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

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

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

---

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

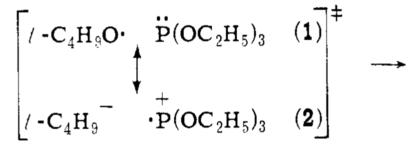
**Juian-Juian L. Fu[1] and Wesley G. Bentrude*[2]**

*Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.* *Received January 29, 1972*

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

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

$$t\text{-}C_4H_9O\cdot + P(OC_2H_5)_3 \longrightarrow$$



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

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

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

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

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

---

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

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

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

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

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

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

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

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

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

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

**Table I.** Products from the Decomposition of Phenylazotriphenylmethane (PAT) in Trimethyl Phosphite (TMP) at 60° [a]

| | % yields of products | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| [PAT][b] | $C_6H_6$ | $PhP(O)(OMe)_2$ | $Ph_3CH$ | $Ph_3CCH_3$ | **7**[h] | $Ph_4C$ | **9**[i] | PhC(O)Ph |
| 0.890 | ~1 | 98.1 | 9.7 | 84.8 | 3.76 | ~0.5 | ~0.5 | 0 |
| 4.99 | ~1 | 97.2 | 8.6 | 84.5 | 3.45 | ~0.5 | ~0.5 | 0 |
| 9.98 | ~1 | 97.2 | 8.1 | 84.2 | 3.59 | ~0.5 | ~0.5 | 0 |
| 15.0 | ~1 | 97.5 | 8.6 | 82.3 | 3.61 | ~0.5 | ~0.5 | 0 |
| 1.14 | ~1 | 98.2 | 12.6 | 81.6 | 2.47 | ~0.5 | ~0.5 | 0 |
| 5.42 | ~1 | 95.5 | 12.4 | 80.4 | 2.55 | ~0.5 | ~0.5 | 0 |
| 10.1 | ~1 | 97.8 | 13.1 | 78.2 | 2.66 | ~0.5 | ~0.5 | 0 |
| 14.9 | ~1 | 98.3 | 13.4 | 80.6 | 2.13 | ~0.5 | ~0.5 | 0 |
| 1.14[c] | ~1 | 97.8 | 15.4 | 43.5 | *g* | *g* | *g* | 14.9 |
| 5.42[c] | ~1 | 94.9 | 17.7 | 39.4 | *g* | *g* | *g* | 16.9 |
| 10.1[c] | ~1 | 97.4 | 18.2 | 45.1 | *g* | *g* | *g* | 15.0 |
| 14.9[c] | ~1 | 97.5 | 17.3 | 51.8 | *g* | *g* | *g* | 13.7 |
| 5.05[d] | 2.42 | 92.5 | 87.1 | 4.9 | 1.22 | 1.89 | 2.46 | 0 |
| 5.11[e] | 29.0 | 27.2 | 59.6 | 0.42 | 0.77 | 5.02 | 4.96[f] | 0 |

[a] Degassed solutions in TMP as solvents. Product yields, sensitivity corrected and based on initial PAT, are the averaged value from duplicate runs. Small peaks (<0.5%) corresponding in retention time to dimethyl methylphosphonate and dimethyl triphenylmethylphosphonate were also detected. [b] mol/l. × $10^2$. [c] Under 1 atm of dry air. 3 ~ 4% of biphenyl was also detected. [d] 3.13 *M* concentration of dimethyl phosphite ($(CH_3O)_2P(O)H$) added. [e] 0.31 *M* concentration of trimethyl phosphite in $(CH_3O)_2P(O)H$ as solvent. [f] ~24% of an unstable **11** [pmr ($CDCl_3$) $\delta$ 3.8 ppm, doublet, $J = 11.0$ Hz] which has very close retention time to **9** (20% SE-30 column) was also detected. [g] These products were not measured in reactions under air atmosphere. [h] 9-Phenylfluorene. [i] 4-Biphenylylidphenylmethane.

consistent with this idea although, if **4** is an intermediate, it is possible that reaction 3 proceeds to product only because the intermediate phosphoranyl radical is trapped in an otherwise reversible process.

Another factor which could influence reactivity in these systems is the stability of the potential phosphoranyl radical intermediate which might, in turn, depend on *bond strengths* and *steric* and *configurational* considerations. The reactivity of the phenyl radical toward trialkyl phosphites is of special interest to the understanding of these reactions, since it is intermediate in polar character, being less electrophilic that *tert*-butoxy or trichloromethyl but more electrophilic than alkyl.[11] In addition, the phosphorus–carbon bond formed in the potential intermediate analogous to **3** will be stronger than when the reacting radical is *tert*-butyl.[16]

That phenyl radical may be reactive with trialkyl phosphites is suggested by the formation of dialkyl phenylphosphonates when phenyl iodide is irradiated with either ultraviolet light[17] or a $^{60}$Co source[18] in the presence of trialkyl phosphite. A possible reaction sequence is (4). The above system possesses two ob-

$$C_6H_5I \xrightarrow{h\nu} C_6H_5\cdot + I\cdot \tag{4}$$

$$C_6H_5\cdot + P(OR)_3 \longrightarrow C_6H_5\dot{P}(OR)_3 \longrightarrow$$

$$C_6H_5P(O)(OR)_2 + R\cdot \xrightarrow{I_2} RI \text{ or } C_6H_5\dot{P}(OR)_3 \xrightarrow[-I_2]{I\cdot \text{ or}}$$

$$C_6H_5\overset{+}{P}(OR)_3I^- \longrightarrow C_6H_5P(O)(OR)_2 + RI$$

jectional features so far as determining the reactivity of the phenyl radical toward a trialkyl phosphite is concerned. First, if free phenyl radicals are involved, the presence of iodine could perturb the intrinsic reactivity of the phenyl by trapping a reversibly formed phosphoranyl radical intermediate. Second, the possibility has been suggested[3a] that the reaction may proceed *via* nucleophilic attack by trivalent phosphorus on electronically excited phenyl iodide. We have therefore employed phenylazotriphenylmethane (PAT)[15a] as a clean thermal source of phenyl radicals which we find to react very rapidly with trimethyl phosphite (TMP) to yield dimethyl phenylphosphonate.[19]

## Results

**Thermal PAT–TMP Reactions.** Reactions were run at 60° on 1–15 × $10^{-2}$ *M* solutions of PAT in TMP as solvent. Yields of products of reactions of degassed solutions as well as those containing oxygen or dimethyl phosphite as potential radical scavengers appear in Table I. Products were analyzed by vpc. Yields of the phenylphosphonate are seen to be constant within the range 96–99% over a 15-fold variation in PAT concentration under degassed conditions. In the presence of oxygen, trityl radicals, which in degassed TMP appear to largely combine with methyl radicals to give 1,1,1-triphenylethane, are diverted to other products, among them benzophenone. However, yields of phenylphosphonate are not affected. High

---

(11) 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 $\rho$ values for abstraction of hydrogen from substituted toluenes, which presumably measure polarity, are for $Cl_3C\cdot$,[12] −1.46 at 50°; for $t\text{-}C_4H_9O\cdot$,[13] −0.35 at 40°; for $CH_3\cdot$,[14] −0.1 at 100°; and for $Ph\cdot$,[15] 0 to −0.4 at 60°.

(12) E. S. Huyser, *J. Amer. Chem. Soc.*, **82**, 394 (1960).

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

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

(15) (a) R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963); (b) W. A. Pryor, J. T. Echols, Jr., and K. Smith, *ibid.*, **88**, 1189 (1966).

(16) The average bond strength $\bar{D}$, 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,[8] for 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], and 75.2 kcal/mol for P (white). For $Me_3P$, $\Delta H_f°(298°, g)$ is −22.5 kcal/mol[8] and for $CH_3\cdot$, 34.0 kcal/mol[ J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966), from which $\bar{D}$ for $Me_3P$ of 67 kcal/mol is calculated]. $\bar{D}$ for $t\text{-}Bu_3P$ is expected to be <67 kcal/mol.

(17) 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).

(18) G. Caspari, H. Drawe, and A. Henglein, *Radiochim. Acta*, **8**, 102 (1967).

(19) A preliminary report of a small portion of this work has been published: W. G. Bentrude, J.-J. L. Fu, and C. E. Griffin, *Tetrahedron Lett.*, 6033 (1968). Reference 18 also reports a limited study of PAT decompositions in phosphite media.

**Table II.** Products from the Decomposition of Phenylazotriphenylmethane (PAT) in Trimethyl Phosphite (TMP)–Dimethyl Phosphite (DMP) Solutions at 60° [a]

| | | | % yields of products[d] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [PAT][b] | [TMP][c] | [DMP][c] | $C_6H_6$ | **14** | **5** | **6** | **13** | **10** | **7** | **8** | **9** | **11** |
| 5.16 | 8.43 | 0.064 | ~1 | 97.6 | 8.66 | 86.2 | 0 | 0.58 | 1.59 | 0.60 | 0.38 | 0 |
| 5.07 | 8.24 | 0.31 | 1.46 | 97.4 | 13.4 | 82.3 | 0 | 0.56 | 1.57 | 0.70 | 0.40 | 0 |
| 5.31 | 6.89 | 1.80 | 1.83 | 94.5 | 46.3 | 46.9 | 1.42 | 0.80 | 1.43 | 0.70 | 0.70 | 0.23 |
| 5.40 | 6.07 | 2.33 | 2.07 | 93.4 | 82.5 | 14.4 | 12.8 | 0.70 | 1.29 | 0.95 | 0.90 | 1.25 |
| 5.05 | 6.05 | 3.13 | 2.42 | 92.5 | 87.1 | 4.98 | 22.0 | 1.26 | 1.22 | 1.89 | 1.22 | 1.23 |
| 5.02 | 5.02 | 4.21 | 3.39 | 85.6 | 90.4 | 1.86 | 35.1 | 0.71 | 0.89 | 0.89 | 1.08 | 2.71 |
| 5.63 | 5.03 | 5.01 | 3.62 | 87.5 | 91.3 | 1.87 | 33.2 | 0.64 | 1.05 | 1.00 | 1.28 | 2.53 |
| 5.11 | 3.42 | 6.08 | 5.05 | 76.4 | 83.2 | 1.20 | 31.3 | 1.01 | 0.84 | 1.51 | 1.55 | 6.53 |
| 4.74 | 1.87 | 7.91 | 10.0 | 68.1 | 75.3 | 0.76 | 36.8 | 1.97 | 0.74 | 4.01 | 4.00 | 13.9 |
| 5.11 | 0.308 | 10.5 | 29.0 | 27.2 | 59.6 | 0.42 | | 6.49 | 0.77 | 5.02 | 4.96 | 23.8 |

[a] Degassed solutions of PAT in mixed TMP–DMP solvents. Yields sensitivity corrected and based on initial PAT. Average values for duplicate runs reported. Errors less than ±3% of reported yield for major products (**5**, **6**, and **10**) and ±5% for minor products. [b] mol/l. × $10^2$. [c] mol/l. [d] Products are: **5**, $Ph_3CH$; **6**, $Ph_3CCH_3$; **7**, 9-phenylfluorene; **8**, $Ph_4C$; **9**, $(4\text{-}C_6H_5C_6H_4)CH(C_6H_5)_2$; **10**, $Ph_3CP(O)(OMe)_2$; **11**, unknown long retention time product; **13**, dimethyl methylphosphonate; **14**, $PhP(O)(OMe)_2$.

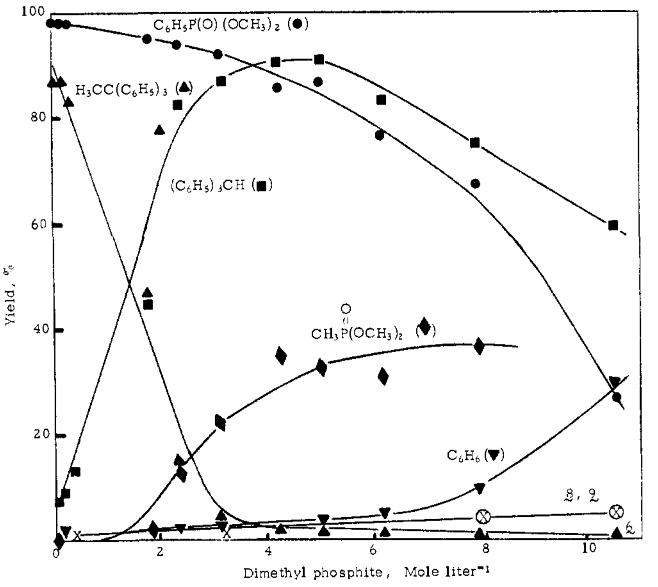


Figure 1. Per cent yields of **14**, dimethyl phenylphosphonate (●); **6**, 1,1,1-triphenylethane (▲); **5**, triphenylmethane (■); **13**, dimethyl methylphosphonate (◆); benzene (▼); **8**, tetraphenylmethane (X); and **9**, *p*-biphenylyldiphenylmethane (○) *vs.* dimethyl phosphite molarity in mixtures of 0.05 *M* PAT with trimethyl phosphite and dimethyl phosphite.

concentrations of dimethyl phosphite (DMP) lead to considerable amounts of benzene formation. Total accountability of phenyl and trityl radicals is generally good and is close to quantitative in degassed TMP as solvent.

We also made a quantitative assessment of the effect of gradual addition of DMP on the apparent products of reaction of phenyl, trityl, and methyl radicals. In all cases accurate vpc sensitivity calibrations using authentic samples were made. These results are listed in Table II and are shown in Figure 1. The greatest effect on yields of products is seen with dimethyl phenylphosphonate and 1,1,1-triphenylethane, both of which are decreased in yield by the hydrogen donor, and with triphenylmethane which is progressively increased in yield. The much lower response to a given amount of hydrogen donor of the phenylphosphonate than that of the other two products is notable.

In other experiments, PAT decomposition in degassed DMP as solvent at [PAT] 0.015–0.23 *M* showed the following distribution of products: benzene, 70–80%; triphenylmethane (**5**), 50–70%; 1,1,1-triphenylethane (**6**), <1%; 9-phenylfluorene (**7**), 3–4%; tetraphenylmethane (**8**), ~5%; 4-biphenylyldiphenylmethane (**9**), ~5%; and dimethyl triphenylmethylphosphonate (**10**), ~3%. It is important to note that in these reactions *no dimethyl phenylphosphonate is formed.* The possibility that a portion of the dimethyl phenylphosphonate formed in competitive reactions in which DMP was present might result from combination of phenyl and $(CH_3O)_2P(O)\cdot$ radicals or from the phosphonation of benzene[20] by the latter species is thereby ruled out (see discussion in the following paper).[21]

The only identified products found in the TMP–DMP studies which could result from $(CH_3O)_2P(O)\cdot$ (likely to be present as a result of hydrogen abstraction) are dimethyl methylphosphonate and dimethyl triphenylmethylphosphonate, both of which were increased in yield by addition of DMP. In addition, an unstable material, **11**, was detected by vpc in amounts up to about 25% based on vpc peak area and normal sensitivities. The latter product was present only in the reactions containing DMP. (A similar material is generated in the presence of diethyl phosphite.) This substance defied attempts to isolate it by vpc in pure form. Small amounts of impure material showed nmr absorptions attributable to $CH_3OP(O)$ ($\delta$ 3.8, doublet, $J = 11$ Hz).

Further insight into the origin of the dimethyl methylphosphonate can be gained from Table III and Figure 2 in which product data from PAT decompositions in solutions containing various amounts of TMP and diethyl phosphite (DEP) are recorded. The influence of DEP on product distributions is basically the same as that of DMP. However, there is one important exception. *Both* dimethyl methylphosphonate and diethyl methylphosphonate are formed. More importantly, although the total yield of these two products at a [TMP]/[DEP] ratio of about one is comparable to that of dimethyl methylphosphonate in the PAT–TMP–DMP reaction with [TMP]/[DMP] = 1, the yield of diethyl methylphosphonate is 6–8 times that of the dimethyl methylphosphonate. This means that only a

---

(20) E. J. Jason and E. K. Fields, *J. Org. Chem.*, **27**, 1402 (1962); E. K. Fields and R. J. Rolih, *Chem. Ind.* (*London*), 999 (1960).

(21) J.-J. L. Fu, W. G. Bentrude, and C. E. Griffin, *J. Amer. Chem. Soc.*, **94**, 7717 (1972).

**Table III.** Products from the Decomposition of Phenylazotriphenylmethane (PAT) in Trimethyl Phosphite (TMP)–Diethyl Phosphite (DEP) Solutions at 60° [a]

| [PAT][b] | [TMP][c] | [DEP][c] | % yields of products[d] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $C_6H_6$ | **14** | **5** | **6** | **13** | **10** | **7** | **16** | **8** + **15** | **9** + **12** |
| 4.94 | 8.12 | 0 | 1.11 | 97.9 | 9.40 | 86.4 | 0 | 0.59 | 1.58 | 0 | 0.68 | 0.46 |
| 4.91 | 7.77 | 0.065 | 1.33 | 98.3 | 11.2 | 81.4 | 0 | 0.54 | 1.55 | 0 | 0.72 | 0.41 |
| 5.11 | 7.84 | 0.19 | 1.51 | 97.3 | 11.7 | 84.1 | 0 | 0.51 | 0.88 | 0 | 0.73 | 0.66 |
| 5.31 | 6.48 | 1.28 | 1.57 | 97.9 | 30.4 | 63.8 | 0 | 0.59 | 0.99 | 0 | 1.25 | 1.58 |
| 5.17 | 5.45 | 2.27 | 2.18 | 91.8 | 64.5 | 28.2 | 0 | 0.52 | 0.70 | 6.48 | 1.74 | 4.11 |
| 4.88 | 3.92 | 3.53 | 3.39 | 89.0 | 94.3 | 4.23 | 4.30 | 0.38 | 0.50 | 29.6 | 1.60 | 4.38 |
| 5.36 | 2.61 | 5.38 | 5.02 | 82.1 | 93.9 | 1.34 | 2.28 | 0.33 | 0.24 | 17.0 | 2.65 | 8.75 |
| 5.08 | 0.73 | 6.50 | 31.8 | 63.9 | 86.5 | 0.55 | 2.51 | 0 | | 13.5 | 9.55 | 25.3 |

[a] Degassed solutions of PAT in mixed TMP–DMP solvents. Yields sensitivity corrected and based on initial PAT. Average values from duplicate runs reported. Errors less than ±3% of reported yield for major products **5**, **6**, and **10** and ±5% of reported yield for others. [b] mol/l. × $10^2$. [c] mol/l. [d] Products are: **5**, $Ph_3CH$; **6**, $Ph_3CMe$; **7**, 9-phenylfluorene; **8**, $Ph_4C$; **9**, $(4\text{-}C_6H_5C_6H_4)CHPh_4$; **10**, $Ph_3CP(O)(OMe)_2$; **12**, unknown long retention time product; **13**, $MeP(O)(OMe)_2$; **14**, $PhP(O)(OMe)_2$; **15**, $Ph_3CP(O)(OEt)_2$; **16**, $MeP(O)(OEt)_2$.

minor portion of the dimethyl methylphosphonate formed in reactions of PAT at high DMP concentrations could have resulted from reaction 5. Since (5)

$$CH_3\cdot + P(OCH_3)_3 \longrightarrow CH_3\dot{P}(OCH_3)_3 \longrightarrow CH_3P(O)(OCH_3)_2 + CH_3\cdot \quad (5)$$

is potentially a chain process, *the reactivity of methyl with TMP must be very low compared to its reactivity toward trityl radicals or hydrogen attached to dialkyl phosphite.* Methyl apparently undergoes abstraction and coupling reactions in the presence of hydrogen donors as a large-scale decomposition of PAT (0.08 *M*) in a solution of TMP (6 *M*) and DMP (3 *M*) gave a gas sample which showed by vpc the presence of methane along with lesser amounts of ethane. These two products were also found in the gases from PAT decomposition in a TMP–DEP mixture.

Other hydrocarbon compounds, **7**, **8**, and **9**, derived from phenyl and trityl radicals, were minor products in all studies. On addition of either DMP or DEP, the yield of **7** decreases slightly from ~2 to ~1% (see Tables II and III). In the PAT–TMP–DMP reactions, the yields of **8** and **9** increase from 0.5 to 5% in a constant 1:1 ratio upon the addition of hydrogen donors DEP or DMP. Unfortunately, in the PAT–TMP–DEP reaction, compounds **8** and diethyl tritylphosphonate (**10**), as well as compounds **9** and the unstable long-retention-time unknown product (**12**) analogous to **11**, are not separable under the glc conditions employed. Combined yields of **8** and **10** are estimated to range 1–10% based on the sensitivity of **8**, while those of **9** and **12** combined vary from 1 to 25% if the sensitivity of **9** is used for both products (see Table III).

## Discussion

The general free-radical nature of the decompositions of PAT in TMP and the likelihood that the formation of $PhP(O)(OCH_3)_2$ is a rapid reaction of Ph· with TMP are discussed below in terms of the products formed and the response of product distribution to added oxygen and to hydrogen donors. Kinetic evidence for the very high reactivity of Ph· toward TMP and the implications of these results so far as our understanding of the factors which control the reactivity of free radicals toward trivalent phosphorus are found in the paper which follows.[21]

In pure TMP, PAT decomposition leads to nearly quantitative (96–99%) formation of dimethyl phenylphosphonate (**14**), but the yield of 1,1,1-triphenylethane (**5**) never exceeds 84% (Table I). This rules out any mechanism in which the reactivity of phenyl with TMP is dependent upon the presence of trityl radicals, for example, sequence 6a, in which the phosphoranyl radical intermediate **17** goes on to form **14**

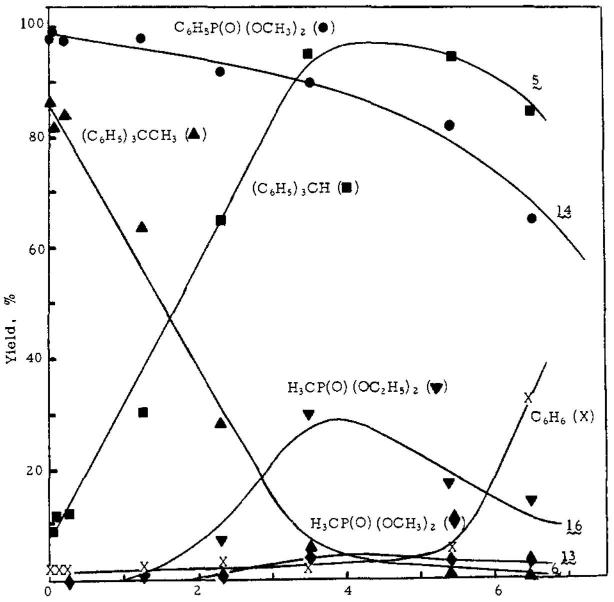
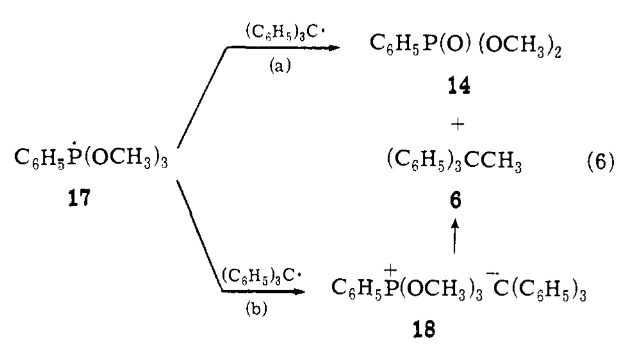


Figure 2. Per cent yields of **14**, dimethyl phenylphosphonate (●); **6**, 1,1,1-triphenylethane (▲); **5**, triphenylmethane (■); **13**, dimethyl methylphosphonate (◆); **16**, diethyl methylphosphonate (▼); and benzene (X) *vs.* diethyl phosphite molarity in mixtures of 0.05 *M* PAT with trimethyl phosphite and diethyl phosphite.

$$C_6H_5\cdot + (CH_3O)_3P \rightleftharpoons \underset{\textbf{17}}{C_6H_5\dot{P}(OCH_3)_3}$$



only as a result of displacement by trityl on the methyl group of **17**.

Other mechanisms requiring trityls can also be envisaged such as electron transfer (6b) to form a phophonium triphenylmethide species, **18**, which then gives product in Arbuzov fashion. That trityl radicals are only incidental to the reaction of phenyl with TMP is also shown by their diversion to other products by oxygen[22] and hydrogen donors while the yield of **14** remains unchanged (Tables I and II, Figures 1 and 2). However, this does not prove that **6** or a portion of **6** does not arise from a reaction like (6) following rate determining formation of **17**. The same may be said (*vide infra*) for $CH_3P(O)(OCH_3)_2$ and $CH_3P(O)(OEt)_2$ formed at high DMP or DEP concentrations in a perhaps surprisingly efficient apparent radical dimerization.

We propose that the PAT–TMP reactions proceed *via* reactions 7–12 which account for the formation of

$$C_6H_5N{=}NC(C_6H_5)_3 \xrightarrow{\Delta} \overline{C_6H_5\text{–}N_2\cdot + \cdot C(C_6H_5)_3} \quad (7)$$

$$\overline{C_6H_5\text{–}N_2\cdot + \cdot C(C_6H_5)_3} \longrightarrow \text{cage products} \quad (8)$$

$$\overline{C_6H_5\text{–}N_2\cdot + \cdot C(C_6H_5)_3} \longrightarrow C_6H_5\cdot + (C_6H_5)_3C\cdot + N_2 \quad (9)$$

$$C_6H_5\cdot + P(OCH_3)_3 \longrightarrow C_6H_5\dot{P}(OCH_3)_3 \longrightarrow C_6H_5P(O)(OCH_3)_2 + CH_3\cdot \quad (10)$$

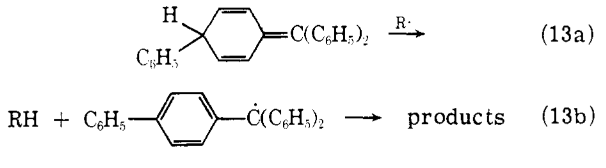
$$CH_3\cdot + \cdot C(C_6H_5)_3 \longrightarrow (C_6H_5)_3CCH_3 \quad (11)$$

$$(C_6H_5)_3C\cdot \xrightarrow{SH} (C_6H_5)_3CH \quad (12)$$

the major products observed. The actual involvement of the potential phosphoranyl radical as a discrete intermediate has not been demonstrated in this case, but extensive evidence[27] has suggested its presence in similar systems.

In degassed TMP solutions, trityl radical appears to be an effective scavenger of the methyl radical formed in reaction 10 as 78~85% of **6** is formed. The main portion of the remaining trityls abstracts hydrogen from some undefined source, perhaps TMP, to form 9–13% of triphenylmethane (**5**). Formation of **5** is commonly noted in PAT decompositions.[30,31] The amount of **5** in our study does not increase with [PAT], and 96–99% of $C_6H_5\cdot$ has been accounted for in the formation of **14**. Thus, abstraction from PAT products by process 13, as proposed[30,31] in other PAT systems, is probably unimportant. The failure of PhH yields to respond to changes in [PAT] means that Ph· is much more reactive toward TMP than toward $CCl_4$, since in the latter solvent wide variations in PhH yield result from changes in [PAT].[15a] In the following paper,[21] Ph· is reported to be 100 times as reactive with TMP as with $CCl_4$.

$$C_6H_5\cdot + (C_6H_5)_3C\cdot \longrightarrow$$



$$R = C_6H_5\cdot \text{ or } (C_6H_5)_3C\cdot$$

As increasing amounts of hydrogen donors are added (Figures 1 and 2, Tables II and III), the percentage of **5** increases accordingly, and methyl radicals are diverted to the formation of methane and ethane. Again, the yield of **14** falls off much slower than the yield of **6**, as expected if *reaction 10 of Ph· with TMP is very fast.* Methyls in the reactions with DMP and DEP present in high concentrations gave dimethyl methylphosphonate (**13**) and diethyl methylphosphonate (**16**), respectively, in addition to methane and ethane. As discussed in the Results section, only a small fraction of **13** could result from attack of methyl on TMP (9). The most likely source of **16**, formed in yields up to 30% in TMP–DEP solutions, and of the major portion of **13** in the TMP–DMP reactions is cross combination of methyl and dialkyl phosphonyl radicals (eq 14). $(RO)_2P(O)\cdot$ is

$$CH_3\cdot + (RO)_2\dot{P}(O) \longrightarrow CH_3P(O)(OR)_2 \quad (14)$$

expected to be present from reaction of the dialkyl phosphite with trityl radicals to give triphenylmethane formed in large amounts in the presence of DMP and DEP. Alternatively, the product methyl dialkylphosphonate may result from ill-defined chemistry involving methyls and the unstable long retention time products **11** and **12** formed in the PAT decompositions in TMP–DMP and TMP–DEP reactions, respectively. The nature of **11** and **12** is largely unknown except for the presence of $CH_3OP(O)$ functionality inferred by pmr in the TMP–DMP system, but it seems reasonable that they must arise from the dialkyl phosphonyl radicals which should be involved in the DEP and DMP reactions and which are largely unaccounted for in the products found.

Methyls are essentially unreactive with TMP as solvent (Table I) probably because they are efficiently trapped by $Ph_3C\cdot$; but as $Ph_3C\cdot$ is removed by reaction with added DMP, it seems that reaction **5** may occur (Figure 2) to some extent. For some reason methyl radicals undergo coupling with $(CH_3)_2P(O)\cdot$ (reaction 14) as well as hydrogen abstraction, whereas phenyls abstract hydrogen at high [DMP] and [DEP] but do not give analogous cross-coupling products. *Compared to Ph·, $CH_3\cdot$ is decidedly less reactive toward TMP.*

---

(22) $Ph_3C\cdot$ is known to be very reactive toward $O_2$[23,24] even though it is relatively inert toward other species. The great reactivity of Ph· with TMP precludes its reaction with oxygen. These results again illustrate that $Ph_3C\cdot$ is not involved in a reaction such as (6a) or (6b). Benzophenone, isolated here, is commonly observed[25] in $Ph_3C\cdot$ systems containing oxygen. TMP is extensively oxidized to trimethyl phosphate as would be expected.[6,26]

(23) J. P. Lorand and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 3294 (1966).

(24) M. Gomberg, *Chem. Rev.*, 1, 91 (1924).

(25) (a) H. Wieland, *Ber.*, **44**, 2550 (1911); (b) H. Wieland and J. Maier, *ibid.*, **64**, 1205 (1931); (c) M. F. Hawthorne, *J. Amer. Chem. Soc.*, 77, 5523 (1955); (d) S. J. Cristol and J. E. Leffler, *ibid.*, **76**, 4468 (1954); (e) P. Gray and G. Williams, *Chem. Rev.*, **59**, 239 (1959); (f) W. H. Starnes, Jr., *J. Amer. Chem. Soc.*, **89**, 3368 (1967); (g) G. W. Clark and J. A. Kampmeier, *Chem. Commun.*, 996 (1970).

(26) S. A. Buckler, *J. Amer. Chem. Soc.*, **84**, 3093 (1962); M. B. Floyd and C. E. Boozer, *ibid.*, **85**, 984 (1963).

(27) Esr studies have identified the radicals $\cdot PCl_4$,[28] $\cdot PF_4$,[29] and $(RO)_xPR'_{4-x}$[5a–c] from reaction of a radical with the appropriate trivalent phosphorus compound. Chemical evidence is also available (ref 5d).

(28) G. F. Kokoszka, and P. E. Brinckman, *J. Amer. Chem. Soc.*, **92**, 1199 (1970); *Chem. Commun.*, 349 (1968).

(29) W. Nelson, G. Jackel, and W. Gordy, *J. Chem. Phys.*, **52**, 4572 (1970); R. W. Fessenden and R. H. Schuler, *ibid.*, **45**, 1845 (1966); P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4363 (1964); J. R. Morton, *Can. J. Phys.*, 41, 706 (1963).

(30) D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 110 (1965); M. J. Perkins, *ibid.*, 5932 (1964); D. H. Hey and J. Peters, *ibid.*, 79, 88 (1960); D. H. Hey and P. Jewfik, *ibid.*, 2402 (1965).

(31) J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Amer. Chem. Soc.*, **88**, 1257 (1966).

As depicted in Tables II and III, not more than 0.6% of dimethyl triphenylmethylphosphonate is formed in PAT decompositions in pure TMP and in TMP–DEP. *The triphenylmethyl radical appears to be almost, if not totally, unreactive toward TMP.* The increase in **10** on adding DMP probably results from reaction 15 which is analogous to reaction 14 involving methyl radicals.

$$(C_6H_5)_3C\cdot + (CH_3O)_2P(O) \longrightarrow (C_6H_5)_3CP(O)(OCH_3)_2 \quad (15)$$

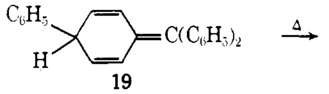
The apparent high reactivity of Ph· and relative unreactivity of $CH_3\cdot$ and $Ph_3C\cdot$ will be discussed in in the following paper[21] in terms of the strengths of the bonds formed in the likely phosphoranyl radical intermediates.

The origin of the minor products, **7–9**, of the PAT–TMP reactions and the effects of added hydrogen donors on their yields are also of interest. These products have little or nothing to do with the question of radical reactivities with trivalent phosphorus, but they are pertinent to the detailed consideration of the mechanism of PAT decomposition and of the effects of structure on radical coupling.

Two of these, **8** and **9**, which are commonly reported to be minor products of PAT decompositions,[30–32] in all probability arise from coupling of trityl and phenyl radicals (reactions 16, 17). Formation of **9** *via* (17) requires that the initially formed substituted 1,3-cyclohexadiene (or quinoid) intermediate undergoes aromatization (a thermally allowed suprafacial [1,5] hydrogen shift) under reaction or analysis conditions.[32] The one-to-one proportion of these low-yield products, **8** and **9**, under a variety of conditions (Tables I and II) indicates that coupling occurs with equal probability at the tertiary central carbon and the para positions of triphenylmethyl. This is in marked contrast to the exclusive coupling of methyls with trityls at the tertiary carbon to yield 1,1,1-triphenylethane (**6**). The accountability of trityls was nearly quantitative, so that no more than minor amounts of *p*-toluyldiphenylmethane could have been formed. Although examples of redissociation of a para-coupling product into free radicals have been observed with the quinoids isodicumyl[33] and 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene (triphenylmethyl radical dimer)[34] it is unlikely that any of the products from the coupling of more reactive radicals such as phenyl and methyl with trityls could undergo redissociation to radicals under the reaction or analysis conditions. Therefore, the proportions of **8** and **9** should be controlled by kinetic rather than thermodynamic factors.

$$C_6H_5\cdot + \cdot C(C_6H_5)_3 \longrightarrow \underset{\mathbf{8}}{(C_6H_5)_4C} \quad (16)$$

$$C_6H_5\cdot + \cdot C(C_6H_5)_3 \longrightarrow$$

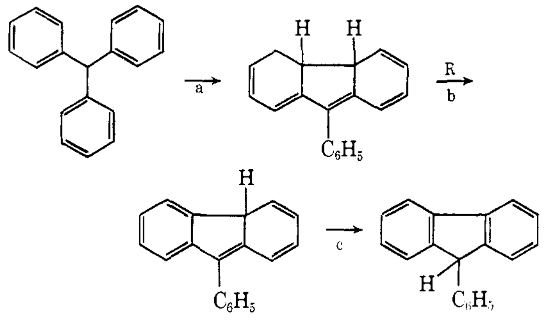


**19**

$$\underset{\mathbf{9}}{4\text{-}C_6H_5C_6H_4C(H)(C_6H_5)_2} \quad (17)$$

The results of a number of studies of attack by radicals on $Ph_3C\cdot$ have been summarized by Lorand and Bartlett.[23] The proportions of central carbon and para coupling are to a large extent controlled by steric considerations. The exclusive central atom attack on $Ph_3C\cdot$ by methyl and 50:50 central–para couplings of $Ph_3C\cdot$ with Ph· observed in this study are consistent with this view. In an earlier study, Kampmeier, *et al.*,[31] noted a 4:1 para–central atom coupling ratio for phenyl. Since it was necessary for these workers to determine relative amounts of para coupling products by indirect analyses of the products of apparent reaction of 4-biphenylyldiphenylmethyl radicals with *tert*-butyl thiyl radical, some discrepancy between our results and theirs may not be surprising. The possibility that the quinoid para-coupling intermediate **19** could be consumed by radical addition instead of conversion to **9** in our reactions cannot be excluded. However, the generally constant **8**/**9** ratio (Table II) seems contrary to this idea. Steric effects resulting from superior solvation of phenyl radical in di-*tert*-butyl sulfide, the solvent used in the earlier study,[31] could be important. The relatively constant amounts of **8** and **9** formed when concentration of TMP exceeds 5 *M* (Table II) suggest that **8** and **9** result from cage reactions at high [TMP]. But as [TMP] is lowered, noncage Ph· and $Ph_3C\cdot$ combination occurs outside the solvent cage along with hydrogen abstraction reactions of phenyl which give benzene. The insensitivity of the yields of **8** and **9** to [PAT], Table I, is also consistent with the idea that **8** and **9** are cage products in TMP as solvent. The TMP seems to scavenge all kinetically free phenyl radicals.

The yield of 9-phenylfluorene (**7**) appears to be decreased by the addition of DMP and DEP toward a minimum value of less than 1%. The generation of **7** requires an abstracting species (eq 18), and the above trend could signify that the added hydrogen donor diverts R· so that (18b) does not occur. It may well be likely that $Ph_3C\cdot$ is the species diverted by DMP or DEP to form **5** (*vide supra*) rather than **7**. (Step 18c, a thermally disallowed 1,3 shift, may be nonconcerted or benefit from the aromaticity of the product, **7**).



(18)

A portion of **7** formed may be cage product with R· = Ph· (eq 18). Tables I–III show that some benzene (~1%) is formed even when TMP appears to scavenge all kinetically free phenyls. The small constant amounts of benzene formed in pure TMP over a wide range of [PAT] may well be cage product. Cage reaction 18, R· = Ph·, has been previously suggested.[15a] How-

---

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

(33) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 137 (1966).

(34) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

ever, this is contrary to the later report of Pryor and Smith[32] that ArH is not a cage product, since its yield at very low initial PAT and *p*-nitrophenylazotriphenylmethane concentrations drops rapidly toward zero, and also since ArH is not formed when $I_2$ or $CBr_4$ is added.[34a]

In summary, the above studies show that thermal decompositions of PAT in TMP and mixtures of TMP with various hydrogen donors give products consistent with the occurrence of free-radical processes. Ph· appears to be the active species in formation of dimethyl phenylphosphonate in a reaction not dependent on triphenylmethyl radicals. Ph· reacts very rapidly with TMP, whereas $CH_3\cdot$ shows a very low reactivity. $Ph_3C\cdot$ is almost, if not totally, inert toward TMP.

## Experimental Section

**Proton magnetic resonance (pmr) spectra** were recorded using either a Varian A-60 or a Varian A-56/60 spectrometer with tetramethylsilane (TMS) as an internal standard. Chemical shifts are in parts per million (ppm) downfield from TMS. Standard notations are used to denote peak multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

**Gas-liquid chromatography (glc)** was done on the following instruments: an F & M Model 810, dual-column chromatograph with thermal conductivity detector and temperature programmer, and an Aerograph Model A 90-P3 chromatograph equipped with a manual collector assembly, a linear temperature programmer, and thermal conductivity detector.

**Quantitative analyses** were performed using 6 ft × 0.25 in. 20% SE-30 on 60–80 Chromosorb W (regular) and 10 ft × 0.25 in. 20% 3,3′-oxydipropionitrile on 40–60 Chromosorb W (regular) columns and one of the following methods.

**Method A. Absolute Calibration.** Solutions of accurately weighed samples of the compound for which the calibration curve was required were prepared in 2- or 5-ml volumetric flasks. The solvent was carbon tetrachloride or dimethyl phosphite. Exact volumes of each of these solutions were injected and analyzed several times by glc (conditions were the same as those used in analyzing for the compound in the reaction mixture). Peak areas were measured by a planimeter (Gelman Instrument Co., No. 49108). The sensitivity calibration curve was obtained by plotting the average values of peak areas against the number of mmoles of the compound injected. An exact amount of the unknown solution, which had been diluted to known volume, was then injected several times, and an average area value was determined. The amount of sample present in the unknown solution was calculated from the following relationship.

$$\text{mmoles}_x = \text{area}_x \cdot (\text{mmoles/area})_{\text{calibration}}$$

Analysis of an unknown solution was always preceded and followed by the known standards. Reproducibility was ≤5%.

**Method B. Internal Standardization.** Solutions of various mole ratios of the compound ($x$) and a standard ($s$) were prepared and chromatographed using multiple injections. The solvent was benzene or dimethyl phosphite. The peak areas were measured by the Model 227 Disc chart integrator. The correct factor ($F_x$) was determined from the following relationship by the least-squares method.

$$F_x = (\text{area}_x/\text{area}_s)/(\text{moles}_x/\text{moles}_s)$$

The moles of product ($x$) in the unknown solution in which a certain amount of standard ($s$) had been added were calculated. The reproducibility in this study was ≤3%. Data in Table I were obtained by method A; those in Tables II and III by method B.

**Materials.** Solvents and reagents for synthesis were carefully purified before use. Authentic samples of the following products of reaction were synthesized by known procedures and characterized by physical constants and spectral data: dimethyl phenylphosphonate;[17] diethyl phenylphosphonate;[17] dimethyl methylphosphonate;[35] diethyl methylphosphonate;[35] 1,1,1-triphenylethane;[36] dimethyl[37] and diethyl[38] triphenylmethylphosphonate. Tetraphenylmethane, 4-biphenylyldiphenylmethane, and 9-phenylfluorene were gifts from Professors J. A. Kampmeier and W. A. Pryor to whom we are grateful. Triphenylmethane was obtained from Aldrich Chemical Co. and recrystallized from benzene.

**Phenylazotriphenylmethane** (**PAT**) was prepared by the reduction of *N*-phenyl-*N′*-triphenylmethylhydrazine[39] (27 g, 0.77 mol) with excess hydrogen peroxide (40 ml, 30%) according to a modification of the procedure of Bridger and Russell.[15a] Material of highest purity could be obtained when the reduction was carried out at 0° for 2 days and the unreacted hydrazine removed by treatment with anhydrous hydrogen chloride. The product was twice recrystallized by first dissolving it in warm dichloromethane and then adding an equal volume of absolute ethanol. Well-formed crystals resulted upon standing in a freezer (−40°) for several hours. The crystals were dried under vacuum at 0–10° for 10 hr to give PAT: yield 55%; mp 111–112° (vacuum sealed tube) (lit.[15a] mp 110–112°); pmr ($CCl_4$) $\delta$ 7.17 ppm (m); ir ($CCl_4$) 3049 m, 1592 m, 1486 s, 1439 s, 1182 m, 1145 m, 1033 m, 719 m, 699 vs, 687 $cm^{-1}$ s.

As a test of purity, 0.096 *M* PAT in carbon tetrachloride was decomposed as described by Bridger and Russell.[15a] The benzene–chlorobenzene ratio was determined by glc using a 10 ft × 0.25 in. 20% 3,3′-oxydipropionitrile on 40–60 Chromosorb W column at 86° (isothermal) with a helium flow rate of 80 ml/min. The benzene–chlorobenzene ratio was found to be 0.079–0.087, which is well within the limits of 0.070–0.099 accepted by Bridger and Russell as a criterion of purity. If the ratio was higher than the minimum value, precipitation of the hydrochloride salt of the hydrazo compound from an ether solution of PAT, reoxidation, and recrystallization were used to reduce it to the minimum benzene–chlorobenzene ratio.

**PAT Thermal Reactions.** The following general procedure was used in all thermal reactions of PAT except as noted. Pyrex reaction ampoules were carefully washed with aqueous nitric acid and ammonium hydroxide solutions, rinsed with distilled water, oven-dried, and then capped with rubber serum caps and thoroughly flushed with pure nitrogen before use. Solutions containing TMP and various amounts of DMP, DEP, and cyclohexene were made up by weight in glass-stoppered volumetric flasks. In the cases in which the substrate was sensitive toward oxygen, serum cap-stoppered, nitrogen gas-flushed volumetric flasks were used. Solutions containing desired concentrations of PAT were then made up from the above mixtures using standard volumetric procedures. The actual weight of added substrate mixtures was also recorded so that the number of moles of all potential reactants was actually known. Known amounts (~1 ml) of these PAT solutions were weighed into the sample ampoules by means of a long needle syringe with care taken to ensure that no reactants adhered to the walls of the tubes. Each solution was weighed into two different ampoules to duplicate results. The reaction mixtures were degassed at $10^{-5}$–$10^{-6}$ mm with three successive freeze–thaw cycles before sealing under vacuum. The sealed tubes were placed in a light-proof constant temperature bath at 60 ± 0.1° for more than 10 half-lives of PAT (4 hr). After reaction, the ampoules were stored in liquid nitrogen until they were analyzed. Immediately before analysis, the ampoules were opened in a pure nitrogen atmosphere and sealed with rubber serum caps. A proper internal standard was then weighed in. In the cases in which method A was used for the quantitative analysis, analyses of unknown solutions were always

---

[34a] Note Added in Proof. After this paper was submitted, a full account of the effect of adding radical scavengers, $I_2$ and $CBr_4$, to PAT decompositions was published: W. A. Pryor, K. Smith, J. T. Echols, Jr., and D. L. Fuller, *J. Org. Chem.*, 37, 1753 (1972). Pryor, *et al.*, reported benzene yields to be reduced to the range zero to <0.5% by added $I_2$ or $CBr_4$. As noted in the following paper[21] we find application of a 1% benzene correction to our competitive TMP–DMP studies at 0.05 *M* PAT (Table II, next paper) is necessary, and this is also clearly shown by application to our data of the graphical analysis method of Pryor, *et al.*, which is presented in the above paper. This is further evidence for the formation of about 1% benzene from 0.5 *M* PAT in pure TMP. We and the Pryor group both agree that the amount of cage product benzene formed on thermolysis of PAT is much less than that previously estimated by extrapolation procedures (≥3%). It is doubtful that resolution of the question of whether zero or 1% of the phenyls from PAT give benzene by cage reaction is worth further effort.

[35] A. H. Ford-Moore and J. H. Williams, *J. Chem. Soc.*, 1465 (1947).

[36] H. Gilman and B. J. Gai, *J. Amer. Chem. Soc.*, **82**, 6326 (1960).

[37] K. Dimroth and A. Nürrenbach, *Chem. Ber.*, **93**, 1649 (1960).

[38] A. E. Arbuzov and C.-L. Chang, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 11, 1945 (1963); H. H. Hatt, *J. Chem. Soc.*, 2412 (1929); A. E. Arbuzov and V. S. Abramov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 35 (1959).

[39] M. Gomberg and H. W. Berger, *Chem. Ber.*, **36**, 1088 (1903); S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, 75, 5504 (1953).

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.

**Acknowledgment.** The research was supported by a grant from the National Science Foundation (GP-22885).

---

# 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

---

(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 $\rho$ values for abstraction of hydrogen from substituted toluenes, which presumably measure polarity, are for $Cl_3C\cdot$,[6] −1.46 at 50°; for $t\text{-}C_4H_9O\cdot$,[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].