# THE REACTION OF ALKYL RADICALS WITH ALKYL DIPHENYLPHOSPHINITES

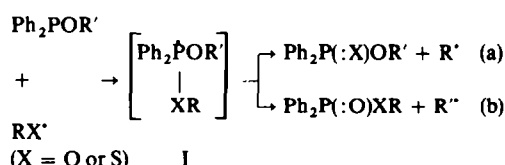R. S. DAVIDSON

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**Abstract**—Methyl and i-propyl radicals have been found to react with methyl diphenylphosphinite to give respectively, methyldiphenylphosphine oxide and i-propyldiphenylphosphine oxide. t-Butyl radicals under similar conditions, initiated the transformation of the ester to methyldiphenylphosphine oxide. Benzyl radicals were found to be unreactive. Phenyl radicals, obtained from phenylazotriphenylmethane, were found to react with a number of alkyl diphenylphosphinites to give triphenylphosphinine oxide plus alkyltriphenylmethane. Cyclopentyl and cyclohexyl diphenylphosphinites were found to react abnormally in that they gave cycloalkene instead of cycloalkyltriphenylmethane. Reactions are postulated as occurring by attack of the alkyl radical upon the trivalent phosphorus ester to give a phosphoranyl radical which subsequently decomposes to give phosphine oxide plus an alkyl radical.
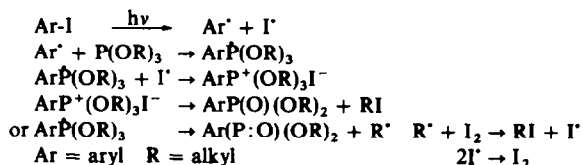
SEVERAL examples of the reactions of alkoxy,[1,2] thioalkyl[1-3] and peroxy[1-3] radicals with trivalent phosphorus esters have been previously reported. These reactions are postulated as occurring by attack of the radical upon the phosphorus ester to give a phosphoranyl radical (I) which subsequently breaks down to give oxidized phosphorus compound plus an alkyl radical. Although in principle, either reaction (a) or (b)

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\begin{array}{c}
\text{Ph}_2\text{POR}' \\
+ \\
\text{RX}^\cdot \\
(\text{X = O or S})
\end{array}
\rightarrow
\left[
\begin{array}{c}
\text{Ph}_2\overset{\cdot}{\text{P}}\text{OR}' \\
| \\
\text{XR}
\end{array}
\right]
\begin{array}{l}
\rightarrow \text{Ph}_2\text{P}(:\text{X})\text{OR}' + \text{R}^\cdot \quad \text{(a)} \\
\rightarrow \text{Ph}_2\text{P}(:\text{O})\text{XR} + \text{R}'' \quad \text{(b)}
\end{array}
$$

$$\text{I}$$

can occur, the one leading to R (i.e. reaction a) is the most frequently encountered. Dimethylamino radicals have been found to oxidize alkyldiphenylphosphinites to give alkyl radicals by reaction (b).[4] In the reaction of dimethylamino radicals with methyl diphenylphosphinite it was found that methyldiphenylphosphine oxide was produced and it was suggested that it had been formed by attack of Me radicals upon the phosphorus ester.

$$\text{Me}^\cdot + \text{Ph}_2\text{POMe} \rightarrow \text{Ph}_2\text{P}(:\text{O})\text{Me} + \text{Me}^\cdot \qquad (i)$$
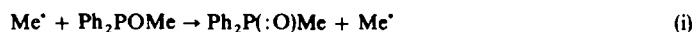
A number of previously reported reactions seemed to support the suggestion that alkyl radicals can attack trivalent phosphorus esters. Thus photolysis of aryl halides in the presence of trivalent phosphorus esters, in which aryl radicals are undoubtedly produced,[5] leads to oxidized phosphorus compounds.[1,5] Photolysis of trimethyl-

$$
\begin{array}{l}
\text{Ar-I} \xrightarrow{\text{h}\nu} \text{Ar}^\cdot + \text{I}^\cdot \\
\text{Ar}^\cdot + \text{P(OR)}_3 \rightarrow \text{Ar}\overset{\cdot}{\text{P}}(\text{OR})_3 \\
\text{Ar}\overset{\cdot}{\text{P}}(\text{OR})_3 + \text{I}^\cdot \rightarrow \text{ArP}^+(\text{OR})_3\text{I}^- \\
\text{ArP}^+(\text{OR})_3\text{I}^- \rightarrow \text{ArP(O)(OR)}_2 + \text{RI} \\
\text{or ArP(OR)}_3 \rightarrow \text{Ar(P:O)(OR)}_2 + \text{R}^\cdot \quad \text{R}^\cdot + \text{I}_2 \rightarrow \text{RI} + \text{I}^\cdot \\
\text{Ar = aryl} \quad \text{R = alkyl} \qquad\qquad\qquad 2\text{I}^\cdot \rightarrow \text{I}_2
\end{array}
$$

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phosphite gives dimethylmethylphosphinate probably by attack of Me radicals upon the phosphite.[7]

$$Me^{\cdot} + (MeO)_3P \rightarrow (MeO)_2P(:O)Me + Me^{\cdot}$$

Recently it has been reported[8] that photolysis of triethylphosphite gives the radicals IIa and IIb and Et radicals. The radicals were positively identified by electron spin resonance spectroscopy.

$$(EtO)_2P\!-\!O^{\cdot} \qquad (EtO)_2\overset{+}{P}$$
$$\mid$$
$$O^-$$

IIa          IIb
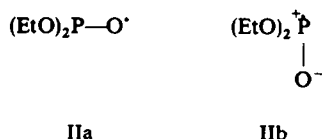
In order to determine the reactivity of trivalent phosphorus esters towards alkyl radicals, several azoalkanes were decomposed photolytically in the presence of methyl diphenylphosphinite. The methyl diphenylphosphinite was not decomposed under the reaction conditions. The results of these reactions are shown in Table 1.

TABLE 1. PRODUCTS FROM THE PHOTOLYSIS OF BENZENE SOLUTIONS OF AZOALKANES IN THE PRESENCE OF METHYL DIPHENYLPHOSPHINITE

| Azoalkane | | Radical produced | Products |
|---|---|---|---|
| MeN=NMe | (X.S.) | Me$^{\cdot}$ | Ph$_2$P(:O)Me  (80%)[a] |
| i-PrN=NPr(i) | (Equimolar amount) | iPr$^{\cdot}$ | Ph$_2$P(:O)Pr(i)  (33%) |
| | | | Unchanged Ph$_2$POMe  (67%) |
| PhCH$_2$N=NCH$_2$Ph | (Equimolar amount) | PhCH$_2$$^{\cdot}$ | No oxidized phosphorus compounds |
| | | | Bibenzyl  (45%) |
| t-BuN=NBu(t) | (Equimolar amount) | tBu$^{\cdot}$ | Unchanged Ph$_2$POMe  (59%) |
| | | | Ph$_2$P(:O)Me  (22%) |

[a] Yields of isolated material. All other yields were determined by PMR spectroscopy.

The formation of methyl and isopropyldiphenylphosphine oxides in the reactions with methyl and iso-propyl radicals respectively, confirms that alkyl radicals can oxidize trivalent phosphorus esters. The fact that benzyl radicals did not bring about oxidation undoubtedly reflects the stability of the radical. The relatively unreactive t-butyl radicals reacted in a similar manner to the dimethylamino radicals in that they initiated the chain reaction of Me radicals with methyl diphenylphosphinite.

$$tBu^{\cdot} + Ph_2POMe \rightarrow Ph_2P(:O)Bu(t) + Me^{\cdot} \qquad \text{(ii)}$$
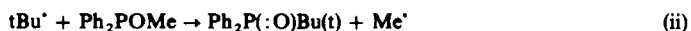
Investigation of the products of this reaction by PMR spectroscopy failed to reveal the presence of any t-butyldiphenylphosphine oxide. This suggests that the Me radicals are formed predominantly by the chain reaction (i) and not by the initiation reaction (ii). The failure of t-butyl radicals to bring about oxidation of trivalent phosphorus esters to give phosphorus compounds containing a ³-butyl group has been previously reported by Walling and Rabinowitz.[9]

The reaction of a variety of alkyldiphenylphosphinites with Ph radicals was also investigated in order to determine what effect, if any, the alkyl group had upon the reaction. Phenylazotriphenylmethane was used as the source of Ph radicals since it is

readily available and can be decomposed either photolytically or thermally, the triphenylmethyl radicals produced by the decomposition were found, in a number of cases, to act as a trap for the alkyl radicals produced in the reaction.[9] The results of the reactions are shown in Table 2.

TABLE 2. PRODUCTS FROM THE DECOMPOSITION OF PHENYLAZOTRIPHENYLMETHANE IN BENZENE SOLUTIONS OF ALKYL DIPHENYLPHOSPHINITES

| Phosphinite | Method of decomposition | Yield of $Ph_3PO$ (%) | Radical produced | Triphenylmethyl radical adduct |
|---|---|---|---|---|
| $Ph_2POMe$ | Thermal, 80° | 68 | $Me^{\cdot}$ | $MeCPh_3{}^a$ (34%) |
| $Ph_2POPr(i)$ | $h\nu$ | 68 | $Pr(i)$ | $iPrCPh_3{}^b$ (39%) |
| $Ph_2POCH_2{}^{\cdot}C_6H_{11}$ | $h\nu$ | 44 | $C_6H_{11}CH_2{}^{\cdot}$ | $C_6H_{11}CH_2CPh_3{}^a$ (24%) |
| $Ph_2POCH_2Ph$ | $h\nu$ | 58 | $PhCH_2{}^{\cdot}$ | $PhCH_2CPh_3{}^a$ (40%) |

[a] Yield of isolated material.
[b] This product was contaminated with some triphenylmethane and could not be obtained crystalline.

Surprisingly little phenylation of the solvent (always present in vast excess) occurred in these reactions. For example, an 18% yield of biphenyl was formed in the reaction with benzyl diphenylphosphinite. This observation is further confirmation for the suggestion[10] that attack of Ph radicals upon the P atom of trivalent phosphorus compounds is extremely rapid. In the time between the rejection of the communication reporting these results and the writing up of this paper, Bentrude *et al.* have reported their studies on the thermal decomposition of phenylazotriphenylmethane in the presence of trimethylphosphite.[11] The results are in agreement with those reported in this paper.

The oxidation of cyclohexyldiphenylphosphinite by Ph radicals was found to produce very little cyclohexyltriphenylmethane and instead cyclohexene was formed. By the use of chlorobenzene as solvent for the reaction, it was possible to show that benzene is not produced in the reaction and therefore the cyclohexene could not have arisen by Ph radicals abstracting hydrogen from cyclohexyl radicals or the intermediate phosphoranyl radical III. A relatively large amount of triphenylmethane was produced



III
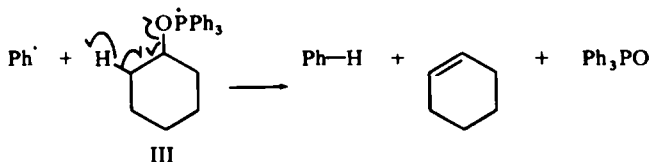
and it is suggested that it is formed by abstraction of hydrogen from the phosphoranyl radical (III). When phenylazotriphenylmethane is decomposed in cyclohexane, cyclohexyltriphenylmethane, but not cyclohexene, is formed. Thus triphenylmethane cannot be formed by abstraction of hydrogen from cyclohexylradicals by triphenylmethyl radicals. 2-i-Propyl-4-methylcyclohexyl diphenylphosphinite and cyclopentyl diphenylphosphinite were found to react with Ph radicals to give the corresponding cycloalkene. The none formation of benzene is not surprising in the light of the rapid attack of Ph radicals upon P atom of the trivalent phosphorus ester.

The ease of oxidation of trivalent phosphorus esters by such radicals as Me, suggests that this reaction may well occur in the desulphurization of thioalkyl and deoxygenation of alkoxy radicals by trivalent phosphorus esters and therefore affect the yield of alkyl radicals produced in these reactions.[8, 12]

The utility of the oxidation of trivalent phosphorus compounds by alkyl radicals as a means of generating alkyl radicals, is being further investigated.

## EXPERIMENTAL

All reactions were carried out under $O_2$-free nitrogen. Petroleum ether refers to the fraction b.p. 60–80°. PMR spectra were recorded for solns in $CDCl_3$ using a Varian A-60 spectrometer.

*Preparation of azoalkanes.* Azomethane and 2,2'-azobispropane were prepared by the method of Renaud and Leitch.[13] The azomethane was absorbed in benzene and this soln used for the reaction. 2,2'-Azobisisobutane was prepared by the method of Stevens[14a] in which t-butylamine is oxidized by iodine pentafluoride. Azotoluene was prepared according to the method of Bickel and Waters[14b] in which 1,2-dibenzylhydrazine is oxidized by mercuric oxide. No attempt was made to purify this azo compound.

*Photochemical decomposition of azoalkanes in the presence of methyl-diphenylphosphinite.* A 450 W. Hanovia medium press Hg. lamp was surrounded by a water-cooled "Pyrex" jacket, "Pyrex" tubes, containing the soln to be irradiated, were clamped around the "Pyrex" jacket. With the exception of the reaction with azomethane, reaction mixtures consisted of a benzene soln (10 ml) of the azoalkane (1 mmole) containing the phosphinite (1 mmole). In the case of the reaction with azomethane, the benzene soln contained an excess of the azoalkane (about 5 mmole). In all cases the $N_2$ evolution was between 70 and 90% of the theoretical.

*Isolation of the products from photolysis of azomethane in the presence of methyl diphenylphosphinite.* Evaporation of the benzene under reduced press gave a solid residue which was crystallized from benzenepet. ether to give methyldiphenylphosphine oxide m.p. and mixed m.p. (from petroleum ether–benzene) 110–111°, doublet at τ 8·08 ($J_{PH}$ 13 c/s).

*Analysis of the reaction products from photolysis of 2,2'-azobispropane in the presence of methyl diphenylphosphinite.* Evaporation of the benzene under reduced press gave an oil which was analysed by PMR spectroscopy. By comparison of the integrated area under the Me peaks (doublet at τ 6·55 $J_{PH}$ 14 c/s) of the methyl diphenylphosphinite present, with the area under the Me peaks (quartet at τ 8·9 $J_{PH}$ 13 c/s $J_{CH}$ 7 c/s) of the isopropyldiphenylphosphine oxide it was found that there was 67% unchanged phosphinite present and 33% phosphine oxide had been produced. An IR spectrum of the reaction showed that both phosphine oxide and phosphinite were present.

*Analysis of the reaction products from photolysis of 2,2'-azobisisobutane in the presence of methyl diphenylphosphinite.* Evaporation of the benzene under reduced press gave an oil which was analysed by PMR spectroscopy. The reaction mixture was shown to contain 59% unchanted phosphinite and 22% methyldiphenylphosphine oxide. An IR spectrum of the reaction mixture showed that both phosphine oxide and phosphinite were present.

*Analysis of the reaction products from photolysis of azotoluene in the presence of methyldiphenylphosphinite.*

*Analysis of the reaction products from photolysis of 2,2'-azobisisobutane in the presence of methyl diphenylphosphinite.* Evaporation of the benzene under reduced press gave an oil which was analysed by PMR spectroscopy. The reaction mixture was shown to contain 59% unchanged phosphinite and 22% methyldiphenylphosphine oxide. An IR spectrum of the reaction mixture showed that both phosphine oxide and phosphinite were present.

*Analysis of the reaction products from photolysis of azotoluene in the presence of methyldiphenylphosphinite.* GLC analysis of the reaction indicated that bibenzyl (45%) had been formed. This was confirmed when the mixture was analysed by PMR spectroscopy. The latter also showed that no phosphinite had been used up.

*The thermal decomposition of phenylazotriphenylmethane in the presence of methyl diphenylphosphinite.* A benzene soln (17 ml) of the azo compound (1·2 g) containing the phosphinite (0·7 g) was heated under reflux for 18 hr. Removal of the solvent by evaporation gave a residue which on trituration with pet ether gave triphenylphosphine oxide (68%) m.p. and mixed m.p. (from EtOH) 155–156°. The mother liquors were chromatographed on silica. Elution with a pet ether–benzene (10%) mixture gave 1,1,1-triphenylethane m.p. 95°,[15] singlet at τ 7·9.

*Irradiation of benzene solutions of phenylazotriphenylmethane containing alkyl diphenylphosphinites.* The solns were irradiated in "Pyrex" tubes, in the same way as in the azoalkane reactions.

*Photolytic decomposition of phenylazotriphenylmethane in the presence of methyldiphenylphosphinite.* A benzene soln (10 ml) of the azo compound (0·32 g) containing the phosphinite (0·2 g) was photolysed for 16 and a half hr. Analysis of the reaction mixture by PMR spectroscopy showed that 1,1,1-triphenylethane (66%) had been produced and that there was 42% unchanted phosphinite. Work up of the reaction mixture as in the thermal decomposition gave triphenylphosphine oxide (55%) and the 1,1,1-triphenylethane (48%).

*Photolytic decomposition of phenylazotriphenylmethane in the presence of i-propyl diphenylphosphinite.* A benzene soln (20 ml) of the azo compound (0·64 g) containing the phosphinite (0·45 g) was photolysed for 16 and a half hr. Removal of the solvent by evaporation gave a residue which crystallized from a pet ether benzene mixture to give triphenylphosphine oxide (68%) m.p. and mixed m.p. (from EtOH) 155–156°. The mother liquors were chromatographed on silica. Elution with a pet ether–benzene (10%) mixture gave a fraction which would not crystallize. The fraction was shown, by PMR spectroscopy, to be mainly 1,1-dimethyl-2,2,2-triphenylethane (quartet at $\tau$ 6·5r and doublet at $\tau$ 9·2 $J_{CH}$ 6 c/s) and the contaminant to be triphenylmethane.

*Photolytic decomposition of phenylazotriphenylmethane in the presence of cyclohexylmethyl diphenylphosphinite.* A benzene soln (40 ml) of the azo compound (1·28 g) containing the phosphinite (1·0 g) was irradiated for 5 hr. Removal of the solvent by evaporation gave an oil which on trituration with pet ether gave triphenylphosphine oxide (44%), m.p. and mixed m.p. (from EtOH) 154–156°. The mother liquors were chromatographed on silica. Elution with a pet. ether–benzene (10%) mixture gave an oil (1·24 g) which crystallized from pet ether to give 1-cyclohexyl-2,2,2-triphenylethane (24%) m.p. 133·5–134·5°. (Found: C, 91·87, H, 8·27. Calc. for $C_{26}H_{28}$: C, 91·75, H, 8·25%). The mother liquors were shown, by PMR spectrscopy, to be a mixture of 1-cyclohexyl-2,2,2-triphenylethane and triphenylmethane.

*Photolytic decomposition of phenylazotriphenylmethane in the presence of benzyl diphenylphosphinite.* A benzene soln (20 ml) of the azo compound (0·70 g) containing freshly prepared, crude phosphinite (0·52 g) was irradiated for 16 hr. A control reaction showed that the phosphinite was not decomposed under these conditions. Analysis of the reaction mixture by GLC showed that biphenyl (18%) had been produced. Removal of the solvent from the reaction mixture gave a residue which crystallized from a pet. ether–benzene mixture to give triphenylphosphine oxide (58%). The mother liquors crystajlized from EtOH to give 1,2,2,2-tetraphenylethane (40%) m.p. (from Et :H) 142–144° lit. m.p. 144°.[16]

*Photolytic decomposition of phenylazotriphenylmethane in the presence of cyclohexyl diphenylphosphinite.* A benzene soln (10 ml) of the azo compound (0·32 g) containing the phosphinite (0·337 g) was irradiated for 5 hr. Analysis of the reaction mixture by GLC showed that cyclohexene (26%) had been produced. Removal of the solvent gave an oil which crystallized from a pet ether–benzene to give triphenylphosphine oxide (40%) m.p. and mixed m.p. (from EtOH) 155–156°.

When the reaction was carried out with chlorobenzene as solvent, cyclohexene was shown to be produced, by GLC, in 23% yield. Benzene formation could not be detected.

*Photolytic decomposition of phenylazotriphenylmethane in the presence of 2-i propyl-4-methylcyclohexyl diphenylphosphinite.* A benzene soln (20 ml) of the azo compound (0·64 g) containing the phosphinite (0·64 g) was irradiated for 16 hr. GLC analysis of the reaction mixture showed that 2-i-propyl-4-methylcyclohex-1-ene (50%) had been produced. Removal of the solvent by evaporation gave an oil which crystallized from a pet ether–benzene to give triphenylphosphine oxide (50%) m.p. and mixed m.p. (from EtOH) 154–156°.

*Photolytic decomposition of phenylazotriphenylmethane in the presence of cyclopentyl diphenylphosphinite.* A benze e soln (15 ml) of the azo compound (0·48 g) containing the phosphinite (0·37 g) was irradiated for 8 hr. GLC analysis of the mixture showed that cyclopentene (32%) had been formed. Removal of the solvent and crystallization of the residue from a pet ether–benzene gave triphenylphosphine oxide (50%) m.p. and mixed m.p. (from EtOH) 155–156°.

*Preparation of alkyl diphenylphosphinite.* These were prepared by reaction of chlorodiphenylphosphine with the appropriate alcohol in the presence of pyridine. Benzyl diphenylphosphinite cannot be purified by distillation since it undergoes thermal rearrangement to benzyl diphenylphosphine oxide. Cyclohexyl diphenylphosphinite had b.p. 174–176° (3 mm), cyclohexylmethyl diphenylphosphinite had b.p. 158–162° (1 mm), 2-i-propyl-4-methylcyclohexyl diphenylphosphinite had b.p. 162–170° (0·1 mm) and cyclopentyl diphenylphosphinite had b.p. 168–170 (3 mm).

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