ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 12, pp. 2007–2008. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.G. Kirakosyan, G.H. Minasyan, V.S. Hakobyan, M.H. Injikyan, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 12, pp. 2054–2055.

LETTERS TO THE EDITOR

Phosphorylation of Ethyl Acetoacetate and Acetylacetone in the Conditions of Todd–Atherton Reaction

V. G. Kirakosyan, G. H. Minasyan, V. S. Hakobyan, and M. H. Injikyan

Scientific and Technological Center of Organic and Pharmaceutical Chemistry, National Academy of Sciences of Armenia,
pr. Azatutyana 26, Yerevan, 0014 Armenia
e-mail: virab.kir@rambler.ru

Received April 16, 2012

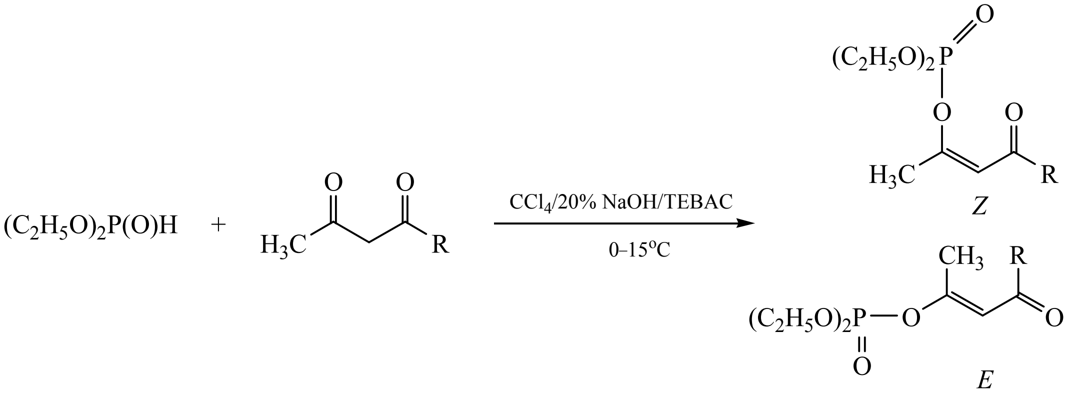
DOI: 10.1134/S1070363212120183

The keto-enol CH-acids are known to be phosphorylated at the oxygen atom [1, 2]. The phosphorylation of dialkyl bromomalonates with triethylphosphite results in enolophosphates [1]. The latter were obtained also via the phosphorylation of tetraalkylammonium salts of β-dicarbonyl compounds with diethyl chlorothiophosphate under the phase-transfer catalysis [2].

The reaction of diethyl phosphite with ethyl acetoacetate and acetylacetone in the presence of carbon tetrachloride, 20% aqueous alkali, and triethylbutylammonium chloride (TEBAC) at 0–15°C followed by stirring for 3 h without cooling gave ethyl 3-(diethoxyphosphoryloxy)but-2-enoate **I** and 4-(diethoxyphosphoryloxy)-3-penten-2-one **II** in 63 and 70% yield, respectively. According to the ^{1}H NMR data, compounds **I** and **II** formed as mixtures of *Z*,*E*-isomers in the ratio of 75:25 in the case of compound **I** and 85:15 in the case of compound **II**.

Under the Todd–Atherton reaction conditions, the keto-enol CH-acids were found to be also phosphorylated of the oxygen atom. It is in agreement with the reaction course of the corresponding ambident ions with the strong electrophiles. The newly synthesized phosphates can be the starting materials for the synthesis of a large range of the phosphoryl compounds.

(*Z*,*E*)-Ethyl 3-(diethoxyphosphoryloxy)but-2-enoate (I). To a mixture of 6.9 g (0.05 mol) of diethyl phosphite, 15.4 g (0.1 mol) of carbon tetrachloride, 6.5 g (0.05 mol) of ethyl acetoacetate, and 1.06 g (0.005 mol) of triethylbutylammonium chloride was added dropwise 16 ml of 20% aqueous sodium hydroxide solution at vigorous stirring and cooling to 0°C, so that the reaction temperature did not exceed 15°C. After stirring for 3 h at room temperature the organic layer was separated and dried with Na_2SO_4. The resulting phosphate was distilled in a vacuum. Yield 8.379 g (63%), bp 140–142°C (3 mm Hg). IR spectrum, ν, cm^{-1}: 1250, 1230, 1190, 1100 (P=O, P–O–C, C–O–C), 1700 ($COOC_2H_5$), 1640, 810 (C=C).



I, II

I, R = OC_2H_5; **II**, R = CH_3.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.27 t (3H, $COOCH_2C\underline{H}_3$, *J* 7.1, *Z*) and 1.28 t (3H, $COO·CH_2C\underline{H}_3$, *J* 7.1, *E*), 1.38 t (6H, $OCH_2C\underline{H}_3$, *J* 7.1), 2.17 d (3H, CH_3C=, $^3J_{HH}$ 1.6, $^4J_{HP}$ 0.9, *Z*) and 2.40 d (3H, CH_3C=, *J* 0.9, *E*), 4.08–4.31 m (8H, $OC\underline{H}_2CH_3$), 5.29 m (1H, =CH, *E*) and 5.79 m (1H, =CH, *Z*). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 14.4 (CH_3), 16.2 d (CH_3, *J* 6.7), 18.6 d (CH_3, *J* 4.7), 21.8 s (CH_3), 59.8 and 60.1 (OCH_2), 64.8 d (OCH_2, *J* 6.0) and 64.9 d (OCH_2, *J* 6.3), 105.4 d (CH, *J* 8.3) and 106.3 d (CH, *J* 5.3), 158.1 d (C=, *J* 6.6), 163.3 d (=C, *J* 8.8), 163.5 (CO), 166.3 (CO). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –2.71, –3.37. Found, %: C 45.05; H 7.78; P 11.58. $C_{10}H_{19}O_6P$. Calculated, %: C 45.11; H 7.89; P 11.65.

The reaction with acetylacetone was performed similarly.

(*Z,E*)-4-(Diethoxyphosphoryloxy)-3-penten-2-one (II). Yield 8.26 (70%)**,** bp 140–141°C (5 mm Hg). IR spectrum, ν, cm^{-1}: 1250, 1190, 1150 (P=O, P–O–C), 1680 ($COCH_3$), 1640, 810 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.35 t (6H, $OCH_2C\underline{H}_3$, $^3J_{HH}$ 7.1, $^4J_{HP}$ 1.2), 2.16 d. d (3H, CH_3C=, $^3J_{HH}$ 1.7, $^4J_{HP}$ 1.0), 2.26 s (3H, CH_3CO, *J* 5.4, *Z*) and 2.31 d (3H, CH_3CO, *J* 0.8, *E*), 4.21 d. q (4H, CH_3CH_2O, $^3J_{HP}$ 8.2, $^3J_{HH}$ 7.1), 5.44 m (1H, =CH, *Z*) and 6.19 m (1H, =CH, *E*). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 16.3 d (CH_3, *J* 6.8), 19.1 d (CH_3, *J* 5.6), 21.7 (CH_3), 31.3 and 32.3 (CH_3), 65.0 d (OCH_2, *J* 6.2), 112.6 d (CH), 115.2 m (CH), 158.4 d (C=, *J* 6.7), 195.9 (CO), 197.1 (CO). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –2.89, –2.91. Found, %: C 45.64; H 7.15; P 13.06. $C_9H_{17}O_5P$. Calculated, %: C 45.76; H 7.20; P 13.13.

The IR spectra were recorded on an UR-20 instrument. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were registered on a Varian Mercury-300 spectrometer operating at 300.08, 121.75, and 75.46 MHz for the ^{1}H, ^{31}P, and ^{13}C nuclei, respectively, at 303 K relative to internal TMS (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P).

REFERENCES

1. Thompson, J.E., *J. Org. Chem.*, 1965, vol. 30, p. 4276.
2. Kolind-Andersen, H. and Lawesson, S.O., *Acta Chem. Scand. (B)*, 1975, vol. 29, p. 430.