Stability/Lability Characteristics of 1, 2, and 10 in D_2O. The reaction mixtures contained 0.005 M substrate and, in most cases, an additive, and were monitored by ^1H NMR with $Me_3Si(CH_2)_3SO_3Na$ as internal standard. The results are summarized in Table I. In entries 1 and 5, 1 decomposed to 7 and 8. Due to poor resolution and partial overlap of the SO_2CH_2 with the Me_3N^+ signal, it was indeterminable whether or not partial hydrogen–deuterium exchange within the former group accompanied 1's decomposition. The presence of $ArSO_2CD{=}CH_2$ (**7**-*d*) was likewise uncertain by ^1H NMR. In entries 11 and 12, 2 decomposed to 7 and 9, whose possible deuterium contents were uncertain. The limited solubility of 2 at 25 °C (Kraft temperature >25 °C) precluded the use of more concentrated KOD solutions in cleavage studies. At higher temperatures in such solutions, 2 should undergo rapid cleavage to 7 and 9. In entries 13, 15, and 16, 10 underwent isotopic exchange as it decomposed to 11 and 9 (Na^+). Also, in entries 15 and 16, **7**-*d* was detected. In no run was $4\text{-}n\text{-}C_{12}H_{25}C_6H_4SO_2CDH(D)CH_2OD$ or $4\text{-}MeC_6H_4SO_2CDH(D)CH_2OD$ detected, which would have resulted from Michael-like addition of D_2O to 7 and 11, respectively.

Acknowledgment is made to the U.S. Army Research Office, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Marathon Oil Company for support of this research.

Registry No. 1, 103752-44-9; 2, 103752-45-0; 3, 20025-90-5; 4, 57011-90-2; 5, 103752-35-8; 5 (sulfonyl), 103752-36-9; 5 (sulfonyl amine), 103752-37-0; 6, 103752-38-1; 6 (sulfonyl), 103752-39-2; 6 (alcohol), 103752-40-5; 6 (sulfonyl alcohol), 103752-41-6; 7, 60523-06-0; 8, 92939-04-3; 10, 103752-46-1; $4\text{-}HOC_6H_4NHCOMe$, 103-90-2; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_2OPh$, 589-10-6; $Br(CH_2)_2OH$, 540-51-2; $4\text{-}C_{12}H_{25}C_6H_4SO_2(CH_2)_2OSO_2Me$, 103752-42-7; $4\text{-}NH_2C_6H_4OH$, 123-30-8; $4\text{-}MeC_6H_4S(CH_2)_2OPh$, 94001-61-3; $4\text{-}MeC_6H_4SO_2(CH_2)_2OPh$, 28611-88-3.

---

[14] **Note Added in Proof:** At 50 °C in 0.1 M KOD–D_2O, 0.005 M 2 decomposed completely to 7 and 9 within 10 min.

Reactions of Carbenes and Photoexcited Ketones with Phosphorus Compounds

Angelo Alberti*

Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni, CNR, 40064 Ozzano Emilia, Italy

David Griller and A. S. Nazran

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

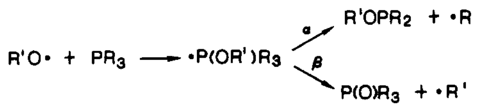
Gian Franco Pedulli*

Istituto di Chimica Organica, 09100 Cagliari, Italy

Received December 24, 1985

The photoinduced reactions of aromatic carbonyl compounds and diaryldiazomethanes with phosphorus derivatives were investigated by EPR and laser flash photolysis techniques. Triplet ketones reacted with tetraethyl pyrophosphite via a mechanism akin to a homolytic displacement (S_H2) process at an almost diffusion controlled rate (k_{300} = (7.96 ± 0.04) × 10^8 M^{-1} s^{-1} for benzophenone). Triplet benzophenone reacted very rapidly with tetraphenyldiphosphine (k_{300} = 2 × 10^8 M^{-1} s^{-1}). Tetraethyl pyrophosphite also underwent homolytic attack by triplet diphenylcarbene (k_{300} = (7.4 ± 0.7) × 10^6 M^{-1} s^{-1}) to give a diradical intermediate (or transition state) which, by β-fragmentation, gave $Ph_2\dot{C}OP(O)(OEt)_2$. Product studies supported the proposed mechanism. In contrast with diphenylcarbene, fluorenylidene appeared to react via a nonradical mechanism.

Tervalent phosphorus compounds, PR_3, undergo attack by oxygen-centered radicals, $^\bullet OR'$, to give phosphoranyl intermediates, which have been often detected by EPR.[1] The phosphoranyl radicals decompose by cleavage either of one of the P–R bonds (α-scission) or of the O–R′ bond (β-scission).[2,3] For the α-scission the overall reaction amounts to a homolytic substitution S_H2 of R by OR′ (eq 1), while in the latter case oxidation of the tervalent to a pentavalent phosphorus occurs (eq 2). The relative importance with which one of the two routes is chosen depends essentially on the relative strength of the P–R and O–R′ bonds; thus, for R = Ph and R′ = *t*-Bu, triphenylphosphine oxide is obtained in high yield (reaction 2), while if R′ is a primary or secondary alkyl group variable amounts of substitution and oxidation products are recovered depending on the nature of the alkyl.[2,3]



$$R'O^\bullet + PR_3 \longrightarrow {}^\bullet P(OR')R_3 \xrightarrow{\alpha} R'OPR_2 + {}^\bullet R \quad (1)$$

$$R'O^\bullet + PR_3 \longrightarrow {}^\bullet P(OR')R_3 \xrightarrow{\beta} P(O)R_3 + {}^\bullet R' \quad (2)$$

Tervalent phosphorus compounds are also attacked by carbon centered radicals to give phosphoranyls, which may subsequently undergo α- or β-scission. The latter route is generally observed when reacting phenyl or vinyl radicals with phosphites.[3] Reaction 3 also occurs slowly with R′ = methyl or isopropyl. However, *tert*-butyl radicals do not react readily with phosphites.[2]

$$^\bullet R' + P(OR)_3 \rightarrow {}^\bullet P(OR)_3R' \rightarrow (O)P(OR)_2R' + {}^\bullet R \quad (3)$$

In principle, homolytic displacement or oxidation could be brought about by other species containing unpaired electrons, such as triplet state molecules. We are not aware of any reports of homolytic reactions of the kind described in eq 1–3 which are carried out by triplet analogues of alkoxyl radicals, e.g., excited ketones, or triplet analogues

---

[1] Roberts, B. P. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Heyden: London, 1980; Vol. 6, p 225.

[2] Ingold, K. U.; Roberts, B. P. In *Free Radical Substitution Reactions*; Wiley-Interscience: New York, 1971; pp 116–133.

[3] Bentrude, W. G. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. II, pp 595–663.

0022-3263/86/1951-3959$01.50/0

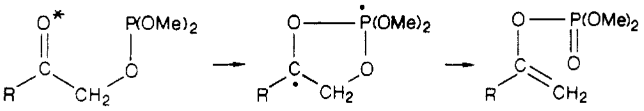
Table I. ESR Spectral Parameters for Radicals $R_2\dot{C}OP(OEt)_2$ (I) and $R_2\dot{C}OP(O)(OEt)_2$ (II)

$R_2C(O)$	radical	$a(^{31}P)$, G	a(other nuclei), G	g	T, K
benzophenone	I	14.97	3.26 ($4H_o$), 1.28 ($4H_m$), 3.59 ($2H_p$)	2.0028	403
	II	30.56	3.32 ($4H_o$), 1.31 ($4H_m$), 3.66 ($2H_p$)	2.0028	403
di-2-thienyl ketone	I	10.66	5.35 ($2H_3$), 1.11 ($2H_4$), 4.55 ($2H_5$)	2.0037	393
9-thioxanthone	I	14.44	0.94 ($H_{1,8}$), 3.77 ($H_{2,7}$), 1.07 ($H_{3,6}$), 3.36 ($H_{4,5}$)	2.0037	403
	II	28.26	0.97 ($H_{1,8}$), 3.78 ($H_{2,7}$), 1.04 ($H_{3,6}$), 3.34 ($H_{4,5}$)	2.0036	403
anthraquinone	I	10.40	2.93 ($H_{1,8}$), 0.94 ($H_{2,4,5,7}$), 3.31 ($H_{3,6}$)	2.0036	373
	II	27.46	3.12 ($H_{1,8}$), 0.89 ($H_{2,7}$), 3.46 ($H_{3,6}$), 1.08 ($H_{4,5}$)	2.0036	373

of carbon centered radicals, e.g., triplet carbenes. In fact, triplet benzophenone is actually photoreduced by triphenylphosphine (eq 4).[4]

$$Ph_2C(O)^* + PPh_3 \rightarrow Ph_2C^{2\bullet} + (O)PPh_3 \quad (4)$$

No intermolecular reactions of phosphites with ketones have been observed. However, dimethyl β-ketoethyl phosphites have been found to photorearrange to dimethyl vinyl phosphates.[5] This rearrangement is perhaps the only example of a homolytic reaction by triplets on phosphorus compounds and has been explained in terms of an intramolecular attack of the excited ketone on phosphorus (eq 5; c.f. eq 2).



(5)

On the other hand, carbenes are well-known to react with phosphines to give phosphorus ylides (eq 6) which are commonly used as reagents for the Wittig reaction.[6]

$$R_2C^{2\bullet} + PR_3 \rightarrow R_2C{=}PR_3 \leftrightarrow R_2C^-P^+R_3 \quad (6)$$

In order to gain more insight into the reactivity of triplet state molecules with tervalent phosphorus compounds we have carried out an EPR and laser flash photolysis investigation, combined with product studies where possible, of the photoinduced reactions of several carbonyl compounds or diphenyldiazomethane with phosphorus derivatives. We have found that with tetraethyl pyrophosphite, triplet ketones give an S_H2 reaction similar to 1, while triplet diphenyl carbene behaves analogously to carbon-centered radicals, such as phenyl or vinyl, and gives attack at the phosphorus atom followed by β-scission of a P–O bond.

Experimental Section

Materials. Diphenyldiazomethane[7] and diazofluorene[8] were prepared according to standard methods and were respectively purified by sublimation at room temperature or by recrystallization from hexane. 9-Methyleneanthrone was synthesized as reported in the literature.[9] Commercial tetraethyl pyrophosphite (TEPP) was distilled before use. All other chemicals were of high grade purity and were therefore used as received. Benzene was washed with concentrated sulfuric acid and then with water; it was then dried over magnesium sulfate and was finally distilled from calcium hydride.

Product Studies. Photolysis of diphenyldiazomethane (0.06 M) with tetraethyl pyrophosphite (0.164 M) in benzene was carried out by using a tungsten lamp until the characteristic pink color of the diazo compound had disappeared. The product distribution was determined by GC/mass spectrum (Hewlett-Packard 5995 fitted with a 10-m, 0.2-mm diameter cross-linked methyl silicon column). In the reaction between triplet benzophenone and TEPP product studies could not be carried out because the conversion was very low.

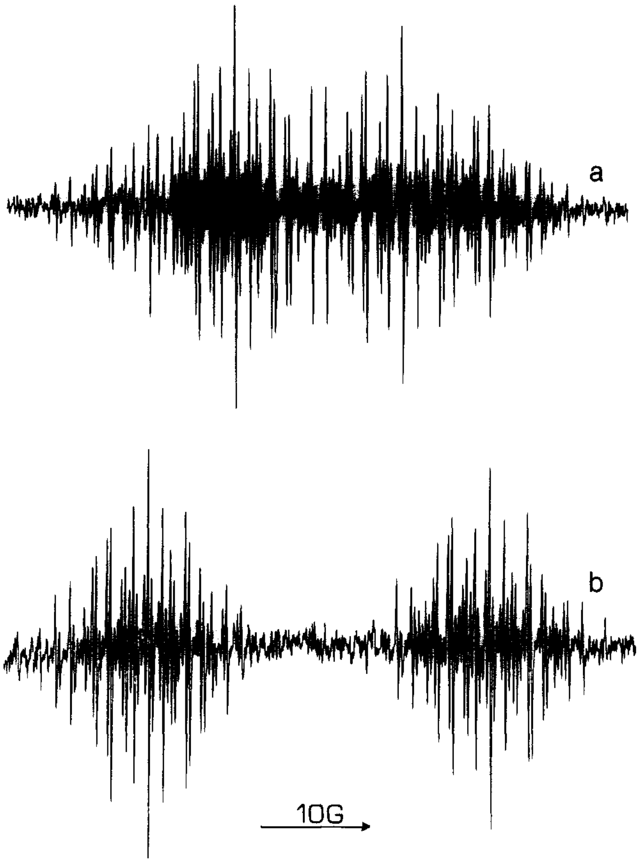


Figure 1. EPR spectra observed at 400 K upon photolysis of *tert*-butylbenzene solutions of benzophenone and TEPP in the absence (a) and in the presence (b) of $(t\text{-BuO})_2$.

Apparatus. EPR spectra were recorded with a Bruker ER 200 D spectrometer. Radicals were generated by photolysis of nirogen-purged benzene or *tert*-butylbenzene solutions containing the appropriate diazomethane or carbonyl compound and a phosphorus derivative. Typical concentrations of the samples were ca. 0.1 M in ketone, 0.2–0.4 M of the phosphorus compound, and, when present, 1 M in di-*tert*-butyl peroxide. The light from the photolysis source, a 1-kW high-pressure mercury lamp, was filtered through an aqueous solution of $CoSO_4$ (0.21 M) and $NiSO_4$ (1.14 M), to avoid heating the sample.

Laser flash photolysis experiments were carried out by using equipment that has been described elsewhere.[10] In experiments involving triplet benzophenone, a nitrogen laser (337 nm, 1 mJ per pulse, 8-ns width) was used as the excitation source, whereas an excimer laser (308 nm, 10 mJ per pulse, 8-ns width) was used to photolyze diphenyldiazomethane in order to generate diphenylcarbene. All samples were carefully deoxygenated by nitrogen purging, and in carbene experiments a flow system was used so as to avoid problems associated with sample depletion.

---

(4) Wescott, L. D., Jr.; Sellers, H.; Poh, P. *J. Chem. Soc., Chem. Commun.* **1970**, 586.

(5) Griffin, C. E.; Bentrude, W. G.; Johnson, G. M. *Tetrahedron Lett.* **1969**, 969.

(6) Kirmse, W. In *Carbene Chemistry*; Academic: New York, 1971; Chapter 11.

(7) Smith, L. I.; Howard, K. L. In *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III; p 351.

(8) Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4475.

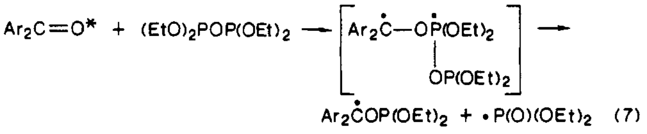
(9) de Barry Barnett, E.; Matthews, M. A. *Chem. Ber.* **1926**, *59*, 767.

(10) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 2146.

Results and Discussion

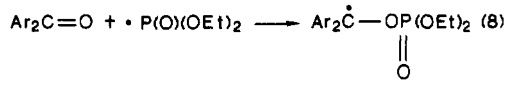
EPR Studies. Photoreaction of Ketones with TEPP. Irradiation at ca. 400 K of a deoxygenated solution of benzophenone and TEPP gave an EPR spectrum due to two radicals (see Figure 1a), characterized by similar g factors and proton hyperfine splitting (hfs) constants and exhibiting significantly different ^{31}P splittings (Table I). The spectral parameters were consistent with the structures $Ph_2\dot{C}OPR_n$. By repetition of the reaction with di-*tert*-butyl peroxide added to the solution, the more intense spectrum, i.e., the one characterized by the smaller phosphorus splitting, $a(^{31}P)$ 14.57 G, could no longer be observed while the one exhibiting $a(^{31}P)$ 30.56 G resulted greatly enhanced (Figure 1b). Since the reaction of t-BuO• with TEPP is known to afford triethoxyphosphonyl radicals,[11] we attribute the latter spectrum to radical $Ph_2\dot{C}OP(O)(OEt)_2$ arising from addition of $\cdot P(O)(OEt)_2$ to benzophenone.

An S_H2 displacement at phosphorus accounts for the observation of two paramagnetic species in the absence of peroxide, eq 7 and 8. Thus, attack of the photoexcited benzophenone triplet at the phosphorus atom of TEPP leads to an intermediate biradical (or transition state) which by α-scission affords I and $\cdot P(O)(OEt)_2$ radicals. Addition of the latter to benzophenone gives II. This reaction sequence in fact explains, in the absence of peroxide, the greater intensity of the spectrum due to I which is the radical species formed in the primary reaction step. The disappearance of I in the presence of $(t\text{-BuO})_2$ is likely due to attack of TEPP by *tert*-butoxyl radicals, which being diffusion controlled,[12] effectively competes with that by benzophenone triplet.[13] The mechanism described in reactions 7 and 8 has also been invoked to account for the observed radicals in the photoreaction of TEPP with some quinones.[15]



$$\mathrm{Ar_2C{=}O^*} + \mathrm{(EtO)_2POP(OEt)_2} \longrightarrow \left[\mathrm{Ar_2\dot{C}{-}O}\underset{\substack{|\\ \mathrm{OP(OEt)_2}}}{\dot{\mathrm{P}}}\mathrm{(OEt)_2}\right] \longrightarrow \mathrm{Ar_2\dot{C}OP(OEt)_2} + \cdot\mathrm{P(O)(OEt)_2} \quad (7)$$

I



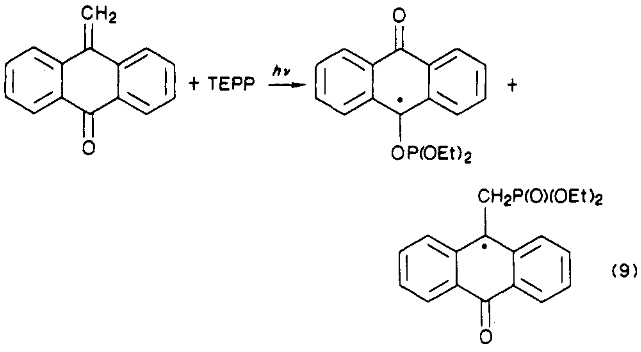
$$\mathrm{Ar_2C{=}O} + \cdot\mathrm{P(O)(OEt)_2} \longrightarrow \mathrm{Ar_2\dot{C}{-}O}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{P}}\mathrm{(OEt)_2} \quad (8)$$

II

When benzophenone was replaced by anthraquinone (AQ) similar results were obtained. Both the diethoxyphosphinyl I and diethoxyphosphonyl II adducts could be observed at 373 K in *tert*-butylbenzene. Again, addition of peroxide resulted in the detection of only species II.

Photolysis of di-2-thienyl ketone and thioxanthen-9-one in the presence of TEPP gave only their phosphinyl adducts I over a wide range of temperatures. With thioxanthen-9-one addition of di-*tert*-butyl peroxide resulted in the appearance of a weak spectrum attributable to II. With fluorenone, on the other hand, no radical adducts of either kind could be detected.

The photochemical reaction of 9-methyleneanthrone with TEPP again gave rise to two different paramagnetic species, neither of which could be related to the expected radicals I and II. One of them proved to be the diethoxyphosphinyl adduct of anthraquinone, while the other was identified as the adduct resulting from addition of $\cdot P(O)(OEt)_2$ radical to the exocyclic carbon–carbon double bond [$a(^{31}P)$ 51.14 G, $a(H_{2,8})$ 0.82 G, $a(H_{3,7})$ 3.33 G, $a(H_{4,6})$ 1.02 G, $a(H_{5,7})$ 2.97 G, $a(CH_2)$ 7.45 G, g 2.0034 at 298 K].



III

Since before irradiation 9-methyleneanthrone did not reveal impurities of anthraquinone, it seems that the initially formed radical I is readily oxidized by adventitious oxygen. The observation of III is an indication that $\cdot P(O)(OEt)_2$ adds to the C=C double bonds more easily than to the C=O double bonds.

We also reacted TEPP with an aryl alkyl ketone as *tert*-butyl phenyl ketone. Photolysis at 383 K resulted in the appearance of an intense spectrum interpretable in terms of the following hyperfine couplings: $a(2H)$ 1.50 G, $a(2H)$ 4.35 G, $a(1H)$ 4.95 G, $a(^{31}P)$ 14.55 G, and $a(^{31}P)$ 27.03 G and g 2.0029. These parameters are characteristic of $Ph((EtO)_2P(O))\dot{C}OP(OEt)_2$, (IV),[16] which is presumably formed through reaction sequence 10 and 11.

$$PhC(O)\text{-}t\text{-}Bu \xrightarrow{h\nu} Ph\dot{C}O + t\text{-}Bu^{\bullet} \quad (10)$$

$$Ph\dot{C}O + (EtO)_2POP(OEt)_2 \xrightarrow{S_H2} Ph(P(O)(OEt)_2)CO + {}^{\bullet}P(OEt)_2 \rightarrow Ph((OEt)_2(O)P)\dot{C}OP(OEt)_2 \quad (11)$$

Photoreaction of Ketones with Other Phosphorus Compounds. In our search for other homolytic displacement reactions involving triplet ketones and phosphorus compounds, we extended our investigation to the photoreaction of benzophenone and anthraquinone with triethyl phosphite, $P(OEt)_3$, diphenylphosphine, $HPPh_2$, and tetraphenyldiphosphine, Ph_2PPPh_2. With $P(OEt)_3$ no EPR signals were detected, in agreement with previous results.[5] With $HPPh_2$ only hydrogen abstraction occurred, as indicated by the detection of $Ph_2\dot{C}OH$ and $^{\bullet}AQH$ in the temperature range 250–410 K. The reaction of benzophenone with tetraphenyldiphosphine gave rise to a strong spectrum of $Ph_2\dot{C}OPPh_2$ (see Table II), while with anthraquinone, no diphenylphosphinyl adduct was observed.

Due to the photolability of the P–P bond[17] a mechanism involving photochemical fragmentation of Ph_4P_2 into $Ph_2P^{\bullet}$ radicals with subsequent addition to the C=O bond can

---

[11] Davies, A. G.; Griller, D.; Roberts, B. P. *J. Am. Chem. Soc.* **1972**, *94*, 1782.

[12] Burkey, T. J.; Griller, D.; Lunazzi, L.; Nazran, A. S. *J. Org. Chem.* **1983**, *48*, 3704.

[13] The formation of t-BuO• radicals can be due to direct photolysis of $(t\text{-BuO})_2$ or to energy transfer from benzophenone triplet to the peroxide.[14]

$$Ph_2C{=}O^* + (t\text{-BuO})_2 \xrightarrow{k = 3.4 \times 10^6\,M^{-1}\,s^{-1}} Ph_2C{=}O + 2t\text{-BuO}^{\bullet}$$

In the present case, the latter route seems rather unlikely in view of the low rate of the above reaction if compared with the quenching of benzophenone triplet by TEPP (vide infra).

[14] Scaiano, J. C.; Wubbels, G. G. *J. Am. Chem. Soc.* **1981**, *103*, 640.

[15] Alberti, A.; Hudson, A.; Pedulli, G. F.; McGimpsey, W. G.; Wan, J. K. S. *Can. J. Chem.* **1985**, *63*, 917.

[16] Alberti, A.; Degl'Innocenti, A.; Pedulli, G. F.; Ricci, A. *J. Am. Chem. Soc.* **1985**, *107*, 2316.

[17] Chen, K. S.; Foster, T.; Wan, J. K. S. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1238.

Table II. ESR Spectral Parameters of the Adducts of Benzophenone (BP) and Anthraquinone (AQ) with Other Phosphorus-Centered Radicals

substrate	PR_n	$a(^{31}P)$, G	a(other nuclei), G	g	T, K
BP	PPh_2	16.09	3.27 ($4H_o$), 1.26 ($4H_m$), 3.67 ($2H_p$)	2.0029	293
	PPh_2	15.67			243
	$P(O)Ph_2$	25.10	3.27 ($4H_o$), 1.29 ($4H_m$), 3.60 ($2H_p$)	2.0028	373
	$P(S)Et_2$	35.23	3.90 ($4H_o$), 1.26 ($4H_m$), 3.66 ($2H_p$)	2.0029	253
AQ	$P(O)Ph_2$	20.59	3.03 ($H_{1,8}$), 0.90 ($H_{2,7}$), 3.38 ($H_{3,6}$), 1.05 ($H_{4,5}$)	2.0036	393
	$P(O)Ph_2$	21.00			343
	$P(S)Et_2$	24.48	3.01 ($H_{1,8}$), 0.96 ($H_{2,4,5,7}$), 3.32 ($H_{3,6}$)	2.0036	323

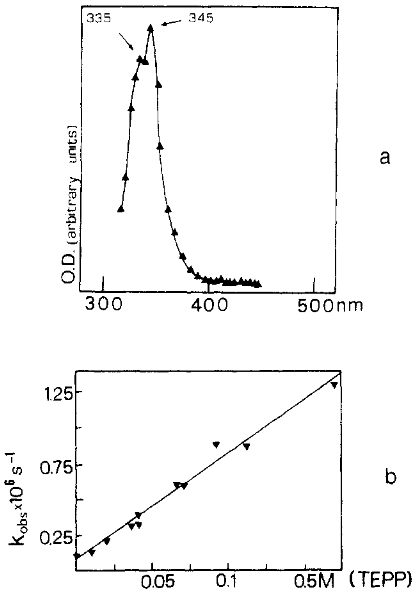


Figure 2. (a) Transient absorption spectrum of $Ph_2\dot{C}P(O)(OEt)_2$ obtained by laser flash photolysis of diphenyldiazomethane in the presence of TEPP. (b) Plot of k_{obsd} for the quenching of triplet diphenylcarbene at 298 K vs. TEPP concentration in benzene solvent.

be postulated. However, on the basis of laser flash photolysis experiments (vide infra), the formation of $Ph_2\dot{C}OPPh_2$ can be regarded as the result of a homolytic displacement on phosphorus by benzophenone triplet.

When the photoreaction of benzophenone with Ph_4P_2 is carried out at high temperature ($T > 373$ K), a second radical with $a(^{31}P)$ ca. 25 G is formed. This radical has been identified as the diphenylphosphonyl adduct $Ph_2\dot{C}OP(O)Ph_2$, by comparison with the authentic radical generated by reacting benzophenone with $HP(O)Ph_2$ in the presence of di-*tert*-butyl peroxide. Anthraquinone behaves similarly since at 373 K the reaction with Ph_4P_2 affords the $P(O)Ph_2$ adduct (Table II). The formation of the two diphenylphosphonyl adducts can be attributed to the high sensitivity of polyphosphines to oxidizing agents.[18]

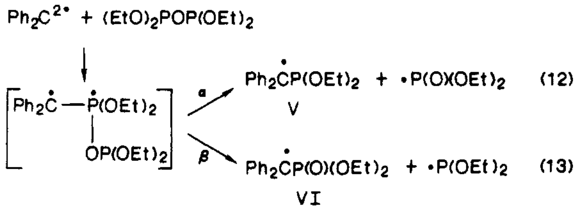
Other pentavalent phosphorus compounds as $HP(O)(OEt)_2$, $HP(O)Ph_2$, or $(Et_2(S)P)_2$ were also used as substrates. With diethyl phosphite or diphenylphosphine oxide and anthraquinone at low temperatures, photolysis gave only the radicals arising from hydrogen abstraction, while above 373 K the diethoxyphosphonyl and diphenylphosphonyl adducts were detected.

A similar behavior was also shown by benzophenone when reacted with $HP(O)Ph_2$, while in the reaction with $HP(OEt)_2$, $Ph_2\dot{C}OH$ was the only detectable radical up to 413 K.

The observation of these species is consistent with an initial hydrogen abstraction by the ketone or quinone triplets and subsequent attack of the resulting phosphonyl to the C=O double bond.

The photoreaction of benzophenone and AQ with tetraethylbiphosphine disulfide leads to the detection of $R_2\dot{C}OP(S)Et_2$ (see Table II) arising from addition to the carbonyl group of $^{\bullet}P(S)Et_2$ radicals formed by photocleavage of the P–P bond.[15]

Photoreaction of Diphenyldiazomethane with TEPP. The photolysis of Ph_2CN_2 (ca. 0.28 M) and TEPP (ca. 0.72 M) in deoxygenated benzene at room or higher temperature gave an EPR spectrum characterized by the following parameters: $a(^{31}P)$ 29.49 G, $a(4H_o)$ 2.88 G, $a(4H_m)$ 1.22 G, $a(2H_p)$ 3.15 G, g 2.0025 at 333 K. The hfs constants are therefore consistent with an α-substituted diphenylmethyl radical presumably arising by attack of triplet diphenylcarbene on the pyrophosphite. In principle the initially formed biradical intermediate (or transition state) could fragment by α- or β-scission (eq 12 and 13), thus leading respectively to radical V or VI. We, however, identify the observed radical as **VI** by comparison of the ^{31}P splitting with those reported for related systems.



Consistently, the two homologous radicals $t\text{-}BuCH_2\dot{C}HP(OEt)_2$[19] and $t\text{-}BuCH_2\dot{C}HP(O)(OEt)_2$[20] are characterized by similar proton couplings and g factors but by markedly different ^{31}P splittings, i.e., 95.8 G for the former and 41.3 G for the latter.

When taking into account that the two phenyl rings reduce the spin density at the radical center by ca. 35% (see for instance $^{\bullet}CH_3$ and $^{\bullet}CHPh_2$ where a_H is 22.83 and 14.7 G,[21] respectively) we expect an $a(^{31}P)$ splitting of ca. 60 G for radical V and of ca. 27 G for radical VI.

We may therefore conclude that the reaction route followed by diphenylcarbene is represented by eq 13 and that, like the $R\dot{P}(OR)_3$ phosphoranyl in reaction 3, the intermediate biradical undergoes β-fragmentation to give radical VI.

Tetraethyl pyrophosphite seems to be the only tervalent phosphorus derivative undergoing a homolytic reaction with triplet diphenylcarbene. In fact, no EPR signals were detected when reacting diphenyldiazomethane with the other aforementioned phosphorus compounds, i.e., PPh_3, $P(OEt)_3$, and Ph_4P_2, under similar experimental conditions. The failure to observe paramagnetic species has probably to be attributed to the formation of phosphorus ylides as

---

(18) Smith, D. J. H. In *Comprehensive Organic Chemistry*; Barton, D. H., Ollis, W. D., Sutherland, I. O., Eds.; Pergamon: New York, 1979; Vol. 2, p 1179.

(19) Baban, J. A.; Cooksey, C. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 781.

(20) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1979**, 373.

(21) Bassindale, A. R.; Bowles, A. J.; Hudson, A.; Jackson, R. A.; Schreiner, K.; Berndt, A. *Tetrahedron Lett.* **1973**, 3185.

outlined in eq 6, although we did not pursue this point.

It is remarkable that diazofluorene when photolyzed in the presence of TEPP does not afford any detectable radical. This may be due to the fact that both the singlet and triplet states are extremely short-lived and attack solvent molecules very readily. Moreover, the singlet–triplet gap is so small[22] that the triplet may bring about singlet-like reactions such as ylide formation, insertion, etc.[23]

Laser Flash Photolysis. Photolysis of degassed solutions of diphenyldiazomethane (6.2×10^{-5} M) in benzene led to the detection of triplet diphenylcarbene ($\lambda_{max} \simeq 318$ nm). In the absence of any quencher the triplet decayed in about 5 μs. Addition of TEPP to the solution quenched the triplet absorption spectrum and gave rise to a new optical absorption band at λ_{max} 345 nm (Figure 2a) which grew concurrently with decay of triplet diphenylcarbene. Rate constants, k_1, for the reaction of $^3Ph_2C^{2\bullet}$ with TEPP were obtained by monitoring the decay of the carbene at 318 nm and the growth of VI at 345 nm. The observed rate constants, k_{obsd} for both processes are related to the rate constant of interest k_1 by eq 14, where k_0 represents the rate constant for the disappearance of the carbene in the absence of TEPP.

$$k_{obsd} = k_0 + k_1[\mathrm{TEPP}] \qquad (14)$$

The plot of k_{obsd} vs. the pyrophosphite concentration, which is shown in Figure 2b, gave the value $k_1 = (7.4 \pm 0.7) \times 10^6\ M^{-1}\ s^{-1}$.

A similar method was used to measure rate constants for the reaction of benzophenone triplet with TEPP and with tetraphenyldiphosphine. When the decay of triplet benzophenone was monitored at 525 nm, rate constants were determined to be $(7.96 \pm 0.04) \times 10^8\ M^{-1}\ s^{-1}$ and $2 \times 10^8\ M^{-1}\ s^{-1}$, respectively. The similarity of these two values indicates that the two reactions proceed through the same mechanism, i.e., that also tetraphenyldiphosphine undergoes a homolytic displacement by benzophenone triplet (vide supra).

From a comparison of the rate constants for the reaction of TEPP with benzophenone and with *tert*-butoxyl radicals ($2.85 \times 10^9\ M^{-1}\ s^{-1}$)[12] it can be inferred that ketones photoexcited in their triplet state exhibit a reactivity akin to that of alkoxyl radicals.

Product Studies. The photoreaction of diphenyldiazomethane with tetraethyl pyrophosphite afforded a quite complex product mixture. However, the following materials containing the Ph_2C moiety were identified:

$Ph_2CHP(O)(OEt)_2$ (VII)	36.7%
$Ph_2C(P(OEt)_2)P(O)(OEt)_2$ (VIII)	12.2%
$Ph_2C{=}NN{=}CPh_2$	26.5%
$Ph_2C{=}O$	7.8%
$Ph_2C{=}CPh_2$	4.9%
$Ph_2CHCHPh_2$	2.1%
unidentified	9.7%

The isolation of products VII and VIII is consistent with the proposed reaction mechanism (eq 13) as the former may arise from VI via hydrogen abstraction, possibly from another molecule of TEPP, and the latter by recombination of VI with the displaced diethoxyphosphinyl radical $^\bullet P(OEt)_2$.

Benzophenone may result from oxygen contamination, while the other products may arise from reactions 15 to 18.

$$Ph_2C^{2\bullet} + Ph_2CN_2 \rightarrow Ph_2C{=}NN{=}CPh_2 \qquad (15)$$

$$Ph_2C^{2\bullet} + RH \rightarrow Ph_2\dot{C}H + {}^\bullet R \qquad (16)$$

$$2\ Ph_2\dot{C}H \rightarrow Ph_2CHCHPh_2 \qquad (17)$$

$$2\ Ph_2C^{2\bullet} \rightarrow Ph_2C{=}CPh_2 \qquad (18)$$

Summary

Triplet ketones react with tetraethyl pyrophosphite and with tetraphenyldiphosphine via a mechanism analogous to the homolytic substitution, S_H2, process. With the other investigated tervalent phosphorus compounds containing stronger phosphorus–ligand bonds, no evidence was obtained supporting the occurrence of this reaction.

A homolytic reaction also takes place between TEPP and triplet diphenylcarbene and the intermediate biradical (or transition state) fragments via β-scission; the resulting radicals are responsible for the formation of the major products containing phosphorus. No free radicals were detected by reacting diphenylcarbene with other phosphorus compounds. Fluorenylidene, where the singlet manifold is readily accessible, does not display radical reactivity even with tetraethyl pyrophosphite.

Acknowledgment. We are indebted to "Progetto Finalizzato Chimica Fine e Secondaria" del CNR for financial support. This paper is issued as NRCC Publication 26097.

Registry No. AQ, 84-65-1; $P(OEt)_3$, 122-52-1; $HPPh_2$, 829-85-6; Ph_2PPPh_2, 1101-41-3; $HP(O)(OEt)_2$, 762-04-9; $HP(O)Ph_2$, 4559-70-0; $(Et_2(S)P)_2$, 3790-23-6; diphenyldiazomethane, 883-40-9; ethyl pyrophosphite, 21646-99-1; benzophenone, 119-61-9; di-2-thienyl ketone, 704-38-1; thioxanthen-9-one, 492-22-8; fluorenone, 486-25-9; 9-methyleneanthrone, 4159-04-0; *tert*-butyl phenyl ketone, 938-16-9.

---

[22] Grasse, P. B.; Brauer, B. E.; Zupanic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

[23] Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227.