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LETTERS TO THE EDITOR

Acylation and Sulfonation of the Enol Form of Phosphorylated Aldehydes

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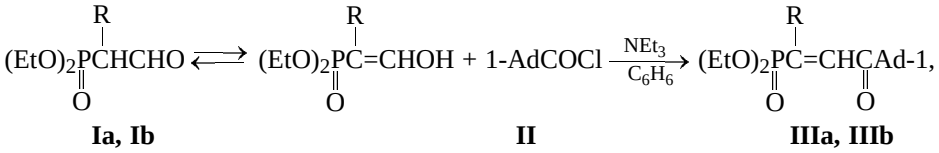
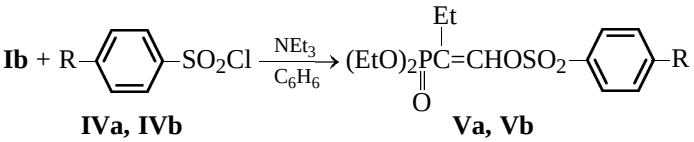
Acylation with acetyl chloride of phosphorylated aldehydes $(RO)_2P(O)CH(R')CHO$ characterized by a keto–enol equilibrium was reported in [1]. It was interesting to examine the possibility of acylating the enol form of α-phosphorylated aldehydes **Ia** and **Ib** with 1-adamantylcarbonyl chloride **II**. The reaction was performed in the presence of triethylamine and yielded the corresponding diethyl [2-(1-adamantylcarbonyloxy)vinyl]phosphonates **IIIa** and **IIIb**.



Ia, Ib **II** **IIIa, IIIb**

I, III, R = Me (**a**), Et (**b**).

2-(Diethoxyphosphoryl)butanal **Ib** is sulfonated with arenesulfonyl chlorides **IVa** and **IVb** to give the corresponding diethyl 2-arenesulfonyloxyvinylphosphonates **Va** and **Vb**.



IVa, IVb **Va, Vb**

IV, V, R = H (**a**), Me (**b**).

The structure of the products of these reactions suggests the probable spectrum of their biological effect. This assumption is based on biological effects of a series of vinyl sulfonates [2] and adamantane-containing compounds [3].

Diethyl [1-methyl-2-(1-adamantylcarbonyloxy)-vinyl]phosphonate IIIa. A 3.9-g portion of chloride **II** was slowly added with stirring at 20°C to a solution of 3.8 g of **Ia** and 2 g of triethylamine in 50 ml of dry benzene. The mixture was stirred for 1 h at room temperature and 1 h at 60°C. After 12 h, the precipitate of triethylammonium chloride was filtered off, and the solvent was removed from the filtrate to leave an oily residue which crystallized within several days. Recrystallization from dry pentane gave 3.7 g (53%) of **IIIa**, mp 65–66°C. The IR spectrum of the product is similar to the spectrum of $(CH_3O)P(O)C(CH_3)=CHOC(O)CH_3$ (as far as the main structural groups are concerned [1]) and contains additional bands in

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the region of 2835 cm^{-1} (ν_{CH} in the adamantane core). Found, %: C 60.70; P 8.60. $C_{18}H_{29}O_5P$. Calculated, %: C 60.67; P 8.70. Esters **IIIb**, **Va**, and **Vb** were prepared similarly.

Diethyl [1-ethyl-2-(1-adamantylcarbonyloxy)-vinyl]phosphonate IIIb was prepared from 2.7 g of **II**, 1.4 g of triethylamine, and 2.8 g of **Ib**; yield after vacuum distillation 1.9 g (38%), bp 150–153°C (0.2 mm), n_D^{20} 1.4990. Found P, %: 8.30. $C_{19}H_{31}O_5P$. Calculated P, %: 8.38.

Diethyl (1-ethyl-2-benzenesulfonyloxyvinyl)-phosphonate Va was prepared from 0.8 g of **Ib**, 0.4 g of triethylamine, and 0.7 g of **IVa** in 15 ml of dry benzene; yield 1 g (77%), bp 165–166°C (0.03 mm), d_4^{20} 1.1773, n_D^{20} 1.4910. IR spectrum, ν, cm^{-1}: 1050–1030 (C–O–C), 1200–1195 and 1390–1385 (S=O), 1250–1245 (P=O), 1670–1665 (C=C). Found, %: P 8.78; S 9.05. $C_{14}H_{21}O_6PS$. Calculated, %: P 8.90; S 9.19.

Diethyl [1-ethyl-2-(*p*-toluenesulfonyloxy)vinyl]-phosphonate Vb was prepared from 1.1 g of **Ib**, 0.5 g of triethylamine, and 1 g of **IVb** in 20 ml of dry benzene; yield 1.1 g (59%), bp 137–139°C (0.07 mm), n_D^{20} 1.4853. Found, %: P 8.48; S 8.76. $C_{15}H_{23}O_6PS$. Calculated, %: P 8.56; S 8.84.

The IR spectra were recorded on an IKS-29 spectrophotometer (thin films).

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