ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 3, pp. 440–441. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © V.E. Shishkin, E.V. Mednikov, Yu.V. Popov, O.V. Anishchenko, M.I. Bondareva, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 3, pp. 417–418.

Condensation of N-Substituted Alkyl(dibutoxyphosphoryl)acetimidates with Tribromoacetaldehyde

V. E. Shishkin, E. V. Mednikov, Yu. V. Popov, O. V. Anishchenko, and M. I. Bondareva

Volgograd State Technical University, pr. Lenina 28, Volgograd, 400131 Russia
e-mail: tons@vstu.ru

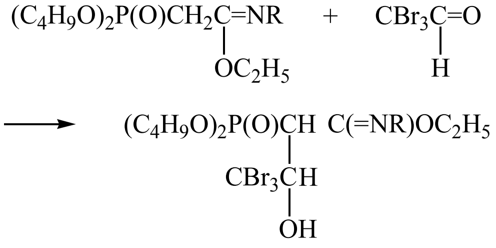
Received August 4, 2009

Abstract—N-Substituted alkyl(dibuthoxyphosphoryl)acetimidates enter into the reaction with tribromoacetaldehyde under mild conditions without catalyst to form products of addition to the carbonyl group, N-substituted ethyl-(4,4,4-tribromo-3-hydroxy-2-dibutoxyphosphoryl)butanimidates.

DOI: 10.1134/S1070363210030114

Recently we established that N-substituted alkyl (dialkoxyphosphoryl)acetimidates showed CH-acidic properties due to the lability of methylene hydrogen atoms located between electron-withdrawing dialkoxyphosphoryl and imine groups [1]. Utilizing these properties, we developed new methods of preparation of phos-phorylated imidates containing various functionalities [2, 3]. Extending this direction and continuing the study of CH-acidic properties of phosphorylated imidates, we examined condensation of N-substituted alkyl(dialkoxyphosphoryl)acetimidates with tribromoacetaldehyde. The products of condensation of trihaloaldehydes with different phosphorus-nitrogen containing compounds are known to exhibit high pesticide and fungicidal activities [4].

N-Substituted ethyl(dibutoxyphosphoryl)acetimidates react with tribromoacetaldehyde to yield the products of addition to the carbonyl group, N-substituted ethyl-(4,4,4-tribromo-3-hydroxy-2-dibutoxyphosphoryl)-butanimidates.



$$(C_4H_9O)_2P(O)CH_2\underset{OC_2H_5}{\underset{|}{C}}{=}NR \quad + \quad CBr_3\underset{H}{\underset{|}{C}}{=}O$$

$$\longrightarrow \quad (C_4H_9O)_2P(O)\underset{\underset{\underset{OH}{|}}{CBr_3CH}}{\underset{|}{CH}}\ C(=NR)OC_2H_5$$

R = $CH_3C(O)$; $C_6H_5C(O)$; $(CH_3)_3Si$; $(CH_3O)_2P(O)$.

As the investigation subjects we used imidates containing butoxy groups on the phosphorus atom, as the least toxic, and also acetyl, benzoyl, trimethylsilyl, and dimethoxyphosphoryl substituents at the nitrogen atom. These imidates are known to show a versatile biological activity. It is known that condensation of CH-acidic compounds with carbonyl compounds (Knoevenagel reaction) occurring in the presence of catalysts with water elimination, is a special case of aldol-crotonic condensation, where the used methylene components have especially high acidity owing to the two reactive hydrogen atoms. In the case of N-substituted phosphorylated acetimidates the condensation of the latter with tribromoacetaldehyde proceeds under mild conditions free of catalysts and without water elimination. This is due to weaker CH-acidic properties of phosphorylated imidates in comparison with the malonate.

The reaction with tribromoacetaldehyde proceeds in the absence of catalyst due to the high electrophilicity of the carbonyl group activated with the strong inductive electron-withdrawing effect of the tribromomethyl group.

Reaction of N-substituted phosphorylated imidates with tribromoacetaldehyde was carried out at the molar ratio 1:1. This reaction occurs with heat evolution. Imidates in these reactions differ little from each other by reactivity. All the obtained N-substituted ethyl-(4,4,4-tribromo-3-hydroxy-2-dibutoxyphosphoryl)-butanimidates are viscous yellow liquids, well soluble in alcohol, dioxane, poorly soluble in the saturated hydrocarbons, and insoluble in water. Structure and composition of the compounds obtained were confirmed by the elemental analysis data, molecular refraction, and IR spectroscopy.

Besides the absorption bands characteristic of the initial N-substituted dialkoxyphosphorylacetimidates at 1660–1675 (C=N), 1220-1260 (P=O), 1740 (C=O), 1090–1116 (C–O–C), and 980–1060 cm^{-1} (P–O–C), the IR spectra of the synthesized compounds contain also a wide band at 3190–3280 cm^{-1} belonging to the stretching vibrations of OH-group and a strong band at 740–742 cm^{-1} originating from C–Br bond vibrations.

Hence, the approach to N-substituted ethyl-(4,4,4-tribromo-3-hydroxy-2-dibutoxyphosphoryl)butanimidates was elaborated. This method is characterized by the simplicity of the experimental conditions and high yields of the target products (86–93%).

EXPERIMENTAL

The IR spectra were recorded on a SPECORD M 82 instrument. Spectra of liquid substances were registered from a thin layer.

Ethyl-*N*-dimethoxyphosphoryl-(4,4,4-tribromo-3-hydroxy-2-dibutoxyphosphoryl)-butanimidate. To a solution of 3 g (0.0077 mol) of ethyl-*N*-dimethoxyphosphoryl(dibutoxyphosphoryl)acetimidate in 5 ml of dioxane was added a solution of 2.2 g (0.0077 mol) of tribromoacetaldehyde in 1 ml of dioxane. At mixing the solution self-heated and turned bright yellow. The reaction mixture was allowed to stand for 2 h at 40°C, after that the solvent was removed. The crude product was distilled (P_{res} 1–2 GPa, T_{bath} 40°C). Yield 4.6 g (89%), n_D^{20} 1.4872, d_4^{20} 1.5899, MR_D 120.88, calc. 121.62. Found, %: N 2.23, P 8.89. $C_{16}H_{32}O_8P_2NBr_3$. Calculated, %: N 2.09, P 9.28.

Ethyl-*N*-trimethylsilyl-(4,4,4-tribromo-3-hydroxy-2-dibutoxyphosphoryl)butan-imidate was prepared similarly from 5 g (0.014 mol) of ethyl-*N*-trimethylsilyl(dibutoxyphosphoryl)acetimidate and 3.93 g (0.014 mol) of tribromoacetaldehyde. Yield 7.6 g (86%), n_D^{20} 1.4886, d_4^{20} 1.4162, MR_D 127.89, calc. 128.41. Found, %: N 2.23, P 4.71. $C_{17}H_{31}O_5PNBr_3Si$. Calculated, %: N 2.22, P 4.94.

Ethyl-*N*-benzoyl-(4,4,4-tribromo-3-hydroxy-2-dibutoxyphosphoryl)butanimidate was prepared similarly from 4 g (0.01 mol) of ethyl-*N*-benzoyl(dibutoxyphosphoryl)acetimidate and 2.8 g (0.01 mol) of tribromoacetaldehyde. Yield 6 g (91%), n_D^{20} 1.5354, d_4^{20} 1.3319, MR_D 155.07, calc. 155.55. Found, %: N 2.25, P 4.71. $C_{21}H_{31}O_6PNBr_3$. Calculated, %: N 2.11, P 4.67.

Ethyl-*N*-acetyl-(4,4,4-tribromo-3-hydroxy-2-dibutoxyphosphoryl)butanimidate was prepared similarly from 5 g (0.016 mol) of ethyl-*N*-acetyl(dibutoxyphosphoryl)acetimidate and 4.4 g (0.016 mol) of tribromoacetaldehyde. Yield 9 g (93%), n_D^{20} 1.4884, d_4^{20} 1.3186, MR_D 114.13, calc. 114.82. Found, %: N 2.38, P 5.62. $C_{16}H_{29}O_6PNBr_3$. Calculated, %: N 2.33, P 5.15.

REFERENCES

1. Shishkin, V.E., Mednikov, E.V., Anishchenko, O.V., and No, B.I., *Dokl. Ross. Akad. Nauk*, 2001, vol. 380, no. 5, p. 645.
2. Shishkin, V.E., Mednikov, E.V., Anishchenko, O.V., and No, B.I., RF Patent no. 220328, MPK 7C 07 F9/40, *Volgograd. Gos. Univ.*, 2003.
3. Shishkin, V.E., Mednikov, E.V., and Anishchenko, O.V., *Zh. Obshch. Khim.*, 2005, no. 3, p. 411.
4. Purdela, D. And Vylchanu, R., *Khimiya organicheskikh soedinenii fosfora* (Chemistry of Organophosphorus Compounds), Moscow: Khimiya, 1972.