REACTION OF BENZALACETONE WITH DIMETHYLPHOSPHOROUS ACID

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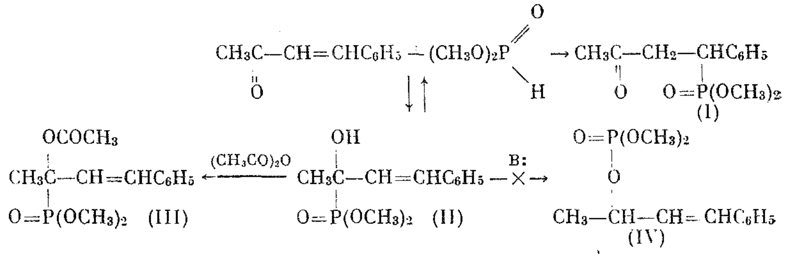
Previously [1] it was shown that dimethyl phosphite in the presence of MeONa reacts with benzalacetone to give the dimethyl ester of 1-phenyl-2-acetylethylphosphonic acid (I). However, it was recently discovered [2] that the reaction of dialkyl phosphites with benzalacetones, substituted in the aromatic ring, gives the adducts of the enol, and not the keto form.

We studied the reaction of benzalacetone with dimethyl phosphite in the presence of both MeONa and Et_2NH and found that, depending on the amount of MeONa, the reaction goes with the formation of either the β-ketophosphonate (I) or the α-hydroxyphosphonate (II). A small amount of the alcoholate favors the formation of the α-hydroxyphosphonate (II). The β-ketophosphonate (I) is obtained under the conditions given in [2], or even with a somewhat smaller amount of the alcoholate. The reaction proceeds at room temperature. Product (I) could be isolated in the crystalline form.

In the presence of a milder catalyst, like Et_2NH, the α-hydroxyphosphonate (II) is also formed at ~20°C in ~100% yield, which is easily acetylated with Ac_2O. Thermography disclosed that the α-hydroxyphosphonate (II) is thermally unstable, and after melting it decomposes into the starting components. The decomposition begins at 130°C and is complete at 160°C. Both sodium methylate and triethylamine lower the decomposition temperature, but fail to cause the phosphonate—phosphate rearrangement to (IV). However, in the presence of MeONa the α-hydroxyphosphonate (II) is easily converted to the β-ketophosphonate (I).



EXPERIMENTAL

Dimethyl Ester of 4-Phenyl-2-hydroxy-3-butenyl-2-phosphonic Acid (II). a) To a solution of 0.73 g of benzalacetone and 0.55 g of dimethyl phosphite in absolute ether was added 3 drops of a saturated MeONa solution in MeOH. Here the temperature of the reaction mixture rose by 3°C. Crystals of the α-hydroxyphosphonate (II) deposited after 10 min. The product was filtered and washed with absolute ether; yield 57%. The yield of (II) is increased to 70% when the amount of dimethyl phosphite is doubled.

b) Compound (II) deposited from a solution of equimolar amounts of benzalacetone, dimethyl phosphite, and Et_2NH in absolute ether in 3 h after adding the catalyst; yield 100%, mp 132-133°C (from methyl ethyl ketone). Infrared spectrum (ν, cm^{-1}): 1025, 1056 (POC); 1230 (P=O); 3265 (OH). Found: C 56.31; H 7.09; P 12.36%. $C_{12}H_{17}O_4P$. Calculated: C 56.24; H 6.68; P 12.09%.

Dimethyl Ester of 4-Phenyl-2-acetoxy-3-butenyl-2-phosphonic Acid (III). A mixture of 0.6 g of the α-hydroxyphosphonate, 0.7 g of Ac_2O, and a drop of conc. H_2SO_4, after holding at ~20°C for 12 h, was

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dissolved in benzene, washed with water, and dried over $MgSO_4$. The thick oil that remained after removal of the benzene crystallized after standing in the refrigerator. The yield of (III) was 76%, mp 46-47°C (from petroleum ether). Infrared spectrum (ν, cm^{-1}): 1025, 1052 (POC), 1185 ($POCH_3$) 1230, 1250 (acetate CO) and (P=O), 1735 (C=O). Found: C 56.34; H 6.44; P 10.41%. $C_{14}H_{19}O_5P$. Calculated: C 56.37; H 6.42; P 10.30%.

Dimethyl Ester of 1-Phenyl-2-acetylethylphosphonic Acid (I). a) Using the method given in [2], to a solution of 4.7 g of benzalacetone and 3.5 g of dimethyl phosphite in 20 ml of absolute benzene was added 0.2 g of dry MeONa in a dry nitrogen stream. The reaction was accompanied by marked heating up. Based on the IR spectral data, (I) was formed. The composition of the reaction mixture did not change after refluxing for ~10 h. Distillation in a high vacuum gave a fraction with bp 124°C ($5.5 \cdot 10^{-4}$ mm); n_D^{20} 1.5133. The next day the product crystallized; yield 21.7%, mp of (I) 69-70°C (from petroleum ether). Infrared spectrum (ν, cm^{-1}): 1040, 1063 (POC); 1255 (P=O), 1710 (C=O). Found: C 56.44; H 6.82; P 12.05%. $C_{12}H_{17}O_4P$. Calculated: C 56.24; H 6.68; P 12.09%.

b) To 0.9 g of α-hydroxyphosphonate (II) in absolute ether was added 10 drops of a saturated MeONa solution in MeOH. The oil, obtained after removal of the ether, crystallized on cooling. The yield of crude (I) was 70%. Based on the IR spectra data, it is slightly contaminated with benzalacetone.

CONCLUSIONS

1. In the presence of an equimolar amount of diethylamine or a catalytic amount of sodium methylate, dimethylphosphorous acid adds to the carbonyl group of benzalacetone to give the dimethyl ester of 4-phenyl-2-hydroxy-3-butenyl-2-phosphonic acid.

2. An equimolar amount of sodium methylate favors the formation of the dimethyl ester of 1-phenyl-2-acetylethylphosphonic acid.

LITERATURE CITED

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2. R. S. Tewart and R. Shukla, Indian J. Chem., 10, 823 (1972).