radical can account for this discrepancy. The absolute values of the angles in DHP agree well with those predicted by molecular models and so one would expect any difference predicted between positions 7 and 12 to be accurate to a few degrees, and thus a different explanation of the nmr data must be sought.

Experimental Section

Infrared spectra were measured on a Beckman IR-5A spectrometer. Electron spin resonance spectra were recorded with a Varian 4502 X-band spectrometer which was modified for the endor experiments as described in ref 11. Melting points are uncorrected.

The synthesis of the following compounds have been reported previously: 7,12-dihydropleiadene,[19] 1-chloro-7,12-dihydropleiadene,[19] 1-methyl-7,12-dihydropleiadene,[9] 7,12-*o*-phenylene-7,12-dihydropleiadene,[20] 7,12-dihydropleiadene-7,7-d_2,[2a] 1-methyl-7,12-dihydropleiadene-7,7-d_2,[9] and 1-methyl-7,12-dihydropleiadene-*12,12*-d_2.[9]

To obtain 1-trideuteriomethyl-7,12-dihydropleiadene, the following sequence was followed. Using the procedure of Newman and Boden,[21] 1-chloro-7,12-dihydropleiadene was treated with cuprous cyanide in *N*-methylpyrrolidone to give 1-cyano-7,12-dihydropleiadene: mp 177.5–178.5°; $\nu_{C\equiv N}$ (Nujol) 4.51 μ; M^+ *m/e* 255.

Anal. Calcd for $C_{19}H_{13}N$: C, 89.39; H, 5.13; N, 5.48. Found: C, 89.42; H, 5.14; N, 5.45.

The nitrile was hydrolyzed with basic peroxide using the method of Noller[22] to give 1-carboxamido-7,12-dihydropleiadene: mp 250° dec; ir (Nujol) 2.99, 3.15, and 6.08 μ; M^+ *m/e* 273. The amide was hydrolyzed by the method of Sperber, *et al.*,[23] using *n*-butyl nitrite to yield 1-carboxy-7,12-dihydropleiadene: mp 236–240°; ν_{OH} 3.6–3.9 μ (b); $\nu_{C=O}$ 5.92 μ; M^+ *m/e* 274. The acid was treated with diazomethane to give the methyl ester which was reduced with aluminum chloride and lithium aluminum deuteride. This yielded after sublimation 1-trideuteriomethyl-7,12-dihydropleiadene which contained some alcohol ($-CD_2OH$) as shown by mass spectrometry. The mixture was used to obtain the endor spectrum of 1-trideuteriomethyl-7,12-dihydropleiadene since any remaining alcohol would form a diamagnetic alkoxide salt on reduction with potassium rather than a radical anion and, thus, would not interfere with the experiment.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(19) M. P. Cava and R. H. Schlesinger, *Tetrahedron*, 21, 3073 (1965).

(20) P. T. Lansbury and A. Lacher, unpublished results.

(21) M. S. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961).

(22) C. R. Noller, "Organic Synthesis," Collect. Vol. II, Wiley, New York, N. Y., p 586.

(23) N. Sperber, D. Papa, and E. Schwenk, *J. Amer. Chem. Soc.*, **70**, 3091 (1948).

Radical Intermediates in the Oxygenation of Phenylmagnesium Bromide. Evidence from Aromatic Phenylation

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Abstract: In a mixture of bromobenzene and diethyl ether, the oxygenation of phenylmagnesium bromide gives bromobiphenyls. The isomer distributions are similar to those obtained when bromobenzene reacts with phenylazotriphenylmethane or benzoyl peroxide, well-recognized sources of phenyl radicals. Thus, phenyl radicals are implicated as intermediates in the oxygenations. This is consistent with reaction mechanisms involving electron-transfer steps such as $PhMgBr + O_2 \rightarrow Ph\cdot + MgO_2Br$, or $PhMgBr + ROO\cdot \rightarrow Ph\cdot + ROOMgBr$, where R could be H.

Oxygenations of aliphatic Grignard reagents are believed to proceed through a two-stage reaction sequence (eq 1 and 2).[2] There is strong evidence that

$$RMgX + O_2 \longrightarrow ROOMgX \quad \text{oxidation stage} \qquad (1)$$

$$ROOMgX + RMgX \longrightarrow 2ROMgX \quad \text{metathesis stage} \qquad (2)$$

the oxidation stage involves free alkyl radical intermediates.[3-5] For this stage, a chain sequence of a type suggested by Russell is the most likely mechanism (eq 3 and 4).[6] The initiation step could be an electron-transfer reaction of the Grignard reagent with oxygen (eq 5). Apparently the metathesis stage does not proceed through free alkyl radicals.[5]

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (3)$$

$$ROO\cdot + RMgX \longrightarrow ROOMgX + R\cdot \qquad (4)$$

$$RMgX + O_2 \longrightarrow R\cdot + MgO_2X \qquad (5)$$

The oxygenation behavior of aryl Grignard reagents contrasts with that of alkyl Grignards. While high yields of alcohols (60–90%) are obtained from alkyl Grignard reagents, from phenylmagnesium bromide in diethyl ether phenol yields are poor (10–20%).[3] Benzene, biphenyl, 1-phenylethanol, and ethanol are major products (10–25% yields), while small quantities of such products as quinone, *p,p'*-terphenyl, diphenyl ether, and *p,p'*-biphenol have been reported.

Some of these products suggest that radicals are intermediates in the reactions. Thus, biphenol suggests phenoxy radicals. The ethanol and 1-phenylethanol are clearly derived from the solvent. This has been the basis of suggestions that phenyl radicals are intermediates in the oxygenations and that they attack the solvent.[7]

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(1) Based on a thesis submitted by A. C. Farrar in partial fulfillment of the requirements for an M.S. degree from The University of Georgia.

(2) C. Walling and S. A. Buckler, *J. Amer. Chem. Soc.*, 77, 6032 (1955).

(3) M. E. H. Howden, J. Burdon, and J. D. Roberts, *ibid.*, **88**, 1732 (1966).

(4) R. C. Lamb, P. W. Ayers, M. K. Toney, and J. F. Garst, *ibid.*, **88**, 4261 (1966).

(5) C. Walling and A. Cioffari, *ibid.*, **92**, 6609 (1970).

(6) G. A. Russell, *ibid.*, **76**, 1595 (1954).

(7) H. Hock, K. Kropf, and F. Ernst, *Angew. Chem.*, **71**, 541 (1959).

Table I. Products of Oxygenation of Phenylmagnesium Bromide in Bromobenzene–Diethyl Ether

Expt	$[G]_0$,[a] M	Conditions	PhOH	PhC_6H_4Br	PhH	$PhCHOHCH_3$
		Practical Magnesium				
26-1	0.25	Rapid O_2	0.11[b]	0.13		0.0091
26-2	0.25	Slow O_2	0.10	0.16		0.0095
26-3	0.25	Rapid O_2, excess DEE	0.07	0.08		0.015
28-1	0.06	Rapid O_2	0.13	0.19		0.028
28-2	0.06	Slow O_2	0.11	0.23	0.52	0.031
28-3	0.06	Rapid O_2, excess DEE	0.06	0.11	0.26	0.030
		Single-Crystal Magnesium				
29	0.24	Rapid O_2	0.22	0.12		0.095

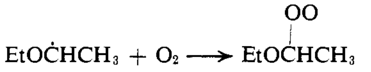
[a] Initial concentration of PhMgBr. [b] All yields are in moles per mole of initial Grignard reagent.

Table II. Bromobiphenyl Isomer Distributions

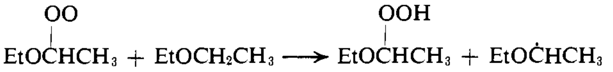
Expt	Ortho, %	Meta, %	Para, %
26-1	62	27	11
26-2	59	29	12
26-3	64	28	8
28-1	58	27	15
28-2	61	29	10
28-3	53	30	17
29	53	32	15
Av of above	58	29	13
PAT[a]	55	30	15
BP (80°)[b]	49	33	17

[a] Obtained in this work from a room temperature decomposition of phenylazotriphenylmethane in bromobenzene. [b] From the decomposition of benzoyl peroxide in bromobenzene: D. R. Augood, J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3412 (1953).

However, it is not necessary to assume that *phenyl* radicals are involved. It could be, for example, that oxygenation leads to the normal radical chain oxidation of diethyl ether (eq 6 and 7). 1-Phenylethanol

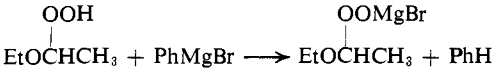


$$\mathrm{EtO\dot{C}HCH_3} + \mathrm{O_2} \longrightarrow \mathrm{EtO\overset{\overset{OO}{|}}{C}HCH_3} \quad (6)$$

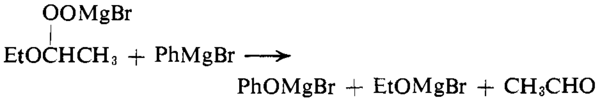


$$\mathrm{EtO\overset{\overset{OO}{|}}{C}HCH_3} + \mathrm{EtOCH_2CH_3} \longrightarrow \mathrm{EtO\overset{\overset{OOH}{|}}{C}HCH_3} + \mathrm{EtO\dot{C}HCH_3} \quad (7)$$

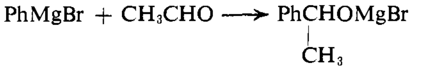
would be the expected product if the ether hydroperoxide reacted further to give acetaldehyde, which would then react with phenylmagnesium bromide (eq 8–10).



$$\mathrm{EtO\overset{\overset{OOH}{|}}{C}HCH_3} + \mathrm{PhMgBr} \longrightarrow \mathrm{EtO\overset{\overset{OOMgBr}{|}}{C}HCH_3} + \mathrm{PhH} \quad (8)$$



$$\mathrm{EtO\overset{\overset{OOMgBr}{|}}{C}HCH_3} + \mathrm{PhMgBr} \longrightarrow \mathrm{PhOMgBr} + \mathrm{EtOMgBr} + \mathrm{CH_3CHO} \quad (9)$$



$$\mathrm{PhMgBr} + \mathrm{CH_3CHO} \longrightarrow \mathrm{Ph\underset{\underset{CH_3}{|}}{C}HOMgBr} \quad (10)$$

One likely route would involve a hydroperoxide–Grignard metathesis reaction (eq 9). Thus, benzene, phenol, ethanol, and 1-phenylethanol are the rational products of reactions *not* involving phenyl radicals. Consequently, the facts outlined above do not constitute clear evidence for phenyl radical intermediates in oxygenations of phenylmagnesium bromide. We sought such evidence through a trapping procedure.

Phenyl radicals are so unreactive toward oxygen[8] that yields of aromatic phenylation products in decompositions of benzoyl peroxide are actually *enhanced* by the presence of oxygen.[9] Presumably, oxygen efficiently dehydrogenates intermediate phenylcyclohexadienyl radicals (eq 11). Thus, an aromatic substrate

$$\mathrm{Ph}\cdot + \mathrm{ArH} \longrightarrow \mathrm{PhArH}\cdot \xrightarrow{O_2} \mathrm{PhAr} + \mathrm{HOO}\cdot \quad (11)$$

would be an ideal trap for intermediate phenyl radicals in the oxygenation of phenylmagnesium bromide. The substitution pattern in the biaryls would be expected to be that which is characteristic of homolytic aromatic phenylation of the chosen substrate.

Accordingly, we oxygenated phenylmagnesium bromide in bromobenzene–diethyl ether. To maximize the probabilities of reactions of phenyl radicals with bromobenzene, as much of the diethyl ether as could be removed by low-temperature (60°) distillation was stripped off following Grignard preparation. Aliquots of the Grignard solutions were then subjected to several treatments: (a) immediate anaerobic protolysis with acetic acid, (b) "rapid oxygenation" by bubbling a stream of dry, CO_2-free oxygen through the Grignard solution, (c) "slow oxygenation" by passing a stream of oxygen over a slowly stirred solution of the Grignard reagent, and (d) readdition of diethyl ether followed by rapid oxygenation. The first treatment served as part of the analysis for the initial concentration of phenylmagnesium bromide, while the latter three treatments were carried out in hopes that they would yield readily interpretable variations in product yields.

Upon oxygenation, Grignard solutions prepared from either practical grade "Grignard" magnesium or from a single crystal of magnesium (considered to be the highest purity we could readily obtain) gave significant yields of bromobiphenyls (Table I). In experiment 28-2, the total yield of phenol, bromobiphenyls, benzene, and 1-phenylethanol was 89%. Readdition of diethyl ether before oxygenation resulted in a diminished total yield of these products (experiment 28-3).

The bromobiphenyl isomer distribution coincides with those obtained from reactions of recognized sources of phenyl radicals with bromobenzene (Table II). In no case was more than 5% of the ultimately formed quantity of bromobiphenyls present in the Grignard

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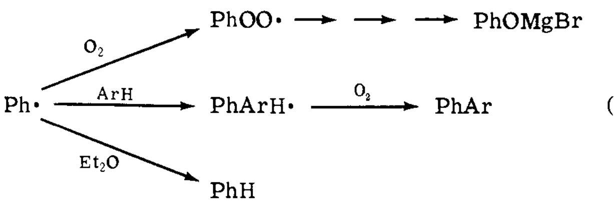
[8] G. A. Russell and R. F. Bridger, *J. Amer. Chem. Soc.*, **85**, 3765 (1963).

[9] R. T. Morrison, J. Cases, N. Samkoff, and C. A. Howe, *ibid.*, **84**, 4152 (1962).

solutions before oxygenation. Hence, greater than 95% of the homolytic phenylation of bromobenzene occurred during the oxygenation phases of the experiments. Thus, at least 10–25% of the original phenylmagnesium bromide leads to phenyl radicals.

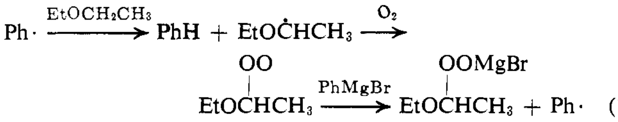
Variations in yields with the method of oxygenation are too small to justify interpretation; and so are the variations with diethyl ether concentration among the relative yields of phenol, bromobiphenyls, and benzene. If there had been significant yield variations, it would have been tempting to attempt to interpret them in terms of the competitions outlined in eq 12.



(12)

The lack of significant variations could be an indication that there are other operative pathways, besides those shown explicitly in eq 12, to benzene and phenol.

For example, reaction along the lowest branch of eq 12 could rationally lead to phenol as well as benzene (eq 13). Ethanol, 1-phenylethanol, and phenol could



$$\mathrm{Ph\cdot} \xrightarrow{\mathrm{EtOCH_2CH_3}} \mathrm{PhH} + \mathrm{EtO\dot{C}HCH_3} \xrightarrow{\mathrm{O_2}} \mathrm{EtO\overset{\overset{OO}{|}}{C}HCH_3} \xrightarrow{\mathrm{PhMgBr}} \mathrm{EtO\overset{\overset{OOMgBr}{|}}{C}HCH_3} + \mathrm{Ph\cdot} \qquad (13)$$

be concomitantly formed through reactions 9 and 10. It is amusing to note that this would lead to precisely the same stoichiometry as reactions 6–10.

Another potential pathway to phenol and benzene follows through the aromatic phenylation reaction (eq 11). Equation 11 and 14 could constitute a chain reaction. In any event, once reaction 11 were accomplished, there would be present a substance with an acidic hydrogen. Reaction of PhMgBr with HOO· itself could proceed to benzene, but if reaction 15 (proton transfer) does not compete well with reaction 14 (electron transfer), then HOOMgBr or some species derived from it by later reactions could be the acid giving rise to benzene. Further, it is quite likely that HOOMgBr or some derived species could react with PhMgBr to produce phenol. Thus, even if there were variations in the fractions of the reaction proceeding through the branches of eq 12, some of these variations would not necessarily lead to detectable changes in the product ratios.

$$\mathrm{HOO\cdot} + \mathrm{PhMgBr} \longrightarrow \mathrm{HOOMgBr} + \mathrm{Ph\cdot} \qquad (14)$$

$$\mathrm{HOO\cdot} + \mathrm{PhMgBr} \longrightarrow \mathrm{PhH} + \mathrm{BrMgO_2} \qquad (15)$$

Although the yield of bromobiphenyls is sensibly the same whether practical or pure magnesium is used, the yield of phenol appears sensitive to metal purity, more phenol being formed with the pure magnesium. A possible interpretation is that neither the efficiency of phenyl radical production from phenylmagnesium bromide nor the partitioning of phenyl radicals among their possible reaction pathways is affected by the purity of the magnesium, but that the nature or extents of reactions of the various peroxide and superoxide salts formed in the radical reactions may be affected by impurities.

The amount of biphenyl present in a reaction mixture after oxygenation was invariably 10–30% *smaller* than in the corresponding solution of the Grignard reagent after anaerobic protolysis. This suggests that a biphenyl precursor is present in the Grignard solutions, one which yields biphenyl upon treatment with acetic acid but which yields less biphenyl upon oxygenation and subsequent protolysis. Biphenylylmagnesium bromide would be one such biphenyl precursor, and this is a rational explanation of our findings. In an earlier report it was found that the reaction of chlorobenzene with magnesium in chlorobenzene gives biphenylylmagnesium chloride as well as phenylmagnesium chloride.[10]

In summary, our experiments provide strong evidence for phenyl radical intermediates in oxygenations of phenylmagnesium bromide, but the detailed reaction pathways remain uncertain.

Experimental Section

Analyses. Qualitative. From a large-scale oxygenation of a phenylmagnesium bromide solution, prepared as described below from practical grade magnesium, phenol, biphenyl, 2-bromobiphenyl, 3-bromobiphenyl, and 4-bromobiphenyl, were isolated. The phenol was obtained by extraction with aqueous base, and the others were obtained by preparative vpc of the neutral fraction (1.5 ft × 0.5 in. 5% Carbowax 20-M-TPA on 60–80 Chromosorb W, DMCS treated, at 220°). The physical properties, infrared spectra, nmr spectra, and vpc retention times agreed with those of authentic samples. Other products (benzene, 1-phenylethanol) were identified on the basis of retention times alone, determined by coinjection with authentic samples on several columns.

Quantitative. All quantitative product analyses were obtained by vpc using flame ionization detection, internal standards, and electronic digital integration. Product, [internal standard], (column), temperature: benzene, [toluene], (5 ft × 1/8 in. 20% Flexol Plasticizer 8N8 on 60–80 Chromosorb W, DMCS treated), 50°; phenol, biphenyl, 1-phenylethanol, [bibenzyl], (5 ft × 1/8 in. 20% FFAP on 60–80 Chromosorb W, DMCS treated), 200°; bromobiphenyls, [fluorene], (3 ft × 1/8 in. Bentone-34 on 60–80 Chromosorb W, DMCS treated), 190°.

Grignard Preparation and Assay. In experiment 26, Mg turnings[11] (2.43 g, 0.10 g-atom) reacted with bromobenzene (200 ml) containing diethyl ether (50 ml) under an atmosphere of purified nitrogen. Simple distillation at 60° removed excess volatiles (diethyl ether and benzene, the latter detected by vpc). Aliquots were treated as described in the main text. In the case of aliquots to which diethyl ether was added, equal volumes of stripped Grignard solution and diethyl ether were mixed.

When an aliquot of the stripped Grignard solution was heated to 86°, no further benzene distilled. Thus, the stripping procedure removes benzene quantitatively. After a 5-ml aliquot of the stripped Grignard solution had been acidified with 1 ml of glacial acetic acid, benzene was determined by vpc. From this, the concentration of phenylmagnesium bromide was estimated. The yield of phenylmagnesium bromide was 0.50 mol/mol of Mg. Biphenyl was

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[10] R. H. F. Manske and A. E. Ledingham, *Can. J. Chem.*, 27, 158 (1949).

[11] In experiments with "pure" magnesium, we employed turnings (carbide bit, at no time was the magnesium allowed to touch a metal surface) from a single crystal of magnesium obtained from Alfa Inorganics, Ventron Division. In private correspondence, Professor E. C. Ashby indicated to us his belief, based on experiments with Grignard reagents using magnesium from many sources, that the single-crystal metal used here is the best magnesium commercially available at this time. Although the manufacturer would not warranty purity higher than 99.99% at the time we purchased our sample, they did indicate that it was manufactured in the same manner that has been used in previous years. In a quotation to Professor Ashby dated March 20, 1969, the manufacturer indicated a purity of 99.9995% for such single crystals.

also determined by vpc, yield 0.16 mol/mol of Mg. Because at least some of the biphenyl determined in this manner was probably present before acidification as biphenylylmagnesium bromide (see main text), we regard this assay method as superior to conventional titrations for the purposes of our experiments. While the figures given in this section apply only to experiment 26, the method was employed in each experiment.

Reactions of Phenylmagnesium Bromide with Oxygen. Rapid oxygenations were carried out for 4 hr and slow oxygenations for 7 days. Temperatures were maintained between 20 and 30°. Before analyses, product mixtures were acidified with glacial acetic acid.

Acknowledgments. This research was supported by a grant from the National Science Foundation. We are grateful to Professor E. C. Ashby for discussions concerning the purities of commercially available magnesium.

Free-Radical Chemistry of Organophosphorus Compounds. I. Reactions of Phenyl Radicals from Phenylazotriphenylmethane with Trimethyl Phosphite

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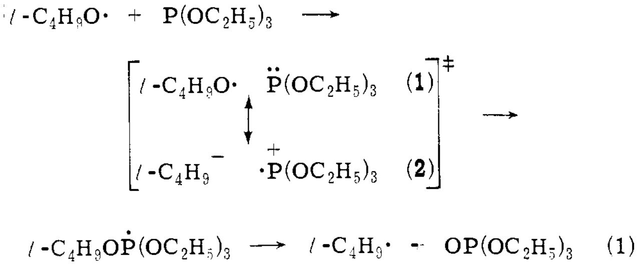
Received January 29, 1972

Abstract: Studies of the products of decomposition of phenylazotriphenylmethane (PAT) in trimethyl phosphite show dimethyl phenylphosphonate to be formed in 96–99% yields based on theoretically available Ph·. Additions of high concentrations of hydrogen donors, dimethyl (DMP) and diethyl phosphite (DEP), divert some of the phenyl radicals to benzene and also affect the distribution of the other products of PAT decomposition—triphenylmethane, 1,1,1-triphenylethane, 9-phenylfluorene, tetraphenylmethane, and 4-biphenylyldiphenylmethane. These results are interpreted in terms of the decomposition of PAT to give Ph·, N_2, and $Ph_3C\cdot$ followed by rapid reaction of the relatively electroneutral phenyl radical with TMP to give dimethyl phenylphosphonate. Methyl radicals, formed in the Ph·–TMP system, appear to yield primarily 1,1,1-triphenylethane in pure TMP and methane and $CH_3P(O)(OCH_3)_2$ or $CH_3P(O)(OC_2H_5)_2$ at high $[HP(O)(OR)_2]$. $CH_3P(O)(OR_2)$ probably results primarily from combination of $CH_3\cdot$ with $(RO)_2P(O)\cdot$. A small portion of $CH_3P(O)(OCH_3)_2$ likely results from an inefficient reaction of $CH_3\cdot$ with TMP under these conditions. Tetraphenylmethane, 4-biphenylyldiphenylmethane, and benzene appear to be cage products in degassed TMP as solvent.

Although it has been known for over a decade that certain free radicals undergo reaction at the phosphorus atom of trivalent phosphorus derivatives,[3] the factors which govern reactivity in such systems are not at all well understood. *E.g.*, alkoxy radicals and thiyl radicals transfer oxygen and sulfur, respectively, to phosphorus in very rapid reactions which may involve intermediate phosphoranyl radicals such as **3**.[3c,4] However, the *tert*-butyl radicals formed in reaction 1 are not reactive with triethyl phosphite[6] even though reaction 2 is thermodynamically very favorable.[7] It has been suggested[7] that *polar structures* such



$$t\text{-}C_4H_9O\cdot + P(OC_2H_5)_3 \longrightarrow \left[\begin{array}{ll} t\text{-}C_4H_9O\cdot & \ddot{P}(OC_2H_5)_3 \quad (\mathbf{1}) \\ \quad\updownarrow & \\ t\text{-}C_4H_9^{-} & \cdot\overset{+}{P}(OC_2H_5)_3 \quad (\mathbf{2}) \end{array}\right]^{\ddagger} \longrightarrow$$

$$\underset{\mathbf{3}}{t\text{-}C_4H_9O\dot{P}(OC_2H_5)_3} \longrightarrow t\text{-}C_4H_9\cdot + OP(OC_2H_5)_3 \qquad (1)$$

$$t\text{-}C_4H_9\cdot + P(OC_2H_5)_3 \not\longrightarrow t\text{-}C_4H_9P(O)(OC_2H_5)_2 + C_2H_5\cdot \qquad (2)$$

as **2** may stabilize the transition state for formation of **3**. With less electrophilic radicals, such as alkyls, contributors analogous to **2** should be less important. The apparent reactivity[10] of trichloromethyl radicals toward trialkyl phosphites (sequence 3) appears to be

$$Cl_3C\cdot + P(OR)_3 \rightleftharpoons Cl_3CP(OR)_3 \xrightarrow[-Cl_3C\cdot]{CCl_4} \underset{\mathbf{4}}{Cl_3C\overset{+}{P}(OR)_3Cl^{-}} \longrightarrow Cl_3CP(O)(OR)_2 + RCl \qquad (3)$$

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[1] Taken in part from the Ph.D. thesis of J.-J. L. Fu, University of Utah, June 1971; University Fellow, 1967–1970.

[2] University of Utah; to whom inquiries should be addressed.

[3] For reviews of the reactions of free radicals with trivalent phosphorus intermediates, see (a) C. Walling and M. S. Pearson, *Top. Phosphorus Chem.*, 3, 1 (1966); (b) J. I. G. Cadogan, *Advan. Free-Radical Chem.*, 2, 203 (1967); W. G. Bentrude, *Annu. Rev. Phys. Chem.*, **18**, 283 (1967). (c) For a recent esr study of these reactions, see J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969).

[4] Esr[5a–e] and chemical evidence[5d] for 3 has recently been found.

[5] (a) P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6033 (1972); (b) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem.*, **83**, 800 (1971); (c) G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 2528 (1972); (d) W. G. Bentrude and R. A. Wielesek, **91**, 2406 (1969); W. G. Bentrude and T. B. Min, *ibid.*, **94**, 1025 (1972).

[6] C. Walling and R. Rabinowitz, *ibid.*, **81**, 1243 (1959).

[7] *E.g.*, for the analogous reaction, $CH_3\cdot + (CH_3O)_3P \rightarrow CH_3\cdot + CH_3P(O)(OCH_3)_2$, ΔH may be estimated to be -43.7 kcal/mol. This estimate is based on the measured[8] $\Delta H1^\circ$ (298°, g) for $(CH_3O_3P$ (-168.3 kcal/mol) and calculated[9] $\Delta H_f{}^\circ$ (298°, g) for $CH_3P(O)(OCH_3)_2$.

[8] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London and New York, 1970.

[9] -211.9 kcal/mol: D. A. Bafus, E. J. Gallegos, and R. W. Kiser, *J. Phys. Chem.*, 70, 2614 (1966), by the method of J. L. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1969).

[10] See R. E. Atkinson, J. I. G. Cadogan, and J. T. Sharp, *J. Chem. Soc. B*, 138 (1969), and references cited therein.