Structure and Decomposition of a Staudinger Reaction Intermediate [1-Methyl-(or phenyl-)3-tris(dimethylamino)phosphoranylidenetriazene]

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Unstable intermediates $(Me_2N)_3PN_3R$ have been isolated from Staudinger reactions between hexamethylphosphorous triamide and methyl or phenyl azides. N.m.r. data strongly support the presence of a linear skeletal P=N–N=N framework in these compounds. Kinetic studies of the thermal decomposition of the phenyl derivative in methoxybenzene has afforded activation parameters ($\Delta H^‡$ 95 kJ mol^{-1}; $\Delta S^‡$ −40 J mol^{-1} K^{-1}) indicative of a constrained transition state for this decomposition.

REACTIONS between three-co-ordinate phosphorus nucleophiles and organic azides to produce iminophosphoranes [equation (1)] were discovered in 1919 by Staudinger.[1]

$$R^1_3P + R^2N_3 \longrightarrow R^1_3P{:}NR^2 + N_2 \qquad (1)$$

There have been a number of studies of the mechanism of reactions of this type [2,3] and it is generally accepted that an intermediate adduct often plays a part.[3] We have now isolated rather unstable adducts from reactions between hexamethylphosphorous triamide and methyl or phenyl azide.[4] Structural studies strongly support the presence of a $P=N-N=NR^2$ linear skeletal arrangement in the adducts. The characteristics and kinetics of the thermal decomposition of the adduct from phenyl azide have been examined in order to elucidate the mechanism of this particular Staudinger reaction.

EXPERIMENTAL

Materials.—Hexamethylphosphorous triamide was a redistilled commercial sample. ^1H N.m.r. spectroscopy indicated that the content of proton-containing impurities was well below 1%. Methyl and phenyl azides were prepared by published procedures.[5]

Instrumentation.—I.r. spectra were determined on a Beckman IR-5 spectrometer; u.v. spectra on a Cary 14 spectrometer, ^1H n.m.r. spectra on a Varian A-60 spectrometer, ^{31}P n.m.r. spectra on a Varian HA-100 spectrometer, and ^{13}C n.m.r. spectra on a Bruker HX-90 spectrometer by Fourier transform methods.

Kinetics.—The apparatus used was a simplified version of one described in the literature.[3] Magnetic stirring was used to eliminate the problem of leakage at the stirring gland. The gas burette was not thermostatted, but laboratory temperatures, checked during runs, were constant within ±1°.

1-*Phenyl*-3-*tris*(*dimethylamino*)*phosphoranylidenetriazene* (I; R = Ph).—A solution of hexamethylphosphorous triamide (6·32 g, 0·039 mol) in diethyl ether (50 ml) was added dropwise to a stirred solution of phenyl azide (4·61 g, 0·039 mol) in diethyl ether (50 ml) maintained at or below 5°. Yellow crystals of the adduct were formed during the addition. The mixture was then cooled to −35° and filtered. The crystalline product was recrystallized from diethyl ether to yield the adduct (6·3 g, 57%), which was too unstable to give reliable elemental analytical figures. It was characterized by its spectral parameters (see later) and by its quantitative thermal decomposition.

When a solution of the adduct in methoxybenzene was heated at 130° it yielded nitrogen and phenyliminotris(dimethylamino)phosphorane [5] quantitatively.

The 1-methyl analogue (I; R = Me) was prepared analogously from hexamethylphosphorous triamide and methyl azide. It was thermally unstable at room temperature and so was only characterized spectrally (see later) and by its decomposition to nitrogen and methyliminotris(dimethylamino)phosphorane.[5]

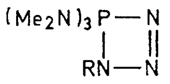
RESULTS AND DISCUSSION

Structures of the Adducts.—I.r. spectral data indicate that the adducts are not in equilibrium with any substantial amounts of their components in solution. Phenyl azide has an intense i.r. absorption at 2125 cm^{-1} which is attributed to the antisymmetric mode of the N_3 fragment;[6] the analogous band of methyl azide is at 2090 cm^{-1}. The recrystallized adduct from phenyl azide and hexamethylphosphorous triamide has only one notable absorption between 1700 and 2800 cm^{-1}, either in the solid state (KBr) or in solution (CCl_4 or CH_2Cl_2), a medium intensity band at 2006 cm^{-1}. The methyl azide adduct, which is impossible to purify because of its ready thermal decomposition, has a sharp weak band at 2040 cm^{-1}. These new bands near 2000 cm^{-1} may be genuine skeletal absorptions of the PN_3 system. There is no trace of bands attributable to free azide in the spectra of solutions of the compounds, however. It seems, therefore, that the adducts are not in mobile equilibrium with detectable amounts of their components in solution, as is the case for certain other Staudinger reactions.[3]

Several valence bond structures can be drawn for the adducts, *e.g.* a linear phosphoranylidenetriazene structure

$$(Me_2N)_3P{:}N{\cdot}N{:}NR \qquad (I)$$

$$(Me_2N)_3P{:}\overset{+}{N}R{\cdot}N{:}\overset{-}{N} \qquad (II)$$



(III)

(I), a dipolar branched chain structure (II), or a heterocyclic formulation (III). The u.v. spectrum of the

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[1] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.

[2] L. Horner and A. Gross, *Annalen*, 1955, **591**, 117.

[3] J. E. Leffler and R. D. Temple, *J. Amer. Chem. Soc.*, 1967, **89**, 5235 and references therein.

[4] Farberfabriken Bayer A.G., Ger. Pat. 1,104,958/1960 (*Chem. Abs.*, 1962, **56**, 10,041e).

[5] H. Goldwhite, P. Gysegem, S. Schow, and M. Swyke, preceding paper.

[6] L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1968, p. 62.

phenyl azide adduct (Table 1) strongly suggests that it contains a more extended conjugated system than that in phenyl azide itself; new intense longer wavelength bands appear at 300 and 310 nm. However all three formulations (I)—(III) would at least be compatible with this observation.

TABLE 1

U.v. spectra

Compound	Solvent	Conc. (M)	$\lambda_{max.}$/ nm	$\varepsilon_{max.}$/ l mol^{-1} cm^{-1}
PhN_3	Cyclohexane	$5·95 \times 10^{-5}$	249	10 800
			278	2350
			286	1850
$PhN_3P(NMe_2)_3$	Et_2O	$4·80 \times 10^{-5}$	223	12 400
			290	13 400
			300	14 900
			310	14 200
$PhN{:}P(NMe_2)_3$	Et_2O	$3·00 \times 10^{-5}$	257	16 900
			290	2060

N.m.r. spectra (Table 2) give more discriminatory information which points towards structure (I) as the best formulation. Thus in the methyl azide adduct $[(Me^A)_2N]_3PN_3Me^B$ there is no detectable coupling between the phosphorus nucleus and the Me^B protons whereas the Me^A groups show $^3J_{HCNP}$ 9·6 Hz. In both structures (II) and (III) all the methyl protons are three bonds removed from phosphorus and would be expected to show P,H coupling. However in structure (I) Me^B has its protons five bonds removed from phosphorus, and such a long-range coupling would be expected to be small or undetectable.

TABLE 2

N.m.r. spectra

^{1}H Spectra [a]

	$[(CH_3)_2N]_3P$	$[(CH_3)_2N]_3PN_3CH_3$		$[(CH_3)_2N]_3P{:}NCH_3$	
δ	2·45	2·68	3·37	2·40	2·70
$J_{H,P}$	9·0	9·6	0	9·5	23·3

	$[(CH_3)_2N]_3PN_3C_6H_5$		$[(CH_3)_2N]_3P{:}NC_6H_5$	
δ	2·60	6·8—7·2	2·30	6·1—6·9
$J_{H,P}$	10·0	m	9·8	m

^{31}P Chemical shifts [b]

	$(Me_2N)_3P$	$(Me_2N)_3PN_3Me$	$(Me_2N)_3P{:}NMe$
δ	$-99·6$	$-40·7$	$-32·6$

^{13}C Spectra [c]

	$[(CH_3)_2N]_3P$	$[(CH_3)_2N]_3P{:}O$	$[(CH_3)_2N]_3PN_3CH_3$	
δ	$-75·5$	$-36·8$	$-37·1$	$-48·7$
$J_{C,P}$	37	3·7	0	0

	$C_6H_5N_3$	$[(CH_3)_2N]_3P{:}NC_6H_5$	
δ	-119 to -130	$-37·1$	-120 to -129
$J_{C,P}$	m	0	m

[a] Neat liquids; δ in p.p.m. downfield from internal Me_4Si; J in Hz. [b] Neat liquids; δ in p.p.m. (downfield negative) from 85% H_3PO_4 (external). [c] Solutions (20%) in C_6D_6; δ in p.p.m. (downfield negative) from internal Me_4Si; J in Hz.

Supporting evidence was obtained from ^{31}P chemical shifts. The ^{31}P signal of trisdimethylaminophosphine is at $-99·6$ p.p.m. whereas that of the methyl azide adduct is at $-40·7$ and that of the phenyl azide adduct at $-41·2$ p.p.m. Thermal decomposition of the methyl azide adduct yields the imide $(Me_2N)_3P{:}NMe$ with δ_P $-32·6$ p.p.m. The closeness of this last value to those of the adducts argues for a similarity of electronic structure, best accounted for by structure (I). The five-co-ordinate phosphorane (III) would be expected to show a much higher field signal than an acyclic four-co-ordinate phosphorus compound.[7]

^{13}C N.m.r. data also agree with structure (I). The ^{13}C chemical shift of Me^A in the methyl azide adduct ($-37·1$) is very similar to that of the methyl groups in the imide $(Me_2N)_3P{:}NPh$ ($-37·1$) and that in hexamethylphosphoric triamide ($-36·8$ p.p.m.). A surprising feature is the variation in the magnitude of $^2J_{CNP}$. In the three-co-ordinate hexamethylphosphorous triamide this coupling is rather large (36·6 Hz); in the corresponding four-co-ordinate hexamethylphosphoric triamide $^2J_{CNP}$ is only 3·7 Hz. However in the methyl azide adduct there is no detectable C,P coupling (*i.e.* $J < 1$ Hz) nor is there detectable Me,P coupling in the imide $(Me_2N)_3P{:}NPh$. The explanation of these differences is not obvious at present. The $^3J_{HCNP}$ values for coupling between hydrogen (attached to carbon) and phosphorus do not show any marked variations which could be attributed to major hybridization changes at carbon or at phosphorus. It has been demonstrated that in some three-co-ordinate phosphorus compounds $^2J_{CNP}$ values are strongly dependent on conformation.[8] It is difficult to invoke conformational arguments for the present observations since the observed $^2J_{CNP}$ values are averaged over all conformations. Rotational barriers about PN bonds are low for these compounds.[5]

Thermal Decomposition of the Adducts.—Both adducts decomposed thermally to give quantitative yields of nitrogen and phosphorus imides [equation (2)]. For

$$(Me_2N)_3PN_3R \longrightarrow N_2 + (Me_2N)_3P{:}NR \qquad (2)$$

(I; R = Me) this reaction proceeded rapidly ($t_{\frac{1}{2}} < 1$ h) at room temperature; for the phenyl derivative reaction at room temperature was slow, but decomposition was rapid at 100°.

Because of the formal similarity between the linear skeletal arrangements of the adducts (P:N·N:NR) and azo-compounds (RN:NR), which generally decompose thermally by radical pathways, some tests were carried out for radical intermediates in the decomposition of the more stable phenyl azide adducts. CIDNP experiments, in which solutions of the adduct were put into a preheated n.m.r. probe at temperatures at which the half-life of the adduct was a few minutes, gave no evidence of n.m.r. emission. The only peaks seen were the normal absorptions of starting material and products. The adduct did not seem to be very susceptible to photochemically induced decomposition; after 16 h irradiation (ethereal solutions; borosilicate glass flask; Rayonet 16 × 8 W lamp reactor) there was barely any detectable decomposition. Irradiation of the adduct with a 500 W

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[7] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. P. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227.

[8] M. P. Simonnin, R. M. Lequan, and F. W. Wehrli, *J.C.S. Chem. Comm.*, 1972, 1204.

mercury lamp in tetrahydrofuran glass at −130° did not produce any detectable e.s.r. signals.

These negative indications, together with the generally clean nature of the reaction, and the insignificant yields of side products, tend to argue against radical intermediates in the reaction. We then studied the kinetics of thermal decomposition.

After a qualitative survey, methoxybenzene was chosen as the solvent, and the kinetics were followed gasometrically, by monitoring nitrogen evolution, over the temperature range 106—130 °C. Over this range the reaction was found to be accurately first order in adduct.

TABLE 3

Rate constants for thermal decomposition of the adduct (I; R = Ph) in methoxybenzene

T/K	10^3k/s^{-1}	T/K	10^3k/s^{-1}
379	1·64	393	5·09
385	2·95	395	5·85
387	3·59	397	7·18
388	3·89		

Rate constants are listed in Table 3 and give rise to the following activation parameters: $\Delta H^\ddagger$ 95·1 ± 3 kJ mol^{-1}; $\Delta S^\ddagger$ −39·9 ± 8 J mol^{-1} K^{-1}. (The estimated errors are standard deviations based on a least squares treatment of the data in Table 3.)

Mechanism of Decomposition.—Previous studies of Staudinger reactions between arylphosphines and aryl azides have shown that the mechanism in the absence of acid catalysis is as shown in equations (3) and (4),

$$\mathrm{P} + \mathrm{AZ} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \qquad (3)$$

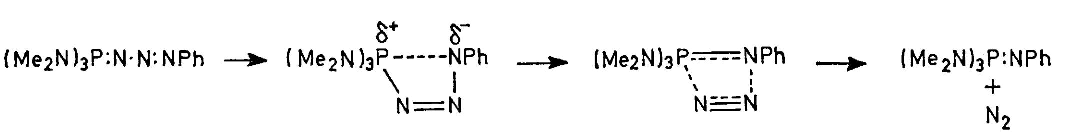
$$\mathrm{C} \xrightarrow{k_2} \mathrm{PN} + \mathrm{N_2} \qquad (4)$$

where P is the phosphine, AZ is the azide, C is the intermediate adduct, and PN is the phosphine imide product. The reaction between hexamethylphosphorous triamide and phenyl azide is compatible with this scheme with the following added constraints: k_{-1} must be very small, and may even be zero, since no reversible formation of adduct is observed; k_1 must be much larger than k_2 since the adduct is isolable and decomposes only slowly at room temperature (*i.e.* $k_1 \gg k_{-1}$; and $k_1 \gg k_2$).

It has also been previously demonstrated that in the reaction between phenyl azide and triphenylphosphine the nitrogen which ends up in the phosphine imide is derived quantitatively from the one which was originally adjacent to the aryl ring of the azide[3] [equation (5)].

$$\mathrm{Ph}N{=}\overset{+}{\mathrm{N}}{=}\overset{-}{\mathrm{N}} + \mathrm{Ph_3P} \longrightarrow \mathrm{N_2} + \mathrm{Ph}N{=}\mathrm{PPh_3} \qquad (5)$$

If this observation is considered together with the demonstration of the linear, rather than branched, skeleton of the adduct in the present work, and with the observation of a substantial negative entropy of activation in the adduct decomposition, then the mechanism which best accommodates all these data is one involving a concerted reaction with a constrained cyclic transition state, as has been previously suggested[3] [equation (6)]. It is not clear whether, in this reaction, a heterocyclic phosphorane (III; R = Ph) is formed as a high energy intermediate. The data neither require nor exclude such an intermediate.



(6)

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