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Abstract

Full Text

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DIETHYL ESTER OF 1-ETHOXYCYCLOHEXENE-1-PHOSPHINIC-2 ACID

In previous communications (^{1}) we showed that esters of cyclohexanone-2-phosphinic acid cannot be obtained by the Arbuzov rearrangement reaction or by the Michaelis—Becker reaction.

The diethyl ester of cyclohexanone-2-phosphinic acid was obtained by a roundabout route: through the diethyl phosphorous ester of the enol form of the ester of cyclohexanone-2-phosphonic acid (III), by transesterification with ethyl alcohol (^{2}). The comparatively low yield of the phosphorous ester of cyclohexenolphosphinic acid and the insufficiently good reproducibility of the experiment led us to determine the reasons for this, and also to seek other routes for the synthesis of the ester of cyclohexanonephosphinic acid.

The reaction between dibromocyclohexanone and triethyl phosphite, described by us in a brief communication (^{2}), is accompanied by the formation of a considerable amount of lower-boiling fractions and depends strongly on the conditions under which the experiment is carried out. Further study of these fractions showed that they contain diethyl phosphorous acid, triethyl phosphate, the diethyl ester of cyclohexanone-2-phosphonic acid, and unsaturated compounds, including diene compounds. One of the reasons for the complex course of the reaction may be the influence of the conformation of the starting dibromocyclohexanone, which led us to carry out experiments on the action of triethyl phosphite and sodium diethyl phosphite on cis- and trans-2,6-dibromo- and 2,6-dichlorocyclohexanones.

One route for the synthesis of the diethyl phosphorous ester of the enol form of the ester of cyclohexanone-2-phosphonic acid (III) could have been the bromination of diethyl cyclohexenyl phosphate (I) with bromosuccinimide, followed by the action of triethyl phosphite on the resulting monobromide.

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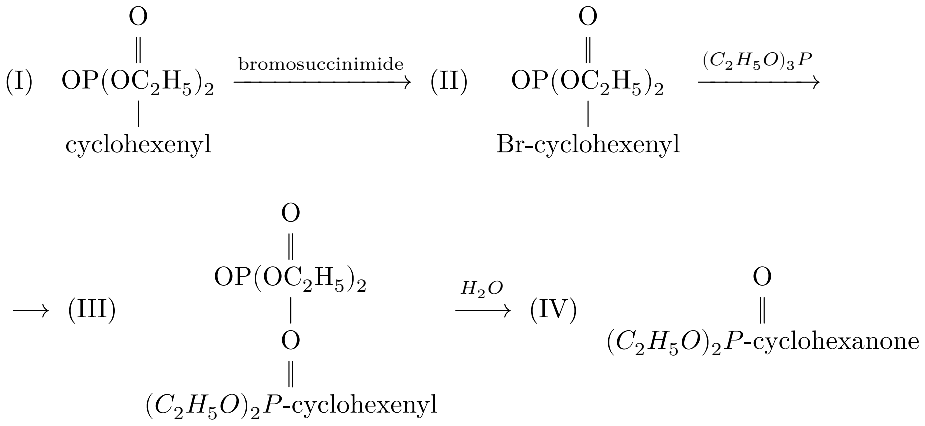
Fig. 1. IR spectrum of acid chloride IX (film)

Figure 1: Fig. 1. IR spectrum of acid chloride IX (film)

Fig. 2. IR spectrum of the diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid (X) (film)

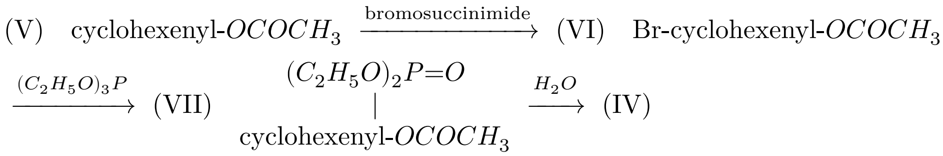
Figure 2: Fig. 2. IR spectrum of the diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid (X) (film)



$$\text{(I)}\quad \begin{array}{c}\text{O}\\ \|\\ \text{OP(OC}_2\text{H}_5)_2\\ |\\ \text{cyclohexenyl}\end{array} \xrightarrow{\text{bromosuccinimide}} \text{(II)}\quad \begin{array}{c}\text{O}\\ \|\\ \text{OP(OC}_2\text{H}_5)_2\\ |\\ \text{Br-cyclohexenyl}\end{array} \xrightarrow{(C_2H_5O)_3P}$$

$$\longrightarrow \text{(III)}\quad \begin{array}{c}\text{O}\\ \|\\ \text{OP(OC}_2\text{H}_5)_2\\ |\\ \text{O}\\ \|\\ (C_2H_5O)_2P\text{-cyclohexenyl}\end{array} \xrightarrow{H_2O} \text{(IV)}\quad \begin{array}{c}\text{O}\\ \|\\ (C_2H_5O)_2P\text{-cyclohexanone}\end{array}$$

This route did not lead to the desired results. Nor did another variant of the synthesis of diethyl phosphonocyclohexanone give positive results:



$$\text{(V)}\quad \text{cyclohexenyl-}OCOCH_3 \xrightarrow{\text{bromosuccinimide}} \text{(VI)}\quad \text{Br-cyclohexenyl-}OCOCH_3$$

$$\xrightarrow{(C_2H_5O)_3P} \text{(VII)}\quad \begin{array}{c}(C_2H_5O)_2P{=}O\\ |\\ \text{cyclohexenyl-}OCOCH_3\end{array} \xrightarrow{H_2O} \text{(IV)}$$

The principal product of the reaction proved to be the diethyl cyclohexenyl ester of phosphorous acid (I).

I. F. Lutsenko and M. Kirillov $(^3)$ showed that, by the addition reaction of phosphorus pentachloride to enol acetates, one can arrive at α-phosphonaldehydes and α-phosphonketones.

We have not yet been able to select suitable conditions for carrying out this reaction of phosphorus pentachloride in the case of the enol acetate

Fig. 1. IR spectrum of acid chloride IX (film)

Fig. 2. IR spectrum of the diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid (X) (film)

of cyclohexanone. We succeeded in carrying out the synthesis of the diethyl ester of cyclohexanone-2-phosphinic acid by an analogous route, starting from 1-ethoxycyclohexene.

$$(\mathrm{VIII}) \xrightarrow{+\mathrm{PCl}_5} \text{chlorinated complex} \xrightarrow{\mathrm{SO}_2} (\mathrm{IX}) \xrightarrow{\mathrm{C}_2\mathrm{H}_5\mathrm{OH}} (\mathrm{X}) \xrightarrow{\mathrm{H}_2\mathrm{O}} (\mathrm{XI}) \rightleftharpoons (\mathrm{IV})$$

By adding phosphorus pentachloride to ethoxycyclohexene (VIII), followed by treatment of the complex with sulfur dioxide, the acid chloride (IX) was obtained with b.p. 136°/2 mm, d_D^{20}1.3009; n_D^{20}1.5275; MR_D found 57.52, $C_8H_{13}O_2Cl_2P$ calculated 55.43.

The spectrum of the combinational scattering of light of acid chloride (IX) had the following frequencies (in cm^{-1}): 165 (6 sh), 180 (3), 248(5), 296(2), 321(3), 347(2), 371(2), 398(7), 408(2), 450(2 dw.), 491(5), 502(2), 529(3sh), 571(2), 604(0), 674(1), 736(1), 825(4), 866(3), 907(1), 967(3), 1016(0), 1033(2), 1080(4), 1143(2), 1181(5), 1227(0), 1258(6), 1279(2), 1368(1), 1421(7), 1446(4), 1456(2), 1552(2sh)*, 1591(0), 1611(10sh)**, 1662(2), 2657(0), 2728(0), 2863 (5dw.), 2896 (5sh), 2937(8sh), 2979(4).

In the IR spectrum of product IX (Fig. 1), absorption of medium intensity at 1660 and very strong absorption at 1611 appear, corresponding to the C=C bond of the cyclohexene ring, which is under the strong influence of the P=O group and two chlorine atoms. The strong broad band in the absorption region of the P=O group has three maxima: 1272, 1255, and 1234 cm^{-1}.

* May be a repeat line from the exciting mercury line f.
** The line width is ~ 30 cm^{-1}.

By esterification of acid chloride IX with ethyl alcohol, the expected diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid (X) was obtained, with b.p. 122-123°/1 mm, d_0^{20} 1.0860; n_D^{20} 1.4735. MR_D found 67.82, $C_{12}H_{23}O_2P$ calculated 67.46.

The Raman spectrum of diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid (X) had the following frequencies (in cm^{-1})*: 258(2), 270(2), 328(1), 354(2), 437(1), 502(0), 521(0), 563(0), 586(0), 612(1), 653(0), 677(1), 712(1), 750(2), 812(2), 828(2), 865(2), 910(2), 949(1), 967(0), 1034(2), 1083(2), 1100(3), 1119(2), 1149(1), 1176(2), 1236(1), 1282(2), 1338(1), 1364(2), 1388(1), 1430(2), 1442(4), 1456(3), 1480(0), 1636(4), 1665(3), 2723(0), 2843(3), 2870(4), 2898(3), 2931(6), 2981(4), 3064(1).

Fig. 3. U.-v. absorption spectra: **1** —diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid (X) in CH_3OH; **2** —diethyl ester of cyclohexanone-2-phosphinic acid in isooctane

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Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

The i.-r. spectrum of product X is shown in Fig. 2. Instead of the strong broad band 1611 observed in the i.-r. spectrum of acid chloride IX (Fig. 1), in the i.-r. spectrum of diethyl ester of 1-ethoxycyclohexene-1-phosphinic acid (X) there is an absorption of medium intensity at 1636, coinciding with the frequency 1632 corresponding to the C=C bond of the enol form (XI) of diethyl ester of cyclohexanone-2-phosphinic acid (see Fig. 4). The values of the frequencies of the stretching vibrations of the C=C bonds in the Raman spectra of products IX and X change analogously.

Fig. 4. I.-r. spectrum of diethyl ester of cyclohexanone-2-phosphinic acid: **1** –in film, **2** –in hexane, $c \simeq 4.5$ wt. %, $d = 0.1$ mm; **3** –in iso-C_4H_9OH, $c \simeq 1$ wt. %, $d = 0.03$ mm

The u.-v. spectrum of diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid (X) (Fig. 3) is also close in the character of absorption to the u.-v. spectrum of diethyl ester of cyclohexanone-2-phosphinic acid, recorded in isooctane solution, where the equilibrium is strongly shifted toward the enol form (^{2}).

By saponification of ester X with acidified water, diethyl ester of cyclohexanone-2-phosphinic acid was obtained, with b.p. 111–113°/1 mm, d_0^{20} 1.1231; n_D^{20} 1.4660. The constants fully coincided with those of the ester described by us earlier (^{2}).

The i.-r. spectrum of the ester obtained also coincided with the spectrum of diethyl ester of cyclohexanone-2-phosphinic acid obtained by transesterification of ester III (Fig. 4). In the i.-r. spectrum of diethyl ester of cyclohexanone-2-phosphinic acid, as well as in the spectrum of combinational scattering (^{2}), frequencies 1710 and 1632 appear, characteristic of the ketone (IV) and enol (XI) forms, respectively. In a hexane solution the positions of these bands, found in the spectrum of the liquid ester, are retained in the IR spectrum, and a considerable change in their intensities is observed: the intensity of the 1710 band decreases and that of the 1632 band increases strongly. This indicates a shift of the equilibrium in hexane solution toward the enol form. The strong decrease in the intensity of the 1632 band in isobutyl alcohol solution (Fig. 4, 3) is associated with a decrease in the amount of the enol form of the ester in the more polar solvent.

In the absorption region of the $P = O$ group in hexane solution, the intensity

* The spectrum has a dark background.

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of the 1255 peak decreases and the absorption at 1195 increases strongly. The possibility is not excluded that the $P = O$ group of the enol form participates in the formation of an intramolecular hydrogen bond.

Experimental Part

Action of phosphorus pentachloride on ethoxycyclohexene. Ethoxycyclohexene, b.p. 55°/14 mm, n_D^{20} 1.4589, was obtained by removal of an ethanol molecule from the acetal of cyclohexanone, prepared by the reaction of cyclohexanone with tetraethoxysilane (^{4}), by heating in vacuo (170–188 mm) in the presence of camphorsulfonic acid and quinoline (^{5}).

Ethoxycyclohexene (37.6 g), dissolved in benzene, was added dropwise with stirring and cooling to a suspension of 124.4 g of PCl_5 in 200 ml of abs. benzene. After standing for two days at room temperature, the reaction mixture was treated with SO_2 until the precipitate had dissolved completely. Distillation in vacuo gave fractions: 1) 86—92°/2.5 mm; 2) 128—136°/2 mm.

By distillation of the higher fraction, the acid chloride of 1-ethoxycyclohexene-1-phosphinic-2 acid was isolated, b.p. 136°/2 mm, d_0^{20} 1.3009; n_D^{20} 1.5275–22 g. MR_D found 57.52, $C_8H_{13}O_2Cl_2P$ calculated 55.43.

$C_8H_{13}O_2Cl_2P$. Found %: P 12.53; 12.64; Cl 29.23; 28.70
Calculated %: P 12.75; Cl 29.16

Preparation of diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid. To a solution of 30 g of the acid chloride of 1-ethoxycyclohexene-1-phosphinic-2 acid, b.p. 136°/2 mm, in 100 ml of abs. ether, with stirring and cooling, a mixture of 25 g of triethylamine and 17.5 ml of ethanol (20% excess) was added dropwise. After separation of triethylamine hydrochloride, the residue was distilled in vacuo. Obtained: 16.3 g (50% of theory) of diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid: b.p. 122—123°/1 mm, d_0^{20} 1.0860; n_D^{20} 1.4735; MR_D found 67.82, $C_{12}H_{23}O_4P$ calculated 67.46.

$C_{12}H_{23}O_4P$. Found %: P 12.32; 12.22
Calculated %: P 11.82

Saponification of diethyl ester of 1-ethoxycyclohexene-1-phosphinic-2 acid was carried out by shaking the ester in a separatory funnel with dilute HCl (1 : 10). The solution was extracted repeatedly with ether. The ether extract was dried with Na_2SO_4, and the ether was removed. Distillation of the residue in vacuo gave diethyl ester of cyclohexanone-2-phosphinic acid with b.p. 111—113°/1 mm; d_0^{20} 1.1231; n_D^{20} 1.4660 (^{2}).

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