction products. At 160-170° (0.5 hour) the yield of triphenyl phosphate reaches 92.5%. In the interaction of triphenyl phosphite with ω-bromoacetophenone at 120-140° for 1 hour (in vacuo, 14-17 mm Hg), triphenyl phosphate (88.1%), hydrogen bromide (61%), and phenylacetylene (49.6%) were obtained:

$$(C_6H_5O)_3P + BrCH_2COC_6H_5 \rightarrow (C_6H_5O)_3P(O) + C_6H_5 - C \equiv CH + HBr.$$

A similar course of the reaction was also observed in the case of the interaction of triphenylphosphine with ω-bromoacetophenone (^{2}). The lower yield of phenylacetylene in comparison with triphenyl phosphate is explained by its greater tendency toward polymerization (^{3}) and hydrobromination under the conditions of the reaction and distillation of its products. The decreased yield of hydrogen bromide is due to its loss during the reaction in vacuo and vacuum distillations, as well as to its addition to phenylacetylene.

On boiling equimolecular amounts of triphenyl phosphite and ω-bromoacetophenone in anhydrous benzene, toluene, or xylene, and also at 120-130° (without solvent), an addition product—an adduct—is formed. The rate of formation of the adduct depends on the reaction temperature. Thus, for example, at 80° (in benzene) the yield of the adduct after 43 hours reaches 21.4%; at 110° (in toluene) after 9 hours, 95%; at 138-140° (in xylene) after 2.5 hours, 25%; and at 120-130° (without solvent) after 2.5 hours, 30%. As can be seen, the optimum temperature for formation of the adduct is 110°. At a higher temperature (120° and above), the rate of thermal decomposition of the adduct exceeds the rate of its formation. By analogy with the addition products of α-halocarbonyl compounds to triphenylphosphine ($^{4-6}$), we assign to the product of addition of ω-bromoacetophenone to triphenyl phosphite the structure of an enolphosphonium salt (^{1}).

The adduct is a crystalline substance; at 120° and above it decomposes with formation of triphenyl phosphate, phenylacetylene, and hydrogen bromide. It is a highly reactive compound: in air it "fumes," decomposing under the influence of atmospheric moisture. It reacts very vigorously with water, alcohols, and acetic acid (and also with other compounds having an active hydrogen) with evolution of heat:



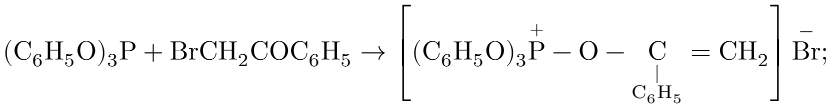
$$\left[(C_6H_5O)_3\overset{+}{P}-O-\underset{C_6H_5}{C}=CH_2\right]\overset{-}{Br}+ROH \rightarrow (C_6H_5O)_3P(O)+C_6H_5COCH_3+RBr,$$

(I)

where $R = H, CH_3, C_2H_5, CH_3CO$.

On decomposition of the adduct with water, triphenyl phosphate (90%), acetophenone, and hydrogen bromide were obtained. On decomposition with ethanol—triphenyl phosphate, ethyl bromide, and acetophenone. Decomposition of the adduct with anhydrous acetic acid gave triphenyl phosphate, acetophenone, and acetyl bromide.

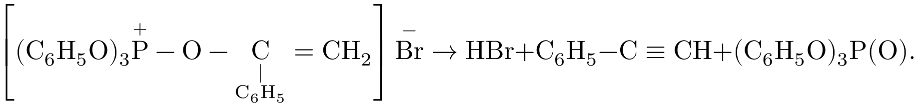
Thus, when the reaction is carried out under more severe conditions (120° and above), it proceeds in two phases: phase I—the addition of ω-bromoacetophenone to triphenyl phosphite with formation of an adduct apparently having the structure of an enolphosphonium salt (I)



$$(C_6H_5O)_3P + BrCH_2COC_6H_5 \rightarrow \left[(C_6H_5O)_3\overset{+}{P}-O-\underset{C_6H_5}{C}=CH_2\right]\overset{-}{Br};$$

(I)

phase II—thermal decomposition of the adduct with formation of triphenyl phosphate, phenylacetylene, and hydrogen bromide:



$$\left[(C_6H_5O)_3\overset{+}{P}-O-\underset{C_6H_5}{C}=CH_2\right]\overset{-}{Br}\rightarrow HBr+C_6H_5-C\equiv CH+(C_6H_5O)_3P(O).$$

(I)

Experimental Part

Reaction of triphenyl phosphite with ω-bromoacetophenone without solvent

On heating 55.9 g of triphenyl phosphite and 35.82 g of bromoacetophenone at 120–132° at 14 mm Hg for one hour, 10.5 g of a substance with b.p. 84–86° (at 14 mm), n_D^{20} 1.5450, were distilled off. From the latter, phenylacetylene was identified in the form of silver phenylacetylide (7), with a yield of 49.6%. On attempting to distill this fraction, resinification of the phenylacetylene fraction is observed for the most part; apparently its polymerization and hydrobromination occur. The phenylacetylene isolated by distillation had the following constants: b.p. (85 mm), n_D^{20} 1.5480, d_4^{20} 0.9427. According to (8): b.p. 86° (at 90 mm), n_D^{20} 1.5484, d_4^{20} 0.9285. The residue after removal of the phenylacetylene fraction was washed with water in ether solution. By titration of the aqueous solution, 61% hydrogen bromide was found. Vacuum distillation gave triphenyl phosphate in 88.1% yield: b.p. 225–230° (at 2 mm), m.p. 49–50° (from hexane + acetone).

$C_{18}H_{15}O_4P$. Found %: P 9.62; 9.44
Calculated %: P 9.51

Reaction of triphenyl phosphite with ω-bromoacetophenone in solution

Reaction in benzene medium. 31.0 g of triphenyl phosphite and 19.9 g of bromoacetophenone were boiled in 150 ml of anhydrous benzene. After 2 hours, precipitation of the adduct began in the form of an oily product insoluble in benzene. Over 43 hours, 6.32 g (21.4% based on reacted bromoacetophenone) of light-yellow crystals formed. The latter were washed with anhydrous ether and dried in a vacuum desiccator over P_2O_5.

Found %: P 6.49; 6.32; Br 15.75; 15.26 (hydrolysis with water and titration of hydrog
15.06 (by Stepanov).
$C_{26}H_{22}BrO_4P$ Calculated %: P 6.09; Br 15.71

Reaction in toluene. Similarly, when 31.0 g of triphenyl phosphite and 19.9 g of bromoacetophenone were boiled in 150 ml of anhydrous toluene for 9 h, 48.3 g (95%) of the adduct was obtained.

Reaction in xylene. Similarly, when 31.0 g of triphenyl phosphite and 19.9 g of bromoacetophenone were boiled in 150 ml of anhydrous technical xylene for 2.5 h, 12.7 g (25%) of the adduct was obtained. At 120–130° (without solvent), in 2.5 h the yield of the adduct is 30%.

Decomposition of the Adduct

Decomposition with water. When 0.2 g of water was added to 5.1 g of the adduct, strong heating and evolution of hydrogen bromide in the form of fumes were observed. After washing out the hydrogen bromide with water, 2.98 g (90%) of triphenyl phosphate was obtained, and the presence of acetophenone was shown qualitatively with the aid of 2,4-dinitrophenylhydrazine.

Decomposition with ethanol. Into the reaction were taken 15.3 g of the adduct and 15 ml of anhydrous ethanol. When ethanol was added to the adduct, the latter dissolved with strong heating and simultaneous distillation of the ethyl bromide formed (2.6 g). The duration of decomposition was 15 min. Triphenyl phosphate and acetophenone were isolated by distillation.

Decomposition with acetic acid. When 31.0 g of triphenyl phosphite, 19.9 g of ω-bromoacetophenone, and 6.0 g of glacial acetic acid were boiled in 150 ml of anhydrous toluene for 1.5 h, 2 g of acetyl bromide was distilled off. By vacuum distillation of the reaction mass, 47.6 g (91.4%) of triphenyl phosphate and 3.91 g (32.6%) of acetophenone were isolated.

The reaction of triphenyl phosphite with ω-bromoacetophenone was studied in anhydrous benzene, toluene, xylene, and without solvent. It was shown that in anhydrous benzene, toluene, or xylene, and also at 120–130° (without solvent), the product of addition of ω-bromoacetophenone to triphenyl phosphite (the adduct) is formed; this is a thermally insufficiently stable and highly reactive compound, readily reacting with compounds containing active hydrogen.

It was established that at a higher temperature (120–140° and above), triphenyl phosphate, phenylacetylene, and hydrogen bromide are formed, which are products of thermal decomposition of the adduct. A mechanism for the course of the latter reaction has been proposed.

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