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Abstract

Full Text

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ON THE REACTIONS OF TRI-(-CYANOISOPROPYL) PHOSPHITE, ETHYL DI-tert.-(, , -TRICHLOROBUTYL) PHOSPHITE, AND TRI-(, , -TRICHLOROETHYL) PHOSPHITE WITH CHLORAL

Aldehydes react with trialkyl phosphites with the formation of esters of α-alkoxyalkylphosphinic acids (^{1}). According to the data of (^{2}), the reaction in the indicated direction proceeds only with aromatic aldehydes. With aliphatic aldehydes the reaction proceeds in a more complex manner.

α-Halogen-substituted aldehydes react with trialkyl phosphites by the Perkow reaction, with the formation of mixed dialkylvinyl esters of phosphoric acid (^{3}).

We have found that tri-(α-cyanoisopropyl) phosphite (I) reacts with chloral in another direction, with the formation of the di-α-cyanoisopropyl ester of α-hydroxy-(β,β,β-trichloroethyl)phosphonic acid (II), with elimination of methacrylic acid nitrile. The reaction proceeds at room temperature. Ester (II) is a crystalline substance with m.p. 150-151°. Its structure was proved by analytical data and the IR spectrum (Fig. 1). In the IR spectrum, in the region of $\nu(\mathrm{P}=\mathrm{O})$, a split band is observed with maxima at 1267 and 1252 cm^{-1}, and a broad band ν(O—H) at 3290 cm^{-1}. A strong sharp band at 1100 cm^{-1} is assigned to the deformation vibration of the OH group.

The formation of ester (II) may be represented by the following scheme:

$$\begin{aligned}
\text{(I)}\quad & (\mathrm{CH_3})_2\mathrm{C(CN)}{-}\mathrm{O}{-}\mathrm{P}\left[\mathrm{O}{-}\mathrm{C(CH_3)_2CN}\right]_2 + \mathrm{O{=}CH{-}CCl_3} \longrightarrow \\
& \left[(\mathrm{CH_3})_2\mathrm{C(CN)}{-}\mathrm{O}{-}\mathrm{P^+}\left(\mathrm{O^-}{-}\mathrm{CH}{-}\mathrm{CCl_3}\right)\left(\mathrm{O}{-}\mathrm{C(CH_3)_2CN}\right)_2\right] \longrightarrow \\
& \left((\mathrm{CH_3})_2\mathrm{C(CN)O}\right)_2\mathrm{P}(=O){-}\mathrm{CH(OH)}{-}\mathrm{CCl_3} + \mathrm{CH_2{=}C(CH_3){-}CN}
\end{aligned}$$

(II)

In the intermediate complex, the hydrogen of the methyl radical is split off in the form of a proton and passes to the negatively charged oxygen, with formation of a hydroxy group. The elimination of methacrylic acid nitrile is evidently facilitated by the presence of the electronegative CN group. From this point of view it was of interest to carry out the reaction between chloral and tri-tert.-(β,β,β-trichlorobutyl) phosphite, the preparation of which was described by Dewey (^{4}) and Sanin (^{5}). On repeating Dewey' s experiment, however, we did not obtain the full phosphite, but obtained di-tert.-(β, β, β-trichlorobutyl) phosphorous acid with m.p. 44–45° (^{6}). This same m.p. (44–45°) was given by Dewey and Sanin for the full phosphite.

The structure of di-tert.-(β, β, β-trichlorobutyl) phosphorous acid (III) was proved by analysis and by the identity of its IR spectrum with the spectrum of di-tert.-(β, β, β-trichlorobutyl) phosphorous acid obtained by us by hydrolysis of di-tert.-(β, β, β-trichlorobutyl) chlorophosphite.

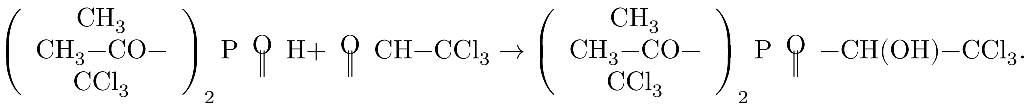
With chloral, di-tert.-(β, β, β-trichlorobutyl) phosphorous acid with m.p.

44–45° gave, by the usual reaction of dialkylphosphorous acids with aldehydes, $^{(6)}$ the di-tert-(β, β, β-trichlorobutyl) ester of α-hydroxy-β, β, β-trichloroethylphosphinic acid (IV) with m.p. 181–182°, which did not give a depression of the melting point with ester (IV) obtained by us from the interaction of chloral with acid (III), synthesized by hydrolysis of di-tert-(β, β, β-trichlorobutyl) chlorophosphite.

The IR spectrum of ester (IV) is shown in Fig. 2A.

In the spectrum of (IV) in Vaseline oil (Fig. 2A) there are two bands, 1257 and 1240 cm^{-1}, in the region of $\nu(\mathrm{P=O})$, and a broad band $\nu(\mathrm{O-H})$ at 3270 cm^{-1}, attributable to vibrations of an associated hydroxyl.

Fig. 1. IR absorption spectrum of di-α-cyanoisopropyl ester of α-hydroxy-β, β, β-trichloroethylphosphinic acid (II). *a*—absorption bands of Vaseline oil.



$$\left(\begin{array}{c}CH_3\\ CH_3{-}CO{-}\\ CCl_3\end{array}\right)_2 P\overset{O}{\|}H + \overset{O}{\|}CH{-}CCl_3 \rightarrow \left(\begin{array}{c}CH_3\\ CH_3{-}CO{-}\\ CCl_3\end{array}\right)_2 P\overset{O}{\|}{-}CH(OH){-}CCl_3.$$

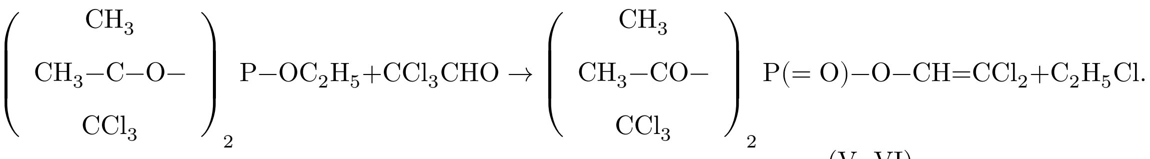
(III) (IV)

In the IR spectrum of a solution of (IV) in CCl_4 (Fig. 3), as the solution is diluted, a gradual disappearance of the band of bound hydroxyl and the appearance of a strong sharp band* at 3576 cm^{-1}, evidently attributable to vibrations of free hydroxyl, are observed. In addition, the spectrum contains a band at 3500 cm^{-1}, the intensity of which increases with dilution; it may be assigned to vibrations of hydroxyl participating in the formation of an intramolecular hydrogen bond.

In the region of $\nu(\mathrm{P=O})$, instead of the 1257 cm^{-1} band with a small side band at 1240 cm^{-1}, three bands of approximately equal intensity appear in the IR spectra of solutions of (IV) in CCl_4 and CS_2, with maxima at 1281, 1271, and 1257 cm^{-1}. These changes may be explained by the possible participation of the $\mathrm{P=O}$ group in the formation of a hydrogen bond.

We carried out the reaction between chloral and mixed di-tert-(β,β,β-trichlorobutyl) ethyl phosphite (V). The reaction proceeds at at room temperature with heating and leads to the formation of: 1) ester (IV) with m.p. 180-180.5° (a mixed-melting-point depression was not observed; the IR spectrum coincided with the spectra in Fig. 2A) and 2) a product with m.p. 78-80°, which proved to be di-tert-(β,β,β-trichlorobutyl)-(β,β-dichlorovinyl) phosphate (VI). The formation of (VI) is due to the Perkow reaction:

Fig. 2. IR absorption spectra: **A**—di-tert-β,β,β-trichlorobutyl ester of α-hydroxy-β,β,β-trichloroethylphosphinic acid (IV); **B**—di-tert-β,β,β-trichlorobutyl-(3,3-dichlorovinyl)phosphate (VI).



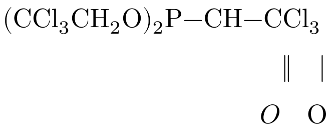
$$\left(\begin{array}{c}CH_3\\ CH_3{-}C{-}O{-}\\ CCl_3\end{array}\right)_2 P{-}OC_2H_5+CCl_3CHO \rightarrow \left(\begin{array}{c}CH_3\\ CH_3{-}CO{-}\\ CCl_3\end{array}\right)_2 P(=O){-}O{-}CH{=}CCl_2+C_2H_5Cl.$$

(V, VI)

In the IR spectrum of (VI) (Fig. 2B) there is an intense band $\nu(P=O)$ at 1278 cm^{-1} and a weak band $\nu(C=C)$ at 1652 cm^{-1}. In the $\nu(O-H)$ region there are no absorption bands.

The formation of (IV) must be accompanied by elimination of ethylene. The mechanism of this reaction has not yet been elucidated by us.

As one further example of the interaction of chloral with complete phosphites containing electronegative groups in the ester radicals, we used tri-(β,β,β-trichloroethyl) phosphite (7). The reaction proceeds at room temperature. The reaction product with m.p. 157-158° proved, by analysis and IR spectrum, to be the di-β,β,β-trichloroethyl ester of α-hydroxy-β,β,β-trichloroethylphosphinic acid (VII).



$$\begin{array}{lcc}(CCl_3CH_2O)_2P{-}CH{-}CCl_3 & & \\ \qquad\qquad\qquad\quad\ \| \quad | & & \\ \qquad\qquad\qquad\quad O \quad OH & & \end{array}$$

(VII)

Fig. 3. IR absorption spectra of the di-tert-β,β,β-trichlorobutyl ester of α-hydroxy-β,β,β-trichloroethylphosphinic acid (IV) in CCl_4 solution; 1 $-C=0.02$; 2 $-C=0.01$ mol/L

The IR spectrum of (VII) is presented in Fig. 4. In the spectrum there are bands $\nu(P=O)$ at 1260 cm^{-1}, $\nu(O-H)$ at 3250 cm^{-1}, a strong band of the

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* Similar absorption at 3585 cm^{-1} was found by us in the spectra of solutions of chlorotone in CCl_4.

deformation vibration of the hydroxyl group at 1100 cm^{-1}, and no $\nu(\mathrm{C}=\mathrm{C})$ band.

Experimental Part

The IR spectra were obtained on a Hilger H-800 infrared spectrophotometer with a NaCl prism and on an IKS-14 spectrophotometer with a LiF prism. **Reaction of tri-(α-cyanoisopropyl) phosphite with chloral.** On mixing equimolecular amounts of the components, warming by 2° occurred. On the following day the main mass had crystallized. After recrystallization from benzene the crystals had m.p. 150–151°.

Found, %: P 8.88, 8.81; Cl 29.19, 29.24
$C_{10}H_{14}O_4N_2PCl_3$. Calculated, %: P 8.52; Cl 29.25

Di-α-cyanoisopropyl ester of α-hydroxy-β,β,β-trichloroethylphosphonic acid (III).

In addition to the crystals, a liquid fraction was isolated which, on distillation, for the most part polymerized. A few drops of methacrylic acid nitrile distilled over: b.p. 74–82°; d_0^{18} 0.8560.

Found, %: C 71.67, 71.63; H 7.41
C_5H_5N. Calculated, %: C 71.71; H 7.52

(IR spectrum: $\nu(\mathrm{C}=\mathrm{C})$ 1625, $\nu(\mathrm{C}\equiv\mathrm{N})$ 2220 cm^{-1}.)

Preparation of tri-tert-(β,β,β-trichlorobutyl) phosphite. In the reaction of phosphorus trichloride (0.1 mole) with chloral hydrate (0.3 mole) in dry pyridine (0.33 mole) and dry benzene under the conditions of Dewey (4), we isolated di-tert-(β,β,β-trichlorobutyl) phosphorous acid, m.p. 44–45° (6).

Found, %:	P 8.07, 8.00;	Cl 52.99, 53.00
$C_8H_{13}O_3PCl_6$. Calculated, %:	P 7.73;	Cl 53.06

In the reaction of equimolecular amounts of this acid and chloral, the di-tert-β,β,β-trichlorobutyl ester of α-hydroxy-β,β,β-trichloroethylphosphinic acid was obtained (m.p. 181–182° from petroleum ether, b.p. 70–100°). The ester gives no depression of the melting point with the product obtained by the reaction of chloral with di-tert-(β,β,β-trichlorobutyl)phosphorous acid.

Fig. 4. IR absorption spectrum of the di-β,β,β-trichloroethyl ester of α-hydroxy-β,β,β-trichloroethylphosphinic acid (VII). *a* —absorption bands of Vaseline oil.

Reaction of mixed di-tert-(β,β,β-trichlorobutyl) ethyl phosphite (8) **with chloral.** When chloral was added to mixed di-tert-(β,β,β-trichlorobutyl) ethyl phosphite (equimolecular amounts), heating to the boiling point of chloral was observed. The mixture was cooled with cold water. On the following day the entire mass crystallized. After recrystallization from petroleum ether (b.p. 70-100°), two types of crystals were obtained:

1) M.p. 79-80°.

Found, %:	*P* 6.52, 6.67;	*Cl* 55.13, 55.29
$C_{10}H_{13}O_4PCl_8$. Calculated, %:	*P* 6.05;	*Cl* 55.42

Di-tert-(β,β,β-trichlorobutyl)-(β,β-dichlorovinyl) phosphate (VI).

2) M.p. 180-180.5°.

Found, %:	*P* 6.31, 6.33;	*Cl* 57.91, 57.88
$C_{10}H_{14}O_4PCl_9$. Calculated, %:	*P* 5.65;	*Cl* 58.20

Di-tert-β,β,β-trichlorobutyl ester of α-hydroxy-β,β,β-trichloroethylphosphinic acid (IV). It gives no depression of the melting point with the product obtained by the reaction of chloral with the acid from di-tert-(β,β,β-trichlorobutyl) chlorophosphite.

Reaction of tri-(trichloroethyl) phosphite (7) **with chloral.** On mixing equimolecular amounts of the components, no heating occurred. On the following day crystals formed, m.p. 157-158° (from petroleum ether, b.p. 70-100°)—the di-β,β,β-trichloroethyl ester of α-hydroxy-β,β,β-trichloroethylphosphinic acid (VII).

Found, %:	*P* 6.95, 6.92;	*Cl* 64.44, 64.40
$C_6H_6O_4PCl_9$. Calculated, %:	*P* 6.30;	*Cl* 64.83

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CITED LITERATURE

1. V. S. Abramov, DAN, **95**, 991 (1954).
2. V. A. Ginsburg, A. Ya. Yakubovich, ZhOKh, **30**, 3979 (1960).
3. W. Perkow, E. Krockow, K. Knoevenagel, Ber., **88**, 662 (1955); J. F. Allen, O. H. Johnson, J. Am. Chem. Soc., **77**, 2871 (1955); F. W. Lichtenthaler, Chem. Rev., **61**, 607 (1961).

4. W. Davey, Ind. and Eng. Chem., **42**, 1841 (1950).
5. P. I. Sanin, E. S. Shepeleva, B. V. Kleimenov, *Chemistry and Technology of Fuels and Oils*, No. 8, 24 (1960).
6. V. S. Abramov, V. K. Khairullin, ZhOKh, **26**, 844 (1956).
7. W. Gerrard, W. I. Green, R. I. Phillips, J. Chem. Soc., 1954, 1148.
8. V. S. Abramov, V. K. Khairullin, ZhOKh, **27**, 442 (1957).

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