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Abstract

Full Text

Chemistry

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On the Structure of the Products of the Interaction of Certain α-Haloketones of the Carbocyclic Series with Triethyl Phosphite and Sodium Diethyl Phosphite

In recent years we have undertaken a study of esters of β-ketophosphinic acids (1). The initial aim of the investigations was to determine whether keto-enol tautomerism is present in esters of β-ketophosphinic acids.

It turned out, however, that the A. E. Arbuzov rearrangement reaction of triethyl phosphite with α-haloketones, by means of which esters of β-ketophosphinic acids were obtained, proceeds in a complex manner, and, along with the expected esters of β-ketophosphinic acids, mixed esters of phosphoric acid are formed (2). This complicated the study of esters of β-ketophosphinic acids and explained certain deviations in the chemical and physical properties of the esters of β-ketophosphinic acids that we observed (3).

Our investigations showed that the Michaelis–Becker reaction in the case of the interaction of sodium diethyl phosphite with α-haloketones also proceeds in a complex manner and leads, along with esters of β-ketophosphinic acids, to the formation of esters of epoxyphosphinic acids (4).

In the present communication we give the data obtained by us on the structure of the products of the interaction of triethyl phosphite or sodium diethyl phosphite with α-chlorocyclohexanone, α-chloro-α-methylcyclohexanone, α-chlorocyclopentanone, and the ester of bromopyruvic acid.

In 1955 A. N. Pudovik (5) showed that the product of the action of triethyl phosphite on α-chlorocyclohexanone is a mixed ester of phosphoric acid (I), containing the ester radical of the enol form of cyclohexanone. On transesterification with ethyl alcohol it gave triethyl phosphate and cyclohexanone.

$$\text{-chlorocyclohexanone} + \mathrm{P(OC_2H_5)_3} \longrightarrow \mathrm{I} \xrightarrow{\mathrm{C_2H_5OH}} \text{cyclohexanone} + \mathrm{(C_2H_5O)_3P{=}O}$$

$$\mathrm{I:}\quad \text{cyclohexenyl } \mathrm{O{-}P({=}\,O)(OC_2H_5)_2}$$

To the product of the interaction of α-chlorocyclohexanone with sodium diethyl phosphite he assigned the structure of the diethyl ester of α-phosphonocyclohexanone. We carried out a study of the products of the interaction of α-bromocyclohexanone with triethyl phosphite and showed that in this case as well a mixed ester of phosphoric acid (I) is obtained, which was confirmed both by chemical data and by the spectrum of combined light scattering.

Study of the product of the interaction of α-chlorocyclohexanone with sodium diethyl phosphite showed, however, that it is neither an unsaturated ester of phosphoric acid nor an ester of phosphonocyclohexanone. On transesterification with ethyl alcohol it was recovered unchanged. With 2,4-dinitrophenylhydrazine it did not give a dinitrophenyl-

hydrazone. Its Raman spectrum did not contain the frequency of a carbonyl group. All these data indicated that the product obtained has the structure of the diethyl ester of epoxycyclohexanephosphinic acid (II).

This assumption was confirmed by us by synthesis of ester (II) according to the following scheme [4]:

$$[\alpha\text{-chlorocyclohexanone}] + \mathrm{HOP(OC_2H_5)_2} \longrightarrow [\text{chlorohydroxycyclohexylphosphinate}] \xrightarrow[\text{in alcohol}]{\text{KOH}} [\text{epoxy}$$

The ester of epoxycyclohexanephosphinic acid had the following constants: b.p. 112-114°/2.5 mm, n_D^{20} 1.4571, d_4^{20} 1.1193, MR_D 57.01—close to those of the Michaelis–Becker reaction product. The Raman spectra of both products coincided completely.

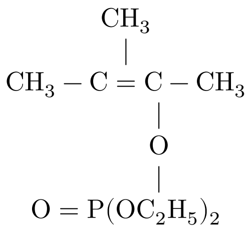
Thus, as in the case of aliphatic α-haloketones [4], the product of the action of sodium diethyl phosphite on α-chlorocyclohexanone proved to be the ester of epoxycyclohexanephosphinic acid, and not α-phosphonocyclohexanone.

It was somewhat unexpected that, in the case of α-chloro-α-methylcyclohexanone, the products of the action on it of triethyl phosphite and sodium diethyl phosphite had similar constants and similar Raman spectra.

Both preparations, on transesterification with ethyl alcohol, gave triethyl phosphate and methylcyclohexanone and thus proved to be methylcyclohexenyldiethyl ester of phosphorous acid (III); the Arbuzov rearrangement reaction and the Michaelis–Becker reaction in this case lead to one and the same unsaturated ester of phosphorous acid.

It is interesting to note that, as we have found, in another case as well—in the case of methyl α-bromoisopropyl ketone, where there is a halogen at a tertiary carbon—the rearrangement reaction and the Michaelis–Becker reaction lead to one and the same product, an unsaturated ester of phosphorous acid (IV). This was proved by a transesterification reaction with ethyl alcohol, leading to methyl isopropyl ketone and triethyl phosphate, and by Raman spectra.

[methylcyclohexenyl diethyl phosphite]
III


$$\mathrm{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=\underset{\underset{\underset{\displaystyle O=P(OC_2H_5)_2}{|}}{\underset{|}{O}}}{C}-CH_3}$$
IV

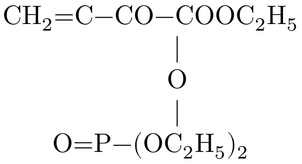
[epoxycyclopentylphosphinate]
V

The product previously obtained by us from the interaction of α-chlorocyclopentanone with sodium diethyl phosphite, as additional investigations showed, proved to be the ester of epoxycyclopentanephosphinic acid (V). It did not give a 2,4-dinitrophenylhydrazone and was not transesterified by ethyl alcohol. Its Raman spectrum contained neither the frequencies of a carbonyl group nor of a $C = C$ bond.

Additional study of the product of the action of sodium diethyl phosphite on α-bromocamphor showed that it is a mixed unsaturated ester of phosphorous acid (VI). On transesterification with ethyl alcohol it gave camphor and triethyl phosphate.

The unsaturated ester of phosphoric acid (VII) also proved to be the product previously obtained by us from the action of sodium diethyl phosphite on bromopyruvic ester.

VI


$$\mathrm{CH_2{=}C{-}CO{-}\underset{\underset{\underset{\displaystyle O{=}P{-}(OC_2H_5)_2}{|}}{\underset{|}{O}}}{C}OOC_2H_5}$$
VII

The material presented in this communication shows the complex course of the reaction between α-haloketones and sodium diethyl phosphite, leading to the formation of unsaturated esters of phosphoric acid, esters of epoxyphosphinic acids, and in some cases also esters of β-ketophosphinic acids (4)—depending on the nature of the halide, the reaction conditions, and the substituting alkyl radicals.

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