preceded and followed by the known standards. The same general procedure was used to prepare control reactions containing the expected products. All products were found to be stable at the reaction temperature.

Larger scale reactions from which products were isolated were run on an approximately 1-g PAT scale. All products were isolated by glc and were identified by comparing their physical and chemical properties with authentic samples. *Pmr spectra of PAT reaction mixtures showed that the products detected by glc analysis were not formed in the chromatograph.* Gaseous products were withdrawn by a gas-tight syringe and analyzed by glc on a Porapak S column.

For the thermal decomposition of PAT in trimethyl phosphite under air, the solutions were prepared and sealed at atmospheric pressure without degassing and then were decomposed and analyzed in the usual manner.

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Free-Radical Chemistry of Organophosphorus Compounds. II. Reactivity of Phenyl Radical toward Trimethyl Phosphite and the Mechanism of the Corresponding Photo-Arbuzov Reaction with Phenyl Iodide

Juian-Juian L. Fu,[1] Wesley G. Bentrude,*[2] and Claibourne E. Griffin[3]

Contribution from the Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112, and Department of Chemistry,
University of Toledo, Toledo, Ohio 43606. Received January 29, 1972

Abstract: In competitive kinetic experiments, phenyl radical from the thermal decomposition of phenylazotriphenylmethane (PAT) at 60° is shown to react with trimethyl phosphite (TMP) *ca.* 100 times as rapidly as it abstracts chlorine from CCl_4. Under the same conditions, hydrogen abstraction from cyclohexene and dimethyl or diethyl phosphite (DEP) is found to be 4.1 and 2.9 times, respectively, as fast as reaction of phenyl with CCl_4. Photolysis at 60° of phenyl iodide in solution with various TMP and DEP mixtures gives extrapolated ratios of rate constants essentially the same as found from PAT decompositions. It is concluded that Ph· is the phenylating species in these reactions as well. A second-order rate constant for reaction of Ph· with TMP at 60° of 10^6–10^7 mol^{-1} l. sec^{-1} is estimated. It is suggested that the high reactivity of Ph· and the relative unreactivity of $CH_3\cdot$ toward TMP are a result of the greater strength of the P–C bond formed in the phosphoranyl radical intermediate $R\dot{P}(OCH_3)_3$, where R = Ph·, and possible resonance stabilization of this intermediate by the phenyl substituent.

The preceding paper[4] emphasized product studies of the decomposition of phenylazotriphenylmethane (PAT) in trimethyl phosphite (TMP) and mixtures of TMP with dimethyl phosphite (DMP) and diethyl phosphite (DEP). It was concluded that the products formed and their response to variations of medium could be consistently interpreted in terms of rate-determining thermolysis of PAT to give Ph·, N_2, and $Ph_3C\cdot$ (reactions 1 and 2) followed by a very rapid

$$PhN{=}NCPh_3 \xrightarrow{\Delta} \overline{PhN_2\cdot + \cdot CPh_3} \qquad (1)$$

$$\overline{PhN_2\cdot + \cdot CPh_3} \longrightarrow Ph\cdot + N_2 + \cdot CPh_3 \qquad (2)$$

reaction (3 and 4) of Ph· with TMP to yield dimethyl

$$Ph\cdot + (CH_3O)_3P \longrightarrow \underset{\mathbf{1}}{Ph\dot{P}(OCH_3)_3} \qquad (3)$$

$$Ph\dot{P}(OCH_3)_3 \longrightarrow PhP(O)(OCH_3)_2 + CH_3\cdot \qquad (4)$$

phenylphosphonate. As discussed previously,[4] the reactivity of Ph· toward TMP is of special interest so far as increasing our understanding of the factors which determine the reactivity of radicals toward trivalent phosphorus. This is because Ph· is of intermediate polarity,[5] being more electrophilic than alkyl radicals, which do not react with trialkyl phosphites, but less so than the extremely reactive alkoxy and thiyl species. However, the newly formed carbon–phosphorus bond in the potential phosphoranyl radical intermediate in this reaction, **1**, is likely to be considerably stronger than that in similar species resulting from alkyl radical attack.[11] Further, the phosphoranyl radical with

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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] University of Toledo.

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

[5] The order of electronegativities, *tert*-butoxy > phenyl > methyl > cyclohexyl, has been established: H. Pritchard and H. Skinner, *Chem. Rev.*, **55**, 745 (1955); A. F. Gaines and F. M. Page, *Trans. Faraday Soc.*, **62**, 3086 (1966); Krishnaji and S. Chandra, *J. Sci. Ind. Res.*, **27**, 135 (1968) [*Chem. Abstr.*, **69**, 46136b (1968)]. Hammett ρ values for abstraction of hydrogen from substituted toluenes, which presumably measure polarity, are for $Cl_3C\cdot$,[6] −1.46 at 50°; for t-$C_4H_9O\cdot$,[7] −0.35 at 40°; for $CH_3\cdot$,[8] −0.1 at 100°; and for Ph·,[9,10] 0 to −0.4 at 60°.

[6] E. S. Huyser, *J. Amer. Chem. Soc.*, **82**, 394 (1960).

[7] C. Walling and J. A. McGuinness, *ibid.*, **91**, 2053 (1969); H. Sakurai and A. Hosomi, *ibid.*, **89**, 458 (1967).

[8] W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jomonville, *J. Org. Chem.*, **34**, 2018 (1969).

[9] R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3745 (1963).

[10] W. A. Pryor, J. T. Echols, Jr., and K. Smith, *ibid.*, **88**, 1189 (1966).

[11] The average bond energy, $\overline{D}$, for Ph_3P is 77 kcal/mol, based on gas-phase heats of formation ($\Delta H_f°$) at 298°K, for Ph_3P of 78.5 kcal/mol,[24] and Ph· of 78.5 kcal/mol [S. W. Benson and E. Whittle, private communication. See R. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 4578 (1967), for a slightly older value].

Table I. Decomposition of Phenylazotriphenylmethane (PAT) in Dimethyl Phosphite–Carbon Tetrachloride Solutions at 60°

[PAT][a]	$[CCl_4]/[(CH_3O)_2P(O)H]$[b]	% yield: C_6H_6[c]	% yield: C_6H_5Cl[c]	k_H/k_{Cl}[d]
8.99	0.207	86.3	5.42	3.09
7.35	0.559	79.4	14.2	2.88
7.59	1.01	72.3	23.8	2.81
8.20	2.80	52.0	43.2	2.97
7.19	6.30	34.5	56.8	3.16
0.568	1.01	74.9	25.0	2.87
1.19	1.01	74.5	24.7	2.90
2.82	1.01	73.9	24.1	3.06
5.33	1.01	71.3	23.8	2.80
5.99	1.01	63.7	21.6	2.72
8.27	1.01	59.0	20.0	2.67
15.0	1.01	51.3	19.6	2.23
			Av	2.85 ± 0.24[e]

[a] Mol l.$^{-1}$ × 10^2. [b] Mole ratio. [c] Based on the initial amount of PAT added. [d] $k_H/k_{Cl} = [CCl_4]([C_6H_6] - [C_6H_6]_0)/[(CH_3O)_2P(O)H]\cdot[C_6H_5Cl]$; $[C_6H_6]$ is the amount of benzene produced in decomposition of PAT in CCl_4–$(CH_3O)_2P(O)H$ while $[C_6H_6]_0$ is the amount of benzene produced in decomposition of PAT in CCl_4 with similar concentration and can be obtained from Figure 1. [e] Standard deviation, one σ limit.

phenyl on phosphorus may benefit from resonance stabilization.

In this paper, we present competitive kinetic data consistent with the presence of free Ph· as the active phenylating species in the reaction with TMP and from which an estimate of the rate constant for phenylation at 60° can be made. It is shown as well that the formation of dimethyl phenylphosphonate on photolysis of PhI–TMP solutions probably also involves free Ph

Results

Competitive Reactions. Phenyl from PAT with TMP, CCl_4, and Hydrogen Sources. In order to obtain an estimate of the reactivity of phenyl radicals with TMP, we have determined the relative rates of reaction of this species toward TMP and toward CCl_4. This is a particularly useful measurement, since the comparative reactivities of CCl_4 and a great number of hydrocarbons and other hydrogen donors (k_{Cl}/k_H) have been previously determined.[9] Ideally, direct competitive studies would be desirable. However, TMP and other trivalent phosphorus compounds undergo spontaneous ionic and radical reactions with CCl_4.[12] We therefore measured the rate constant for the reaction of phenyl with TMP (k_P) *vs.* that of its reaction with several hydrogen donors (k_H) and then combined this with k_{Cl}/k_H values previously measured by others or determined as part of this research. Agreement between k_P/k_H values using the three hydrogen donors, dimethyl phosphite (DMP), diethyl phosphite (DEP), and cyclohexene, was quite good.

The first competition studied was that between DMP and CCl_4. The ratio k_H/k_{Cl} was determined from the amounts of benzene and chlorobenzene formed at the completion of the reaction and was calculated using expression 5. Of course, this approach is justified

$$k_H/k_{Cl} = [CCl_4][C_6H_6]/[C_6H_5Cl][(CH_3O)_2P(O)H] \quad (5)$$

only if: (a) reactions 6 and 7 are of the same kinetic order in $C_6H_5\cdot$ and first order in DMP and CCl_4; (b) the ratio $[DMP]/[CCl_4]$ remains constant during the reaction; and (c) reactions 6 and 7 are the only sources of benzene and chlorobenzene. Effects of changing

$$C_6H_5\cdot + HP(O)(OCH_3)_2 \xrightarrow{k_H} C_6H_6 + \cdot P(O)(OCH_3)_2 \quad (6)$$

$$C_6H_5\cdot + CCl_4 \xrightarrow{k_{Cl}} C_6H_5Cl + Cl_3C\cdot \quad (7)$$

the $[CCl_4]/[DMP]$ ratio on the k_H/k_{Cl} value are seen in data compiled in Table I. The constancy of k_H/k_{Cl} and the lack of effect of changes in PAT concentration indicate that assumption a is valid. The large excesses of DMP and CCl_4 should assure the constancy of the concentration of these reactants (assumption b). A possible complication, however, is reaction between DMP and CCl_4. Diphenylphosphine oxide has been shown[13] to react with CCl_4 at room temperature, and $(RO)_2P(O)Cl$ has been isolated as a product in the reaction of dialkyl phosphites with CCl_4 in the presence of a tertiary amine.[14] Chloroform is also formed in the reaction which may proceed according to

$$(RO)_2P(O)\cdot + CCl_4 \longrightarrow (RO)_2P(O)Cl + \cdot CCl_3$$

$$CCl_3 + (RO)_2P(O)H \longrightarrow (RO)_2P(O)\cdot + HCCl_3$$

But in our competitive experiments <2% $CHCl_3$ was detected, and no major amount of unknown product which might be the dimethyl phosphorochloridate was present. Apparently, the triphenylmethyl radicals present in the system effectively inhibit chain reactions.

Since small amounts of benzene are formed at normal PAT concentrations even in non-hydrogen-containing media such as CCl_4,[9] it is necessary to subtract the amount of benzene formed in this way from the total measured benzene (assumption c). Two methods of making this correction have been employed in the past. In the method of Bridger and Russell,[9] the amount of benzene formed in carbon tetrachloride at a given PAT concentration is subtracted from the amount of benzene formed in a competitive reaction employing the same concentration of PAT. Pryor, *et al.*,[10] attempt to correct for products formed in the solvent cage and also for those products resulting from reaction with materials formed during the reaction. This is done by extrapolating the yields of benzene and chlorobenzene,

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

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

(14) G. M. Steinberg, *J. Org. Chem.*, 15, 637 (1950).

Table II. Decomposition of Phenylazotriphenylmethane in Trimethyl Phosphite-Dimethyl Phosphite Solutions at 60°

$[PAT]^a$	$\frac{[(CH_3O)_3P]^b}{[(CH_3O)_2P(O)H]}$	% yield: $C_6H_6{}^c$	% yield: $C_6H_5P(O)(OCH_3)_2{}^c$	$k_P/k_H{}^d$
5.31	3.83	1.84	94.1	29.2
5.31	3.83	1.82	94.9	30.2
5.40	2.60	2.05	92.7	34.0
5.40	2.60	2.08	95.1	33.9
5.05	1.93	2.42	92.5	33.8
4.99	1.06	3.39	85.6	33.8
5.63	1.00	3.58	86.7	33.6
5.63	1.00	3.65	88.3	34.5
5.11	0.562	5.06	76.3	33.4
5.11	0.562	5.03	76.5	33.8
4.74	0.236	9.99	68.1	32.1
5.11	0.028	39.0	27.2	34.7
			Av	33.1 ± 1.7[e]

[a] Mol $l.^{-1} \times 10^2$. [b] Mole ratio. [c] Based on the initial amount of PAT added. [d] Calculated from eq 8.[15a] There is 1% of benzene formed in the decomposition of 0.05 *M* PAT in trimethyl phosphite. [e] Standard deviation, one σ limit.

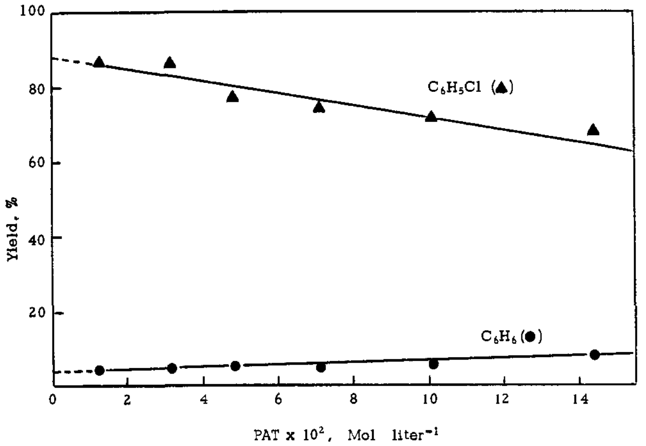

Figure 1. Per cent yields of benzene (●) and chlorobenzene (▲) *vs.* PAT molarity in CCl_4.

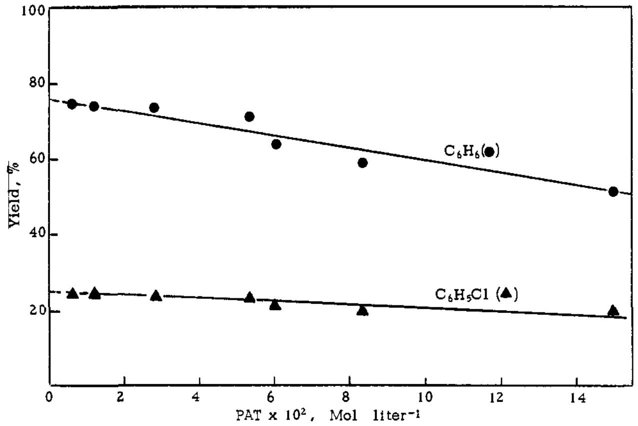

Figure 2. Per cent yields of benzene (●) and chlorobenzene (▲) *vs.* PAT molarity in a mixture of CCl_4 and $(CH_3O)_2P(O)H$ (mol ratio 1.01).

formed at a constant ratio of $[RH]/[CCl_4]$ and varying concentrations of PAT, to zero PAT concentration (infinite dilution). The amount of benzene which results from PAT decompositions in CCl_4, extrapolated to zero concentration of PAT, is then subtracted from the yield of benzene found at zero [PAT] in the competition reaction. (However, in a footnote to a later communication, Pryor and Smith[15] state that at very low concentrations of PAT in CCl_4, the yield of benzene drops precipitously toward zero.) In Figure 1 is shown the effect of variation of PAT concentration on the amounts of C_6H_6 and C_6H_5Cl formed in pure CCl_4. The values of k_H/k_{Cl} listed in Table I are derived by applying the correction of Bridger and Russell using the data of Figure 1. In Figure 2 are displayed variations of C_6H_6 and C_6H_5Cl yields at a given $[DMP]/[CCl_4]$ value. Application of the method of Pryor, *et al.*, to these data gives a k_H/k_{Cl} value of 2.91, within experimental error of that derived by the first method (2.85 ± 0.24).[15a]

To allow calculation of k_P/k_{Cl} for TMP using the k_H/k_{Cl} data obtained for the DMP-CCl_4 system, it was then necessary to determine k_P/k_H for the competitive reactions of TMP and DMP with phenyl, using expression 8. The values for dimethyl phenylphosphonate and C_6H_6 in expression 8 are the percentage yields. The 1% correction applied to the C_6H_6 yield corresponds to the amount of benzene formed in decomposition of PAT in pure TMP at the [PAT] used in the competition experiments.[15a] It is necessary in these competitions that $PhP(O)(OCH_3)_2$ not arise from other sources. In the preceding paper, the possible coupling of Ph· with $(CH_3O)_2PO\cdot$ was excluded. Values of k_P/k_H obtained at 12 different ratios of [DMP]/[TMP] are compiled in Table II and show an average of 33.1 ± 1.7. Thus a k_P/k_{Cl} value of 96 ± 12 is obtained.

$$\frac{k_P}{k_H} = \frac{[(CH_3O)_2P(O)H](C_6H_5P(O)(OCH_3)_2)}{[(CH_3O)_3P]((C_6H_6) - 1)} \tag{8}$$

As a cross check, cyclohexene was used as a hydrogen donor. Calculated k_P/k_H values for four concentrations of TMP and cyclohexene appear in Table III. Disregarding the last value determined at low concentrations of TMP, where the constancy of [TMP] may be a poor assumption, an average value for k_P/k_H of 23.3 ± 2.6 is calculated. Bridger and Russell reported[9] for cyclohexene a k_H/k_{Cl} of 4.4 at 60°. Thus, a k_P/k_{Cl} value of 102 ± 11 results, in agreement within

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[15] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **89**, 1741 (1967).

[15a] NOTE ADDED IN PROOF. Use of the graphical analysis published by Pryor, *et al.*, after this paper had been submitted (W. A. Pryor, K. Smith, J. T. Echols, Jr., and D. L. Fuller, *J. Org. Chem.*, **37**, 1753 (1972)) gives essentially the same values for k_H/k_{Cl} and k_P/k_H and a benzene correction for the latter competition of about 1%.

Table III. Decomposition of Phenylazotriphenylmethane in Trimethyl Phosphite-Cyclohexene Solutions at 60°

[PAT][a]	$[(CH_3O)_3P]^b/[C_6H_{10}]$	% yield C_6H_6[c]	% yield $C_6H_5P(O)(OCH_3)_2$[c]	k_P/k_H[d]
0.053	0.13	19.6	60.3	24.6
0.054	0.032	41.5	31.6	24.6
0.050	0.014	48.9	13.9	20.7
0.050	0.011	62.9	12.4	18.2

[a] Mol l.$^{-1}$. [b] Mole ratio. [c] Based on the amount of PAT initially added. [d] $k_P/k_H = [C_6H_5P(O)(OCH_3)_2][C_6H_{10}]/[C_6H_6 - 1\%][(CH_3O)_3P]$.

Table IV. Decomposition of Phenylazotriphenylmethane in Trimethyl Phosphite-Diethyl Phosphite Solutions at 60°

[PAT][a]	$[(CH_3O)_3P]^b/[(C_2H_5O)_2P(O)H]$	% yield C_6H_6[c]	% yield $C_6H_5P(O)(OCH_3)_2$[c]	k_P/k_H[d]
0.053	5.07	1.57	97.9	33.9
0.052	2.40	2.21	92.4	31.8
0.052	2.40	2.15	91.1	33.0
0.049	1.11	3.40	89.2	33.5
0.049	1.11	3.38	88.8	33.6
0.054	0.48	5.02	82.1	33.8
			Av	33.3 ± 0.8[e]

[a] Mol l.$^{-1}$. [b] Mole ratio. [c] Based on the initial amount of PAT added. [d] $k_P/k_H = [C_6H_5P(O)(OCH_3)_2][(C_2H_5O)_2P(O)H]/[C_6H_6 - 1\%]\cdot[(CH_3O)_3P]$. [e] Standard deviation, one σ limit.

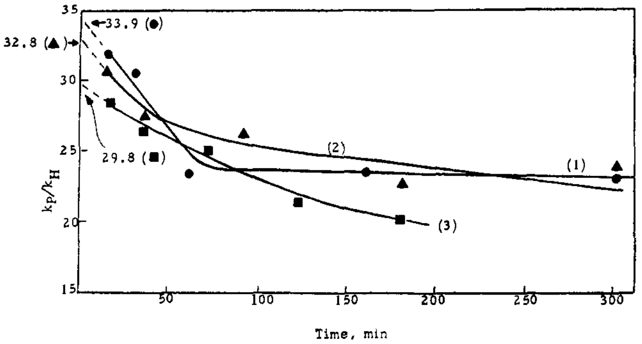

Figure 3. Kinetic data of the photolytic reaction of iodobenzene with trimethyl phosphite (TMP)–dimethyl phosphite (DMP) mixtures at 60°: (1) 5.88 × 10^{-2} M C_6H_5I, [TMP]/[DMP] = 0.0361 (●); (2) 7.31 × 10^{-2} M C_6H_5I, [TMP]/[DMP] = 0.218 (▲); (3) 8.17 × 10^{-2} M C_6H_5I, [TMP]/[DMP] = 0.755 (■).

experimental error with that calculated from the DMP competition.

Alternately, one may view the k_P/k_H figure for the TMP–cyclohexene system as allowing a check of the Bridger and Russell[9] value of k_H/k_{Cl} for cyclohexene. Assuming k_P/k_{Cl} of 96 (*vide supra*) to be accurate, k_P/k_H of 23 gives for k_H/k_{Cl} (cyclohexene) a value of 4.2, in good agreement with Bridger and Russell.

Finally, Table IV records the results of a similar determination of k_P/k_H from competitive reactions of TMP and diethyl phosphite. Clearly, the reactions are unaffected by a change in substituents on phosphorus in the dialkyl phosphite hydrogen donor from methoxy to ethoxy. The precision in this determination of k_P/k_H is slightly better than that with DMP.

Competitive Reactions. Phenyl Iodide–TMP–DMP System. Photolysis of aryl iodide–trialkyl phosphite solutions[16] provides a valuable and efficient synthesis of dialkyl arylphosphonates in what amounts to a photochemical equivalent of the Arbuzov rearrangement.

$$\text{Ar-I} + (RO)_3P \xrightarrow{h\nu} ArP(O)(OR)_2 + RI$$

Although a free-radical arylation mechanism seems highly probable for this reaction,[16] a nucleophilic displacement by phosphorus on electronically excited aryl iodide has also been suggested.[17] In order to ascertain whether or not the same species is responsible for the formation of dimethyl phenylphosphonate in the PAT and phenyl iodide systems, a comparison of the relative reactivities of the potential phenyl radical intermediates from C_6H_5I toward TMP and DMP with those of phenyls from PAT was sought. Photoreaction of phenyl iodide with trialkyl phosphites is accompanied at 60° by thermal Arbuzov rearrangement of the phosphite, a reaction which is catalyzed by the alkyl iodide formed in the photoprocess. Thus, the concentration of TMP could not be assumed constant. To overcome this difficulty, amounts of benzene and dimethyl phenylphosphonate formed in competitive reactions were measured as a function of time and extrapolated to time zero. Results of this procedure are shown graphically in Figure 3 from which an average value for k_P/k_H of 32.2 ± 2.1 is obtained. The actual error is probably larger in view of the extrapolation procedure, but the k_P/k_H value nonetheless is close to that determined for phenyl radicals from thermal PAT decomposition at 60°.

Discussion

Previous results[4] show clearly that decomposition of PAT in TMP leads to the very rapid phenylation of TMP with the ultimate formation of dimethyl phenylphosphonate (**14**). Futher evidence for the correctness of eq 3[4] can be found in the above competitive reaction data and from comparisons of the PAT and phenyl iodide systems. A quantitative estimate of the Ph· reactivity toward TMP can also be made.

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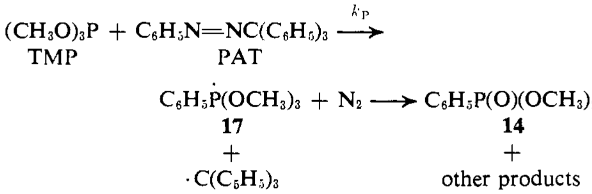
(16) J. B. Plumb, R. Obrycki, and C. E. Griffin, *J. Org. Chem.*, **31**, 2455 (1966); C. E. Griffin, R. B. Davidson, and M. Gordon, *Tetrahedron*, **22**, 561 (1966); R. Obrycki and C. E. Griffin, *J. Org. Chem.*, **33**, 632 (1968).

(17) C. Walling and M. S. Pearson, *Top. Phosphorus Chem.*, **3**, 1 (1966).

Relative Reactivity Comparisons. PAT and Phenyl Iodide Systems. Data given in Table III and Figure 3 show that the reactive species in the phenylation of TMP in the PAT systems and in the phenyl iodide system have the same relative reactivities toward TMP and toward the hydrogen source DMP, *i.e.*, k_P/k_H = 31–35. This result is consistent with there being a common intermediate responsible for phenylation and hydrogen abstraction in both systems. Considering that PAT thermolysis[9,10] and phenyl iodide photolysis[18] are generally found to be sources of the phenyl radical and that photochemically generated and thermally generated phenyl radicals behave similarly in aromatic substitution,[19] the logical conclusion is that phenyls are the reactive species in both TMP reactions. If one considers the agreement of k_P/k_H values to be coincidental, two other possible free-radical schemes for the PAT system may be proposed. In one all the phenylation occurs *via* direct attack of the phosphite on PAT to give a phosphoranyl radical **17**, N_2, and trityl radical (reaction 9). At increasing concentrations of DMP (low TMP concentrations), the normal thermolysis of PAT is able to compete and gives phenyls which react only with DMP (reactions 10 and 11).



$$\underset{\text{TMP}}{(CH_3O)_3P} + \underset{\text{PAT}}{C_6H_5N{=}NC(C_6H_5)_3} \xrightarrow{k_P} \underset{\substack{\mathbf{17}\\ +\\ \cdot C(C_5H_5)_3}}{C_6H_5\dot{P}(OCH_3)_3} + N_2 \longrightarrow \underset{\substack{\mathbf{14}\\ +\\ \text{other products}}}{C_6H_5P(O)(OCH_3)_2} \quad (9)$$

$$C_6H_5N{=}NC(C_6H_5)_3 \xrightarrow{k_d} C_6H_5\cdot + N_2 + \cdot C(C_6H_5)_3 \quad (10)$$

$$C_6H_5\cdot + (CH_3O)_2P(O)H \xrightarrow{k_H} C_6H_6 + (CH_3O)_2\dot{P}(O) \quad (11)$$

$$C_6H_5\cdot + P(OCH_3)_3 \xrightarrow{k_{P'}} \mathbf{17} \longrightarrow \mathbf{14} + \cdot CH_3 \quad (12)$$

This is ruled out, however, by the competition experiments which showed a constant value of k_P/k_H to be calculated from variations of the [DMP]/[TMP] ratio in which *both* concentrations were changed. The expression for $d(C_6H_5P(O)(OCH_3)_2)/d(C_6H_6)$ for the above scheme in which all free phenyls react with DMP would show a zero-order dependence on [DMP] (eq 13) but, in fact, responds in first-order fashion to [DMP].

$$d(C_6H_5P(O)(OCH_3)_2)/d(C_6H_6) = (k_P/k_d)[\text{TMP}] \quad (13)$$

A second alternative in which **14** is formed both by TMP attack on PAT (reaction 9) *and* by reaction of free phenyls with TMP (reaction 12) is also ruled out. In such a system (reactions 9–12) the ratio of benzene to **14** would be dependent on a more complicated expression (14) involving [DMP] and [TMP].

$$\frac{d(C_6H_6)}{d(C_6H_5P(O)(OCH_3)_2)} = \frac{k_dk_H[\text{DMP}]/[\text{TMP}]}{k_Pk_{P'}[\text{TMP}] + k_Hk_P[\text{DMP}] + k_dk_{P'}} \quad (14)$$

Reactivity of Phenyl Radical toward TMP. The very high reactivity of phenyl toward TMP is seen by the previously stressed[4] finding that TMP traps virtually all kinetically free phenyl radicals. An estimate of k_P at 60° for phenyl with TMP can be made by use of gas-phase data[20] for hydrogen abstraction by phenyl from isobutane ($\log A = 8.8$; $E_a = 6.7$ kcal/mol) and values of $k_H(\text{isobutane})/k_{Cl}(CCl_4)$[9] (calculated) and $k_P/k_{Cl}(CCl_4)$ (this work) in solution. In this way, k_P(TMP) is determined at 60° to be 4.6×10^6 mol^{-1} l. sec^{-1}. If it is assumed that 10^9 is a reasonable A value for bimolecular attack of phenyl at phosphorus, then an estimate of E_a for k_P(TMP) of 3.6 kcal/mol arises.

Thus, in spite of the fact that phenyl radical is not a strongly electronegative species, it is extremely reactive toward TMP. For this reason, factors other than polar ones should be considered. Consistent with this idea is the fact that the rates of competitive reactions of a series of arylphosphonites, p-$XC_6H_4P(OMe)_2$ with *tert*-butoxy radical, are unaffected by variation in substituent X, even though rates of ionic methylation with CH_3I are.[21]

Evidence for the irreversible nature of the reaction of Ph· with TMP (15a) comes from the finding that reaction 15b of dimethyl phenylphosphonite with *tert*-butoxy radical fails to give any *tert*-butyl dimethyl phosphite.[21] The quantitative formation of dimethyl phenylphosphonate from both reactions is shown in eq 15 in terms of a common phosphoranyl radical intermediate. The above-estimated k_P and E_a values therefore apply to step 15a.

In terms of a reaction *via* a phosphoranyl radical, the thermodynamics of formation of such an intermediate clearly must be favorable if reaction is to proceed very rapidly. The enthalpy change for phosphoranyl radical intermediate formation (ΔH_{PZ_4}) can be divided, perhaps arbitrarily, into three contributing terms: the phosphorus orbital rehybridization energy; the strength of the bond to phosphorus being formed; and any resonance stability imparted to the phosphoranyl radical by the substituents on phosphorus. On this basis the great reactivity of phenyl and relative unreactivity of methyl radical toward TMP, noted in this study, are readily explained. Using average bond strengths[22] ($\bar{D}_{PZ_3}$) for the corresponding trivalent compounds PZ_3 as a measure of relative strengths of the new PZ bond to be formed in the phosphoranyl intermediate predicts ΔH_{PZ_4} for Z equal to RO· ($\bar{D}_{PZ_3}$, 84 kcal/mol[23]) or Ph· ($\bar{D}_{PZ_3}$, 77 kcal/mol[11]) to be considerably more favorable than for Z equal to CH_3· ($\bar{D}_{PZ_3}$, 67 kcal/mol[26]). It is also possible that the phenylation reaction is aided by resonance interaction involving the odd electron on phosphorus and the phenyl substituent. Thus a reaction which is very favorable

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[19] P. G. Naylor and N. Kharasch, *Int. Sci. Chem. Rep.*, **2** (1968); D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 3963 (1955).

[20] F. J. Duncan and A. F. Trotman-Dickenson, *ibid.*, 4672 (1962).

[21] J.-J. L. Fu, submitted for publication.

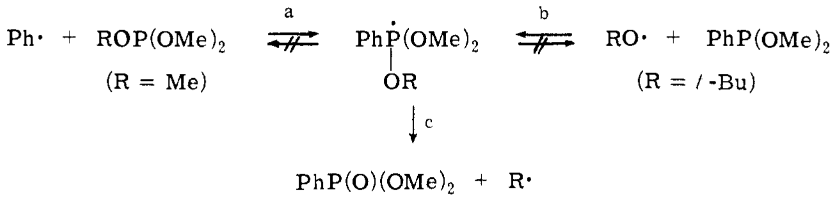
[22] $\bar{D}_{PZ_3}$ was calculated for each case using the gas-phase heat of formation at 298°K, $\Delta H_f°(298,g)$, and the appropriate $\Delta H_f°(298,g)$ for the phosphorus atom and Z·.

[23] For $(C_2H_5O)_3P$, $\Delta H_f°(298,g)$ is −195.9 kcal/mol;[24] $\Delta H_f°(298,g)$ for C_2H_5O· is −6.7 kcal/mol.[25]

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

[25] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

[26] For Me_3P, $\Delta H_f°(298,g)$ is −22.5 kcal/mol;[24] for CH_3·, 34.0 kcal/mol.[25]



(15)

thermodynamically overall[27] may not occur unless bond strength and resonance factors make formation of the intermediate $\cdot PZ_4$ favorable. These ideas will be expanded to cover other examples in a subsequent paper. The great difference in reactivities of various radicals toward TMP suggests its possible use as a selective scavenger.

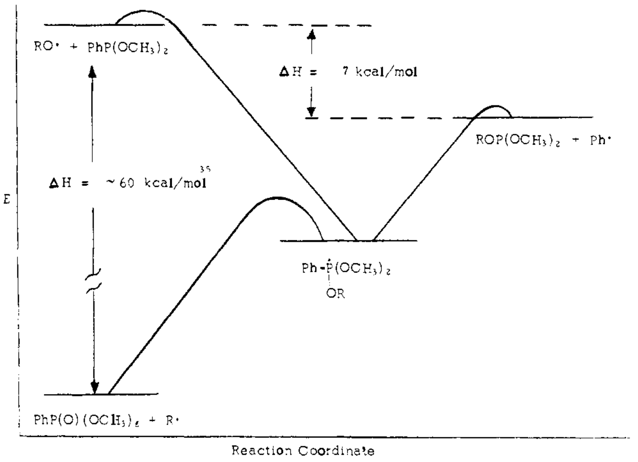


Figure 4. Energy diagram for phenyl and alkoxy radical reactions with trivalent phosphorus.

Based on the relative average bond strengths for $(RO)_3P$ and Ph_3P and the irreversibility of the Ph· reaction with $(MeO)_3P$, the energy diagram shown in Figure 4 can be constructed.[29] The irreversibility of the reaction of Ph· with $(CH_3O)_3P$ means that it is very likely an exothermic process which, of course, dictates that the reaction of RO· with $PhP(OCH_3)_2$ (eq 15b) must be, as shown in Figure 4, irreversible and even more exothermic. The relatively high barrier for β scission is in keeping with the value of 10 kcal/mol estimated very recently for this step by Davies, *et al.*[33]

Experimental Section

The general procedures for the thermal PAT decompositions (60.0 ± 0.1°) were given in detail in the preceding paper.[4] The same analytical procedures, methods A and B, were also employed. Data in Table I were determined by method A, those in Tables II–IV by method B.

Phenyl Iodide Photoreactions. The same general procedure described for the PAT reactions[4] was used. The light source was a 654A-36 200-W Hanovia mercury vapor lamp. Both Vycor and Pyrex reaction tubes were used. The light was placed in a water-cooled quartz thimble, and sample tubes were placed as close as possible to the sides of the thimble. Competitive reactions, in degassed Pyrex ampoules, were carried out in a water bath at 60 ± 1°. Each solution prepared was weighed equally into six ampoules. The reactions were quenched by removing the ampoules at the appropriate time intervals and cooling them in a liquid nitrogen bath. Both the appearance of products and disappearance of starting materials were followed by glc. Values of k_P/k_H were determined using expression 8 (except that no correction was applied to the benzene yield) and plotted in Figure 3. Control experiments indicated that phenyl iodide did not react with the substrates under conditions of glc analysis and that the products were stable under conditions of photolysis and analysis.

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(27) *E.g.*, for the 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[24] $\Delta H_f°$(298,g) for $(CH_3O)_3P$ and calculated[28] $\Delta H_f°$(298,g) for $CH_3P(O)(OCH_3)_2$.

(28) −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).

(29) Esr studies have identified the radicals $\cdot PCl_4$,[30] $\cdot PF_4$,[31] and $(RO)_xPR'_{4-x}$[32,33] from reaction of a radical with the appropriate trivalent phosphorus compound. Chemical evidence is also available.[34]

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(35) Based on $\Delta H_f°$ values for PZ_3[24] and OPZ_3[24] and $\Delta H_f°$ for the process t-BuO· → t-Bu· + O (ref 25).