Unstable Intermediates. Part CXLIX.[1] An Electron Spin Resonance Study of various Phosphinyl Radicals formed by Solid-state Radiolysis

By **Brian W. Fullam, Shuddhodan P. Mishra, and Martyn C. R. Symons,*** Department of Chemistry, The University, Leicester LE1 7RH

One of the major products when a range of trivalent phosphorus compounds was exposed to ^{60}Co γ-rays at 77 K was shown by e.s.r. spectroscopy to be the corresponding phosphinyl radical, $\dot{P}R_2$. These radicals, which include $\dot{P}H_2$, $\dot{P}(Me_2CH)_2$, $\dot{P}(OMe)_2$, $\dot{P}(SMe)_2$, $\dot{P}Ph_2$, $\dot{P}Ph(Cl)$, and $\dot{P}Cl_2$, are all characterised by a ^{31}P parallel hyperfine coupling constant in the 240—290 G range and a perpendicular coupling close to zero. The conditions under which these radicals are formed, and the mechanisms involved, are outlined and discussed.

CONSIDERABLE interest has recently been shown in the formation of various phosphorus-centred radical intermediates, both in the liquid-phase[2] and in the solid-state.[3] Although radicals of the general types $\dot{P}L_3$ and $\dot{P}L_4$ are now well known,[2,3] very few of the type $\dot{P}L_2$ have been recorded. In fact, clear identification has only been provided for $\dot{P}H_2$,[4] $\dot{P}F_2$,[5,6] and $\dot{P}Cl_2$ [7,8] so far as we are aware. It has been claimed that photolysis of $(Ph_2P)_2$ in benzene at 77 K gives $Ph_2\dot{P}$,[9] but the six-line e.s.r. spectrum assigned to this radical bears no resemblance to those now reported, and we consider that the assignment must be in error (see Discussion section).

Recently, Ingold[10] has tentatively suggested that a transient species detected during the reaction of photochemically generated t-butoxyl radicals and phosphine, having A_{iso} (^{31}P) = 83·3 G, is $\dot{P}(OR)_2$ (R = H or Me_3C) and a similar species having $A_{iso}(^{31}P)$ = 78·5 G, formed during photolysis of tetraethoxydiphosphine in d-t-butyl peroxide at room temperature, is $\dot{P}(OEt)_2$. Our present results for the radical $\dot{P}(OMe)_2$, briefly mentioned elsewhere,[11] strongly support this assignment.

EXPERIMENTAL

Diphenylphosphine chloride, di-isopropylphosphine chloride (Maybridge Chemicals), and trimethyl phosphite (B.D.H. Chemicals) were used without further purification, bulb-to-bulb distillation of the chloride causing no appreciable change in the spectra. Trimethyl thiophosphite and triethyl thiophosphite were made by the addition of the respective disulphide to powdered white phosphorus in solvent acetone, under a nitrogen atmosphere.[12] The reaction $2P + 3Me_2S_2 \longrightarrow 2(MeS)_3P$ was catalysed by the addition of a small quantity of 15N-KOH and required no heating. The resulting thiophosphites were used without further purification, since their ^{31}P n.m.r. spectra, after removal of acetone, showed the presence of only one phosphorus compound. A purified sample of diethyl thiophosphine chloride was kindly provided by Professor S. Trippett. Samples were irradiated in a ^{60}Co Vickrad cell for *ca.* 1 h at a nominal dose rate of 4 Mrad h^{-1}. E.s.r. spectra were run at 77 K on a Varian E3 spectrometer and samples were annealed above this temperature and re-cooled for further measurement.

DISCUSSION

Interpretation of Spectra.—All the spectra under consideration (Figures 1—4) are characterised by two parallel type features separated by *ca.* 270 G, and ill defined ' perpendicular ' features in the free-spin region, frequently overlapped by lines from other species. The major interpretative problem lies in extracting the perpendicular (*x* and *y*) information. In several instances, all we can say is that A (^{31}P) = 0, with the large uncertainty of *ca.* ±5 G. In a few cases clear $\pm\frac{1}{2}$ features were resolved, but since the *g*-tensors are not quite axial some interpretative ambiguity remains.

$\dot{P}H_2$ *and* $\dot{P}R_2$ *Radicals.*—The PH_2 radical was clearly identified by Gordy and his co-workers in rare-gas matrices, but only the isotropic spectrum was observed despite the low temperature (4·2 K). In an endeavour to obtain the anisotropic spectrum for $\dot{P}H_2$ we reasoned that to prevent rapid rotation it would be necessary to anchor the radical by hydrogen bonding. Accordingly, we irradiated solutions of phosphine in concentrated aqueous solutions of sulphuric acid (*ca.* 90% H_2SO_4), the solvent being cooled during the addition and then frozen rapidly to avoid oxidation. Although PH_3^+ was the major phosphorus-containing radical product, parallel features assignable to stationary $\dot{P}H_2$ radicals were clearly discerned during the annealing process. These became far better defined when solutions in D_2SO_4 (D_2O) (equilibrated to ensure exchange) were utilised. This gave $\dot{P}D_2$ (together with a trace of $\dot{P}HD$), the resulting data being given in the Table. Intense central lines (SO_4^- and SO_3^-) concealed the ' perpendicular ' region.

---

[1] Part CXLVIII is considered to be G. W. Neilson and M. C. R. Symons, *J.C.S. Perkin II*, 1973, 397.

[2] See, for example, J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969, **91**, 3944; P. J. Krusic, W. Mahler, and J. K. Kochi, *ibid.*, 1972, **94**, 6033; A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738.

[3] See, for example, M. Geoffrey and E. A. C. Lucken, *Mol. Phys.*, 1971, **22**, 257; A. Begum and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 1589.

[4] R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, 1966, **45**, 1747.

[5] W. Nelson, G. Jackel, and W. Gordy, *J. Chem. Phys.*, 1970, **52**, 4572.

[6] M. S. Wei, J. H. Current, and J. Gendell, *J. Chem. Phys.*, 1970, **52**, 1592.

[7] G. F. Kokoska and F. E. Brinkman, *Chem. Comm.*, 1968, 349; *J. Amer. Chem. Soc.*, 1970, **92**, 1199.

[8] M. S. Wei, J. H. Current, and J. Gendell, *J. Chem. Phys.*, 1972, **57**, 2431.

[9] J. K. S. Wan and S. K. M. Wong, *Spect. Letters*, 1970, **3**, 135.

[10] K. U. Ingold, *J.C.S. Perkin II*, 1973, 420.

[11] M. C. R. Symons, *Mol. Phys.*, 1972, **24**, 885.

[12] U.S.P. 3,341,632 (Cl, 260–971) 1967.

Using the known isotropic coupling (Table), this gives $2B(\dot{P}H_2) = 195$ G. This is almost identical with the value obtained for $\dot{P}(Me_2CH)_2$ (196·5 G), both values being very close to that corresponding to unit spin-density on phosphorus (206 G) that we have previously proposed,[13] and to the revised value calculated from the wavefunctions of Froese [14] (201 G). This suggests that hydrogen-bonding has indeed held the radical firmly and prevented even the libration that commonly occurs in matrices at 77 K.[15] It also strongly supports our use of the calculated data for neutral phosphorus atoms,[13,14] in preference to the values listed by Hurd and Coodin.[16]

E.s.r. data for a range of phosphinyl radicals

		^{31}P Hyperfine tensor components (G) [a]				Other hyperfine coupling data				g-Tensor components			
Radical	Source	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$2B$	$A_{\parallel}$	$A_{\perp}$	A_{iso}		g_x	g_y	g_z	g_{av}
PH_2	PH_3	275		80 [b]	195					2·002			
$P(CHMe_2)_2$	$ClP(CHMe_2)_2$	290	~0	96·7	193·3	13			(^{1}H)				
PPh_2	$ClPPh_2$	268	−13	78·7	189·3					2·000	2·005	2·009	2·0047
$P(OMe)_2$	$P(OMe)_3$	285								2·002			
$P(OEt)_2$ [c]	$P_2(OEt)_4$			78·5									2·002
$P(SMe)_2$	$P(SMe)_3$	237·6								2·002			
$P(SEt)_2$	$ClP(SEt)_2$	245	−15	71·8	173·7					2·002	2·0013	2·021	2·012
$P(SPr^i)_2$	$P(SPr^i)_3$	246	−15	71·8	173·7					2·002	*ca.* 2·018	*ca.* 2·018	2·0127
PF_2 [d]	PF_3	308·1	−27·2	84·6	223·5					2·0027	2·0016	2·0016	
[e]	P_2F_4	307	−83	47	260								
[f]				35									
PCl_2	PCL_3	272·5	−22·5	75·8	196·7	16·5	~0	5·5	(^{35}Cl)	$1·995_3$	2·0187	2·0187	
[g]	PF_3	269	−28	71·0	198·0	15	0	5·0	(^{35}Cl)	2·001	2·021	2·021	
[h]		293	−30·5	77·3	215·7	17·5	<0·3	5·8	(^{35}Cl)	$2·002_4$	1·999	1·999	

[a] 1 G = 10^{-4} T. [b] Ref. 4. [c] Ref. 10. [d] Ref. 5. [e] Ref. 6. [f] Ref. 21. [g] Ref. 7. [h] Ref. 8.

The $\dot{P}(CHMe_2)_2$ radical was formed directly in good yield from $ClP(CHMe_2)_2$ by dissociative electron capture at 77 K (Figure 1). In marked contrast, in our extensive studies of trialkylphosphines we have never detected features for such $\dot{P}R_2$ radicals.

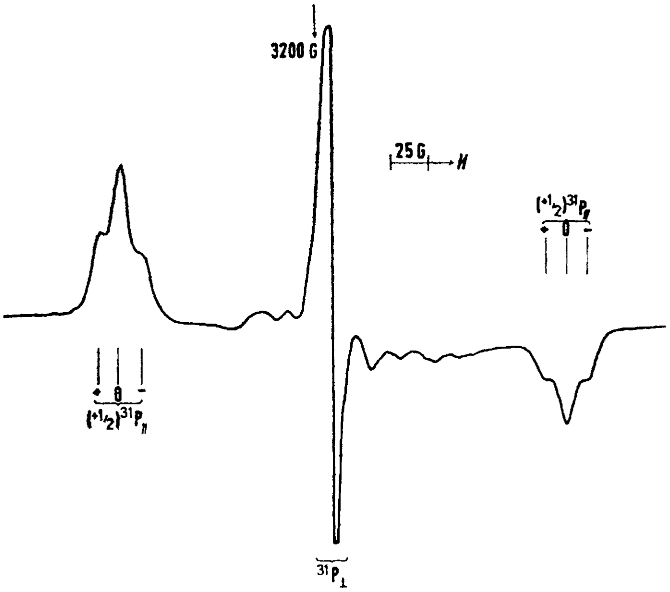

FIGURE 1 First-derivative e.s.r. spectrum for Pr^i_2PCl after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $Pr^i_2\dot{P}$ radicals

$\dot{P}(SR)_2$ *Radicals*.—These radicals are formed very readily during radiolysis of organophosphorus–sulphur compounds, a typical spectrum being given in Figure 2. The value of $A_{\parallel}$ (^{31}P) for $\dot{P}(SMe)_2$ is appreciably less than the values for the diethyl and di-isopropyl derivatives, which almost certainly means that these $\dot{P}(SMe)_2$ radicals are librating slightly at 77 K. This was supported by the fact that $A_{\parallel}$ (^{31}P) for these radicals fell monotonically when the temperature was increased above 77 K, in contrast with the values for the other two radicals, which were temperature insensitive below *ca.* 140 K. Furthermore, $A_{\perp}$ for $\dot{P}(SMe)_2$ was close to zero at 77 K, whereas an appreciable perpendicular coupling was detected for the other two radicals. These results incidentally confirm that the small ^{31}P coupling for $A_{\perp}$ is negative, as we have assumed in deriving the A_{iso} values listed in the Table.

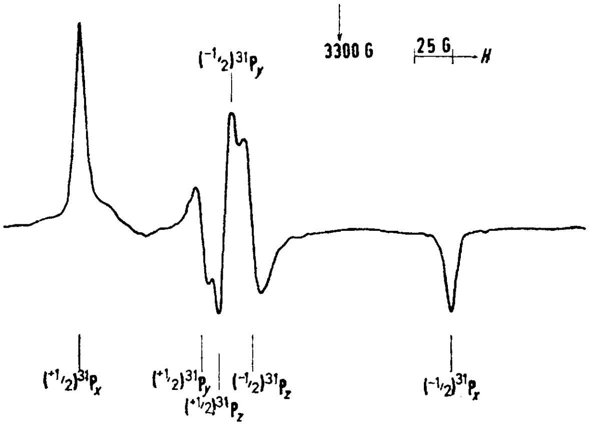

FIGURE 2 First-derivative e.s.r. spectrum for $(Pr^iS)_3P$ after exposure to ^{60}Co γ-rays at 77 K and partial annealing, showing features assigned to $(Pr^iS)_2\dot{P}$ radicals

The $\dot{P}Ph_2$ *Radical*.—This radical was formed in good

---

[13] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

[14] Calculated from the data of C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

[15] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 3075.

[16] C. M. Hurd and P. Coodin, *J. Phys. Chem. Solids*, 1967, **28**, 523.

yield from the chloride, Ph_2PCl, as expected (Figure 3). The results show conclusively that there can be only minor delocalisation of the unpaired electron onto the aromatic π-systems. This important result accords with several other recent findings. For example, delocalisation into the aromatic rings for $Ph_2\dot{P}O$ and $Ph\dot{P}O_2^-$ is undoubtedly small.[17] However, in these cases the radicals are pyramidal at phosphorus and poor π-delocalisation is expected for this reason. We [18] have recently drawn attention to the fact that the results of Gray *et al.*[19] for the radical $Ph_2\dot{A}s$ also established that delocalisation into the π-systems is very small indeed.

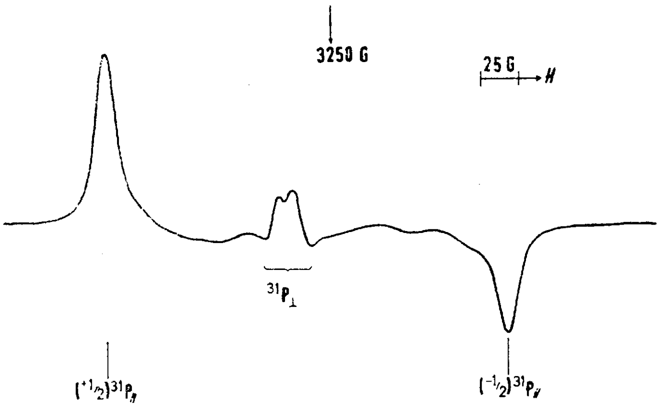

FIGURE 3 First-derivative e.s.r. spectrum for Ph_2PCl after exposure to ^{60}Co γ-rays at 77 K and partial annealing, showing features assigned to $Ph_2\dot{P}$ radicals

$\dot{P}F_2$, $\dot{P}Cl_2$, and related Radicals.—There have been divergent reports for the radical $\dot{P}F_2$, as indicated in the Table.[20] The results of Gordy *et al.*[5] and of Current *et al.*[6] agree that $A_\parallel$ (^{31}P) = 307 G, but the perpendicular values differ possibly because of the difficulties involved in interpreting powder spectra. However, Gordy *et al.*[5] found that $\dot{P}F_2$ in PF_3 was rotating isotropically at 77 K which fixes the isotropic coupling unambiguously at 84·6 G and hence confirms their perpendicular value of (—)27·2 G obtained at 4·2 K. These results link in very well with the others given in the Table, and this suggests that the species with A_{iso} (^{31}P) = 35 G also thought to be PF_2 [21] is incorrectly assigned.

Our results for PCl_2 in PCl_3 previously reported [22] agree fairly well with those reported by Brinckman and Kokoska,[7] but the g value assignments are very different from those more recently reported by Wei *et al.*[8] We have therefore checked our results and reproduce our e.s.r. spectrum for $\dot{P}Cl_2$ in PCl_3 (Figure 4) in order to establish that '$g_\perp$' is in fact clearly greater than $g_\parallel$ (Table). It could be argued that since Wei *et al.*[8] computer simulated their $\dot{P}Cl_2$ spectra, their results are more reliable: in fact, however, the simulation does not reproduce the experimental spectrum in the vital area of intensities. Thus the low-field parallel lines in the spectra are clearly more intense than the high-field parallel components and this must mean that '$g_\perp$' is $>g_\parallel$.

The parallel value of 293 G obtained by Wei *et al.*[8] suggests that the radical in PCl_3 is librating. Since the magnitude of $A_\perp$ is lower for the librating radical, it must be negative, as was assumed.[8] This gives $A_{iso}(^{35}Cl) \doteqdot 7$ G and $2B \doteqdot 216$ G. Using our normal $2B°$ value of 201·4 G,[14] this gives a spin-density close to, but greater than, unity. Thus, even if delocalisation onto the two chloride ligands is negligible, the estimated spin-density is too high, and this led Wei *et al.*[8] to favour the calculated $2B°$ values of Hurd and Coodin.[16] As stressed above, there are good reasons for favouring the value of *ca.* 201·4 G for neutral radicals, and we prefer to suggest that the increase for PF_2 and PCl_2 arises because the high relative electronegativity of the ligands confers a small positive charge on the phosphorus atom. This slightly contracts the orbitals close to phosphorus thus increasing the coupling and rendering the $2B°$ value of 201·4 G too small.

Trends in Isotropic Hyperfine Coupling Constants.—The most striking feature of the isotropic ^{31}P coupling constants is their remarkable constancy despite the large assortment of ligands. Thus they range from *ca.* 72 to *ca.* 97 G, whereas the range for comparable nitrogen radicals $\dot{N}L_2$ is from *ca.* 7 G ($Ph\dot{N}H$) [23] to *ca.* 20 G ($\dot{N}Cl_2$) [8] [or, since the latter result is suspect, *ca.* 17 G ($\dot{N}F_2$)].[24] We suggest that the major cause of this difference in behaviour is the smaller tendency to delocalise the unpaired electron onto the ligands in the phosphorus compounds. This can be appreciated by comparing the

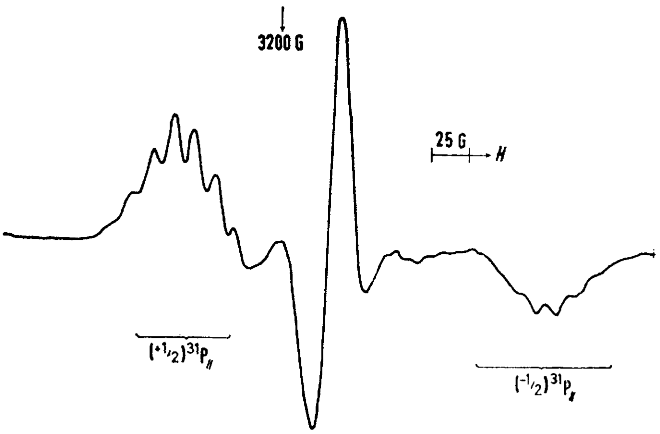

FIGURE 4 First-derivative e.s.r. spectrum for PCl_3 after exposure to ^{60}Co γ-rays at 77 K and partial annealing, showing features assigned to $\dot{P}Cl_2$ radicals

---

[17] M. Geoffrey and E. A. C. Lucken, *Mol. Phys.*, 1972, **24**, 335.

[18] A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1973, **95**, 3483.

[19] J. R. Preer, F. D. Tsay, and H. B. Gray, *J. Amer. Chem. Soc.*, 1972, **94**, 1875.

[20] M. C. R. Symons, *Ann. Rev. Phys. Chem.*, 1969, **20**, 219.

[21] H. Bernstein, J. R. Morton, and J. K. Wan, *Canad. J. Chem.*, 1966, **44**, 1957.

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

[23] R. V. Lloyd and D. F. Wood, *Mol. Phys.*, 1971, **20**, 735.

[24] P. H. Kasai and E. B. Whipple, *Mol. Phys.*, 1965, **9**, 497.

value for $A_{\mathrm{iso}}(^{14}\mathrm{N})$ for the anilino-radical $\mathrm{Ph\dot{N}H}$[23] of 7·77 G with that for $\dot{\mathrm{N}}\mathrm{H}_2$ (10·3 to ~14 G)[25,26] or $\dot{\mathrm{N}}\mathrm{Me}_2$ (~14·8 G),[27] which, together with the relatively large ring-proton hyperfine coupling constants[23] confirm the occurrence of very extensive ring delocalisation. This contrasts with the small decrease in $2B$ (^{31}P) on going from $\dot{\mathrm{P}}(\mathrm{Alk})_2$ to $\dot{\mathrm{P}}\mathrm{Ph}_2$, and the absence of any detectable ring-proton hyperfine interaction.

There is a clear increase in $A_{\mathrm{iso}}(^{31}\mathrm{P})$ on going from $\dot{\mathrm{P}}\mathrm{H}_2$ to $\dot{\mathrm{P}}(\mathrm{Alk})_2$, just as is found on going from $\dot{\mathrm{N}}\mathrm{H}_2$ to $\dot{\mathrm{N}}(\mathrm{Alk})_2$.[25-27] Following a suggestion by Rao and Symons,[26] the latter trend has been linked with an increase in bond-angle on replacing H by alkyl,[28] and it may well be that there is a similar increase in bond angle for the phosphorus radicals.

The low value of A_{iso} for the $\dot{\mathrm{P}}(\mathrm{SR})_2$ radicals probably reflects their greater tendency towards delocalisation, and this may be a key to the reason why nitrogen and phosphorus seem to differ so markedly in this respect. Thus for nitrogen, and the majority of ligands, π-interaction involves overlap of $2p(\pi)$-orbitals, which is known to be efficient. With phosphorus, $3p$–$2p(\pi)$ interaction seems to be far less efficacious, but for $3p$–$3p(\pi)$ orbitals the size and energy matching is greatly improved and delocalisation consequently enhanced.

It is interesting to compare the downward trend in $A(^{31}\mathrm{P})$ on going from $\dot{\mathrm{P}}\mathrm{F}_2$ (84·6 G) to $\dot{\mathrm{P}}\mathrm{Cl}_2$ (*ca.* 75 G) with the reported upward trend on going from $\dot{\mathrm{N}}\mathrm{F}_2$ (*ca.* 16·8 G) to $\dot{\mathrm{N}}\mathrm{Cl}_2$ (20 G). Following the argument about orbital matching outlined above, this trend seems quite reasonable, delocalisation being favoured for $\dot{\mathrm{P}}\mathrm{Cl}_2$ on the one hand and $\dot{\mathrm{N}}\mathrm{F}_2$ on the other. However, the reported data for $\dot{\mathrm{N}}\mathrm{Cl}_2$ are unexpected in that the magnitude of the 'perpendicular' coupling to ^{35}Cl (−17 G) is larger than predicted by comparison with α-chloroalkyl radicals,[29] whilst the very asymmetric form of the ^{14}N coupling tensor components (40, 14, 6) is also unlikely for this radical. From the published powder spectra, which are extremely difficult to interpret because of their complexity, we would suggest that the ^{14}N coupling is better taken as $A_{\parallel} = +40$, $A_{\perp} \approx \pm 5$ G, whence $A_{\mathrm{iso}}(^{14}\mathrm{N}) =$ 16·7 or 10·0 G. The latter seems too low, but the former value accords well with that for $\dot{\mathrm{N}}\mathrm{H}_2$.

We thank Mr. J. A. Brivati for experimental assistance, the S.R.C. for a grant to B. W. F., and the Commonwealth Scholarship Commission in the United Kingdom for a fellowship to S. P. M.

[4/362 *Received*, 25*th February*, 1974]

---

[25] S. N. Forev, E. L. Cochran, V. A. Bowers, and C. K. Jen, *Phys. Rev. Letters*, 1958, **1**, 91.

[26] K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2163.

[27] W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, 1970, **92**, 5235.

[28] K. F. Purcell and W. C. Danen, *J. Amer. Chem. Soc.*, 1972, **94**, 7613.

[29] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1973, **69**, 1425.