November, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **53**, *3225—3231 (1980)* 3225

Monochromatic Light-induced Reactions of Benzophenone Hydrazones and the *N*-Acetyl Derivatives in Carbon Tetrachloride in the Presence of Oxygen[1)]

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(Received December 24, 1979)

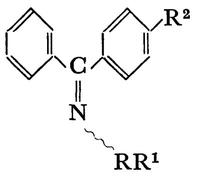
Irradiation of hydrazones of benzophenone, 4-methylbenzophenone and 4-methoxybenzophenone in carbon tetrachloride with monochromatic light in the presence of oxygen afforded the corresponding azine, resulting from N–N bond cleavage, as the major product together with the hydrazone hydrochloride. In contrast to the hydrazones, benzophenone acetylhydrazone in carbon tetrachloride in the presence of oxygen afforded an unstable hydroperoxide as the only product, on photolysis with monochromatic light (288±8 nm); this product was transformed spontaneously into benzophenone on evaporation of the solvent at room temperature. 4-Methylbenzophenone acetylhydrazone and 4-methoxybenzophenone acetylhydrazone reacted in a manner similar to benzophenone acetylhydrazone. Irradiation of benzophenone diacetylhydrazone with 266±8 nm light under conditions analogous to the photo-reactions of hydrazones and acetylhydrazones resulted in loss of an acetyl group, resulting in N–CO bond cleavage to afford acetylhydrazone. The mechanism of the photooxygenation of benzophenone acetylhydrazones is interpreted in terms of chlorine radical-induced autoxidation.

In previous papers,[2)] it was reported that steroidal cyclic ketone acetylhydrazones afforded various yields of lactams on photolysis in the presence of oxygen, while the corresponding hydrazones gave the azines under similar conditions. It was of interest to compare the behavior of alicyclic ketone hydrazone and acetylhydrazone with that of aromatic ketone hydrazone and acetylhydrazone when they were irradiated in the presence of oxygen under similar conditions.

In this paper, we report results of photoinduced oxygenation of some benzophenone acetylhydrazones and diacetylhydrazones in carbon tetrachloride. A comparison is made with the behavior of the parent hydrazones under similar conditions. To avoid secondary photodecompositions[3)] as much as possible, all the photolyses were undertaken with monochromatic light.

Results

Benzophenone hydrazone (**1**),[4)] 4-methoxybenzophenone hydrazone (**3**),[5)] 4-methylbenzophenone hydrazone (**5**),[6)] their *N*-acetyl derivatives (**2**, **4**, and **6**), and *N*-diacetyl derivative (**7**) were prepared by the standard methods.



1 $R=R^1=R^2=H$
2 $R=R^2=H$, $R^1=Ac$
3 $R=R^1=H$, $R^2=OCH_3$
4 $R=H$, $R^1=Ac$, $R^2=OCH_3$
5 $R=R^1=H$, $R^2=CH_3$
6 $R=H$, $R^1=Ac$, $R^2=CH_3$
7 $R=R^1=Ac$, $R^2=H$

The 4-substituted hydrazones, **3** and **5**, and their *N*-acetyl derivatives, **4** and **6**, used for the photoreactions were a mixture of *E* and *Z* isomers, as indicated by their NMR spectra (Table 1). All the hydrazones exhibited two strong absorption maxima due to $\pi\rightarrow\pi^*$ transitions in their UV spectra in dioxan, one at 277—278 nm and the other at 223—234 nm. The absorption at the longer wavelength showed a hypsochromic shift and a hyperchromic effect in methanol, as expected for the $\pi\rightarrow\pi^*$ transitions.

The acetylhydrazones also exhibited two absorption maxima, stronger than the hydrazones, attributable to $\pi\rightarrow\pi^*$ configurations.[7)] The absorptions at the longer wavelength in methanol exhibited bathochromic shifts to 285—288 nm in dioxan. As for the hydrazones, the shorter wavelength absorptions (222—231 nm) in dioxan exhibited hypsochromic shifts to 205—208 nm and a hyperchromic effect in methanol.

Photolysis. A solution of benzophenone acetylhydrazone (**2**) (30 mg in 4 ml of carbon tetrachloride containing oxygen) was irradiated with monochromatic light of 288±8 nm generated by a JASCO CRM-FA grating spectro-irradiator. The progress of the reaction was monitored by the NMR and UV spectra. The irradiation caused the gradual disappearance of the absorption maximum at 288 nm in the UV spectrum, and two singlets due to NH and acetyl protons at τ 1.82 and τ 7.74 emerged in the NMR spectrum. Irradiation for 110 h resulted in the disappearance of the UV absorption maximum at 288 nm and the replacement of the signals due to NH and acetyl protons by a 3-H singlet at τ 7.99 and a 1-H singlet at τ 7.79. In fact, examination of the solution by TLC disclosed the absence of the starting material and the formation of a single product much more polar than the starting material. The addition of aqueous potassium iodide to the solution liberated iodine immediately. The NMR spectrum of the photolyzed solution at 75° showed little change in the spectrum, indicating that the product in solution was stable at that temperature. However, the evaporation of the solvent caused a total decomposition of the product. The NMR spectrum of the residue after removal of the

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TABLE 1. NMR PARAMETERS (100 MHz) FOR BENZOPHENONE HYDRAZONES, THE *N*-ACETYL DERIVATIVES, AND THE AZINES IN CCl_4 ($CDCl_3$) SOLUTION [CHEMICAL SHIFTS (τ) AND SPLITTINGS (Hz; in parenthesis)]

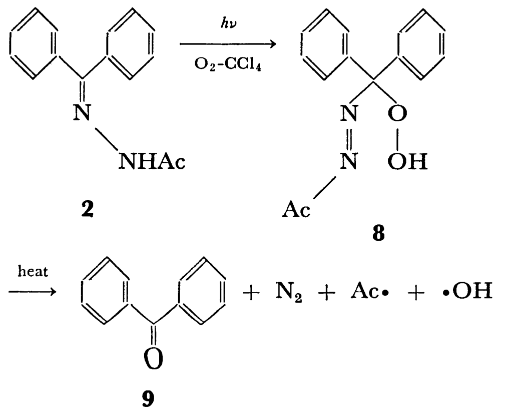
Compound	NH or NH_2	Aromatic protons	$COCH_3$	OCH_3	CH_3
1	4.76(s)	2.36—2.96(m)	—	—	—
1a)	4.63(s)	2.32—3.02(m)	—	—	—
2	1.82(s)	2.30—2.90(m)	7.74(s)	—	—
2a)	1.65(s)	2.30—2.96(m)	7.56(s)	—	—
3ab)	4.89 br(s)	3.24(d) (9.0) 3 and 5H; 2.36—3.06 (m) other aromatic protons	—	6.24(s)	—
3bb)	4.7 br	3.04(d) (9.0) 3 and 5H; 2.45—2.93 other aromatic protons	—	6.31(s)	—
4	1.81(s) (0.6H) and 1.99(s) (0.4H)	3.22(d) (9.0) 3 and 5H (1.2H), 2.87(d) (9.0) 3 and 5H (0.8H), 2.27—3.00(m) other aromatic protons	7.69(s)	6.21(s) (1.8H) and 6.13(s) (1.2H)	—
5b)	5.08 br	2.89(d) (9.0) 3 and 5-H; 2.30—2.78 (m) other aromatic protons	—	—	7.69(s)
5b)	4.62 br	2.85(d) (9.0) 3 and 5-H; 2.40—2.80 (m) other aromatic protons	—	—	7.57(s)
6	1.87(s) (0.53H) and 1.95(d) (0.47H)	2.29(d) (9.0) 3 and 5H (1.1H), 2.75(s) (9.0) 3 and 5H (0.9H); 2.24- *ca.* 2.90(m) other aromatic protons	7.71(s)	—	7.65(s) (1.6H) and 7.55(s) (1.4H)
7	—	2.31—2.91(m)	7.80(s)	—	—
14a)	—	3.19(d) (8.4) 3, 5, 3′ and 5′H, 2.92(d) (8.4) 2, 6, 2′ and 6′H; 2.67—3.24(m) other aromatic protons	—	6.32(s) (3.6H) and 6.08(s) (2.4H)	—
16a)	—	2.40—2.95(m)	—	—	7.68(s) (2.5H) and 7.61(s) (3.5H)

a) Values in $CDCl_3$. b) *Z-E* configuration of these compounds are undetermined.

TABLE 2. THE YIELDS OF BENZOPHENONES IN THE PHOTOLYSIS OF BENZOPHENONE ACETYLHYDRAZONES IN CARBON TETRACHLORIDE WITH MONOCHROMATIC LIGHT

Compound	Wavelength of the irradiation light (nm)	Time of irradiation (h)	Yield of benzophenones (%)
2	288±8	110	60
2a)	286±8	168	0
4	289±8	43	73
6	289±8	48	63

a) Solvent: dioxan.

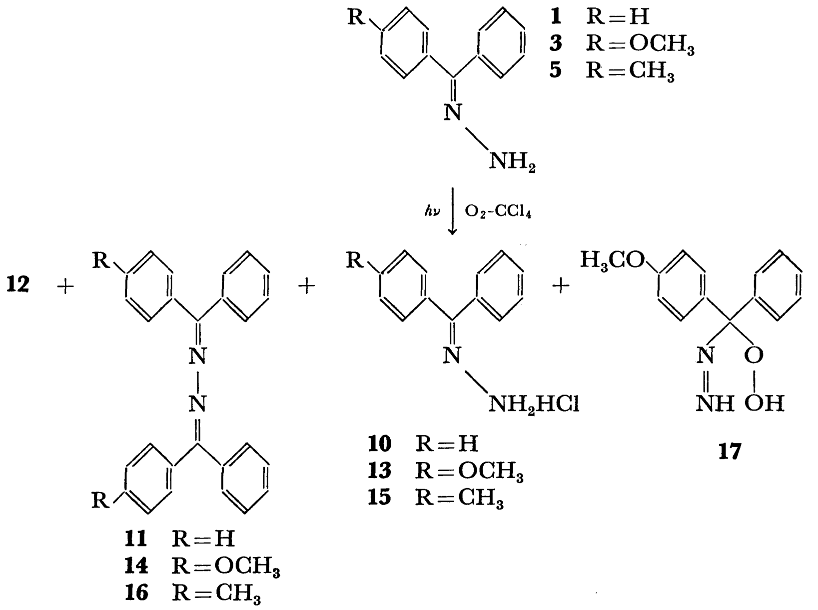


Scheme 1.

solvent disclosed that the signal due to the acetyl group had vanished, and it was actually the spectrum of benzophenone which was isolated in 79% yield by preparative TLC. These observations confirmed that a highly unstable intermediate was formed, which decomposed spontaneously to afford benzophenone upon evaporation of the solvent.

A hydroperoxide structure **8** accommodates all the NMR spectral results, the chemical properties and the result of TLC (Scheme 1). Two singlets at τ 7.99 and 7.79 are ascribable to the acetyl and the hydroperoxide protons. The hydroperoxide proton signals usually resonate at τ −0.3 to −0.75.[8,9] The considerable upfield shift is attributable to shielding by the aromatic ring.

In contrast to the benzophenone acetylhydrazone, irradiation of benzophenone hydrazone (**1**) itself with monochromatic light (270±8 nm) for 72 h under conditions comparable to the case of *N*-acetyl derivative afforded three products: **10**, **11**, and **12** (Scheme 2). Product **10**, which gradually separated as a solid on the wall of the vessel while being irradiated, was identified as benzophenone hydrazone hydrochloride[10] (25% yield). Product **11**, mp 161—163 °C, was iden-



Scheme 2.

Table 3. Products and the yields in the photolysis of benzophenone hydrazones in carbon tetrachloride with monochromatic light

Compound	Wavelength of light (nm)	Time of irradiation (h)	Yields of products (%)		
			The azine	The ketone	The hydrochloride
1	277±8	72	50	0	25
3	279±8	20	7	25	32
5	276±8	11	47	0	31

tified as benzophenone azine by a comparison with a specimen prepared by the reported method.[4] The third product, **12**, mp 230—232 °C, the structure of which has not been deduced, exhibited the molecular ion at *m/e* 418 in the mass spectrum and a single absorption maximum at 307 nm in the UV spectrum.

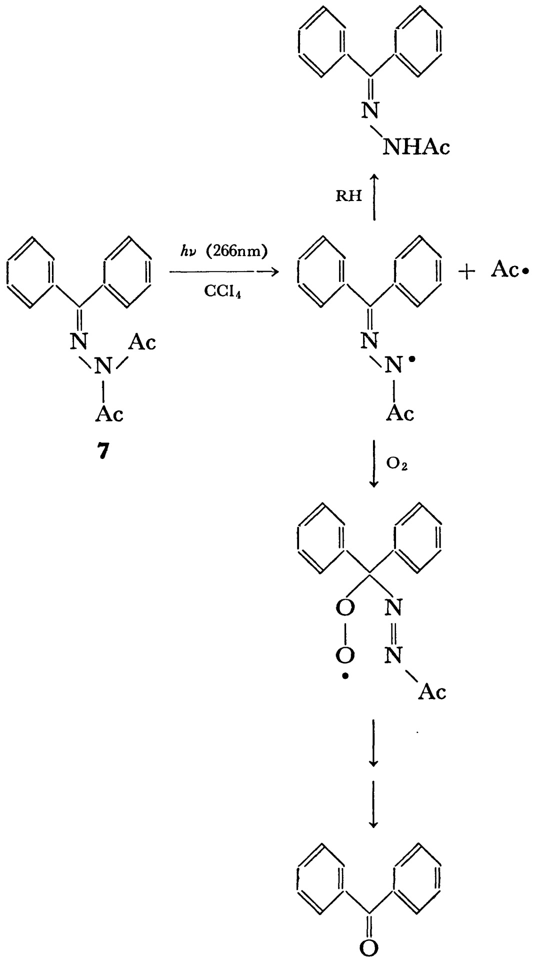
Irradiation of other two nuclear substituted acetylhydrazones **4** and **6** in carbon tetrachloride with monochromatic light gave results parallel with those for acetylhydrazone **2**. The reaction conditions and the yields of the product ketone are shown in Table 2.

In order to obtain further information with regard to the role of the solvent, photolysis of benzophenone acetylhydrazone (**2**) in dioxan with monochromatic light (286±8 nm) was carried out under conditions similar to those in carbon tetrachloride. However, no trace of hydroperoxide was found after 168 h irradiation and the starting material was recovered.

Irradiation of nuclear substituted hydrazone **5** in carbon tetrachloride with appropriate monochromatic light provided results parallel to the case of the hydrazone **1**. It is notable, however, that while the irradiation of the hydrazones **1** and **5** did not afford any parent ketones, the irradiation of the hydrazone **3** afforded a significant amount of the parent ketone formed *via* a hydroperoxide **17**. The reaction conditions and the yields of products are shown in Table 3.

These results are in a sharp contrast with the results by Binkley,[16] who reported that irradiation of benzophenone hydrazone (**1**) in oxygen-free methanol, with Vycor-filtered light, afforded diphenylmethane (26%) and benzophenone (34%). Repetition of this photolysis in the presence of oxygen with monochromatic light showed the photoreaction in methanol to be slower than that in carbon tetrachloride and confirmed the formations of only diphenylmethane and benzophenone as the products. Photolysis in dioxan with Vycor-filtered light was also carried out. Diphenylmethane was again the major product (28%), accompanied by the azine (3%) and the parent ketone (15%). The formation of diphenylmethane by irradiation in this aprotic solvent in the presence of oxygen seems to suggest that the reaction does not involve radical species and that the methylene proton(s) of diphenylmethane may be provided by an ionic intramolecular proton transfer from the amino group, although no experiments in deuteriodioxan were undertaken.

Finally, photolysis of benzophenone diacetylhydrazone **7** in carbon tetrachloride with monochromatic light (266±8 nm) was carried out in order to define further structural requirement for the formation of the hydroperoxide. It was expected that the photoinduced transformation of **7** may be slower than that of acetylhydrazone **2**, since the former did not have a hydrogen on the nitrogen center. However, the disappearance of **7** was found to complete in a period even shorter than in the case of benzophenone acetylhydrazone (90 h). The NMR spectrum of the solution exhibited four sharp singlets at τ 6.42, 7.62, 7.78, and 8.02 in 1:0.7:0.2 ratio, a broad singlet at τ 1.38, and a multiplet at τ 2.22 to 2.80. Examination of the product by TLC disclosed the formation of virtually two products, the Rf values of which were identical with those of benzophenone and benzophenone acetylhydrazone (**2**). These two compounds were isolated by preparative TLC in 77 and 20% yields. Two singlets at τ 1.38 and 7.78 in the photolyzed solution can be attributable to benzophenone acetylhydrazone (**2**). Other singlets in the solution could be due to volatile products resulting from the reaction of the acetyl radical.



Scheme 3.

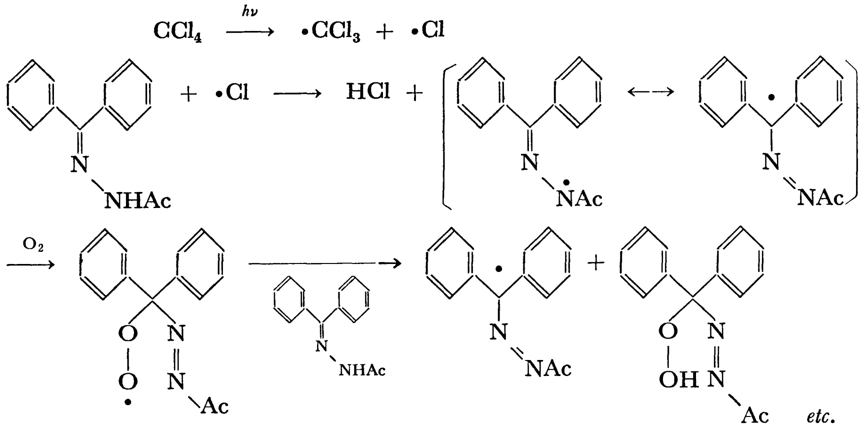
Discussion

There are at least two possible mechanistic pathways for the formation of the hydroperoxides (*e.g.*, **8**) from the acetylhydrazones. One is *via* a radical-induced autoxidation observed for benzaldehyde phenylhydrazones by Busch and Dietz.[9,11] Another is by sensitized oxygenation, as observed for acetone phenylhydrazone by Schenck and Wirth.[12] In this case, singlet oxygen is involved.[13]

Of these two mechanisms, involvement of singlet oxygen, which might be generated *via* sensitization by the acetylhydrazone itself, is ruled out, since no hydroperoxides are formed in the photolysis in dioxan. Thus, oxygenation through the autoxidation remains as a mechanistic possibility. To compare the present reaction with the autoxidation of benzaldehyde phenylhydrazone, benzophenone acetylhydrazone **2** in benzene was subjected to autoxidation under the conditions analogous to the autoxidation of benzaldehyde phenylhydrazone.[11] However, no hydroperoxide **8** was formed under these conditions and irradiation was necessary to obtain hydroperoxide **8** from acetylhydrazone **2**.

One of the probable autoxidation pathways for the hydroperoxide formation is depicted in Scheme 4. In this pathway, a chlorine atom generated from carbon tetrachloride abstracts a hydrogen attached to the amide nitrogen of the acetylhydrazone to form a stabilized amidyl radical and to initiate a chain reaction. Generation of chlorine atoms from carbon tetrachloride under the experimental conditions was confirmed by the formation of the hydrochlorides **10**, **13**, and **15** in the photolysis of the hydrazones. It should be noted that this autoxidation process for the acetylhydrazones predominates over other processes such as N–N bond cleavage, which is almost only reaction in monochromatic photolysis of benzophenone hydrazones, and N–CO bond cleavage.

In contrast to the acetylhydrazone, the parent hydrazones are virtually unreactive toward oxygen under irradiation, with the exception of 4-methoxybenzophenone hydrazone (**3**) in which 25% of the parent



Scheme 4.

ketone was formed together with the azine (Table 3). The major reaction in the hydrazone photolysis is the homolysis of the N–N bond to afford the imino radicals. The homolysis probably takes place from the excited singlet state of the hydrazones since it occurs even in the presence of oxygen.[14)] For the hydrazones, generation of a nitrogen-centered radical *via* the abstraction by electrophilic chlorine atom is probably more difficult than for the acetylhydrazones, owing to the lower stabilization of the radicals to be formed.

In this connection, it is notable that only 4-methoxybenzophenone hydrazone (**3**) afforded the hydroperoxide (as indicated by the formation of the parent ketone). We explain this in terms of the polar effects that frequently influence radical reactions.[15)] The reactions involving electrophilic chlorine atom have a considerable ionic character.[15)] In the present case, the electron-donating methoxyl substituent should stabilize the transition state and facilitate the hydroperoxide formation. The electron-donating effect of a methoxyl group also may play a role in accelerating the attack by the chlorine atom on the hydrogen atom attached to the nitrogen. The difference in the products in the photo-reaction of benzophenone hydrazones in carbon tetrachloride and those in methanol or dioxan is appreciable. Although the exact reason for this difference is not clear, it is likely that a photochemical N–N bond cleavage in the hydrazone is facilitated by the protonation of the amino group with the hydrogen chloride generated by irradiation.

The foregoing experiments showed that a primary photochemical reaction of the diacetylhydrazones is the cleavage of one of the N–CO bonds[17)] rather than the N–N bond cleavage. The N–CO bond cleavage is followed by competitive processes: *i.e.*, the combination of the amidyl radical with oxygen or with hydrogen from another substrate or chlorine abstraction of the amidyl radical from the solvent. These processes may lead to the observed products. We noted previously[2)] that in the photolysis of acetyl- and diacetylhydrazones of some steroidal alicyclic ketones, no azine resulting from N–N bond cleavage was formed. The present results with regard to acetyl- and diacetylhydrazones of aromatic ketones seem to be parallel to the previous results[2)] in that no azine was found in the products.

Experimental

For instruments used and general procedure see part 30.[18)] The mass spectra were taken with a Hitachi RMU-6E spectrometer (ion source temperature 200 °C; ionizing voltage 80 eV) with the exception of **5**. The mass spectrum of **5** was taken with a Hitachi JMS-D 300 spectrometer (ion source temperature 175 °C and ionizing voltage 70 eV).

Benzophenone Hydrazone (1). This hydrazone was prepared by the described procedure,[4,10)] mp 97—99 °C (lit,[4)] mp 97—98 °C). UV $\nu_{\max}$ (dioxan) 278 nm (ε: 11500), $\nu_{\max}$ (CH_3OH) 281 nm (ε: 23000), $\nu_{\max}$ (CCl_4) 288 nm (ε: 24000); MS, *m/e* (rel. intensity) 196 (M^+, 100%).

Benzophenone Acetylhydrazone (2). Benzophenone hydrazone (1.8 g) and acetic anhydride (7 ml) in pyridine (10 ml) were stirred for 63.5 h at room temperature. After the addition of methanol, the solvent was removed by the addition of benzene and the residue was dissolved in chloroform. The organic layer was washed with 2 mol dm^{-3}-hydrochloric acid and water successively and dried (Na_2SO_4). After removal of the solvent, the residue was recrystallized from diethyl ether to afford benzophenone acetylhydrazone (1.64 g), mp 106—107.5 °C. Found: C, 74.84; H, 5.57; N, 11.50%. Calcd for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76%. UV $\nu_{\max}$ (dioxan) 286 nm (ε: 18700); $\nu_{\max}$ (CH_3OH) 281 nm (ε: 23000); $\nu_{\max}$ (CCl_4) 288 nm (ε: 24000); IR, 3179 (NH), 1688 (NHCO), 1332, 1311, 1290, 1127, 1020, 954, 784, and 770 cm^{-1}; MS, *m/e* (rel. intensity) 238 (M^+, 60%), 196 (100), and 195 (89).

4-Methoxybenzophenone Hydrazone (3). 4-Methoxybenzophenone (3 g) and hydrazine hydrate (15 ml) in ethanol (30 ml) were refluxed for 22 h. A part of the solvent was removed and the crystals which appeared were collected by filtration, (1.77 g). These were a 2:3 mixture of *E* and *Z* isomers, judged by the NMR spectrum, but recrystallization from ethanol twice afforded a more abundant single isomer, mp 95—96.5 °C, which gave a single peak due to the methoxyl at τ 6.24 (lit,[5)] α-form, mp 95—96 °C). Found: C, 74.15; H, 6.29; N, 12.32%. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 11.38%. UV $\nu_{\max}$ (dioxan) 278 nm (ε: 15000); $\nu_{\max}$ (CH_3OH) 278 nm (ε: 17400); $\nu_{\max}$ (CCl_4) 279 nm (ε: 12600); IR 3422 and 3309 (NH_2), 1609, 1251, 1073, 1028, and 838 cm^{-1}. MS, *m/e* (rel. intensity) 226 (M^+, 100), 195, and 128 (50).

4-Methoxybenzophenone Acetylhydrazone (4). The hydrazone **3** (1.5 g) and acetic anhydride (5 ml) in pyridine (7.5 ml) were stirred for 18 h at room temperature. After work-up as usual, the residue was recrystallized from acetone to yield the acetylhydrazone (1.47 g), mp 98—99 °C. Found: C, 71.65; H, 6.01; N, 10.51%. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44%. UV $\nu_{\max}$ (dioxan) 285 nm (ε: 18800); $\nu_{\max}$ (CH_3OH) 287 nm (ε: 22400); $\nu_{\max}$ (CCl_4) 289 nm (ε: 17500); IR 3180 (NH), 1665 (CONH), 1605, 1507, 1334, 1303, 1243, 1169, 1128, 1037, 843, 779, and 698 cm^{-1}. MS, *m/e* (rel. intensity) 268 (M^+, 79), 226 (78), and 225 (100).

4-Methylbenzophenone Hydrazone (5). 4-Methylbenzophenone (3 g) and hydrazine hydrate (15 ml) in ethanol (30 ml) were refluxed for 10 h. A part of the solvent was removed and the crystals which appeared were collected by filtration to yield the hydrazone (2.90 g). This was a 2:1 mixture of *E* and *Z* isomers, judged by the NMR spectrum. Recrystallization from ethanol twice afforded a more abundant single isomer, which showed a single peak due to the methyl (τ 7.57), mp 87.5—88.5 °C (lit,[6)] mp 80—81 °C). UV $\nu_{\max}$ (dioxan) 277 nm (ε: 12000); $\nu_{\max}$ (CH_3OH) 272 nm (ε: 12000); $\nu_{\max}$ (CCl_4) 276 (ε: 11800); IR 3360 (NH_2), 1579, 1076, and 832 cm^{-1}. MS, *m/e* (rel. intensity) 210 (M^+, 100), 195 (20), and 194 (20).

4-Methylbenzophenone Acetylhydrazone (6). The hydrazone **5** (1.5 g) and acetic anhydride (10 ml) in pyridine (15 ml) were stirred for 17 h at room temperature. After the addition of methanol, the solvent was removed by the addition of benzene. The residue was dissolved in diethyl ether. The solution was washed with water and dried (Na_2SO_4). The usual work-up gave a residue which was recrystallized from diethyl ether. (659 mg), mp 95—96 °C. Found: C, 76.37; H, 6.41; N, 11.05%. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10%. UV $\nu_{\max}$ (dioxan) 288 nm (ε: 19100); $\nu_{\max}$ (CH_3OH) 285 nm (ε: 19800); $\nu_{\max}$ (CCl_4) 289 nm (ε: 18400). IR 3180 (NH), 1674 (NHCO), 1336, 1309, 1297, 1113, 1020, 960, 832, and 778 cm^{-1}. MS, *m/e* (rel. intensity) 252 (M^+, 71%), 210 (98), and 209 (100).

Photolysis of Benzopenone Acetylhydrazone (2) in the Presence of Oxygen with Monochromatic Light (286±8 nm). *In Carbon Tetrachloride*: Benzophenone acetylhydrazone (**2**) (30 mg) in purified carbon tetrachloride[19] (4 ml) saturated with oxygen in a quartz vessel was placed in the chamber of a CRM-FA grating spectro-irradiator and was irradiated. The progress of the reaction was monitored by UV spectroscopy. The intensity of the absorption maximum at 288 nm gradually diminished during irradiation and after 110 h the absorption maximum nearly vanished. The NMR spectrum also showed that the signals of the starting material were replaced by those of the product (see text). The solvent was evaporated and the residue was purified by preparative TLC with a 1:1 mixture of benzene and diethyl ether to afford benzophenone (18 mg). A small amount of a more polar unidentified compound (3 mg) was obtained.

In Dioxan: Benzophenone acetylhydrazone (100 mg) in dioxan (Dotite Spectrosol, Wako, Japan) (4 ml) was irradiated with 286±8 nm wavelength light for 168 h. The absence of the hydroperoxide in the solution was proved by TLC and the absence of the parent ketone was confirmed by the NMR spectrum of the product after evaporation of the solvent.

Photolysis of 4-Methoxybenzophenone Acetylhydrazone (4) in the Presence of Oxygen with Monochromatic Light (288±8 nm). 4-Methoxybenzophenone acetylhydrazone (**4**) (30 mg) in purified carbon tetrachloride (4 ml) saturated with oxygen in a quartz vessel was irradiated for 43 h as for benzophenone acetylhydrazone. After removal of the solvent, the residue showed two spots in TLC (benzene). This was subjected to preparative TLC to afford two fractions. The more mobile fraction (22 mg) was nearly pure 4-methoxybenzophenone. The less mobile fraction (few mg) was unidentified gum.

Photolysis of 4-Methylbenzophenone Acetylhydrazone (6) in the Presence of Oxygen with Monochromatic Light (294±8 nm). 4-Methylbenzophenone acetylhydrazone (**6**) (30 mg) in purified carbon tetrachloride (4 ml) saturated with oxygen in a quartz vessel was irradiated for 48 h, as done for benzophenone acetylhydrazone. After removal of the solvent, the residue showed two spots on TLC (benzene), but the less mobile spot was very weak. Preparative TLC of the residue afforded two fractions. The more mobile fraction (19 mg) was nearly pure 4-methylbenzophenone. The less mobile fraction (6 mg) was an unidentified gum.

Photolysis of Benzophenone Hydrazone (1) in Dioxan in the Presence of Oxygen with Vycor-filtered Light. Benzophenone hydrazone (**1**) (500 mg) in dioxan (220 ml) was irradiated with a Hanovia 450-W high pressure Hg arc with a Vycor-filter until the starting material disappeared (24 h). After removal of the solvent, the oily residue was subjected to preparative TLC with benzene to afford three fractions. The most mobile fraction (120 mg) was diphenylmethane and the next mobile fraction (28 mg) was benzophenone. The 3rd fraction (194 mg) was still a mixture, which was subjected to preparative TLC with a 3:1 benzene and hexane. Three developments afforded major two fractions. The more mobile fraction (14 mg) was the azine **11** which was recrystallized from ethanol. The less mobile fraction (40 mg) was benzophenone.

Photolysis of Benzophenone Hydrazone (1) in the Presence of Oxygen with Monochromatic Light (270±8 nm). *In Carbon Tetrachloride*: Benzophenone hydrazone (30 mg) in purified carbon tetrachloride (4 ml) containing oxygen in a quartz vessel was irradiated with monochromatic light for 72 h, as done for *N*-acetylbenzophenone hydrazone (**2**). During the irradiation, a solid appeared in the solution. The solid (9 mg) was collected by filtration and was recrystallized from methanol to yield hydrazone hydrochloride **10**, mp 166—167 °C (lit,[10] mp 183 °C). This was identified by its mass spectrum. Removal of the solvent from the filtrate afforded the residue (17 mg). This was subjected to preparative TLC with a 4:1 benzene–diethyl ether mixture to afford four fractions. The most mobile fraction (15 mg) was identified as benzophenone azine (**11**), which was recrystallized from methanol (5 mg), mp 161—163 °C (lit,[4] mp 162—164 °C). The second and third mobile fractions (4 mg and 3 mg) were unidentified gums. The fourth fraction (5 mg) was recrystallized from methanol to yield crystals (**12**), mp 230—232 °C. UV ν_{max} (CCl_4) 307 and 280 nm (inflexion); ν_{max} ($CHCl_3$) 1707 and 1111 cm^{-1}; MS, *m/e* (rel. intensity) 418 (M^+, 2), 223 (15), and 196 (100).

In Methanol: Benzophenone hydrazone (**1**) (2 mg) in methanol (Dotite Spectrosol, Wako, Japan) (4 ml) was irradiated with monochromatic light (273±8 nm). Irradiation for 5 h completed the photo-decomposition. After evaporation of the solvent, the residue was subjected to preparative TLC with a 4:1 benzene and diethyl ether mixture to afford seven fractions. All the fractions except the most mobile one was very minor. The most mobile fraction was again subjected to preparative TLC with a 1:3 hexane and benzene mixture to afford more mobile diphenylmethane and less mobile benzophenone. Both compounds were identified by comparisons of the UV spectra and the TLC behaviors with those of the authentic materials.

Photolysis of 4-Methoxybenzophenone Hydrazone (3) in the Presence of Oxygen with Monochromatic Light (277±8 nm). The hydrazone (20 mg) in carbon tetrachloride (3 ml) containing oxygen was photolyzed for 20 h. The solid (11 mg) which separated was collected and recrystallized from methanol–diethyl ether to afford hydrochloride **12** (2 mg), mp 127—130 °C. The residue (13 mg) obtained by evaporation of the filtrate was subjected to preparative TLC with 1:5 hexane and benzene to afford three fractions. The most mobile fraction (1.5 mg) was azine **13** which was identified by a comparison with the specimen prepared by a ground state reaction. The second mobile fraction (5 mg) was 4-methoxybenzophenone. The least mobile fraction (7.5 mg) was an unidentified gum.

Photolysis of 4-Methylbenzophenone Hydrazone (5) in the Presence of Oxygen with Monochromatic Light (287±8 nm). The hydrazone (30 mg) in carbon tetrachloride (4 ml) was photolyzed for 11 h. The solid (11 mg) which separated was collected and recrystallized from methanol to afford hydrochloride **15** (5 mg), mp 138—139 °C. The residue (20 mg) obtained by the evaporation of the filtrate of the photolyzed solution was subjected to preparative TLC with a 4:1 benzene and diethyl ether mixture to afford two fractions. The mobile fraction was again purified by preparative TLC with a 5:1 benzene and hexane mixture to afford the azine **16** (14 mg), which was identified by a comparison with the authentic specimen prepared by a ground state reaction.

Preparation of 4-Methoxybenzophenone Azine (13). 4-Methoxybenzophenone (400 mg), hydrazine hydrate (0.3 ml), and potassium hydroxide (1 g) were refluxed in ethanol (3 ml) for 20 h. A part of the solvent was removed and the solution was extracted with chloroform. The chloroform solution was neutralized with 2 mol dm^{-3} hydrochloric acid, washed with water, and dried (Na_2SO_4). Evaporation of the solvent left the residue which was purified by preparative TLC with a 1:5 hexane and benzene mixture to afford an oily azine **15** (450 mg). This azine could not be induced to crystallize. IR (CCl_4) 1614, 1516, 1398, 1458, 1308, 1249, 1176, 1042, 724, and 698 cm^{-1}.

Preparation of 4-Methylbenzophenone Azine (15). 4-Methylbenzophenone (400 mg), hydrazine hydrate (0.3 ml) and potassium hydroxide (1 g) in ethanol (3 ml) were refluxed for 3 h. A part of the solvent was removed by a rotary evaporator and the solution was extracted with dichloromethane. The dichloromethane solution was worked up as done for 4-methoxybenzophenone azine. The product was purified by preparative TLC with a 1:5 hexane and benzene mixture to afford an oily azine **15** (69 mg). This was recrystallized from methanol-diethyl ether (31 mg), mp 137—138 °C. IR 1607, 1588, 1322, 1303, 1177, 823, 767, 718, and 694 cm^{-1}.

Attempted Autoxidation of Benzophenone Acetylhydrazone (2). In the Presence of Hydrogen Peroxide and Oxygen. Benzophenone acetylhydrazone (60 mg) in benzene (10 ml) and 30% hydrogen peroxide (1 drop) were stirred under air for 288 h at room temperature. TLC showed that no product other than the starting material was present in the solution.

In the Presence of Oxygen: Benzophenone acetylhydrazone (100 mg) in benzene (0.6 ml) was bubbled with oxygen and the solution was stirred for 96 h in an atmosphere of oxygen at room temperature. After removal of the solvent, the residue was recrystallized from diethyl ether to afford the starting material (26 mg). Removal of the solvent left a residue which was subjected to preparative TLC with a 1:3 benzene and dichloromethane to afford two fractions. The more mobile fraction (39 mg) was examined by the NMR spectrum, which showed no aromatic protons. The less mobile fraction (30 mg) was the starting material.

Benzophenone Diacetylhydrazone (7). Benzophenone hydrazone (2.014 g) and acetic anhydride (10 ml) in pyridine (10 ml) were stirred for 20 h at 70—80 °C. After the addition of methanol, the reaction mixture was worked up as done for the preparation of benzophenone acetylhydrazone. After removal of the solvent, the residue was subjected to column chromatography (Wako gel C-200; 45 g). Elutions with benzene and benzene containing increasing amounts of chloroform afforded two fractions. The less polar fraction (1.845 g) was recrystallized from diethyl ether to afford benzophenone diacetylhydrazone, mp 121—124 °C. Found: C, 72.86; H, 5.66; N, 9.81%. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99%; UV ν_{max} (MeOH) 208 nm (ε: 25000), and 245 nm (ε: 16000); ν_{max} (dioxan) 253 nm (ε: 14000).

Photolysis of Benzophenone Diacetylhydrazone (7) in the Presence of Oxygen with Monochromatic Light (266±8 nm) in Carbon Tetrachloride. Benzophenone diacetylhydrazone (**7**) (30 mg) in purified carbon tetrachloride (3 ml) in a quartz vessel was placed in the chamber of a CRM-FA grating spectroirradiator and was irradiated. The progress of the reaction was monitored by TLC, which showed the disappearance of the starting material after 90 h. After evaporation of the solvent, the residue was subjected to preparative TLC (Merck, silica gel 60F-254) with a 1:1 mixture of benzene and diethyl ether to afford two fractions. The more mobile fraction (15 mg) was benzophenone and the other (5 mg) was benzophenone acetylhydrazone.

We thank Mrs. T. Okayama for the measurements of NMR spectra.

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14) Benzophenone hydrazone and the *N*-acetyl derivative showed neither detectable fluorescence nor phosphorescence in EPA matrix at 77 K as in other compounds having a C–N double bond in which *syn-anti* isomerization is possible; quantum yields of the emissions were lower than 10^{-6}. We are grateful to Drs. T. Takemura and K. Fujikawa of Research Insitute of Applied Electricity, Hokkaido University, for their help in the measurements of the emission spectra.

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