

Photochemistry of Phenyl Alkyl Ketones in the Presence of Organophosphorus(V) Compounds

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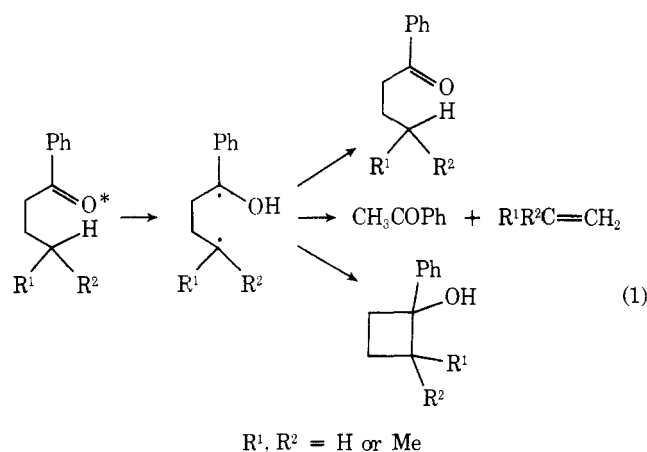
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Triphenylphosphine oxide, as well as organic phosphates [(MeO)₃PO, (PrO)₃PO, and (PhO)₃PO], interact with the biradicals produced in the photochemistry of phenyl alkyl ketones (e.g., valerophenone), increasing the yields of photofragmentation and cyclization. The effect is presumed to result from the formation of a complex between the organophosphorus substrate and the intermediate biradical.

When a solution of a phenyl alkyl ketone bearing γ -hydrogen atoms is irradiated with UV light, it undergoes fragmentation and cyclization processes, known as the Norrish type II reaction.² The intermediacy of biradicals in the reaction from the triplet state has been proposed from studies of solvent effects and the photochemistry of optically active molecules.²⁻⁵ This proposal was confirmed by Wagner,⁵⁻⁶ who successfully trapped the biradicals from valerophenone and γ -methoxyvalerophenone, and by a series of examples of biradical interception which followed this report.⁷⁻¹³ More recently the biradicals of reaction have been detected directly in laser photolysis experiments.¹⁴

The biradicals have lifetimes in the range of 30–100 ns, depending on the solvent.^{12,14}

During a study of the quenching ability of several group 5 organometallics, we observed evidence indicating that P=O double bonds interact efficiently with the biradicals produced in the photochemistry of phenyl alkyl ketones bearing γ -hydrogen atoms.¹⁵ For example, while organophosphines and organic phosphates are efficient quenchers of carbonyl triplets,¹⁵⁻¹⁷ triphenylphosphine oxide causes an increase in the yield of photofragmentation of valerophenone in benzene. The effect is proposed to result from the interaction of the intermediate biradical (see reaction 1) with the organophosphorus substrate.



The effect on the quantum yields is similar to that of polar solvents¹⁸ and oxygen,⁸ where it has been proposed to result from bonding interactions (hydrogen bonding in the case of alcohols) which prevent the reabstraction reaction.

We report in this paper a study of the photochemistry of valerophenone in the presence of triphenylphosphine oxide and trimethyl, tri-*n*-propyl, and triphenyl phosphates. Butyrophenone and γ -methylvalerophenone have also been examined in the case of trimethyl phosphate.

Results and Discussion

Figure 1 shows the effect of trimethyl phosphate on the

quantum yields of photofragmentation of butyrophenone and γ -methylvalerophenone. For comparison we have also included a plot showing the effect of *tert*-butyl alcohol in the case of γ -methylvalerophenone calculated from literature parameters.¹⁸ The effect on the cyclobutanols is similar but relatively smaller (see below).

Scheme I shows the mechanism proposed to account for the effect. It is the same type of mechanism proposed for the effect of alcohols and oxygen.^{8,18} We note that no assumptions are made regarding the structure of the intermediate BP or the nature of the molecular interactions involved.

In the absence of triplet quenching, eq 2 is expected to represent the behavior of the system, where τ_B is the biradical lifetime, P_{II}^0 and P_{II}^∞ are the probabilities of fragmentation from ¹B and BP, and Φ_{II} and Φ_{II}^0 are the quantum yields of

Scheme I

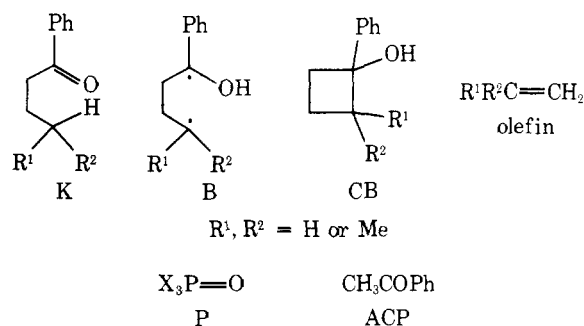
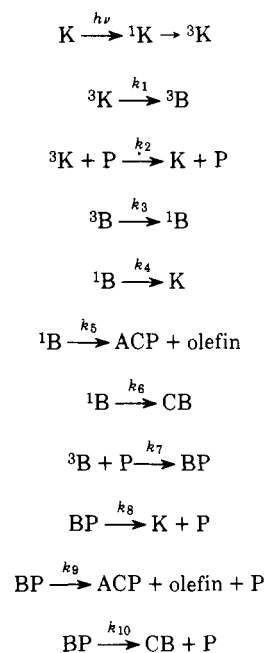


Table I. Effect of 0.02 M Organophosphorus Compounds on the Photochemistry of Phenyl Alkyl Ketones in Benzene at 30 °C

| Ketone | Registry no. | Substrate | Registry no. | Φ_{II}/Φ_{II}^0 | Φ_{CB}/Φ_{II} | $k_{7\tau_B}^a$ | k_7^b | r^{2c} |
|-------------------------------|--------------|-----------------------------|--------------|-------------------------|-----------------------|-----------------|---------------------|--------------------|
| Valerophenone | 1009-14-9 | Ph ₃ PO | 791-28-6 | 1.48 | 0.16 | 18 | 5.3×10^8 | 0.995 |
| | | (MeO) ₃ PO | | 1.35 | 0.19 | 12 | 3.5×10^8 | 0.993 |
| | | (PrO) ₃ PO | 513-08-6 | 1.44 | 0.18 | 16 | 4.7×10^8 | 0.989 |
| | | (PhO) ₃ PO | 115-86-6 | 1.06 | $\sim 0.22^d$ | 1.7 | 5.0×10^7 | 0.999 ₉ |
| Butyrophenone | 495-40-9 | (MeO) ₃ PO | 512-56-1 | 1.37 | <i>e</i> | 16 | $5.0 \times 10^8^f$ | 0.999 |
| γ -Methylvalerophenone | 2050-07-9 | (MeO) ₃ PO | | 1.42 | <i>e</i> | 6 | 1.7×10^8 | 0.999 ₆ |
| Valerophenone | | <i>t</i> -BuOH ^g | | 1.03 | | 0.63 | 1.8×10^7 | |
| | | Pyridine ^g | | 1.15 | | 4.4 | 1.3×10^8 | |
| | | None ^g | | 1.0 | 0.22 | | | |

^a In units of M⁻¹. ^b In units of M⁻¹s⁻¹, based on lifetimes from ref 8c. ^c Coefficient of determination from the least-squares treatment of eq 2. ^d $k_{7\tau_B}$ too small to allow an accurate measurement. ^e Not measured. ^f Based on $\tau_B = 33$ ns, obtained in oxygen-scavenging studies (R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, in press. ^g From ref 18.

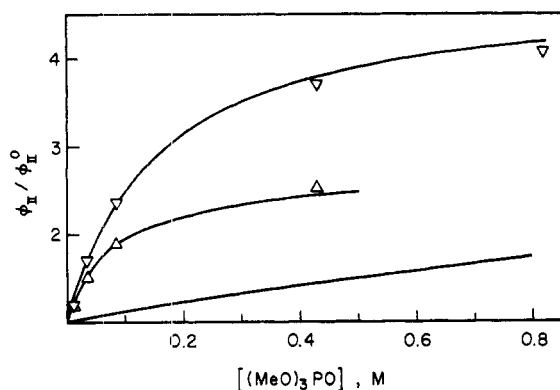


Figure 1. Effect of trimethyl phosphate on the yields of photofragmentation of butyrophenone (Δ) and γ -methylvalerophenone (∇). The lower curve corresponds to *tert*-butyl alcohol and γ -methylvalerophenone (see text).

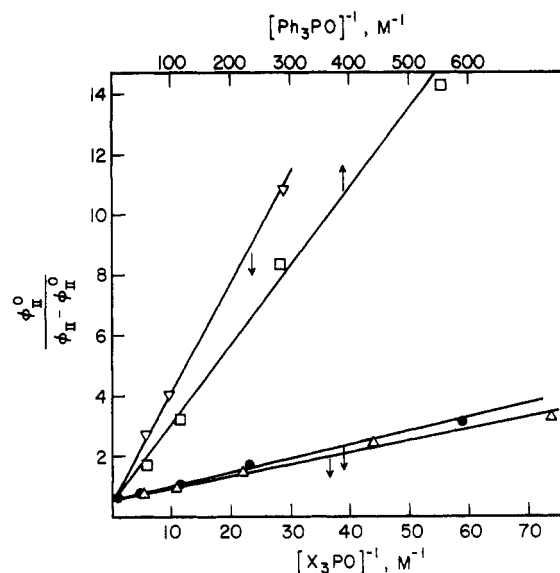


Figure 2. Results according to eq 2 for valerophenone in benzene interacting with (MeO)₃PO (\bullet , lower scale), (PrO)₃PO (Δ , lower scale), (PhO)₃PO (∇ , lower scale), and Ph₃PO (\square , upper scale).

fragmentation in the presence and absence of P.

$$\frac{\Phi_{II}^0}{\Phi_{II} - \Phi_{II}^0} = \frac{P_{II}^0}{P_{II}^\infty - P_{II}^0} \left(1 + \frac{1}{k_{7\tau_B}[P]} \right) \quad (2)$$

Figure 2 shows the plots of $\Phi_{II}^0/(\Phi_{II} - \Phi_{II}^0)$ vs. $[P]^{-1}$ for several organophosphorus compounds reacting with the biradicals from valerophenone.¹⁹ The same type of plots can be made for the cyclobutanols [plotting $\Phi_{CB}^0/(\Phi_{CB} - \Phi_{CB}^0)$ instead of $\Phi_{II}^0/(\Phi_{II} - \Phi_{II}^0)$]. These plots lead to the same values of $k_{7\tau_B}$; however, since the effect on the yields of cyclobutanols is smaller and they are more difficult to measure experimentally, the points are subject to considerably more error than the fragmentation data.

We have carried out a number of experiments trying to detect new products and/or consumption of the organophosphorus compound. We have failed to detect any consumption of reagent or formation of any products other than the fragmentation and cyclization products which are characteristic of the Norrish type II process. For example, in the case of (MeO)₃PO with valerophenone, $\Phi_{\text{products}}/\Phi_{-P} \geq 200$, where Φ_{-P} is the yield of consumption of (MeO)₃PO and Φ_{products} is the yield of acetophenone plus cyclobutanols, which, within experimental error, agrees with the consumption of valerophenone.

Table I shows a comparison of the effect on fragmentation and cyclobutanols for 0.02 M organophosphorus compounds, as well as the values of $k_{7\tau_B}$ calculated using eq 2 and k_7 values based on experimental lifetimes.¹²⁻¹⁴ The mechanism of Scheme I assumes that the overall process is kinetically controlled, that is, that reaction 7 is not reversible. Alternatively we could propose an equilibrium-controlled process. In this

case $k_{7\tau_B}$ would be replaced by $K_{\text{eq}\tau_B}(k_8 + k_9 + k_{10})$. As in the case of alcohols,¹⁸ it is impossible to decide from quantum yields studies which is the mechanism that best represents the behavior of the system.

Up to this point our discussion of the results has been limited to kinetic arguments. An interesting question is which type of interaction is the cause of the changes in quantum yields observed. In the case of alcohols,¹⁸ hydrogen bonding is believed to be responsible for the enhancement of quantum yields; i.e., the engagement of the hydroxylic group in the biradical in hydrogen bonding prevents the reverse hydrogen transfer to produce the parent ketone, resulting in an increase of the yields of fragmentation and cyclization.

In principle, one could invoke the same type of interactions in the case of X₃PO compounds, which are known to form hydrogen bonds efficiently.²⁰ However, we believe that the alkyl end of the biradical is also involved in the process. The dependence of $k_{7\tau_B}$ values (and k_7) on γ substitution (see Table I) seems to support this idea. Further, an interaction of this type could be to a certain extent responsible for the large differences in reactivity between some of the X₃PO compounds and alcohols (e.g., Ph₃PO is nearly 30 times more efficient than *tert*-butyl alcohol).²¹

The values of $k_{7\tau_B}$ follow the order butyrophenone > valerophenone > γ -methylvalerophenone and should reflect the order of k_7 values since direct^{12,14} and indirect¹³ measure-

ments of τ_B show that it is largely independent of the substitution at the τ position. If the alkyl end of the biradical were to add to the P–O double bond or interact in such a way as to decrease the P–O bond order, we could expect the rate of this process to follow the inverse order of that observed in the α cleavage of phosphoranyl radicals, which follow the order primary < secondary < tertiary,^{22,23} in agreement with our experiments. Although no detailed study has been reported on the addition of radicals to the P=O bond, Levin et al.²⁴ have reported evidence that the process occurs when methyl radicals are generated in the presence of (EtO)₃PO. We have made several attempts to detect the presence of phenyl radicals (in the case of Ph₃PO, see Experimental Section) in the hope that BP would undergo α cleavage. All our experiments produced negative results, suggesting that either BP does not have a phosphoranyl-type structure or it is too short-lived for the process of α cleavage to compete with other modes of decay.

A few experiments with other phosphorus(V) compounds are worth mentioning. (PhO)₂P(O)OH and (MeO)₂P(O)OH do not seem to have any significant effect on the quantum yields. Presumably, intramolecular hydrogen bonding tends to make them inefficient.

A series of experiments was carried out with Ph₃PSe and Ph₃PS in the case of valerophenone. The latter does not seem to have much effect on the yields of fragmentation; however, the ratio of fragmentation-to-cyclization yields is increased slightly. For example, for 0.06 M Ph₃PS, the value of $(\Phi_{II}\Phi_{CB}^0)/(\Phi_{CB}\Phi_{II}^0) = 1.08$, suggesting that the substrate is in fact interacting with the biradical. It seems likely that some quenching of the triplet state tends to compensate the effect. In the case of Ph₃PSe, extensive quenching and the difficulties in obtaining very pure samples make any conclusion highly speculative.

The interaction of the biradical produced in the Norrish type II reaction with good hydrogen bonding solvents such as alcohols and wet acetonitrile has been frequently used to measure limiting quantum yields for the type II reaction,^{18,25} a parameter which for simple ketones measures the quantum yield of biradical production. The high efficiency of organophosphorus compounds can probably extend the applicability of these techniques to systems where high concentrations of hydroxylic compounds are not desirable, as is the case of polymers, where the type II process plays an important role in photodegradation.²⁶

In conclusion, phosphine oxides and trisubstituted organic phosphates interact efficiently with type II biradicals, producing a marked increase in the yields of fragmentation and a small increase in the case of cyclization. In all the examples examined (see Table I), the yields extrapolated at infinite substrate concentration add, within experimental error, to one. The kinetics of the reaction are consistent with a mechanism involving the formation of a complex between the intermediate biradical and the organophosphorus compound. While the involvement of hydrogen bonding in the biradical–X₃PO interaction cannot be discounted, it seems certain that the alkyl end plays an important role.

Experimental Section

Materials. Butyrophenone and valerophenone were Aldrich products. γ -Methylvalerophenone was a generous gift from Dr. K. U. Ingold. Triphenylphosphine oxide (K & K), triphenyl phosphate (Aldrich), and triphenylphosphine sulfide (Aldrich) were recrystallized. Tri-*n*-propyl phosphate (Matheson), trimethyl phosphate (Aldrich), and dimethyl phosphate (ICN) were distilled under vacuum. TLC and/or VPC checks were carried out in all cases. Benzene was a Fisher (Certified, ACS) product. Dodecane and mesitylene (Aldrich, Gold Label) were distilled prior to use and carbon tetrachloride

(Mallinckrodt, spectroquality) was distilled twice.

Irradiations. The samples (1 cm³) were contained in matched Pyrex tubes made of precision bore tubing (i.d. 0.2500 ± 0.0002 in, made of Corning 7740 glass, Lab Crest Scientific). They were degassed by three freeze–pump–thaw cycles to a residual pressure of ca. 10^{–6} Torr. The samples were irradiated in a merry-go-round apparatus, using a Rayonet reactor fitted with 16 RPR-3500 lamps. Conversions (based on parent ketone) were kept below 2%, except during the attempts to detect consumption of the organophosphorus compound.

Analyses. Quantitative analyses of type II products were carried out by gas chromatography, using 5% DC-11 silicone oil on a Chromosorb W column and FID. This and other columns, as well as TLC, were used in a number of unsuccessful attempts to detect new products.

Search for Evidence of Phenyl Radicals. A number of experiments were carried out with the valerophenone–Ph₃PO system in an attempt to trap phenyl radicals. We looked in vain for the formation of benzene, using *n*-dodecane and mesitylene as solvents, or chlorobenzene, using carbon tetrachloride as solvent.

Spectra. The UV spectra of all the ketone–organophosphorus compound pairs were examined using a Cary 14 spectrophotometer. No evidence for association in the ground state was observed.

Actinometry. Whenever necessary, the photofragmentation of valerophenone in benzene [$\Phi(\text{acetophenone}) = 0.30$]¹⁸ was used as an actinometer.

Registry No.—(PhO)₂P(O)OH, 838-85-7; Ph₃PS, 3878-45-3; (MeO)₂P(O)OH, 813-78-5.

Supplementary Material Available: Tables II–IV showing quantum yields (4 pages). Ordering information is given on any current masthead page.

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