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Photoinduced Alcoholysis of α,α,α-Tribromoacetophenone to Benzoylformate

Yasuji IZAWA, Katsuhiro ISHIGURO, and Hideo TOMIOKA*

Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514

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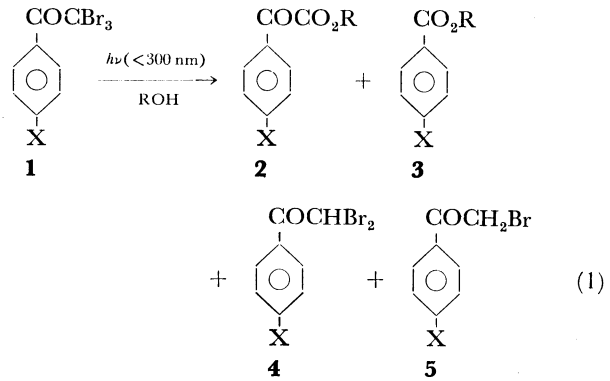
Irradiation of *p*-substituted α,α,α-tribromoacetophenones (**1**) in O_2-saturated alcohols (MeOH, prim. and sec. alcohols) afforded a new alcoholysis product, benzoylformate (**2**), in good yield (75—85%) along with benzoate and radical (reduction) products. Sensitization experiments showed that **2** was derived from the triplet excited **1**. Formation of **2** as well as the decomposition rate of **1** were greatly accelerated by oxygen, presumably as a result of the involvement of the normally forbidden $S_0 \rightarrow T_1$ transition of **1** due to the oxygen-**1** charge transfer complex. Independent synthesis and reaction of possible intermediates in the photoalcoholysis of **1** leading to **2** suggested that **2** was formed from spontaneous (dark) reactions of initial photoalcoholysis product, α,α-dibromo-α-alkoxyacetophenone.

Since photoinduced solvolysis reactions of nitrophenyl phosphates were first discovered by Havinga *et al.*,[1] related reactions were found to occur with other aromatic esters, ethers, halides, *etc.*, reacting with a variety of nucleophiles.[2] Interest has increased in this new domain of chemistry, not only from the stand-point of the reaction mechanism but also from a synthetic viewpoint. These reactions often proceed to a high degree of conversion—resulting in good yields of products which are sometimes difficult to prepare by other reactions. Although the investigations in this field had been mainly focussed on the aromatic photosubstitutions, since the report[3] by Zimmerman and Sandel on the photosolvolysis of benzyl acetate in aqueous dioxane to form benzyl alcohol, a considerable amount of work has been reported[4-9] on the photochemistry of benzyl compounds, mainly benzyl halides, in nucleophilic solvents. It has been reported that products resulting from both heterolysis and homolysis of the benzyl-heteroatom are formed either upon direct irradiation or upon photosensitization. Apart from work with benzyl halides there has been increasing interest paid recently to photolysis of alkyl and cycloalkyl halides.[10,11] Contrary to the earlier belief that only radical intermediates are involved, it becomes clear that cationic, as well as free radical, intermediates may also play an important role in the solution-phase photochemistry of simple alkyl halides. Competing ionic and radical photobehavior has also been observed[12-14] for haloalkenes. However, there are only a few reports on the study of photochemical behavior of α-halo carbonyl compounds. Although the intervention of an α-keto carbonium ion has been suggested in the photoelimination[15] and photorearrangement[16] of some α-halo ketones, few attempts have been made to trap α-keto carbonium ions intermolecularly with nucleophiles. We have already shown that the intermediate generated photolytically from α-halo esters can be trapped by phosphite[17] and electron-rich aromatic nuclei.[18] As an extension of this study, we examined the photolysis of α,α,α-trichloroacetophenone in alcohols and found[19] that a new photoalcoholysis product benzoylformate was formed, albeit in low yield (≈10%), along with other radical products. The formate clearly arose from nucleophilic trapping of ionic species. Since thermal (dark) nucleophilic attack of alcohol on trihaloacetophenone is known to occur exclusively at the carbonyl function to give benzoate (haloform reaction), the formation of formate in the present photoalcoholysis reaction is quite significant and in sharp contrast with the other photosolvolysis reactions in which the type of photoproducts is mostly similar to that obtained in the dark reaction. Thus, it is of obvious interest to get deeper insight into the nature of this novel photoalcoholysis. We wish to report here that tribromoacetophenone undergoes the photoalcoholysis much more efficiently than the trichloro analog, forming benzoylformate in much higher yield (75—85%). The present study also reveals the important role of oxygen, the excited state intermediates leading to photoalcoholysis, and the chemical intermediates leading to benzoylformate.

Results and Discussion

Irradiation of an oxygen-saturated solution of α,α,α-tribromoacetophenone (**1a**) in MeOH for 2 h resulted in the formation of methyl benzoylformate (**2a**, R=Me, 76%) as the main product along with small amounts of methyl benzoate (**3**, R=Me, ≈1%), di- (**4**), and monobromoacetophenones (**5**) (<5%). The identity of these products was confirmed by comparison with authentic samples. Control experiments showed that there was no reaction under identical conditions in the absence of light. Plots of the product yields determined by GC as a function of irradiation time in MeOH (Fig. 1) suggest that esters (**2** and **3**) and the dibromide (**4**) are the primary photoproducts of tribromoacetophenone, but that monobromide (**5**) is apparently derived from **4**. Control experiments also showed that irradiation of **4** in MeOH gave **5**



(1)

a: X=H, **b**: X=MeO, **c**: X=Br, **d**: X=CN.

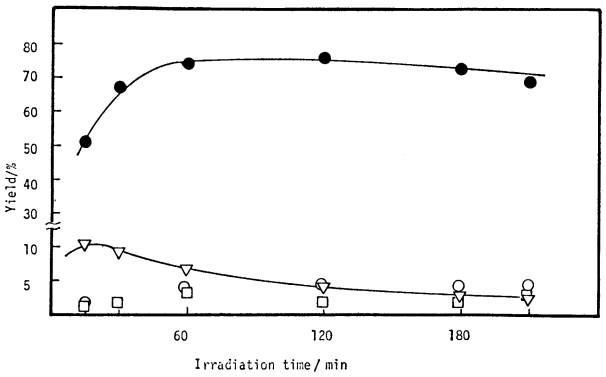


Fig. 1. Yields of **2a** (●), **3a** (□), **4a** (▽), and **5a** (○) during irradiation of **1a** in non-degassed methanol.

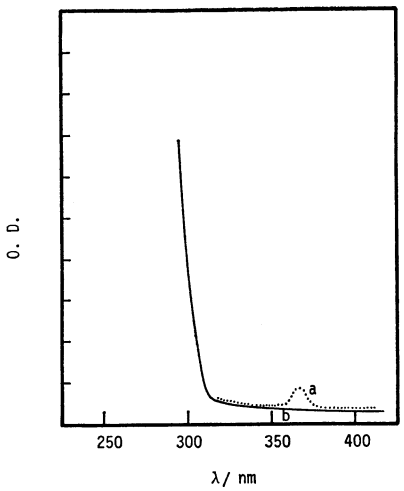


Fig. 2. Absorption bands induced by saturation with oxygen; a) saturated with oxygen, b) after degassing by bubbling argon.

along with small amounts of the esters (**2** and **3**). The latter two acetophenones apparently arise at least principally *via* radicals. On the other hand, the major photoproduct **2** clearly arises from nucleophilic trapping of ionic species. This alcoholysis is applicable to a wide variety of alcohols as summarized in Table 1. Yields of formate **2** were generally good (75—85%) for MeOH and the primary and secondary alcohols, but decreased rather sharply with tertiary alcohol-concomitant with formation of several by-products, *e.g.*, benzaldehyde. This is in a marked contrast with the similar photolysis[19] of trichloroacetophenone in an alcohol, where the yields of formate are generally low (≈10%) and the main products are radical products, *e.g.*, dichloroacetophenone. Photolysis of trifluoroacetophenone in alcohol gave neither the alcoholysis product nor radical products.

Effects of Oxygen. Since oxygen has been shown[10] to have a marked effect on some photosolvolytic processes, we next examined the effect of oxygen on the present photoalcoholysis reaction. The results summarized in Table 2 indicate that oxygen has a marked effect on the product ratio. When the solution was purged with oxygen for 30 min before irradiation, the formation of the formate (**2**) as well as the rate of decomposition of **1** were substantially increased. But when the solution was deoxygenated by bubbling argon, both the formation of **2** and the decomposition rate were suppressed, concomitant with appreciable increase in the dibromide (**4**). In connection with the acceleration of the reaction by oxygen, we have examined the UV absorption spectra of **1** in the presence and absence of oxygen. Oxygen-saturated tribromoacetophenone shows a contact charge transfer spectrum with oxygen at around 363 nm, which disappears on bubbling with argon (Fig. 2). The involvement of the charge-transfer (CT) complex in the photoalcoholysis reaction was shown by irradiating the CT band selectively with monochromatic light. Thus, when the irradiation of the monochromatic light of 363 nm was carried out in the presence of oxygen, the yield of the formate was about three

Table 1. Yields of **2**—**5** from irradiations of **1** in ROH[a]

Tribromo-acetophenone	ROH	Irradiation time/h	Yield/%[b]			
			2	**3**	**4**	**5**
1a	MeOH	2.0	76.4(76.0)	5.5	4.3	1.2
	EtOH	1.0	81.5(76.6)	1.9	3.6	1.5
	n-PrOH	2.0	73.3(69.0)	≈1	5.0	2.3
	i-PrOH	2.0	76.4(70.3)	≈1	4.2	≈1
	n-BuOH	2.0	76.4	≈1	3.2	1.3
	i-BuOH	3.5	86.8	≈1	2.5	1.0
	s-BuOH	2.0	75.5	≈1	3.2	≈1
	t-BuOH[c]	3.5	4.9	3.6	2.3	≈1
1b	MeOH	2.0	61.9	4.4	5.8	≈1
1c	MeOH	2.0	86.2	7.8	3.2	≈1
1d	MeOH	2.0	59.0	3.5	5.4	≈1

a) Irradiations were performed on a 40 mM (1 M = 1 mol dm^{-3}) solution of **1** in Pyrex tubes at 10 °C. The solution was purged with oxygen before irradiation. b) Determined by GC. The maximum yields of **2** from time-conversion curves (See Fig. 1) were indicated. Yields in parentheses refered to isolated product based upon **1** used. c) PhCHO was formed in ≈40% yield.

Table 2. Effect of oxygen on photoreaction **1a** in MeOH[a]

Conditions[b]	λ/nm	Irradiation time/min	Conversion %	Yield/%[c]			
				2a	**3a**	**4a**	**5a**
O_2	Hg[d]	15	65.6	51.0	2.0	10.4	1.2
	Hg[d]	30	91.4	67.5	2.0	8.6	2.0
	363[e]	70	—	32.0	<1	≈1	<1
	265[e]	70	—	9.8	<1	5.4	2.0
Ar	Hg[d]	15	51.2	18.0	1.7	20.3	1.3
	Hg[d]	30	84.5	25.7	3.9	19.9	1.4
	363[e]	70	—	11.2	<1	≈1	<1
	265[e]	70	—	12.4	<1	6.5	1.5

a) Irradiations were performed on a 40 mM solution of **1a** in Pyrex tubes at 10 °C. b) The solution was purged with oxygen (O_2) or argon (Ar) for 30 min before irradiation. c) Determined by GC. d) 300W high pressure mercury lamp. e) Monochromatic light from 250W Xenon lamp.

Table 3. Effect of sensitizer and quencher on photoreaction of **1a** in MeOH[a]

Additive	Yield/%[b]			
	2a	**3a**	**4a**	**5a**
None	51.0	2.0	10.4	1.2
Ph_2CO[c]	66.3	1.3	2.3	<1
1,3-Pentadiene[d]	30.8	<1	13.8	3.5
Cyclohexene[d]	35.7	<1	16.9	4.2
Hydroquinone[d]	32.5	<1	15·8	5.2

a) Irradiations were preformed on a 40 mM solution of **1a** in oxygen-saturated MeOH in Pyrex tubes at 10 °C for 15 min. b) Determined by GC. c) About 5-fold excess of Ph_2CO was added as a triplet sensitizer. Irradiated with monochromatic light of 366 nm. d) 0.5 mM.

times that obtained in the similar irradiation in the absence of oxygen. The yield of **2** was not appreciably altered by oxygen when the absorption maximum of **1** (265 nm) was irradiated. It should be noted that the product distributions exhibited a wavelength dependence. That is, the yield of radical products was higher at 265 nm than at 363 nm.

Sensitization and Quenching Studies. When the irradiation was carried out in the presence of benzophenone as a triplet sensitizer with monochromatic light of 366 nm, where >98% of the incident light was absorbed by the sensitizer, the yield of **2** was essentially unaltered with its rate of formation being accelerated (Table 3). This indicates that **2** is essentially derived from the triplet excited state of **1**. Addition of 1,3-pentadiene as a triplet quencher in the reaction caused a marked decrease in the formate formation (Table 3). However, the examination of the product distributions as a function of the concentration of 1,3-pentadiene showed that the formation of dibromide, as well as the decomposition rate of **1**, increased as the concentration of the quencher was increased. The data are presented graphically in Fig. 3 in the usual form of a Stern-Volmer plot. A possible explanation is that 1,3-pentadiene is not acting as a triplet quencher, but as a hydrogen-atom donor. This was easily confirmed by the findings that the Stern-

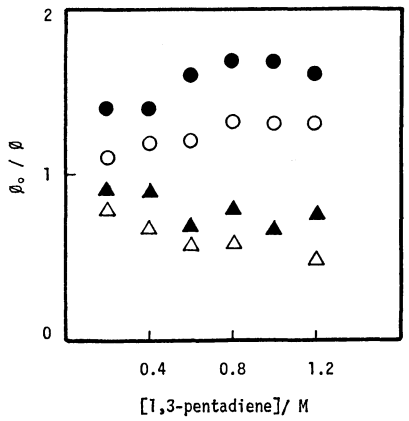


Fig. 3. Effect of 1,3-pentadiene on the quantum yield for formation of **2a** (●), **3a** (○), and **4a** (▲) from **1a** (△) in methanol.

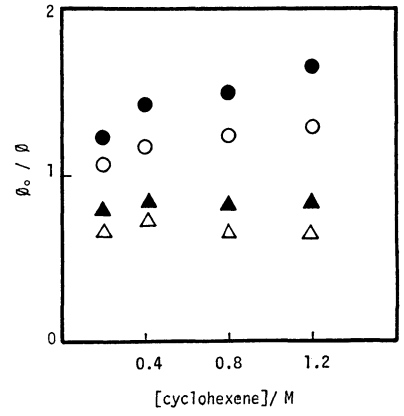


Fig. 4. Effect of cyclohexene on the quantum yield.

Volmer plot using cyclohexene, a good hydrogen donor, also resulted in similar dependence of product distributions (Fig. 4). These results can be interpreted as indicating that there is a delicate balance between ionic (photoalcoholysis) and radical (photoreduction) pathways.

Effects of Solvent. The present photoalcoholysis can be similarly carried out in a mixture of MeOH and solvent (1:10 v/v), instead of absolute MeOH. As summarized in Table 4, however, the product

Table 4. Effect of solvent on photoreaction of **1a** in MeOH[a]

Solvent	Yield/%[b]			
	2a	**3a**	**4a**	**5a**
MeCN	38.1	<1	15.9	2.9
Et_2O	23.4	2.4	19.9	6.1
EtOAc	23.5	<1	16.8	4.2
$CHCl_3$	27.7	1.4	15.7	3.5
PhH	52.5	3.2	3.2	<1
CCl_4	64.1	1.0	<1	<1
None[c]	51.0	2.0	10.4	1.2

a) Irradiations were performed on a 40 mM solution of **1a** in oxygen-saturated mixtures of MeOH and solvent (1:10 v/v) in Pyrex tubes for 15 min. b) Determined by GC. c) Absolute MeOH was used as solvent.

distributions were somewhat sensitive to the nature of solvent employed. Notably, the significant increase in the yield of **2** was observed in CCl_4 and benzene, while the yield was decreased concomitant with the appreciable increase in **4** and **5** in other solvents. Apparently, the difference reflects in part the hydrogen donor ability of solvents. A good hydrogen donor like ether favors the radical pathway by trapping radicals to give **4** and **5** in competition with ionic process leading to **2** and **3**. The heavy-atom effect in the case of CCl_4 facilitates the intersystem crossing of the excited singlet state to the triplet. CCl_4 is therefore the best co-solvent for the photoalcoholysis.

Effects of Substituents. A number of *p*-substituted tribromoacetophenones were irradiated in an attempt to learn whether there might be any effect of ring substituents on the photoalcoholysis. The results summarized in Table 1 indicate that, just as with tribromoacetophenone itself, the principal products of the substituted tribromoacetophenones were the corresponding benzoylformates, with small amounts of benzoates and dibromoacetophenones also being formed. Thus, neither strong electron-donating nor -withdrawing substituents caused much change in the yield of **2**. This is to be noted in connection with the facts that many photosolvolytic reactions of aryl compounds have been shown[2,20] to be dramatically affected by ring substituents. For example, Grinter *et al.*[21] have shown in the photohydrolysis of monosubstituted benzylidyne trifluorides that *m*-chlorobenzylidyne trifluoride shows hardly any reactivity under the conditions where the *m*-hydroxy derivative undergoes photohydrolysis. Such a marked sensitivity to ring substituents often limits the photosolvolytic method as a general synthetic procedure, although its mechanistic implications are very important. The fact that the present photoalcoholysis can be applicable, regardless of the aryl substituents, opens a route to the benzoylformates from the readily available tribromoacetophenones.

Reaction Mechanism. From the above results it is seen that tribromoacetophenones afford new photosolvolytic products, benzoylformates, which are most easily rationalized as resulting from nucleophilic trapping of a cationic intermediate. The corresponding free radical (reduction) products are also observed in lower yield. These results pose two main questions as to the reaction mechanism. (1) Are the excited state intermediates leading to photoalcoholysis the same as those leading to homolysis? That is, where does branching occur in the photoreaction scheme? (2) What are the possible chemical intermediates in the formation of benzoylformate **2**?

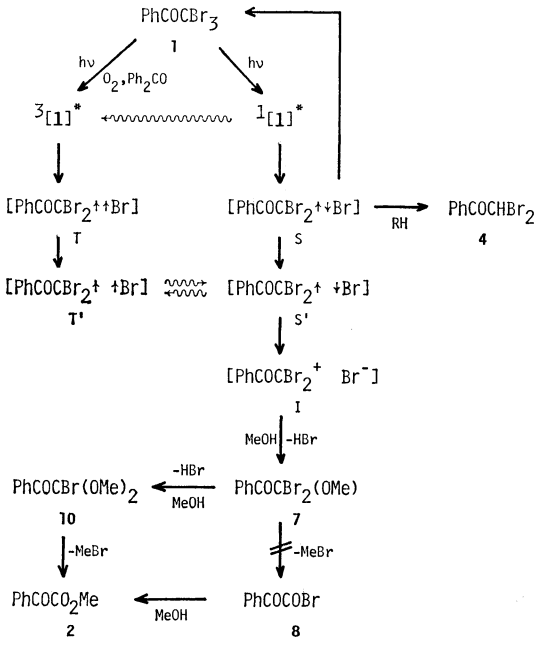
(1) Previous works in this field have examined the effect of sensitizer on the competing ionic and radical photobehavior of halides. It has been indicated[9] in the photolysis of benzyl halides in nucleophilic solvents that, in general, the triplet states produced by sensitization favor heterolysis, whereas the excited states produced as a result of direct light absorption disfavor heterolysis compared with homolysis. The present results (effects of benzophenone photosensitizer and solvent) also indicate that the benzoylformate comes from a triplet excited state of **1**. In their interesting work on photosolvolysis of alkyl iodide, Kropp and his coworkers have proposed[10] that ionic intermediates are not produced directly from the photoexcited state, but that the photoexcited state decays by homolysis to a radical pair, which may undergo radical reactions or may undergo electron transfer to afford an ion pair, which would then undergo carbocation reactions.

$$R\text{-}X \xrightarrow{h\nu} [R\cdot X\cdot] \xrightarrow[\text{transfer}]{\text{electron}} [R^+X^-] \qquad (2)$$

This is mainly based on the observation that irradiation of alkyl halide in an alcohol saturated with oxygen resulted in simultaneous quenching of the formation of the free radical product and the ionic product, suggesting trapping of the radical by oxygen in competition with the electron transfer process. The reductive work-up of the resulting mixture affords alcohol arising from peroxide. In the present photoalcoholysis, presence of oxygen also caused quenching of the formation of the radical product (**4**, **5**), but it increased the formation of alcoholysis product. Similar marked acceleration of photoalcoholysis by oxygen has been observed[22] in the irradiation of α,α,α-trichlorotoluene in alcohol and explained in terms of the involvement of the normally forbidden $S_0 \rightarrow T_1$ transition of trichlorotoluene due to the trichlorotoluene–oxygen charge-transfer (CT) complex. Moreover, such complexes of organic compounds with oxygen have been frequently observed[23] and are responsible for some photochemical reactions[24] in the presence of oxygen. Since the present photoalcoholysis product is derived from the triplet excited state of **1**, the effect of oxygen is attributable to the CT complex which facilitates the intersystem crossing. However, we cannot eliminate the possibility that some of the formate may arise from the reaction of oxygen with an initially formed radical *via* homolytic C–Br cleavage. A possible test of this, involving an $^{18}O_2$ tracer experiment, is in progress and will be reported later. The effects of hydrogen donor on the product distributions are more intriguing in this respect. Thus, the addition of a hydrogen donor, *e.g.*, 1,3-pentadiene, cyclohexene, and hydroquinone, always resulted in a marked in-

crease in the reduction product at the expense of the formate. This is most conveniently explained in terms of the idea that radical and ionic photoproducts from **1** are coupled, as shown in Eq. 2, through the common intermediacy of the radical pair. Appreciable increase in the apparent decomposition rate of **1** in the presence of a hydrogen donor suggests that there is substantial recombination within the radical pair to regenerate the starting bromide **1**. The origin of the solvent effect, in which the use of poor hydrogen donor solvent affords increased yields of ionic product, is also thought to be at least in part due to decreased opportunity for the common radical pair to abstract hydrogen from the solvent. The markedly increased ionic behavior of bromides as compared with their chloro analog also reflects that chlorine atoms abstract hydrogen from the solvent cage (in competition with the electron transfer process) more readily than bromine atoms do.

The mechanism of a route from triplet substrates to solvolysis products is very important. Recently, McKenna and his coworkers have studied the photosolvolysis of benzyl halides and suggested[6] that the formation of photosolvolysis product from triplet substrates must include interconversion of loose singlet and triplet radical pairs, followed by electron transfer in the singlet pair to give a solvent-separated ion pair (see Scheme 1). The present results can be equally well explained by this suggestion. Presumably, singlet radical pairs (S) are very reactive and might either undergo recombination to **1** or abstract hydrogen from the solvent to give dibromoacetophenone (**4**), before they form loose radical pairs (S'). Triplet radical pairs (T), on the other hand, are less reactive and have enough lifetime to shift to loose radical pairs (T') where the partners are already adequately separated to form a solvent-separated ion pair (I).



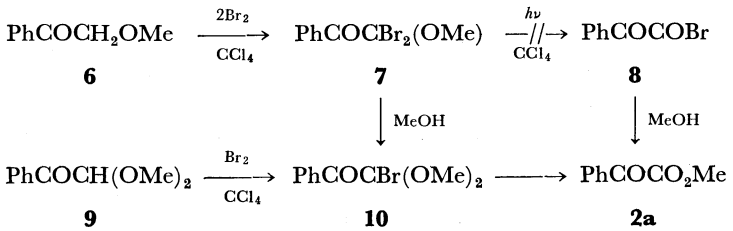
Scheme 1.

(2) There are *a priori* several intermediates for the formation of **2** from the photoalcoholysis of **1**. In the photohydrolysis of monosubstituted benzylidyne trifluoride, Grinter and his coworkers[21] have isolated benzoyl fluoride as an intermediate. Sugimori and his coworkers[22] have also suggested that ethyl chloride and intermediary benzoyl chloride are generated from α-ethoxy-α,α-dichlorotoluene in the photoethanolysis of α,α,α-trichlorotoluene. α-Methoxy-α,α-dibromoacetophenone (**7**), a possible initial photoalcoholysis product, was easily prepared by bromination of α-methoxyacetophenone (**6**) in CCl_4. **7** was, however, stable in non-hydroxylic solvent either upon standing in dark or upon prolonged irradiation. When dissolved in MeOH at room temperature, **7** reacted instantaneously to give methyl benzoylformate (**2**) almost quantitatively. More conveniently, when bromination of **6** was carried out in MeOH, **2** was obtained in quantitative yield. Bromination of α,α-dimethoxyacetophenone (**9**) in CCl_4 resulted in a 1:1 mixture of α-bromo-α,α-dimethoxyacetophenone (**10**) and methyl benzoylformate. The former was gradually changed to the formate upon standing at room temperature. These facts indicate that benzoylformyl bromide (**8**) is not generated in the present photoalcoholysis and that the initial photoalcoholysis product **7** reacted spontaneously with MeOH to give **2** probably *via* dimethoxybromoacetophenone (**10**).

Experimental

Instrumentation. UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO IR-G recording spectrometer, and ^1H NMR spectra were determined with a JEOL JNM-MH-100 NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. GC analyses were performed on a Yanagimoto Model G-180 instrument with flame ionization detector using a 2.0 m×4.0 mm column packed with (A) 5% PEG 6000 and (B) 5% OV-17 on 60—80 mesh Diasolid L.

Materials. Mono- (**5a—d**),[25] di- (**4a—d**),[26] and tribromoacetophenones (**1a—d**)[26] were prepared by bromination of corresponding acetophenones. Trifluoroacetophenone was prepared[27] by the Friedel-Crafts reaction.



Scheme 2.

Authentic benzoylformates (**2a**—**d**) were prepared[28] from the corresponding dichloroacetophenone followed by esterification. All alcohols were dried and distilled before use.

Irradiation for Product Isolation. In a typical run, a solution of tribromoacetophenone (300 mg) in MeOH (30 ml) was placed in a Pyrex tube. The solution was purged with oxygen at 0 °C for 20—30 min before irradiation. The tube was then septum-sealed and irradiated with a high-pressure, 300W, Hg lamp with a water-cooled jacket. The progress of the reaction was monitored by GC. After irradiation for 2 h, the mixtures were concentrated on a rotary evaporator and chromatographed on 2.0×30 cm^2 silica gel (Woelm, activity III) column with $CHCl_3$ as eluent to give methyl benzoate ($\approx$2 mg, $\approx$1%), methyl benzoylformate (110 mg, 80%), and a mixture of mono- and dibromoacetophenone, all of which showed the same NMR spectra and GC retention times as authentic samples.

Irradiation for Analytical Purposes. Irradiations outlined in Tables 1—4 were carried out on 40 mM solution of **1** in alcohol in a Pyrex tube of 5.0 ml capacity. The progress of the reaction was monitored by GC analysis of aliquots removed periodically from the irradiation mixture in order to obtain time-conversion curves for each product. The identity of the products was confirmed either by GC comparison with authentic samples prepared as above or by separation of each of the components by column chromatography, followed by spectroscopic identification. A purge of the samples with the gas (O_2 or Ar) was carried out at 0 °C with vigorous stirring by a magnetic stirring bar.

Sensitized irradiations were conducted by using a Ritsu MC-20 radiating monochromator (250-W Xenon arc lamp) so as to assure absorption of most of incident light by the photosensitizer; when sensitized irradiation was carried out in Pyrex tubes containing 131 mM benzophenone ($\varepsilon \approx 70$ at 366 nm) and 25 mM **1a** ($\varepsilon \approx 1.0$ at 366 nm) with light of 366 nm wavelength from the monochromator, more than 98% of the incident light was absorbed by the sensitizer.

For quenching studies, a stock solution of **1** in MeOH was prepared, and 3 ml portions were added to Pyrex tubes containing varying amounts of quenchers. The tubes were then septumsealed and placed in the "merry-go-round" for irradiation. The irradiation was generally interrupted at about 30% completion in order to minimize error associated with product decomposition.

Bromination of α-Methoxyacetophenone. *(A) In CCl_4*: To a stirred solution of α-methoxyacetophenone[29] **6** (0.45 g, 3.0 mmol) in CCl_4 (20 ml) was added dropwise a solution of Br_2 (0.49 g, 3.0 mmol) in the same solvent (2.0 ml) at room temperature, and the mixture was further stirred for an additional 1 h. Evaporation of the solvent *in vacuo* gave crude α-methoxy-α-bromoacetophenone as a yellow oil: 0.63 g, 92%; ^{1}H NMR 3.62 (s, 3H), 6.37 (s, 1H), 7.20—8.10 (m, 5H).

To a refluxing solution of crude α-methoxy-α-bromoacetophenone (0.63 g, 2.7 mmol) in CCl_4 (20 ml) was added dropwise a solution of Br_2 (0.46 g, 2.8 mmol) in the same solvent, and the mixture was refluxed for an additional 1 h. Evaporation of the solvent *in vacuo* gave crude α-methoxy-α,α-dibromoacetophenone **7** as a yellow oil: 0.67 g, 80%; ^{1}H NMR 3.79 (s, 3H), 7.00—8.10 (m, 5H).

7 (0.67 g, 2.2 mmol) was dissolved in MeOH 10 ml) and left for 30 min at room temperature. Evaporation of the solvent gave methyl benzoylformate (**2a**) almost quantitatively.

(B) In MeOH: A solution of Br_2 (1.0 g, 6.3 mmol) in MeOH (4 ml) was added dropwise to a refluxing solution of **6** (0.46 g, 3.1 mmol) in the same solvent (20 ml), and the mixture was further boiled for an additional 1 h. Evaporation of the solvent *in vacuo* gave crude **2a** (0.47 g, 92%).

*Bromination of α,α-Dimethoxyacetophenone (**9**).* When **9**[30] was reacted with equivalent bromine in refluxing CCl_4, the crude product after evaporation of the solvent was shown to be 1:1 mixture of **10** and **2a** by NMR analysis, which also revealed that **2a** was increased at the expense of **10** upon standing at room temperature and that **2a** was the exclusive product after standing overnight.

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