Free-Radical Chemistry of Organophosphorus Compounds. IV.[1] Polar, Bond Strength, and Resonance Effects on Phosphoranyl Radical Formation

Wesley G. Bentrude,* Juian-Juian L. Fu,[2] and Peter E. Rogers

Contribution from the Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112. Received September 26, 1972

Abstract: Competitive reactions of *t*-BuO· with a series of X-$C_6H_4P(OCH_3)_2$ [X = *p*-MeO, H, *p*-Cl, and *m*-CF_3] were run to test the importance of polar substituent effects on the rates of such reactions. Rate differences were found to be negligible. (A rate constant for the case X = H of $3.1–3.7 \times 10^8\ M^{-1}\ sec^{-1}$ at 65° was estimated.) This is in contrast to the Michaelis–Arbuzov reactions of the same series of $ArP(OCH_3)_2$ with CH_3I which doubtless have very dipolar transition states. For these processes relative second-order rates at 40.2° varied over a 15-fold range and were correlated by the Hammett relation using σ rather than σ^+ values ($\rho = -1.74$). Gross general reactivity trends in free-radical oxidation, Arbuzov, and displacement reactions of trivalent organophosphorus compounds are shown to be explainable in terms of a *tentative* scheme, subject to further testing, which depends on the thermodynamics of phosphoranyl radical formation, ΔH_{PZ_4}. In this treatment ΔH_{PZ_4} is made dependent on the value of the orbital reorganization energy (ORE) and two, variable, substituent-dependent terms: *bond energy* (ΔH_{PZ}) and *resonance energy* in the intermediate $\cdot PZ_4$ (RE). The possibility that polar effects may play a secondary role in affecting transition state energies or ORE is suggested. Certain reactions not well explained in these terms are also discussed.

Certain free radicals are known to be extremely reactive toward trivalent organophosphorus compounds; *e.g.*, a recent estimate[3] places k_1 (30°) for reaction sequence 1 at $1.6 \times 10^8\ M^{-1}\ sec^{-1}$. Similarly, transfer of sulfur to trivalent phosphorus by RS· is

$$t\text{-BuO}\cdot + P(OEt)_3 \xrightarrow{k_1} t\text{-BuO}\dot{P}(OEt)_3$$
$$(\log k_1 = 9.83 - 2.24/2.303RT)^3 \qquad (1)$$
$$t\text{-BuO}\dot{P}(OEt)_3 \xrightarrow{k_2} t\text{-Bu}\cdot + OP(OEt)_3$$

very fast overall.[4] The reaction of phenyl radicals with trimethyl phosphite at 60° has a rate constant estimated[1] at $10^6–10^7\ M^{-1}\ sec^{-1}$ which places E_a at 3–4 kcal/mol (if $A = 10^9$).

$$Ph\cdot + P(OMe)_3 \longrightarrow Ph\dot{P}(OMe)_3 \longrightarrow PhP(O)(OMe)_2 + Me\cdot \qquad (2)$$

By contrast, potential reactions analogous to eq 2 of alkyl radicals with trialkyl phosphites proceed in a sluggish manner, if at all. *tert*-Butyl radicals from reaction 1 do not yield *t*-BuP(O)(OMe)$_2$.[5a] Potentially more reactive methyl radicals from reaction 2 are mostly consumed by reaction with H donors or $Ph_3C\cdot$.[6] This is in spite of the fact that the reaction of Me· with $(MeO)_3P$ to give $(MeO)_2P(O)Me$ may be estimated to be exothermic by −44 kcal/mol.[7]

Some years back it was proposed[5a] that the great reactivity of RO· and RS· toward $P(OR')_3$ might be the result of stabilization of the transition state for phosphoranyl radical formation by the contribution of polar structures, *e.g.*, **2**. The results reported in this

$$\underset{\mathbf{1}}{RO\cdot\ddot{P}(OR')_3} \longleftrightarrow \underset{\mathbf{2}}{RO^{-+}\dot{P}(OR')_3} \longleftrightarrow \underset{\mathbf{3}}{RO–\dot{P}(OR')_3}$$

paper stem from an effort to evaluate this idea as well as the effects of bond strengths and resonance factors on the ease of phosphoranyl radical intermediate formation. We herein present a tentative scheme based on the latter two factors to explain much of the variation in reactivity of free radicals toward trivalent phosphorus.

Results

A series of arylphosphonites, X-$C_6H_4P(OMe)_2$, **4–7**, was synthesized and was found to be oxidized to the corresponding arylphosphonates, **8–11**, by reaction with *tert*-butoxy radicals from thermal decomposition of di-*tert*-butyl hyponitrite, a well-established source of *tert*-butoxy radicals[10] (eq 3 and 4). Competitive reactions involving pairs of arylphosphonites were then run to test the response of the rates of oxidation by *tert*-butoxy radicals to changes in substituent X in an attempt to assess the importance of transition state structure **12a**. Finally, the relative reactivities of the arylphosphonites toward MeI were determined (reac-

---

(1) For part II in this series, see J.-J. L. Fu, W. G. Bentrude, and C. E. Griffin, *J. Amer. Chem. Soc.*, **94**, 7717 (1972); part III, ref 17.

(2) Taken in part from the Ph.D. Thesis of J.-J. L. Fu, University of Utah, June, 1971; University Fellow, 1967–1970.

(3) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, **10**, 738 (1971); *J. Chem. Soc., Perkin Trans. 2*, 993 (1972).

(4) Reaction of *n*-BuS· with $P(OEt)_3$ has been estimated to have a rate constant of $2.5 \times 10^8\ M^{-1}\ sec^{-1}$ at 70°; C. Walling and M. Pearson, *J. Amer. Chem. Soc.*, **86**, 2262 (1964).

(5) (a) C. Walling and R. Rabinowitz, *ibid.*, **81**, 1243 (1959). For more recent references dealing with the question of polar effects in free-radical reactions with trivalent organophosphorus compounds, see (b) M. B. Floyd and C. E. Boozer, *ibid.*, **85**, 984 (1963); (c) Y. Ogata and M. Yamashita, *J. Chem. Soc., Perkin Trans. 2*, 730 (1972). (d) A recent determination of the relative reactivities of hydrocarbons and Ph_3P toward *tert*-butoxy radicals shows that $(EtO)_3P$ and Ph_3P have similar reactivities toward such radicals [W. H. Starnes, Jr., and N. P. Neureiter, *J. Org. Chem.*, **32**, 333 (1967)] which supports the reactivity trends reported by Walling and Pearson[4] determined by direct competitive methods.

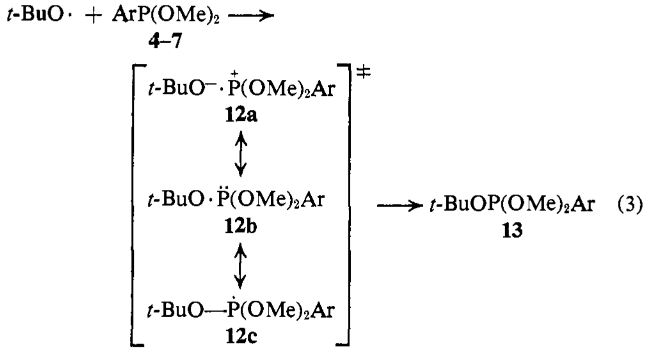
(6) J.-J. L. Fu and W. G. Bentrude, *J. Amer. Chem. Soc.*, **94**, 7710 (1972).

(7) $\Delta H_f°$ (298 g) for $CH_3P(O)(OCH_3)_2$ has been estimated [D. A. Bafus, E. J. Gallegos, and R. W. Kiser, *J. Phys. Chem.*, **70**, 2614 (1966)] by the method of Franklin[8] to be −211.9 kcal/mol. The experimental $\Delta H_f°$ (298 g) for $(CH_3O)_3P$ is +168.3 kcal/mol.[9]

(8) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(9) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

(10) H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967).



$$t\text{-BuO}\cdot + \underset{\mathbf{4\text{–}7}}{\text{ArP(OMe)}_2} \longrightarrow \left[\begin{array}{c} t\text{-BuO}^{-}\cdot\overset{+}{\dot{\text{P}}}\text{(OMe)}_2\text{Ar} \\ \mathbf{12a} \\ \updownarrow \\ t\text{-BuO}\cdot\ddot{\text{P}}\text{(OMe)}_2\text{Ar} \\ \mathbf{12b} \\ \updownarrow \\ t\text{-BuO—}\dot{\text{P}}\text{(OMe)}_2\text{Ar} \\ \mathbf{12c} \end{array}\right]^{\ddagger} \longrightarrow \underset{\mathbf{13}}{t\text{-BuOP(OMe)}_2\text{Ar}} \qquad (3)$$

$$\mathbf{13} \longrightarrow t\text{-Bu}\cdot + \underset{\mathbf{8\text{–}11}}{\text{OP(OMe)}_2\text{Ar}} \qquad (4)$$

tion 10) in order that a model reaction having a dipolar transition state would be available for comparison.

Syntheses of Arylphosphonites. Known procedures or variations thereof were used to prepare the phosphonites $X\text{-}C_6H_4P(OMe)_2$, where X = *p*-MeO (**4**), *p*-H (**5**), *p*-Cl (**6**), and *m*-CF_3 (**7**). With the exception of **4**, products of high purity were obtained. All samples of **4** contained approximately 8% by weight of an impurity with boiling point very close to that of **4** (vpc evidence). This impurity was observed to be unchanged in amount in all reactions of **4**. The exact amount of **4** in a given sample was calculated from its gas chromatogram by the method described in the Experimental Section.

Reactions of Individual Arylphosphonites with Excess *t*-BuO·. The decomposition of an excess amount of di-*tert*-butyl hyponitrite (DBH) at 65° ($t_{1/2}$ = 29 min)[10] in degassed 0.20–0.42 *M* solutions of **4–7** in benzene gave within experimental error quantitative oxidation of **4–7** to the corresponding arylphosphonates, **8–11** (Table I). Of the DBH decomposed, 43–53% was accounted for in formation of **8–11**. Gaseous products, 17–21% of acetone and 21–27% of *tert*-butyl alcohol were also found (yields based on added DBH). Phosphonites **4–7** were reasonably stable to the temperatures and times of the reaction (control experiments 1 and 2, 4 and 5, etc.). Phosphonite **4** gave 5–6% of a side product, *p*-$MeOC_6H_5P(O)(Me)OMe$, formed by unknown processes only during reaction with DBH added. Minor amounts of oxide were formed in controls of **4** and **5**. Kinetic studies have shown the rate of decomposition of DBH in benzene to be unaffected by added triethyl phosphite in the concentration range used in the studies of Tables I and II.[11] We have assumed that this rules out in the present system the possibility that DBH might be decomposed by some sort of bimolecular mechanism involving attack by trivalent phosphorus.

Competitive Reactions. Under the same reaction conditions, benzene solutions of **5** with **4**, **6**, and **7** were allowed to compete for *t*-BuO·. Results of these competitions appear in Table II. Appropriate control reactions to establish the stability of reactants were again carried out. Phosphonite pairs, usually in several molar ratios, were run in excess amounts compared to theoretically available radicals from DBH. Quantitative accountability in terms of amounts of phosphonites **4–7** consumed and moles of **8–11** formed was excellent. Of the DBH decomposed, 80–95% was accounted for by products **8–11**. The ability of **4–7** as *tert*-butoxy radical scavengers is attested to by the failure to detect more than 1–2% of acetone or *tert*-butyl alcohol by vpc.

Table I. Decomposition of Excess Di-*tert*-butyl Hyponitrite (DBH) in Benzene Solutions of Dimethyl Arylphosphonites[a]

			% yields of products[d]		
Expt no.	[DBH][e]	[Phosphonite][f]	Unreacted phosphonite	Phosphonate[g]	Phosphinate
1[b,i]	0	2.00 (**4**)	98.5	1.73 (**8**)	0
2[c]	0	2.00 (**4**)	98.1	1.81 (**8**)	0
3[j]	2.08	1.98 (**4**)	0	94.4 (**8**)	5.62[h]
4[b]	0	2.39 (**5**)	96.5	3.51 (**9**)	0
5[c]	0	2.39 (**5**)	96.4	3.65 (**9**)	0
6[j]	2.00	2.18 (**5**)	0	99.6 (**9**)	0
7[b]	0	4.68 (**5**)	101	0 (**9**)	0
8[c]	0	4.68 (**5**)	100	0 (**9**)	0
9[k]	4.78	4.15 (**5**)	0	100 (**9**)	0
10[b]	0	4.40 (**6**)	99.9	0 (**10**)	0
11[c]	0	4.40 (**6**)	99.6	0 (**10**)	0
12[k]	4.28	3.88 (**6**)	0	98.9 (**10**)	0
13[b]	0	4.22 (**7**)	99.4	0 (**11**)	0
14[c]	0	4.22 (**7**)	100	0 (**11**)	0
15[k]	4.09	3.78 (**7**)	0	99.9 (**11**)	0

[a] Solutions were degassed and decomposed at 65° for 5 hr except as noted in footnote *b*. [b] Solutions were degassed and sealed and then kept at ~0° before glc analyses. These reactions together with those labeled *c* serve as control reactions. [c] The degassed solutions were heated at 65° for 5 hr. [d] Calculated yields were based on the initial amount of phosphonite added. Sensitivities of all compounds were calibrated using an internal standard, nitrobenzene, anisole, or tridecane. At least three samples of each run were analyzed by glc. Averaged values of duplicate runs are reported. The maximum errors involved were less than ±3% of the reported values. [e] Mol $l.^{-1} \times 10$. Ideally, each mole of DBH should produce 2 mol of *tert*-butoxy radical. [f] Mol $l.^{-1} \times 10$, specific phosphonite used indicated in parentheses. [g] Phosphonate produced indicated in parentheses: **8**, *p*-$CH_3OC_6H_4P(O)(OCH_3)_2$; **9**, $C_6H_5P(O)(OCH_3)_2$; **10**, *p*-$ClC_6H_4P(O)(OCH_3)_2$; **11**, *m*-$CF_3C_6H_4P(O)(OCH_3)_2$. [h] Specific phosphinate produced, *p*-$CH_3OC_6H_4P(O)(CH_3)(OCH_3)$. [i] The concentration of **4** indicated and the % yields of products shown were all based on pure **4** present in sample (see Results). [j] 17–21% of acetone and 21–27% of *tert*-butyl alcohol were also obtained. The yields of these two compounds were calculated based on the initial amount of DBH added. [k] The peaks of acetone and *tert*-butyl alcohol on the glc column used in this experiment overlapped.

Since reactant concentrations did not remain constant during reaction, the relative reactivities of **4–7** were calculated from integrated rate expressions based on disappearance of **4–7** (eq 5) or formation of **8–11**

$$\frac{k_X}{k_H} = \ln \frac{[X\text{-}C_6H_4P(OMe)_2]_\infty}{[X\text{-}C_6H_4P(OMe)_2]_0} \bigg/ \ln \frac{[C_6H_5P(OMe)_2]_\infty}{[C_6H_5P(OMe)_2]_0} \qquad (5)$$

(eq 6) where 0 and ∞ indicate concentrations of re-

$$\frac{k_X}{k_H} = \frac{\ln \dfrac{[X\text{-}C_6H_4P(OMe)_2]_0 - [X\text{-}C_6H_4P(O)(OMe)_2]_\infty}{[X\text{-}C_6H_4P(OMe)_2]_0}}{\ln \dfrac{[C_6H_5P(OMe)_2]_0 - [C_6H_5P(O)(OMe)_2]_\infty}{[C_6H_5P(OMe)_2]_0}} \qquad (6)$$

actants or products at the beginning of the reaction and after 5 hr at 65° (10 half-lives). As shown in Table II, the k_X/k_H ratios calculated by (5) and (6) are nearly identical as expected for the near-quantitative conversions observed. As required by this treatment, k_X/k_H is independent of the phosphonite ratio.

---

(11) T. B. Min, unpublished results from this laboratory.

Table II. Competitive Reactions of **4**, **6**, and **7** with **5** for *tert*-Butoxy Radicals from DBH in Benzene at 65°[a]

					% yields of products[b]						
Phosphonite	[DBH][c]	[Phosphonite][c]	[**5**][c]	Mol ratio of phosphonites	Unreacted phosphonite **4**, **6**, or **7**	**5**	Phosphonates[d] **8**, **10**, or **11**	**9**	Phosphinate	$k_X{}^f/k_H$	k_X/k_H (av)
4[g,h]	0	4.62	4.92	0.939	98.5	97.6	1.32	1.70	0		
4[i]	0	4.62	4.92	0.939	98.1	98.0	1.40	1.80	0		
4	2.35	4.16	4.43	0.939	43.5	52.1	52.7	48.4	3.21[e]	1.18–1.24[j] 1.15–1.21[j]	1.20 ± 0.06
6[h]	0	4.13	4.48	0.922	97.7	100.0	0	0	0		
6[i]	0	4.13	4.48	0.922	100.2	100.0	0	0	0		
6	3.31	3.80	4.13	0.920	27.0	27.9	72.6	71.8	0	1.03 1.02	
6[h]	0	15.0	3.55	4.23	99.6	99.7	0	0	0		
6[i]	0	15.0	3.55	4.23	99.5	100.0	0	0	0		
6	3.63	13.5	3.20	4.22	69.5	70.0	30.0	30.2	0	1.01 1.00	
6[h]	0	2.85	13.6	0.210	99.9	99.4	0	0	0		
6[i]	0	2.85	13.6	0.210	99.0	99.7	0	0	0		
6	3.89	2.57	12.3	0.209	51.7	51.0	49.6	49.3	0	0.969 1.02	1.01 ± 0.02
7[h]	0	4.21	4.26	0.989	99.7	100.5	0	0	0		
7[i]	0	4.21	4.26	0.989	100.6	100.0	0	0	0		
7	2.43	3.92	3.96	0.990	44.7	46.0	55.2	54.5	0	1.05 1.03	
7[h]	0	11.8	3.53	3.34	99.6	99.3	0	0	0		
7[i]	0	11.8	3.53	3.34	99.9	100.2	0	0	0		
7	3.17	10.8	3.21	3.37	61.2	60.9	37.5	37.9	0	0.984 0.990	
7[h]	0	5.13	10.5	0.489	99.2	100.6	0	0	0		
7[i]	0	5.13	10.5	0.489	100.0	100.0	0	0	0		
7	2.95	4.45	9.16	0.486	58.4	58.9	41.4	41.2	0	1.02 1.01	1.01 ± 0.02

[a] Solutions were degassed and heated at 65° for 5 hr except as noted. [b] Based on the initial amount of corresponding phosphonite added. By vpc using internal standards and measured relative sensitivities. At least three samples of each run were analyzed by glc. Average values of duplicate runs were reported. The maximum error involved was less than ±3% of the reported values. [c] Mol $l.^{-1}$ × 10. [d] **8**, p-$CH_3OC_6H_4P(O)(OCH_3)_2$; **9**, $C_6H_5P(O)(OCH_3)_2$; **10**, p-$ClC_6H_4P(O)(OCH_3)_2$; **11**, m-$CF_3C_6H_4P(O)(OCH_3)_2$. [e] p-$CH_3OC_6H_4P(O)(CH)_3$-(OCH_3). [f] First value of k_X/k_H was calculated from eq 5, and second from eq 6. [g] The concentration of **4** and % yields of products shown were all based on pure **4** present in sample (see Results). [h] Solutions were degassed and sealed and then kept at 0° before glc analyses. These reactions together with (*i*) serve as control reactions. [i] The degassed solutions were heated at 65° for 5 hr. These reactions served as the stability controls under reaction conditions. These phosphonite percentages were used for the k_X/k_H calculation. [j] Values reported were corrected for the oxidation product present in the starting material and for the isomerization product present in the final reaction mixture (see Results).

The competitions between **4** and **5** were complicated somewhat by the formation of oxides (**8** and **9**) of **4** and **5** and the rearrangement product of **4**, p-$MeOC_6H_5P(O)(OMe)CH_3$, even in the controls (Table II). The final yields of these products were corrected by subtracting the amounts of **8** and **9** formed in the control experiment and then either adding the yield (3.21%) of isomerization product, p-$MeOC_6H_4P(O)(Me)OMe$, to $[\mathbf{4}]_\infty$ or subtracting it from $[\mathbf{4}]_0$. These two approaches assume the two extreme possibilities, *i.e.*, that all the isomerization occurs either at the beginning or at the end of the reaction. By this method a range k_X/k_H of 1.18–1.24 was obtained from expression 4 and 1.15–1.21 from (5).

If it is assumed that the effect of MeO is real and not a result of errors which accompany the assumptions employed in the competitive reactions of **4**, a Hammett correlation of the data may be attempted. Expressions 7 and 8 are obtained, depending on whether σ or σ^+

$$\log (k_X/k_H) = -0.0989\sigma + 0.0309 \quad (r = 0.786) \quad (7)$$

$$\log (k_X/k_H) = -0.0615\sigma^+ + 0.0193 \quad (r = 0.895) \quad (8)$$

values are used. Neither correlation is a very good one as shown by the correlation coefficients, and the substituent effect, if real, is minor.

Absolute Rate of t-BuO· Reaction with $PhP(OMe)_2$. In order that an estimate of the absolute rate constant, k_3, for reaction 3 with phosphonite **5** (Ar = Ph) might be obtained, a competition was carried out for t-BuO· between **5** (reaction 3) and cyclohexene (reaction 9).

$$t\text{-BuO}\cdot + c\text{-}C_6H_{10} \xrightarrow{k_9} t\text{-BuOH} + c\text{-}C_6H_9\cdot \quad (9)$$

From k_3/k_9 and k_1/k_9, obtained from the analogous competition between $(EtO)_3P$ and cyclohexene, k_3/k_1 was determined. The results of these experiments appear in Table III. Cyclohexene was used in excess and products were determined by glc. Two methods were employed to determine the final amounts of $(EtO)_3P$ or $PhP(OCH_3)_2$ (kinetic expressions in footnotes *a* and *b* of Table III). In method A the yield of oxidized product was subtracted from starting trivalent phosphorus compound. Alternately by method B, the remaining $(EtO)_3P$ or $PhP(OMe)_2$ was measured directly.

The results in Table III show $PhP(OMe)_2$ to be 1.3 to 1.6 times as reactive toward *tert*-butoxy radicals at 65° as is $(EtO)_3P$. The rate expression of Davies, *et al.*,[3] for reaction 1, $\log k_1 = 9.83 - 2.24/2.303RT$, gives a value for k_1 (65°) of 2.38 × 10^8 M^{-1} sec^{-1}. Therefore, k_3 must be 3.1 to 3.7 × 10^8 M^{-1} sec^{-1}, somewhat below the 10^9–10^{10} values usually assumed for diffusion-con-

Table III. Determination of k_3/k_1 by Competitive Kinetics

Temp, °C	k_1/k_9[a]		k_3/k_9[b]		k_3/k_1[c]	
	Method A	Method B	Method A	Method B	Method A	Method B
65[d]	110 ± 3 (5)[e]	129 ± 6 (5)	138 ± 7 (5)	210.7 ± 7 (4)	1.25 ± 0.1[g]	1.63 ± 0.12
65[f]	130 ± 10 (4)	166 ± 8 (3)	162 ± 2 (3)	255 ± 5 (3)	1.25 ± 0.12	1.54 ± 0.11
20[d]	187 ± 5 (3)	199 ± 5 (3)	172 ± 2 (3)	253 ± 10 (3)	0.92 ± 0.4	1.27 ± 0.08

[a] $k_1/k_9 = ([\text{c-C}_6\text{H}_{10}]/[t\text{-BuOH}]) \ln ([(\text{EtO})_3\text{P}]_0/[(\text{EtO})_3\text{P}]_\infty)$. [b] $k_3/k_9 = ([\text{c-C}_6\text{H}_{10}]/[t\text{-BuOH}]) \ln ([\text{PhP(OMe)}_2]_0/[\text{PhP(OMe)}_2]_\infty)$. [c] Based on average values. [d] Di-*tert*-butyl peroxide photolysis. [e] Values in parentheses indicate number of replications; ratio of c-C_6H_{10}/phosphorus species, 13–18. [f] Thermolysis of di-*tert*-butyl hyponitrite. [g] Error limits, one standard deviation (σ).

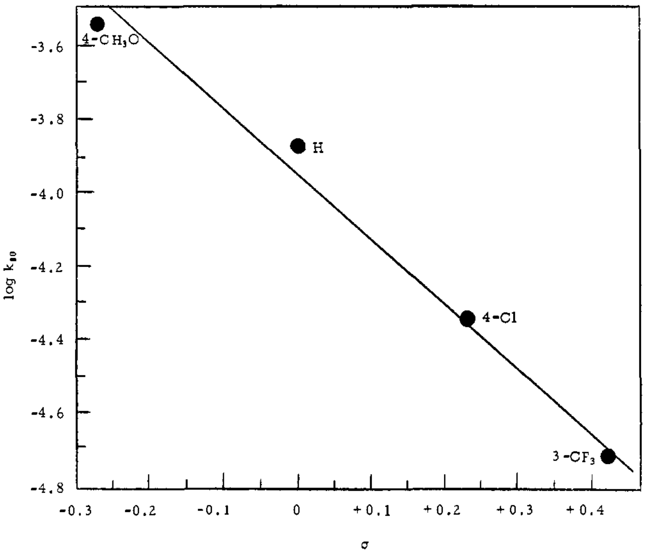


Figure 1. Hammett plot for Michaelis–Arbuzov reactions of iodomethane with dimethyl arylphosphinites, eq 11.

Table IV. Rate Data for Reactions of Iodomethane with Dimethyl Arylphosphonites in Benzene at 40.2°

Phosphonite	[Phosphonite][a]	[Iodomethane][a]	Pseudo-first-order rate constant, k_{10}'[b]	Second-order rate constant, k_{10}[c]
4	17.0	34.2	10.2 (r = 1.00) 9.71 (r = 0.992)	29.8, 28.4 Av 29.1 ± 1.0
5	17.7	33.1	4.46 (r = 0.996) 4.45 (r = 0.997)	13.5, 13.4 Av 13.5 ± 0.07
6	22.7	32.2	1.49 (r = 0.999) 1.45 (r = 0.998)	4.61, 4.49 Av 4.53 ± 0.08
7	17.4	33.7	0.658 (r = 0.998) 0.642 (r = 0.998)	1.95, 1.91 Av 1.93 ± 0.03

[a] Mol $\text{l.}^{-1} \times 10^2$. [b] $\text{Sec}^{-1} \times 10^5$. The first value was obtained by following disappearance of **4–7**, and the second from appearance of product. The least-squares method was used to obtain k_{10}'. The correlation coefficient is shown as r. [c] $\text{Mol}^{-1}\ \text{l. sec}^{-1} \times 10^5$, $k_{10} = k_{10}'/[\text{CH}_3\text{I}]$, corresponds to k_{10} of eq 10.

trolled reaction between uncharged species.[12] The competitions of Table II, therefore, appear to be meaningful. The E_a for reaction 3 is probably about 2 kcal/mol and judging from the effect of temperature of k_1/k_3 (Table III) slightly lower than E_a for (1).

Michaelis–Arbuzov Reactions of Dimethyl Arylphosphonites. It is generally postulated[13] that the Michaelis–Arbuzov reactions of trivalent phosphorus esters with alkyl halides proceed by rate-determining formation of phosphonium ions. In order that a model system might be available in which a positive charge is developed on phosphorus in the rate-determining step, the kinetics of the pseudo-first-order reactions (eq 10)

$$\text{ArP(OMe)}_2 + \text{MeI} \underset{\text{slow}}{\xrightarrow{k_{10}}} \text{Ar}\overset{+}{\text{P}}(\text{OMe})_2\text{MeI}^- \underset{\text{fast}}{\longrightarrow} \text{ArP(O)(OMe)Me} + \text{MeI} \qquad (10)$$

of methyl iodide with **4–7** in benzene at 40.2° were studied. The reactions were shown to be clearly pseudo first order for 2–3 half-lives. As shown in Table IV, the rate constants determined by least-squares treatments of data obtained by following disappearance of **4–7** or appearance of product phosphinates **8–11** were nearly identical. A plot using the averaged second-order rate constants, Figure 1, gave a better correlation with σ (eq 11) than with σ^+ (eq 12).

$$\log k = -1.74\sigma - 3.95 \quad (r = 0.994) \qquad (11)$$

$$\log k = -0.892\sigma^+ - 4.15 \quad (r = 0.934) \qquad (12)$$

Discussion

t-BuO·–ArP(OMe)$_2$ System. Several recent esr[3,14] and chemical[15] studies have confirmed the presence of phosphoranyl radicals during the reactions of *tert*-butoxy radicals with trivalent phosphorus compounds. In fact, all combinations of $t\text{-BuO}\dot{\text{P}}(\text{OEt})_x\text{Et}_{3-x}$ now have been observed by esr. It therefore seems reasonable to discuss the oxidation of **4–7** by t-BuO· in terms of reactions 3 and 4 and intermediate **13**.

Reaction of t-BuO· with PhP(OMe)$_2$ (3,4) gives product **9** quantitatively. There is no evidence for displacement of Ph· to give t-BuOP(OEt)$_2$. Added (EtO)$_3$P, which would rapidly consume some of any displaced phenyls, fails to yield PhP(O)(OEt)$_2$. Reaction 2, discussed earlier, also gives product **9** quantitatively.[6] Reactions 2 and 11 may be combined as represented by eq 13 and Figure 2 on the assumption that phosphoranyl radical **14** is common to both. For process (1) E_a is estimated at 2.24 kcal/mol.[3] The data

---

(12) A value of $1.0 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ for benzene at 20°, calculated from the modified Debye equation, appears in "Photochemistry," J. G. Calvert and J. N. Pitts, Jr., Ed., Wiley, New York, N. Y., 1966, p 627. We calculate from the Smoluchowski equation [M. V. Smoluchowski, *Physik. Z.*, 17, 557, 583 (1916); *Z. Phys. Chem.* (*Leipzig*), **92**, 129 (1917)] an encounter rate of $1.2 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ at 65°.

(13) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967, pp 37–45.

(14) (a) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969); (b) P. J. Krusic, W. Mahler, and J. K. Kochi, *ibid.*, **94**, 6033 (1972); (c) G. B. Watts and K. U. Ingold, *ibid.*, **94**, 2528 (1972); (d) G. B. Watts, D. Griller, and K. U. Ingold, *ibid.*, **94**, 8784 (1972); (e) A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **40**, C33 (1972).

(15) (a) W. G. Bentrude and T. B. Min, *J. Amer. Chem. Soc.*, **94**, 1025 (1972); (b) W. G. Bentrude and R. A. Wielesek, *ibid.*, **91**, 2406 (1969).

Table V. Pertinent Average Bond Strength ($\bar{D}$) and $\Delta H_f°$ Data[a]

Compd	$\Delta H_f°$(298, g), kcal/mol	Ref	Radical or atom	$\Delta H_f°$(298, g), kcal/mol	Ref	Bond	$\bar{D}$, kcal/mol	D, kcal/mol
$(EtO)_3P$	−195.9	9	EtO·	−6.7	*d*	P–O	84	
Me_3P	−22.5	9	Me·	34.0	*d*	P–C	67	
Et_3P	−32.8	*b*	Et·	25.7	*d*	P–C	62	
	−11.8	9	Et·	25.7	*d*	P–C	55	
Ph_3P	78.5	9	Ph·	78.5	*e*	P–C	77	
$(Me_2N)_3P$	−45.0	*c*	$Me_2N\cdot$	29.3	*d*	P–N	69	
$(EtO)_3PO$	−284.5	9	O	59.6	*d*	P═O		148

[a] White phosphorus as reference state [$\Delta H_f°$ (298, g) = 75.2 kcal/g-atom: D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand.* (*U. S.*), *Tech. Note*, No. 270-3 (1968). [b] H. A. Skinner, *Advan. Organometal. Chem.*, **2**, 49 (1964), from $\Delta H_c°$ data of W. F. Lautsch, P. Erzberger, and A. Trober, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **1**, 31 (1958). Cox and Pilcher[10] calculate $\Delta H_f°$ (298, g) for Et_3P from the same data of −11.8 kcal/mol. The value depends on the products assumed. We have used the Skinner number because it seems more reasonable and agrees with a recent analysis of kinetic results: K. W. Egger and T. L. James, *Trans. Faraday Soc.*, **66**, 2560 (1970). [c] S. B. Hartley, unpublished results quoted in S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev., Chem. Soc.*, **17**, 204 (1963). [d] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [e] S. W. Benson and E. W. Whittle, private communication. For a slightly older value, see A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 4578 (1967).

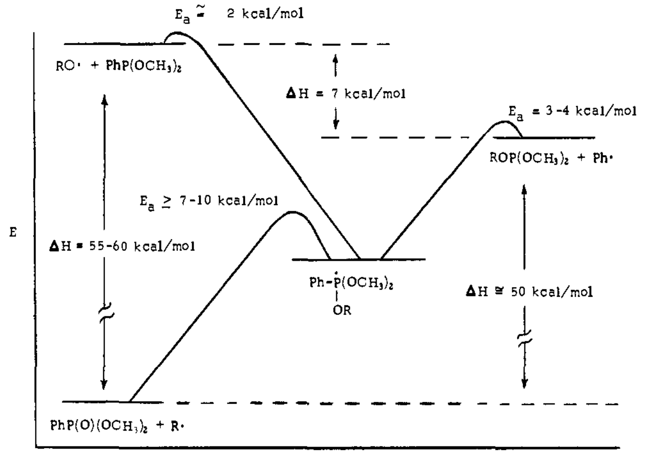
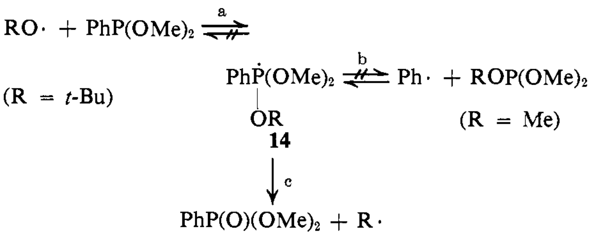


Figure 2. Energy diagram for phenyl and alkoxy radical reactions with trivalent phosphorus.



$$\begin{array}{l} \mathrm{RO\cdot} + \mathrm{PhP(OMe)_2} \underset{\not\leftarrow}{\overset{a}{\rightarrow}} \\ (R = t\text{-}\mathrm{Bu}) \qquad \underset{\substack{|\\ \mathrm{OR}\\ \mathbf{14}}}{\mathrm{Ph\dot{P}(OMe)_2}} \underset{\not\rightarrow}{\overset{b}{\leftarrow}} \mathrm{Ph\cdot} + \underset{(R\,=\,\mathrm{Me})}{\mathrm{ROP(OMe)_2}} \\ \qquad\qquad\quad \downarrow c \\ \qquad\qquad \mathrm{PhP(O)(OMe)_2} + \mathrm{R\cdot} \end{array} \tag{13}$$

of Table III suggest that E_a for reaction 11 is also of the order of 2 kcal/mol as the A factors for these reactions would be expected to be similar. The low E_a's for reactions 13a and 13b are depicted in Figure 2.

The enthalpy changes shown in Figure 2 were calculated using the bond energy and average bond strength data from Table V. Calculation of overall ΔH for oxygen transfer (−57 kcal/mol) requires also the reaction heat for the process t-BuO· → t-Bu· + O (91 kcal/mol from $\Delta H_f°$ data in footnote *d*, Table V) and assumes that $D_{P=O}$ for $(EtO)_3PO$ is a good approximation for $PhP(O)(OMe)_2$. Since (13b) shows no evidence of reversibility, it likely has E_a greater than the 8–10 kcal/mol required[3,14d] for β scission when R is t-Bu (unless A values are a controlling factor). Considering the fact that E_a for (13b) is 3–4 kcal/mol, this means that

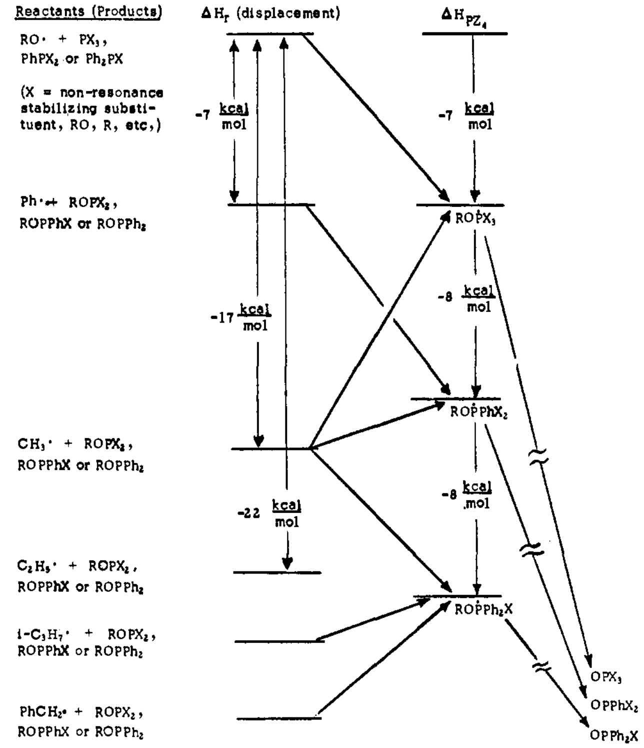


Figure 3. Energetics (ΔH) of phosphoranyl radical formation as a function of bond strengths and resonance energy.

step 13b must be exothermic by at least 3–6 kcal/mol to account for the high E_a for the reverse of (13b). Step 13a, therefore, must be exothermic by at least 10–13 kcal/mol. Clearly, the postulated step (13a) is irreversible and E_a estimates (~2 kcal/mol) apply to that step rather than any combination of steps (13a) and β scission.

The Michaelis–Arbuzov reaction rates of the series of arylphosphonites **4**–**7** with methyl iodide respond as expected for a reaction whose rate-determining transition state places a partial positive charge on phosphorus [reaction sequence 10]. Although ground-state stabilization would have a parallel effect on Michaelis–Arbuzov rates, in all likelihood a major portion of the rate variation reflects interaction of the aryl group with the charge of phosphorus. The hybridization about phosphorus in the transition state **12** for reaction

Table VI. Arbuzov-Like Radical Reactions of Trivalent Organophosphorus

	Reaction	Ref
(1)	$Cl_3C\cdot + (RO)_3P \rightarrow Cl_3CPO(OR)_2 + R\cdot(RCl)$	*a*
(2)	$Ph\cdot + (MeO)_3P \rightarrow PhPO(OMe)_2 + Me\cdot$	1, 6
(3)	$ClCH{=}CH\cdot + P(OEt)_3 \rightarrow ClCH{=}CHPO(OEt)_2 + Et\cdot$	*b*
(4)	$CH_3COCH_2\cdot + P(OEt)_3 \rightarrow CH_3COCH_2PO(OEt)_2 + Et\cdot$	*c*
(5)	$Me\cdot + (MeO)_3P \xrightarrow{\text{very slow}} MePO(OMe)_2 + Me\cdot$	6
(6)	$Et\cdot + (MeO)_3P \nrightarrow EtPO(OMe)_2 + Me\cdot$	This work
(7)	$t\text{-}Bu\cdot + P(OEt)_3 \nrightarrow t\text{-}BuPO(OEt)_2 + Et\cdot$	5a
(8)	$t\text{-}Bu\cdot + PhP(OMe)_2 \nrightarrow t\text{-}BuPO(OMe)Ph + Me\cdot$	This work
(9)	$Et\cdot + PhCH_2OP(OEt)_2 \rightarrow EtP(O)(OEt)_2 + PhCH_2\cdot$	*d*
(10)	$C_6H_5\cdot + Ph_2POR \rightarrow (C_6H_5)_3PO + R\cdot$	*e*
(11)	$Me\cdot + Ph_2POR \rightarrow MePOPh_2 + R\cdot$	*e*
(12)	$i\text{-}Pr\cdot + Ph_2POR \rightarrow i\text{-}PrPOPh_2 + R\cdot$	*f*
(13)	$Me_2N\cdot + Ph_2POR \rightarrow Me_2NP(O)Ph_2 + R\cdot$	
(14)	$t\text{-}Bu\cdot + Ph_2POR \xrightarrow{\text{very slow}} t\text{-}BuPOPh_2 + R\cdot$	*e*
(15)	$PhCH_2\cdot + Ph_2POR \nrightarrow PhCH_2POPh_2 + R\cdot$	*e*

[a] R. E. Atkinson, J. I. G. Cadogan, and J. T. Sharp, *J. Chem. Soc. B*, 138 (1969). [b] W. M. Daniewski, M. Gordon, and C. E. Griffin, *J. Org. Chem.*, **31**, 2083 (1966). [c] H. Tomioka, Y. Izawa, and Y. Ogata, *Tetrahedron*, **24**, 5739 (1968). [d] E. R. Hansen and P. E. Rogers, unpublished results from this laboratory. [e] R. S. Davidson, *Tetrahedron*, **25**, 3383 (1969). [f] R. S. Davidson, *Tetrahedron Lett.*, 3029 (1968).

3 clearly is not identical with that of reaction 10. Nevertheless, *the results of the competitive radical reactions fail to give any evidence for the importance of structure* **12a** *in the transition state of reaction 3.*

It is conceivable that polar effects in reactions such as (1) and (3) are in fact largely responsible for an E_a which is so low (~2 kcal/mol) that changes in substituent X perturb E_a only slightly resulting in essentially unmeasurable rate changes. However, as will be outlined below, we believe it is very likely that the great reactivity of *tert*-butoxy radicals toward trivalent phosphorus is *primarily* the result of the relatively great strength of the P–O bond formed in the phosphoranyl radical $RO\dot{P}X_3$ and the resulting exothermicity of that step. Polar transition state effects could be of *secondary importance* where alkoxy radicals are concerned but should only result in changes in rate when very drastic alterations in reactant polarity are made. The relative reactivities[4,5d] toward *tert*-butoxy radicals of the series n-Bu_3P, $(EtO)_3P$, Ph_3P (1.2:1.0:0.49), which are similar to those noted on autoxidation,[5d] may represent such a case. The slightly lower value of E_a for *tert*-butoxy radical reaction with Et_3P, 1.34 kcal/mol,[14e] compared with that for reaction with $(EtO)_2P$, 2.24 kcal/mol,[3] also is consistent with this view. Furthermore, the rates of autoxidations of Ph_2POMe, $PhP(OMe)_2$, and $P(OMe)_3$ decrease somewhat in the order given with $\rho^* = -0.38$ ($r = 0.928$).[5c,15c]

Other Free-Radical Reactions at Trivalent Phosphorus. In the introduction to this paper, mention was made of the great reactivity of phenyl radicals with trialkyl phosphites and the reluctance of methyl and *tert*-butyl radicals to undergo a reaction analogous to (2). Such processes may be considered to be free-radical analogs of the very well-known Michaelis–Arbuzov reaction. The failure of the alkyl radical initiated Arbuzov reactions is not a result of an unfavorable overall ΔH for reaction; *e.g.*, $\Delta H_r{}^{298}$ for process 14, which is quite slow, can be estimated to be about −44 kcal/mol,[7] a value similar in magnitude to that for reaction 2 ($\Delta H_r{}^{298}$ about −50 kcal/mol) and for reaction 1 ($\Delta H_r{}^{298} = -57$ kcal/mol). Since the potential methyl radical reactions were carried out either in the presence of triphenylmethyl radical traps or of good hydrogen donor conditions,[6] we have photolytically decomposed azoethane in $(MeO)_3P$ as solvent (see Experimental Section). $EtP(O)(OMe)_2$, to be expected from reaction of ethyl radicals in a manner analogous to (14), was absent in the products. In Table VI is compiled a listing of the potential reactions of the free radical Arbuzov type showing which ones do occur and those which have been attempted and are either very slow or do not take place at all.

$$Me\cdot + (MeO)_3P \longrightarrow Me\dot{P}(OMe)_3 \longrightarrow MeP(O)(OMe)_2 + Me\cdot \quad (14)$$

Free-radical displacements at trivalent phosphorus also are well known; *e.g.*, displacement often accounts for a major portion of product of reaction of alkoxy radicals with trivalent phosphorus (eq 15) and more

$$RO\cdot + PXYZ \longrightarrow RO\dot{P}XYZ \longrightarrow ROPYZ + X\cdot \quad (15)$$

rarely those of thiyl radicals.[16] To a first approximation, ease of displacement appears to depend on the strength of the P–X bond to be broken.[17] Certain other displacements occur on reaction with alkyl and phenyl radicals, *e.g.*, eq 16–19. On the other hand, the relatively stable radicals $(CH_3)_2\dot{C}CN$ and $Ph_3C\cdot$ were found[18] to be unreactive toward PCl_3. In reaction 18

(15c) Note Added in Proof. The rates of reaction of *tert*-butylperoxy radicals at −95° with a series of PX_3, with X covering the polarity range from halogen to alkyl, have recently been reported. Reactivities followed σ^* with $\rho^* = -0.75$: E. Furimsky and J. A. Howard, *J. Amer. Chem. Soc.*, **95**, 369 (1973). The increased ρ^* observed may be a result of the low temperatures used and/or the decreased reactivity of the *tert*-butylperoxy radicals compared to *tert*-butoxys.

(16) W. G. Bentrude, E. R. Hansen, W. A. Khan, and P. E. Rogers, *J. Amer. Chem. Soc.*, **94**, 2867 (1972).

(17) For example, for reaction of t-BuO· with a series of $XP(OEt)_2$, displacement of X· appears to predominate when $\bar{D}_{PX_3}$ is less than about 75 kcal/mol. See paper III in this series: W. G. Bentrude, E. R. Hansen, W. A. Khan, T. B. Min, and P. E. Rogers, *J. Amer. Chem. Soc.*, **95**, 2286 (1973). A picture based on bond strengths alone may well be oversimplified, however.

(18) L. Dulog, F. Nierlich, and A. Verhelst, *Chem. Ber.*, **105**, 874 (1972). On consideration of $\bar{D}_{PX_3}$ for $P(CH_3)_3$ (67 kcal/mol) and PCl_3 (77 kcal/mol), it is surprising that the reaction with t-Bu· occurs at all. Apparently the electronegative chlorines are P–C bond strengthening in $RPCl_2$. ($\bar{D}_{PX_3}$ value for PCl_3 calculated from $\Delta H_f{}^\circ$ (298, g) of PCl_3,[19] Cl·,[19] and white P.[19]) See also R. A. Bowie and O. C. Musgrave, *J. Chem. Soc. C*, 566 (1966) for formation of $PhPCl_2$ in low yields from photolysis of PhI/PCl_3 solutions.

displacement occurs in preference to the radical Arbuzov alternative which would yield $PhCH_2(Et)P(O)OEt$ and ethyl radical.

$$t\text{-Bu}\cdot + PCl_3 \longrightarrow t\text{-BuPCl}_2 + Cl\cdot \quad (16)^{18}$$

$$Ph\cdot + PCl_3 \longrightarrow PhPCl_2 + Cl\cdot \quad (17)^{18}$$

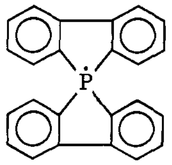
$$Et\cdot + PhCH_2P(OEt)_2 \longrightarrow EtP(OEt)_2 + PhCH_2\cdot \quad (18)^{20}$$

$$Et\cdot + t\text{-BuP(OEt)}_2 \not\longrightarrow EtP(OEt)_2 + t\text{-Bu}\cdot \quad (19)^{20}$$

Bond Strength and Resonance Effects on Reactivity. If the basic assumption[3,14,15] is made that reactions of free radicals at trivalent phosphorus centers (free radical Arbuzovs, oxidations, and displacements) all proceed *via* a phosphoranyl radical intermediate, then for any such reaction to be rapid, phosphoranyl radical formation must be not too unfavorable thermodynamically. Otherwise, a competitive reaction will consume the reactant radical even though *overall* the Arbuzov, displacement, or oxidation process might be very exothermic. The ensuing paragraphs outline an approach by which much *but not all* of the reactivity data for such systems may be interpreted in terms of the effects of bond strengths and resonance stabilization on the thermodynamics of phosphoranyl radical formation.

In Figure 3 we express diagrammatically the thermodynamics of phosphoranyl radical formation for a variety of reactant radicals, $Z\cdot$, and trivalent phosphorus compounds, PX_3. Figure 3 is most simply understood in the following way. The enthalpies of the reactants $RO\cdot$ and PX_3 are set equal ($X = Ph\cdot$, $RO\cdot$, R_2N, alkyl, halogen, etc.). Then, assuming that $\bar{D}_{PX}$ is not greatly affected by the nature of the other substituents on phosphorus (*i.e.*, $\bar{D}_{PX}$ for $ROPX_2$ and $(RO)_2PX$, *e.g.*, equals $\bar{D}_{PX}$ for PX_3), the energetics (ΔH) of displacement of $X\cdot$ by $RO\cdot$ can be readily calculated and depicted (column 2 of Figure 3). If the enthalpy of formation of $RO\dot{P}X_3$ from reaction of $RO\cdot$ with PX_3 is called ΔH_{PZ_4}, then ΔH_{PZ_4} for formation of $RO\dot{P}X_3$ from reaction of various $X\cdot$ with $ROPX_2$ ($X \neq Ph$) is established. In view of the low activation energies observed for reaction of $RO\cdot$ with various PX_3, the value of -7 kcal/mol assigned *arbitrarily* to the formation of $RO\dot{P}X_3$, where X is any substituent but phenyl, in Figure 3 is not unreasonable. If it is then assumed that each phenyl substituted for X in $RO\dot{P}X_3$ lowers the energy of $RO\dot{P}X_3$ by 8 kcal/mol, the remainder of Figure 3 readily is constructed. A further refinement of this approach would include consideration of alteration of ΔH_{PZ_4} as a result of affects of differences in substituent electronegativities on the stability of $RO\dot{P}X_3$, etc.[21] The right-hand column of Figure 3 shows potential radical-Arbuzov and oxygen-transfer products which would result from β-scission processes available to $\cdot PZ_4$.[21]

One piece of data which may be cited as possible evidence for the odd-electron delocalizing abilities of aryl substituents in phosphoranyl radical intermediates is the small isotopic hyperfine splitting constant (A_P), 17.9 *G*, noted for radical **15**.[22] (This value may be compared to splittings of 700–1100 G for radicals of the type $(RO)_xPR_{4-x}$[3,14].) Alternate explanations of the above esr data are possible, however.[22b] Kinetic evidence consistent with an unusual stability of the intermediate $ROO\dot{P}Ph_3$ in autoxidation of Ph_3P also has been presented.[5c]



15

An alternate approach to the construction of Figure 3 which more clearly defines the contributions of various factors is to divide the energy change for formation of a phosphoranyl radical into three contributing terms: the strength of the bond to phosphorus being formed (ΔH_{PZ}); any resonance stability imparted to the phosphoranyl radical by substituents on phosphorus (RE); and the orbital reorganization energy involved in rehybridization about phosphorus. These factors may be expressed in the form of eq 20. Figure 3 results if

$$\Delta H_{PZ_4} = ORE + \Delta H_{PZ} + RE \quad (20)$$

for each case the value of $\bar{D}_{PX_3}$ (Table V) is used for ΔH_{PZ}; -8 kcal/mol for the resonance stability (RE) imparted by each phenyl substituent is assumed; and a constant, arbitrary value of 77 kcal/mol is assigned to ORE. For example, ΔH_{PZ_4} for the reaction of t-BuO$\cdot$ with $PhP(OR)_2$ is calculated to be -15 kcal/mol ($+77 - 84 - 8$).

Examination of Figure 3 reveals that the energetics of phosphoranyl radical formation in any particular case depend on the *strength of the bond* in $\cdot PZ_4$ being formed and any resonance stabilization imparted to $\cdot PZ_4$ by its substituents. *The scheme of Figure 3 is proposed as a very tentative one and must be subjected to further tests.* Expecially open to question is the magnitude of RE assigned to phenyl substituents. With Figure 3 as now constructed, essentially three cases may be distinguished. For those in which ΔH_{PZ_4} is very favorable (case I), the reacting radical is trapped rapidly and irreversibly[15] and then awaits α or β scission. At the opposite extreme, the reason for the unreactivity of very stable radicals is apparent. Formation of $\cdot PZ_4$ does not occur at all (case II). Near the middle of

---

(19) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand. (U. S.), Tech. Note*, No. 270-3 (1968).

(20) E. R. Hansen and P. E. Rogers, unpublished results from this laboratory.

(21) Electron-withdrawing electronegative substituents are known to have a stabilizing effect on pentacovalent phosphorus compounds, especially if they are allowed to occupy the axial positions in the trigonal bipyramidal structure; see, *e.g.*, D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *J. Amer. Chem. Soc.*, **91**, 5243 (1969).

(22) (a) D. Hellwinkel, *Chem. Ber.*, 102, 528, 548 (1969); (b) R. Rothius, T. K. J. Luderer, and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, 91, 836 (1972). The latter authors obtained a low-temperature spectrum resulting from interaction of the odd electron with 8 hydrogens and from which 0.80 of the total spin density could be assigned to the rings. The rest was presumed to reside on carbons neither hydrogen nor phosphorus substituted. It was proposed that the odd electron is delocalized over the two aromatic rings of a *single* biphenyl portion of the molecule. We believe that a possible alternative explanation is that the odd electron is delocalized by interaction with only the axial or equatorial rings of a trigonal bipyramidal structure in which the odd electron is equatorial or appreciable spin density may be present at only two carbon atoms of each of four phenyl rings which are configurationally equivalent as a result of a rapid pseudorotation which interchanges them. Further studies on the structure of **15** are awaited with interest.

Figure 3 formation of $\cdot PZ_4$ may be marginally favorable or even slightly exothermic (case III). Reversibility can then become an important alternative to α and β scission. The success of a given reaction then will depend on the competition between α or β scission and reversal to regenerate $Z\cdot + PZ_3$. It now seems worthwhile to discuss reactivities of specific known systems in relation to Figure 3.

Figure 3 and eq 20 predict that reactions of alkoxy radicals should be very favorable energetically (case I), a consequence of the P–O bond strength $[\Delta H_{PZ}(\bar{D}_{P(OEt)_3}) = -84$ kcal/mol]. Phenyl radical reactions have negative predicted ΔH_{PZ_4} because of the relatively strong P–C bond formed $[\Delta H_{PZ} = -77$ kcal/mol] and the resonance energy term. The value of ΔH_{PZ} for the vinyl radical (Table VI, reaction 3) should be similar to that of phenyl, and the observed reaction is consistently explained. The unreactivity (Table VI, eq 5–7) of the alkyl radicals, methyl, ethyl, and *tert*-butyl[23] when X is methoxy or ethoxy is predicted by this treatment because of the relatively weak P–C bonds formed and relatively high activation energies for β scission. However, when two phenyl substituents are attached to phosphorus in the reactant, the resonance energy term makes adduct formation favorable for methyl and ethyl in agreement with experiment using methyl radicals[24] (eq 11, Table VI). A single phenyl substituent is not sufficient to make the *t*-Bu· reactive toward trivalent phosphorus (eq 8, Table VI) but a sluggish reaction ensues when two phenyls are present on phosphorus (eq 14, Table VI). More stable radicals such as benzyl,[23] as expected, do not react even with $(C_6H_5)_2$-POR (Table VI, eq 14), because ΔH_{PZ} is too small (case II). (ΔH_r (displacement) for $PhCH_2\cdot$ probably should be much more negative than is shown in Figure 3 in view of the resonance energy of benzyl radical.) Isopropyl radical,[23] intermediate in stability between ethyl and benzyl, is reactive[24] with Ph_2POR (Table VI, eq 12). The reaction of dimethylamino radical ($\Delta H_{PZ} = -69$ kcal/mol) with diphenylphosphinites occurs as predicted (Table VI, eq 13), but this radical should be found to be relatively less reactive with trimethyl phosphite, if the predictions of eq 20 hold.

Phenyl substituents have the affect[17] of increasing the β/α scission ratio in reactions of $RO\cdot$ with PX_3. If the exothermicity of both processes is decreased by phenyl stabilization of the phosphoranyl radical, the relative activation free energies will change also, and α scission may even become endothermic. Alternatively, a phenyl substituent may lower the activation energy for β scission independently of that for α scission. In this view the role of phenyl is to allow an otherwise completely reversible phosphoranyl radical formation (case III) to give product.

As noted above, with certain radicals near the center of Figure 3, $\cdot PZ_4$ may be reversibly accessible *via* a mildly endothermic reaction (case III) but fail to yield radical-Arbuzov product because β scission has too high an activation energy. In the oxidation of triethyl phosphite by *tert*-butoxy radical, E_a for β scission is known to be 8–10 kcal/mol[14b,d] but is probably considerably higher for C–O cleavage to give radicals less stable than *t*-Bu. Reaction of *t*-BuO· with various alkylphosphonites[16,17] gives only alkyl displacement product (eq 21)

$$t\text{-BuO}\cdot + \text{RP(OEt)}_2 \longrightarrow t\text{-BuO}\dot{\text{P}}\text{(OEt)}_2\text{R} \longrightarrow t\text{-BuOP(OEt)}_2 + \text{R}\cdot \qquad (21)$$

Weak esr signals assignable to $t\text{-BuO}\dot{\text{P}}\text{Et(OEt)}_2$ have been observed[14e] when *t*-BuO· is generated in the presence of $EtP(OEt)_2$. If ethyl displacement in this system does indeed proceed *via* the above phosphoranyl radical as intermediate, then $\Delta G^{\ddagger}$ for α scission is clearly lower than that for β scission. One would then expect the addition of an alkyl radical to a trialkyl phosphite (eq 14) to be highly reversible and not lead to Arbuzov rearrangement unless a C–O β cleavage of very low activation energy were available. Reaction 9 of Table VI supports this view. β scission to give the relatively stable $PhCH_2\cdot$ from $Et\dot{P}(OEt)_2OCH_2Ph$ now competes with α scission. (A portion of phosphate also results from reaction of $PhCH_2O\cdot$ with $EtP(OEt)_2$.)[16,17] In addition, an esr signal assigned to $Et_2\dot{P}(OEt)_2$ results in generation of Et· in a solution of $EtP(OEt)_2$.[14e] These observations strongly suggest that reactions of alkyl radicals (except benzyl) with $(RO)_3P$ are of the case III type.[24a]

Displacement reactions 16 and 17 require that $R\dot{P}Cl_3$ be accessible if the process is two-step. It has been suggested[18] that PCl_3 should be more reactive with nucleophilic radicals such as *t*-Bu than is $(CH_3O)_3P$ because of differences in direction of the molecular dipole in the two molecules. In terms of Figure 3, an alternative interpretation is that a facile α scission traps $t\text{-Bu}\dot{P}Cl_3$ (which may be stabilized by delocalization of the odd electron on to the chlorine) and leads to product[25] whereas β scission of $t\text{-Bu}\dot{P}(OCH_3)_3$ does not compete with reversal of its formation. Alternately, the displacements by phenyl and *tert*-butyl may be concerted processes. In either event, the reported[18] greater efficiency of the reaction with phenyl radical is consistent with the relative stabilities of Ph· and *t*-Bu·. The failure noted of $(CH_3)_2\dot{C}CN$ and $Ph_3C\cdot$ is predictable in terms of Figure 3. The unreactivity[20] of *tert*-butylphosphonite (eq 19) compared to $PhCH_2P(OEt)_2$ (eq 18) toward Et· indicates that in such displacements the P–C bond to the leaving radical is broken in the rate-determining step. This idea can be accommodated by either a one- or two-step displacement mechanism. Steric effects assignable to the bulky *tert*-butyl substituent could also be important. The mechanistic details of such displacements remain to be worked out.

Certain aspects of the reactivity of free radicals with trivalent phosphorus are not well interpreted, however, in terms of eq 20 and Figure 3. Two examples are reactions 1 and 4 of Table VI. In the former case it has been established that reactions of CCl_4 with trialkyl

---

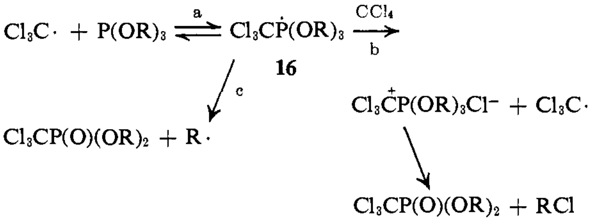
(23) $\bar{D}_{PR_3}$ values for R = *t*-Bu, *i*-Pr, or $PhCH_2$ are not known but are presumably lower than for Me and Et. Combustion heats for a variety of PR_3 would be most welcome. Even more desirable would be a series of bond dissociation energies so as to avoid the problems associated with use of *average* bond energies.

(24) R. S. Davidson, *Tetrahedron*, **25**, 3383 (1969).

(24a) Note Added in Proof. It has been reported recently that esr signals assigned to $CH_3\dot{P}(OR)_3$ are observed on photochemical decomposition of azomethane in the presence of trialkyl phosphites. These signals were not observed with ethyl radicals: A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 2224 (1972). These findings are completely consistent with our notion that alkyl radicals add reversibly to trialkyl phosphites and that the stability of the resulting phosphoranyl radical is dependent on the strength of the phosphorus–carbon bond formed.

(25) With $(EtO)_2PCl$, *t*-BuO· gives a displacement/oxidation ratio based on products of ~1:1; see ref 17.

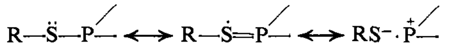
phosphites contain a free-radical component, and process 22a does seem like a reasonable first step. But



(22)

the possibility is that this is a special case in which reversible formation of **16** involving the stable trichloromethyl radical is followed by a rapid trapping reaction (22) in the absence of which step (22c) alone would not give measurable amounts of $Cl_3CP(O)(OR)_2$.[26] Reaction 4 of Table VI may also be somewhat unique in that the acetonyl radical, if present, is formed by photolysis of chloroacetone. Molecular chlorine might act in this case like CCl_4 to trap the phosphoranyl radical formed.

The extremely high reactivities of thiyl radicals are not within the expectations of eq 20 and Figure 3 based on ΔH_{P-S}[27] unless a very large resonance energy term is included (structure **17**). Resonance stabilization by



17a **17b** **17c**

phenyl in $\cdot PZ_4$ was discussed previously, and the −8 kcal/mol resonance stabilization arbitrarily assigned to phenyl may be compared to the −19 kcal/mol stabilization experienced by CH_3 when one of its hydrogens is replaced by a phenyl group to give $PhCH_2\cdot$ or −13 kcal/mol difference in stabilities of $CH_3CH_2\cdot$ and $PhCH_2\cdot$.[28] Divalent sulfur α to the developing radical center reduces $\Delta H^{\ddagger}$ for azo compounds by ~11 kcal/mol.[29] Polar effects may also be operative in the $RS\cdot$ reaction or a single-step mechanism which avoids the phosphoranyl radical may obtain.[30] In regard to the polar effect possibilities, the relative rates from competitions,[4] $(n\text{-}C_4H_9)_3P > (C_2H_5O)_3P > (C_6H_5)_3P > (C_6H_5O)_3P$, are about in the order predicted by consideration of structure **57c**. An evaluation of polar effects on thiyl and trichloromethyl reactivity appears to be in order.

A potentially useful consequence of the great differences in reactivity between alkyl and alkoxy radicals is that trialkyl phosphites are essentially selective scavengers, rapidly consuming alkoxy but not alkyl radicals.

Experimental Section

Proton magnetic resonance (pmr) spectra were recorded with a Varian A-60 or A-56/60 spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are in δ parts per million (ppm) downfield from TMS. Peak multiplicity is noted by: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (ir) spectra were recorded on a Beckman IR-5A spectrophotometer. Only medium or strong intensity bands are recorded except for those weak bands important for structural assignment. Abbreviations are: vw, very weak; w, weak; m, medium; s, strong; vs, very strong. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Synthesis of Dimethyl Phenylphosphonite (5). Phenylphosphonous dichloride (43 g, 0.24 mol) was mixed with 200 ml of ice-cooled, dry pentane under nitrogen. With constant stirring, methanol (15.4 g, 0.481 mol) and triethylamine (48.6 g, 0.480 mol) in 100 ml of pentane were added dropwise. The mixture was warmed to room temperature and refluxed for another 0.5 hr after which the white precipitate (triethylamine hydrochloride) was filtered by quickly pouring the mixture into a large separatory funnel which had in the bottom a plug of glass wool covered with a layer of glass beads. The pentane solution was forced through the glass wool with positive nitrogen pressure into a vented flask protected from moisture by a calcium chloride drying tube. Most of the pentane was removed by placing the flask in a 45° oil bath and maintaining a flow of N_2 over the surface of the liquid. The remaining solution was distilled giving **5**: yield 60%; bp 101–102° (15 mm) or 55.5° (1.25 mm), lit.[31] 102–104° (15 mm).

Dimethyl phenylphosphonate (9) was prepared either from TMP and iodobenzene by the method of Plumb, Obrycki, and Griffin[32] or by oxidation of **5** with nitrogen dioxide as follows. To **5** (8.6 g, 0.05 mol) in 20 ml of dichloromethane cooled in an ice bath was added, dropwise, with constant stirring a nitrogen dioxide–saturated dichloromethane solution (50 ml, brown color). The temperature of the reaction mixture was kept always under 30°. The appearance of a green color indicated completion of oxidation. After the solvent was evaporated, the residue was distilled: yield 90%; bp 79° (2.0 mm), lit.[33] 79–80° (2.0 mm).

4-Methoxyphenylphosphonous dichloride was prepared in a very low yield by a modification of the procedure of Gefter.[34] A mixture of anisole (90 g, 0.83 mol), anhydrous ferric chloride (60 g, 0.40 mol), and phosphorus trichloride (114 g, 0.83 mol) was stirred and refluxed under the dry nitrogen gas for 5 hr. Hydrogen chloride gas was copiously evolved and was absorbed by a water trap. The reddish brown reaction mass was twice extracted with ligroin (bp 60–90°), the ligroin was evaporated, and the residue was vacuum distilled: yield 10%; bp 71° (0.2 mm), lit.[34] 104° (1.0 mm).

Dimethyl 4-methoxyphenylphosphonite (4) was obtained from the phosphonous dichloride and methanol using the procedure outlined for **5**. An impurity (8%, glc) which was nonseparable from **4** was encountered in all preparations and remained unchanged during all studies being carried on **4**: yield of **4**, 60%; bp 40–42° (0.05 mm); pmr (neat) δ 3.47 (d, 6 H, J_{HP} = 11.0 Hz, CH_3OP), 3.65 (s, 3 H, 4-$C\mathit{H}_3OC_6H_4P$), 6.86 (doublet of doublets, 2 H, $J_{HH'}$ = 8.5 Hz, $J_{H'P}$ = 2.0 Hz, 4-$CH_3OC_6\mathit{H}_2'H_2P$), 7.50 (doublet of doublets, 2 H, $J_{HH'}$ = 8.5 Hz, J_{HP} = 6.0 Hz, 4-$CH_3OC_6H_2'\mathit{H}_2P$); ir (film) 3050 w, 2941 m, 2830 w, 1595 s, 1500 s, 1465 m, 1400 vw, 1300 m, 1250 vs, 1180 m, 1110 m, 1044 vs, 1013 vs, 830 m, 800 m, 745 s, 715 s cm^{-1}.

Dimethyl 4-methoxyphenylphosphonate (8) was prepared by N_2O_4 oxidation of **4** in a manner similar to the procedure described for the preparation of **9**: yield 80%; bp 116–117° (0.12 mm); lit.[35] 113–114° (0.1 mm); pmr (neat) in agreement with literature report.[35]

4-Chlorophenylphosphonous bis(diethylamide) was synthesized using a modification of a procedure given in the literature.[36] To a clean, dry, nitrogen-flushed, three-necked, round-bottom flask fitted with a stirrer, addition funnel, reflux condenser, and nitrogen bubbler, a few pieces of iodine crystals and magnesium turnings (14.6 g, 0.601 mol) were added. After the iodine was vaporized by a flame and the flask contents were cooled to room temperature, 50 ml of anhydrous ether was added. A solution of *p*-bromochlorobenzene (76.5 g, 0.400 mol) and anhydrous ether (400 ml) was

---

[26] $Ph_4P^+Cl^-$ is isolated from photolysis of Ph_5P in CCl_4, quite possibly *via* an abstraction step involving $Ph_4P\cdot$ and CCl_4 analogous to (22b): G. A. Razuvaev and N. A. Osanova, *Dokl. Akad. Nauk SSSR*, **104**, 552 (1955); *Zh. Obshch. Khim.*, 26, 2531 (1956). A similar process may be suggested for the formation of $Ph_4P^+I^-$ on PhI photolysis in Ph_3P; J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, 27, 4711 (1962).

[27] We are unaware of a value for $\bar{D}_{PX_3}$ for X = SR but expect it to be considerably less than for PR_3 or $P(OR)_3$.

[28] Estimated for data: J. A. Kerr, *Chem. Rev.*, 66, 465 (1966).

[29] A. Ohno and Y. Ohnishi, *Tetrahedron Lett.*, 4405 (1969).

[30] Esr evidence for the intermediates $MeS\dot{P}(OEt)_3$ and $n\text{-}Bu_3\dot{P}SMe$ has recently been published: A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **38**, C8 (1972). We suspect that as E_a for β cleavage in intermediates ($RO\dot{P}Z_3$ or $RS\dot{P}Z_3$) decreases with lowered strength of the bond undergoing scission an E_a of zero may be approached at which time oxygen or sulfur transfer would become concerted.

[31] A. N. Pudovik and V. K. Krupnov, *J. Gen. Chem. USSR*, **38**, 1239 (1968).

[32] J. B. Plumb, R. Obrycki, and C. E. Griffin, *J. Org. Chem.*, 31, 2455 (1966).

[33] K. D. Berlin and M. E. Peterson, *J. Org. Chem.*, 32, 125 (1967).

[34] E. L. Gefter, *J. Gen. Chem. USSR*, 33, 3481 (1963).

[35] R. Obrycki and C. E. Griffin, *J. Org. Chem.*, 33, 632 (1968).

[36] H. Schindlbauer, *Monatsh. Chem.*, **96**, 1936 (1965).

added at a sufficient rate to keep the ether refluxing gently. Addition was completed in 2 hr, and the mixture was allowed to reflux for an additional hour after which the excess magnesium turnings were filtered off under dry nitrogen. To a solution of bis(diethylamino)chlorophosphine[37] (82.0 g, 0.389 mol) and pyridine (92.0 g, 1.16 mol) in 200 ml of anhydrous ether cooled in an ice bath was added rapidly the above Grignard solution. The reaction mixture was warmed to room temperature, refluxed for 4 hr, kept overnight in a cold room (~10°), and filtered under dry nitrogen. After removing the solvent under reduced pressure on a rotary evaporator, distillation through a Vigreux column yielded pure 4-chlorophenylphosphonous bis(diethylamide), yield 80%: bp 135° (1.3 mm), lit.[36] 163–168° (10 mm); pmr (neat) δ 1.07 (t, 12 H, J_{HH} = 7.0 Hz, $(CH_3CH_2)_2NP$), 2.93, 3.08 (doublet of quartets, 8 H, J_{HP} = 9.5 Hz, J_{HH} = 7.0 Hz, $(CH_3CH_2)_2NP$), 7.05–7.43 (m, 4 H, 4-ClC_6H_4P); ir (film) 3050 vw, 2959 s, 2924 m, 2857 m, 1572 w, 1475 m, 1460 m, 1374 s, 1195 s, 1181 s, 1080 m, 1014 s, 920 s, 822 s, 793 m, 749 m, 666 m cm^{-1}.

4-Chlorophenylphosphonous dichloride was prepared from the reaction between 4-chlorophenylphosphonous bis(diethylamide) and dry hydrogen chloride:[36] yield 75%; bp 83.5–84° (1.3 mm), lit.[36] 115–118° (9 mm); pmr (neat) δ 7.12–7.73 (m, 4-$ClC_6H_4PCl_2$); ir (film) 3040 vw, 1572 m, 1480 m, 1390 m, 1088 s, 1015 m, 818 s, 745 s cm^{-1}.

Dimethyl 4-Chlorophenylphosphonite (6). The general procedure used in the preparation of **5** was employed for the synthesis of **6** from methanol and the above dichloride: yield 50%; bp 79–80° (1.35 mm), lit.[38] 107–109° (5 mm); pmr (neat) δ 3.45 (d, 6 H, J_{HP} = 10.5 Hz, CH_3OP), 7.20–7.55 (m, 4 H, 4-ClC_6H_4P); ir (film) 3050 vw, 2976 w, 2933 m, 2833 w, 1580 m, 1481 m, 1451 w, 1389 m, 1179 m, 1086 s, 1044 vs, 1015 vs, 823 s, 745 vs, 722 s cm^{-1}.

Dimethyl 4-chlorophenylphosphonate (10) was synthesized by oxidation of **6** with nitrogen dioxide in a manner similar to that given for the preparation of **9**: yield 95%; bp 107–108° (1.1 mm), lit.[39] 95.6° (0.1 mm); pmr ($CDCl_3$) δ 3.73 (d, 6 H, J_{HP} = 11.0 Hz, $CH_3OP(O)$), 7.26–7.85 (m, 4 H, 4-$ClC_6H_4P(O)$); ir (film) 3050 w, 2994 w, 2941 m, 2849 w, 1585 s, 1486 m, 1393 m, 1253 vs, 1186 s, 1134 s, 1093 s, 1055 vs, 1022 vs, 818 vs, 789 vw, 739 m cm^{-1}.

3-Trifluoromethylphenylphosphonous Bis(diethylamide). By the general procedure outlined in the preparation of 4-chlorophenylphosphonous bis(diethylamide), 3-trifluoromethylphenylmagnesium bromide (from 3-bromobenzotrifluoride (130 g, 0.578 mol) and magnesium turnings (30 g, 1.2 mol)) were allowed to react with bis(diethylamino)chlorophosphine (82 g, 0.4 mol) and pyridine (95 g, 1.2 mol) in absolute ether at −5° to give the desired product: yield 70%; bp 112–113° (1.30 mm); pmr (neat) δ 1.10 (t, 12 H, J_{HH} = 7.0 Hz, $(CH_3CH_2)_2NP$), 2.99, 3.15 (doublet of quartets, 8 H, J_{HP} = 9.5 Hz, J_{HH} = 7.0 Hz, $(CH_3CH_2)_2NP$), 7.28–7.85 (m, 4 H, 3-$CF_3C_6H_4PN$); ir (film) 3049 vw, 2967 m, 2924 m, 2857 w, 1600 vw, 1464 w, 1418 w, 1377 m, 1325 s, 1183 s, 1167 s, 1129 s, 1104 s, 1074 s, 1015 s, 921 s, 800 m, 709 w, 702 m, 668 w, 652 w cm^{-1}.

3-Trifluoromethylphenyldichlorophosphine was prepared from the reaction of the above diamide with anhydrous hydrogen chloride:[36] yield 81%; bp 54–55° (1.4 mm); pmr (neat) δ 7.35–8.18 (m, 3-$CF_3C_6H_4PCl_2$); ir (film) 3050 vw, 1605 w, 1414 w, 1325 vs, 1174 s, 1136 vs, 1106 s, 1073 s, 801 m, 709 w, 694 s, 651 w cm^{-1}.

Dimethyl 3-trifluoromethylphenylphosphonite (7) was synthesized from the above phosphonous dichloride and methanol using the same procedure given for the preparation of **5**: yield 30%; bp 58.5–59° (1.45 mm); pmr (neat) δ 3.50 (d, 6 H, J_{HP} = 10.6 Hz, CH_3OP), 7.28–7.93 (m, 4 H, 3-$CF_3C_6H_4P$); ir (film) 3050 vw, 2976 w, 2933 m, 2825 s, 1600 w, 1460 w, 1420 w, 1330 vs, 1318 s, 1170 vs, 1130 vs, 1075 s, 1045 vs, 1015 vs, 805 m, 752 s, 726 m, 709 m, 701 m, 652 m cm^{-1}.

Anal. Calcd for $C_9H_{10}F_3O_2P$: C, 45.39; H, 4.23; P, 13.01. Found: C, 45.08; H, 4.06; P, 13.52.

Dimethyl 3-Trifluoromethylphenylphosphonate (11). Oxidation of the corresponding phosphonite (**7**) by nitrogen dioxide according to the procedure given in preparation of **9** gave **11**: yield 60%; bp 88–90° (1.25 mm); pmr ($CDCl_3$) δ 3.77 (d, 6 H, J_{HP} = 11.0 Hz, $CH_3OP(O)$), 7.51–8.12 (m, 4 H, 3-$CF_3C_6H_4P(O)$); ir (film) 3050 vw, 2976 w, 2941 m, 2833 w, 1610 m, 1462 w, 1430 m, 1330 vs, 1316 s, 1258 vs, 1172 vs, 1130 vs, 1075–1020 vs (broad band), 833 s, 807 m, 772 m, 699 s, 654 m cm^{-1}.

Anal. Calcd for $C_9H_{10}F_3O_3P$: C, 42.53; H, 3.97; P, 12.19. Found: C, 42.76; H, 4.11; P, 12.22.

Methyl methylarylphosphinates were synthesized in very routine fashion from the corresponding dimethyl arylphosphonites (**4–7**) by reaction with methyl iodide according to the procedure of Neimysheva, *et al.*,[38] with the exception of methyl methylphenylphosphinate prepared from the phenylphosphonite according to Harwood and Grimsley.[40] All except the phosphinate from **4**, isolated by preparative glc, were purified by vacuum distillation. These compounds were readily characterized by pmr spectroscopy.

Di-*tert*-butyl hyponitrite was prepared according to the procedure described by Traylor.[10] It was recrystallized from absolute ethanol-pentane and was dried under a stream of nitrogen at −65°.

Di-*tert*-butyl Hyponitrite (DBH) Thermal Reactions. Pyrex reaction ampoules were carefully washed with aqueous HNO_3 and ammonium hydroxide, rinsed with distilled water, oven dried, and then capped with rubber serum caps and thoroughly flushed with pure nitrogen before use. Standard solutions containing DBH, **4**, **5**, **6**, or **7**, were made up by weight in benzene in serum-capped, N_2-flushed volumetric flasks. Solutions containing desired concentrations of DBH and reactants **4–7** were then made up in volumetric flasks from the above mixtures using standard volumetric procedures. The actual weights of added substrate solutions were also recorded so that the number of moles of all reactants was accurately known. Known amounts of these solutions were weighed into the sample ampoules by means of a long-needle syringe ensuring no reactants adhered to the walls. Reaction ampoules were degassed at 10^{-5}–10^{-6} mm with three successive freeze–thaw cycles before sealing *in vacuo*. The sealed tubes were heated at 65.0 ± 0.1° for 10 half-lives of DBH (5 hr). Glc analyses were carried out by the internal standard method using an F&M Model 810 dual column instrument with thermal conductivity detectors with 10% poly(*m*-phenyl ether) (six-ring) on 60–80 Chromosorb W (AW) columns and also F&M Model 700, dual column chromatograph equipped with FID on 10% silicone gum rubber (UCC-W-982) on 60–80 Diatoport S columns. Sensitivity plots of area ratio *vs.* mole ratio contained from three to seven points exclusive of origin and had correlation coefficients of 0.999–1.000. Areas were measured with a Model 227 Disc integrator. Each solution was analyzed several times and results averaged. Products isolated by preparative glc from reaction mixtures had spectral properties identical with those of authentic samples.

To analyze accurately by glc the reactions which involved **4** and its inseparable impurity, the following procedure was used. The expressions below show the relation among: total weight of two given impure samples (W^1, W^2); the areas of pure **4** [$A_4{}^1$ and $A_4{}^2$] and the impurity ($A_I{}^1$ and $A_I{}^2$) for a given volume of injected sample; and the sensitivity factors (weight/area) for the pure **4** (S_4) and the impurity (S_I). From gas chromatograms of samples containing somewhat different amounts of **4** and the impurity, values of S_4 and S_I were determined. In this way the absolute amount of pure **4** in any sample could be determined accurately.

$$(A_4{}^1)(S_4) + (A_I{}^1)(S_I) = W^1$$

$$(A_4{}^2)(S_4) + (A_I{}^2)(S_I) = W^2$$

Azobisethane Photodecomposition in Trimethyl Phosphite. A 1 *M* solution of azobisethane in neat trimethyl phosphite was placed in a serum-capped Pyrex tube, thoroughly flushed with pure nitrogen, and then irradiated for 36 hr with a 654 A-36 Hanovia 200-W medium-pressure lamp. After this time glc analysis on an SE-30 column showed the azo compound to be nearly all consumed. No traces of $EtP(O)(OMe)_2$ could be detected although it would have been well separated from the other peaks in the chromatogram.

Kinetics of MeI Reactions with $ArP(OMe)_2$. A solution of iodomethane with the internal standard was made by carefully weighing the compounds and benzene solvent into a nitrogen-filled 10-ml volumetric flask. A solution of the phosphonite was made up in a similar way. The two solutions were then placed in a large lightproof, thermostated oil bath maintained at 40.2 ± 0.1°. After a minimum of 15 min, 5-ml aliquots of each solution were withdrawn and weighed rapidly into a nitrogen-flushed 100-ml Pyrex test tube which was sealed with a rubber serum cap. The reaction tube was shaken for 30 sec and returned to the bath. At appropriate intervals, under positive nitrogen pressure, approximately

---

[37] P. G. Chantrell, C. A. Pearce, C. R. Toyer, and R. Twaits, *J. Appl. Chem.*, 14, 563 (1964).

[38] A. A. Neimysheva, V. I. Savchuck, and I. K. Knunyants, *J. Gen. Chem. USSR*, **36**, 520 (1966).

[39] R. Obrycki and C. E. Griffin, *Tetrahedron Lett.*, 5049 (1966).

[40] H. J. Harwood and P. W. Grimsley, Jr., *J. Amer. Chem. Soc.*, **82**, 423 (1960).

0.5-ml samples of the reaction mixture were withdrawn from the tube by means of a long-needle hypodermic syringe inserted through the serum cap, quenched by cooling to liquid nitrogen temperature, and then analyzed by glc immediately. The reaction was followed quantitatively by measuring the relative area ratio of both the reactant and product *vs.* the internal standard. The time of reaction was measured from the beginning of shaking to the instant of quenching. Rate constants were calculated from 9 to 13 separate determinations of concentrations in the region 10–85% reaction. Control experiments indicated that iodomethane was not reactive toward the phosphonites under conditions of glc analysis and that the internal standard was inert toward the reactants under all circumstances. The products were stable and were isolated from glc and identified.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Thallium in Organic Synthesis. XXXII. Oxidative Rearrangement of Olefins Using Thallium(III) Nitrate (TTN)[1-3]

Alexander McKillop,[4a] John D. Hunt,[4a]
Frank Kienzle,[4b,c] Eric Bigham,[4b] and Edward C. Taylor[4b]*

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, Norfolk, England, and the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received June 27, 1972*

Abstract: Thallium(III) nitrate (TTN) effects rapid rearrangement of olefins to carbonyl compounds. Examination of other thallium(III) salts has shown that some control over the reaction pathway can be achieved by varying the nature of the associated anion and the reaction conditions. The scope, limitations, and synthetic utility of TTN oxidations of olefins are defined.

Although oxidation of unsaturated systems with electrophilic metal salts is of long established synthetic and mechanistic interest, the majority of these processes are unique with respect to both oxidant and substrate, and meaningful correlations on the relative reactivities of metal salts are disappointingly few. The most notable exceptions are metalation and oxymetalation reactions.[5,6] Both processes have long been known with mercury(II) salts, and there are now examples of metalation and/or oxymetalation reactions with lead(IV), thallium(III), palladium(II), platinum(II), gold(III), and, possibly, rhodium(III) salts.[5,6] These reactions thus appear to be characteristic of metal ions which can be regarded as "soft"[7] or as having "class b"[8] character. Within this general context the reactions of unsaturated, nonaromatic substrates with the isoelectronic salts of mercury(II), thallium(III), and lead(IV) are of particular interest. The oxidation potentials of the ions are in the order Hg < Tl < Pb; two comparative studies of oxymetalation of olefins with the acetates of the three metals have established the intermediate position of the thallium salt.[9,10] In this and subsequent papers we describe the results of our investigations on oxythallation reactions with particular emphasis on the use of thallium(III) nitrate (TTN) as oxidant.

Oxidation of olefins with mercury(II), thallium(III), or lead(IV) salts can lead to a variety of products depending on the nature of the metal cation, the anion, the solvent, and the structure of the olefin. Oxymercuration with mercury(II) acetate has been extensively investigated,[6] and the synthetic scope of mercury(II) salt oxidation has been recently reviewed[11] and further extended by the introduction of mercury(II) trifluoroacetate[12] and nitrate.[13] The analogous reactions with thallium(III)[6,14] and lead(IV)[6,15] acetate have been studied much less comprehensively, and in contrast to oxymercuration there are few synthetically useful procedures based on oxythallation or oxyplumbation. Thus, treatment of olefins with lead(IV) acetate generally gives complex mixtures of products,[15] while stable oxymercuration adducts are formed with mercury(II) salts.[6] Oxythallation adducts have been isolated only occasionally,[9,16-18] and a variety of products derived by subsequent decomposition of the oxythallation adducts may be formed.[9,10,14,18-27]

---

[1] Part XXXI: A. McKillop, R. A. Raphael, and E. C. Taylor, *J. Org. Chem.*, 37, 4204 (1972).

[2] We gratefully acknowledge partial financial support of this work by Eli Lilly and Co., the Ciba Pharmaceutical Co., and G. D. Searle and Co.

[3] Preliminary communication: A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Lett.*, 5275 (1970).

[4] (a) University of East Anglia; (b) Princeton University; (c) NRCC Postdoctoral Fellow, 1968–1970.

[5] W. Kitching, *Organometal. Chem. Rev.*, 3, 35 (1968).

[6] W. Kitching, *ibid.*, 3, 61 (1968).

[7] R. G. Pearson, *Surv. Progr. Chem.*, 7, 1 (1969).

[8] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev., Chem. Soc.*, 12, 265 (1958).

[9] H.-J. Kabbe, *Justus Liebigs Ann. Chem.*, 656, 204 (1962).

[10] J. B. Lee and M. J. Price, *Tetrahedron*, 20, 1017 (1964).

[11] H. Arzoumanian and J. Metzger, *Synthesis*, 527 (1971).

[12] H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, 91, 5646 (1969).

[13] H. C. Brown and J. T. Kurek, *ibid.*, 91, 5647 (1969).

[14] P. M. Henry, *Advan. Chem. Ser.*, No. 70, 126 (1968).

[15] R. Criegee, "Oxidation in Organic Chemistry, Part A," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 335–350.

[16] K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

[17] R. Criegee, *Angew. Chem.*, 70, 173 (1958).

[18] W. Kruse and T. M. Bednarski, *J. Org. Chem.*, 36, 1154 (1971).

[19] R. R. Grinstead, *ibid.*, 26, 238 (1961).

[20] C. B. Anderson and S. Winstein, *ibid.*, 28, 605 (1963).

[21] W. D. Ollis, K. L. Ormand, and I. O. Sutherland, *J. Chem. Soc. C*, 119 (1970).

Taylor, et al. / Oxidative Rearrangement of Olefins Using Thallium Nitrate