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LETTERS TO THE EDITOR

Features of the Reaction of 7,7-Dichlorobicyclo[4.1.0]heptane with Phosphorus Trichloride

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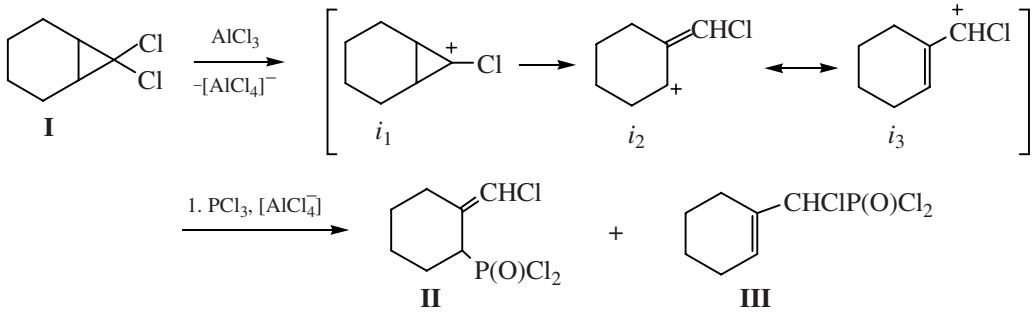
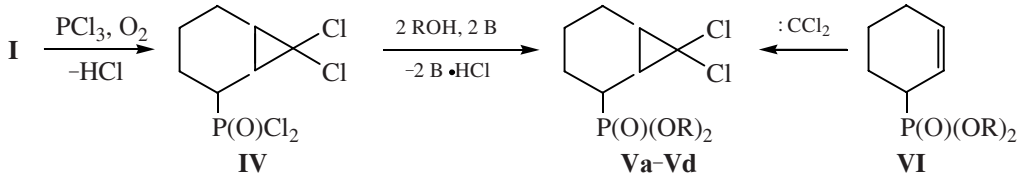
Halo derivatives of bicyclic hydrocarbons have not been explored in the Kinnear–Perren–Clay reaction [1, 2]. We showed for the first time that 7,7-dichlorobicyclo [4.1.0]heptane (**I**) react with equimolar amounts of phosphorus trichloride and anhydrous aluminum trichloride under mild conditions. Two phosphonic dichlorides were formed (δ_P 46 and 51 ppm) in a 1 : 1 ratio upon controlled hydrolysis of the intermediate complex. According to the IR spectrum, they are unsaturated compounds ($\nu_{C=C}$ 1630 and 1640 cm^{-1}). The ^1H NMR spectrum shows multiplets at 5.66–6.00, 4.55, 3.44 and 0.95–2.55 ppm, implying the presence of ring ethylene and methylene protons and PCH protons. These data together with the elemental analysis allowed the products to be assigned the structures of isomeric [2-(chloromethylene)cyclohexyl]phosphonic (**II**) and [chloro(cyclohex-1-enyl)methyl]phosphonic (**III**) dichlorides.



We succeeded in preserving the bicyclic structure of noncarane by performing the reaction of **I** with phosphorus trichloride with oxygen bubbling. In this case, according to ^1H, ^{31}P NMR and IR spectral data, 7,7-dichlorobicyclo[4.1.0]hept-2-ylphosphonic dichloride (**IV**) formed.



R = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**).

The suggested scheme of the process was confirmed also by an independent synthesis, which involved the preparation of 7,7-dichlorobicyclo[4.1.0] hept-2-ylphosphonates from dichloride **IV** and also by dichlorocarbene addition to dialkyl (cyclohexenyl) phosphonates **VI**. The constants and spectral characteristics of esters **Va–Vd** obtained by these two procedures were identical.

7,7-Dichlorobicyclo[4.1.0]hept-2-ylphosphonic dichloride (IV). Yield 18%, mp 158–160°C (1 mm Hg), d_4^{20} 1.4926, n_D^{20} 1.5397. IR spectrum, ν, cm^{-1}: 3030 (C–H), 1270 (P=O), 730–760 (C–Cl), 575 (P–Cl). ^1H NMR spectrum, δ, ppm: 0.93–2.23 m (9H, C_7H_9). ^{31}P NMR spectrum, δ_P, ppm: 54.66. Found, %: C 29.71; H 3.18; Cl 50.44; P 11.08. $C_7H_9Cl_4OP$. Calculated, %: C 29.82; H 3.22; Cl 50.30; P 10.99.

The IR spectra were registered on a UR-20 instrument (KBr prism, thin film). The ^1H NMR spectra were measured on a Bruker WM-250 instrument (200 MHz) in $(CD_3)_2SO$ relative to internal DMSO. The $^{31}P–\{^1H\}$ NMR spectra were recorded on a Bruker WP-80 spectrometer (32.44 MHz) relative to external 85% H_3PO_4.

REFERENCES

1. Clay, J.P., *J. Org. Chem.*, 1951, vol. 16, p. 892.
2. Kinnear, A.M. and Perren, E.A., *J. Chem. Soc.*, 1952, no. 9, p. 3437.