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LETTERS TO THE EDITOR

Reactions of 2-Alkoxy-7,7-dichlorobicyclo[4.1.0]heptanes with Phosphorus Trichloride

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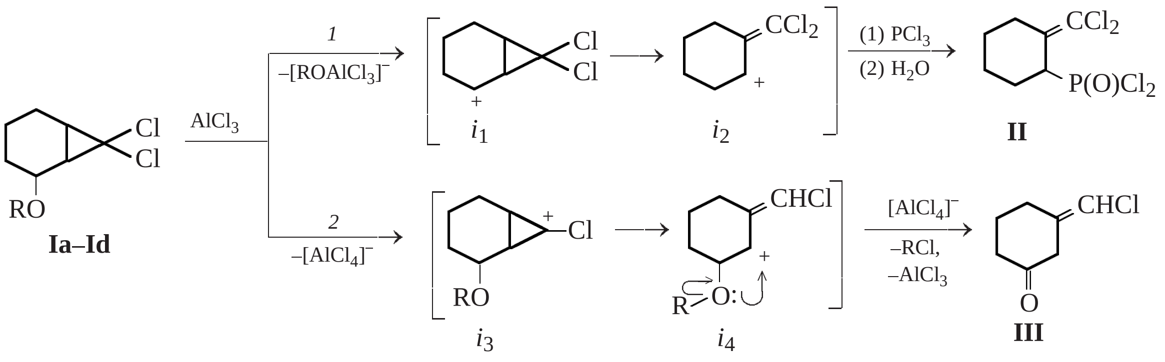
Bicyclic terpene hydrocarbons of the carane, carene, thujane, thujene series, etc., widely occur in plants in the form of such functional derivatives as alcohols, ketones, carboxylic acids, or esters which exhibit a broad spectrum of biological activity [1]. These properties may be enhanced by introducing phosphorus-containing groups into their structure. In this connection, we have studied the reactions of some derivatives of these hydrocarbons with phosphorus trichloride. Readily accessible 2-alkoxy-7,7-dichlorobicyclo[4.1.0]heptanes **Ia**–**Id** were used as starting compounds. We found that they react with phosphorus trichloride in the presence of Lewis acids, e.g., of anhydrous aluminum trichloride, with the opening of the small ring and formation of 2-dichloromethylenecyclohexylphosphonic acid dichloride (pathway *1*).



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

However, the yield of phosphonic dichloride **II** does not exceed 30%, which is apparently caused by the possibility of stabilization of carbocation i_2 by deprotonation leading to 3-dichloromethylenecyclohexene, which readily polymerizes. The reaction may also occur at the three-membered ring (pathway *2*) to form 3-chloromethylenecyclohexanone **III**.

2-Dichloromethylenecyclohexylphosphonic dichloride. To a suspension of 5.5 g of aluminum trichloride in 5 g of phosphorus trichloride, 6.8 g of 7,7-dichloro-2-ethoxybicyclo[4.1.0]heptane was added dropwise with stirring. The dark brown liquid complex thus formed was dissolved in 50 ml of dichloromethane and treated with 4.5 g of water at 0°C. The white precipitate obtained was filtered off and washed with 20 ml of dichloromethane. Distillation of the filtrate gave 1.5 g (20%) of acid dichloride **II**, bp 128–130°C (5 mm Hg), d_4^{20} 1.4863, n_D^{20} 1.5341. IR spectrum, ν, cm^{-1}: 1600 (C=C), 1275 (P=O), 730

(C–Cl), 575, 536 (P–Cl). ^{1}H NMR spectrum, δ, ppm: 1–3 m (9H, C_6H_9). ^{31}P NMR spectrum, δ_P, ppm: 52. Found, %: C 29.71; H 3.18; Cl 50.14; P 10.80. $C_7H_9Cl_4OP$. Calculated, %: C 29.82; H 3.22; Cl 50.30; P 10.99. Distillation of the low-boiling fraction gave 3-chloromethylenecyclohexanone **III** in 27% yield, bp 105–107°C (13 mm Hg), d_4^{20} 1.2479, n_D^{20} 1.5082. IR spectrum, ν, cm^{-1}: 1710 (C=O), 1590 (C=C). Found, %: Cl 39.51. C_7H_9ClO. Calculated, %: Cl 39.60. 2,4-Dinitriphenylhydrazone, mp 159°C. Found, %: C 47.92; H 4.14; Cl 10.79; N 17.30. $C_{13}H_{13}Cl \cdot N_4O_4$. Calculated, %: C 48.08; H 4.03; Cl 10.92; N 17.25.

The IR spectra were recorded on a UR-20 spectrometer, KBr prism, thin film. The ^{1}H NMR spectra were taken on a Bruker WM-250 (250 MHz) device in DMSO-d_6 against its residual protons. The ^{31}P NMR spectra were obtained on a Bruker WP-80 spectrometer (32.44 MHz) against external 85% phosphoric acid.

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