solution in sulfolane into the preincubated reaction mixture. Buffering of the solution when needed was made according to the procedure developed by Ritchie.[41] The concentrations of CN^- were determined by pH reading and a calibration curve of OH^- concentration in the same media.

Acknowledgment. We thank Dr. S. S. Shaik, Prof. Z. Rappoport, and Prof. W. P. Jencks for helpful discussions.

Registry No. 1 (X = Y = NO_2), 25945-85-1; 1 (X = Y = CN), 1989-32-8; 1 (X = H; Y = NO_2), 74373-02-7; 2 (Nu = CN; X = Y = NO_2), 86120-10-7; 2 (Nu = OMe; X = Y = NO_2), 82615-43-8; 2 (Nu = CN; X = H; Y = NO_2), 86120-11-8; 2 (Nu = OMe, X = H; Y = NO_2), 86120-12-9.

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Photochemistry of Phenyl Alkyl Ketones in the Presence of Triphenylphosphine

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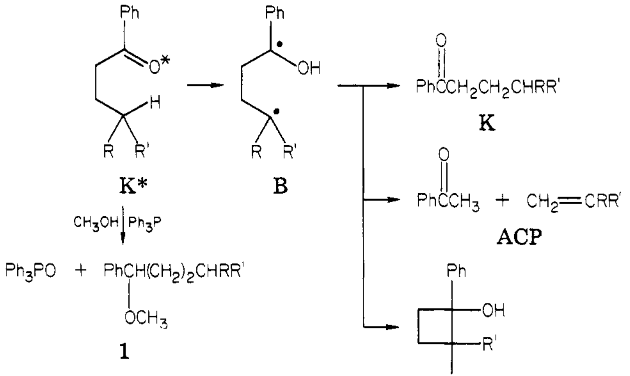
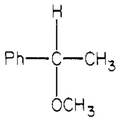
Photolysis of butyrophenone, valerophenone, γ-methylvalerophenone, and acetophenone in methanol in the presence of triphenylphosphine gave triphenylphosphine oxide and 1-phenyl-1-methoxyalkanes in addition to the expected Norrish type II products. Kinetic studies of these photoreactions by steady-state measurements show that triplet-state ketones are quenched by Ph_3P but that the corresponding biradicals do not interact with Ph_3P.

Scheme I



a, R = R' = H
b, R = CH_3; R' = H
c, R = R' = CH_3



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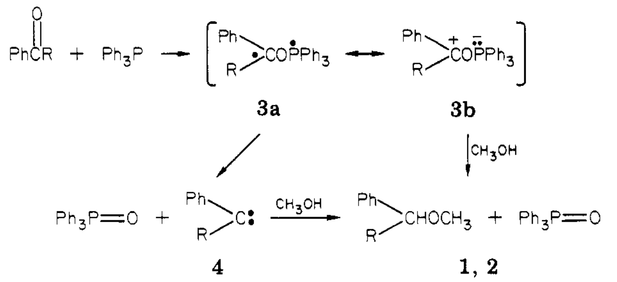
Scheme II



Studies of the Norrish type II reaction of phenylalkanones[1,2] have made significant contributions to our understanding of ketone photochemistry in recent years.[3-9] As shown in Scheme I, the key step of Norrish type II reactions is the generation of a biradical B, which can fragment to acetophenone (ACP) and an olefin or cyclize to a cyclobutanol (CB). Direct proofs of the intermediacy of biradicals have been gained from trapping experiments[3] and from direct observations in laser flash photolysis.[4] In connection with kinetic studies, interactions of a variety of quenchers with the triplet and biradical states of phenylalkanones have been studied.[6-12] The biradicals have been shown to undergo H abstraction,[3,7] electron transfer,[4] addition to double bonds and oxygen,[11] and paramagnetic interaction.[8] For example, while organic phosphines and phosphites[14] are quenchers of carbonyl triplet states,[13-17] organic phosphates interact with the biradicals to promote the Norrish type II reaction.[10] Photolysis of aryl ketones in the presence of triphenylphosphine has been shown to give the phosphine oxide and various products that can be derived from phosphoranes and/or carbenes.[18] In the

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aromatic ketone sensitized photoreduction of bis(acetylacetonato)copper(II) in the presence of Ph_3P as a stabilizing coordinating ligand,[19,20] Ph_3P can react with such intermediates as biradicals and/or excited-state complexes. We here report on the photolysis of several aromatic ketones in the presence of Ph_3P.

Results and Discussion

Irradiation of butyrophenone (0.06 M) in methanol in the presence of triphenylphosphine (0.05 M) under nitrogen through a Pyrex filter gave acetophenone, 1-phenylcyclobutanol (CBa), triphenylphosphine oxide, and 1-methoxy-1-phenylbutane (**1a**); the last two compounds were obtained in 74% and 32% yields, respectively, and their yields were lower when the concentration of Ph_3P was lower. The structure of ether **1a** was based on elemental analysis and on spectroscopic data; the strong peaks at *m/e* 121 and 91 indicated the fragments of $(M^+ - C_3H_7)$ and $C_7H_7^+$, and the ^1H NMR signals at 4.08 (t, 1 H) and 3.20 ppm (s, 3 H) indicated the presence of a methoxy ether linkage. Trace amounts of other high-boiling compounds were also detected in GC analysis, but a phosphorane was not identified. In similar photolyses of valerophenone (Kb), γ-methylvalerophenone (Kc), and acetophenone in the presence of Ph_3P, the corresponding ethers **1b**, **1c**, and **2** were obtained in addition to triphenylphosphine oxide and the Norrish type II products as shown by GC analysis. These ethers were not isolated but were identified by GC–MS; the diagnostic peaks in all of their spectra were the parent peak at *m/e* 121 (100%) for $C_6H_5CH(OCH_3)^+$ and a strong peak at *m/e* 91 for $C_7H_7^+$. Under comparable conditions with the concentration of Ph_3P at 0.04 M, the yields of **1a** and **2** were about the same (~10%), but those of **1b** and **1c** were only 5.9% and 2.3%, respectively. The drastic decreases in the latter were apparently caused by the intervention of the Norrish type II reaction, which was particularly facile for Kb and Kc.

Fox's mechanistic proposal[18] may be extended to account for the reaction pattern as in Scheme II. Phenyl-conjugated phosphoranes are relatively stable and react with methanol to give phenylalkanes[21] but not benzyl ethers **1** and **2**. Ethers **1** and **2** are more likely formed either from carbene intermediates **4** (such a reaction pattern is well-known)[22] or directly from the phosphoranide **3b** by the nucleophilic addition of methanol. In view of the well-proven existence of certain phosphoranides,[23] **3b** is a more probable intermediate in the reaction scheme; it can be regarded as a resonance form of the biradical **3a**. We believe that efficient interception of **3b** by methanol prevents the formation of the corresponding phosphoranes.

In order to learn more about the effects of Ph_3P on the photolysis of aryl ketones, kinetic investigations were undertaken. The reaction scheme shown in eq 1–10 is proposed to represent the primary steps of the photoreaction, in analogy to the scheme of previous workers.[7,10]

$$\mathrm{K} \xrightarrow{h\nu} \mathrm{K\ (singlet)} \rightarrow {}^*\mathrm{K\ (triplet)} \tag{1}$$

$$^*\mathrm{K} \xrightarrow[\mathrm{CH_3OH}]{k_2} \mathrm{K + H\ abstraction} + \Delta \tag{2}$$

$$^*\mathrm{K} \xrightarrow{k_3} \mathrm{B} \tag{3}$$

$$^*\mathrm{K} + \mathrm{Ph_3P} \xrightarrow{k_4} [\mathrm{K{\cdot}PPh_3}]\ (\mathbf{3}) \tag{4}$$

$$[\mathrm{K\text{-}PPh_3}] \xrightarrow[\mathrm{CH_3OH}]{k_5} \mathrm{PhCH(OCH_3)R}\ (\mathbf{1}\text{ and }\mathbf{2}) + \mathrm{Ph_3P{=}O} \tag{5}$$

$$[\mathrm{K\text{-}PPh_3}] \xrightarrow{k_6} \mathrm{K + PPh_3} \tag{6}$$

$$\mathrm{B} \xrightarrow{k_7} \mathrm{K} \tag{7}$$

$$\mathrm{B} \xrightarrow{k_8} \mathrm{PhCOCH_3 + CH_2{=}CRR'} \tag{8}$$

$$\mathrm{B} \xrightarrow{k_9} \mathrm{PhC(OH)CH_2CH_2CRR'\ (CB)} \tag{9}$$

$$\mathrm{B + PPh_3 \rightarrow K + PPh_3 + products} \tag{10}$$

In this scheme, $[K\text{-}PPh_3]$ represents the complex **3**, the formation of which may involve charge-transfer interactions and other steps but is simplified as in eq 4. The intersystem crossing for singlet ketone to the triplet state is regarded to be complete within the time scale of the ensuing reactions.[12] Equation 10 represents unspecified interactions of the biradicals with Ph_3P, in which we assume that ethers **1** are not formed as there is no rational mechanism for such a reaction. This scheme leads us to the following equations on the basis of the steady-state approximation:

$$\Phi^0/\Phi = 1 + (k_4\tau_T + k_{10}\tau_B)[\mathrm{Ph_3P}] + k_4\tau_T k_{10}\tau_B[\mathrm{Ph_3P}]^2 \tag{11}$$

where $\tau_T = (k_2 + k_3)^{-1}$, the lifetime of the triplet-state ketone, and $\tau_B = (k_7 + k_8 + k_9)^{-1}$, the lifetime of the biradical, and

$$1/\Phi_e = 1/\beta + 1/(\beta k_4\tau_T[\mathrm{Ph_3P}]) \tag{12}$$

where $\beta = k_5/(k_5 + k_6)$, Φ^0 and Φ are the quantum yields of aryl ketone disappearance or acetophenone–cyclobutanol appearance in the absence and presence of Ph_3P, and Φ_e is the quantum yield of the formation of ethers **1** or **2**.

Equation 11 contains the square of the concentration of Ph_3P, arising from quenching of two reactive intermediates. The equation becomes a typical Stern–Volmer eq 13 when this term becomes negligibly small compared with cumulative experimental errors.

$$\Phi^0/\Phi = 1 + (k_4\tau_T + k_{10}\tau_B)[\mathrm{Ph_3P}] \tag{13}$$

The quantum yields of phenylalkanone disappearance and ether **1** formation for photolysis of Ka, Kb, and Kc in the presence and absence of Ph_3P were determined by using a merry-go-round irradiation setup and GC analysis to afford Φ^0, Φ, and Φ_e (Table I). For comparison, photolysis of acetophenone under similar conditions was also carried out and the quantum yields of acetophenone disappearance, Φ^0 and Φ, and the formation of ether **2**, Φ_e, were also determined. Similar experiments for quenching of triplet-state benzophenone by Ph_3P were carried out by utilizing HPLC to measure the quantum yield of benzophenone disappearance; HPLC analysis was necessary because of the decomposition of benzopinacol on a GC

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Table I. Photodecomposition of Phenylalkanones in the Presence of Ph_3P in MeOH at Room Temperature[a]

1. Butyrophenone (100×10^{-3} M)[a]

$[Ph_3P]$ (10^{-3} M)	0	2.5	5	7.5	10	15	20
Φ^0/Φ	1.00	1.07	1.56	1.80	1.70	2.30	
Φ_e			0.024	0.031	0.042	0.043	0.045

slope = 0.138 ± 0.020, intercept = 13.7 ± 2.5, R = 0.9692

2. Valerophenone (100×10^{-3} M)

$[Ph_3P]$ (10^{-3} M)	0	10	15	20	30	35	40
Φ^0/Φ	1.00	1.30	1.52	1.78	1.87	2.20	2.44
Φ_e		0.020	0.028	0.031	0.42		0.45

slope = 0.391 ± 0.020, intercept = 11.68 ± 1.19, R = 0.9962

3. γ-Methylvalerophenone (100×10^{-3} M)

$[Ph_3P]$ (10^{-3} M)	0	10	20	30	40
Φ^0/Φ	1.00	1.03	1.24	1.29	1.34
Φ_e		0.008	0.015	0.019	0.025

slope = 1.125 ± 0.045, intercept = 11.89 ± 2.67, R = 0.9984

4. Acetophenone (33×10^{-3} M)

$[Ph_3p]$ (10^{-3} M)	0	2	3	4	6	8	10	12
Φ^0/Φ	1.00	1.19	2.54	1.86	2.28	2.56	2.91	3.29
Φ_e		0.023	0.031	0.035	0.040			

slope ≃ 0.058, intercept ≃ 14.34

5. Benzophenone[b] (50×10^{-3} M)

$[Ph_3P]$ (10^{-3} M)	0	5	7.5	10	15	20	25	30	35
Φ^0/Φ	1.00	1.37	1.35	1.59	2.34	2.87	3.15	3.56	4.00

[a] Slope, intercept, and R values were derived from plots according to eq 12 by using Φ_e values. [b] The benzophenone disappearance was monitored by HPLC; other ketones were monitored by GC.

Table II. Summary of Kinetic Data

ketones	$k_4\tau_T + k_{10}\tau_B$, M^{-1}	$k_4\tau_T$, M^{-1}	τ_T, ns	τ_B, ns	10^9k_4,[a] M^{-1} s^{-1}	10^8k_{10},[b] M^{-1} s^{-1}
butyrophenone	87 ± 12	99 ± 32	(70)[d]	(110)[d]	1.4	<2
valerophenone	34 ± 3	30 ± 5	16[e]	102[e]	1.9	<1
γ-methylvalerophenone	9.4 ± 1.6	10 ± 3	4.7[e]	97[e]	2.1	<0.3
acetophenone	202 ± 10[c]	~250	(200)[f]		~1.0	
benzophenone	91 ± 4[c]		260[g]		0.35	

[a] These data were obtained from columns 3 and 4 except for the last two compounds. [b] The upper limit of the rate constants calculated from column 2 by taking into account probable errors. [c] These values are $k_4\tau_T$ since no biradical is involved. [d] Estimated values from the results obtained by flash photolysis in benzene (personal communication from Dr. J. C. Scaiano). [e] References 4 and 9. [f] Extrapolated from the value obtained by flash photolysis in ethanol and 2-propanol.[24] [g] Reference 25.

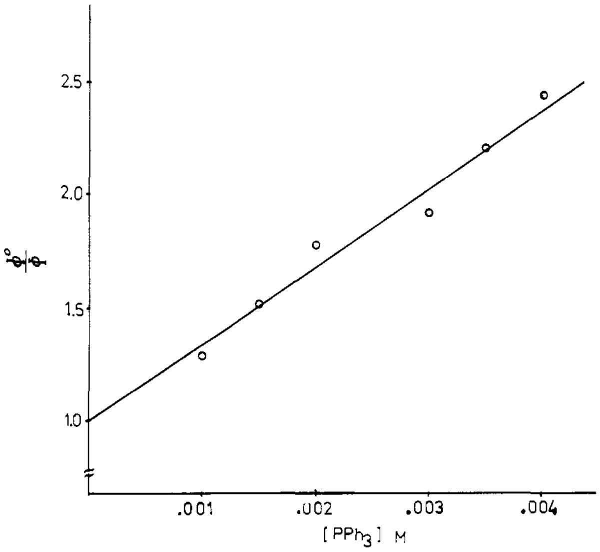

Figure 1. Stern–Volmer plot of valerophenone photolysis in the presence of Ph_3P in methanol: correlation coefficient = 0.9865 for the best linear fit.

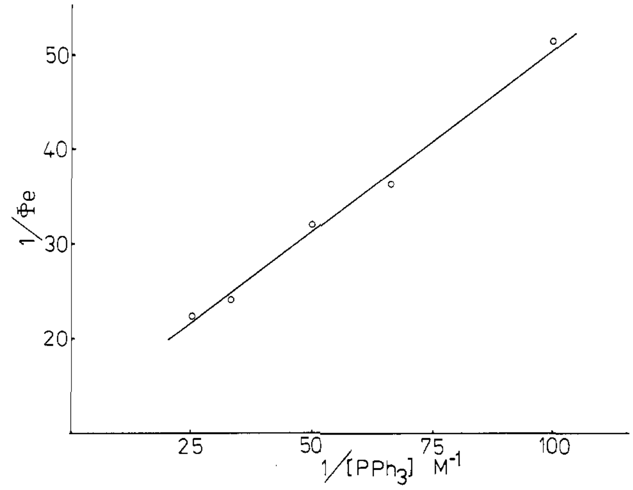

Figure 2. Reciprocal of quantum yield of **1b** vs. reciprocal of Ph_3P concentration; irradiation of valerophenone in methanol.

column. Stern–Volmer plots were made from these quantum yields Φ^0 and Φ, and that for the photodecomposition of valerophenone is shown in Figure 1. Detailed analysis according to quadratic and linear fits showed that the latter case was satisfactory, indicating that eq 13 could represent the quenching kinetics. The slopes of these plots afforded $k_4\tau_T + k_{10}\tau_B$ for each quenching (Table II). The reciprocals of Φ_e were also plotted against $1/[Ph_3P]$; the example for valerophenone photolysis is shown in Figure 2. The quenching rates $k_4\tau_T$ were obtained from intercept/slope in each case according to eq 12 and are listed in Table II.

As shown in Table II, the values of $(k_4\tau_T + k_{10}\tau_B)$ and those of $k_4\tau_T$ determined from different monitors Φ and Φ_e are essentially identical within experimental error, suggesting the absence of interaction between the biradicals and Ph_3P as in eq 10. To confirm this point, valerophenone photodecomposition in the presence of various concentrations of Ph_3P was examined by simultaneously monitoring the formation of acetophenone (ACP), the cyclobutanol (CBb), and the disappearance of valerophenone. The quantum yields obtained from this experiment were analyzed by using the Stern–Volmer relation, eq 13, individually to give $(k_4\tau_T + k_{10}\tau_B) = 34 \pm 3$, 37 ± 4, and 34 ± 2, respectively, for each monitor. The close agreement among these three values shows that the biradical does not interact with Ph_3P to any significant extent, i.e., that eq 10 is not applicable. This conclusion is in contrast to the report that triphenylphosphine oxide enhances the yields of Norrish type II product, e.g. ACP and CB, via complex formation.[10]

It is desirable to know the rate constants for eq 4 and 10 in order to understand the quantitative relation of these two reactions to the overall pattern. This requires the values of lifetimes τ_T and τ_B; some of these are available but others can only be estimated. Because of the experimental errors in the determination of $(k_4\tau_T + k_{10}\tau_B)$ and $k_4\tau$, the rate constants calculated in Table II must be regarded as approximate. In particular, k_{10} can only be estimated from the upper limit of the error ranges of other. However, the rate constants k_4 for the Ph_3P quenching of triplet-state ketones, obtained from eq 12, are in reasonably good agreement with some published data. For example, the interaction of triplet-state benzophenone with Ph_3P has been studied by steady-state[14,18] and laser flash photolysis[18] techniques, giving $k_4 = 6 \times 10^8$ and 3.6×10^8 M^{-1} s^{-1} in benzene[14,18] and 3.2×10^8 M^{-1} s^{-1} in acetonitrile.[13,14] Likewise, the k_4 for butyrophenone measured by flash photolysis in benzene[13,16] is 1.8×10^9 and 2.4×10^9 M^{-1} s^{-1}. These figures when compared to those in Table II suggest that the interaction of triplet-state ketones with Ph_3P does not depend significantly on the solvent.

Experimental Section

General Conditions and Materials. Acetophenone, butyrophenone, valerophenone (all Aldrich), and γ-methylvalerophenone (Fluka) were distilled prior to use. The latter three were shown to be free of acetophenone by GC analyses. Benzophenone (Aldrich) was recrystallized several times from ethanol. Methanol was distilled twice.

Ultraviolet spectra were obtained with a Cary 17 spectrophotometer, infrared spectra with Perkin-Elmer 457 spectrophotometer, ^1H NMR spectra with a Varian A56/60 spectrometer in $CDCl_3$ with Me_4Si as an internal standard, and ^{13}C NMR spectra with a Varian XL100 spectrometer. A Hewlett-Packard (Model 5985) spectrometer was used to perform GC coupled with mass spectrometry. The HPLC machine was constructed with a LDC Model 711 solvent delivery system, a Rheodyne Model 7120 syringe-loading sample injector, a Partisil PXS 10/25 Whatman analytical column, and a LDC Model 1203 UV monitor (254 nm). Analytical vapor-phase chromatographic analyses were performed on a Varian 1200 (FID) with 5% Carbowax 20M or 10% SE-30 capillary columns using anisole as an internal standard. The cyclobutanols, CBa, CBb, and CBc, were prepared by photolysis of butyrophenone, valerophenone, and γ-methylvalerophenone and were identified by GC–MS; CBa m/e (relative intensity) 148 (M^+, 8), 120 (29), 105 (100), 77 (51), 78 (22); CBb m/e (relative intensity) 162 (M^+, 3), 134 (28), 133 (36), 120 (99), 105 (100), 91 (11), 78 (34), 77 (31); CBc m/e 176 (relative intensity) (M^+, 0.6), 148 (6), 133 (4), 120 (100), 105 (64), 78 (25), 77 (20). The mixtures were used for the identification of these GC peaks. Preparative separations were carried out on a Varian Aerograph 1700 using a 20% SE-30 column.

Irradiation Conditions. A large-scale preparative irradiation was carried out in a cylindrical immersion photocell using a 450-W medium-pressure Hanovia lamp in a Pyrex water-cooled jacket with cut off at 300 nm.

Quantum yield determinations were carried out in small phototubes in a "merry-go-round" system. The Pyrex phototubes (1.2-cm diameter × 10-cm length) were equipped with a mercury-sealed gas inlet and outlet. The light source was the same as in the large-scale preparative photolysis. A solution of butyrophenone (0.1 M) in benzene ($\Phi = 0.36$) or of benzophenone–benzhydrol in benzene ($\Phi = 0.74$)[20] was used as an actinometer.

Photolysis of Butyrophenone in the Presence of Ph_3P. A methanol solution (280 mL) containing butyrophenone (2.49 g, 0.06 M) and triphenylphosphine (3.7 g, 0.05 M) was irradiated under nitrogen for 5 h. The progress of the reaction was followed by GC. The photolysate was evaporated under vacuum to yield a solid–liquid residue. The solid (1.5 g) was filtered and shown by GC and GC–MS analysis to be PPh_3 and Ph_3PO in a 1:3 ratio. The filtrate was distilled under vacuum. The residue (2.2 g) was shown to contain Ph_3P and 80% Ph_3PO. The distillate (2.3 g) was separated by preparative gas chromatography to give three compounds: acetophenoe, 1-phenyl-1-methoxybutane (**1a**), and a mixture of butyrophenone with a minor amount (5–7%) of 1-phenylcyclobutanol (CBa) in yields of 21%, 31%, and 48%, respectively. The last two compounds eluted close to each other from GC. Ether **1a**: MS, m/e (relative intensity) 164 (M^+, 0.8), 122 (8.8), 121 (100), 91 (16.6), 77 (15.0); IR (Nujol) 3100–3040, 2970–2880, 1500, 1460, 1100 and 710 cm^{-1}; ^1H NMR ($CDCl_3$) 7.30 (s, 5 H), 4.08 (t, 1 H), 3.20 (s, 3 H), 2.10–1.20 (m, 4 H), 0.81 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 143.2 (s), 129.7 (d), 128.7 (d), 128.1 (d), 84.55 (d), 57.23 (q), 40.96 (t), 19.68 (t), 14.64 (q). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.58; H, 9.66.

In a separate experiment, a methanol solution (4 mL) containing butyrophenone (0.056 g, 0.094 M) and Ph_3P (0.021 g, 0.02 M) was irradiated for 7 h in a Pyrex tube under nitrogen. The photolysate was analysed by GC to give acetophenone (14.7%), ether **1a** (4.7%), butyrophenone (75%), and 1-phenylcyclobutanol (CBa ~2.5%) in addition to other minor peaks (<1%).

Photolysis of Phenylalkanones in the Presence of Ph_3P. Methanol solutions (4 mL) containing a ketone (0.06 M) and Ph_3P (0.04 M) were deaerated with purified nitrogen and were irradiated for 4–5 h. Anisole was added as an internal standard, and analysis by GC (SE-30 capillary column) and GC–MS indicated acetophenone, cyclobutanols (CB), the starting ketones, and the corresponding ethers **1a** (10.3%), **1b** (5.9%), **1c** (2.3%), and **2** (9.9%). The ethers **1b**, **1c**, and **2** were not isolated. Their MS data were as follows: 1-phenyl-1-methoxypentane (**1b**) m/e (relative intensity) 178 (M^+, 0.9), 122 (8), 121 (100), 91 (9) and 77 (8); 1-phenyl-1-methoxy-4-methylpentane (**1c**) m/e (relative intensity) 192 (0.8), 122 (8), 121 (100), 91 (9) and 77 (8); 1-phenyl-1-methoxyethane (**2**) m/e (relative intensity) 137 ($M^+ + 1$, 0.7), 136 (M^+, 6.5), 122 (8), 121 (100), 105 (20), 91 (8), 77 (18).

Quantum Yield Determinations—Kinetic Study. Quantum yield studies were carried out by simultaneous irradiation of several samples in a "merry-go-round". Phototubes containing 4-mL methanol solutions of 0.1 M ketones (acetophenone 0.04 M and benzophenone 0.05 M) and concentrations of triphenylphosphine ranging from 0.001–0.04 M were deaerated with purified nitrogen and irradiated. Irradiation times were chosen to cause 5–10% conversion of ketones. In cases where the disappearance of ketone was measured, the conversion was <30%. After irradiation the samples were analyzed by GC using anisole as an internal standard. In photolyses of butyrophenone and γ-methylvalerophenone, the concentrations of acetophenone and ethers **1a** and **1c** were determined. For valerophenone photolysis, the concentrations of all Norrish type II reaction products were determined. In acetophenone photolysis, the disappearance of acetophenone and the formation of ether **2** were analyzed. For determination of the quenchng rate constant of the benzophenone triplet state by triphenylphosphine, benzophenone disappearance was measured by HPLC analysis using anisole as an internal standard and 5% ethyl acetate in hexane as the solvent.

In the Stern–Volmer plots, the strength (A) of a chromatographic peak relative to the standard peak was taken to represent the percent formation or disappearance of a given compound. For the phenylalkanone disappearance and acetophenone–cyclobutanol appearance, ratios of the relative strength in the absence (A^0) and in the presence (A_x) of Ph_3P were taken as $\Phi^0/\Phi = A^0/A_x$ for the plotting of eq 13. The quantum yields of the formation of ethers 1 and 2, Φ_e in eq 12, were calculated from the percent yields of the ethers, which were obtained from a predetermined calibration curve against the anisole internal standard.

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Registry No. **1a**, 81631-43-8; **1b**, 78522-84-6; **1c**, 86259-54-3; **2**, 4013-34-7; CBa, 935-64-8; CBb, 82245-43-0; CBc, 81759-40-2; butyrophenone, 495-40-9; valerophenone, 1009-14-9; γ-methylvalerophenone, 2050-07-9; acetophenone, 98-86-2; methanol, 67-56-1; triphenylphosphine, 603-35-0.

Formation and Reactions of Dewar 4-Pyrimidinones in the Photochemistry of 4-Pyrimidinones at Low Temperature. 2

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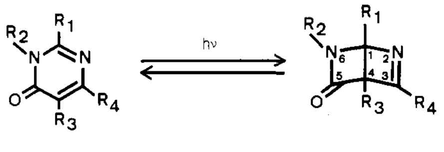
The photochemistry of the 4-pyrimidinones **1b–l** in liquid NH_3–ether solution at −40 °C or in methanol at −10 to −40 °C was studied. Irradiation of **1b–g** at low temperature gave the corresponding Dewar 4-pyrimidinones (**2b–g**), whose physical properties (IR, NMR, and UV) were determined. The photolysis of **1h–j** in methanol at −10 to −20 °C gave methanol adducts **5–7** which suggested the formation of the Dewar 4-pyrimidinones **2h–j**. However, the intermediate **2h** could not be detected in liquid NH_3–ether solution at −40 °C. The hydrogen of the imino group increases sharply the reactivity of **2h–j**. Irradiation of **1k** and **1l** in liquid NH_3–ether solution at −40 °C gave the crystalline product **3** and inseparable products, respectively, which did not suggest the formation of **2k** and **2l**. Presumably, the excited 4-pyrimidinone **1k** directly reacts with ammonia before electrocyclization. The 4-pyrimidinone **1l** may decompose by excitation. The reactions of the Dewar 4-pyrimidinones **2a–j** in methanol and in methanol containing sodium methoxide were studied. The products were the β-lactam **4**, imino ether **5**, and acetals **6–8**. The Dewar 4-pyrimidinones **2e–g** gave inseparable products and two unidentified products in methanol, respectively.

Recently, we have reported the photochemical reactions of 4-pyrimidinones in protic solvents.[1-3] The structures of the products suggested strongly that a Dewar 4-pyrimidinone is an intermediate. Low-temperature photolysis of 4-pyrimidinones was then undertaken in order to obtain the Dewar 4-pyrimidinones. 1,3,6-Trimethyl-5-oxo-2,6-diazabicyclo[2.2.0]hex-2-ene (Dewar 4-pyrimidinone **2a**) was photochemically formed from 2,3,6-trimethyl-4-(3*H*)-pyrimidinone (**1a**) in liquid NH_3–ether solution at −40 °C, and the reaction of **2a** in protic solvents revealed that the Dewar 4-pyrimidinone **2a** is the intermediate (Scheme I).[3]

In the previous report,[1] several attempts to obtain β-lactams from some 4-pyrimidinones in methanol were unsuccessful. For example, 3,6-dimethyl-2-phenyl-4-(3*H*)-pyrimidinone (**1c**) was irradiated in methanol at 30–35 °C to give inseparable product(s). No corresponding β-lactam was obtained. The results suggested that either little or no photochemical reaction occurs or that the formed Dewar 4-pyrimidinone does not undergo a solvolysis reaction in methanol. The mechanistic question was resolved by application of the low-temperature method to 4-pyrimidinones **1b–l**. Experiments with the 4-pyrimidinones **1b-l** permitted examination of the generality of the photochemical electrocyclization of 4-pyrimidinones since replacement of the alkyl group with hydrogen, aryl, or thiomethyl provides insight into the solvolysis reactions of the Dewar 4-pyrimidinones in methanol.

Scheme I



1a-g **2a-g**

Results and Discussion

Photochemistry of 4-Pyrimidinones 1b–l at Low Temperature. Irradiation of 4-pyrimidinones **1b–l** has been carried out in liquid NH_3–ether solution at −40 °C or in methanol at −10 to −40 °C under a nitrogen atmosphere with a high-pressure mercury lamp through quartz or a Pyrex glass filter. The 4-pyrimidinones **1b–g** under irradiation gave mixtures of 5-oxo-2,6-diazabicyclo-

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