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THERMAL DECOMPOSITION OF PHOSPHORYLATED HEMIMERCAPTALS

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The reaction of diphenylchlorophosphine with the hemimercaptal of chloral in the presence of triethylamine by analogy with the work of Nikonorov [1] gives α -ethylthio- β , β , β -trichloro-ethyl diphenylphosphonite (I):

$\begin{array}{c} \text{SEt} & \text{SEt} \\ | \\ \text{Ph}_2\text{PCl} + \text{HOCHCCl}_3 \xrightarrow[-\text{Et}_3\text{N} \cdot \text{HCl}]{} \\ \end{array} \xrightarrow[\text{Ph}_2\text{POCHCCl}_3]{} \\ \begin{array}{c} \text{(I)} \end{array}$

The structure of (I) was indicated by ¹H NMR, ³¹P NMR, and IR spectroscopy. The PMR spectrum of (I) in CCl₄ has signals for the thioethyl group at 1.10 and 2.62 ppm, ³J_{HH} = 7.5 Hz, the methine proton at δ 5.27 ppm. ³J_{HP} = 7.0 Hz, and phenyl protons at 7.08-7.62 pp; δ ³¹P = 123 ppm. The IR spectrum has bands at 495, 531 (CS), 1055 (POC), 3060 and 3072 cm⁻¹ (CH_{arom}).

Phosphinite (I) is unstable, and upon heating or prolonged maintenance at 20°C it decomposes to form S-ethyl diphenylthiophosphinite (II) and chloral, which could not be isolated since this aldehyde reacts with (I) to give the Perkov reaction products (III) and (IV):

 $(I) \xrightarrow{\Delta} Ph_2PSEt + [Cl_3CCHO] \xrightarrow{Ph_2POCHCCl_3} Ph_2PSEt + Ph_2POCH=CCl_2 + ClCHCCl_3 \\ (II) \qquad (II) \qquad (III) \qquad (IV)$

The structure of this product was indicated by IR, ¹H NMR, and ³¹P NMR spectroscopy as well as by comparison of their physical indices with those reported in the literature [2-7]. In addition, diphenylchlorophosphine is formed as a side product during distillation.

Phosphorylated hemimercaptal (V) is also formed in the reaction of diphenylchlorophosphine with the hemimercaptal of dimethyl acetyl phosphonate. Phosphonite (V) also undergoes thermal decomposition to diphenylthiophosphonite (IIb) and dimethyl acetyl phosphonate (VI). In this case, acetyl phosphonate (VI) may be isolated as a pure compound since (VI) is apparently less reactive toward phosphonite (V) than chloral.



It is interesting that the decomposition of (I) is accelerated upon the addition of catalytic amounts of acids ($H_2SO_4 > CH_3CO_2H > Et_3N \cdot HC1$). On the other hand, in the presence of a base (Et₃N), (I) is not altered upon heating at 90°C for 3 h. We may assume that the acid cat-

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alysis of this decomposition may be carried out by substitution of the alkoxyl group by the acid anion [8] with subsequent dissociation of the chloral hemimercaptal formed to chloral and a mercaptan, which reacts with Ph_2PX to give a thiophosphonite, thereby regenerating the acid:

$SEt \qquad SEt \\ | \\ Ph_2POCHCCl_3 + HX \rightleftharpoons Ph_2PX + HOCHCCl_3 \\ SEt \\ HOCHCCl_3 \rightleftharpoons EtSH + Cl_3CCHO$

$Ph_2PX + EtSH \rightarrow Ph_2PSEt + HX$ etc. .

Phosphorylated hemimercaptals (I) and (V) may formally be considered as the product of insertion of a carbonyl group at the P-SR bond. The facility and direction of the decomposition of (I) and (V) indicate that the pathway which reverses the insertion reaction is most favored for activated carbonyl compounds such as chloral and acetyl phosphonate.

EXPERIMENTAL

The ³¹P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz with 85% H₃PO₄ as the standard. The PMR spectra were taken on a Varian T-60 spectrometer at 60 MHz for 25-30% solutions relative to TMS as the internal standard. The IR spectra were taken on a UR-20 spectrometer.

 $\frac{\alpha-\text{Ethyl}-\beta,\beta,\beta-\text{trichloroethyl Diphenylphosphonite (I) and Its Thermal Decomposition. A sample of 15.0 g (68 mmoles) diphenylchlorophosphine was added dropwise over 20 min with stirring and cooling to -30°C to a mixture of 14.3 g (68 mmoles) <math display="inline">\beta,\beta,\beta-\text{trichloro}-\alpha-\text{hydroxyethyl}$ sulfide and 6.9 g (68 mmoles) triethylamine in 100 ml ether. Filtration gave 9.0 g (95.7%) triethylamine hydrochloride with mp 254°C [9]. The solvent was removed from the filtrate in vacuum. Phosphonite (I) was obtained in the residue; the spectral data are given in the text. Repeated distillation of the residue gave 3.5 g (33.3%) $\beta,\beta-\text{dichlorovinyl diphenyl phosphonate, bp 152-154°C (8•10⁻³ mm) [2] with <math display="inline">\delta P$ 31 ppm [3], 3.5 g (42.2%) S-ethyl diphenylthiophonite with bp 142-143°C (7•10⁻³ mm) [4] and δP 25 ppm [5], 2.9 g (38.7%) diphenylchlorophosphine with bp 117-119°C (0.8 mm), n_D²⁰ 1.6357, and δP 83 ppm [6], and 3.2 g (41.6%) α,β , $\beta,\beta-\text{tetrachloroethyl ethyl sulfide with bp 100°C (10 mm), n_D²⁰ 1.5340 [7].$

<u>a-Propylthio-a-dimethylphosphonoethyl Diphenylphosphonite (V) and Its Thermal Decomposition.</u> A sample of 15.8 g (72 mmoles) diphenylchlorophosphine was added dropwise over 30 min with stirring and cooling to -30° C to a mixture of 16.3 g (72 mmoles) dimethyl a-hydroxy-a-propylthioethyl phosphonate and 7.3 g (72 mmoles) triethylamine in 200 ml ether. Filtration gave 9.6 g (98.0%) triethylamine hydrochloride, mp 254°C [9]. The solvent was removed from the filtrate in vacuum. Phosphonite (V) was obtained in the residue, δ P 114 and 8 ppm. Distillation of the residue gave 11.1 g (59.7%) S-propyl diphenylthiophosphonite with bp 126-128°C (8•10⁻³ mm) [4] and δ P 26 ppm and 5.8 g (53.2%) acetyl dimethyl phosphonate with bp 90-91°C (10 mm), n_D²⁰ 1.402 [10]. δ P = -1 ppm.

CONCLUSIONS.

The reaction of diphenylchlorophosphine with β , β , β -trichloro- α -hydroxyethyl ethyl sulfide in the presence of triethylamine leads to the formation of α -ethylthio- β , β , β -trichloroethyl diphenylphosphonite. The reaction of diphenylchlorophosphine with dimethyl α -hydroxy- α -propylthiophosphonate in the presence of triethylamine gives α -propylthio- α -dimethylphosphonoethyl diphenylphosphonite. The phosphorylated hemimercaptals obtained are thermally unstable and decompose to S-alkyl diphenylthiophosphonites and the corresponding carbonyl compounds.

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EFFECT OF THE MEDIUM ON THE RATE OF THE DEGENERATE

REARRANGEMENT OF 1,2,3,4,5-PENTAMETHYL-1,3-CYCLOPENTADIENE

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In analyzing the common features and discrepancies in the structural-kinetic relationships of rearrangements proceeding by 1,2 shift of the migrant in "long-lived" carbocationic and neutral compounds, the question arises as to the ability to compare data obtained in different media. The rate of the rearrangements of long-lived carbocations with H, Me, and Ph as the migrants is usually only slightly sensitive to variation of the medium [1]. On the other hand, the data on the solvent effect on the rate of rearrangement of neutral compounds are not unequivocal. Thus, a number of workers have shown that the rate of the 1,2 shift of H [2, 3], CH=CHR [4], CHO [5], and SiMe₃ [6] in cyclopentadiene and indene systems is virtually independent of the solvent. On the other hand, Miller [3] and Schulman [7] found a marked effect of the medium on the rate of the 1,2 shift of the phenyl group and hydrogen atom in such systems.

In the present work, we studied the effect of the medium on the rate of the degenerate rearrangement of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (I) which proceeds, as shown in our previous work [8], by the 1,2 shift of a hydrogen atom:



Diene (I) was selected for study since such methylated cyclopentadienes are promising models for elucidating the common features and discrepancies in the structural-kinetic relationships of the rearrangements of neutral structures and carbocations [8, 9].

The rearrangement kinetics was studied by the labeled atom method relative to the change in the intensities of the signals for the 5-CD₃ (I₁) and 1,2,3,4-CD₃ groups (I₂) over time in the ²H NMR spectrum for a mixture of deuterated analogs of (I) having CD₃ groups at C¹, C², and C⁵ (the ratio of the isotopomers at the onset was 30:62:8). The rate constants for the 1,2 shift of the hydrogen atom were calculated using the following equation without taking account of isotope effects which are apparently insignificant [8]:

 $C_{1}e^{r_{1}kt} + C_{2}e^{r_{2}kt} = \frac{4-N}{N+1}$ (1)

where N = I_1/I_2 , $C_1 = -0.658$, $C_2 = 0.0578$, $r_1 = (-5 + \sqrt{5})/2$, $r_2 = (-5 - \sqrt{5})/2$, k is the 1,2 shift rate constant, and t is the time. Table 1 shows that the rate of the 1,2 shift is only slightly dependent on the nature of the solvent over a broad range of parameters characterizing the solvent properties dielectric constant (ε_{20} ° from 1.9 to 29.6), polarity (Y from

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