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PHOTOINDUCED REACTIONS—XXVIII

COMPETITION BETWEEN INTRAMOLECULAR HYDROGEN ABSTRACTION AND FRAGMENTATION IN THE PHOTOREACTION OF HINDERED AROMATIC KETONES AND A CORRELATION WITH THE MASS SPECTRA[1]

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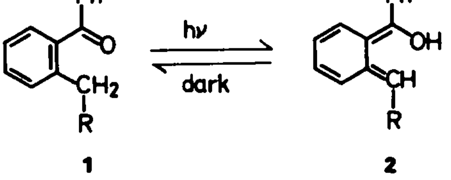
Abstract—The photoreactions of various alkyl 2,4,6-trimethylphenyl ketones bearing a sterically hindered CO group have been investigated. Depending upon the bulkiness of the alkyl side chain, two types of reactions have been observed. Intramolecular hydrogen abstraction leading to formation of a novel benzocyclobutenol is predominant with a less bulky alkyl side chain and fragmentation leading to a carbonyl–alkyl bond fission with a more bulky one. A correlation is found between the photoreactions and the mass spectrometric decomposition of the ketones. These photoreactions have been interpreted in terms of stereoelectronic requirements for the hydrogen abstraction from the n,π* triplet state. Unusual photoreduction of 2,4,6-trimethylbenzophenone is also reported.

It is well known that *o*-alkylbenzophenones of type **1** do not undergo usual photoreduction leading to pinacols even in hydrogen-donating solvents but result in the formation of photoenols **2** which revert to the parent ketones in the dark.[2,†] The photochemical disappearance of *o*-methylbenzophenone (**1**; R = H) is very slow as $\phi = 0{\cdot}01$.[2d] Analogous photoenolization of other *o*-alkylaryl ketones has been reported,[3,4] although irradiation of 2,4- or 2,5-dimethylacetophenones yields the corresponding pinacol and a diaroylethane which is considered to be formed presumably *via* a photoenol of type **2**.[5] In view of recent observations[6] concerning the steric effect on photochemical behavior of aliphatic and alicyclic ketones, it appeared worthwhile to investigate the photoreaction of highly hindered aromatic ketones such as **3**, where photoenolization might be difficult because of their steric environment.



1 **2**

Irradiation of 2,4,6-trimethylacetophenone (**3a**) in isopropyl alcohol using a high-pressure mercury lamp filtered through Pyrex resulted in the formation of an isomeric product in 70% yield. Its IR spectrum shows an OH band but no CO band. The NMR

[†] Recently, Heindel *et al.*[2e] have reported that photoreduction of 2-methylbenzophenones indeed occurs in isopropyl alcohol to give the corresponding pinacols in competition with photoenolization.

spectrum exhibits a singlet at δ 6·68 (two aromatic protons), three singlets at δ 2·27, 2·22 (two aromatic Me's), and 1·64 (an aliphatic Me), and an AB quartet at δ 3·25 and 3·01 (two protons, $J = 13$ Hz). On pyrolysis at 200° the product reverted to the starting ketone **3a** in essentially quantitative yield. The mass spectrum, which is virtually the same as that of the starting ketone **3a**, also indicates that the product has a tendency to revert to **3a**. From the above results, a benzocyclobutenol structure **4a** was assigned for the photoproduct.

Under similar conditions, 2,4,6-trimethylpropiophenone (**3b**) yielded the corresponding benzocyclobutenol **4b** in 63% yield, whose chemical and spectral properties were quite analogous to those of **4a**. Irradiation of 2,4,6-trimethylisobutyrophenone (**3c**) in isopropyl alcohol also gave the corresponding benzocyclobutenol **4c** in 61% yield, and as a byproduct 2,4,6-trimethylbenzoic acid (**5**) was isolated in 7% yield. The former product exhibits similar properties to those of **4a** and **4b**.

The photoreaction of 2,4,6-trimethylpivalophenone (**3d**), which has a very bulky alkyl side chain, was somewhat complex. Upon irradiation in isopropyl alcohol, it gave a mixture of products which was found, by TLC analysis, to consist of at least seven compounds. The main products were found to be 2,4,6-trimethylbenzoic acid (**5**) and isobutylene both of which were obtained in 48% yield. The corresponding benzocyclobutenol could not be detected in this case. Irradiation in benzene of **3d** also gave the trimethylbenzoic acid **5** in 46% yield. On the other hand, irradiation in methanol gave 35% of **5** and a benzocyclobutenol **4e** in 4% yield.

The results clearly indicate that the photochemical behavior of the aromatic ketones **3** bearing two Me groups in both *ortho* positions is different from that of *o*-methylphenyl ketones **1** which usually photoenolize to **2**, and that the course of reaction is affected by the steric environment of the CO group of **3**, namely, as the CO group becomes sterically more hindered, the benzocyclobutenol formation is more suppressed and the fragmentation to 2,4,6-trimethylbenzoic acid (**5**) becomes more important. The degree of the steric hindrance of the CO group in the trimethylphenyl ketones **3** can be estimated from the CO stretching band and from the chemical shift of the *ortho* Me group whose NMR signal appears at δ 2·17 for **3a**, **3b** and **3c** and at δ 2·06 for **3d** (Table 1), whereas the *ortho* Me signal of *o*-methylbenzophenone appears at δ 2·23. It is known that the shift toward higher magnetic field is due to noncoplanarity of the CO group with benzene ring.[7]

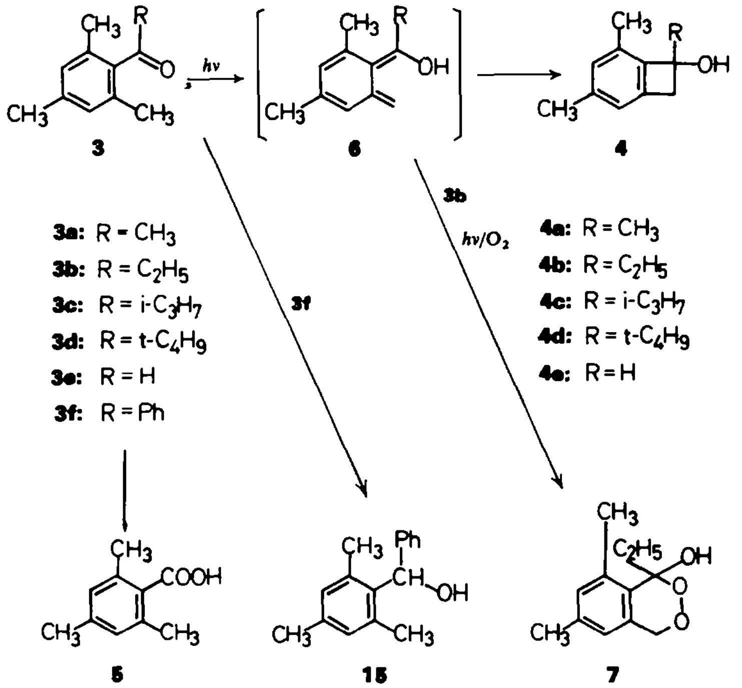
Although long chain aliphatic ketones bearing a γ-H atom are known to form cyclobutanols by photochemical intramolecular hydrogen abstraction,[8] the present results provide the first example of photochemical formation of benzocyclobutenols from *o*-methylphenyl ketones. For the benzocyclobutenol formation from **3** the following three pathways (Eqns 1, 2, and 3) may be considered.

$$\mathbf{3} \xrightarrow[n,\pi^*]{h\nu} \underset{\text{(singlet)}}{[\mathbf{3}]^{*S}} \rightarrow \mathbf{4} \qquad (1)$$

$$\mathbf{3} \xrightarrow[n,\pi^*]{h\nu} \underset{\text{(singlet)}}{[\mathbf{3}]^{*S}} \rightarrow \underset{\text{(triplet)}}{[\mathbf{3}]^{*T}} \rightarrow \mathbf{4} \qquad (2)$$

$$\begin{tikzcd} \mathbf{3} \arrow[r, "h\nu"] & {[\mathbf{3}]^{*S}} \arrow[r] & {[\mathbf{3}]^{*T}} \arrow[r] & \text{photoenol } \mathbf{6} \arrow[r] \arrow[lll, bend left] & \mathbf{4} \end{tikzcd} \qquad (3)$$

As demonstrated by Wagner and Hammond[9] and by Dougherty[10] in the case of cyclobutanol formation from long chain aliphatic ketones, both the singlet (Eq. 1) and triplet (Eq. 2) excited states of **3**, possibly by n,π* excitation, may be responsible for the γ-hydrogen abstraction leading directly to **4**. In order to obtain information on the multiplicity of the excited state, quenching experiments were carried out. The photochemical benzocyclobutenol formation from **3a** in isopropyl alcohol was efficiently quenched by a triplet quencher, piperylene. Therefore, the pathways (Eqs. 2 and 3) involving the triplet excited state of **3a** are more favorable, although the first pathway (Eq. 1) cannot be rigorously ruled out. The results obtained in the quenching experiments do not conflict with the third pathway (Eq. 3). In this pathway, the triplet excited state of **3** is converted to a photoenol **6** which then reverts thermally to the ketone **3** or cyclizes to the benzocyclobutenol **4** either thermally or photochemically. Zwicker *et al.*,[2b] using a flash photolysis technique, have detected triplet state intermediates in the photoenolization of *o*-benzylbenzophenone (**1**; R = Ph) to **2** (R = Ph), and they have concluded that the enol is not formed directly from the n,π* singlet.



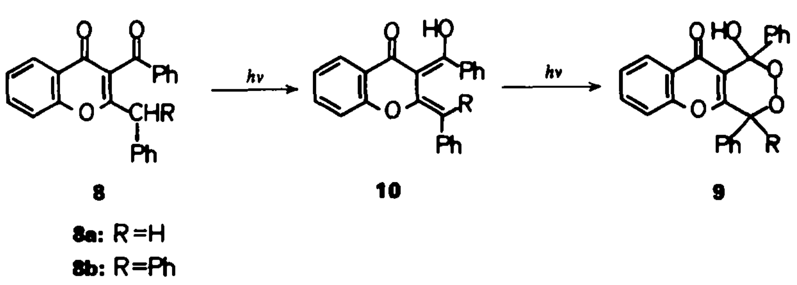


TABLE 1. SPECTRAL DATA AND PHOTOCHEMICAL REACTIONS OF THE 2,4,6-TRIMETHYLPHENYL KETONES **3**

Ketones **3**	Mass spectral peak			Chemical shift of 2- and 6-methyl (δ)	$\nu_{C=O}$ (cm^{-1})	Product yield (%)	
	rel. int.		ratio of $M^+/(M-R)^+$				
	M^+	$(M-R)^+$				**4**	**5**
3a: R = Me	33	100	0·33	2·17	1695	70	—
3b: R = Et	9	100	0·09	2·17	1695	63	—
3c: R = *i*-Pr	3	100	0·03	2·17	1693	61	7
3d: R = t-Bu	2	100	0·02	2·06	1687	—	48
3e: R = H	71	100	0·71	—	—	33	14
3f: R = Ph	123	100	1·23	1·98	—	—[a]	—
Pivalophenone	5	100	0·05	—	—	—	—[b]

[a] 2,4,6-Trimethylbenzhydrol (**15**) was obtained in 50% yield.

[b] Hydrobenzoin (**14**) resulted from Type I cleavage was obtained in 42% yield.

In the early stage of this investigation it was considered that photoenol **6** may not be formed from **3** because of steric repulsion between the 6-Me and the alkyl groups (R in formula **6**) but a benzocyclobutenol may be formed directly from the excited state of **3**, however, the following evidence demonstrates that photoenolization of **3** does indeed occur. First, 2,4,6-trimethylisobutyrophenone (**3c**), recovered after insufficient irradiation in MeOD, contained about two deuterium atoms in the Me groups at the 2- and 6-positions.† Second, the benzocyclobutenol **4c** was stable under the irradiation conditions and did not revert to the starting ketone **3c**. Third, irradiation of 2,4,6-trimethylpropiophenone (**3b**) in cyclohexane in the presence of oxygen afforded an oxygen adduct **7** in 65% yield.

The peroxide nature of the adduct was confirmed by its ability to generate iodine from potassium iodide. The IR spectrum shows an OH band at 3450 cm^{-1} and no CO band. The NMR spectrum exhibits two singlets at δ 6·95 and δ 6·75 (two vinyl protons), an AB-type quartet at δ 5·95 and δ 4·77 (J = 15 Hz; methylene protons), a broad singlet at δ 3·55 (OH), two singlet at δ 2·47 and δ 2·30 (two aromatic Me's), a quartet at δ 2·07 (J = 7 Hz, $\underline{CH_2}$-Me), and a triplet at δ 0·68 (J = 7 Hz), CH_2—$\underline{CH_3}$).

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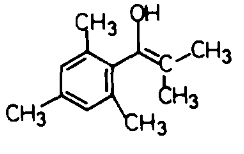
† Simultaneously, the isopropyl-methine hydrogen was completely exchanged by a further deuterium atom. The result shows that another type of photoenolization (formula i) occurs during irradiation of **3c**. Isobutyrophenone itself did not undergo such a photoenolization under the same conditions and was recovered unchanged. A similar type of photoenolization of acetophenone has been reported, although the irradiation was done in the presence of phenol.[5]



i

From these spectral data and by considering the analogous transformations of 2-benzyl- and 2-benzhydryl-3-benzoylchromones (**8a** and **8b**) to oxygen adducts (**9a** and **9b**) under similar conditions,[11]† a cyclic peroxide structure **7** is proposed for the oxygen adduct. Henderson and Ullman[11] demonstrated that the formation of peroxide **9** resulted from the photochemical oxygenation of photoenol intermediate **10** analogous to **6**. As suggested by these authors, the formation of peroxides **7** can be interpreted by the attack of singlet oxygen[13] which might be generated from ground state triplet oxygen by an energy transfer from the excited triplet **3b**.

In spite of the above results which indicate the formation of photoenol **6** in the course of the photoreaction of **3**, one cannot differentiate between two pathways (Eqs 2 and 3) for the formation of benzocyclobutenol **4** because of reversibility between **3** and **6** under the reaction conditions. However, from the fact that 2,4,6-trimethylpivalophenone (**3d**) did not give the corresponding benzocyclobutenol **4d** but 2,4,6-trimethylbenzoic acid (**5**), it appears that the third pathway (Eq. 3) is favored over the second pathway (Eq. 2). If the reaction proceeds by the second pathway, a benzocyclobutenol **4d** would be also expected to form from **3d**. In other words, it is expected that photoenol **6d** is so sterically crowded that it cannot be formed from the triplet state of **3d**. In fact, 2,4,6-trimethylpivalophenone recovered from the reaction mixture after insufficient irradiation in MeOD did not contain any deuterium. This clearly indicates that 2,4,6-trimethylpivalophenone (**4d**) does not form photoenol **6d** but undergoes mainly fragmentation to 2,4,6-trimethylbenzoic acid (**5**) and isobutylene. It, therefore, may be concluded that the photoenol **6** is the intermediate in the formation of the benzocyclobutenol **4** as shown in Eq. 2. An analogous benzocyclobutene formation from an *o*-quinone dimethide intermediate, which is formed from various types of compounds either photochemically or thermally, has been reported.[14] The facile formation of the benzocyclobutenol **4** from the photoenol **6** can be easily rationalized by the sterically crowded structure of the latter which relieves its steric hindrance by the transformation into the former.[14a] However, data available at present cannot distinguish between two pathways, photochemical or thermal, from **6** to **4**.

TABLE 2. QUENCHING EXPERIMENT FOR THE PHOTOCHEMICAL DISAPPEARANCE OF **3d**

Concentration (mol/l.)		**3d** Remaining after 3·5 hr Irradiation (%)
3d	Piperylene	
$0{\cdot}5 \times 10^{-3}$	0	34
$0{\cdot}5 \times 10^{-3}$	1×10^{-2}	86
$0{\cdot}5 \times 10^{-3}$	4×10^{-2}	95

We next investigated the mechanism of the fragmentation of 2,4,6-trimethylpivalophenone (**3d**) leading to 2,4,6-trimethylbenzoic acid (**5**) and isobutylene. This reaction was also efficiently quenched by a triplet quencher, piperylene (Table 2). The quenching experiment and the fact that **3d** did not undergo photoenolization suggest that **3d** undergoes Type I cleavage, mostly from its triplet excited state, leading

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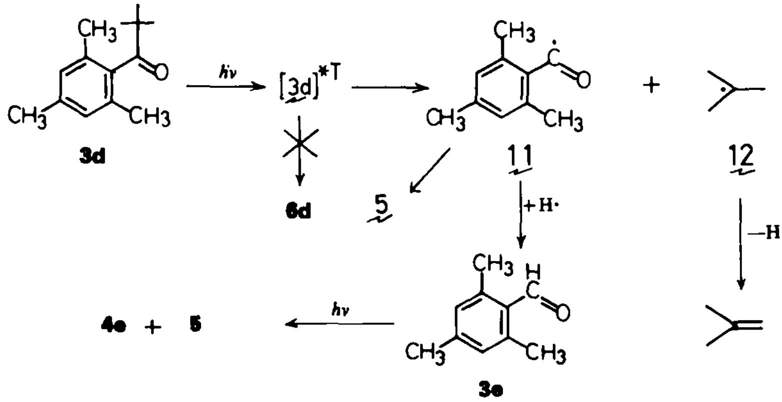
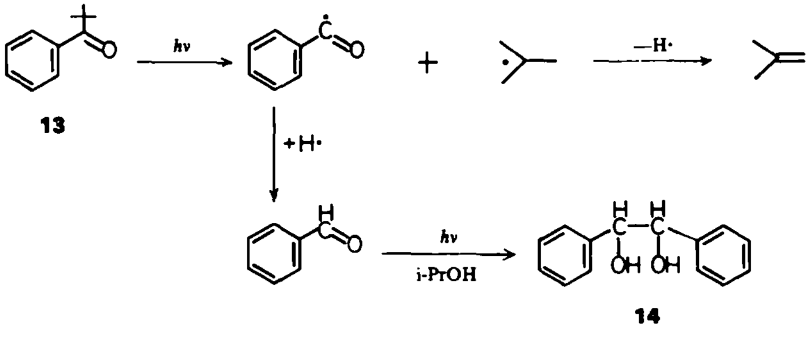
† An analogous oxygen-adduct formation from 2-methylacetophenone was recently reported.[12]

to the 2,4,6-trimethylbenzoyl radical **11** and t-butyl radical **12**. A similar Type I cleavage of t-butyl alkyl ketones was recently reported by Yang and Feit,[6a] who proposed that both n,π^* triplet and singlet excited states are responsible for the reaction. As shown in Scheme 1, the t-butyl radical **12** loses an H atom to give isobutylene. On the other hand, the benzoyl radical **11** may abstract an H atom from the solvent or the starting material **3d** to give 2,4,6-trimethylbenzaldehyde **3e** which is photochemically oxidized with oxygen contained in the nitrogen gas to give 2,4,6-trimethylbenzoic acid (**5**)† or is photochemically cyclized to a benzocyclobutenol **4e**.

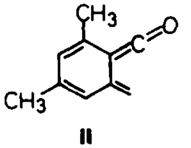
SCHEME 1



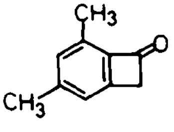
SCHEME 2



† For the formation of mesitoic acid (**5**) from **3c** and **3d**, possible pathways involving a ketene (ii) and a benzocyclobutenone (iii) intermediates were also considered. However, these possibilities were eliminated by the fact that no methyl mesitoate was detected in the photolysis of **3d** in methanol and that, in the IR spectrum of the photolyzed mixture of **3d** in benzene, no band near 2100 nor 1780 cm^{-1} corresponding to ii and iii was observed. Furthermore, the direct formation of **5** from the benzoyl radical **11** should be also considered.



ii



iii

In fact, the intermediary formation of 2,4,6-trimethylbenzaldehyde (**3e**) was supported by the fact that **3e**, upon irradiation under similar conditions in isopropyl alcohol, gave the benzocyclobutenol **4e** and 2,4,6-trimethylbenzoic acid (**5**) in 33 and 14% yield, respectively. This was also supported by the photolysis of pivalophenone (**13**) itself which underwent Type I cleavage in isopropyl alcohol to give isobutylene (40%) and hydrobenzoin (**14**; 42%). A pathway involving benzaldehyde as an intermediate is illustrated in Scheme 2.

The above two type of reactions, intramolecular cyclization and fragmentation of the trimethylphenyl alkyl ketones **3** can be also interpreted by a stereoelectronic concept for hydrogen abstraction reactions by the n,π^* triplet state of alkyl ketones.^{6b,15} According to Turro and Weiss,^{6b} the H atom on the γ-C atom can facilely form a 6-membered transition state in which the C—H bond axis is directed toward the half-vacant n orbital of the CO oxygen atom. Two extreme conformations for the n,π^* excited state of 2,4,6-trimethylphenyl alkyl ketones **3** are illustrated in Fig. 1. The conformation **a** of Fig. 1 meets such a stereo-electronic requirement for the intramolecular hydrogen abstraction of **3a**, **3b**, and **3c** (in part) leading to the benzocyclobutenols **4** *via* the photoenol **6**, although it is assumed that **3a**, **3b**, and **3c** have somewhat distorted conformations (non-coplanarity of the benzene and CO groups) in the ground state judging from the chemical shift of Me groups at 2- and 6-positions (see above).

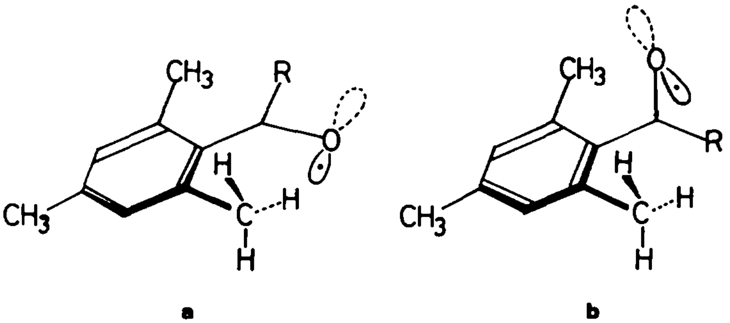
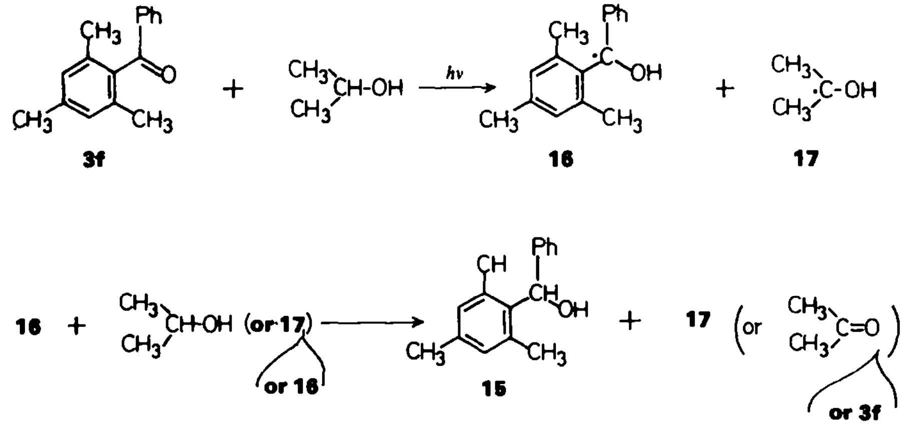


Fig. 1

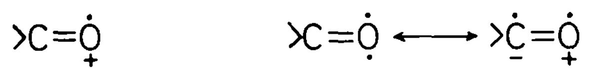
On the other hand, the chemical shift of the corresponding Me groups and the IR band of the CO group of **3d** (Table 1) indicate that **3d** may have conformation **b** in its excited state. Such a conformation would not undergo intramolecular hydrogen abstraction leading to benzocyclobutenol **4e** but does undergo Type I cleavage leading to 2,4,6-trimethylbenzoic acid. This argument was further supported by the unusual photoreduction of 2,4,6-trimethylbenzophenone (**3f**) which seems to have conformation **b** in its excited state. Irradiation of **3f** in isopropyl alcohol with a high-pressure mercury lamp through Pyrex gave 2,4,6-trimethylbenzhydrol (**15**) as the major product (50% yield). The trimethylbenzophenone **3f** recovered after insufficient

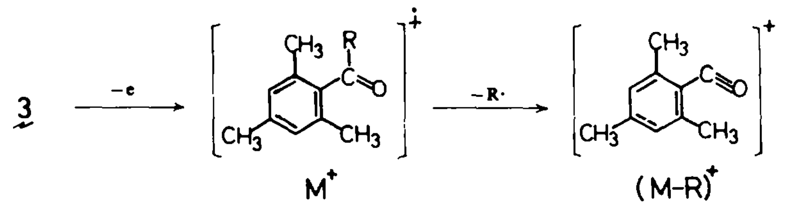
SCHEME 3



irradiation in MeOD did not contain any deuterium as observed in the case of 2,4,6-trimethylpivalophenone (3d).† The formation of **15** from **3f** is rationalized by a pathway illustrated in Scheme 3. The n,x^* excited‡ state of **3f** undergoes neither intramolecular hydrogen abstraction nor Type I cleavage but abstracts an H atom from the solvent molecule to form a ketyl radical **16**. The ketyl radical thus formed further abstracts an H atom from the solvent molecule or the dimethylhydroxymethyl radical **17** to give 2,4,6-trimethylbenzhydrol (**15**) but does not dimerize to the corresponding pinacol because of steric hindrance.

Finally, we wish to mention a correlation between the photoreactions and the mass spectra of the aromatic ketones reported in this paper. Recently, similarities between the photochemical behavior of certain organic compounds and their





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† Hammond *et al.* reported that, in the flash photolysis of 2,4,6-trimethyl-4′-methoxybenzophenone in benzene, a transient was formed with absorption maxima near 400 mμ and the color of the solution persisted for approximately 30 min. The transient was assigned to the photoenol of 2,4,6-trimethyl-4′-methoxybenzophenone.[16] On the contrary, we observed a yellow color in the photolysis of 2,4,6-trimethylbenzophenone in monodeuteriomethanol but deuterium was not found in recovered 2,4,6-trimethylbenzophenone (3f).

‡ The possibility that the reactive excited state of **3f** is the π,π^* triplet cannot be excluded.

principal fragmentation on electron impact have drawn much attention.[17] In particular, photochemical reactions resulting from the n,π* excited state of CO compounds have correlated well with their mass fragmentations.[17a, 17b] Such correlations are considered to be attributable to a similarity between the electronic structures of the molecular ions (**18**) and the n,π* excited state (**19**) of CO compounds. In the present case, a competition between hydrogen abstraction and fragmentation reactions was compared with the ratio of $M^+/(M\text{-}R)^+$ in the mass spectra of the trimethylphenyl ketones **3**.

The results summarized in Table 1 indicate that as the R group becomes bulkier the yield of the benzocyclobutenol **4** decreases and the fragmentation leading to 2,4,6-trimethylbenzoic acid (**5**) becomes more important, although the correlation is not quantitative. The chemical shifts for the 2- and 6-Me groups and the IR frequencies of the CO group (Table 1) are also correlated to the competition reaction. Thus, a lower CO frequency and a higher magnetic shift, both of which indicate a more hindered CO group, compare predominantly with the photochemical fragmentation. 2,4,6-Trimethylbenzophenone (**3f**) does not undergo Type I cleavage in accordance with the highest ratio of $M^+/(M\text{-}R)^+$ but rather an unusual photoreduction because of its highly hindered nature. Pivalophenone (**13**) has a low ratio of $M^+/(M\text{-}R)^+$ and it easily undergoes Type I cleavage.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were obtained on a Japan Spectroscopic Co. Model IRS spectrometer. The NMR spectra were recorded on a Japan Electron Optics C-60-H spectrometer with TMS as an internal standard. Elemental analyses were performed by Elemental Analysis Center of Kyoto University. Mass spectra were recorded by Mass spectrometric analysis laboratory, Pharmaceutical Science, Kyoto University. All irradiations were made with a 450-W high press Hg vapor lamp (Ushio Type UM 450) surrounded by a Pyrex water-cooling jacket under bubbling N_2 unless otherwise indicated.

Photolysis of 2,4,6-*trimethylbenzaldehyde* (**3e**)

A soln of **3e**[18] (2·00 g) in 400 ml isopropyl alcohol was irradiated, until the starting material was not detected by TLC (2 hr). The reaction mixture was evaporated under reduced press to give a slightly yellow viscous oil which was dissolved in benzene and passed through a silica gel column (40 g). Elution with benzene–$CHCl_3$ (1:1) yielded **4e** (664 mg, 33%) as white crystals. Recrystallization from pet ether gave colorless needles: m.p. 91–92°; IR (Nujol) 3250 cm^{-1} (OH); NMR ($CDCl_3$) δ 6·72 (m, 2, aromatic protons), 5·25, 3·53, 2·91 (ABX, 3, $J_{AB} = 14$ Hz, $J_{AX} = 4$ Hz, $J_{BX} \leq 1$ Hz), 2·30 (s, 3, $C\underline{H}_3$), 2·25 (s, 3, $C\underline{H}_3$), and 1·95 ppm (s, 1, $O\underline{H}$). (Found: C, 80·64; H, 8·28. Calc. for $C_{10}H_{12}O$: C, 81·04; H, 8·16%).

Further elution with $CHCl_3$ gave **5** (316 mg, 14%) as colorless crystals: m.p. 155°, which was identified by a comparison of the IR spectrum with that of an authentic sample.[19]

Pyrolysis of 2,4-*dimethylbicyclo*[4.2.0]*octa*-1,3,5-*triene*-8-*ol* (**4e**)

Compound **4e** (70 mg) was placed in a microtesttube and maintained at 200° in an oil bath for 10 min. The resulting light brown oil was identified as **3e** by a comparison of the IR spectrum with that of an authentic sample and a TLC analysis.

Photolysis of 2,4,6-*trimethylacetophenone* (**3a**)

A soln of **3a**[20] (2·00 g) in 450 ml isopropyl alcohol was irradiated as described for 42 hr. Removal of the solvent under reduced press gave a slightly yellow residue which was dissolved in benzene and chromatographed on a silica gel column (40 g). Elution with benzene yielded the unreacted **3a** (504 mg, 25%) as a colorless oil which was identified by a comparison of the IR spectrum with that of **3a** and by a TLC analysis.

Further elution with benzene gave **4a** (1·07 g, 70% based on recovered **3a**) as a white solid. Recrystallization from pet. ether gave colorless plates: m.p. 58–59°; IR (Nujol) 3250 cm^{-1} (OH). The mass spectrum showed a parent peak at *m/e* 162 and the fragmentation pattern was virtually identical with that of **3a**. (Found: C, 81·19; H, 8·98. Calc. for $C_{11}H_{14}O$: C, 81·44; H, 8·70%).

Pyrolysis of 2,4,8-*trimethylbicyclo*[4.2.0]*octa*-1,3,5-*triene*-8-*ol* (**4a**)

Compound **4a** (30 mg) was placed in a microtesttube and maintained at 200° in an oil bath for 15 min. The resulting light brown oil was identified as **3a** by a comparison of the IR spectrum with that of an authentic sample, and by p GLPC analysis.

Photolysis of 2,4,6-*trimethylpropiophenone* (**3b**)

A soln of **3b**[21] (2·00 g) in 450 ml isopropyl alcohol was irradiated as described (44 hr). Removal of the solvent gave a slightly yellow oil which was dissolved in benzene and chromatographed on a silica gel column (40 g). Elution with benzene gave the unreacted **3b** (100 mg) which was identified by a comparison of the IR spectrum with that of an authentic sample. Further elution with benzene–$CHCl_3$ (1 : 1) yielded **4b** (1·20 g, 63% based on recovered **3b**) as a slightly yellow oil which on distillation gave a colorless viscous oil: b.p. 70° (10^{-3} mm); IR (Nujol) 3350 cm^{-1} (OH); NMR ($CDCl_3$) δ 6·67 (s, 1, vinyl protons), 3·22, 2·92 (ABq, 2, $J = 13$ Hz), 2·26 (s, 3, $C\underline{H}_3$), 2·20 (s, 3, $C\underline{H}_3$), 1·92 (q, 2, $J = 7$ Hz, $C\underline{H}_2$—CH_3), and 0·96 ppm (t, 3, $J = 7$ Hz, CH_2—$C\underline{H}_3$). (Found: C, 81·47; H, 9·20. Calc. for $C_{12}H_{16}O$: C, 81·77; H, 9·15%).

Pyrolysis of 2,4-*Dimethyl*-8-*ethylbicyclo*[4.2.0]*octa*-1,3,5-*triene*-8-*ol*

Compound **4b** (25 mg) was placed in a microtesttube and maintained at 200° in an oil bath for 15 min. The resulting light brown oil was identified as **3b** by a comparison of the IR spectrum with that of an authentic sample and by a GLPC analysis.

Photolysis of 2,4,6-*trimethylisobutyrophenone* (**3c**)

A soln of **3c**[22] (2·00 g) in 250 ml isopropyl alcohol was irradiated as described, until the starting material was not detected by a TLC analysis (48 hr). Evaporation of the solvent gave a slightly brown residue which was dissolved in benzene and chromatographed on a silica gel column (40 g). Elution with benzene–$CHCl_3$ (1 : 1) yielded **4c** (1·22 g, 61%) as slightly yellow oil which on distillation gave a colorless viscous oil: b.p. 75° (10^{-3} mm); IR (Nujol) 3400 cm^{-1} (OH); NMR ($CDCl_3$) δ 6·65 (s, 2, aromatic protons), 3·25, 2·80 (ABq, 2, $J = 14$ Hz), 2·5 ~ 1·8 (obscure sept, 1, $J = 7$ Hz, $\underline{CH}(CH_3)_2$), and 0·95 ppm (d, 6, $J = 7$ Hz, $CH(\underline{CH}_3)_2$). (Found: C, 82·06; H, 9·54. Calc. for $C_{13}H_{18}O$: C, 82·06; H, 9·54%).

Further elution with $CHCl_3$ gave **5** (140 mg, 7%) as crystals which was identified by a comparison of the IR spectrum with that of an authentic sample[19] and by a TLC analysis.

Pyrolysis of 2,4-*dimethyl*-8-*isopropylbicyclo*[4.2.0]*octa*-1,3,5-*triene*-8-*ol* (**4c**)

Compound **4c** (100 mg) was placed in a microtesttube and maintained at 200° in an oil bath for 10 min. The resulting light brown oil was identified as **3c** by a comparison of the IR spectrum with that of an authentic sample and by a TLC analysis.

Photolysis of 2,4,6-*trimethylpivalophenone* (**3d**)

A. *In methanol.* A soln of **3d**[23] (1·50 g) in 450 ml MeOH was irradiated as described until the starting material was not detected by a GLPC (7 hr). Evaporation of the solvent under reduced press gave a slightly brown residue which was directly analyzed by GLPC on a column of silicon DC 550 at an oven temp 130°, but methyl 2,4,6-trimethylbenzoate[24] was not detected. The residue was dissolved in pet. ether–benzene (1 : 1) and chromatographed on a silica gel column (40 g). Elution with $CHCl_3$ yielded **4d** (44 mg, 4%) as a white solid which was identified by a comparison of the IR spectrum, TLC and GLPC with those of an authentic sample. Further elution with $CHCl_3$ yielded **5** (424 mg, 35%) as light brown crystals which was identified by a comparison of the IR spectrum with that of an authentic sample[19] and by a TLC analysis.

B. *In isopropyl alcohol.* A soln of **3d** (2·00 g) in 450 ml isopropyl alcohol was irradiated as described. The exhaust gas was led into 10 ml of ice-cooled Br_2 in a 20 ml-testtube, until the starting material was not detected by GLPC (8 hr). The testtube contents were treated with an $NaHSO_3$aq and extracted with ether. The ether layer was washed with water, dried (Na_2SO_4) and evaporated to give 1,2-di-bromoisobutane[25] (895 mg, 47%) as a slightly brown oil which was identified by a comparison of the IR spectrum with that of an authentic sample and by a GLPC analysis. The reaction mixture was evaporated under reduced press to give a slightly brown residue which was dissolved in pet. ether–benzene (1 : 1) and chromatographed on a silica gel column (40 g). Elution with $CHCl_3$ yielded **5** (788 mg, 48%) as a solid. Recrystallization from cyclohexane gave colorless needles; m.p. 156–157°, which were identified by a comparison of the IR spectrum with that of an authentic sample[19] and by a TLC analysis.

C. *In benzene.* A soln of **3d** (2·00 g) in 300 ml benzene was irradiated, until the starting material was not detected by a TLC analysis (8 hr). The reaction mixture was treated in the same manner as in B. to give **5** (751 mg, 46%) as a major product, which was identified by a comparison of the IR spectrum with that of an authentic sample.

Photolysis of 2,4,6-trimethylbenzophenone (3f)

A soln of **3f**[26] (1·500 g) in 400 ml isopropyl alcohol was irradiated as described above (45 hr). Evaporation of the solvent under reduced press gave a slightly yellow residue which was dissolved in benzene–pet. ether (1:1) and chromatographed on a silica gel column (40 g). Elution with benzene–pet. ether (1:1) yielded the unchanged **3f** (100 mg, 6·6%) as a colorless oil which was identified by a comparison of the IR spectrum with that of an authentic sample and by a TLC analysis. Further elution with benzene gave **15** (691 mg, 50% based on recovered **3f**) as a colorless oil which was identified by a comparison of the IR spectrum with that of an authentic sample[27] and by a TLC analysis.

Photolysis of pivalophenone (13)

A soln of **13**[28] (3·00 g) in 450 ml isopropyl alcohol was irradiated under bubbling N_2. The exhaust gas was led into 10 ml Br_2 in a 20 ml-testtube placed in an ice-bath, until the starting material was not detected by TLC (9·5 hr.) The testtube contents were treated with $NaHSO_3$aq and extracted with ether. The ether layer was washed with water, dried (Na_2SO_4), and evaporated to give a slightly brown oil (3·31 g) which was found, by a GLPC analysis, to consist of four products. Among them the major product (40%) was found to be 1,2-dibromoisobutane.[25] Evaporation of the reaction mixture under reduced press gave a brown oil which was dissolved in benzene and chromatographed on a silica gel column (80 g). Elution with $CHCl_3$ **14** (850 mg, 42%) as crystals which was identified by a comparison of the IR spectrum with that of an authentic sample[29] and by TLC analysis.

Photolysis of 2,4,6-trimethylisobutyrophenone (3c) *in monodeuteriomethanol*

A soln of **3c** (350 mg) in 6 ml monodeuteriomethanol was placed in a 20 ml-Pyrex tube. N_2 gas was bubbled for 30 min and the tube was sealed with a glass stopper. The soln was irradiated externally with a 450-W high press Hg vapor lamp (Ushio Type UM 450) for 24 hr. Evaporation of the solvent under reduced press gave a slightly brown oil which was dissolved in benzene–pet. ether (1:1) and chromatographed on a silica gel column (10 g). Elution with benzene–pet. ether afforded the unreacted **3c** (120 mg) as a colorless oil which was identified by GLPC and TLC analyses; NMR ($CDCl_3$) δ 6·77 (s, 2, aromatic protons), 2·25 (s, 3, $\underline{CH_3}$), 2·17 (s, 4, $\underline{CH_3}$), and 1·15 ppm (s, 6, $CD(\underline{CH_3})_2$).

Photolysis of isobutyrophenone in monodeuteriomethanol

A soln of isobutyrophenone (350 mg) in 4 ml monodeuteriomethanol was irradiated as described (7 hr). Evaporation of the solvent under reduced press gave a slightly yellow oil which was dissolved in benzene–pet. ether (1:1) and chromatographed on a silica gel column (10 g). Elution with benzene–pet. ether (1:1) yielded the unreacted isobutyrophenone (243 mg) as a colorless oil which was identified by TLC and GLPC analyses. The NMR spectrum showed that no deuterium was incorporated into the unreacted starting material.

Photolysis of 2,4,6-trimethylpivalophenone (3d) *in monodeuteriomethanol*

A soln of **3d** (130 mg) in 3 ml monodeuteriomethanol was irradiated as described (10 hr). Evaporation of the solvent under reduced press gave a yellow oil which was dissolved in pet. ether and chromatographed on a silica gel column (10 g). Elution with pet. ether–benzene (1:1) gave unreacted **3d** (186 mg) which was identified by GLPC and TLC analyses. The NMR spectrum showed that no deuterium was incorporated into the unreacted starting material. The IR spectrum was completely identical with that of the starting material.

Photolysis of 2,4,6-trimethylbenzophenone (3f) *in monodeuteriomethanol*

A soln of **3f** (300 mg) in 2 ml monodeuteriomethanol was irradiated as described (16·5 hr). Evaporation of the solvent under reduced press gave a slightly yellow oil which was dissolved in pet. ether and chromatographed on a silica gel column (10 g). Elution with pet. ether–benzene (1:1) gave the unreacted **3f** (210 mg) which was identified by a TLC analysis. The NMR and mass spectra showed that no deuterium was incorporated into the unreacted starting material. The IR spectrum was completely identical with that of the starting material.

Photolysis of 2,4,6-trimethylacetophenone (**3a**) *in monodeuteriumethanol*

A soln of **3a** (350 mg) in 3 ml monodeuteriomethanol was irradiated as described (35 hr). Evaporation of the solvent under reduced press gave a slightly yellow oil which was dissolved in pet. ether and chromatographed on a column of silica gel (10 g). Elution with benzene–pet. ether (1 : 1) gave the unreacted **3a** (239 mg) which was identified by TLC and GLPC analyses; NMR ($CDCl_3$) δ 6·77 (s, 2, aromatic protons), 2·24 (s, 3, $\underline{CH}_3$), 2·40 (s, 3, $CO\underline{CH}_3$), and 2·17 ppm (s, 5, $\underline{CH}_3$).

Photolysis of 2,4,6-trimethylpropiophenone (**3b**) *in cyclohexane under oxygen atmosphere*

A soln of **3b** (2·00 g) in 400 ml cyclohexane was irradiated under bubbling O_2 (10 hr). Removal of the solvent under reduced press at 20° gave a viscous residue which was dissolved in benzene–pet. ether (1 : 1) and chromatographed on a silica gel column (40 g). Elution with benzene–pet. ether (1 : 1) gave the unreacted **3b** (790 mg, 39%) as a slightly yellow oil which was identified by comparison of the IR spectrum with that of an authentic sample and by a TLC analysis.

Further elution with benzene–$CHCl_3$ (1 : 1) gave the oxygen adduct 7 (931 mg, 65·6%) as white crystals: m.p. 66–68°; IR (Nujol) 3300 cm^{-1} (OH). (Found: C, 69·01; H, 7·62. Calc. for $C_{12}H_{16}O_3$: C, 69·23; H, 7·69%). This compound liberated I_2 on treatment with NaI in AcOH and decomposed explosively at 160°.

Quenching experiments

A. *2,4,6-Trimethylpivalophenone* (**3d**) *with* 1,3-*pentadiene in isopropyl alcohol.* 1,3-Pentadiene and isopropyl alcohol were distilled prior to use. Ketone **3d** (102 mg, 5×10^{-4} mol) was dissolved in 5 ml isopropyl alcohol and placed in a Pyrex tube. To two of the Pyrex tubes 1,3-pentadiene (690 mg; 10^{-3} mol) and (2·610 g; 4×10^{-2} mol) were added. One tube without any added 1,3-pentadiene was set aside as a control and the three tubes were placed on a cylindrical wall surrounding a 450-W high press Hg vapor lamp (Ushio Type UM 450) with a Pyrex water-cooling jacket. The tubes were irradiated for 3·5 hr. At the end of this time, 100 mg benzophenone was added to each of the tubes as an internal standard and the solvent was removed. The mixture was analyzed by GLPC on a DC-550 silicone on celite column at oven temp of 200° and He flow press of 1·6 Kg/cm^{-2}. The results obtained are summarized in Table 2.

B. *2,4,6-Trimethylacetophenone* (**3a**) *with* 1,3-*pentadiene in isopropyl alcohol.* A soln of **3a** (1·62 g, 10^{-2} mol) and 1,3-pentadiene (13·60 g, 0·2 mole) in 400 ml cyclohexane was irradiated under bubbling N_2 with a 450-W high-press Hg vapor lamp (Ushio Type UM 450) for 24 hr. In this case, GLPC analysis could not be used because the photoproduct **4a** was decomposed to the starting material **3a** during GLPC analysis. However, the TLC analysis of the reaction mixture showed no formation of **4a**. On the other hand, under the same conditions irradiation of **3a** without any added 1,3-pentadiene showed the formation of **4a** by a TCC analysis.

REFERENCES

[1] Part XXVII: T. Matsuura and M. Ikari, *J. Chem. Soc. Japan, Ind. Chem. Soc.* **72**, 179 (1969). Portions of the present work have appeared in a previous communication: T. Matsuura and Y. Kitaura, *Tetrahedron Letters* No. 34 3309 (1967).

[2] [a] N. C. Yang and C. Rivas, *J. Am. Chem. Soc.* **83**, 2213 (1961); [b] E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *Ibid.* **85**, 2671 (1963); [c] A. Beckett and G. Porter, *Trans. Faraday Soc.* **59**, 2051 (1963); [d] J. M. Pitts, Jr., H. W. Johnson and T. Kuwana, *J. Phys. Chem.* **66**, 2456 (1962); [e] N. D. Heindel, E. W. Sarver, and M. A. Pfau, *Tetrahedron Letters* 3579 (1968).

[3] G. Wettermark, *Photochem. Photobiol.* **4**, 621 (1965).

[4] M. Pfau, N. D. Heindel and T. F. Lemke, *C.R. Acad. Sci., Paris* **261**, 1017 (1965).

[5] H. D. Becker, *J. Org. Chem.* **32**, 2140 (1967).

[6] [a] N. C. Yang and E. D. Feit, *J. Am. Chem. Soc.* **90**, 504 (1968); [b] N. J. Turro and D. S. Weiss, *Ibid.* **90**, 2185 (1968).

[7] K. Maruyama, *Bull. Chem. Soc. Japan* **39**, 2722 (1966).

[8] For a review, see D. C. Neckers, *Mechanistic Organic Photochemistry* p. 177. Reinhold, New York, N.Y. (1967).

[9] P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.* **87**, 4009 (1965).

[10] T. J. Dougherty, *Ibid.* **87**, 4011 (1965).

[11] W. A. Henderson, Jr. and E. F. Ullman, *J. Am. Chem. Soc.* **87**, 3424 (1965).

[12] P. Yates, A. C. MacKay, and F. X. Garneau, *Tetrahedron Letters* 5389 (1968).

[13] C. S. Foote, *Accounts of Chem. Research* **1**, 104 (1968).

[14] [a] H. Hart, J. A. Hartlage, R. W. Fish and R. F. Rafos, *J. Org. Chem.* **31**, 2244 (1966); [b] G. Quinckert, W. W. Wiersdorf, M. Finke and K. Opetz, *Tetrahedron Letters* 2193 (1966); [c] M. P. Cava and A. A. Deana, *J. Org. Chem.* **25**, 1481 (1960); [d] Y. Odaira, K. Yamaji, and S. Tsutsumi, *Bull. Chem. Soc. Japan* **37**, 1410 (1964); and refs cited therein.

[15] N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold and A. Glick, *J. Am. Chem. Soc.* **89**, 3950 (1967).

[16] G. S. Hammond, W. G. Herkstroester and L. B. Jones, *J. Am. Chem. Soc.* **88**, 4777 (1966).

[17] [a] N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner and P. D'Angelo, *Ibid.* **87**, 4097 (1965); [b] J. N. Pitts, Jr., J. K. Foote and J. K. S. Wan, *Photochem. Photobiol.* **4**, 323 (1965); [c] F. W. McLafferty, *Analyt. Chem.* **31**, 82 (1956); [d] P. Brown, J. Kossanyi and C. Djerassi, *Tetrahedron* Suppl. I, **8**, 241 (1966); [e] S. Meyerson, I. Puskus and E. K. Fields, *J. Am. Chem. Soc.* **88**, 4974 (1966); [f] A. L. Burlingame, C. Fenselan, W. J. Richter, W. G. Dauben, G. W. Shaffer and N. D. Vietmeyer, *Ibid.* **89**, 3346 (1967); [g] M. M. Bursey, L. R. Dusold and A. Padwa, *Tetrahedron Letters* 2649 (1967); and refs cited therein.

[18] E. C. Horning, *Organic Syntheses* Coll. Vol. III; p. 549. Wiley, New York (1955).

[19] E. C. Horning, *Ibid.* Coll. Col. III p. 553 (1955).

[20] C. R. Noller and R. Adams, *J. Am. Chem. Soc.* **45**, 1889 (1924).

[21] A. Klages, *Ber. Dtsch. Chem. Ges.* **35**, 2255 (1902).

[22] A. Klages, *Ibid.* **37**, 928 (1904).

[23] H. Suzuki, H. Wada, K. Maruyama and R. Goto, *Bull. Chem. Soc. Japan* **39**, 1201 (1966).

[24] H. L. Goering, T. Rubin and M. S. Newman, *J. Am. Chem. Soc.* **76**, 787 (1954).

[25] M. S. Kharasch, W. Hered and F. R. Mayo, *J. Org. Chem.* **6**, 818 (1941).

[26] M. S. Kharasch, R. Morrison, W. H. Urry, *J. Am. Chem. Soc.* **66**, 368 (1944).

[27] P. S. Bailey and J. G. Burr, Jr., *Ibid.* **75**, 2951 (1953).

[28] A. Haller and E. D. Bauer, *C.R. Acad. Sci., Paris*, **148**, 72 (1909).

[29] L. F. Fieser, *Experiments in Organic Chemistry* (3rd Edition), p. 175. Heath, Boston (1957).