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LETTERS TO THE EDITOR

Reactions of Bicyclo[4,1,0]heptane Derivatives with Phosphorus Pentachloride

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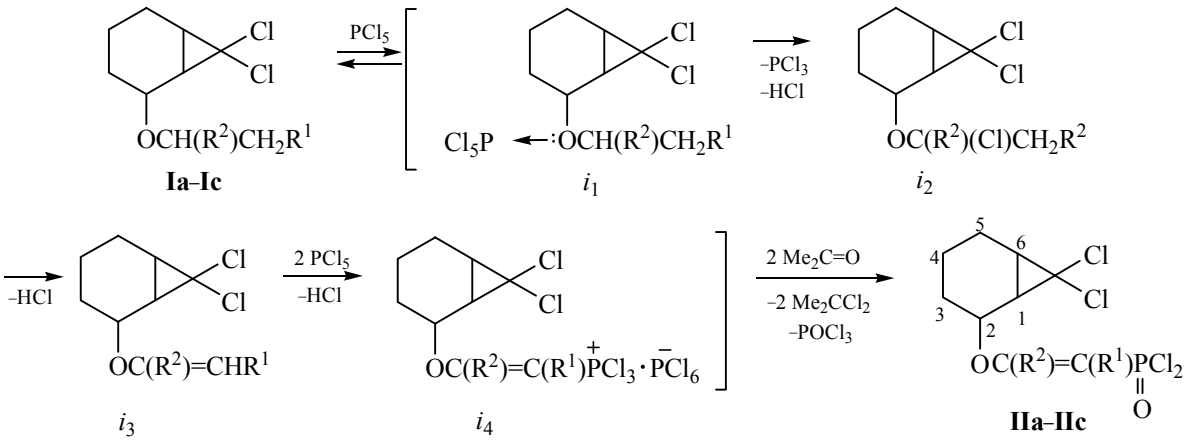
Bicycloalkanes containing three-membered cycle possess the enhanced activity to electrophile reagents action due to raised angular and torsion strains. In this connection the study of reactions of phosphorus pentachloride with bicyclo[4,1,0]heptane derivatives are of significant interest. We pioneered in using as a latter the easily available norcarane, 7,7-dichloro- and 2-alkoxy-7,7-dichloronorcaranes **Ia–Ic**.

Under standard conditions [1], norcarane was found to phosphorylation with a small ring cleavage to form cyclohexylidenemethyl- and 1-chlorocyclohexylmethylphosphonic dichlorides. 7,7-Dichloronorcarane does not react with phosphorus pentachloride under similar conditions that is probably caused by the increased small ring stability. 2-Alkoxy-7,7-dichloronorcaranes **Ia–Ic** are phosphorylated on alkoxyl group to give 2-(7,7-dichlorobicyclo[4,1,0]heptyl-2-oxy)ethenylphosphonic dichlorides **IIa–IIc**. Theoretically possible reaction pathway at the cycle is not observed that is proved by the absence of product with P–C bond when one carried out reaction with 2-methoxy-7,7-dichloronorcarane. This reaction gives rise only to 3-dichloromethylenecyclohexanone, the product of competitive reaction occurring at the three-membered cycle. The possible scheme of the formation of latter was described by us earlier [2].



$R^1 = R^2 = H$ (**a**), R^1 = Me, $R^2 = H$ (**b**), $R^1 = H$, R^2 = Me (**c**).

Dichloroanhydride of 2-(7,7-dichlorobicyclo[4,1,0]-heptyl-2-oxy)-2-methylethenylphosphonic acid (IIc). Yield 48%, bp 182–184°C (1 mm Hg), d_4^{20} 1.3782, n_D^{20} 1.5083. IR spectrum, ν, cm^{-1}: 1600 (C=C), 1275 (P=O), 730 (C–Cl), 575, 535 (P–Cl). ^1H NMR spectrum, δ_H, ppm: 5.01 d (1H, HC=, $^2J_{HP}$ 27 Hz), 4.31 m (1H, OCH), 2.29 d (3H, CH_3, J_{HP} 2 Hz), 1.30–2.15 m (9H, C_6H_9). ^{31}P NMR spectrum, δ_P, ppm: 29. Found, %: C 35.41; H 3.81; Cl 41.79; P 9.27. $C_{10}H_{13}Cl_4O_2P$. Calculated, %: C 35.50; H 3.85; Cl 42.01; P 9.17.

The IR spectra were recorded on a UR-20 device (KBr, film). The ^{1}H NMR spectra were registered on a Bruker WM–250 spectrometer (250 Hz) relative to internal DMSO, solvent $(CD_3)_2SO$. The ^{31}P NMR spectrum was obtained on a Bruker WP-80 (32.44 MHz) external to 85% phosphoric acid.

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