

## CONCLUSIONS

1. The decomposition of the methyl, chloromethyl, and nitromethyl ethers of 2-fluoro-2,2-dinitroethyl alcohol proceeds by the radical route, with the cleavage of  $\text{NO}_2$  from the  $\text{C}(\text{NO}_2)_2\text{F}$  group. The reaction rate is not affected by an oxygen atom in the  $\beta$  position.

2. The decomposition of the azidomethyl and nitroxylmethyl ethers of 2-fluoro-2,2-dinitroethyl alcohol is limited by the decomposition of the  $\text{OCH}_2\text{N}_3$  and  $\text{OCH}_2\text{ONO}_2$  groups. In these cases an  $\alpha$ -oxygen atom lowers the activation energy by 5-6 kcal/mole.

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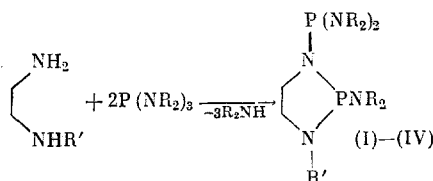
## PREPARATION OF N-PHOSPHORYLATED AND SILYLATED 1,3,2-OXAZA(DIAZA)PHOSPHOLANES AND PHOSPHORINANES

M. A. Pudovik, N. P. Morozova,  
M. D. Medvedeva, and A. N. Pudovik

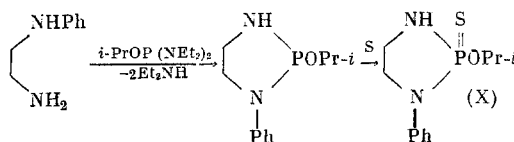
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Triaminophosphines when reacted with N,N'-dialkylethylenediamines give N,N'-dialkyl-1,3,2-diazaphospholanes [1], while their reaction with o-aminophenols in a 2:1 ratio gives N-phosphorylated 1,3,2-oxazaphospholanes [2].

The analogous reaction with monoalkyl- and arylenediamines was studied in the present paper. The previously unknown N-phosphorylated 1,3,2-diazaphospholanes were obtained when the reactants were taken in a 2:1 ratio.



The experiments were run at 110-150°C for 1-2 h, with removal of the formed dialkylamine by distillation. The structure of the products was confirmed by the elemental analysis (Table 1), IR,  $^1\text{H}$  and  $^{31}\text{P}$  NMR, and mass spectra. The IR spectra lack the absorption of a secondary amido group. The  $^{31}\text{P}$  NMR spectra of the obtained compounds each have one broad signal downfield, since the P atoms differ but slightly in chemical shift. The reaction of equimolar amounts of an N-alkyl(phenyl)ethylenediamine with the diamide of an alkylphosphorous acid gives N-alkyl(aryl)-1,3,2-diazaphospholanes, which easily add sulfur to give thiono derivatives.



Previously we had shown that a convenient method for the synthesis of phosphorus-containing heterocycles is the reaction of NH-containing 1,3,2-oxazaphospholanes and phosphorinanes with the full amides of

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 7, pp. 1637-1640, July, 1978. Original article submitted October 10, 1977.

TABLE 1. N-Phosphorylated and N-Silylated 1,3,2-Oxaza(diaza)phospholanes and Phosphorinanes

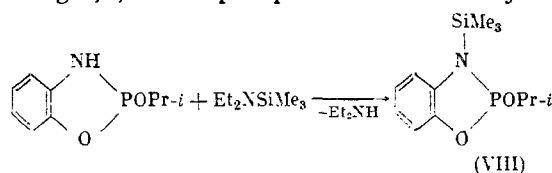


Compound	R	X	Y	R'	Yield, %	bp, °C (p, mm of Hg.)	$d_4^{20}$	$n_D^{20}$	Found, %				Empirical formula	Calculated, %			
									C	H	N	P		C	H	N	P
(I)	(CH <sub>2</sub> ) <sub>2</sub>	N-Ph	P(NMe <sub>2</sub> ) <sub>2</sub>	NMe <sub>2</sub>	16	154 (0.004)	1.1149	1.5865	—	—	21.12	18.52	C <sub>14</sub> H <sub>27</sub> N <sub>5</sub> P <sub>2</sub> *	—	—	21.41	18.96
(II)	(CH <sub>2</sub> ) <sub>2</sub>	N-Ph	P(NEt <sub>2</sub> ) <sub>2</sub>	NEt <sub>2</sub>	26	165 (0.004)	1.0395	1.4661	—	—	16.67	14.71	C <sub>20</sub> H <sub>39</sub> N <sub>5</sub> P <sub>2</sub>	—	—	17.03	15.09
(III)	(CH <sub>2</sub> ) <sub>2</sub>	N-Bz	P(NMe <sub>2</sub> ) <sub>2</sub>	NMe <sub>2</sub>	12	136 (0.004)	1.0940	1.5519	—	—	20.41	18.57	C <sub>15</sub> H <sub>29</sub> N <sub>5</sub> P <sub>2</sub> †	—	—	20.52	18.18
(IV)	(CH <sub>2</sub> ) <sub>2</sub>	N-Bz	P(NEt <sub>2</sub> ) <sub>2</sub>	NEt <sub>2</sub>	13	186 (0.004)	1.0412	1.5032	—	—	16.61	14.59	C <sub>21</sub> H <sub>41</sub> N <sub>5</sub> P <sub>2</sub>	—	—	16.47	14.59
(V)	(CH <sub>2</sub> ) <sub>2</sub>	O	SiMe <sub>3</sub>	OPr- <i>i</i>	40	44 (0.04)	0.9386	1.4412	42.91	9.10	—	14.10	C <sub>8</sub> H <sub>20</sub> NO <sub>2</sub> PSi	43.44	9.09	—	14.09
(VI)	(CH <sub>2</sub> ) <sub>3</sub>	O	SiMe <sub>3</sub>	OPr- <i>i</i>	31	48–50 (0.06)	0.9565	1.4482	46.28	9.36	6.05	13.16	C <sub>9</sub> H <sub>22</sub> NO <sub>2</sub> PSi	45.95	9.93	5.96	13.19
(VII)	(CH <sub>2</sub> ) <sub>3</sub>	O	SiMe <sub>3</sub>	OE <sub>t</sub>	45	41 (0.04)	1.0017	1.4585	43.35	9.18	6.40	13.44	C <sub>8</sub> H <sub>20</sub> NO <sub>2</sub> PSi	43.44	9.05	6.33	13.86
(VIII)	<i>o</i> -C <sub>6</sub> H <sub>4</sub>	O	SiMe <sub>3</sub>	OPr- <i>i</i>	48	84–86 (0.05)	1.0723	1.5313	53.83	7.49	—	11.77	C <sub>12</sub> H <sub>20</sub> NO <sub>2</sub> PSi	53.53	7.43	—	11.52
(IX)	(CH <sub>2</sub> ) <sub>2</sub>	N-Ph	SiMe <sub>3</sub>	OPr- <i>i</i>	49	100–102 (0.004)	1.0278	1.5295	—	—	—	10.16	C <sub>14</sub> H <sub>25</sub> N <sub>2</sub> OPSi	—	—	—	10.47

\* Mol. wt. 327; calculated 327.

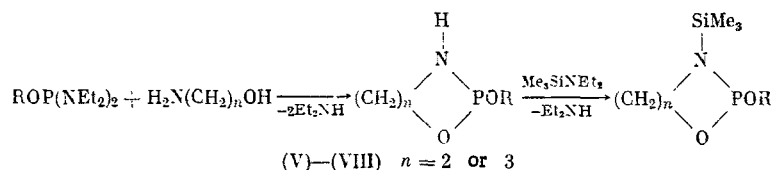
† Mol. wt. 341; calculated 341.

phosphorous acid [3]. Data on the N-silylated phosphorus-containing heterocycles are lacking in the literature. We found that the NH-containing 1,3,2-oxazaphospholanes can be silylated using silylamines:



The structure of (VIII) was confirmed by the elemental analysis, IR, and <sup>1</sup>H and <sup>31</sup>P NMR spectra;  $\delta_{31\text{P}}$  -132 ppm. The absorption of a secondary amino group is absent in the IR spectrum.

A convenient method for the synthesis of N-silylated heterocycle is to run the silylation without isolating the oxazaphospholanes and phosphorinanes. The reaction of equimolar amounts of the alkyl tetraethyldiaminophosphite and either ethanol- or propanolamine represents the first step. When the liberation of diethylamine had ceased the reaction mass was treated with an equimolar amount of trimethylsilyldiethylamine and a catalytic amount of ammonium sulfate, and the heating was continued until the liberation of diethylamine ceased.



A member of the silylated diazaphospholanes, and specifically 2-isopropoxy-1-phenyl-3-trimethylsilyl-1,3,2-diazaphospholane (IX), was also obtained by this method. The structures of (V)-(IX) were confirmed by the IR, PMR, and mass spectra.

## EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument as KBr pellets, while the <sup>31</sup>P NMR spectra were taken on a KGU-4 NMR instrument (10.2 MHz), using 85% H<sub>3</sub>PO<sub>4</sub> as the standard. The PMR spectra were recorded at 60 MHz, and here TMS was used as the standard.

**N-Phosphorylated 1,3,2-Diazaphospholanes (I)-(IV).** A mixture of 0.1 mole of N-phenyl(benzyl)ethylenediamine and 0.2 mole of a hexaalkyltriamidophosphite was heated for 1–2 h at 110–150°. When the liberation of the dialkylamine had ceased the products were vacuum-distilled (see Table 1).

**N-Silylated 1,3,2-Oxaza- and Diazaphospholanes (V)-(VIII).** A mixture of 0.1 mole of an alkyl tetraethyldiamidophosphite and 0.1 mole of an alkanolamine was heated for 1 h at 120–160°. Then 0.1 mole of tri-

methyldiethylamine and a catalytic amount of  $(\text{NH}_4)_2\text{SO}_4$  were added, and the mixture was heated for 1-2 h at 130-160° until the liberation of diethylamine had ceased. The products were vacuum-distilled (see Table 1).

**1-Phenyl-2-isopropoxy-2-thiono-1,3,2-diazaphospholane (X).** A mixture of 4.08 g of N-phenylethylenediamine and 7.02 g of isopropyl tetraethyldiamidophosphite was heated for 1 h at 130-140°. When the liberation of diethylamine had ceased the mixture was treated with 0.96 g of sulfur and then heated for 15 min at 100°. Recrystallization from benzene gave 3.1 g (40%) of (X), mp 110°.  $^{31}\text{P}$  NMR spectrum = -72 ppm; IR spectrum:  $\nu$  3290  $\text{cm}^{-1}$  (NH). Found: N 10.96; P 11.76%.  $\text{C}_{11}\text{H}_{17}\text{N}_2\text{OP}$ . Calculated: N 10.94; P 12.21%.

## CONCLUSIONS

1. The reaction of N-phenyl(benzyl)ethylenediamine with the full amides of phosphorous acid gave a number of N-phosphorylated 1,3,2-diazaphospholanes.

2. The reaction of alkanolamines with the diamides of alkylphosphorous acids, followed by treatment with trimethylsilyldiethylamine in the presence of catalytic amounts of ammonium sulfate, gave N-silylated 1,3,2-oxazaphospholanes and phosphorinanes.

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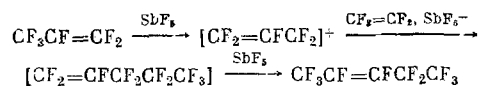
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## ELECTROPHILIC ISOMERIZATION OF FLUORO-CONTAINING OLEFINS

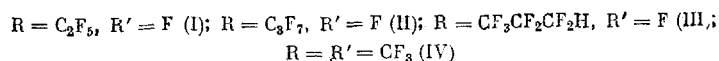
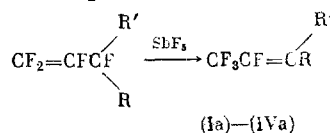
G. G. Belen'kii, G. I. Savicheva,  
E. P. Lur'e, and L. S. German

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Previously we had shown that perfluoropropylene and 2-hydroperfluoropropylene react with fluoro-containing ethylenes in the presence of  $\text{SbF}_5$  to give the corresponding pentenes with the multiple bond in the 2 position [1].



One of the steps of the proposed scheme includes rearrangement under the influence of  $\text{SbF}_5$ , with migration of the multiple bond from the 1 to the 2 position. A similar shift of the multiple bond was confirmed experimentally in the present paper. It proved that terminal fluoro-containing olefins when treated with catalytic amounts of  $\text{SbF}_5$  are smoothly isomerized to the corresponding olefins with the multiple bond in the 2 position, in which connection the rearrangement is stereospecific and leads only to the trans isomers.



The sole exception is perfluoroallylbenzene, the rearrangement of which gives a mixture of the cis- and trans-perfluoropropenylbenzenes in a 1:1 ratio. Both isomers were isolated in the pure state by preparative GLC. The pure cis and trans isomers when treated with  $\text{SbF}_5$  again form equivalent mixtures of the cis- and trans-perfluoropropenylbenzenes.

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