1.5295, d_4^{20} 1.1604. Found: C, 50.69; H, 5.04; P, 10.15%. Calculated for $C_{12}H_{14}NO_3PS$: C, 50.88; H, 4.94; P, 10.95%. ^{31}P NMR spectrum (δ, ppm): 51. PMR spectrum in CCl_4 (δ, ppm, J, Hz): 1.37 t (CH_3C, 3H, $^3J_{HH}$ = 7.0), 2.42 s (CH_3CO, 3H), 6.4 d ($^2J_{HP}$ = 5.0), and 6.5 d ($^2J_{HP}$ = 8.0) (CHP, 1H).

Reaction of (I) with meta-Fluorobenzaldehyde. A sample of 6.2 g aldehyde was added to 8.8 g (I) in the presence of a catalytic amount of $BF_3 \cdot Et_2O$ upon cooling to 0-5°C. Distillation gave 10.5 g (70%) O-ethyl-(1-acetoxy-meta-fluorophenylmethyl)cyanothiophosphonate (IIc) with bp 139-140°C (0.06 mm), n_D^{20} 1.5185, d_4^{20} 1.2475. Found: C, 47.62; H, 3.51; P, 10.08%. Calculated for $C_{12}H_{10}NO_3PSF$: C, 47.84; H, 3.32; P, 10.29%. ^{31}P NMR spectrum (δ, ppm): 50. PMR spectrum in CCl_4 (δ, ppm, J, Hz): 1.8 t ($^3J_{HH}$ = 7.0, CH_3C, 3H), 2.66 s (CH_3CO, 3H), 6.60 d ($^2J_{HP}$ = 4.0) and 6.63 d ($^2J_{HP}$ = 8.0) (CHP, 1H).

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REACTION OF FLUORINE-CONTAINING 1,4,2-OXAZAPHOSPHOLINE WITH OH-NUCLEOPHILES

O. V. Korenchenko, A. Yu. Aksinenko,
V. B. Sokolov, and I. V. Martynov

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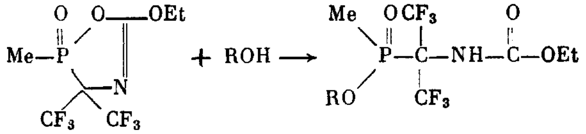
1,4,2-Oxazaphospholine (I) decomposes upon the action of OH-nucleophiles with the formation of phosphonate esters (II).

The synthesis and properties of 1,4,2-oxazaphospholines with a pentacoordinated P^V phosphorus atom have been studied rather extensively [1-3]. On the other hand, the information on the synthesis of 1,4,2-oxazaphospholanes with a tetracoordinated P^V atom is extremely limited and there are no data on their reactivity. In this regard, we undertook a study of the reaction of 1,4,2-oxazaphospholine (I) [4] with OH-nucleophiles, which opens, in our opinion, broad synthetic possibilities for the introduction of fluorine-containing α-aminoalkylphosphoryl fragments into OH-containing molecules.

The ring in (I) is virtually quantitatively opened by water and alcohols at the P-O bond with the formation of the corresponding phosphonic acid and its esters (IIa)-(IIg).



(I) (IIa–g)

R = H (a), Me (b), Et (c), *n*-Pr (d), *n*-Bu (e), *n*-Am(f), *n*-Hex (g).

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TABLE 1. Yields, Properties, and Elemental Analysis Data for (IIa)-(IIg)

Compound	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	Found, %				Chemical formula	Calculated, %			
				C	H	N	P		C	H	N	P
(IIa) *	100	–	–	26,49	3,03	4,48	9,53	$C_7H_{10}F_6NO_4P$	26,51	3,18	4,42	9,77
(IIb)	50	95–96 (1)	1,4044	29,40	3,48	4,49	9,28	$C_8H_{12}F_6NO_4P$	29,01	3,65	4,23	9,35
(IIc)	100	–	1,4140	31,32	4,09	4,19	8,97	$C_9H_{14}F_6NO_4P$	31,31	4,09	4,09	8,95
(IId)	60	90–91 (0,04)	1,4071	33,32	4,64	3,78	8,40	$C_{10}H_{16}F_6NO_4P$	33,43	4,49	3,90	8,62
(IIe)	78	98–99 (0,02)	1,4103	35,76	4,85	3,69	7,85	$C_{11}H_{18}F_6NO_4P$	35,40	4,86	3,75	8,35
(IIf)	80	108–109 (0,02)	1,4120	37,32	5,21	3,60	8,02	$C_{12}H_{20}F_6NO_4P$	37,22	5,21	3,62	8,00
(IIg)	74	116–118 (0,02)	1,4133	39,16	5,70	3,59	7,71	$C_{13}H_{22}F_6NO_4P$	38,91	5,53	3,49	7,72

*Mp, 48-50°C.

TABLE 2. NMR Spectra of (IIa)-(IIg)

Compound	PMR (δ, ppm, J,* Hz)			δ_F*** (intensity)	δP
	EtOC(O)	ROP	NH **		
(IIa)	1,28 t (3H) 4,22 q (2H)	10,85 s (1H)	6,40 d	11,00 s	41,60
(IIb)	1,30 t (3H) 4,18 q (2H)	3,90 d (3H, $^3J_{PH}=18$)	6,30 d	9,38 q, 13,23 q (1 : 1)	44,30
(IIc)	1,30 t (3H) 4,30 q (2H)	1,26 t (3H), 4,14 m (2H)	6,44 d	9,54 q, 13,06 q (1 : 1)	43,10
(IId)	1,30 t (3H) 4,17 q (2H)	0,98 t (3H), 1,74 m (2H), 4,22 m (2H)	6,17 d	9,80 q, 13,97 q (1 : 1)	42,86
(IIe)	1,30 t (3H) 4,22 q (2H)	0,91 t (3H), 1,44 m (2H), 1,70 m (2H), 4,22 m (2H)	6,30 d	9,78 q, 13,97 q (1 : 1)	42,77
(IIf)	1,30 t (3H) 4,21 q (2H)	0,91 t (3H), 1,36 m (4H), 1,72 m (2H), 4,21 m (2H)	6,26 d	9,80 q, 13,90 q (1 : 1)	42,83
(IIg)	1,30 t (3H) 4,20 m (2H)	0,92 t (3H), 1,36 m (6H), 1,72 m (2H), 4,20 m (2H)	6,25 d	9,70 q, 13,90 q (1 : 1)	42,86

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*1.90 d (3H, CH_3P, $^2J_{PH}$ - 16).
**$^3J_{PH}$ - 9.
***$^4J_{FF}$ - 9.

The composition and structures of (IIa)-(IIg) were supported by elemental analysis and ^1H, ^{19}F, and ^{31}P NMR spectroscopy.

The PMR spectra of (II) show characteristic doublets for the methyl group bound to the phosphorus atom at 1.90 ppm with $^2J_{PH}$ = 16 Hz and doublets for the NH protons at 6.2-6.4 ppm with $^3J_{PH}$ = 9 Hz. The ^{19}F NMR spectra of (IIb)-(IIg) show two quartets (at 8-9 and 13-14 ppm with $^4J_{FF}$ = 9 Hz) due to lack of equivalence of the trifluoromethyl groups. The phosphorus atom signals in the ^{31}P NMR spectra of (II) are found at 41-44 ppm, which indicates the phosphine structure of (II) [5].

EXPERIMENTAL

The ^1H, ^{19}F, and ^{31}P NMR spectra were taken on a Bruker CXP 200 spectrometer in $CDCl_3$.

Reaction of 1,4,2-Oxazaphospholine with OH-Nucleophiles. A sample of 0.01 mole water or corresponding alcohol was added dropwise to a solution of 0.01 mole (I) in 10 ml ether at 20°C. The solvent was evaporated after 24 h. Products (IIa) and (IIc) were dried in vacuum, while (IIb) and (IId)-(IIg) were distilled.

The yields, properties, elemental analyses, and NMR spectral data for (IIa)-(IIg) are given in Tables 1 and 2.

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SYNTHESIS OF 5-AZAADENINE DERIVATIVES FROM N-(1,2,4-TRIAZOL-5-YL)AMIDINES

V. A. Dorokhov, A. R. Amamchyan,
V. S. Bogdanov, and B. I. Ugrak

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A method is proposed for the synthesis of N-substituted 5-azaadenines. The condensation of N-(1,2,4-triazol-5-yl)amidines with trichloroacetonitrile gives trichloromethyl derivatives of 1,2,4-triazolo[1,5-a]-1,3,5-triazines, which are converted by the action of primary or secondary amines into N-alkylamino- or N,N-dialkylamino-1,2,4-triazolo-[1,5-a]-1,3,5-triazines (5-azaadenines).

N-(1,2,4-Triazol-5-yl)amidines (TA), which we described in a previous work [1], are used as reagents in heterocyclic synthesis [2]. Thus, the reaction of TA with ethyl orthoformate is a simple, convenient method for obtaining the 5-azapurine system. Fusion of a triazine ring to a triazole ring may apparently be achieved by reactions of TA with other one-carbon synthones. In the present work, TA were used as starting compounds for the synthesis of 5-azaadenines substituted at the exocyclic nitrogen atom.

Free bases of TA obtained in situ from TA hydrochlorides (Ia) and (Ib) react with CCl_3CN to give the corresponding trichloromethyl derivatives of 1,2,4-triazolo[1,5-a]-1,3,5-triazines (IIa) and (IIb) in 58-78% yield.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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