ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 6, p. 1168. © Pleiades Publishing, Ltd., 2013.
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LETTERS TO THE EDITOR

Reactions of Spiro[2.3]hexane-5-carbonyl Chloride with Phosphorus(III) Acids Esters

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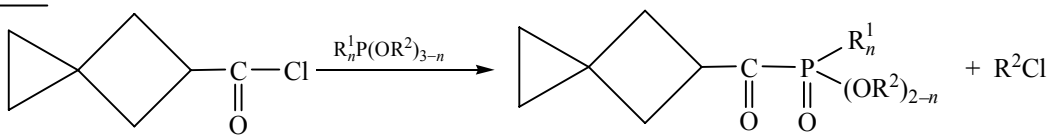
Received February 14, 2013

DOI: 10.1134/S1070363213060303

We have previously shown that the reaction of bicyclo[4.1.0]heptane-7-carbonyl chloride with medium esters of phosphorous and arylphosphonous acids occurs with the retention of the small carbocycle [1]. In continuation of this work it is interesting to study the behavior of carbonyl compounds of spirohexane series in the Arbuzov reaction [2]. Due to the high energy strain of these spiranes one could expect unusual reaction course affording new types of organophosphorus compounds.

We found that spiro[2.3]hexane-5-carbonyl chloride **I** reacts readily with phosphorous and arylphosphonous acids esters. When an equimolar ratio of reagents was used under mild conditions (0–20°C), the attack of the P-nucleophiles occurs on the carbon atom of the carbonyl group. As a result, the reaction produces dialkyl spiro[2.3]hexane-5-carbonyl phosphonates **IIa–IIc** or alkylarylspiro[2.3]hexane-5-carbonyl phosphinates **IId–IIf**.



I **IIa–IIf**

$n = 0$, $R^2 = C_2H_5$ (**a**), C_3H_7 (**b**), C_4H_9 (**c**); $n = 1$, $R^1 = C_6H_5$, $R^2 = C_2H_5$ (**d**), C_3H_7 (**e**), C_4H_9 (**f**).

The structure of compounds **IIa–IIf** was confirmed by the IR and ^{1}H NMR spectroscopy. Thus, in the IR spectra there are low-intensive peaks of the stretching vibrations of the C–H bonds of the three-membered ring in the range of 3090–3095 cm^{-1} and the strong absorption bands of carbonyl, phosphoryl, and ester groups at 1700–1705, 1255–1260, 995–1050 cm^{-1}, respectively. The ^{1}H NMR spectra the three-membered ring protons resonate in a strong field (δ 0.61 ppm). The four-membered ring protons were observed in a weaker field as a doublet at δ 2.77 ppm (4H, CH_2, $^3J_{HH}$ 7.75 Hz) and a multiplet at 3.24 ppm (1H, CH). The protons of alkoxy groups and aromatic ring appear in characteristic areas.

Compound IIa. Yield 75%, bp 151–153°C (5 mm Hg), d_4^{20} 1.1693 g cm^{-3}, n_D^{20} 1.4774.

Compound IIb. Yield 82%, bp 161–162°C (2 mm Hg), d_4^{20} 1.1307 g cm^{-3}, n_D^{20} 1.4765.

Compound IIc. Yield 76%, bp 167–168°C (1 mm Hg), d_D^{20} 1.1006 g cm^{-3}, n_D^{20} 1.4752.

Compound IId. Yield 81%, bp 182–183°C (1 mm Hg), d_4^{20} 1.1992 g cm^{-3}, n_D^{20} 1.5456.

Compound IIe. Yield 78%, oily substance, d_4^{20} 1.1792 g cm^{-3}, n_D^{20} 1.5418.

Compound IIf. Yield 79%, oily substance, d_4^{20} 1.1594 g cm^{-3}, n_D^{20} 1.5378.

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