CYCLOALKYLATION OF COMPOUNDS IN THE SERIES OF PHOSPHORUS-SUBSTITUTED DERIVATIVES OF ACETIC ACID

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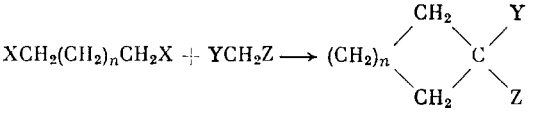
1-Phosphoryl-substituted cyclopropanes, cyclobutanes, and cyclopentanes were obtained by the reaction of phosphoryl-substituted esters and nitriles of acetic acid with α,ω-dihaloalkanes. The influence of the CH-acidity of the starting compounds and electrophilicity of the alkylating agent on the reaction rate was examined.

C-Phosphorylated cyclopropanes comprise a difficultly obtainable class of organophosphorus compounds. They cannot be obtained by the Arbuzov or Michaelis–Becker reactions since nucleophilic substitution in the cyclopropane ring usually proceeds with cleavage of the C–C bonds and opening of the strained ring [1]. A synthesis of phosphorylated cyclopropanes with the participation of carbenes is known [2-4] and also individual synthesis of certain representatives of this class of organophosphorus compounds [1, 5, 6].

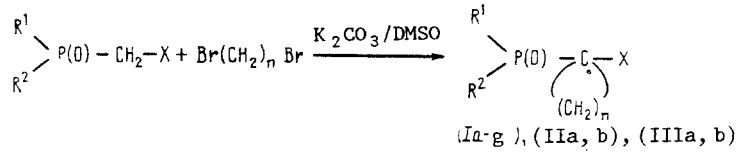
In the present work, the cycloalkylation reaction was used for the synthesis of phosphorylated cyclopropanes, which comprises the action of α,ω-dihaloalkanes on compounds with a mobile methylene group [7]



where X is a halogen atom, Y and Z are electronegative groups. Good results are obtained by carrying out the reaction in DMSO in the presence of potassium carbonate [8].

However, the first attempts to obtain phosphorylated cyclopropanes by this method were unsuccessful, and the alkylation did not take place by the action of dibromoethane on ethyl diethoxyphosphinylacetate, while in the reaction of 1,3-dibromopropane at elevated temperature, a C-alkyl derivatvive was formed [9]. We showed [10] that ethyl diethoxyphosphinylacetate and ethyl ethoxymethylphosphinylacetate undergo the cycloalkylation reaction with dibromoethane in the K_2CO_3/DMSO system at 20°C.

Further study of this reaction using various members of the series of phosphorus-substituted derivatives of acetic acid showed that it is general in character. Thus, it was found that the ethyl ester of diphenylphosphinylacetic acid, as well as phosphorus-substituted acetonitriles react similarly with dibromoethane. By using the electrophilic component of 1,3-dihalopropane and 1,4-dihalobutane the corresponding 1-phosphorus-substituted cyclobutanes (II) and cyclopentanes (III) can be obtained. The yields of the phosphorus-substituted cycloalkanes are from 30 to 70% (Table 1)



(*Ia-g*), (IIa, b), (IIIa, b)

R^1 = Me, OEt, Ph; R^2 = OEt, Ph; X = COOEt, COOBzl, CN; n = 2–4.

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TABLE 1. Physical Constants, Mass Spectral and Elemental Analysis Data of Compounds of Type (I)-(VI)

Compound	R^1	R^2	X	n	Time of reaction, h	Yield, %	Bp, °C (p, mm Hg), Mp, °C	d_4^{20}	n_D^{20}	[M+]/I	Found, %			Formula	Calculated, %		
											C	H	P		C	H	P
(Ib)[a]	OEt	OEt	COOBzl	2	72	71	148(0,01)	1,1850	1,4995	312/20	57,33	6,87	9,89	$C_{15}H_{21}O_5P$	57,66	6,83	9,91
(Id)	Me	OEt	COOBzl	2	90	64	155(0,2)	1,1855	1,5149	–	59,00	6,56	10,45	$C_{14}H_{19}O_4P$	59,57	6,78	10,97
(Ie)	Ph	Ph	COOEt	2	72	30	62–63	–	–	314/100	68,71	5,95	–	$C_{18}H_{19}O_3P$	68,78	6,09	–
(If)	OEt	OEt	CN	2	56	59	102(0,4)	1,1417	1,4460	204/31 [b]	46,56	7,20	15,07	$C_8H_{14}NO_3P$	47,09	6,95	15,25
(Ig)	Me	OEt	CN	2	70	38	97–98(0,2)	1,1228	1,4618	174/10 [b]	48,24	7,06	17,05	$C_7H_{12}NO_2P$	48,56	6,99	17,39
(IIa)	OEt	OEt	COOEt	3	72	29	99–101(0,1)	1,1306	1,4478	265/100 b	–	–	–		–	–	–
(IIb)	Ph	Ph	COOEt	3	72	65	Oil	–	1,5668	329/100 b	–	–	–		–	–	–
(IIIa)	OEt	OEt	COOEt	4	72	55	103(0,06)	1,1817	1,4540	279/11 [b]	–	–	–		–	–	–
(IIIb)	Ph	Ph	COOEt	4	72	47	Oil	–	1,5572	–	–	–	–		–	–	–
(IVa)	OEt	OEt	COOH	2	24	35	77–78	–	–	– [c]	43,64	6,99	13,93	$C_8H_{15}O_5P$	43,25	6,81	13,94
(IVc)	Me	OEt	COOH	2	24	30	131–132	–	–	192/40, 193/100 b,c	43,71	6,98	15,90	$C_7H_{13}O_4P$	43,76	6,82	16,12
(IVc)	Ph	Ph	COOH	2	24	Quant.	175–176	–	–	286/15 [c]	67,96	5,63	10,66	$C_{16}H_{15}O_3P$	67,53	5,28	10,82
(V)	Ph	Ph	COOH	3	24	49	243	–	–	300/18 c	68,31	5,70	10,25	$C_{17}H_{17}O_3P$	68,00	5,71	10,31
(VI)	Ph	Ph	COOH	4	24	32	231	–	–	– [c]	68,57	6,12	9,62	$C_{18}H_{19}O_3P$	68,78	6,09	9,85

[a]Compounds (Ia) (R^1 = R^2 = OEt, X = COOEt and (Ic) (R^1 = Me, R^2 = OEt, X = COOEt), see [10].
[b]$[M + H]^+$.
[c]Neutralization equivalent (compound, found/calculated): (IVa) 222.8 ± 0.5/222.2; (IVb) 191.9 ± 0.5/192.2; (IVc) 286.5 ± 0.5/286.3; (V) 300.0 ± 0.5/300.3; (VI) 313.8 ± 0.5/314.4.

The course of the reaction was monitored by ^{31}P NMR. We should note that in the spectra of the reaction mixtures only the signals of the starting compound and the cyclic end product were recorded. In contrast to the reaction of the malonic ester derivatives with α,ω-dihaloalkanes, where a monoalkylation product was isolated in several cases as the second compound [8], we did not record the presence of such a compound either by ^{31}P NMR or by GLC. This may indicate a higher rate of alkylation for phosphorus-substituted derivatives of acetic acid at the second consecutive stage of the process. It should be noted that increase in the temperature of the reaction mixture results in the resinification and sharp decrease in the yield of the desired end compounds (see [8]). Comparison of the influence of substituents at the active methylene group on the rate of the cycloalkylation reaction gives a clear indication of the interrelationship with the CH-acidity. Thus, phosphonates (pK in DMSO 17.5-19.5 [11]) react more rapidly than phosphinates (pK in DMSO 18.2-20 [11]); the CN-derivatives (pK 17.5 and 18.2) react more rapidly than the carbethoxy groups (pK 19.5 and 20 [11]); the derivatives of phosphinylacetic acid (pK 17.5-20 [11]) react more slowly than malonic ester (pK 16.7 [12]),* while the amide $Ph_2P(O)CH_2CONEt_2$ (pK 22.6 [14]) does not react at all, and the reaction of the latter with dibromethane does not occur, even when the conventional catalyst for such systems, such as 18-crown-6 in DMSO or benzene [15] is used. We should also note that the rate of reaction decreases when dibromoalkanes are replaced by the corresponding dichloroalkanes. When functionally substituted dihaloalkanes (1,3-dichloroacetone or β,β-dichlorodiethyl ether) are used in the cycloalkylation reaction, the starting organophosphorus compound is recovered quantitatively from the reaction.

The cycloalkanes (I)-(III) obtained, with the exception of phosphine oxides (Ie), (IIb), (IIIb), are readily mobile and distillable liquids. Cyclopropanes (I) are thermally stable and do not change on heating for 3 h at 200°C. In contrast to the latter, phosphorylated cyclobutanes (II) and cyclopentanes (III) are less stable: they decompose on prolonged heating and are hydrolyzed by water with cleavage of the P–C bond, giving the corresponding phosphinic acids. This was confirmed by chromato-mass spectrometry and NMR on ^{1}H and ^{31}P nuclei. Thus. the isolation of compounds (II), (III) from the reaction mixtures by repeated washing with small portions of cold water results in their contamination by cleavage products. It was not possible to purify the cycloalkanes completely from polar solvent using other methods, including chromatography. The composition of the synthesized phosphorus-substituted cyclopropanes (I) was confirmed by the elemental analysis and mass spectral data, while the composition of cycloalkanes (II), (III) was confirmed only by means of mass spectra (Table 1).† Moreover, the structure of all the compounds was confirmed spectrally – IR, ^{1}H, ^{13}C, ^{31}P NMR (Table 2). In the IR spectra of the cycloalkanecarboxylic acid esters (I)-(III), a characteristic absorption band of the (C=O) group is observed in the 1730-1745 cm^{-1} region, and also an absorption band of the phosphoryl fragment with a frequency of 1210-1265 cm^{-1}. For cyclopropanes (If, g) the 2245-2250 cm^{-1} band corresponds to the C≡N group. In the ^{31}P NMR spectra of compounds (I)-(III), the chemical shift is in regions corresponding to a given environment of the phosphorus atom. In the PMR spectra, the signals of the cyclopropane ring methylene protons of (Ia-f) appear in the form of a complex multiplet in the 1.10-1.70 ppm region. The signals of the methylene protons in the PMR spectra of cyclobutanes (II) and cyclopentanes (III) were assigned on the basis of the data in [16]. In the ^{13}C NMR spectra, the signals of the quaternary carbon atom in the ring appear in the form of a doublet in the 17-20 ppm region for esters of cyclopropanecarboxylic acids, in the 2.5-4.3 ppm region for nitriles (If, g) and in the 47-53 ppm region for cycloalkanes (II), (III). Thus, a decrease is observed in the direct SSCC $^{1}J_{PC}$ in the series of $^{1}J_{PC}$ $[(RO)_2P(O)]$ > $^{1}J_{PC}$ $[R^1(RO)P(O)]$ > $^{1}J_{PC}$ $[R_2P(O)]$ from 211 to 60 Hz. In the ^{13}C NMR spectra of cyclopropanes (I), taken without uncoupling on the ^{1}H nuclei, the direct SSCC $^{1}J_{CH}$ for the secondary carbon atoms in the ring is 165-170 Hz, which is characteristic for cyclopropane structures. In the mass spectra of 1-phosphorus-substituted cycloalkanes (I)-(III), peaks with considerable intensity of molecular ions $[M^+]$ or $[M + H]^+$ ions are observed. The main primary fragmentation processes of compounds having ethoxyl radicals in the molecule, are due to successive splittings off of ethylene molecules ($\Phi_1 = [M - C_2H_4]^+$) or the corresponding alcohol ($\Phi_2 = [M - C_2H_5OH]^+$). Moreover, for cycloalkanes with this structure, a cleav-

*The pK values of compounds, not available in the literature, were calculated using correlational equations given in [13].

†The content of impurities in compounds (II), (III) is 3-5% according to GLC data.

TABLE 2. Data of IR and ^{1}H, ^{13}C, ^{31}P NMR Spectra of Compounds (I)-(VI)[a]

Compound	IR spectrum, cm^{-1}		^{31}P NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ, ppm; J, Hz				PMR spectrum, δ, ppm; J, Hz
	$\nu_{P=O}$	$\nu_{C=O}$		δ_{C^1}	$^1J_{PC}$	δ_{C^2} $^2J_{PC}$	$\delta_{C=O}$ $^2J_{PC}$	
(Ib)	1240	1735	23,2	18,86	195,0	14,71 –	169,32 br.s	1,25 t (6H, CH_3, $^3J_{HH}$ = =7,0), 1,31–1,51 m (4H, CH_2CH_2), 4,09 m (4H, OCH_2, $^3J_{PH}$=7,2), 5,17 s (2H, CH_2Ph), 7,38–7,55 m (5H, C_6H_5)
(Id)	1220	1745	44,7	20,39	124,0	14,57 –	169,50 d 8,7	1,06 t (3H, CH_3CH_2, $^3J_{HH}$=7,8), 1,11–1,28 m (4H, CH_2CH_2), 1,43 d (3H, CH_3P, $^2J_{PH}$=15,6). 4,82 m (2H, OCH_2), 4,93 s (2H, CH_2Ph), 7,11–7,15 m (5H, C_6H_5)
(Ie)	1210	1730	28,7	17,50	102,0	14,55 –	171,0 d 7,5	0,62 t (3H, CH_3, $^3J_{HH}$ = =6,8), 1,37–1,50, 1,70–1,86 two m (4H, CH_2CH_2), 3,65 q (2H, OCH_2), 7,11–7,96 m (10H, C_6H_5)
(If)	1265	2250[b]	19,7	2,56	211,3	11,69 –	116,5[c] –	1,10 t (6H, CH_3, $^3J_{HH}$ = =7,1), 1,20, 1,25 two br. s (4H, CH_2CH_2), 4,80–4,97 m (4H, OCH_2)
(Ig)	1240	2245	43,02	4,30	124,0	10,55 d 9,8	117,25[c] 14,7	1,60–1,90 m (4H, CH_2CH_2), 1,52 t (3H, CH_3CH_2, $^3J_{HH}$=7,0), 1,82 d (3H, CH_3P, $^2J_{PH}$=15,1), 4,21–4,34 m (2H, OCH_2)
(IIa)	1220	1735	24,4	47,07	137,0	17,38 d[d] 10,5	171,97 ≤0,3	1,04 t (3H, CH_3CH_2OC, $^3J_{HH}$=7,0), 1,11 t (6H, CH_3CH_2OP, $^3J_{HH}$=7,0). 1,69–1,90, 1,96–2,20 two m (2H, $>C^3H_2$), 2,49–2,89 m (4H, $>C^2H_2$), 3,96–4,11 m (6H, OCH_2)
(IIb)	1200	1725	32,0	48,72	60,4	16,71 d[d] 8,9	172,11 3,0	0,57 t (3H, CH_3, $^3J_{HH}$= =7,1), 1,57–1,94 m (2H, $>C^3H_2$). 2,24–2,73 two m (4H, $>C^2H_2$), 3,57 q (2H, OCH_2), 7,02–7,64 m (10H, C_6H_5)
(IIIa)	1250	1730	27,1	53,19	138,5	24,31 d 9,5	170,56 –	1,08, 1,12 two t (9H, CH_3 $^3J_{HH}$=7,1), 1,34–1,52 m (4H, $>C^3H_2$), 1,82–2,00 m (2H, $>C^2H_2$), 2,10–2,21 m (2H, $>C^2H_2$), 3,89–4,05 m (6H, OCH_2)
(IIIb)	1200	1745	28,7	47,05	69,1	24,84 d[d] 3,9	169,05 –	0,76 t (3H, CH_3, $^3J_{HH}$= =7,1), 1,14–1,23 m (4H, $>C^3H_2$), 2,25–2,50 m (2H, $>C^2H_2$), 2,63–2,93 m (2H, $>C^2H_2$), 3,71 q (2H, OCH_2), 7,29–7,92 m (10H, C_6H_5)
(IVa)	1215	1725	24,3	18,26	216,8	15,15 –	172,54 ≤0,5	1,32 t (6H, CH_3, $^3J_{HH}$= =7,0), 1,46–1,53 m (4H, CH_2H_2), 4,12–4,26 m (4H, OCH_2), 11,06 s (1H, OH)

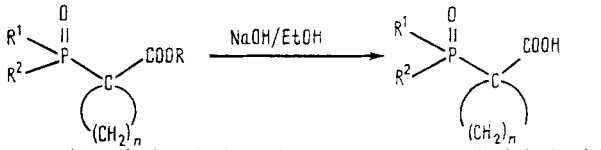
TABLE 2 (continued)

Compound	IR spectrum cm^{-1}		^{31}P NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ, ppm; J, Hz				PMR spectrum, δ, ppm; J, Hz
	$\nu_{P=O}$	$\nu_{C=O}$		δ_{C^1}	$^1J_{PC}$	δ_{C^2} $^1J_{PC}$	$\delta_{C=O}$ $^2J_{PC}$	
(IVb)	1210	1720	52,1	19,58	132,8	14,50d 7,04	171,67d 9,6	1,31 t (3H, CH_3CH_2, $^3J_{HH}$=7,1), 1,29–1,71 m (4H, CH_2CH_2), 1,78d (3H, CH_3P, $^2J_{PH}$=15,5), 4,00–4,24 m (2H, OCH_2), 11,54 s (1H, OH)
(IVc)	1140	1705	36,2	20,53	106,1	14,41 –	172,10d 10,0	1,42, 1,50 two br. s (4H, CH_2), 7,25–7,73 m (10H, C_6H_5), 10,23 s (1H, OH)
(V)	1170	1710	35,5	29,94	62,8	17,70 d[d] 9,7	174,85 –	1,56–1,81, 1,83–2,06 two m (2H, $>C^3H_2$), 2,36–2,81 m (4H, $>C^2H_2$), 7,27–7,69 (10H, C_6H_5), 10,42 s (1H, OH)
(VI)	1155	1705	33,7	–	–	–	–	1,53–1,60 m (4H, $>C^3H_2$), 2,16–2,37 m (4H, $>C^2H_2$), 7,25–7,81 m (10H, C_6H_5)

[a]The NMR spectra were recorded in CCl_4 (Ib, d, f, g): C_6D_6 (Ie), (IIa); $CDCl_3$ (IIb), (IIIa), (IVa-c), (V); CD_3OD (VI).
[b]$\nu_{C\equiv N}$.
[c]$\delta_{C\equiv N}$.
[d]δ_{C^3} 28.15 (IIa), 26.7 (IIb), 31.38 (IIIa), 40.60 (IIIb), 28.54 (V).

age of the C–C bond in the 1-position with the formation of the $\Phi_3 = [M - CO_2 - C_2H_4]^+$ or $\Phi_3' = [M - CN + H]^+$ ions is characteristic. As a result of the above-noted fragmentation processes, stable ions are formed with a mass of 81 for phosphonates, 79 for methyl phosphinates and with a mass of 201 for phosphine oxides. These ions possibly have the structure of H_2PO_3, CH_3PO_2H, and Ph_2PO, respectively.

We obtained the corresponding 1-phosphorus-substituted cycloalkanecarboxylic acids (IV)-(VI) by the hydrolysis of compounds (I)-(III) under alkaline conditions. They are white crystalline substances with a tendency to form hydrates. We should note that during the hydrolysis, cleavage of the P–C bond at the 1-position is also observed, leading to the formation of phosphorus acids of type $R^1R^2P(O)OH$, and correspondingly, to a decrease in the yield of the desired end compounds (IV)-(VI)



(Ia-d),(IIb),(IIIb) (IVa-c),(V),(VI)

R_1 = Me, OEt, Ph; R^2 = OEt, Ph; R = Et, Bzl; n = 2–4.

The composition and structure of compounds (IV)-(VI) were confirmed by the elemental analysis data and by means of IR, ^1H, ^{13}C, ^{31}P NMR and mass spectra (Tables 1, 2). It is of interest to note that upon electron impact on cyclopropanecarboxylic acids (IV) at 250°C, a signal is observed in the mass spectra, corresponding to their dimerization product, although the presence of a dimer before introducing the sample into the ionic source was not confirmed by the spectral data.

The neutralization equivalents of acids (IV)-(VI) found by their titration in 50 vol. % ethanol coincide with the calculated data within the experimental error.

The hydrolysis of cycloalkanes in acid medium proceeds with splitting of both the cyclic structure and the P–C bond. Only in the case of a phosphorus-substituted cyclopropane (Ia) ($R^1 = R^2 = OEt$, X = COOEt) did we obtain the corresponding triammonium salt (VII), in a low yield.

EXPERIMENTAL

The ^1H, ^{13}C, ^{31}P spectra, were recorded on a "Bruker WP-200-SY" spectrometer in CCl_4, benzene-d_6, chloroform-d_2, or methanol-d_4 solutions relative to TMS. For the ^{31}P NMR spectra 85% H_3PO_4 acid was used as an external standard. The exposure regime of the ^{13}C NMR spectra was JMODECHO (the carbon atom signals with even and odd numbers of protons have different polarity). The IR spectra were run on a UR-20 spectrophotometer in a thin layer or in the form of KBr tablets. The samples were examined on "Varian 3400" chromatograph with a DV-5 capillary column and temperature programming from 50 to 275°C. The rate of temperature programming was 4°C/min. A "Finnigan MAT-A-800" ionic trap served as detector, and the energy of the electron impact was 70 eV. The starting compounds were obtained by known methods [11, 17, 18] and had physical constants corresponding to those given in the literature.

Benzyl Ester of Methyl-O-ethylphosphinylacetic Acid. A 10.3 g portion (0.076 mole) of diethyl methylphosphonite was added at 120°C to a solution of 14 g (0.076 mole) of benzyl chloroacetate in 40 ml of p-xylene, and the mixture was boiled for 3 h. The solvent was evaporated at reduced pressure, and the residue was distilled under vacuum. Yield, 8.4 g (43%) of a compound, bp 148-151°C (0.01 mm), n_D^{20} 1.5088. PMR spectrum (δ, ppm; $CDCl_3$): 1.12 t (3H, CH_3CH_2, $^3J_{HH}$ = 5.8 Hz), 1.42 d (3H, CH_3P, $^2J_{PH}$ = 12.5 Hz), 2.86 d (2H, CH_2P, $^2J_{PH}$ = 14.8 Hz), 3.82-4.00 m (2H, OCH_2), 5.01 s (2H, CH_2P), 7.19-7.22 m (5H, C_6H_5). Found, %: C 42.81; H 7.80. $C_7H_{15}O_4P$. Calculated, %: C 43.30; H 7.79.

In a similar way, from 22.7 g (0.3 mole) of chloroacetonitrile and 40.8 g (0.3 mole) of diethyl methylphosphonite, 34.3 g (84%) of O-ethyl methyl(cyanomethyl)phosphinate was obtained, bp 118-119°C (0.4 mm), d_4^{20} 1.1317, n_D^{20} 1.4521. IR spectrum (ν, cm^{-1}): 1260 (P=O), 2245 (C≡N). PMR spectrum (δ, ppm; $CDCl_3$): 1.17 t (3H, CH_3CH_2, $^3J_{HH}$ = 7.5 Hz), 1.48 d (3H, CH_3P, $^2J_{PH}$ = 15.0 Hz), 2.81 d (2H, PCH_2, $^2J_{PH}$ = 17.5 Hz), 3.88 d.q (2H, OCH_2, $^3J_{PH}$ = 3.4 Hz). Found, %: C 40.99; H 6.80; N 9.31. $C_5H_{10}NO_2P$. Calculated, %: C 40.82; H 6.85; N 9.52.

General Method of Cycloalkylation. A mixture of 0.1 mole of the starting organophosphorus compound, 0.2 mole of a dihaloalkane and 0.4 mole of potassium carbonate in 50 ml of DMSO was stirred for the time indicated in Table 1 at ~20°C. A 20 ml portion of water was added, and the organic layer was extracted with ether (3 × 50 ml). The combined extracts were dried over $MgSO_4$. The solvent was evaporated, and the residue was distilled under vacuum or recrystallized.

1-O,O-Diethylphosphonyl-1-cyclopropanecarboxylic Acid (IVa). A solution of 4 g (0.1 mole) of NaOH in 20 ml of 75% alcohol was added at 20°C to 25 g (0.1 mole) of 1-carbethoxy-1-O,O-diethylphosphonylcyclopropane (Ia) and the mixture was stirred for 24 h at 20°C. The mixture was evaporated, 20% H_2SO_4 was added to pH 1, and extraction was carried out with chloroform (3 × 50 ml). The extract was dried over $MgSO_4$, evaporated, and the residue was recrystallized from diethyl ether. Yield, 7.8 g (35%) of (IVa), mp 77-78°C.

Cycloalkanecarboxylic acids (IVb, c), (V), (VI) were obtained in a similar way; their physicochemical constants, the spectral data and elemental analysis data are given in Tables 1 and 2.

Triammonium Salt of 1-Phosphonyl-1-cyclopropanecarboxylic Acid (VII). A 25 g (0.1 mole) portion of 1-carbethoxy-1-O,O-diethylphosphonylcyclopropane (Ia) was boiled for 6 h in 50 ml of concentrated HCl. The mixture was then evaporated to dryness, the residue was dissolved in 20 ml, of a 25% solution of ammonia. The solution was evaporated and the residue was recrystallized from a water–acetone = 1:1 system. Yield, 3.4 g (20%) of salt (VII), mp 216°C (dec.). IR spectrum (ν, cm^{-1}): 1290 (P=O), 1720 (C=O). ^{31}P NMR spectrum: δ 25.1 ppm (D_2O). PMR spectrum (δ, ppm; D_2O): 1.69-1.99 m (4H, CH_2CH_2), 2.32, 2.40 two t (12H, NH_4^+, $^1J_{^{15}NH}$ = 7.9 Hz). Found, %: C 20.02; H 7.80; P 13.12. $C_4H_{18}N_3O_6P$. Calculated, %: C 20.43; H 7.71; P 13.17.

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FUNCTIONALLY SUBSTITUTED ALLENE PHOSPHONATES AND THEIR TRANSFORMATION PRODUCTS.

2.* REACTION OF PHOSPHORUS-CONTAINING 1-METHOXY-2,3-ALKADIENES WITH ORGANOMAGNESIUM COMPOUNDS

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3-Alkyl-1,3-alkadienylphosphonates were obtained by the reaction of phosphorus-containing 1-methoxy-2,3-alkadienes with a Grignard reagent.

It was shown in [2] that phosphorylated allenes can be successfully used in the synthesis of very diverse organophosphorus compounds, in particular phosphorus-containing 1,3-alkadienes, which are prospective monomers for the preparation of fire-resistant plastics and elastomers [3]. One of the methods for the preparation of phosphorus-containing 1,3-alkadienes is based on allene-1,3-diene isomerization of functionally substituted allene phosphonates by the action of various nucleophilic reagents.

In continuation of the investigation of the reactivity of phosphorus-containing allenes with respect to other nucleophilic reagents, we have carried out the reaction of phosphorylated 1-methoxy-2,3-alkadienes (I)-(III) with organomagnesium compounds

*For previous communication, see [1].

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