The Reaction of Trivalent Phosphorus Nucleophiles with Phenyl Azidoformate and 5-Aryloxy-1,2,3,4-thiatriazoles

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Benzoyl azide and phenyl azidoformate react with phosphorous triamides (8) to give isolable phosphazides (11 and 12) which decompose thermally to give the corresponding acylated iminophosphoranes (13 and 14). With 5-aryloxy-1,2,3,4-thiatriazoles (15) and 8, 1:1 reaction products are formed which are best represented by the 2,2-dihydro-1,3,4,5,2-thiatriazaphosphorine (23) structure. This structure assignment is based on thermal degradation studies and on the interpretation of infrared data of the 1:1 adducts; their mass spectra show fragmentation patterns in accordance with their formulation.

As part of our study of the reactions between trivalent phosphorus nucleophiles and organic cyanates (3) and thiocyanates (4), we have examined the interaction of phosphorous triamides with aryl azidoformates and their thiono analogs, namely 5-aryloxy-1,2,3,4-thiatriazoles.

It has been established (5) that reactions which should lead to thiocarbamoyl azides (1, X = S), in reality afford derivatives of 1,2,3,4-thiatriazole (2, X = S). A similar cyclization does not occur with the oxygen analogs, the carbamoyl azides (1, X = O). Phosphoryl azides (6) (3, X = O), thiophosphoryl azides (6) (3, X = S), and diarylphosphinic azides (7) (3, X = O), possess infrared absorptions consistent with the acyclic structure. Cyclization to 4 is not apparent. In analogy to the well-established imidazide-tetrazole equilibrium (8), 1 (X = NR) ⇌ 2 (X = NR), it was to be expected that azidophosphinic imines (3, X = NR) would ring-close intramolecularly to give phosphatetrazoles (4, X = NR). However, infrared studies revealed (9) that they exist in the acyclic form. Nevertheless, it has been suggested (10) that stable complexes of triphenyl phosphine with 2-azidobenzimidazole and 2-azidobenzothiazole are best represented by the cyclic structure 5 (X = S, NH).

Chemical and spectroscopic evidence are presented in this report which show that the reaction products from phosphorous triamides (8) and phenyl azidoformate (10) are indeed acyclic (12), whereas those from 8 and 5-aryloxy-1,2,3,4-thiatriazoles (15) are best represented by the 2,2-dihydro-1,3,4,5,2-thiatriazaphosphorine structure (23).

Triphenyl phosphine (11) and trialkyl phosphites (12) are known to yield addition compounds (6) with phenyl and benzoyl azide (Staudinger reaction), the iminophosphoranes (7, R^1 = phenyl, alkoxyl; R^2 = phenyl, benzoyl) being the stable end products of the reaction. With benzoyl azide (9), compounds 8 react readily to give phosphazides (13) (11) which lose nitrogen on heating as they change to N-benzoyliminophosphoranes (13). We have observed the same behavior with phenyl azidoformate (10). Phosphazides (12, Table I) were the only reaction products of the addition of 8 to 10. Compounds 12 were converted quantitatively to N-phenoxycarbonyliminophosphoranes (14, Table II) in hot toluene. These reactions are illustrated in Scheme 1.

SCHEME 1

$$(R)_3 \equiv P + N_3 - \overset{\overset{O}{\|}}{C} - (O)_n \langle \bigcirc \rangle \longrightarrow (R)_3 \equiv P = N - N = N - \overset{\overset{O}{\|}}{C} - (O)_n \langle \bigcirc \rangle$$

| 8 | 9 (n 0) | 11 (n 0) |
| | 10 (n 1) | 12 (n 1) |

$$\overset{\Delta}{\longrightarrow} (R)_3 \equiv P = N - \overset{\overset{O}{\|}}{C} - (O)_n \langle \bigcirc \rangle + N_2$$

13 (n 0)
14 (n 1)

R = dialkylamino

The phosphazides (11 and 12) and the iminophosphoranes (13 and 14) were characterized by their infrared and ultraviolet spectra (Table III); peaks in the infrared were assigned in the light of well established correlations with special attention of P=N and C=O groups. Compounds 11 and 13 show an intense band near 1360 cm⁻¹ which seems to be characteristic and is in agreement with

literature (9,14) values for P=N (15). In 12 and 14, the P=N absorptions show a shift to lower frequency and a decrease in intensity. In general, these P=N bands appear to be more intense than P=N bands of 7 (R² = phenyl) which are not attached to a carbonyl group. A similar situation exists for P=N-SO₂ compounds (16) and an intense band near 1300-1260 cm⁻¹ is attributed to the entire group rather than P=N alone (17). Some relatively good correlations are apparent for the C=O group. The carbonyl bands are near 1635 cm⁻¹ for 11 and near 1700 cm⁻¹ for 12. In the iminophosphoranes (13 and 14), the carbonyl absorptions show a shift to lower frequency. The phosphazides (11) absorb quite strongly in the ultraviolet, and exhibit maxima near 258 and 318 nm, whereas the uv spectra of 12 exhibit a maximum of high intensity (log ε ≅ 4.5) at 289 ± 1 nm. There is little change in the spectra of solutions of 11 and 12 on changing the solvent from methanol to p-dioxane and benzene. The iminophosphoranes (13) show absorption at 231 nm (log ε ≅ 4.1). In 14, the absorption maximum is shifted to longer wave lengths (271-272 nm) coupled with a decrease in intensity (log ε ≅ 3.2).

The characteristic chemical properties of the 1,2,3,4-

TABLE I

Phosphazides

$$(R)_3 \equiv P = N - N = N - \overset{\overset{O}{\|}}{C} - (O)_n \langle \bigcirc \rangle$$

Compound	R	n	Yield, %	M.p. (a) °C	Formula	C Calcd. Found	H Calcd. Found	N Calcd. Found	P Calcd. Found
11a	$(C_2H_5)_2N-$	0	90.5	89 - 90	$C_{19}H_{35}N_6OP$	57.9 58.0	9.0 9.0	21.3 21.3	7.9 7.8
11b	N-	0	83.6	104.5-105	$C_{22}H_{35}N_6OP$	61.4 61.8	8.2 8.3	19.5 19.6	7.2 7.2
11c	O N-	0	57.6	104 -105 (b)	$C_{19}H_{29}N_6O_4P$	52.3 51.9	6.6 7.0	19.3 19.0	7.1 7.3
12a	$(C_2H_5)_2N-$	1	74.5	74	$C_{19}H_{35}N_6O_2P$	55.5 55.8	8.5 8.5	20.4 20.6	7.6 7.6
12b	N-	1	85.3	127	$C_{22}H_{35}N_6O_2P$	59.2 59.2	7.9 7.9	18.9 19.2	7.0 6.6
12c	O N-	1	84.7	136 -137	$C_{19}H_{29}N_6O_5P$	50.4 50.1	5.3 5.6	18.6 18.7	6.9 7.1

(a) With decomposition. (b) Lit. (11) m.p. 86-87°.

TABLE II

Iminophosphoranes

$$(R)_3 \equiv P = N - \overset{\overset{O}{\|}}{C} - (O)_n - \text{C}_6\text{H}_5$$

Compound	R	n	Dec.,(a) °C	M.p. °C	Formula	Mol.-wght. Calcd. Found	C Calcd. Found	H Calcd. Found	N Calcd. Found	P Calcd. Found
13a	$(C_2H_5)_2N$-	0	30-40	35.5-36	$C_{19}H_{35}N_4OP$	366.5 / 370	62.2 / 61.9	9.6 / 9.9	15.3 / 15.3	9.5 / 9.6
13b	⬡N-	0	60-70	99.5	$C_{22}H_{35}N_4OP$	402.6 / 399	65.7 / 65.5	8.7 / 8.9	13.9 / 13.9	7.7 / 8.0
13c	O⬡N-	0	50-60	165	$C_{19}H_{29}N_4O_4P$	408.5 / 411	55.8 / 56.1	7.1 / 7.4	13.7 / 13.4	7.6 / 7.9
14a	$(C_2H_5)_2N$-	1	90	(b)	$C_{19}H_{35}N_4O_2P$	382.5 / 381	59.6 / 59.5	9.2 / 9.1	14.7 / 14.7	8.1 / 8.4
14b	⬡N-	1	90	(b)	$C_{22}H_{35}N_4O_2P$	418.5 / 392	63.1 / 63.1	8.4 / 8.3	13.4 / 13.7	7.4 / 7.6
14c	O⬡N-	1	70-80	(b)	$C_{19}H_{29}N_4O_5P$	424.4 / 416	53.8 / 54.0	6.8 / 7.1	13.2 / 13.3	7.3 / 7.2

(a) In toluene solution. (b) Colorless resin.

thiatriazole ring are (1) alkaline hydrolysis to azide, carbonate and sulfide, and (2) thermal decomposition to cyano compounds, nitrogen and sulfur (18). Based on the kinetics of the decomposition of 5-alkoxy-1,2,3,4-thiatriazoles (15, R^1 = alkoxy) into alkyl cyanates (19, R^1 = alkyl), nitrogen and sulfur, Jensen et al. (19), proposed a mechanism (path a) which parallels that of ethoxycarbonyl azide (20). A possible explanation for the inability to
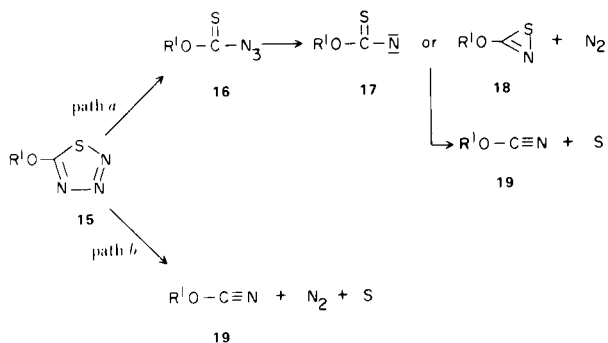
detect the hypothetical thiocarbonyl azide (16), nitrene (17) or thiazirine (18) by either spectroscopic or mass spectrometric measurements (21) may be their short life time or that the decomposition of 15 proceeds via a concerted mechanism as depicted in path b. In summary, under the conditions so far investigated the driving force of this class of compounds toward total fragmentation have been sufficiently large as to prevent the interception of potential intermediates.

The present work was an endeavour to intercept possible intermediates such as 16 by trivalent phosphorus compounds of very high nucleophilicity such as 8. A class of 1,2,3,4-thiatriazoles was accordingly selected, namely 5-aryloxy-1,2,3,4-thiatriazoles (15) which had been previously (22) observed to undergo total fragmentation at 0°, and the extent to which the presence of extraneous trivalent phosphorus nucleophiles interfered with this degradation was examined. In ether solution at -15 to -20°, the strongly exothermic reactions of 15 with 8 resulted in the formation of orange to orange-red crystalline 1:1 reaction

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TABLE III

Ir and Uv Spectral Data of Phosphazides and Iminophosphoranes

| | Phosphazides | | | | | Iminophosphoranes | | | |
| | Uv Data in Methanol | | Ir Data (Potassium bromide) Assignment (cm⁻¹) | | | Uv Data in Methanol | | Ir Data (Potassium bromide) Assignment (cm⁻¹) | |
Compound	Wave Length (nm)	Log ε	C = O	P = N	Compound	Wave Length (nm)	Log ε	C = O	P = N
11a	257	3.900	1635	1385	**13a**	231	4.172	1550	1360
	318	4.416							
11b	258	3.933	1635	1375	**13b**	231	4.108	1545	1360
	319	4.433							
	320 (a)	4.421							
11c	262	3.931	1650	1350	**13c**	232	4.144	1560	1357
	315	4.395							
	315 (a)	4.247							
12a	288	4.502	1703	1300	**14a**	217	3.790	1667	1320
	373	2.637				272	3.262		
12b	290	4.454	1700	1310	**14b**	272	3.160	1660	1325
	289 (b)	4.414							
	289 (c)	4.459							
12c	288 (d)	4.411	1710	1350	**14c**	271	3.121	1655	1320
	287 (b)	4.311							
	283 (c)	4.466							

(a) In acetone solution. (b) In benzene solution. (c) In p-dioxane solution. (d) The solution had not changed after 14 hours at 25°.

products (Table IV). The strongly exothermic reactions were controlled between -20 and -15° by external cooling. It proved unnecessary to dissolve 8c (R = N-morpholino) in ether as it also reacts in the form of a suspension with 15 in solution. The 1:1 reaction products are stable at room temperature and have been stored for more than eight years at ambient temperature without decomposition. The reaction of 15c (R' = 4-chlorophenyl) with triphenylphosphine, which is a weaker nucleophile than 8, proceeded more sluggishly. For example, triphenylphosphine reacted with 15c in ether at considerably higher temperature (25°) with exothermicity; the products were those of total fragmentation, i.e., 4-chlorophenyl cyanate and triphenylphosphine sulfide in addition to nitrogen. In this respect, the behavior parallels that of triphenylphosphine and 5-ethoxy-1,2,3,4-thiatriazole (23) (15, R' = ethyl).
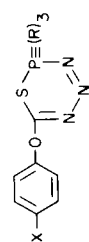
When solutions of the 1:1 adducts in toluene or benzene were heated, nitrogen was evolved and triamidophosphorothioates (24, Table V) were isolated in high yields from these solutions (24). The alternate course, i.e., degradation of the 1:1 adducts to form the acylated iminophosphoranes (25, Scheme 2) was not observed. If these adducts should exist in the (acyclic) phosphazide (22) structure, formation of 25 would be a logical consequence, and in this respect their behavior would parallel that of the oxygen analogs (12) which decompose on

heating to give a quantitative yield of the corresponding acylated iminophosphorane (14). The 1,3,4,5,2-thiatriazaphosphorine (23) structure for the 1:1 adducts of 8 with 15 is in best agreement with their thermal behavior and the formation of the observed degradation products is a logical consequence as shown by the electronic shifts in 23. This assignment is substantiated by infrared and mass spectral data and-is discussed in more detail below.

The reaction pathways available for the 1,3,4,5,2-thiatriazaphosphorine (23) ring include heterolysis of the sulfur-nitrogen bond in 15 to give structure 20 (25) which has exactly the charge distribution needed for the formation of intermediate 21; configuration and charge distribution of 21 would allow for ring closure to 23. A second speculative mechanism would involve nucleophilic attack of the trivalent phosphorus in 8 on the sulfur atom in 15 utilizing the d-orbitals of sulfur. Once the sulfur-nitrogen bond in 26 is weakened, formation of 23 is a logical consequence. Although at the present time we are unable to make a choice between these two mechanisms, we do favor direct nucleophilic attack of phosphorous triamide (8) on the sulfur in 15.

In conformity with a structure like 23, the crystalline 1:1 reaction products of 8 with 15 contain neither covalent nor ionic azide groups as the azide band near 2100 cm⁻¹ is absent from the solid (potassium bromide) and solution

TABLE IV

6-Phenoxy-2,2,2-tris(dialkylamino)-2,2-dihydro-1,3,4,5,2-thiatriazaphosphorines

Compound	R	X	% Yield	M.p. °C(a)	Formula	C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found	P Calcd.	P Found	S Calcd.	S Found	Uv Wave Length (nm)	Log ε
23a	$(C_2H_5)_2N$	H	63.4	71-72	$C_{19}H_{35}N_6OPS$	53.5	53.5	8.3	8.2	19.7	19.7	7.3	7.7	7.5	7.7	259 / 349	3.973 / 4.241
23b	$(C_2H_5)_2N$	CH_3	75.8	72	$C_{20}H_{37}N_6OPS$	54.5	54.9	8.5	8.7	19.1	19.1	7.0	7.3	7.3	7.6	252 / 347	3.980 / 4.271
23c	$(C_2H_5)_2N$	Cl	69.5	132	$C_{19}H_{34}ClN_6OPS$ (b)	49.5	49.8	7.4	7.5	18.3	18.0	6.7	6.9	7.0	7.1	217 / 250 / 350	4.266 / 4.053 / 4.292
23d	$(C_2H_5)_2N$	NO_2	85.1	96	$C_{19}H_{34}N_7O_3PS$	48.4	48.7	7.3	7.2	20.8	20.8	6.6	6.7	6.8	6.6	212 / 273 / 352	4.186 / 4.132 / 4.250
23e	piperidino (N-)	H	79.0	129-130	$C_{22}H_{35}N_6OPS$	57.2	57.0	7.6	7.5	18.2	17.8	6.7	6.9	6.9	7.0	259 / 350	4.008 / 4.276
23f	piperidino (N-)	CH_3	74.0	113	$C_{23}H_{37}N_6OPS$	58.0	58.3	7.8	8.1	17.6	17.7	6.5	6.7	6.7	7.0	251 / 350	3.973 / 4.230
23g	piperidino (N-)	Cl	44.3	146	$C_{22}H_{34}ClN_6OPS$ (c)	53.2	53.5	6.9	6.7	16.9	17.2	6.2	6.0	6.4	6.6	217 / 250 / 350	4.273 / 4.077 / 4.298
23h	piperidino (N-)	NO_2	94.7	102	$C_{22}H_{34}N_7O_3PS$	51.1	51.5	6.8	7.0	19.3	19.6	6.1	6.0	6.3	6.4	215 / 273 / 352	4.129 / 4.085 / 4.194
23i	morpholino (O-N-)	H	85.3	164-165	$C_{19}H_{29}N_6O_4PS$	48.7	48.5	6.2	6.1	17.9	18.3	6.6	7.2	6.8	6.8	220 / 306 / 308 (e)	4.027 / 4.393 / 4.413

TABLE IV (continued)

Compound	R	X	% Yield	M.p. °C (a)	Formula	C Calcd. Found	H Calcd. Found	N Calcd. Found	P Calcd. Found	S Calcd. Found	Uv Data in Methanol Wave Length (nm)	Log ε
23j	$\text{O}\!\!\diagdown\!\!\text{N-}$	CH_3	55.4	146	$C_{20}H_{31}N_6O_4PS$	49.8 49.6	6.5 6.6	17.4 16.9	6.4 6.7	6.6 6.5	307	4.262
23k	$\text{O}\!\!\diagdown\!\!\text{N-}$	Cl	71.6	137	$C_{19}H_{28}ClN_6O_4PS$(d)	45.3 45.6	5.6 5.9	16.7 16.5	6.2 6.5	6.4 6.6	215 256 350	4.192 3.972 4.162
23l	$\text{O}\!\!\diagdown\!\!\text{N-}$	NO_2	54.0	122	$C_{19}H_{28}N_7O_6PS$	44.5 44.7	5.5 5.1	19.1 18.9	6.0 6.2	6.2 6.2	277 347	4.128 4.123

(a) With decomposition. (b) Calcd.: Cl, 7.7; fd, 7.8. (c) Calcd.: Cl, 7.1; fd., 7.1. (d) Calcd.: Cl, 7.1; fd, 6.9. (e) In benzene.

TABLE V

Triamidophosphorothioates

$(R)_3\!\equiv\!P\!=\!S$

Compound	R	Precursor	% Yield	M.p. °C or B.p. °C (mm)	Formula	Mol.-wght. Calcd. Found	C Calcd. Found	H Calcd. Found	N Calcd. Found	P Calcd. Found	S Calcd. Found
24a	$(C_2H_5)_2N\text{-}$	25a 25c	98 91	99-100 (0.01)	$C_{12}H_{30}N_3PS$	279.2 273	51.6 51.8	10.7 10.6	15.1 14.8	11.1 10.9	11.5 11.3
24b	$\diagdown\!\!\text{N-}$	25e 25g	62 78	118	$C_{15}H_{30}N_3PS$	315.3 325	57.2 57.2	9.5 9.8	13.2 13.2	9.8 10.2	10.2 10.4
24c	$\text{O}\!\!\diagdown\!\!\text{N-}$	25i 25k	73 95	141	$C_{12}H_{24}N_3O_3PS$	321.3 319	44.8 45.2	7.5 7.8	13.1 13.0	9.7 9.6	10.0 10.1

(chloroform, carbon tetrachloride) spectra of **23**. However, the ir spectra of **23** show the expected CH stretching vibrations (2970-2960, 2945-2910, 2865-2845) and the CH_2 (and CH_3) deformations near 1460 and 1385 cm^{-1}. Furthermore, the spectra show the C=C stretching vibrations in the 1590 and 1500 cm^{-1} region. The C-O stretching mode of α,β-unsaturated esters (26) gives rise to two strong absorption bands between 1300 and 1250 and 1150 and 1100 cm^{-1}. The bands near 1250 and 1150 cm^{-1} in the spectra of **23** may be tentatively assigned to this vibration. An intense band near 1050 cm^{-1} may be characteristic of the heterocyclic ring system. However, further study of these compounds would be necessary for more accurate assignment of infrared parameters. Compounds **23** absorb strongly in the ultraviolet, and exhibit maxima at 255 ± 5 nm (log $\epsilon \cong$ 4.0) and 350 ± 3 nm (log $\epsilon \cong$ 4.2). In compounds containing the para-nitrophenyl grouping (**23**, d, h, l), the first maximum is shifted toward longer wave lengths (275 ± 2 nm).

SCHEME 2

R = dialkylamino. R' = (4-subst.)-phenyl
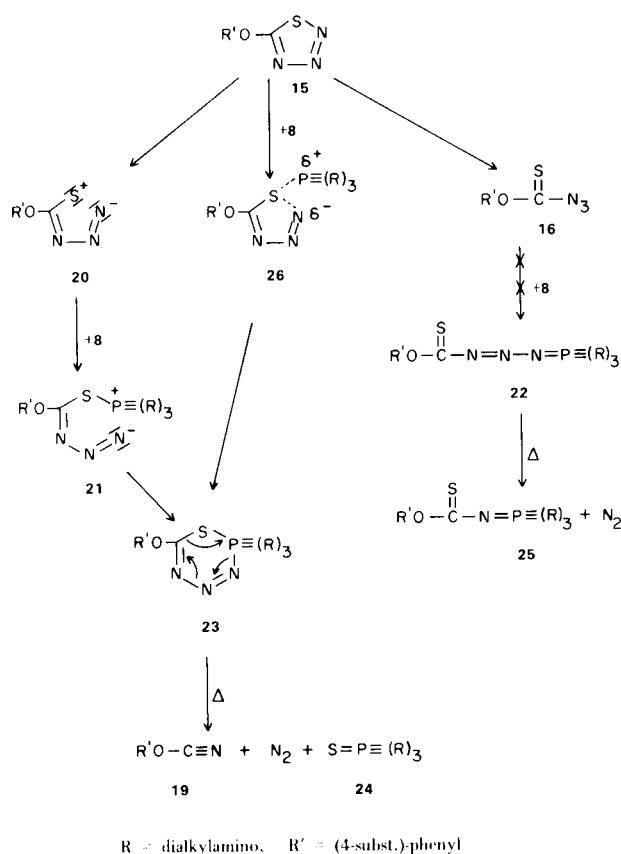
In order to gain a better insight into the structure of **23**, the behavior under electron impact of **23e** (R = piperidino, R' = phenyl) and the two phosphazides, **11b** and

TABLE VI

Mass Spectra

11b (n = 0)
12b (n = 1)
23
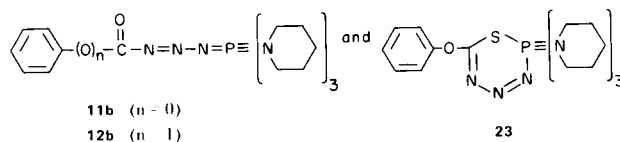
Nominal Mass (m/e)	I (% Abundance) of			Formula Assigned
	11b	12b	23e	
402	6.8	--	--	$(C_5H_{10}N)_3PNC(O)C_6H_5$
325	4.3	3.0	--	$(C_5H_{10}N)_3PNCO$
319	3.7	--	--	$(C_5H_{10}N)_2PNC(O)C_6H_5$
315	--	--	2.8	$(C_5H_{10}N)_3PS$
299	0.1	0.5	0.5	$(C_5H_{10}N)_3PO$
283	0.1	0.1	0.1	$(C_5H_{10}N)_3P$
240	--	0.3	--	$(C_5H_{10}N)_2PNCOH$
236	6.0	--	--	$(C_5H_{10}N)PNC(O)C_6H_5 + 2H$
235	5.7	--	--	$(C_5H_{10}N)PNC(O)C_6H_5 + 1H$
234	2.7	--	--	$(C_5H_{10}N)PNC(O)C_6H_5$
231	--	--	2.4	$(C_5H_{10}N)_2PS$
215	4.6	1.3	0.9	$(C_5H_{10}N)_2PO$
214	0.3	1.4	0.3	
208	--	0.8	--	
199	1.8	1.3	12.5	$(C_5H_{10}N)_2P$
198	3.9	--	0.1	
183	0.6	--	--	
175	--	--	0.1	
170	--	0.6	--	
169	--	0.4	--	
163	--	1.9	--	
157	1.1	0.6	--	$(C_5H_{10}N)PNCO$
156	0.2	0.6	--	
148	--	--	0.5	$(C_5H_{10}N)PSH$
147	--	--	0.3	$(C_5H_{10}N)PS$
146	--	--	0.3	
142	0.3	0.6	--	
141	0.1	1.1	0.1	
132	12.3	0.6	0.2	$(C_5H_{10}N)PO$
131	1.1	0.3	0.1	
130	0.5	0.2	0.2	
121	--	0.2	--	C_6H_5OCO
119	--	0.1	8.3	C_6H_5OCN
116	1.4	1.1	5.4	$(C_5H_{10}N)PH$
115	3.6	0.4	0.5	$(C_5H_{10}N)P$
112	--	2.2	0.1	
105	2.4	--	--	C_6H_5CO
94	--	18.2	3.7	C_6H_5OH
93	--	6.7	0.3	C_6H_5O
91	0.1	--	2.8	
84	37.5	9.9	19.5	$C_5H_{10}N$
77	2.1	5.8	22.8	C_6H_5
74	0.4	2.8	1.8	
70	0.7	2.0	0.5	
66	--	7.3	1.0	
65	--	20.5	3.3	
63	0.2	5.0	3.5	
59	0.1	3.6	0.5	

12b, was investigated; they are listed with their spectra in Table VI. A common feature of the three mass spectra is that the molecular ion is not observed, indicating a great instability of systems containing two adjacent nitrogen atoms (27). The characteristic feature of 11b is the benzoylazido grouping attached to the phosphorous tripiperidide moiety such that upon electron impact nitrogen, phenyl, benzoyl, or piperidino groups may be eliminated. For example, 11b shows a strong peak at m/e 402 which corresponds to M-28 (13b in Table II). The ion at m/e 235 is produced from m/e 402 ion by elimination of a phenyl (m/e 77) group and probably not from the molecular ion. The ion m/e 319, however, is produced by elimination of m/e 84 which is likely the ion of a piperidino group from m/e 402 which on further impact loses a second piperidino group to give the ions at m/e 234. Compound 12b has a phenoxycarbonylazido group attached to the phosphorous tripiperidide moiety. A molecule of nitrogen and the phenoxy (m/e 93) group are eliminated, yielding ion m/e 325 which then loses a piperidino group. In general, 11b and 12b give very similar spectra, except for the phenoxy group and for minor intensity differences. The "thiono analog" of 12b, namely 23e behaves not as anticipated in that the ion m/e 341 which corresponds to that of m/e 325 found in 12b is not present. Instead, strong ions at m/e 315 and m/e 119 are formed both of which are also missing in the mass spectrum of 12b. The ions at m/e 315 (24b in Table V) and m/e 119 (phenyl cyanate) formed by loss of nitrogen are the precursors of many of the ions in the spectrum, fragmenting further by the consecutive elimination of, respectively, piperidino groups and a phenyl moiety.

In conclusion, the above-mentioned fragmentations confirm the structures of 11b and 12b. In the case of 23e however, the observed ions are incompatible with a phosphazide (22) structure, but favor the cyclic 2,2-dihydro-1,3,4,5,2-thiatriazaphosphorine (23) structure.

EXPERIMENTAL

Ultraviolet absorption spectra were determined on a Cary Model 14 recording spectrophotometer. Infrared spectra were recorded on a Perkin Elmer Model 21 spectrometer. Mass spectra were obtained with a CEC 21-110 (direct probe) instrument. The compounds were introduced at 85° and examined at 100° and 5 x 10⁻⁶ mm Hg. Peaks with an intensity greater than 0.05% of the base peak are recorded in Table VI. Molecular weights were determined osometrically in chloroform. All melting and boiling points are uncorrected.

Methods of preparation for many of the starting materials have been described in the literature. These compounds and the appropriate references are as follows: hexaethylphosphorous triamide (28) (8a), phosphorous tripiperidide (29), (8b), phosphorous trimorpholide (30) (8c), benzoyl azide (31) (9, n = 0),

phenyl azidoformate (32) (10, n = 1), 5-phenoxy-1,2,3,4-thiatriazole (22) (15a), 5-(p-tolyloxy)-1,2,3,4-thiatriazole (22) (15b), 5-(4-chlorophenoxy)-1,2,3,4-thiatriazole (22) (15c), 5-(4-nitrophenoxy)-1,2,3,4-thiatriazole (22) (15d).

General Procedure for the Reaction of Phosphorous Triamides (8) with Phenyl Azidoformate (10).

In a typical experiment, a solution of 0.1 mole of hexaethylphosphorous triamide (8a) in 400 ml. of ether was added with stirring at -20° to a solution of 0.1 mole of phenyl azidoformate (10) in 500 ml. of ether. After 10 minutes the turbid solution was cooled to -70° and the pale yellow crystalline solid which precipitated was filtered, washed with cold ether and dried to give phosphazide 12a. Recrystallization from methanol-ether did not change the melting point. Analytical and physical data of a series of phosphazides (11 and 12) are listed in Table I.

Thermal Degradation of Phosphazides (11 and 12).

In a typical experiment, a solution of 0.1 mole of 12a in 200 ml. of toluene was gradually heated with stirring. Between 30-40° the evolution of nitrogen became noticeable. After 1 hour at 90° the yellow solution was concentrated under reduced pressure and kept for 1 day under vacuum (0.001 nm Hg) at 80°. The resulting viscous resin (14a) showed no tendency to crystallize. Tlc analysis (three solvent systems) revealed a single component. Analytical and physical data of a series of acylated iminophosphoranes (13 and 14 are recorded in Table II).

General Procedure for the Reaction of Phosphorous Triamides (8) with 5-Aryloxy-1,2,3,4-thiatriazoles (15).

In a typical experiment, 0.1 mole of hexaethylphosphorous triamide (8a) was added dropwise at -15 to -20° with stirring to a solution of 0.1 mole of 5-phenoxy-1,2,3,4-thiatriazole (15a) in 100 ml. of ether. This addition was exothermic. After 10 minutes an orange red crystalline solid began to precipitate and was removed by filtration. The filter cake was washed with cold ether and dried to give 6-phenoxy-2,2-dihydro-2,2,2-tris(diethylamino)-1,3,4,5,2-thiatriazaphosphorine (23a) in 63.4% yield. The compound was recrystallized from warm (below 40°) ethanol without decomposition. Analytical and physical data of a series of 1,3,4,5,2-thiatriazaphosphorines (23a-I) are listed in Table IV.

Thermal Degradation of 6-Aryloxy-2,2-dihydro-2,2,2-triamino-1,3,4,5,2-thiatriazaphosphorines.

In a typical experiment, 5 g. (185 mmoles) of the above compound (23a) was dissolved in 75 ml. of toluene. This solution was gradually heated to reflux with stirring until evolution of nitrogen had ceased (6 hours). After removal of toluene under reduced pressure, the residual liquid was purified by distillation to give 3.2 g. (98%) of tris(diethylamido) phosphorothioate (24a), b.p. 99-100° (0.01 mm Hg). The purity of the product was 96% (by glc). Analytical and physical constants of a series of triamidophosphorothioates (24) are recorded in Table V.

Reaction of 5-(4-Chlorophenoxy-1,2,3,4-thiatriazole (15c) with Triphenylphosphine.

To a solution of 21.35 g. (0.1 mole) of 15c in 100 ml. of ether was added with stirring at -8° 26.2 g. (0.1 mole) of triphenylphosphine in 150 ml. of ether. The color of the solution changed to yellow. When the temperature was gradually raised to room temperature, nitrogen evolved and the reaction became exothermic causing the ether to boil and a white solid to precipitate. After cooling, filtration yielded 25 g. (85%) of triphenylphosphine sulfide (m.p. 152-153°), identical (by glc, tlc and mixed m.p.) with

an authentic specimen. Concentration of the filtrate afforded a residual liquid which was purified by distillation yielding 15.9 g. (96%) of 4-chlorophenyl cyanate, b.p. 105° (11 mm Hg), m.p. 38-39° (lit. m.p. (22) 38-39°, b.p. 100-101° (10 mm Hg)).

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