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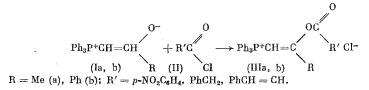
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 β -Oxoalkylidenephosphoranes (I) are an example of ambident anions, in which an inner phosphonium center is present instead of an outer metal cation. In view of this it could be expected that the alkylation and acylation of (I) will initially lead to the predominant formation of the O-substituted products. Actually, as we had shown previously, the alkylation of (I) with alkyl iodides, and also its acylation using (CF₃CO)₂O, proceeds at the O atom [1, 2]. Acetyl chloride and benzoyl chloride react in a similar manner [3-6] [Eq. (1)]. However, in [5, 6] it is stated without structure proof of the products that the acid chlorides of p-nitrobenzoic, phenylacetic, cinnamic, and pyromucic acids acylate (I) only at the C atom [Eq. (2)].

$$Ph_{3}P^{+}CH = C \xrightarrow{O^{-}} (1)$$

$$Ph_{3}P^{+}CH = C \xrightarrow{R^{+}} (C_{1}) \xrightarrow{R^$$

This difference in this direction of the transformation causes astonishment, and consequently we repeated the reactions reported in [5, 6]. It proved that the reaction of (Ia) with the acid chloride of phenylacetic acid in CH_2Cl_2 takes 10 min. The IR spectrum of the reaction mixture has the following intense bands (ν , cm⁻¹): 1450 (Ph-P), 1647 (C = C), 1780 (C = O). The NMR spectrum has only a singlet at 12.4 ppm, which is characteristic for O-substituted salts. These data show that only the O-acylated product (IIIa) is formed, which fails to rearrange for at least a day in C_6H_6 .



When the reaction is run under the conditions given in [6] (in C_6H_6 , for 4 h, ratio of reactants = 1:0.6) the precipitate is not conjugated acid of the starting ylide but instead the acyloxyvinlyphosphonium salt (IIIa). The unreacted starting ylide, which was taken in excess, was isolated from the filtrate instead of the diacylated ylide.

The following reactions serve as chemical confirmation for the structure of the O-acylation product (IIIa). The hydrolysis of (IIIa) gives salt (IVa), which is partially enolized in solution. Infrared spectrum of (IVa) (CH₂Cl₂, ν , cm⁻¹): 1620 (enol C = C), 1725 (ketone C = O). The methanolysis of salt (IIIa) for 3 h at 20°C gives a mixture of three compounds: unreacted (IIIa), salt (IVa), and methyl phenylacetate (Va). Infrared spectrum of reaction mixture (CH₂Cl₂, ν , cm⁻¹): 1640 (C = C), 1780 (C = O) (IIIa); 1620 (C = C), 1725 (C = O) (IVa); 1740 (C = O) (Va).

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TABLE 1. ${}^{31}P - {}^{1}H$ NMR Spectra of Acylated Salts (III) in CH₂Cl₂

R	R'	ð, ppm	R	R'	ð, ppm
Me	PhCH=CH	12,3	Ph	$\begin{vmatrix} p-\mathrm{NO}_2\mathrm{C}_6\mathrm{H}_4\\ \mathrm{PhCH}_2\\ \mathrm{PhCH}_2\\ \mathrm{PhCH}_2 \end{vmatrix}$	14,4
Ph	PhCH=CH	14,4	Me		12,4
Me	p-NO ₂ C ₆ H ₄	12,3	Ph		14,3

 $(IIIa, b) \xrightarrow{H_2O} Ph_3P+CH_2CORCI + PhCH_2COOH (IVa, b) + (IVa, b) + PhCH_2COOM e$ $(IIIa, b) \xrightarrow{MeOH} 3 h (IIIa, b) + (IVa, b) + PhCH_2COOM e$

(Ia, b) + PhCH₂CONH₂ (VIa, b)

Salt (IIIa) when treated with aqueous ammonia in methanol is converted to ylide (Ia) and phenylacetamide. Infrared spectrum of reaction mixture (CH₂Cl₂, ν , cm⁻¹): 1540 (C=O) (Ia); 1690 (C=O), 3415, 3525 (NH₂) (VIa).

The acylation of (Ib) with phenylacetyl chloride proceeds in a similar manner with the difference that in all cases the reaction mixture contains, besides the O-acylated salt, also the conjugated acid of the starting ylide, which is probably formed by the hydrolysis of (IIIb). Infrared spectrum of reaction mixture (CH₂Cl₂, ν , cm⁻¹): 1450 (Ph-P), 1615 (C = C), 1780 (C = O) (IIIb); 1680 (C = O) (IVb). The ³¹P-{¹H} NMR spectrum has singlets at 14.3 ppm (IIIb) and 21.5 ppm (IVb). The reactions of (IIIb) with ammonia and methanol proceed the same as in the case of (IIIa).

According to the ³¹P NMR spectra, the reaction of ylides (Ia, b) with p-nitrobenzoyl chloride and cinnamoyl chloride in CH_2Cl_2 also gives the O-acylated salts (Table 1).

According to the δ values, the O-acylated salts are the Z isomers [1].

As a result, ambident ylides of the (I) type react with acid chlorides only at the O atom to give acyloxyvinylphosphonium salts (III). Their further rearrangement to the C-salts is not observed, probably due to the low nucleophilicity of chloride ion. In view of this the reaction is practically irreversible. We discussed the mechanism of the acylation in more detail in [2].

EXPERIMENTAL

All of the operations were run in absolute solvents. The IR spectra were recorded on a UR-20 spectrophotometer. The spectra of the solutions of the compounds and reaction mixtures were taken in fluorite cells with a layer thickness of 0.1 mm, and the ${}^{31}P - {}^{1}H$ NMR spectra were taken on a Bruker HX-90 instrument (36.43 MHz) from H_3PO_4 as the external standard.

<u>Reaction of (Ia) with Phenylacetyl Chloride.</u> a) To a solution of 0.2 g (0.00063 mole) of ylide (Ia) in 3 ml of C_6H_6 was added 0.083 ml (0.00063 mole) of the acid chloride. After 15 min the crystalline precipitate was filtered to give 0.28 g (95% yield) of (IIIa). Salt (IIIa) was also isolated when CH_2Cl_2 was used as the solvent.

b) The reaction was run under the conditions given in [6]. To 0.32 g (1 mmole) of ylide (Ia) in 5 ml of C_6H_6 was added 0.08 ml (0.6 mmole) of phenylacetyl chloride in 5 ml of C_6H_6 . After 4 h the precipitate was filtered and washed with abs. ether to give 0.28 g of (IIIa) (83.3% yield when based on the acid chloride). The IR spectrum has all of the characteristic bands for (IIIa). The C_6H_6 was distilled from the filtrate and the residue was washed with ether to give 0.11 g (0.35 mmole) of substance, mp 205-206° [7]. Infrared spectrum (CH_2Cl_2 , ν , cm⁻¹): 1540 (P = CC = O). The TLC data confirm the fact that this substance is unreacted ylide (Ia).

Reaction of (Ib) with Phenylacetyl Chloride. To a suspension of 0.38 g (1 mmole) of ylide (Ib) in 5 ml of $C_{6}H_{6}$ was quickly added 0.12 ml (0.9 mmole) of the acid chloride in 5 ml of $C_{6}H_{6}$. After 2 h the copious precipitate was filtered and washed with ether to give 0.47 g (98% yield) of product. Based on the ³¹P NMR data the precipitate contains $\approx 25\%$ of the conjugated acid of the starting ylide (IVb).

CONCLUSIONS

Contrary to the previously described results, the reaction of the β -oxoalkylidenetriphenylpho sphoranes with the acid chlorides of the p-nitrobenzoic, cinnamic, and phenylacetic acids gives only the acyloxyvinylphosphonium salts. As a result, all of the currently known reactions of phosphorus β -ketoylides with acid chlorides lead to the O-acylation products.

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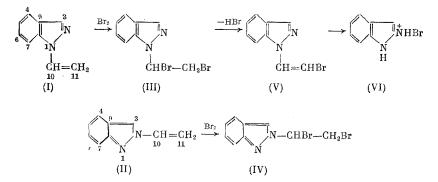
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BROMINATION OF VINYLINDAZOLES

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The direct chlorination or bromination of indazole leads mainly to the 3,5-dihalo derivatives [1]. The reaction of bromine with the vinyl derivatives of indazole was studied in the present paper. It is known that vinylazoles react differently with halogens depending on the basicity, the number and arrangement of the nitrogen atoms in the ring, and also on the polarization of the vinyl group. Thus, the more basic vinylbenzimidazole (K_{as} 75) reacts with halogens to give complexes, while the addition of bromine or chlorine to the vinyl group is characteristic for vinylbenztriazole (K_{as} 15) [2, 3].

It was shown by us that 1-vinylindazole (I) and 2-vinylindazole (II) are brominated in CCl_4 even at $-20^{\circ}C$. The PMR spectra of the reaction mixture testify that, in contrast to vinylbenzimidazole, the initial and main direction of the reaction for indazoles (I) and (II) is the addition of bromine to the vinyl group to give dibromoethylindazoles (III) and (IV):



The structure of 1-(1',2'-dibromoethyl)indazole (III) and 2-(1',2'-dibromoethyl)indazole (IV) is proved by the downfield presence of quartets that belong to the CHBr fragments, and also of the triplets and quartets of the

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