Photochemical Generation of Aryl Phosphonium Ylides

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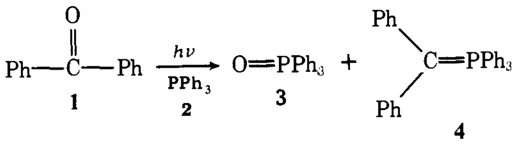
Abstract: A series of diaryl- and arylalkyl ketones have been shown to form phosphonium ylides upon irradiation (45–80%) with long wavelength ultraviolet light in the presence of triphenylphosphine. Although the quantum yield for the process is low (ca. 0.025), the photoreaction appears to be fairly general (in the cases examined) for aryl ketones with n,π^* lowest triplet states. The reaction fails or proceeds very much less efficiently with π,π^* ketones, aldehydes, and aliphatic ketones. A mechanism for ylide formation is suggested. Quenching studies point to the existence of an intermediate formed by the interaction of the excited triplet with phosphine. The relevance of such reactions to the study of exciplex and charge-transfer complexes of ketones and tervalent phosphorus compounds is discussed.

Although phosphonium ylides can be prepared by a variety of techniques,[1] nearly all efficient methods for forming simple nonacylated phosphoranes involve treatment with strong base. We have observed an alternate route for the formation of a family of aryl and diaryl phosphonium ylides in benzene by the direct photochemical interaction of aryl n,π^* ketones with triphenylphosphine and have investigated the mechanism for this method of ylide generation.

In 1970, Wescott and co-workers reported that a light-induced reaction between benzophenone (**1**) and triphenylphosphine (**2**) gave a red-brown air-sensitive solution containing triphenylphosphine oxide (**3**): eq 1. Their supposition that triphenylphosphinediphenylmethylene (**4**) was also formed was supported by the visible spectrum of the reaction mixture, but their inability to isolate the expected product of a normal Wittig reaction of **4** with acetaldehyde precluded a firm assignment.[3]



(1)

Presumably, the success of such a reaction relies on the efficient formation of a strong P-O bond[6] either in the excited state or within a phosphine–carbonyl exciplex.[7] Since the triplet n,π^* state of benzophenone exhibits reactivity reminiscent of alkoxy radicals[8] which are known to react with trivalent phosphorus,[9] either reaction path appears reasonable. Furthermore, the isolation of analogous oxygenation products in the thermal reactions of trialkyl phosphites with aryl ketones[10] or in the photochemical reaction of diphosphines with benzophenone[11] demonstrates the feasibility of carbonyl deoxygenation at trivalent phosphorus.

Results

Upon overnight irradiation with RPR 3500-Å lamps of degassed Pyrex ampules containing a solution of **1** (0.1 M) and **2** (0.2 M) in anhydrous benzene, an intensely red, air-sensitive solution was obtained. About 15% disappearance of **1** had occurred, and GLPC analysis[12] of the photolysate revealed the presence of **3** (73%), biphenyl (14%), benzpinacol (6%), and trace quantities of tetraphenylethylene and three other minor (<2%) unidentified products (yields reported are with respect to reacted **1**). The presence of **4** in the reaction mixture was established by UV-visible spectroscopy[13] as well as by chemical characterization. Triphenylethylene, the expected product of a Wittig reaction of **4** with benzaldehyde,[14] or triphenylbenzhydrylphosphonium bromide and diphenylmethane (a known hydrolysis product of **4**[15]) could be isolated if the reaction mixtures were heated with benzaldehyde or aqueous HBr, respectively. The yield of tetraphenylethylene could be slightly increased (to about 5%) by heating the photolysis mixture at 100 °C for 2 days. Chemical yields of the products of the Wittig reaction with benzaldehyde (40–65%) and the hydrolysis reaction (54–71%) suggest that **4** is formed with an efficiency comparable to that observed for **3**. If conversion of starting material is carried further along, some decrease in yield of such products is observed: the yield of triphenylethylene from the Wittig reaction of benzaldehyde with the photolysis mixture obtained upon irradiation to ca. 46% disappearance of **1** was about 35%.

The rate of formation of **3** by photolysis of degassed ampules containing varying concentrations of **1** and **2** was followed by GLPC.[12] The relative rates for production of **3**, listed in Table I, suggest no dependence on initial benzophenone concentration and sharp dependence on initial triphenylphosphine concentration.

The interception of the n,π^* triplet state of **1** (~0.01 M) by **2** (~10^{-4} M) in benzene was studied by flash photolysis with a nitrogen laser. By observing the disappearance of the triplet benzophenone transient absorption[16] at 530 nm, a quenching constant of 6×10^8 M^{-1} s^{-1} (calculated from literature[7,17]: 3.6×10^8) was found to be strictly first order in triphenylphosphine. Quenching by tri-*n*-butylphosphine was also efficient (8×10^8 M^{-1} s^{-1}) and was found to be first order in phosphine.

Repetition of the photolysis of **1** and **2** in the presence of 1 equiv of isobutene led to trace quantities of 1,1-dimethyl-2,2-diphenylcyclopropane (**6**).[18] If the reaction was allowed to progress to further conversion, slightly larger yields of **6** could be observed (3–5% at ca. 50% conversion).

The rate of formation of **3** by analogous photolysis of other aryl ketones (0.1 M ketone, 0.2 M **2** in degassed benzene) was similarly determined by GLPC. The relative rates for formation of **3** as well as the yield of **3** at ~20% conversion of **1** are listed in Table II. All solutions for which a yield of **3** greater than 10% is reported were found to be air sensitive and reactive with benzaldehyde. No ylides could be detected if tributylphosphine replaced **2** in the reaction or if dialkyl ketones were employed either with **3** or tributylphosphine.

Discussion

Efficiency. The photolysis of a degassed mixture of **1** and **2** results in the formation of **3** and phosphonium ylide **4**. The reaction appears to be fairly general for many diaryl and aryl alkyl n,π^* ketones, but fails or proceeds much less readily with aldehydes and π,π^* ketones. Although the reaction proceeds in low quantum yield (0.025 for benzophenone), the relative cleanness with which the reaction proceeds at low conversion makes it a possible route for the synthesis of some aryl phosphonium ylides in neutral solution.

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Table I. Relative Rates for Formation of Triphenylphosphine Oxide (**3**) in the Photolysis of Benzophenone (**1**) in the Presence of Triphenylphosphine (**2**)[a]

[**1**], M	[**2**], M	rel rate[b]
0.1	0.2	3.1 ± 0.5
0.2	0.1	(1.0)[c]
0.2	0.2	3.8 ± 0.4
0.2	0.5	18 ± 3
0.5	0.2	3.4 ± 0.5

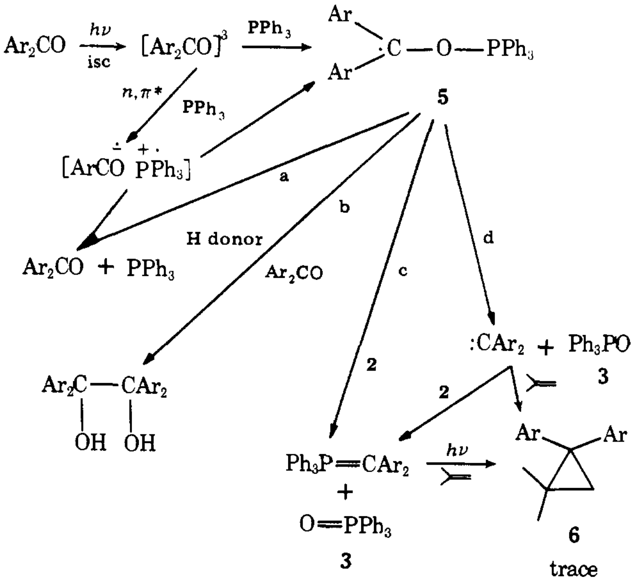
[a] Overnight photolysis in double baffle merry-go-round in a Rayonet photochemical reactor equipped with RPR 3500-Å lamps. [b] Reported rates represent the average of and the variance within four determinations measured at 10–20% conversion. [c] $\Phi = 0.025$.

Mechanism. A plausible mechanism for ylide formation is presented in Scheme I. The initial photochemical excitation, followed by efficient intersystem crossing, is well-documented in a large variety of aryl ketones.[19-21] Capture of benzophenone triplet excited states by trivalent phosphorus compounds is known to be rapid.[17,22] If the benzophenone triplet behaves chemically like an alkoxy radical, such interaction might be expected to give **5**, through the intervention of an exciplex. In view of the known similarity in reactivity of n,π^* ketones and alkoxy radicals,[8] **5** may be best formulated as a triplet biradical, although zwitterionic structures reflecting charge-transfer character or ring-closed structures might equally well be suggested.

Although the kinetics for ylide formation are apparently complex, the dependence of the rate of ylide formation on initial PPh_3 concentration (first and/or higher order) is clear. This fact, together with the near diffusion-controlled quenching of the benzophenone triplet by phosphine observed in the flash experiment, requires the formation of some intermediate species which reacts with an additional molecule(s) of PPh_3 to form product.

The efficiency of a given aryl ketone in forming ylides by this photochemical process seems to be only weakly dependent on electron density in the aryl π system. Although *p*-chloro substituents caused a slight increase in the rate of formation of product and a *p*-methoxy or a *p*-methyl substituent slowed the reaction, the rates were identical within a factor of 3.

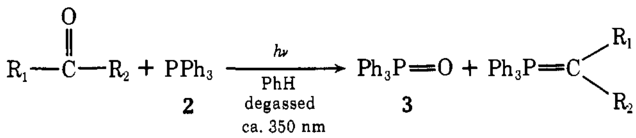
Scheme I. A Possible Mechanism for the Photogeneration of Diaryl Phosphonium Ylides



The small quantum yield for product formation indicates either that the decay of an exciplex precursor of **5** to the ground state is much more efficient than is its collapse to **5** or that a major fate for **5** must be O–P cleavage to ground state molecules[7] (path a). The production of small quantities of benzpinacol could have resulted either from the capture of **5** by a second molecule of benzophenone with subsequent cleavage and hydrogen abstraction leading to the observed product or from a known, inefficient, independent route from the triplet state.[25]

In principle, formation of ylides from **5** could occur either by direct capture of **5** by **2** to give ylide and **3** (path c) or by cleavage to **3** (an observed product) and a diarylcarbene which is captured by a second molecule of **2** (path d). If the former mechanism were operative, dependence of the rate of formation of **3** on the initial concentration of **2** would be expected (as is observed).[24] In the cleavage–capture mechanism, however, such dependence would be observed only if the capture of the

Table II. Photochemical Production of Phosphonium Ylides[a]



$$R_1-\overset{O}{\overset{\|}{C}}-R_2 + \underset{\mathbf{2}}{PPh_3} \xrightarrow[\text{PhH, degassed, ca. 350 nm}]{h\nu} \underset{\mathbf{3}}{Ph_3P{=}O} + Ph_3P{=}C(R_1)(R_2)$$

compound	R_1	R_2	rel rate of production of **3**	yield (**3**)[b]
1	C_6H_5	C_6H_5	1.00	73
7	*p*-Cl-C_6H_4	*p*-Cl-C_6H_4	1.4	81
8	*p*-CH_3-C_6H_4	C_6H_5	0.86	18
9	*p*-OCH_3-C_6H_4	*p*-OCH_3-C_6H_4	0.65	65
10	C_6H_5	CH_3	1.5	71
11	C_6H_5	$CH_2CH_2CH_2CH_3$	0.65	34
12	*o*-CH_3-C_6H_4	C_6H_5	0.10	45
13	C_6H_5	$C_{10}H_9$	0.09	74
14	*p*-NMe_2-C_6H_4	*p*-NMe_2-C_6H_4	0	0
15	$C_{10}H_9$	CH_3	0	0
16	fluorenone		0	0
17	C_6H_5	*o*-OH-*p*-OCH_3-C_6H_3	0	0
18	C_6H_5	H	0.21[c]	18[c]
19	CH_3	CH_3	0	0
20	CH_3CH_2	CH_2CH_3	0	0

[a] Initial concentration of ketone = 0.1 M. [**2**] = 0.2 M. [b] With respect to reacted carbonyl compound at about 20% reaction; average of three runs. [c] Although **3** could be isolated, the characteristic color of ylide was absent in the photolysis of **18**.

carbene by **2** were slower than C–O cleavage in **5**. We view this latter possibility as unlikely since C–O cleavage to form a carbene should have a significant activation barrier while the trapping of diphenylcarbene by phosphines or sulfides would be expected to be very rapid.[1] The absence of dependence of the reaction rate on initial benzophenone concentration in light-opaque solutions is consistent with either mechanism since **1** is involved only in the initial excitation.

The detection of even trace quantities of **6** when the photolysis is conducted in the presence of isobutene might seem to argue for the cleavage–capture sequence since **2** is expected to capture carbenes much more effectively than isobutene. However, since the yield of **6** increases with conversion of starting material, its formation by a secondary route is a real possibility. Since ylides themselves are known to cleave photochemically to carbenes,[26] **6** may have been formed by secondary photolysis of the ylide formed initially. In the presence of excess **2** (as would be the case at low conversions to **4**), most of the carbene formed in this manner is presumably recaptured by **2** to again form **4**.

The observation that acetophenone and butyrophenone can be converted to ylides establishes that any carbene precursor to the ylides cannot be a singlet. Formation of the analogous singlet carbenes in these species would presumably result in production of styrene and 1-phenyl-1-butene, respectively, since intramolecular CH insertion should dominate over intermolecular reaction even in the presence of a trapping agent as effective as **2**. A triplet carbene precursor, however, is still a conceivable intermediate since CH insertion is known to be slow in triplets,[27] and the possibility of interception by phosphine to form ylides is viable.

Generality of the Reaction. Extracting individual rate constants for product formation within a family of ketones is difficult because of variance[20] in ketone lifetime, in rates of nonproduct-forming quenching by phosphine, in rates of competing intramolecular processes and in ketone triplet energies. Table II demonstrates, nonetheless, that substituent effects on the ketone can profoundly influence the efficiency of the reaction. Of the six aryl ketones examined for which efficient photochemical ylide formation can be observed (**1, 7–11**), all exhibit lowest n,π^*-triplet states. Of the four aryl ketones for which no ylide formation is observable (**14–17**), two (**14** and **15**) have been identified as having lowest lying triplets which are π,π^* or CT in character and two (**16** and **17**) have a small separation between n,π^* and π,π^* states, the latter apparently failing to abstract hydrogen efficiently as do most n,π^* ketones.[21] **12**, which is known to deactivate its triplet by photoenolization,[28] suffers a reduction in the efficiency with which it forms ylide. The remaining compound, **13**, possesses a lowest π,π^* triplet. Generalizing these observations on the identity of the triplet configuration required for ylide formation is risky, however, in view of the complexity of the rates of competing processes discussed above.

Also unsuccessful in the photogeneration of ylides were the reactions of **18–20**. It is conceivable that their failure to form ylides could be attributed to a shift in their absorption spectra or to their reactivity with ylides formed. If **18–20** were irradiated in the presence of PPh_3 in benzene, significant quantities of biphenyl were formed. With 3500-Å lamps as excitation source, light is preferentially absorbed by triphenylphosphine, giving rise to phenyl radicals and hence ultimately to biphenyl. If concentrations were manipulated so that the ketone was exclusively excited (with 3000-Å lamps), the ketones **19** and **20** disappeared but no ylide or expected product derived from the ylide was obtained. With benzaldehyde (**18**), small quantities of **3** and stilbene could be isolated. The use of tributylphosphine with **1, 7, 18,** and **20** failed to give any evidence of ylide formation, possibly because the known enhancement of β-cleavage of alkoxyl radical–triphenylphosphine adduct is reduced in the analogous trialkylphosphine adduct.[23] Benzpinacol is formed in high yield when **1** is irradiated in the presence of tri-n-butylphosphine, suggesting the possibility that tri-n-butylphosphine is acting not only as a quencher within the exciplex but also as a hydrogen donor. Although intramolecular photoreactions interfere with the efficiency of photochemical ylide formation (e.g., **12**), capture by **2** is apparently competitive even with γ-hydrogen abstraction. The product of the addition of benzaldehyde to the ylide formed in the photolysis of **11** was shown to contain both diphenyl-C_3 and diphenyl-C_5 olefins, the former presumably being formed by Norrish type II cleavage of **11** and subsequent photoreaction of the **10** thus generated.

Wittig Reactions. The reaction mixtures containing these photochemically generated ylides can be used directly in Wittig reactions or readily isolated from reactants. The reaction of these diaryl ylides with aldehydes having small steric requirements is apparently rapid[2] and we have found reasonable rates of reaction even with benzaldehyde. The reaction of the ylides so formed with their ketone precursors can also occur, but only very slowly. Only very small quantities of tetraphenylethylene could be detected in the reaction mixture of **1** and **2** even after heating at 100 °C for 2 days. This lack of reactivity is undoubtedly due to steric bulk since Wittig reactions are known to be notoriously sensitive to steric effects.[1] Such sluggishness in reactivity is precedented[3] and apparently is responsible for the possibility of accumulating ylides in these reactions. Finding traces of stilbene (but no ylide) in the photoreaction of benzaldehyde suggests that, if generated in the presence of a reactive carbonyl compound, these photoproducts could further participate in chemical reaction. Studies are planned in our laboratory in which a photogenerated ylide could react intramolecularly, potentially then providing a route for the cyclization of α,ω-diketones.

Synthetic Utility. These photoreactions provide a convenient method for generating phosphonium ylides. Their main advantage over conventional preparative sequences lies in the ability to generate the ylides in neutral solution. The reaction is unlikely to supplant conventional techniques for making ylides, however, because high yields of ylide products can only be achieved in highly purified, degassed solvents. Impurities can apparently serve to divert reactivity from ylide formation to alternate pathways. Furthermore, the ylide products formed in the reaction are themselves photolabile and their yields decrease significantly if the reaction is carried to nearly complete destruction of the absorptive ketone. For good yields of ylides, nearly complete exclusion of oxygen is also required since the ylide and its photoprecursors are oxygen sensitive. Since the photoreaction is a low quantum yield process, the requirement for rigorous deaeration is particularly important.

Conclusions

Thus, the present study reveals the utility of a photochemical pathway for the formation of phosphonium ylides in benzene from a variety of diaryl and aryl alkyl ketones. Upon photochemical population of their triplet states, such ketones are chemically intercepted by triphenylphosphine to give a species which can react further with triphenylphosphine to give ylides and triphenylphosphine oxide. In addition to its chemical utility, the characterization of this series of reactions also sheds light on the nature of the excited state interactions of n,π^* ketones with trivalent phosphorus compounds.

Experimental Section

General Photolysis Method. Solutions of dry spectral grade benzene (Mallinckrodt, distilled from Na and stored over molecular sieves) were typically made 0.1 M in ketone and 0.2 M in phosphine. After transfer of 5–25-mL aliquots to Pyrex ampules, the solutions were degassed by a four-cycle freeze-pump-thaw sequence. The ampules were sealed with a flame and suspended either directly (for qualitative studies) on a slowly rotating support or inside a merry-go-round reactor equipped with a double baffle for light alignment (for quantitative and analytical studies) in the cavity of a Rayonet photochemical reactor equipped with RPR 3500-Å lamps. If spectral grade benzene was not employed, additional purification of solvent was required.

Analysis. Ampules were opened in an argon-filled drybox and transferred to appropriate sealed spectroscopic cells for further analysis. Aliquots for gas-liquid phase chromatography (GLPC) were obtained by adding 10 μL of hexadecane (internal standards) to the photolysis mixture and diluting with 50 mL of benzene to dissolve any precipitated **3**. The resulting solutions were taken up in a gas-tight syringe and injected directly. Analytical GLPC analyses were conducted on a 5 ft × $\frac{1}{8}$ in. 5% OV-1 on 80-100 mesh Chromosorb P column in a Varian 2700 gas chromatograph (column A). Preparative separations were accomplished on a 3 ft × $\frac{1}{4}$ in. OV-1 on Chromosorb P (80-100 mesh) in a Varian 3700 gas chromatograph (column B). Ultraviolet and visible spectra were obtained on a Cary 14 spectrophotometer. Mass spectra were obtained on a Du Pont 21-471 spectrometer. Proton nuclear magnetic resonance (NMR) spectra were measured on a Perkin-Elmer R-12 or a Varian A-60 instrument and infrared (IR) spectra were recorded on a Beckmann IR-5A instrument.

All chemical manipulations of photolysis mixtures were conducted in the drybox or in glass apparatus designed for handling air-sensitive compounds.

All chemical yields are reported with respect to reacted ketone. Quantitative analyses were made by a comparison with hexadecane, an internal standard added after the photolysis.

Photolysis of 1 and 2. Upon overnight irradiation of 25 mL of a solution of **1** and **2** prepared in the general method, an intensely red solution was obtained. GLPC analysis showed the presence of **1, 2, 3**, biphenyl, benzpinacol, tetraphenylethylene, and three unidentified minor products. The identity of the products was established by coinjection of authentic samples on column A (200 °C) and by isolation of the first five compounds listed on column B (100→150 °C, 5 °C/min). NMR and IR spectra of the isolated compounds were identical with those of authentic samples. The yields observed are listed in the text.

Chemical Characterization of 4. A sealed ampule containing such a photolysis mixture was heated on a steam bath for 2 days. GLPC analysis (column A) showed a slightly greater fraction of tetraphenylethylene than found immediately after photolysis.

A 5-mL portion of the photolysis mixture was transferred to a 10-mL round-bottomed flask and treated with 5 drops of 5 M aqueous HBr. Cloudiness resulted and the intense red color faded. Upon heating at 100 °C for 1 h and cooling to room temperature, a white precipitate formed. The solution was filtered and analyzed by GLPC (column A, 100→200 °C, 10 °C/min) and was shown to contain **1, 2, 3**, and diphenylmethane.[15] Isolation of the latter was accomplished on column B (100→150 °C, 5 °C/min). The isolated compound had the identical spectral properties of an authentic sample (Aldrich).

The solid (mp 232 °C, dec) was dissolved in 100 mL of Et$_2$O. Upon treatment with NaOEt,[13] **4** was obtained. An additional 15-mL portion of the photolysis mixture was transferred to a 250-mL round-bottomed flask, diluted to 100 mL with dry benzene (to dissolve most of the precipitate crystals) and treated with 160 mg (1.5 mmol) of benzaldehyde. After heating at reflux for 5 h, the reaction mixture was analyzed by thin-layer chromatography (neutral alumina, 50:50 Et$_2$O:petroleum ether). A fluorescent spot corresponding in relative retention time to an authentic sample of triphenylethylene was visible. After stripping the solvent, isolation of this compound (mp 73 °C) on a 5 × $\frac{1}{2}$-in. column of neutral alumina, gave a species whose spectral properties were identical with those of an authentic sample of triphenylethylene.[14]

The visible spectrum of the photolysis mixture was measured after 1:100 dilution with benzene and was identical that of a benzene solution of **4**.

Rates of Formation of 3. The concentrations of **1** and **2** in dry benzene were adjusted to the concentrations listed in Table I. After degassing as in the General Photolysis Method, sealed ampules containing 5 mL of the appropriate solutions were irradiated (16 h, RPR 3500-Å lamps). The resulting solutions were analyzed by GLPC in column A (200 °C) for the concentration of **3** produced with respect to hexadecane internal standard (added after cracking open the photolysis ampules).

Table III

[TPP], M × 10^4	τ_{obsd}, μs	k_q × 10^{-8}	[TBP], M × 10^4	τ_{obsd}, μs	k_q × 10^{-8}
0.0	2.93 ± 0.05		0	3.13	
1.0	2.18 ± 0.05	8.2	0	3.08	
2.0	1.93 ± 0.07	5.9	3	1.51	8.0
3.0	1.59	6.3	4	1.25	8.5
4.0	1.48	5.8	5	1.13	8.1
6.0	1.13 ± 0.04	5.9	30	0.28	7.5
8.0	0.97 ± 0.03	5.8			av: 8.0
10	0.85 ± 0.03	5.9			
30	0.36	5.5			
		av: 6.1			

Quenching of Triplet 1 by Phosphines. A 1 M solution of **1** in spectral grade dry benzene was diluted until its absorption at 337 nm had an optical density of 1.1 (approximately 0.015 M). The solution was placed in a 5-mm rectangular quartz cuvette modified to accept a serum cap through which a hypodermic needle was inserted for in situ gas purging with purified nitrogen for 5 min. With excitation by a nitrogen gas laser (8-ns pulse with maximum energy of 5 mJ per pulse) at right angles to the monitoring geometry, the lifetime of the transient at 530 nm was monitored as incremental additions of **2** or *n*-butylphosphine (1×10^{-4} to 3×10^{-3} M) were made. The effect of added quantities of phosphine on τ and the half-life of the benzophenone triplet are listed in Table III where TPP = triphenylphosphine, TBP = tri-*n*-butylphosphine, and k = the rate constant calculated from the lifetime data for capture of the transient by phosphine. The best linear fit to decay data was obtained when the observed rate constant for decay was set equal to a sum of the rate constant for unimolecular decay (obtained in the absence of phosphine) and the bimolecular rate constant k multiplied by the initial concentration of phosphine. The photodetection equipment, digitization, and computer-controlled data acquisition and processing array have been described.[29]

Photolysis of 1 in the Presence of 2 and Isobutene. To 10 mL of solution of **1** (0.1 M) and **2** (0.2 M) was added 200 mg (~0.2 M) of freshly distilled isobutene. After following the general photolysis procedure and irradiating for 16 h, GLPC analysis (column A, 200 °C) of the reaction mixture revealed major peaks for **1, 2**, and **3** and increased peaks for biphenyl, benzpinacol, and two other unidentified compounds. A trace peak (corresponding to less than 1% of the area of **1** which had disappeared) at the retention time of an authentic sample of **6**[18] was visible on column A, 100→200 °C at 5 °C/min or column B, 150 °C.

Repetition of this reaction with irradiation for 3 days (40-58% conversion of starting material) gave analogous results. The yield of **6** ranged from 3 to 5% in these three runs. The mass spectrum of this product was shown by GC/MS (capillary column, Finnegan) to be identical with that of **6**.

Photolysis of Aryl Ketones in the Presence of 2. Ten-milliliter aliquots of dry benzene were made 0.1 M in ketone and 0.2 M in **2**. After 16-h irradiation with the general photolysis method, analysis for relative rates for formation of **3** was conducted on column A (200 °C). Irradiation times for yield determinations for **11** and **12** were 32 h, for **14-20** 40 h, and **1, 7-10** 18 h. The yields and relative rates reported in Table II are average values of three determinations. Each of the photolysis mixtures which contained **3** was transferred to a 250-mL round-bottomed flask, diluted to 100 mL with benzene and treated with 106 mg of benzaldehyde (1 mmol). After heating at reflux for 5 h, the red colors had faded and the reaction mixtures were cooled, filtered, and stripped of solvent. The hydrocarbon fraction was separated from **2** and **3** by column chromatography (neutral alumina 50:50 Et$_2$O:petroleum ether). The complex mixtures so obtained were stripped of solvent and subjected to mass spectroscopy. A peak of molecular weight of the expected Wittig adduct was observed in the reactions of **1, 7-12**, $C_6H_5CHCArAr'$. No attempts at further product purification were made. In the reaction of **11**, a significant peak at *m/e* 194 could also be detected.

The reaction mixture from the photolysis of **18** was similarly subjected to column chromatographic separation. The hydrocarbon fractions were combined, stripped of solvent, and analyzed by mass spectroscopy. A peak (*m/e* 180) corresponding to stilbene parent was present and GLPC analysis (column B, 100 °C) showed a peak with retention time identical with an authentic sample of *trans*-stilbene.

Quantum Yield for the Photoinduced Disappearance of 1 in the Presence of 2. Solutions of **1** (0.1 M) and **2** (0.2 M) in dry spectral grade benzene were prepared as above and degassed 5-mL samples in sealed Pyrex ampules were irradiated in a double baffle merry-go-round apparatus with RPR 3500-Å lamps to about 10% disappearance of benzophenone. The precise quantity of **1** which had disappeared was determined by GLPC on column A. Light flux, which was found to be nearly invariant over the reaction period, was determined by 5-min exposure of an aqueous potassium ferrioxalate solution immediately before, at the midpoint, and immediately after the irradiation with analysis by standard actinometry techniques.[30] The period of the irradiation was determined on a stopwatch.

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Solid State Photochemistry of *N,N*-Dialkyl-α-oxoamides. Type II Reactions in the Crystalline State

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Abstract: The solid state photochemistry of *N,N*-dialkyl-α-oxoamides (**1**) has been studied. The amides undergo type II cyclization giving β-lactams (**2**) selectively. The selective formation of the lactams via an unprecedented type II reaction in the crystalline state is explainable in terms of the crystal lattice restraints on the molecular motion of the biradical intermediate (**5**) formed by γ-hydrogen abstraction. The nonreactivity of *N*-alkyl-α-oxoanilides toward solid state photolysis was most reasonably explained by their unfavorable s-cis geometries for γ-hydrogen abstraction.

The Norrish type II reaction of ketones is one of the most important photochemical processes of ketones. The reaction takes place both in solution[1] and in the vapor phase.[2] However, that in the solid state has not yet been reported except for polymers such as polyacrylophenones.[3] The question of comparing photoreactivities in the solid and liquid states is an intriguing one. Solid state reactions may differ from those in solution because of the restraints on molecular motions imposed by the crystal lattice on its constituents. Recently, Scheffer and Dzakpasu reported an interesting study of solid state intramolecular hydrogen transfers.[4] Their investigation was mainly concerned with relationships between the solid state conformation of the substrates and the primary photochemical steps. In this paper, we report the first example of type II reaction of carbonyl compounds in the crystalline state, in which the behavior of the biradical formed by γ-hydrogen abstraction is apparently influenced by crystal-lattice restraints.[5]

The substrates chosen in our study are N,N-disubstituted α-oxoamides (**1**). Our previous work[6] on the solution phase photochemistry of these oxoamides showed that the primary step of the reaction was γ-hydrogen abstraction by the ketone carbonyl oxygen to give the biradical (**5**) which undergoes three

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