ESTERS OF β-KETOPHOSPHONIC ACIDS.

COMMUNICATION 9. REACTION OF 2,6-DIBROMO- AND 2,6-DICHLOROCYCLOHEXANONE WITH ONE AND TWO MOLES OF TRIETHYL PHOSPHITE

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In a previous communication we proposed a scheme for the reaction between 2,6-dibromocyclohexanone and two moles of triethyl phosphite to explain the complex course of this reaction (I)

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\begin{align*}
\text{Br} & \quad \text{Br} + \text{P} (\text{OC}_2\text{H}_5)_3 \rightarrow \text{Br} \quad \text{Br} + \text{P} (\text{OC}_2\text{H}_5)_3 \rightarrow \text{Br} \\
\text{OP} (\text{OC}_2\text{H}_5)_2 & \rightarrow \text{OP} (\text{OC}_2\text{H}_5)_2 \\
\text{(IV)} & \rightarrow \text{(IV)} \\
\text{OP} (\text{OC}_2\text{H}_5)_2 & \rightarrow \text{OP} (\text{OC}_2\text{H}_5)_2 \\
\text{(II)} & \rightarrow \text{(II)} \\
\text{Br} & \quad \text{Br} \rightarrow \text{H} \quad \text{Br} \rightarrow \text{H} \\
\text{OP} (\text{OC}_2\text{H}_5)_2 & \rightarrow \text{OP} (\text{OC}_2\text{H}_5)_2 \\
\text{(IV)} & \rightarrow \text{(V)} \\
\text{OP} (\text{OC}_2\text{H}_5)_2 & \rightarrow \text{OP} (\text{OC}_2\text{H}_5)_2 \\
\text{(VI)} & \rightarrow \text{(VI)}
\end{align*}
\]

According to this scheme, the bromoester (IV) which is formed initially can react with a second molecule of triethyl phosphite to give the expected ester (II), or with splitting out of hydrogen bromide to go over to the diene ester (V), which is easily aromatized to the diethyl phenyl ester of phosphoric acid (VI).

To confirm the correctness of the proposed scheme, it was of interest to stop the reaction at the stage of formation of the bromoester (IV) and to show the possibility of its conversion to the diene ester (V) and the aromatic ester (VI) under the conditions that the reaction was carried out. With this purpose we studied the reaction of 2,6-dibromocyclohexanone with one molecule of triethyl phosphite. The reaction went vigorously and on heating above 130° complete decomposition of the reaction products occurred. Even at a bath temperature below 130° partial decomposition occurred on distillation. Therefore, in order to determine the nature of the products initially formed, we obtained the IR spectra before distillation of the reaction mixture and of the separate fractions of the distillate. The product of reaction of trans-2,6-dibromocyclohexanone (ae) with one molecule of triethyl phosphite before distillation had the IR spectrum shown in Fig. 1, Curve 1; in it the broad absorption band in the region of double bonds consists of superimposed bands with a frequency of 1653 cm⁻¹, which should be related to the diene (V), and a shoulder at about 1680 cm⁻¹, which probably is related to the double bond of the bromoester (IV).

The product of vacuum distillation of the reaction mixture with b.p. 39-42° (2 mm) consisted mainly of cyclohexanone. The fraction with b.p. 81-86° (1.5 mm) in the IR spectrum (Fig. 1, Curve 2) had a very intense absorption band at 1680 cm⁻¹, corresponding to the C = O group of cyclohexanone, and strong bands at 1591 and 1491 cm⁻¹, which are characteristic of the diethyl phenyl ester of phosphoric acid (VI) [1]. Thus, the diene ester (V) on distillation obviously is partially* converted to the phenyl ester (VI).

*The frequency 1656 cm⁻¹, which is characteristic of the diene (III), is overlapped by the intense broad band of cyclohexanone at 1680 cm⁻¹.
Purer products were obtained by treatment of the reaction mixture \( [2,6\text{-dibromocyclohexanone} + \text{I MP(OC}_2\text{H}_5)_3] \) with triethylamine. After separation of the triethylamine hydrobromide from the reaction products, we isolated, on distillation, cyclohexanone \([\text{b.p. 44-58°} (2-3 \text{ mm})]\), semicarbazone with m.p. 166-167°, band at 1680 cm\(^{-1}\) in the IR spectrum, UV maximum 224 \(\text{m} \mu\) \[2\], triethyl phosphate \([\text{b.p. 63°} (1 \text{ mm})]\), \(\text{n}\)\(^\text{D} \) 1.4150, IR spectrum], and a fraction with b.p. 105-110° (1 mm), \(\text{n}\)\(^\text{D} \) 1.4775, \(\text{d}\)\(^\text{D} \) 1.1406. With respect to its analysis for phosphorus and its IR spectrum, this fraction coincided with the fraction with b.p. 104-107° (2.5 mm) which was obtained by the action on 2,6-dibromocyclohexanone (trans-form) of two molecules of triethyl phosphite \[1\]. The IR spectrum of the fraction with b.p. 105-110° (1 mm) is given in Fig. 2, Curve 1, and the UV spectrum in Fig. 3. In the IR spectrum there are the frequency 1655 cm\(^{-1}\), which indicates the presence of the diene (V), and the frequency 1591 cm\(^{-1}\), which indicates the presence of the phenyl ester (VI).

In the UV spectrum of this fraction there is an absorption maximum at 262.5 \(\text{m} \mu\) (log \(\varepsilon\) 3.64), which is characteristic of the 1,3-cyclohexadiene system \[3\]. The presence of a conjugated system in the fraction with b.p. 105 to 110° (1 mm) was verified by treating it with maleic anhydride. A fraction was obtained with b.p. 118-119° (2 mm), in the IR spectrum of which (Fig. 2, Curve 2) there appeared, instead of the frequency of the diene bond at 1655 cm\(^{-1}\), absorption bands of the anhydride group at 1777 (s) and 1846 (w) \[4\], and the bands at about 1680 and 1591 cm\(^{-1}\) for the diethyl bromo-6-cyclohexen-1-yl and diethyl phenyl esters of phosphoric acid were preserved, which were found accordingly in the spectrum of the product with b.p. 105-110° (1 mm) before treatment with maleic anhydride (Fig. 2, Curve 1).

As can be seen from our statement, the data obtained are in complete agreement with the previously proposed scheme for the reaction of 2,6-dibromocyclohexanone with triethyl phosphite. Also in accordance with the scheme presented were experiments that we set up on the action of triethyl phosphite \(2 \text{ M}\) on 2,6-dichlorocyclohexanone (trans- and cis-forms). In this case, half of the phosphite used was recovered. From the reaction products we isolated,