Unstable Intermediates. Part 168.[1] Electron Addition to Cyclic Phosphazenes

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Exposure of the following cyclic phosphazenes to ^{60}Co γ-rays at 77 K gives electron-gain centres having e.s.r. spectra characteristic of phosphoranyl radicals: $N_3P_3X_6$ (X = Cl or Br), $N_3P_3Cl_3(NMe_2)_3$, and $N_4P_4X_8$ (X = Cl or Br). This means that, rather than accommodating the extra electron in a delocalised π orbital of a pseudo-aromatic type, the radical anion distorts so that the electron is confined to a single phosphorus atom having a local trigonal-bipyramidal configuration, with the orbital of the unpaired electron on phosphorus directed radially away from the ring.

ELECTRON declocalisation by a π mechanism is frequently invoked in phosphorus(V) compounds, important examples being the phosphobetaines, usually written as $R_2C{=}PL_3$, and the cyclic phosphazenes. The latter show no alternation in P–N bond lengths[2] so an 'aromatic' effect is invoked which requires complete π delocalisation around the ring. An alternative, but less popular, representation involving partial charge separation as in $R_2\overset{-}{\ddot{C}}-\overset{+}{P}L_3$ has been invoked by us[3] to accommodate e.s.r. results for the related radical cations $R_2\dot{C}-\overset{+}{P}L_3$,[3,4] and for similar Group 4 derivatives.[5] A suggestion that trends in the g values for the latter radicals indicate extensive π delocalisation[6] has been refuted.[5] In a preliminary report, we showed that hexachlorocyclophosphazene (phosphonitrilic chloride trimer) gave a phosphoranyl-type centre on electron addition.[7] Previous attempts to add electrons electrolytically to this compound were not successful,[8,9] but electron addition was observed for hexaphenylcyclophosphazene, and it was concluded that extensive delocalisation was occurring in the phosphazene ring system.[8,9] The latter postulate accords with the normal structural model for cyclic triphosphazenes in which extensive p_π–p_π bonding is invoked.

Evidence for π delocalisation comes from several sources.[2] For example, phosphorus–nitrogen bond lengths are usually in the 1.47—1.62 Å region which is much shorter than the normal single bond length (1.77—1.78 Å). The shortest bonds are found for the most

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[1] Part 167, M. C. R. Symons, *J. C. S. Dalton*, 1976, 1568.

[2] H. R. Allcock, *Chem. Rev.*, 1972, **72**, 315.

[3] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1967, 1770.

[4] E. A. C. Lucken and C. Mazeline, *J. Chem. Soc.* (*A*), 1966, 1074; 1967, 439.

[5] A. R. Lyons, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 1063.

[6] J. H. Mackey and D. E. Wood, *Mol. Phys.*, 1970, **18**, 783.

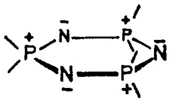
[7] S. P. Mishra and M. C. R. Symons, *J.C.S. Chem. Comm.*, 1973, 313.

[8] H. R. Allcock and W. J. Birdsall, *J. Amer. Chem. Soc.*, 1969, **91**, 7541.

[9] H. R. Allcock and W. J. Birdsall, *Inorg. Chem.*, 1971, **10**, 2495.

electronegative ligands, and the reduction in length is ascribed to skeletal π bonding. Again, various aspects of the vibrational spectra of phosphazenes are interpreted in terms of p_π–d_π bonding.[2] However, u.v. spectra of phosphazenes show none of the expected trends for such delocalisation. Various bonding schemes have been envisaged, the majority of which leave a hybridised 'lone-pair' of electrons (sp^2) on each nitrogen atom directed radially away from the ring, and a π bond between the remaining $2p_z$ orbital on nitrogen (z is normal to the ring) and the $3d_{xz}$ and $3d_{yz}$ phosphorus orbitals.[2] (There is some controversy about the relative importance of these two orbitals.[10,11]) It is even suggested that the axial lone-pair electrons on nitrogen participate in in-plane π bonds involving overlap with the phosphorus $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals. The problem with all such postulates is the very high energy of the $3d$ manifold relative to the $3s$ and $3p$ orbitals. Craig and his co-workers [10,11] have apparently overcome this difficulty by causing the $3d$ orbitals to contract in molecules and hence bringing their energies low enough for significant bonding to occur.

As stressed above, the e.s.r. evidence for $R_2\dot{C}-\overset{+}{P}L_3$ radicals is firmly against this postulate. Instead, we suggest that many, if not all, the special physical characteristics of the phosphazenes can be understood in terms of partial ionic structures such as (I). We then invoke extensive σ delocalisation so as to achieve partial charge neutralisation. This, together with the ionic 'bond', will certainly lead to a contraction of the σ-bonding system. Curiously, such ionic structures are usually dismissed without consideration.[2]



(I)

The aim of the present study was to extend our preliminary work [7] to other cyclic phosphazenes in the hope of learning more about the possibility of π delocalisation and the interactions of these important compounds with electrons. We also hoped to detect the parent radical cations by e.s.r. spectroscopy, since these might also have been expected to exhibit ring delocalisation.

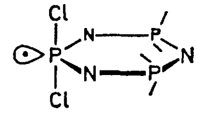
EXPERIMENTAL

Samples of $N_3P_3Cl_6$, $N_4P_4Cl_8$, PCl_5, and PCl_3O (B.D.H.) were of the highest available grade and were used as supplied. Purified $N_3P_3Cl_3(NMe_2)_3$ and $N_3P_3(NMe_2)_6$ were kindly supplied by Dr. D. B. Sowerby.

Samples were irradiated as finely ground powers at 77 K in a Vickrad ^{60}Co γ-ray source at a dose rate of 1.7 Mrad h^{-1} for *ca.* 2.0 h. E.s.r. spectra were measured on a Varian E3 spectrometer at 77 K. Samples were annealed in the insert Dewar flask after decanting the liquid nitrogen, and recooled to 77 K whenever significant changes were noted in the continuously monitored e.s.r. spectra.

RESULTS AND DISCUSSION

$N_3P_3Cl_6$ *and* $N_4P_4Cl_8$.—In both compounds, irradiated at 77 K or at ambient temperature (*ca.* 40 °C), a doublet of septets was obtained (Figure 1) indicative of hyperfine coupling to one phosphorus and two equivalent chlorine atoms. The magnitude of the ^{31}P isotropic coupling is comparable with those for $\dot{P}Cl_4$,[12] $[PCl_3O]^-$ [13,14], and various $[\dot{P}R_2Cl_2]^-$ radicals,[15] and we conclude firmly that the structure of these radicals must be of the type shown in (II). The only reasonable way in which such a radical can be formed is by electron capture.



(II)

Also, the splitting of *ca.* 62 G between the ^{35}Cl and ^{37}Cl features [^{35}Cl and ^{37}Cl both have $I = \frac{3}{2}$, the more abundant (75.4%) ^{35}Cl isotope having the larger magnetic moment] is characteristic of phosphoranyl radicals with two apical chlorine ligands.* It was originally supposed that this well defined chlorine splitting gave the isotropic hyperfine coupling,[7] but it is now realised that these are really 'parallel' features.[16,17] The perpendicular chlorine interaction (usually *ca.* 20 G) is poorly defined because one set appears on the ^{31}P parallel components and the other is centred on the ^{31}P perpendicular features.[17] The present interpretation is indicated in Figure 1 and the data are collected in the Table.

No resolved ^{14}N coupling could be detected in any spectral feature for these phosphoranyl radicals. A quintet from two equivalent nitrogen atoms is expected, but since they are both equatorial the coupling is expected to be small. Liquid-phase studies of phosphoranyl radicals with equatorial nitrogen atoms suggest a coupling of *ca.* 3.5 G.[18] This is close to the limit dictated by our linewidths.

Broad weak features were detected, separated by 700—800 G, for both compounds, and these were enhanced in methanolic solutions. Although no clear ^{14}N or ^{35}Cl interactions could be detected, we suggest that these features are due to phosphoryl radicals formed by elimination of chloride ions [equation (1)]. It is note-

$$N_3P_3Cl_6 + e^- \longrightarrow (III) + Cl^- \qquad (1)$$

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* 1 G = 10^{-4} T.

[10] D. P. Craig and K. A. R. Mitchell, *J. Chem. Soc.*, 1965, 4682.

[11] D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 1962, 4118.

[12] G. F. Kokoszka and F. Brinkman, *J. Amer. Chem. Soc.*, 1970, **92**, 1199.

[13] A. Begum and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2065.

[14] C. M. L. Kerr and F. Williams, *J. Phys. Chem.*, 1971, **75**, 3023.

[15] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1339.

[16] T. Gillbro and F. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 5032.

[17] D. Nelson and M. C. R. Symons, *J.C.S. Dalton*, 1975, 1164.

[18] R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140.

worthy that (III) did not grow at the expense of (II) on annealing and, indeed, that only (II) was detected after irradiation at 40 °C. This must mean that the formation of (III) is decided prior to the formation of (II). Thus we suggest that the extra electron induces two alternative distortions at the originally 'tetrahedral' phosphorus atom. In one an opening of the Cl–P–Cl angle gives the phosphoranyl radical anion (II) and in the other a bond stretching gives the phosphoryl radical (III).

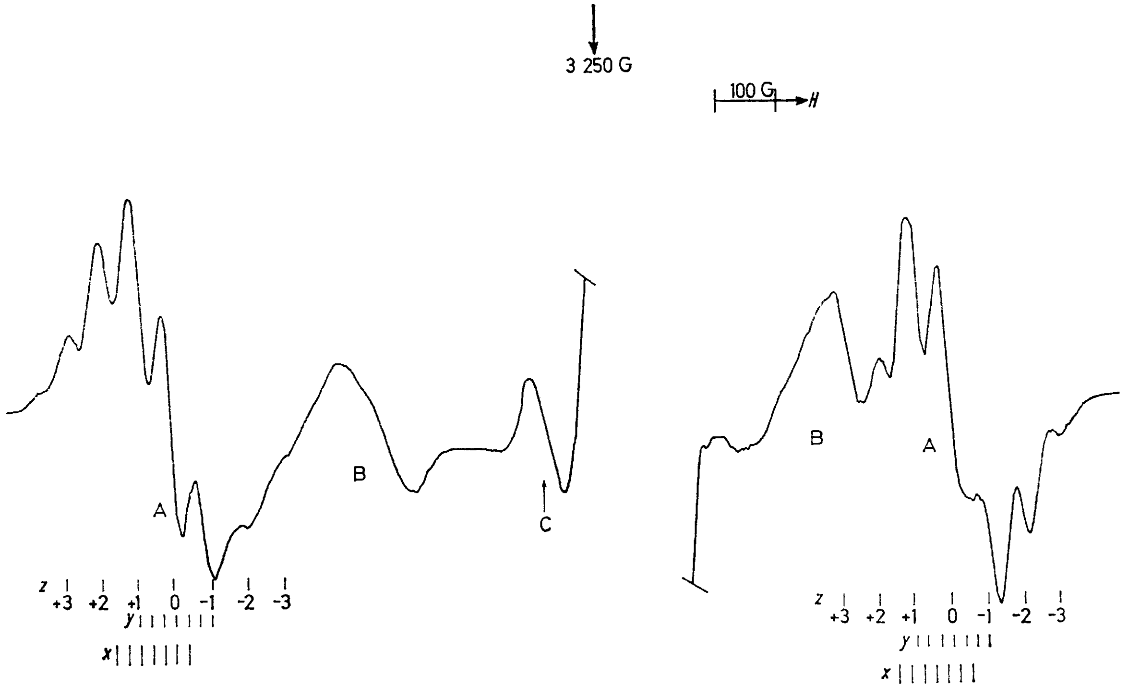
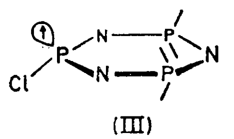


FIGURE 1 First-derivative *X*-band e.s.r. spectrum for hexachlorocyclotriphosphazene after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the radical anion (A), the phosphoryl radical (B), $[Cl_2]^-$ (C), and central features that may be due to the radical cations

Magnetic properties for radical anions of various cyclic phosphazenes and related species

Host	Radical	^{31}P Hyperfine coupling/G [a]			^{35}Cl Hyperfine coupling		
		$A_{\parallel}$	$A_{\perp}$	$A_{iso.}$	$A_{\parallel}$	$A_{\perp}$	$A_{iso.}$
$N_3P_3Cl_6$	$[N_3P_3Cl_6]^-$(II)	1 350	1 300	1 317	62	20	34
$N_4P_4Cl_8$	$[N_4P_4Cl_8]^-$	*b*	*b*	*ca.* 1 300	*ca.* 65	*ca.* 20	35
$N_3P_3Br_6$	$[N_3P_3Br_6]^-$	*b*	*b*	*ca.* 1 200	*ca.* 200	*b*	
$N_3P_3Cl_3(NMe_2)_3$	$[N_3P_3Cl_3(NMe_2)_3]^-$ (V)	*b*	*b*	*ca.* 860	62	*b*	
$N_3P_3Cl_6$	$N_3P_3Cl_5$ (III)	*b*	*b*	*ca.* 750			
$N_4P_4Cl_8$	$N_4P_4Cl_7$	*b*	*b*	*ca.* 700			
$N_3P_3(NMe_2)_6$	$N_3P_3(NMe_2)_5$	500	350	400			
PCl_5	PCl_4	1 350	1 290	1 310	65	20	35 [c]
PCl_3O	$[PCl_3O]^-$	1 417	1 355	1 375.7	69	24	39 [c]

[a] *g* Values *ca.* 2.00. [b] Parallel and/or perpendicular features were poorly defined. [c] S. P. Mishra and M. C. R. Symons, *J.C.S. Dalton*, 1976, 139. Two equivalent chlorine atoms.



(III)

Yet another way in which the extra electron can interact is to give $[Cl_2]^-$ by elimination. Thus, for example, SCl_2O_2 gave $[Cl_2]^-$ as a significant product[19] [equation (2)]. The $[Cl_2]^-$ radical has a characteristic powder

$$SCl_2O_2 + e^- \longrightarrow SO_2 + [Cl_2]^- \qquad (2)$$

spectrum which exhibits a prominent set of lines *ca.* 100 G downfield from the free-spin region.[20] Such features were clearly detected for both compounds, showing that $[Cl_2]^-$ is a minor component. It is not clear which chlorine atoms are involved: we consider that the most likely elimination is from a single phosphorus atom, to give (IV), but intramolecular loss from two different phosphorus atoms or an intermolecular reaction are also possible.

The central regions of the spectra, which should give

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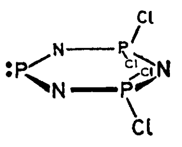
[19] C. M. L. Kerr and F. Williams, *J. Amer. Chem. Soc.*, **1971**, **93**, 2805.

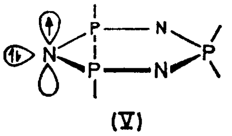
[20] I. Marov and M. C. R. Symons, *J. Chem. Soc.* (*A*), **1971**, 201.

features for the electron-loss centres, were always poorly defined, and no definitive interpretation can be offered. A broad central line gave indications of being a triplet with a 35-G splitting and poorly defined shoulders during the annealing, but reverted to a single feature on cooling to 77 K.



(IV)

Our expectation for $[N_3P_3Cl_6]^+$, for example, is that the ' hole ' will be largely confined to a single nitrogen atom, as in (V), with the possibility of diffusing by jumps around the ring, since for planar ring systems no major distortion is expected on electron loss. Even with slow migration, the solid-state e.s.r. spectrum would be most complicated. The ^{14}N would give parallel features separated by *ca.* 40 G and central perpendicular features with a small, probably unresolved, splitting. Two equivalent ^{31}P nuclei would split these lines into triplets with a fairly isotropic splitting in the 30-G region. Interaction with four equivalent chlorine atoms is less readily predictable but could be quite large (10—20 G) because they occupy favourable positions for ' hyperconjugative ' overlap. Such a complicated spectrum could well give an unresolved powder pattern such as that detected, but we cannot make any definitive assignment.



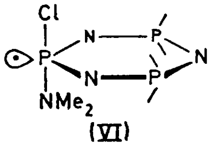
(V)

$N_3P_3Br_6$.—Poorly defined outer features were obtained, similar to those assigned to $[\dot{P}Br_3S]^-$ radicals in irradiated $\dot{P}Br_3S$.[21] The ^{31}P coupling of *ca.* 1 200 G and ^{81}Br coupling of *ca.* 200 G are in good accord with expectation for the phosphoranyl radical anions, but we cannot be more precise about the parameters. Features assignable to $[Br_2]^-$ were detected in the low-field region,[20] but again the central region was insufficiently resolved to warrant assignment.

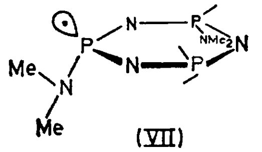
$N_3P_3Cl_3(NMe_2)_3$.—A doublet $[A_\perp(^{31}P) \approx 860$ G] of quartets $[A_\parallel(^{35}Cl)$ 66 G] dominated the outer regions of the e.s.r. spectra. The spectra were too poorly defined to enable us to obtain accurate measurements of $A_\parallel(^{31}P)$ or $A_\perp(^{35}Cl)$, but the form of the spectra suggest that these are quite normal (*i.e. ca.* 980 and *ca.* 20 G respectively). Despite the large decrease in $A(^{31}P)$, we consider that this species is the phosphoranyl radical anion (VI). A decrease in the phosphorus coupling is normal on going to a less-electronegative ligand, and the coupling compares reasonably with that of 794 G for $\dot{P}Et_2Cl(OBu^t)$ in the liquid phase.[15] Also, the parallel chlorine coupling is correct for structure (VI), but too large for the alternative phosphoryl structure.

The spectra give no clear indication of phosphoryl-radical formation, and, once more, the central features, although suggestive of cation formation, were insufficiently resolved for the extraction of parameters.

$N_3P_3(NMe_2)_6$.—In this case, primary phosphoranyl radical anions were not detected, but clear features for phosphoryl radicals were obtained (Figure 2). The ^{31}P hyperfine parameters for this centre (VII), given in the Table, are reasonable when compared with those for $[\dot{P}Me_3]^+$ ($A_\parallel$ 600, $A_\perp$ 290 G) or $\dot{P}Me_2O$ ($A_\parallel$ 535, $A_\perp$ 295 G). Some spectra had indications of unresolved features, presumably from hyperfine coupling to ^{14}N, but we were unable to improve this resolution. It is interesting that we only obtained the phosphoryl radical, $\dot{P}(NMe_2)_2O$, from irradiated $P(NMe_2)_3O$ on irradiation with ^{60}Co γ-rays, there being no trace of the expected phosphoranyl anion. Thus, both these compounds appear to prefer the bond-stretching process to give $[NMe_2]^-$ anion ejection rather than bond bending. We do not understand why this preference should be so marked.



(VI)



(VII)

The central region, shown at lower gain in Figure 2, has been tentatively interpreted in terms of the primary cation. This was better defined, probably because of the absence of chlorine hyperfine coupling, and the reconstruction gives $A_\parallel(^{14}N)$ 45 G, $A_\perp(^{14}N) \approx 0$, and $A(^{31}P) \approx 25$ G. As indicated above, these values are reasonable for structure (V), and, if this is correct, it would seem that electron migration around the ring is slow on the e.s.r. time scale, there being no question of cyclic π delocalisation. This result accords with our evidence that extra electrons are localised, but in this case localisation does not stem from any major distortion.

$N_3P_3Ph_6$.—This gave only a broad central feature (g 2) with no trace of doublets for phosphoranyl or phosphoryl radicals. We have previously shown that electrons prefer to add to the phenyl ligands of $PPhL_3$ molecules to give aromatic anions rather than to phosphorus to give

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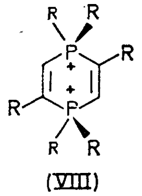
[21] S. P. Mishra, K. V. S. Rao, and M. C. R. Symons, *J. Phys. Chem.*, 1974, **78**, 576.

phosphoranyl radicals unless there are strongly electronegative ligands such as chlorine.[22,23] Thus, from this experience, we would predict electron addition to the ring in the present case. Absence of resolved hyperfine coupling to the ring protons or to ^{31}P is not surprising in the solid state. We suspect that similar electron attachment to aromatic rings must have occurred in the electrolytic-reduction study of Allcock and Birdsall.[8,9] However, it is surprising that in *NN*-dimethylformamide solution the proton and phosphorus hyperfine coupling was not resolved. This may well be because of delocalisation, as suggested,[8,9] but we suspect that this takes the form of electron transfer between two or more aromatic rings rather than *via* the phosphazene ring π system. If the rate of transfer is in the correct range, this could well lead to complete loss of resolution, as observed.



(VIII)

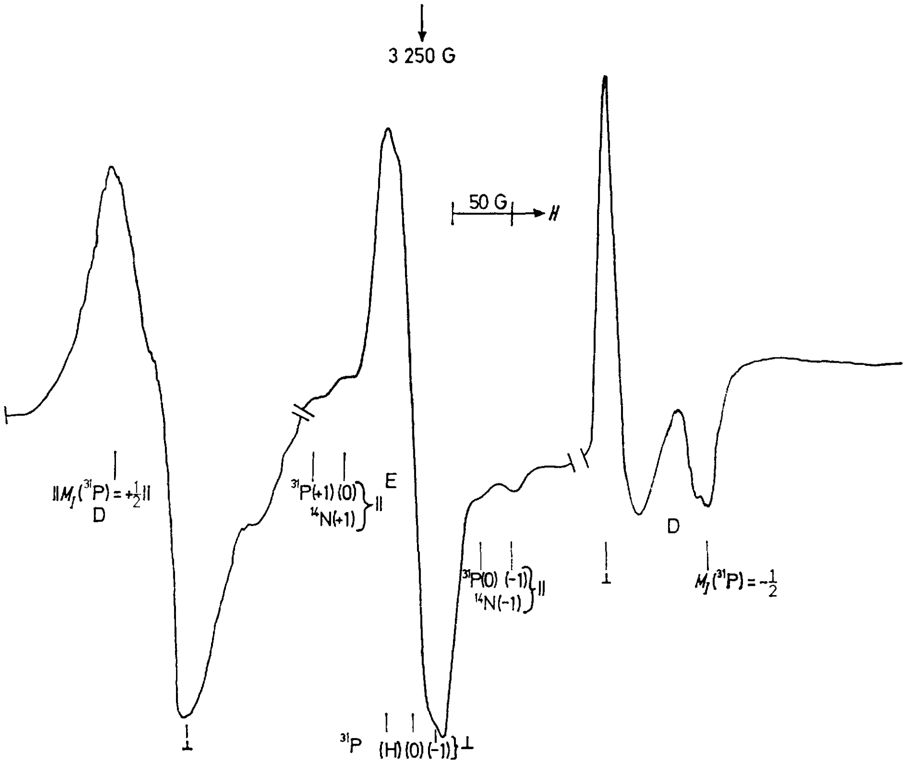


FIGURE 2 First-derivative *X*-band e.s.r. spectrum for hexabis(dimethylamino)cyclotriphosphazene after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the phosphoryl radical (D) and the radical cation (E)

Finally, we recall that electron addition to a range of 1,4-diphosphoniacyclohexa-2,5-diene dications, (VIII), has been shown [24] to result in delocalisation of the electron in the cyclic ring system rather than localisation at a single phosphorus atom. The e.s.r. results show that nearly all the spin density is on the four ethylenic carbon atoms, and the small hyperfine coupling to ^{31}P (*ca.* 15 G) shows that spin density is largely gained *via* spin polarisation as expected.[5] These results make an interesting contrast with those now reported.

We thank Dr. D. B. Sowerby for various phosphazene samples, Mrs. V. Thompson for experimental assistance, and the Department of Chemistry, Banaras Hindu University, India, for study leave (to S. P. M.).

[5/2466 *Received, 18th December,* 1975]

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[22] S. P. Mishra and M. C. R. Symons, *J.C.S. Chem. Comm.*, 1974, 606; *J.C.S. Perkin II*, 1976, 21.

[23] S. P. Mishra and M. C. R. Symons, *J.C.S. Dalton*, 1973, 1494.

[24] R. D. Rieke, R. A. Copenhafer, A. M. Aquiar, M. S. Chattha, and J. C. Williams, *J.C.S. Chem. Comm.*, 1972, 1130.