ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 12, pp. 2523–2524. © Pleiades Publishing, Ltd., 2010.
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LETTERS TO THE EDITOR

Phosphorus-Containing Small Rings: XI.[1] Reaction of 3-Phenyl-2,2-dichlorocyclobutanone with Dialkyl Phosphites

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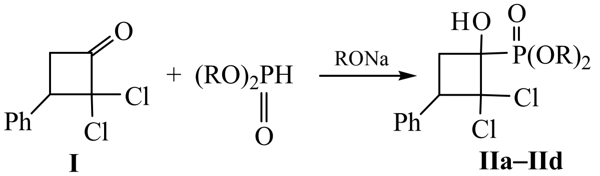
Received March 11, 2010

DOI: 10.1134/S1070363210120212

Cyclobutane derivatives containing carbonyl group have been studied in detail [2]. However the data on the reactions of ketones of the cyclobutane series with hydrophosphoryl compounds are absent in the literature. In this connection we studied for the first time the reaction of 3-phenyl-2,2-dichlorocyclobutanone **I** with dialkyl phosphites. The selection of the initial phosphorylation objects was due both to their accessibility [3] and to the presence of aromatic ring and chlorine atoms along with the strained four-membered ring providing a possibility to further modification of the phosphorylation products into organophosphorus compounds of new types.

The reactions were carried out using equimolar reagent ratio in the presence of a catalytic amount of saturated alcohol solutions of sodium alkoxylate. The formed products were purified by the column chromatography, and their structure was investigated by the methods of IR, ^{1}H and ^{31}P NMR spectroscopy. The spectral data showed that dialkyl (1-hydroxy-3-phenyl-2,2-dichlorocyclobutyl)phosphonates **IIa–IId** formed. This is consistent with the scheme proposed for aliphatic aldehydes and ketones [4]. The reaction of ketone **I** with O-alkylarylphosphonites proceeds analogously.



I **IIa–IId**

R = CH_3 (**a**), C_2H_5 (**b**), C_3H_7 (**c**), C_4H_9 (**d**).

Dimethyl (1-hydroxy-3-phenyl-2,2-dichlorocyclobutyl)phosphonate (IIa). To a solution of 2.2 g of ketone **I** and 1.1 g of dimethyl phosphite in 5 ml of benzene was added 20 drops of the saturated alcohol solution of sodium methoxide while stirring at 25°C. After completion of the weak self-heating (temperature rise up to 40°C) the mixture was stirred for 1 h at 40–50°C and washed with water. The organic layer was dried with anhydrous sodium sulfite and subjected to chromatography on aluminum oxide. Yield 2 g (66%), colorless oil, d_4^{20} 1.4121, n_D^{20} 1.5553. Found, %: Cl 21.81; P 9.53. $C_{12}H_{15}Cl_2O_4P$. Calculated, %: Cl 21.92; P 9.61. ^{1}H NMR spectrum, δ, ppm: 4.73 m (1H, H^3), 3.64 m (2H, H^4), 3.74 d (6H, OCH_3, $^3J_{HP}$ 10.35 Hz), 7.21–7.37 m (5H, C_6H_5), 4.61 s (1H, OH). ^{31}P NMR spectrum: δ_P 20 ppm.

Compounds **IIb-IId** were similarly prepared.

Compound IIb. Yield 76%, $C_{14}H_{19}Cl_2O_4P$, d_4^{20} 1.3424, n_D^{20} 1.5463.

Compound IIc. Yield 81%, $C_{16}H_{23}Cl_2O_4P$, d_4^{20} 1.2916, n_D^{20} 1.5392.

Compound IId. Yield 75%, $C_{18}H_{27}Cl_2O_4P$, d_4^{20} 1.2401, n_D^{20} 1.5332.

The growth-regulating activity of the phosphorus-containing cyclobutanes **IIa–IId** on the germinability of the seeds of agricultural crops was revealed.

The IR spectra were registered on an IR Fourier-spectrometer FSM 1202 (KBr, film). The ^{31}P NMR spectrum was taken on a Bruker WP-80 instrument (32.44 MHz) with external reference 85% H_3PO_4. The

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[1] For communication X, see [1].

^1H NMR spectrum was recorded on a Bruker WM-250 spectrometer with internal reference DMSO.

ACKNOWLEDGMENTS

This work was financially supported by the Analytic Departmental Targeted P*rogram* "*Development of the Scientific Potential of Higher School* (2009–2010)" (project no. 1979).

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