3,2 shift in III is considerably faster than the WM-6,2-WM rearrangement (*cf.* ref 18 and 19).

The $\Delta F^{\pm}$ values (kcal/mol) for the WM-6,2-WM processes are: I, 11.1; II, *ca.* 11.1; 2,7,7-trimethyl-2,5,5-trimethyl-2-norbornyl, *ca.* 11.2; and III, 10.7. This rearrangement is therefore not sensitive to extra methyl substitution. The rapidity of the WM rearrangement allows one to understand more clearly why camphene hydrochloride can *rapidly* rearrange to the thermodynamically more stable isobornyl chloride, a reaction of immense historical importance.[20]

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(20) H. C. Brown, *Chem. Eng. News*, 87 (Feb 13, 1967).

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An Electron Spin Resonance Study of Dialkoxyphosphonyl Radicals, $(RO)_2\dot{P}O$

Sir:

Dialkoxyphosphonyl radicals **2** are recognized to be intermediates in some reactions of dialkyl phosphonates (dialkyl phosphites, **1**),[1] but the esr spectra of the radicals in solution have never been observed. We report here an esr study of the formation and reactions of these radicals, which have been derived from two different sources.

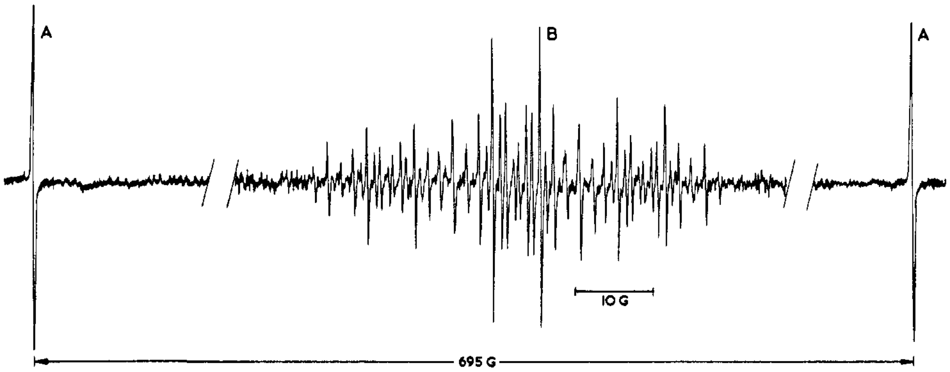

Figure 1. Esr spectrum (at 9.158 GHz) of the diethoxyphosphonyl radical (A), which is replaced by the spectrum of the benzyl radical (B) when benzyl bromide is added to the reaction system.

If di-*tert*-butyl peroxide is photolyzed in an esr cavity[2] in the presence of a dialkyl phosphonate (**1**; R^1 = Me, Et, *i*-Pr, or *n*-Bu, 10–20% (v/v) in peroxide as solvent), alkoxyl radicals abstract the hydrogen which is bonded to phosphorus, and the doublet spectra of the corresponding phosphonyl radicals, **2**, are observed (Figure 1).[3]

$$\textit{tert}\text{-BuOO-}\textit{tert}\text{-Bu} \xrightarrow{h\nu} 2\textit{tert}\text{-BuO}\cdot \tag{1}$$

$$\textit{tert}\text{-BuO}\cdot + \underset{\mathbf{1}}{(R^1O)_2P(O)H} \longrightarrow \textit{tert}\text{-BuOH} + \underset{\mathbf{2}}{(R^1O)_2\dot{P}O} \tag{2}$$

The identical but more intense spectrum of the diethoxyphosphonyl radical was also obtained when di-*tert*-butyl peroxide was photolyzed in the presence of tetraethyl pyrophosphite (**3**). This represents a novel bimolecular homolytic substitution[6] reaction at a phosphorus center (eq 3). In contrast to the reaction

$$\begin{aligned}
&\textit{tert}\text{-BuO}\cdot + \underset{\mathbf{3}}{(EtO)_2POP(OEt)_2} \longrightarrow \\
&\quad \textit{tert}\text{-BuOP(OEt)}_2 + O\dot{P}(OEt)_2 \\
&\qquad \Big\downarrow {\scriptstyle \textit{tert}\text{-BuO}\cdot} \\
&\quad \underset{\mathbf{4}}{(\textit{tert}\text{-BuO})_2\dot{P}(OEt)_2} \longrightarrow \textit{tert}\text{-Bu}\cdot + OP(OEt)_2(O\text{-}\textit{tert}\text{-Bu})
\end{aligned} \tag{3}$$

of *tert*-butoxyl radicals with trialkyl phosphites,[7] no phosphoranyl radical derived from the pyrophosphite could be detected, but, on prolonged photolysis, the spectrum of the phosphoranyl radical **4** ($a(^{31}P)$ = 892 G) derived from *tert*-butyl diethyl phosphite, and of the *tert*-butyl radical which is formed from **4** by β scission,[7] were apparent.

g values and ^{31}P hyperfine splitting constants for the phosphonyl radicals between −10 and −50°, cal-

Table I. Esr Spectra of Dialkoxyphosphonyl Radicals

	g^a	$a(^{31}P)$, G^a
$(MeO)_2\dot{P}O^b$	2.004	700
$(EtO)_2\dot{P}O$	2.005	687
$(i\text{-PrO})_2\dot{P}O$	2.004	685
$(n\text{-BuO})_2\dot{P}O$	2.005	688

[a] g values ±0.001; hyperfine splitting, ±1.0 G. [b] Dichloromethane was added to maintain one liquid phase.

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(1) J. I. G. Cadogan, *Advan. Free Radical Chem.*, 2, 203 (1967); C. Walling and M. S. Pearson, *Top. Phosphorus Chem.*, 3, 1 (1966).

(2) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. B*, 1823 (1971).

(3) When hydroxyl radicals, generated from the Ti^{III}–H_2O_2 couple, were caused to react with dialkyl phosphonates in an aqueous flow system the only radicals detected were those formed by abstraction of hydrogen from the alkoxy groups.[4,5] The spectra obtained under our conditions indicate that abstraction of hydrogen from the alkoxy groups was much slower than abstraction of the hydrogen bound to phosphorus.

(4) E. A. C. Lucken, *J. Chem. Soc. A*, 1354 (1966).

(5) A. R. Metcalfe and W. A. Waters, *ibid.*, *B*, 340 (1967).

(6) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971; A. G. Davies and B. P. Roberts, *Nature Phys. Sci.*, 229, 221 (1971).

(7) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, 10, 738 (1971).

Table II. Hyperfine Coupling Constants in the β-Phosphonylalkyl Radicals **5**

		Hyperfine coupling constants, G $(\mathrm{EtO})_2\mathrm{P(O)}\underset{\mathrm{H^1}}{\mathrm{C}}\text{—}\underset{\mathrm{H^2}}{\mathrm{C}}\text{—}\underset{\mathrm{H^3}}{\mathrm{C}}$			
Olefin	Radical **5**	a^{31}(P)	a(H^1)	a(H^2)	a(H^3)
$CH_2{=}CMe_2$	$(EtO)_2P(O)CH_2\dot{C}(CH_3)_2$[a]	112.5	13.5		22.9
$CH_2{=}CHCH_2Pr$	$(EtO)_2P(O)CH_2\dot{C}HCH_2Pr$[b]	93.0	16.8	21.5	27.4
$CH_2{=}CHCH_2Bu$	$(EtO)_2P(O)CH_2\dot{C}HCH_2Bu$[c]	94.1	16.5	21.5	27.4

[a] −60°. [b] −70°. [c] −80°.

culated from the observed line positions and the Breit-Rabi formula, are listed in Table I. No further splitting from the alkyl groups was detected. No signals were observed when the photolyses were carried out in the absence of the peroxide.

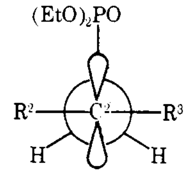
The addition of dialkyl phosphonates to olefins usually in the range 100–130°, and under the influence of peroxides, azo compounds, or uv irradiation, is generally accepted to involve a radical-chain mechanism with the propagating steps shown in eq 4 and 5.[1]

$$(R^1O)_2P\dot{O} + CH_2{=}CR^2R^3 \longrightarrow \underset{\mathbf{5}}{(R^1O)_2P(O)CH_2\dot{C}R^2R^3} \quad (4)$$

$$(R^1O)_2P(O)CH_2\dot{C}R^2R^3 + (R^1O)_2P(O)H \longrightarrow (R^1O)_2P(O)CH_2CHR^2R^3 + (R^1O)_2\dot{P}O \quad (5)$$

If a terminal olefin (*ca.* 10% v/v) is added to either the phosphonate or the pyrophosphite reaction system described above, the spectrum of the phosphonyl radical is quenched and that of the radical **5** becomes apparent at low temperature. Values of the hyperfine coupling constants are given in Table II.

The low values of the a(H^1) coupling constants imply that rotation about the C^1–C^2 bond is restricted, with a preferred conformation in which the C^1–P bond eclipses the p orbital containing the unpaired electron, as shown in formula **6**.



6

A hyperconjugative interaction has recently been suggested to account for such conformational preferences.[8]

When ethyl bromide (*ca.* 10% v/v) was added to either the phosphonate or pyrophosphite reaction systems at −28°, the spectrum of the phosphonyl radical was almost completely quenched, and that of the ethyl radical became apparent. Presumably the phosphonyl radical (like the trialkylsilyl radical[9]) abstracts a bromine atom as in eq 6 (R^1 = Me, Et, or *i*-Pr; R^2 = Et).[10]

$$(R^1O)_2PO + R^2Br \longrightarrow (R^1O)_2P(O)Br + R^2\cdot \quad (6)$$

The isomeric butyl bromides similarly gave the spectra of the corresponding butyl radicals, the signal strengths (*tert*-Bu· > *sec*-Bu· ≫ *i*-Bu· > *n*-Bu·) reflecting mainly the ease of abstraction of bromine by reaction 6. Benzyl bromide similarly gave rise to the spectrum of the benzyl radical, which is illustrated in Figure 1. Allyl bromide gave a strong spectrum of the allyl radical, and no addition of the phosphonyl radical to the double bond was apparent at −28°.

With *n*-butyl chloride a strong signal from the phosphonyl radical was still observed and the spectrum of the *n*-butyl radical was not apparent in the range +8 to −28°. With *tert*-butyl chloride at −42° a very weak signal from the *tert*-butyl radical was detected in addition to that from the phosphonyl radical, but at −2° the intensity of the *tert*-butyl radical spectrum had increased considerably at the expense of the phosphonyl radical.

In the phosphonate reaction system, the alkyl radical may abstract a hydrogen atom, so that reactions 6 and 7 combine into a chain process, where, under our conditions, reaction 7 is much slower than reaction 6.[11]

$$R^2\cdot + (R^1O)_2P(O)H \longrightarrow R^2H + (R^1O)_2\dot{P}O \quad (7)$$

Kinetic studies of the reactions described in this paper are now in progress.

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(8) A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, 1068 (1971).

(9) A. Hudson and R. A. Jackson, *ibid.*, 1323 (1969).

(10) Photolysis of a solution of ethyl bromide and diethyl phosphonate (or triethylsilane) in di-*n*-butyl ether gave rise to a weak spectrum of the ethyl radical. This probably arises by photolytic cleavage of the alkyl halide followed by abstraction of hydrogen from the phosphonate (or silane) by the bromine atom produced. Photolysis of the alkyl halide as the major route to alkyl radicals is ruled out by the observation of a strong esr spectrum of the *tert*-butyl radical when *tert*-butoxyl radicals were generated *thermally* at 80° from di-*tert*-butyl hyponitrite in a mixture of diethyl phosphonate and *tert*-butyl bromide in di-*tert*-butyl peroxide solvent. No *tert*-butyl radicals were detected when *tert*-butoxyl radicals were allowed to react with diethyl phosphonate at 80° in the absence of *tert*-butyl bromide.

(11) Dimethyl phosphonate has been reported to reduce carbon tetrabromide to bromoform,[12] but we have evidence that this is a heterolytic process. Diarylphosphine oxides are said[13] to reduce carbon tetrachloride and bromotrichloromethane to chloroform. The mechanism was thought to involve the diarylphosphonyl radical as a chain carrier.

$$Ar_2\dot{P}O + CCl_3X \longrightarrow Ar_2P(O)X + \dot{C}Cl_3$$

$$Ar_2P(O)H + \dot{C}Cl_3 \longrightarrow Ar_2\dot{P}O + CHCl_3$$

(12) G. Kamai and F. M. Khairasova, *Tr. Kazan. Khim. Tekhnol. Inst.*, **23**, 127 (1957); *Chem. Abstr.*, **52**, 9946 (1958).

(13) P. C. Crofts, I. M. Downie, and K. Williamson, *J. Chem. Soc.*, 1240 (1964).

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