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1,2-OXAPHOSPHOL-3-ENE DERIVATIVES BY CYCLOHALOGENATION OF 2-(1,2-ALKADIENYL)-2-OXO-1,3,2-DIOXAPHOSPHOLANES

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Abstract In our investigations of reactions of electrophilic addition to allene organophosphorus compounds we have shown that in the halogenation of 2-(1,2-alkadienyl)-2-oxo-1,3,2-dioxaphospholanes in inert solvents, the 1,2-dienylphosphonate system of bonds (O=P-C=C=C) is involved in the reaction with the halogen. As a result the cycloaddition of reagent takes place followed by opening of the dioxaphospholane ring and formation of 1,2-oxaphosphol-3-ene derivatives. The structure of the compounds 2a-e and 3a-d was established by analyses of the ir and ^{1}H- and ^{31}P-nmr spectra.

Methods of preparation and interesting chemical transformations of the phosphorus containing heterocycles have been described every year in numerous papers and recently in a monograph [1]. The development of phosphorus heterocyclic chemistry was much enhanced by five- membered heterocyclization of 1,2-alkadienephosphonate system of π-bonds, observed during the interaction of phosphorylic allenes with electrophilic reagents [2-5]. A considerable part of our studies was dedicated on this reaction, which is an addition-eliminating process, connected with formation of 1,2-oxaphosphol-3-ene derivatives [5-11]:

E = Cl, Br, I, RS, ArS, ArSe or $ClSO_2$

X = Cl, Br or I

As a continuation of our investigations in this field we have studied the halogenation of 2-(1,2-alkadienyl)-2-oxo-1,3,2-dioxaphospholanes. These compounds [12,13] are interesting in that their phosphonate part has five-membered ring, which includes the phosphorus. Therefore such a combination of an allenic bond with dioxaphospholane ring would have a substantial influence on the reaction path. Indeed in this case cycloaddition of the halogens was found followed by opening of the dioxaphospholane ring and formation of a new five- membered cycle (see the scheme bellow). The reactions were carried out in a nonpolar solvent (CCl_4, $CHCl_3$ and others) at a temperature from -5° to 0°C. The compounds 2a-e have been prepared, using SO_2Cl_2, too.

The structures of 2a-e and 3a-d were proved by spectroscopic investigations.

TABLE 1. Spectroscopic Characteristics of 1,2-Oxaphosphol-3-ene Derivatives

No	R (X)	R^1 (R^2)	Chemical shift δ, ppm					Coupl. const. J Hz	ir Spectra cm^{-1}	
			R	CHR^1	CHR^2	CH_3 (H)	^{31}P	R^1CH-P (P-H)	P=O	C=C
2a	Me (Cl)	H (H)	1.63	4.34	3.96	1.59 (6.22)	27.6	10.5 (23.5)	1245	1588
b	Et (Cl)	H (H)	Me 0.90 CH_2 1.86	4.40	3.73	1.56 (6.25)	28.0	9.5 (23.6)	1265	1586
c	Me (Cl)	Me (H)	1.56	Me 1.37 H 4.65	3.58	1.52 (6.09)	-	8.8 (22.4)	1265	1588
d	Et (Cl)	Me (H)	Me 0.88 CH_2 1.83	Me 1.39 CH 4.78	3.55	1.51 (6.05)	27.8	8.2 (23.6)	1245	1582
e	Et (Cl)	Me (Me)	Me 0.86 CH_2 1.80	Me 1.36 H 4.64	Me 1.36 H 4.04	1.50 (6.12)	-	7.2 (24.0)	1245	1580
3a	Me (Br)	H (H)	1.64	4.40	3.55	1.58 (6.31)	-	9.8 (24.6)	1238	1580
b	Et (Br)	H (H)	Me 0.92 CH_2 1.88	4.67	3.53	1.58 (6.35)	28.2	9.6 (25.0)	1235	1575
c	Me (Br)	Me (H)	1.68	Me 1.53 H 4.80	3.58	1.64 (6.39)	28.2	9.2 (24.0)	1240	1570
d	Et (Br)	Me (H)	Me 0.94 CH_2 1.89	Me 1.49 H 4.85	3.52	1.64 (6.30)	28.4	9.6 (24.5)	1240	1570

Fig. 1 The ^{1}H-nmr spectrum of 4-methyl-2-(3-methyl-1,2-pentadienyl)-2-oxo-1,3,2-dioxaphospholane 1d

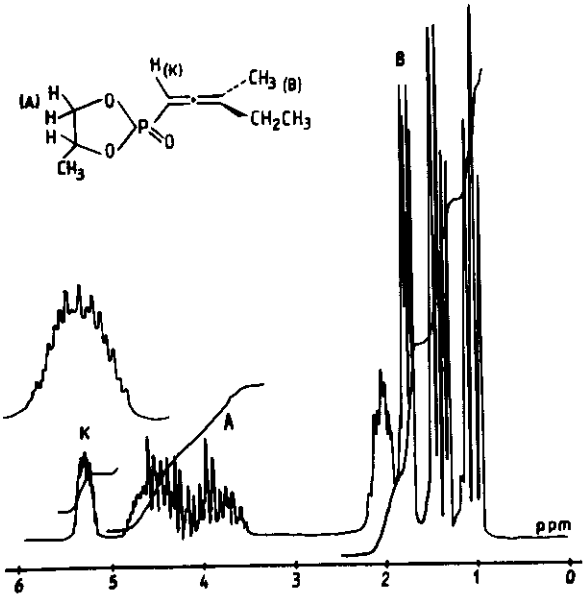
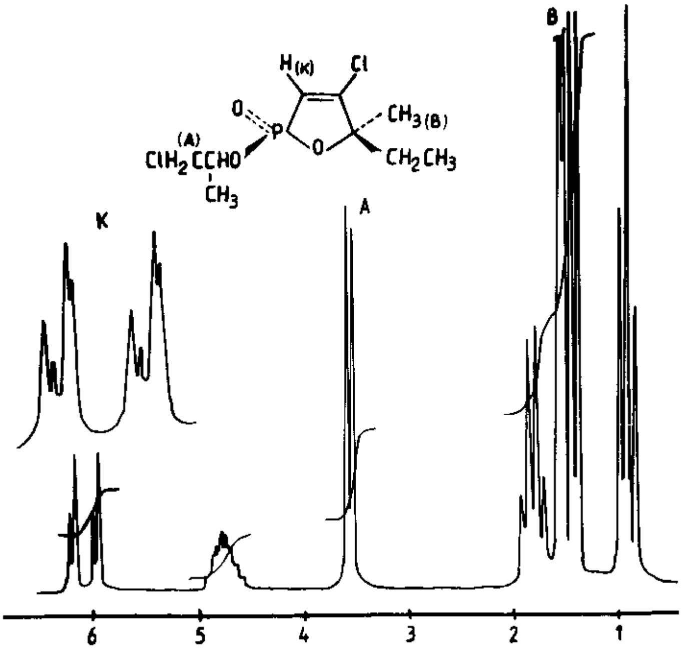


Fig. 2 The ^{1}H-nmr spectrum of 5-methyl-5-ethyl-4-chloro-2-(1-methyl-2-chloroethoxy)-2-oxo-1,2-oxaphosphol-3-ene 2d

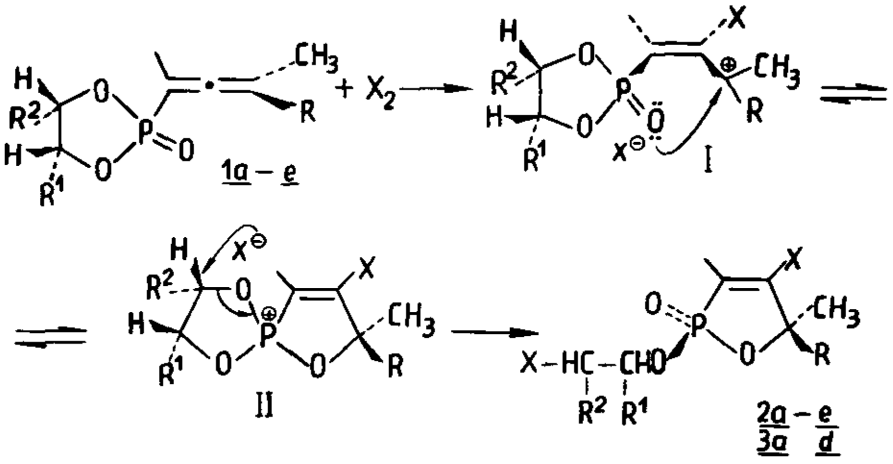


During the halogenation, in ir spectra of the 1a-e, the absorbtion band corresponding to the allene bond (1950 cm^{-1}) gradually disappears and a new band, characterizing the double bond in the oxaphospholenic ring (1570 - 1590 cm^{-1}) is observed. Comparing the ^{1}H-nmr spectrum of the initial phosphonate 1d (Fig. 1) with the spectrum of 2d obtained after chlorination of 1d (Fig. 2), one can see, that the coupling characteristic for the allenic phosphonates (Fig. 1) in Fig. 2 is not present, but the new typical coupling for the oxaphospholenes appears. This is confirmed by the absence of coupling interactions between H_A and ^{31}P in 2d (δ 3.55, $^3J_{HH}$ 4.8 Hz), while the same protons in the 1d gives a complex multiplet (δ 3.86, $^3J_{HP}$ 7.8 Hz, $^3J_{HH}$ 6.0 Hz). Moreover, the proton H_K in 1d is several quartets (δ 5.28, $^2J_{HP}$ 7.7 Hz, $^5J_{HH}$ 3.4 Hz) while in 2d it consists of four doublets (δ 6.06, $^2J_{HP}$ 23.7 Hz). The protons H_B in the dioxaphospholane 1d in a higher field give two doublets (δ 1.73, $^{5}J_{HP}$ 7.6 Hz, $^{5}J_{HH}$ 3.4 Hz), while in 2d they appear as two singlets (δ 1.50, 1.52). The chemical shift of the ^{31}P observed after these structural transformation does not change significantly (δ 31.5 ppm for 1d and 28.2 ppm for 2d), because in both cases phosphorus is included in five-membered heterocycles and it is in tetracoordination state.

In the molecules of all the synthesized products there is more than one center of chirality, i.e. the compounds are mixtures of racemic diastereoisomers. The stereoisomers can be partially observed in the ^{1}H-nmr spectra, which makes the latter even more complicated. For example, the spectrum of 2d, containing three chirality centers (see Fig. 2), only the proton H_K gives four doublets corresponding to four diastereomers. It is noteworthy that when interpreting the spectra we have taken the average signal values (Table 1) and thus have neglected the presence of isomers. The integral intensities of the signals in the spectra of all compounds 2a-e and 3a-d correspond to the proposed structure. In Table 2 are shown some of the physical constants of the synthesized compounds and their elemental analytical data.

Our studies revealed that the cyclohalogenation of 1a-e is highly stereoselective reaction. The ^{1}H-nmr spectral data concerning the reaction mixture obtained after chlorination and bromination of 1c, for instance, show that complete transformation of the allene to oxaphospholenes 2c and 3c has taken place. In these spectra peaks

SCHEME



for the protons of 1c or any compounds from other reactions were not observed. All the experimental results are confirming the high reactivity of the allenephosphonate group (O=P-C=C=C), with halogens. Most probably in the first stage of the reaction a free carbenium ion (I) is formed (see the Scheme). As a result of the nucleophilic attack of the phosphorylic oxygen to (I), the spiro compound (II) is obtained. Apparently a fast rearrangement of Arbuzov type takes place as involving opening of the dioxaphospholane ring and addition of the halide anion to the aliphatic part of the obtained alkoxy group. When the substituents at the two C atoms of the dioxaphospholane are different, opening of the cycle occurs at the less substituted C atom. For example, compounds, 2c, 2d, 3c and 3d are obtained from 1c

TABLE 2. Physical Constants and Analyses of 2a-e and 3a-d

No	Yield %	bp, °C (p, mm)	n_D^{20}	d_4^{20}	Found, %		Formula	Calcul., %	
					X	P		X	P
2a*	69 (72)	102-103 (0.5)	1.4870	(-)	28.75 29.02	12.15	$C_7H_{11}Cl_2O_3P$	28.93	12.63
b	63 (70)	122-123 (1.0)	1.4860	1.3008	27.17 27.48	11.85	$C_8H_{13}Cl_2O_3P$	27.36	11.95
c	64 (79)	100-101 (0.5)	1.4812	(-)	27.22 27.65	11.81	$C_8H_{13}Cl_2O_3P$	27.36	11.95
d	67 (80)	101-102 (0.5)	1.4826	(-)	25.90 26.18	11.18	$C_9H_{15}Cl_2O_3P$	25.96	11.34
e	64 (75)	113-114 (0.5)	1.4805	1.2242	24.38 24.75	10.45	$C_{10}H_{17}Cl_2O_3P$	24.68	10.78
3a	72	149-150 (0.5)	(-)	(-)	46.67 46.91	8.87	$C_7H_{11}Br_2O_3P$	47.85	9.27
b	64	163-164 (1.0)	1.5219	(-)	45.50 45.78	8.75	$C_8H_{13}Br_2O_3P$	45.92	8.90
c	67	142-143 (0.5)	1.5158	(-)	45.75 46.08	8.64	$C_8H_{13}Br_2O_3P$	45.92	8.90
d	65	148-149 (0.5)	1.5140	(-)	43.78 43.92	8.65	$C_9H_{15}Br_2O_3P$	44.15	8.55

* The yields in the parentheses are obtained by reaction of 1a-e with SO_2Cl_2.

and 1d by rupturing of the R^2CH-O bond. This can be easily explained taking into account the greater energy density of this bond, as compared with the other C-O bond. The difference in the bond-energies is due to the influence of the substituents on the polarization of the bond. It is evident that the location of the bond rupture can be affected also to some extent by the effect of sterical hindrance of the substituent on the reaction center at the R^1CH group, which makes difficult the nucleophilic attack of the halide anion.

EXPERIMENTAL

^1H-nmr spectra were measured on JNM-PS-10 (100 MHz) and Tesla BS-487 B (80 MHz) spectrometers as solutions in $CDCl_3$ with internal standard TMS. The chemical shift of ^{31}P was measured on a spectrometer with working frequency 16.2 MHz and internal stsndard trimethyl phosphate. The ir spectra were determined on a spectrophotometer UR-10.

4-Halogeno-2-(2-halogenoalkoxy)-5-methyl-5-alkyl-1,2-oxaphosphol-3-ene-2-oxides. Equimolar amount of the halogen dissolved in dry inert solvent (CCl_4, $CHCl_3$ etc.) is added slowly, at -5° - 0°C, to a solution of 2-(2-methyl-1,2-alkadienyl)-2-oxo-1,3,2-dioxaphospholane 1a-e, with stirring. The reaction mixture is stirred for an hour more, and after that the solvent is evaporated off, and the residue is distilled two times in vacuo. Thus obtained compounds are colourless, odourless liquids, with high viscosity, crystallizing in a short period of time when stored. The compounds 2a-e are obtained when sulfuryl chloride is added to 1a-e within the same reaction conditions as above.

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