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LETTERS TO THE EDITOR

Synthesis of Dialkyl 1-Methyl-2,2-dichlorocyclopropylcarbonylphosphonates and Alkyl (1-Methyl-2,2-dichlorocyclopropylcarbonyl)arylphosphinates

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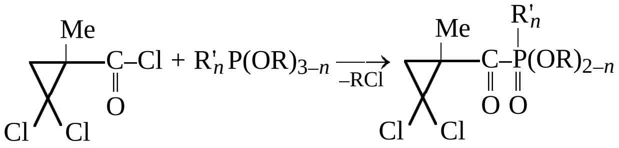
One of the promising directions in synthesis of phosphorylated small carbocycles is the reaction of three-coordinate phosphorus derivatives with functional derivatives of cyclopropane and cyclobutane [1, 2]. Among such derivatives, halocyclopropanes are the most widely used, whereas representatives of other classes were used only in a few works. In this connection, continuing our previous studies [3, 4] and aiming to broaden the synthetic potential of cyclopropanecarboxylic acid derivatives, we have studied the reaction of 1-methyl-2,2-dichlorocyclopropylcarbonyl chloride **I** with esters of phosphorus(III) acids. Acid chloride **I** contains two electrophilic centers, of which the carbonyl carbon atom is the most reactive. Therefore, at equimolar reactant ratio and under mild conditions (20–70°C), the nucleophilic attack of trialkyl phosphites and dialkyl arylphosphonites occurs at the sp^2-hybridized carbon atom. The reaction follows the classic scheme of the Arbuzov reaction and yields dialkyl 1-methyl-2,2-dichlorocyclopropylcarbonylphosphonates and alkyl (1-methyl-2,2-dichlorocyclopropylcarbonyl)arylphosphinates.



I **IIa**–**IIj**

n = 0, R = Et (**a**), *i*-Pr (**b**), Bu (**c**), $ClCH_2CH_2$ (**d**); n = 1, R'= Ph, R = Me (**e**), $MeOCH_2CH_2$ (**f**); R' = 4-MeC_6H_4, R = Me (**g**); R' = 4-$Me_2NC_6H_4$, R = Me (**h**), Et (**i**), *i*-Pr (**j**).

Compounds **IIa**–**IIc** are also formed by the reaction of acid chloride **I** with sodium dialkyl phosphites.

The structures of **IIa**–**IIj** were confirmed by IR and ^1H and ^{31}P NMR spectroscopy. In particular, in the ^1H NMR spectrum of **IIa**–**IId**, the methylene protons of the three-membered ring give the doublets with δ 2.09–2.12 and 2.16–2.22 ppm and the coupling constant $^2J_{HH}$ 7.5 Hz. The protons of the methyl group bound to the ring give a characteristic singlet at 1.50–1.52 ppm. The ^{31}P NMR spectra of phosphonates **IIa**–**IId** contain signals with δ_P 15.8–18.1 ppm. The IR spectra of **IIa**–**IIj** contain strong bands of stretching vibrations of the C=O, P=O, P–O–C, and CCl_2 groups at 1710–1715, 1245–1265, 985–1095, and 755–765 cm^{-1}, respectively, and also a weak band at 3090–3100 cm^{-1} (ν_{C-H}).

Evaluation of the biological activity of the compounds showed that $(1–5)\times10^{-3}$% aqueous solutions of **IIa**–**IIg** stimulate the energy of germination and the laboratory germinating capacity of cereal seeds. Below we give for the products obtained the number of compound, its empirical formula, yield (%), bp (p,

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mm), d_4^{20}, n_D^{20}: **IIa**, $C_9H_{15}Cl_2O_4P$, 39, 139–140 (2), 1.2720, 1.4708; **IIb**, $C_{11}H_9Cl_2O_4P$, 62, 130–132 (2), 1.2047, 1.4661; **IIc**, $C_{13}H_{23}Cl_2O_4P$, 75, 160–162 (4), 1.1087, 1.4578; **IId**, $C_9H_{15}Cl_4O_4P$, 56, –, 1.3234, 1.4893; **IIe**, $C_{12}H_{13}Cl_2O_3P$, 46, 121–123 (4), 1.2934, 1.5213; **IIf**, $C_{14}H_{17}Cl_2O_4P$, 57, 173–175 (4), 1.2262, 1.5020; **IIg**, $C_{13}H_{15}Cl_2O_3P$, 41, 148–150 (4), 1.2603, 1.5145; **IIh**, $C_{14}H_{18}Cl_2NO_3P$, 58, 178–180 (1), 1.3308, 1.5546; **IIi**, $C_{15}H_{20}Cl_2NO_3P$, 61, 186–188 (0.5), 1.3105, 1.5490; **IIj**, $C_{16}H_{22}Cl_2NO_3P$, 64, 194–196 (0.5), 1.2812, 1.5461.

The ^1H and ^{31}P NMR spectra were taken on a Bruker WP-80 spectrometer (80 and 32.44 MHz, respectively) against external HMDS and 85% phosphoric acid. The IR spectra were measured on a UR-20 spectrometer in a thin layer, NaCl prism.

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