Tetrahedron. Vol. 28, pp. 2383 to 2394. Pergamon Press 1972. Printed in Great Britain

TETRAZOLO-AZIDO ISOMERIZATION IN HETEROAROMATICS—IV

REACTIONS OF TETRAZOLOPOLYAZINES WITH TRIPHENYLPHOSPHINE[1]

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(*Received in Japan* 4 *December* 1971; *Received in the UK for publication* 26 *January* 1972)

Abstract—Formation of iminophosphoranes from tetrazolopolyazines and triphenylphosphine has been studied kinetically in various solvents, and the mechanism explained as nucleophilic attack of the phosphine moiety on the trazolo ring. In the equilibrium system of tetrazolopolyazine (**9**) and azidopyrazine (**9a**) in chloroform, it is concluded that tetrazolo and azido moieties react competitively with triphenylphosphine. The mechanism of the reaction of tetrazolopolyazines with triphenylphosphine in chloroform is discussed on a phosphinium radical cation intermediate proposed.

THE EQUILIBRIA of several N-heterocycles bearing an azido group adjacent to the annular nitrogen with the tetrazolo form have been investigated spectroscopically. However, only a few studies on the chemical nature of tetrazolo-azido tautomerism have been reported.[2]

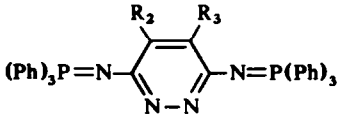
In continuation of our previous work on the tautomerization of tetrazolopolyazines and tetrazolopyridines,[2,3] we report here a comparative study of the reactions of tetrazolopolyazines and azido-pyridazone with triphenylphosphine (TPP), to obtain evidence for the mechanism of the nucleophilic attack of the phosphine moiety at the tetrazolo ring.

RESULTS

Reactions of tetrazolopolyazines and azidopyridazone with TPP. The model compounds (**1–8**) and (**9**) were prepared from the corresponding hydrazino compounds and sodium nitrite by our previously reported method.[2] Compound **11** was synthesized from 1-phenyl-3,5-dichloropyridazone-6 (**10**) and sodium azide (Scheme 1).

The reactions of tetrazolo[1,5-*a*]pyridazines (**2–4** and **6–8**), 5,6-diphenyltetrazolo[1,5-*a*]pyrazine (**9**) and 1-phenyl-3-chloro-5-azidopyridazone-6 (**11**) with TPP in various solvents at room and reflux temperature afforded the iminophosphorane derivatives (**12–14**, **15–17**, **19** and **20**, respectively). These results are summarized in Scheme 2 and Table 1.

Interestingly, **1** and **5** did not react with TPP, even in refluxing chlorobenzene. The reactions of **6–8** with excess TPP did not afford bis-iminophosphorane compounds (**18**) but gave the corresponding monosubstituted compounds **15–17**.



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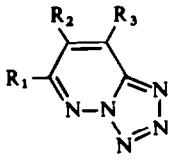
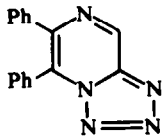
SCHEME 1.



	R_1	R_2	R_3
1	H	H	H
2	Cl	H	H
3	Cl	Me	H
4	Cl	H	Me
5	OMe	H	H
6	N_3	H	H
7	N_3	Me	H
8	N_3	H	Me



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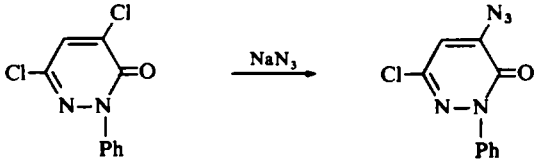
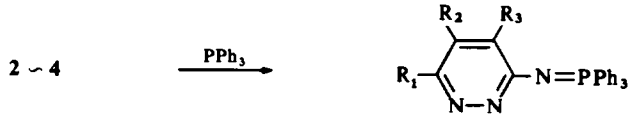
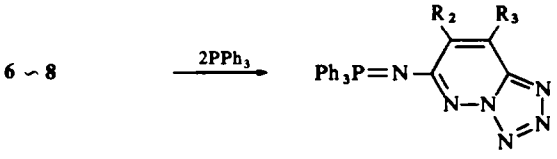


10 **11**

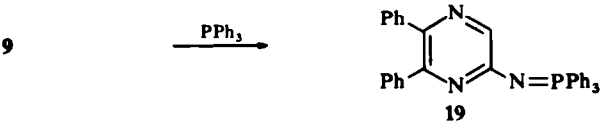
SCHEME 2.



	R_1	R_2	R_3
12	Cl	H	H
13	Cl	Me	H
14	Cl	H	Me



	R_2	R_3
15	H	H
16	Me	H
17	H	Me



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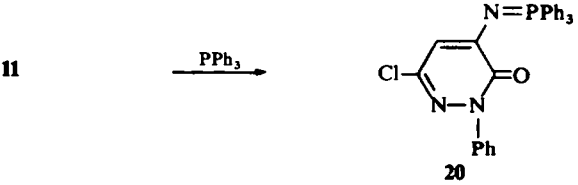

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TABLE 1. REACTIONS OF TETRAZOLOPOLYAZINES AND AZIDOPYRIDAZONE WITH TPP IN VARIOUS SOLVENT

Compound No.	Solvent	Temp. (°C)	Time (hr)	Compound No.	Product Yield (%)	M.p. (°C)	IR (KBr) $\nu_{N=P}(cm^{-1})$	UV (EtOH) λ_{max}(mu)	NMR ($CDCl_3$) τ
1	PhCl	115	10	Recovery of starting material					
2	PhCl	100	7	**12**	78	174–176	1418	263(ε = 15200)	3·18(s, 2-H) 2·03–2·92(m, 15-H)
3	PhCl	110	22	**13**	80	215–217	1420	261(ε = 18000)	7·81(s, 3-H) 3·75(s, 1-H) 2·50–2·73(m, 15-H)
4	PhCl	110	22	**14**	75	199–201	1420	262(ε = 18000)	7·62(s, 1-H) 3·10(s, 1-H) 2·30–2·73(m, 15-H)
5	PhCl	130	22	Recovery of starting material					
6	EtOH	25	1·0	**15**	100	231–233	1419 1429 1442	309(ε = 2450)	2·80(d, *J* 9 Hz, 1-H) 2·00–2·65 (m, 16-H)
6	PhCl	100	10	**15**	100				
7	EtOH	25	1·0	**16**	100	250–252	1420 1483	308(ε = 4260) 218(ε = 37800) (Sh)	7·42(s, 1-H) 1·03–2·68 (m, 16-H)
8	EtOH	25	1·0	**17**	95	242–244	1418 1438	307(ε = 2380) 223(ε = 27700) (Sh)	7·43(s, 3-H) 2·99(s, 1-H) 1·96–2·70(m, 15-H)
9	EtOH	25	1·0	**19**	95	276–278	1425 1447	350(ε = 13000) 299(ε = 24000)	2·09–3·35 (m, 25-H) 1·68(s, 1-H)
11	EtOH	25	1·0	**20**	94	202–204	1425	336(ε = 20200)	3·40(s, 1-H) 2·11–2·78 (m, 20-H)

Kinetic studies of the reactions of tetrazolopolyazines and azidopyridazone with TPP. With a view to obtaining kinetic information on the above mentioned reactions, the reaction of the rates of compounds **2**, **3**, **4**, **9**, and **11** with TPP were measured in DMSO, $CHCl_3$, and AcOH by UV spectrometry: the results are summarized in Tables 2, 3, and 4.

Second-order kinetics were clearly observed at each approximate concentration in all runs. However, the reaction rates of compounds **6**, **7**, and **8** with TPP could not be measured by UV spectrophotometry because of overlapping of the absorption maxima of both the azido- and iminophosphorane compounds. The rate measure-

TABLE 2. THE REACTION RATES OF TETRAZOLOPYRIDAZINES WITH TPP $v = k_2$ (TETRAZOLOPYRIDAZINES) (TPP)

Compound No.	Solvent	Temp. (°C)	$k_2(M^{-1}sec^{-1})$	Relative rate	$\Delta H^{\ddagger}$ (Kcal/mol)	$\Delta S^{\ddagger}$ (e.u)
	$CHCl_3$	32	$3{\cdot}92 \times 10^{-6}$			
		55	$5{\cdot}70 \times 10^{-5}$			
		32	$5{\cdot}56 \times 10^{-6}$			
		55	$4{\cdot}27 \times 10^{-5}$			
2	DMSO	89	$5{\cdot}30 \times 10^{-4}$			
		100	$9{\cdot}58 \times 10^{-4}$	1·0	17·2	−26·6
		110	$1{\cdot}94 \times 10^{-3}$			
	$CHCl_3$	55	$5{\cdot}62 \times 10^{-5}$			
	DMSO	55	$4{\cdot}21 \times 10^{-5}$			
3		89	$5{\cdot}23 \times 10^{-4}$			
		100	$9{\cdot}55 \times 10^{-4}$	1·0	16·5	−28·4
		110	$1{\cdot}83 \times 10^{-3}$			
	DMSO	89	$3{\cdot}35 \times 10^{-5}$			
4		100	$5{\cdot}74 \times 10^{-5}$	0·06	14·2	−40·6
		110	$9{\cdot}82 \times 10^{-5}$			

TABLE 3. REACTION RATES OF **11** WITH TPP $v = k_2(11)$ (TPP)

Solvent	Temp.(°C)	$k_2(M^{-1}sec^{-1})$	$\Delta H^{\ddagger}$ (Kcal/mol)	$\Delta S^{\ddagger}$ (e.u)
DMSO	20	$2{\cdot}18 \times 10^{-1}$		
	25	$2{\cdot}98 \times 10^{-1}$	8·20	−33·4
	28	$3{\cdot}24 \times 10^{-1}$		
	37	$4{\cdot}88 \times 10^{-1}$		
$CHCl_3$	14	$8{\cdot}75 \times 10^{-2}$		
	20	$1{\cdot}50 \times 10^{-1}$		
	25	$2{\cdot}31 \times 10^{-1}$	14·8	−11·8
	28	$2{\cdot}83 \times 10^{-1}$		
$CHCl_3 + I_2$	20	$9{\cdot}18 \times 10^{-2}$		
AcOH	20	$1{\cdot}72 \times 10^{-1}$		
	25	$2{\cdot}45 \times 10^{-1}$	10·1	−27·6
	28	$2{\cdot}78 \times 10^{-1}$		
	37	$4{\cdot}58 \times 10^{-1}$		

TABLE 4. REACTION RATES OF **9** WITH TPP $v = k_2(9)$ (TPP)

Solvent	Temp. (°C)	$k_2(M^{-1}sec^{-1})$	Relative rate	$\Delta H^{\ddagger}$ (Kcal/mol)	$\Delta S^{\ddagger}$ (e.u)
DMSO	22	$3{\cdot}95 \times 10^{-3}$			
	27	$4{\cdot}49 \times 10^{-3}$	1·00	11·5	−31·2
	32	$6{\cdot}03 \times 10^{-3}$			
	37	$8{\cdot}83 \times 10^{-3}$			
	42	$1{\cdot}09 \times 10^{-2}$			
$CHCl_3$	22	$9{\cdot}00 \times 10^{-3}$			
	27	$1{\cdot}41 \times 10^{-2}$	3·14	13·8	−21·0
	32	$1{\cdot}95 \times 10^{-2}$			
$CHCl_3 + I_2$	27	$1{\cdot}36 \times 10^{-2}$			
AcOH	21	$1{\cdot}93 \times 10^{-2}$			
	27	$2{\cdot}98 \times 10^{-2}$	6·64	12·7	−23·2

TABLE 5. REACTION RATES OF **9**, and **9a** WITH EXCESS TPP AT 37°C

Solvent	9(M)	TPP(M)	TPP/9	$K_{obs}(sec^{-1})$
DMSO	0·005	0·025	5	$1{\cdot}83 \times 10^{-4}$
	0·005	0·035	7	$3{\cdot}00 \times 10^{-4}$
	0·005	0·050	10	$4{\cdot}57 \times 10^{-4}$
	0·005	0·075	15	$6{\cdot}38 \times 10^{-4}$
	9a			$k_2(M^{-1}sec^{-1})$
AcOH				$5{\cdot}29 \times 10^{-2}$
DMSO				$6{\cdot}72 \times 10^{-2}$*
				$6{\cdot}45 \times 10^{-2}$*
				$6{\cdot}19 \times 10^{-2}$*
				$5{\cdot}64 \times 10^{-2}$*

* Calculated from $5{\cdot}29 \times 10^{-2} \times \frac{\text{rate const. of 11 in DMSO(at 20} \sim 37°)}{\text{rate const. of 11 in AcOH (at 20} \sim 37°)}$

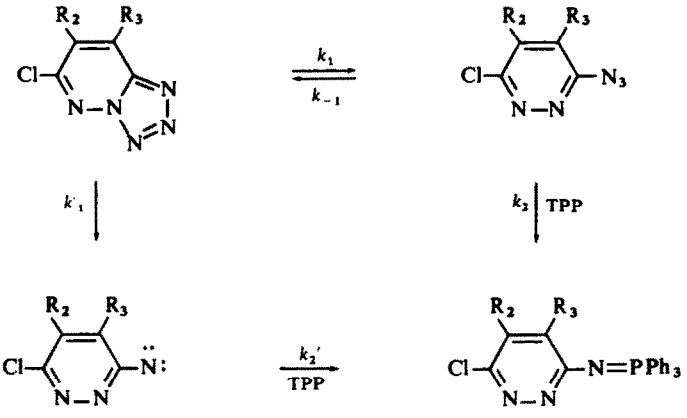
ments at various temperatures afforded the activation energy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) for each reaction. The reaction of **9** with excess TPP, both in DMSO and in AcOH at 37°, was demonstrated to be pseudo-first order as shown in Table 5.

DISCUSSION

The substituent effect plays an important role in reactions of tetrazolopolyazine derivatives with TPP; electron attracting substituents such as a chloro group appear to be effective in destabilizing the tetrazolo ring resulting in the formation of the iminophosphorane, while electron-releasing substituents such as methoxy- and iminophosphoranyl groups stabilize the tetrazolo ring and suppress the reaction. For compounds **1**–**5**, a complete absence of the azido form at room temperature has been reported.[2] In fact, no azido absorption was observed for these compounds ir $CHCl_3$, DMSO, and DMSO containing equivalent TPP even at elevated temperature (100 and 110°) by IR and NMR spectral inspections.

Similarly with compounds **6–8** having both fused-tetrazolo and azido moieties, no equilibria with the diazido forms were observed even at 50–100°; while compound **7** is isomerized to **8** in DMSO at 89 and 94°.[4] If either the azido tautomer or the nitrene derivable from **2**, **3**, and **4** reacts with TPP, then first-order kinetics should be obtained which are determined by k_1 and k_1' as shown in Scheme 3, since the azido- and nitrene moieties could react very rapidly with TPP at elevated temperature (80–110°). However, neither the azido tautomer nor the nitrene were observed by spectral inspection or by the thermal condition, and the reaction rates measured showed second-order kinetics. The rate constants for compounds **2**, **3**, and **4** with TPP in DMSO at 89, 100 and 110° were relatively smaller than those for **11** in DMSO even at 20, 25 and 28°.

SCHEME 3.

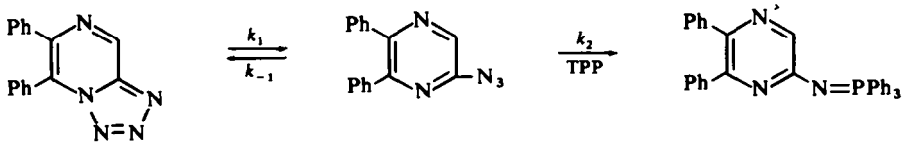


On the other hand, the reaction rate of compound **4**, bearing a methyl group adjacent to the tetrazolo ring, was very slow; the rate ratio of compounds **4**/**2** was 0·06 at 100°, though that of compounds **2**/**3** was 1·0 at 100°. The slow rate might originate from steric repulsion of the methyl group by TPP rather than from the inductive effect of the methyl group. Similar phenomena have been observed for the reaction rate of *o*-methyl phenyl azide with TPP.[5] These facts show that TPP attacks at the N-1 atom of the tetrazolo[1,5-*b*]pyridazine system.

As already reported,[2] IR and NMR inspections have shown that compound **9** exists only as the tetrazolo form in DMSO even at elevated temperature (about 80°C), as the azido-tetrazolo tautomer equilibrium mixture in $CHCl_3$ and exclusively as the azido form in AcOH. The temperature effect on the equilibrium constant (K) of **9** in CHCl is calculated to be 0·30 at 25°, 0·38 at 38°, and 0·52 at 58° respectively, from the ratios of its intensity of the ring proton signals of the azido tautomer to those of the tetrazolotautomer. Thus, the isomerization is found to be endothermic with the heat of tautomerization $\Delta H = 4{\cdot}8 \pm 0{\cdot}5$ kcal/mol (Fig 1).

Further, the equilibrium constant in $CHCl_3$ was unchanged at various concentrations of **9**. Here, we can correlate the equilibrium with the kinetic results obtained for the reaction of **9** with TPP in DMSO.

SCHEME 4.



9 **9a** **19**

If we assume an equilibrium ($K = k_1/k_{-1}$) between **9** and **9a**, followed by the reaction of **9a** with TPP, i.e. a two-step mechanism, then the rate of formation of **19** is expressed as eq. 1.

$$\frac{d[\mathbf{19}]}{dt} = k_2[\mathbf{9a}][\text{TPP}] \tag{1}$$

Since, spectra shows that exact azido-tetrazolo equilibrium does not exist, we can approximate a steady state on **9a**.

Hence, we obtain eq. 2.

$$\frac{d[\mathbf{9a}]}{dt} = k_1[\mathbf{9}] - k_{-1}[\mathbf{9a}] - k_2[\mathbf{9a}][\text{TPP}] = 0$$

$$[\mathbf{9a}] = \frac{k_1[\mathbf{9}]}{k_{-1} + k_2[\text{TPP}]}$$

$$\frac{d[\mathbf{19}]}{dt} = k_2[\mathbf{9a}][\text{TPP}] = \frac{k_1k_2[\mathbf{9}][\text{TPP}]}{k_{-1} + k_2[\text{TPP}]} \tag{2}$$

Under conditions where the concentration of TPP is much larger than that of **9**, the concentration of TPP can be taken as constant throughout the reaction period.

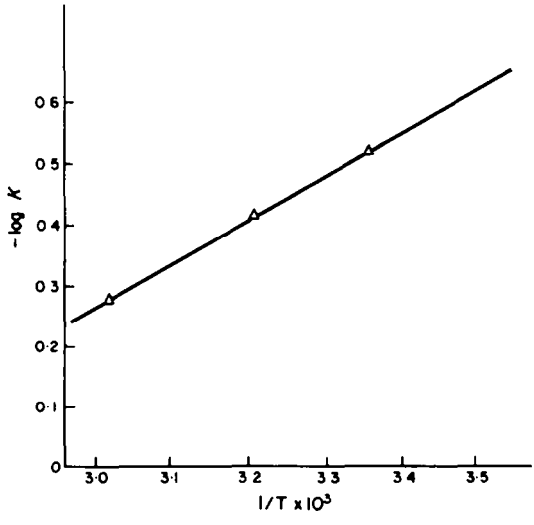


FIG 1. Effect of temperature on the equilibrium constant (K) for **9** in $CHCl_3$

$$\frac{k_1k_2[\mathrm{TPP}]}{k_{-1}+k_2[\mathrm{TPP}]}=k_c \tag{3}$$

Thus, k_c is the pseudo-first order rate constant varying TPP and we get eq. 4.

$$\frac{d[\mathbf{19}]}{dt}=k_c[\mathbf{9}] \tag{4}$$

According to the magnitudes of k_1, k_{-1} and k_2, the situation can be further divided into the following cases (a), (b) an (c).

(a) $k_2[\mathrm{TPP}] \ll k_1$ and k_{-1}
From eq. (4), we have

$$\frac{d[19]}{dt}=(k_1/k_{-1})\,k_2[\mathbf{9}][\mathrm{TPP}], \quad \text{and} \quad k_c=(k_1/k_{-1})k_2[\mathrm{TPP}].$$

The combination of [**9a**] with TPP, slow compared to the rapid equilibration, is the rate-determining step (case (a)).

(b) $k_2[\mathrm{TPP}] \gg k_1$ and k_{-1}

$$\frac{d[\mathbf{19}]}{dt}=k_1[\mathbf{9}] \quad \text{and} \quad k_c=k_1$$

The first equilibrium step becomes the rate-determining step (case (b)).

(c) $k_2[\mathrm{TPP}] \simeq k_1$ and k_{-1}
Here, the relation is represented by eqs (2) and (3) (case (c)).

(d) If the reaction of **9** with TPP proceeds without intervention of **9a** and produces **19** with the second-order rate constant of k_2', we have

$$\frac{d[\mathbf{19}]}{dt}=k_2'[\mathbf{9}][\mathrm{TPP}] \tag{5}$$

Under the condition of excess TPP, we have

$$\frac{d[\mathbf{19}]}{dt}=k_c'[\mathbf{9}] \quad \text{where} \quad k_c'=k_2'[\mathrm{TPP}] \quad (\text{case (d)}).$$

This relation should be the same as that in case (a). Cases (a)–(d) are graphically shown by plotting k_c of k_c' against concentration of TPP.

The pseudo first-order rate constant k_{obs} obtained at various concentrations of TPP at 37° are shown in Table 5. A plot of k_{obs} *vs.* [TPP] gives a straight line as shown in Fig 2, thus excluding cases (b) and (c). From the slop, $(k_1/k_{-1})k_2$ or k_2' can be evaluated as shown in Table 5. If we can evaluate k_2 in DMSO, then the equilibrium constant ($K=k_1/k_{-1}$) at 37° can be determined. We estimated k_2 from the reaction rate constant of **9a** with excess TPP in AcOH and from the relative ratio of the reaction rates of **11** in DMSO and AcOH. Thus, we estimated k_2 as $5{\cdot}64 \sim 6{\cdot}72 \times 10^{-2}$ and then obtained the value 0·15–0·13 for K; the equilibrium constant is apparently inconsistent with the experimental fact that the azido tautomer is not detected spectrally in DMSO. The calculated value of $8{\cdot}57 \times 10^{-3}$ corresponds to the second-order rate constant of **9** with TPP in DMSO at 37°, indicating case (d). Even if there are some errors in the estimation of k_2, the value is still inconsistent with the

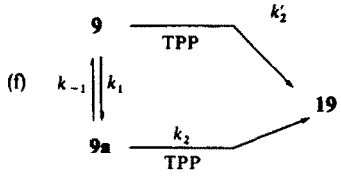
undetectable K value indicated by spectrophotometry, since the k_2 value in DMSO is expected to be close to the value in AcOH.

Consequently, it is reasonable to assume that destabilization of the tetrazolo ring by nucleophilic attack of TPP results in the formation of iminophosphorane. In the apparent rapid pre-equilibrium system **9** ⇌ **9a** in $CHCl_3$, we can consider the following cases; (e) and (f).

(e) $$\mathbf{9} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{9a} \xrightarrow[\text{TPP}]{k_2} \mathbf{19}$$

$$\frac{d[\mathbf{19}]}{dt} = k_2 K[\mathbf{9}][\text{TPP}] \tag{6}$$

(f)



$$\frac{d[\mathbf{19}]}{dt} = (k_2' + k_2K)[\mathbf{9}][\text{TPP}] \tag{7}$$

Here, we calculated k_2K by estimating k_2 as in the above described approximation, and $(k_2' + k_2K)$ by estimating k_2' from the rate constant of the reaction of **9** with TPP in DMSO, and by the relative ratio of the rates of the reaction of **2** with TPP in $CHCl_3$ and DMSO (Table 2). The observed and calculated rate constants are summarized in Table 6.

TABLE 6. CALCULATED AND OBSERVED RATE CONSTANT OF THE REACTION OF **9** ⇌ **9a** WITH TPP IN $CHCl_3$

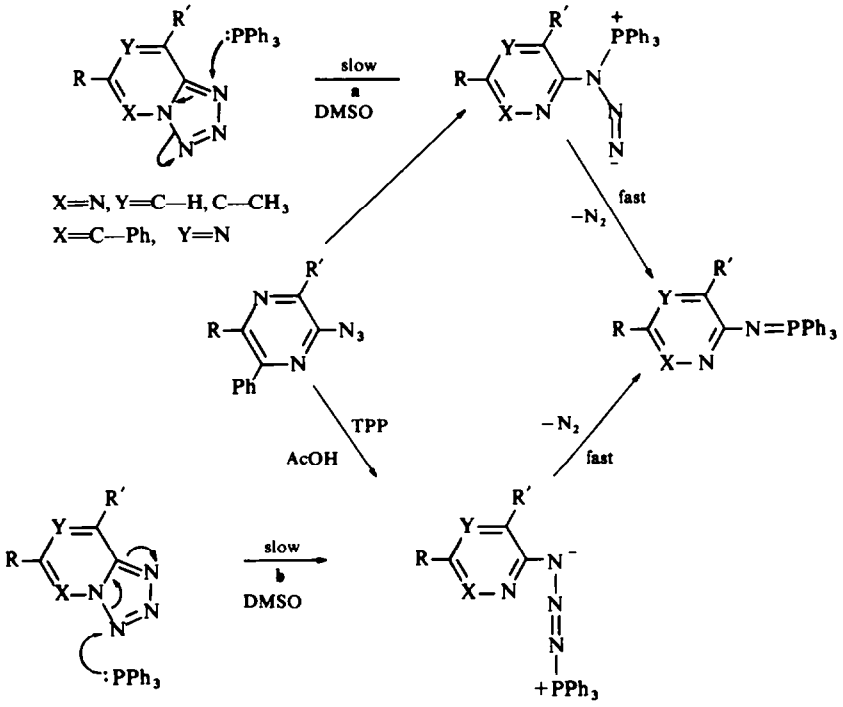
Temp/°C	k_2	k_2'	K*	k_2K	$k_2' + k_2K$	k_{obs} ($M^{-1}sec^{-1}$)
22	$1{\cdot}84 \times 10^{-2}$	$5{\cdot}61 \times 10^{-3}$	0·29	$5{\cdot}34 \times 10^{-3}$	$1{\cdot}10 \times 10^{-2}$	$9{\cdot}00 \times 10^{-3}$
27	$2{\cdot}98 \times 10^{-2}$	$6{\cdot}38 \times 10^{-3}$	0·32	$9{\cdot}54 \times 10^{-3}$	$1{\cdot}59 \times 10^{-2}$	$1{\cdot}41 \times 10^{-2}$
32	$4{\cdot}12 \times 10^{-2}$	$8{\cdot}56 \times 10^{-3}$	0·34	$1{\cdot}40 \times 10^{-2}$	$2{\cdot}26 \times 10^{-2}$	$1{\cdot}95 \times 10^{-2}$

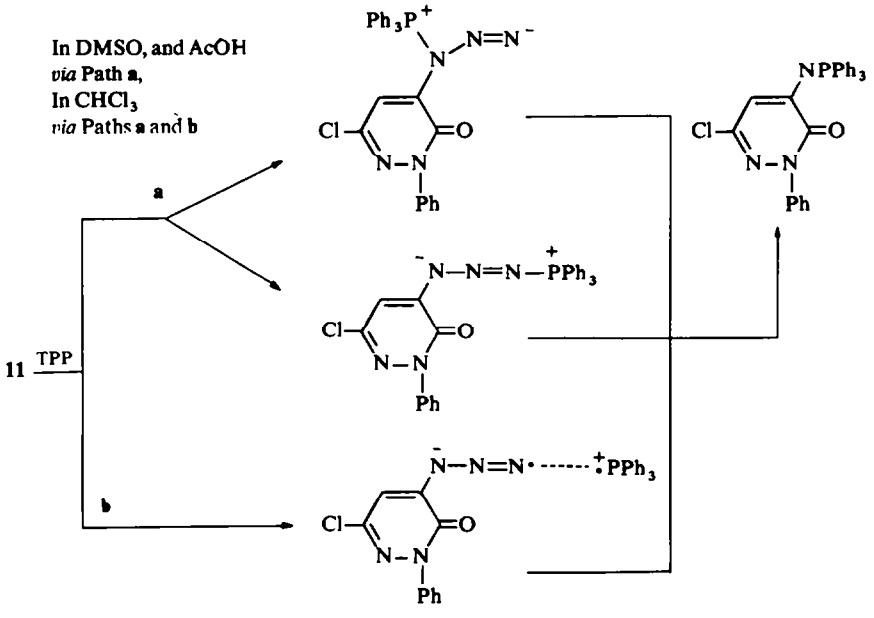
*K: Equilibrium constant (calculated from Fig 1).

It is to be noted that while considerable deviation between k_2K and the observed rate constants is admitted, $(k_2' + k_2K)$ is in accordance with the observed rate constant; that the reaction of **9** with TPP can take place without the intervention of the azido form, even in DMSO, suggests the iminophosphorane formation occurs by competitive reaction paths, as described by eq. (7).

Finally, there is an additional comment which may be made on the rate studies. As we previously suggested,[2] the involvement of a charge-transfer complex (radical

SCHEME 5.


X=N, Y=C—H, C—CH3
X=C—Ph, Y=N
slow
a
DMSO
fast
−N2
TPP
AcOH
slow
b
DMSO
−N2
fast


In DMSO, and AcOH
via Path a,
In CHCl3
via Paths a and b
11
TPP
a
b

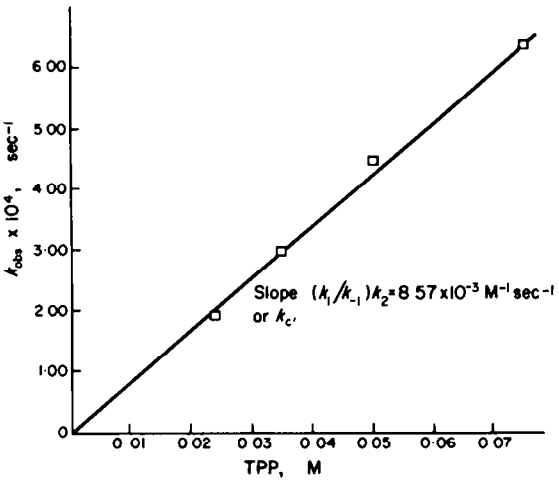


FIG 2. Correlation of k_{obs} and TPP at 37°C

ion pair) in the transition state of the reaction of azidopyridine derivatives with TPP in $CHCl_3$ is suggested by the activation entropy of $+6 \backsim -2$ eu, and by the rate retardation on adding a radical inhibitor; the activation entropy in $CHCl_3$ is significantly different from that in DMSO. In addition, a phosphinium radical cation intermediate has been postulated in several organic reactions of phosphorous compounds.[6–8] Such a mechanism demands a higher $\Delta H^{\ddagger}$ and a lower negative $\Delta S^{\ddagger}$ because of the high degree of freedom in the transition state. In the reaction of **11** with TPP in $CHCl_3$, the value of $-11{\cdot}8$ eu for the activation entropy suggests dual reaction pathways; *via* the charge-transfer complex (path **a**) and *via* the betaine for (path **b**), the existence of path **a** being supported by the fact that radical inhibitors such as iodine slightly retard the rate in $CHCl_3$ (Table 3). However, in the reaction of **9** with TPP in $CHCl_3$, the value of $-21{\cdot}0$ eu for the activation entropy is normal for these reactions in various solvents, so the reaction would seem to proceed only *via* the betaine intermediate. This assumption is also supported by the fact that addition of a radical inhibitor does not retard the rate in $CHCl_3$ (Table 4). The overall mechanisms concluded for these reactions with TPP in various solvents are shown in Scheme 5.

EXPERIMENTAL

M.ps were measured on a Yanagimoto micro apparatus and are uncorrected. The microanalyses were performed on a Perkin–Elmer 240 elemental analyser, while the IR and UV spectra were obtained on JASCO Model IR-S and ORD/UV-5 spectrometers, respectively. The NMR spectra were recorded with a JEOL Model C-60-XL spectrometer with TMS as internal standard.

1-Phenyl-3-chloro-5-azido-pyridazone-6 (**11**). 1-Phenyl-3,5-dichloropyridazone-6 (2·4 g) was dissolved in 70 ml of hot EtOH (70%). The solution was cooled to 40°, and NaN_3 (0·72 g) in 100 ml of water was then added in one portion. The mixture was heated at 75–80° for 3–4 hr. and excess solvents evaporated under reduced pressure. Extraction of the residue with $CHCl_3$ afforded colorless crystals (60–70%), m.p. 117° (decomp.); ν (KBr) 2170 cm^{-1} (N_3), τ ($CDCl_3$) 3·32 (s, 1H), 2·40–2·69 (m, 5H), λ_{max} (EtOH) 326 (8400), 297 (6800), 222 nm (ε 14200). (Calc for $C_{10}H_6N_5OCl$: C, 48·50; H, 2·44; N, 28·28. Found: C, 48·41; H, 2·51; N, 28·23%).

Compound **11** (0·2 g) in toluene (10 ml) was refluxed for 4 hr. After evaporation of solvent *in vacuo*, the residue was purified by silica-gel chromatography ($CHCl_3$—MeOH) to give 1-phenyl-3-chloro-5-amino-pyridazone-6 (0·13 g, m.p. 181–185°), which was identified with an authentic sample.[9]

Reactions of tetrazolopolyazines and 1-phenyl-3-chloro-5-azidopyridazone-6. General method: A mixture of tetrazolopolyazines (0·001 mol) and/or 1-phenyl-3-chloro-5-azido-pyridazone-6 (0·001 mol) with TPP (0·0011 mol) in the respective solvent was stirred at room temperature, and or heated in an oil bath. The solvent was evaporated *in vacuo*, and the residue recrystallized from EtOH-C_6H_6. Physical and spectral data are summarized in Table 1. (Calc for $C_{22}H_{17}N_3PCl$(12): C, 67·78; H, 4·40; N, 10·78. Found: C, 67·94; H, 4·49; N, 10·94. Calc for $C_{23}H_{19}N_3PCl$(13): C, 68·40; H, 4·75; N, 10·41. Found: C, 68·48; H, 4·81; N, 10·34. Calc for $C_{23}H_{19}N_3PCl$(14): C, 68·40; H, 4·75; N, 10·41. Found: C, 68·53; H, 4·62; N, 10·42. Calc for $C_{22}H_{17}N_6P$(15): C, 66·59; H, 4·29; N, 21·19. Found: C, 66·49; H, 4·33; N, 21·00. Calc for $C_{23}H_{19}N_6P$(16): C, 67·31; H, 4·67; N, 20·48. Found: C, 67·30; H, 4·59; N, 20·55. Calc for $C_{23}H_{19}N_6P$(17): C, 67·31; H, 4·67; N, 20·48. Found: C, 67·35; H, 4·55; N, 20·48. Calc for $C_{34}H_{26}N_3P$(19): C, 80·45; H, 5·16; N, 8·28. Found: C, 80·44; H, 5·26; N, 8·24. Calc for $C_{28}H_{21}N_3OPCl$(20): C, 69·78; H, 4·39; N, 8·72. Found: C, 69·88; H, 4·42; N, 8·59%).

Kinetics. The reaction was started by rapid addition of tetrazolopolyazines and/or 1-phenyl-3-chloro-5-azido-pyridazone-6 to an equimolar solution ot TPP in DMSO, in $CHCl_3$, or AcOH, both reactants having previously reached temperature equilibrium in a thermostat. The reaction was carried out under stirring in a glass-stopped flask as a homogeneous system. Aliquots were taken out at appropriate time intervals. The reaction was stopped by dilution with EtOH. Products were determined by UV spectrophotometry at the maximum of the wave length and the molar extinction coefficient (ε) of either the reaction product or the starting material. The k value is fairly constant up to 60–80% conversion.

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