Tetrahedron. Vol 27, pp. 1597 to 1606. Pergamon Press 1971. Printed in Great Britain

PHOTOINDUCED REACTIONS—XLVIII

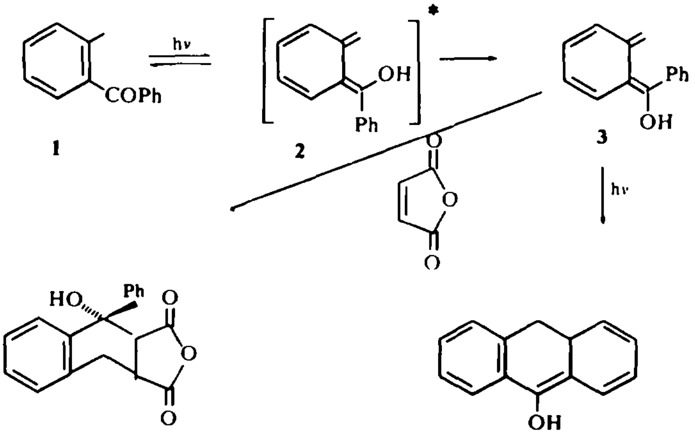
STERIC AND SUBSTITUENT EFFECTS ON PHOTOREACTIONS OF 2,4,6-TRIALKYLPHENYL KETONES[1]

Y. Kitaura and T. Matsuura
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, Japan

(*Received in Japan* 2 *October* 1970; *Received in the UK for publication* 17 *November* 1970)

Abstract—Steric and substituent effects on the photochemical reaction of 2,4,6-trialkylphenyl ketones has been investigated. A striking steric effect was observed in the photoreaction of 2,4,6-trialkylbenzophenones. The more hindered the carbonyl group, the more readily photoenolization occurs resulting in intramolecular cyclization leading to benzocyclobutenol derivatives. With 2,4,6-trialkylacetophenones, such a steric effect was not observed in the cyclization and photoenolization reactions. These reactions have been interpreted in terms of the excited state nature responsible for these reactions.

It has been shown that *o*-methylbenzophenone (**1**) undergoes reversible photo enolization to give **3** *via* the n, π* triplet state, accompanied by slow photoreduction in hydrogen-donating solvents.[2] A transient species (λ_{max} 405 mμ) having a lifetime of 10 sec was obtained on flash photolysis of **1** in cyclohexane and was assigned the enol structure **3**. However, flash photolysis of a solution of *o*-methylbenzophenone (**1**) in isopropyl alcohol, produced the long-lived (> 1 hr) yellow species[3] (absorption at 340–440 mμ) to which the intramolecularly cyclized structure **4** was assigned.[4] In the photoenolization reaction of *o*-methylbenzophenone (**1**), the geometry of the photoenol product **3** is the transoid structure which is opposite to that required for internal abstraction of a methyl hydrogen atom by the excited carbonyl oxygen in **1**.

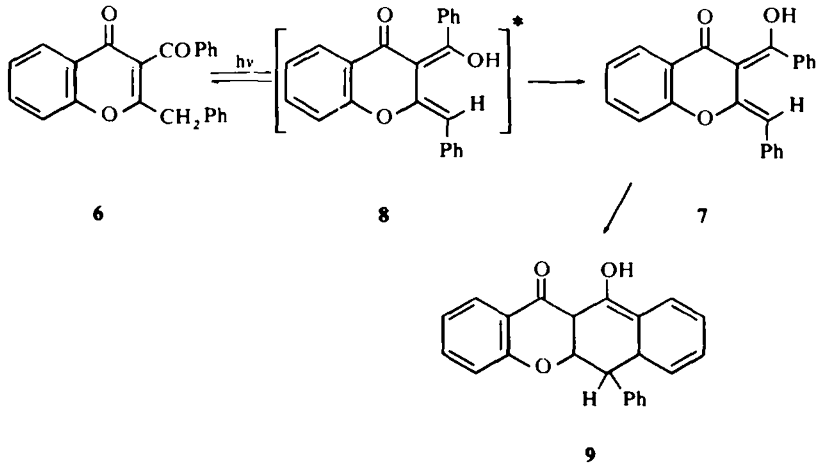


1 **2** **3**

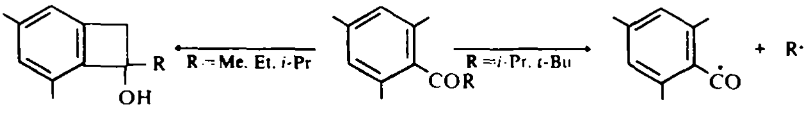
5 **4**

The geometry shown in **3** was also demonstrated by the ability of **3** to undergo photocyclization to give **4**[4] and by the stereochemistry of its maleic anhydride adduct **5**.[5] Since the photoenol **3** appeared to be formed in one photochemical step through a triplet of the ketone **1**, the reaction must lead directly to an excited (presumably triplet) photoenol **2** capable of subsequent geometrical isomerization to **3**.

Similarly, a chromone **6** reacts through its triplet state to give a geometrically rearranged photoenol **7** which may also be formed through an intermediate triplet photoenol **8** and undergoes photocyclization to give **9** *via* excited singlet state of **7**.[6]



It has been reported that alkyl 2,4,6-trimethylphenyl ketones bearing a sterically hindered group, depending on the bulkiness of alkyl side chain, undergo two types of the photoreactions: one, intramolecular photocyclization *via* a photoenol intermediate to give benzocyclobutenols, and the other, fragmentation leading to a carbonyl-alkyl bond fission (Scheme 1).[7] These photoreactions have been interpreted in terms of stereoelectronic requirements[8] for the hydrogen abstraction from the n, π^* triplet.



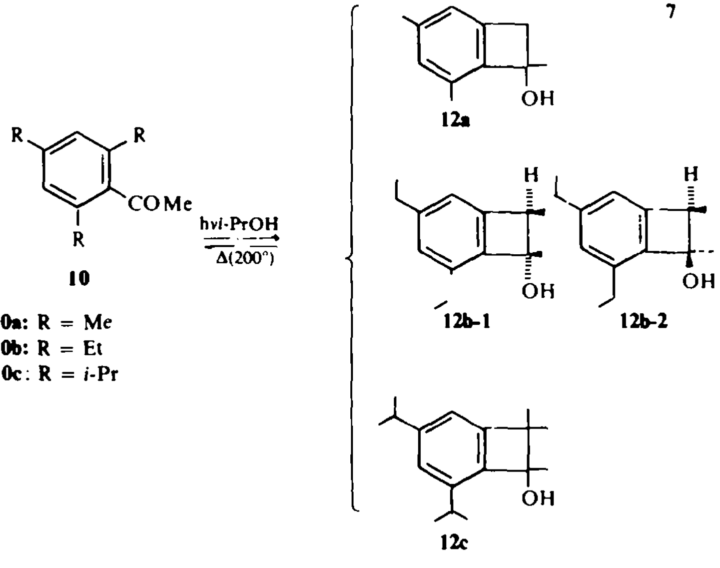
Scheme 1

In view of this observation concerning the steric effects on photochemical behaviour of ketones, it was of interest to investigate further the photoreaction of hindered aromatic ketones such as **10** and **11**. In this paper we report (1) the effect of noncoplanarity of the CO group and benzene ring in **10** and **11** on the rate of the cyclization reaction, (2) the correlation of the excited state nature responsible for cyclization with steric factors and, (3) the stereochemistry of photoenol intermediates and cyclization products.

RESULTS AND DISCUSSION

Photolysis of 2.4.6-trialkylphenyl methyl ketones **10**. Irradiation of 2.4.6-trimethylacetophenone (**10a**) gave a benzocyclobutenol **12a** in 70% yield.[7] Irradiation of 2.4.6-triethylacetophenone (**10b**) in isopropyl alcohol under nitrogen using a high-pressure mercury vapour lamp (Pyrex) gave a single benzocyclobutenol derivative (**12b-1** or **12b-2**) in 78% yield. Its IR spectrum shows an OH band at 3350 cm^{-1} and no CO absorption. The NMR spectrum ($CDCl_3$) exhibits three singlets at δ 6·38 (two aromatic protons), 2·15 (one OH proton) and 1·50 (an aliphatic Me proton), two quartets at δ 3·32 (one benzyl proton, $J = 7$ Hz) and 2·60 (four benzyl protons, $J = 7$ Hz), two triplets at δ 1·20 (Me proton, $J = 7$ Hz) and 1·23 (Me proton, $J = 7$ Hz) and a doublet at δ 1·25 (Me proton, $J = 7$ Hz). On pyrolysis at 200°, the product reverted to the starting material **10b** in essentially quantitative yield. From the above results, a benzocyclobutenol structure **12b-1** or **12b-2** was assigned for the photoproduct. The same product was obtained in benzene cyclohexane. In all cases, the NMR spectra measured in four different solvents, $CDCl_3$, CCl_4, CD_3COCD_3 and CD_3SOCD_3, were quite similar, indicating that the photocylization of **10b** proceeds stereospecifically.

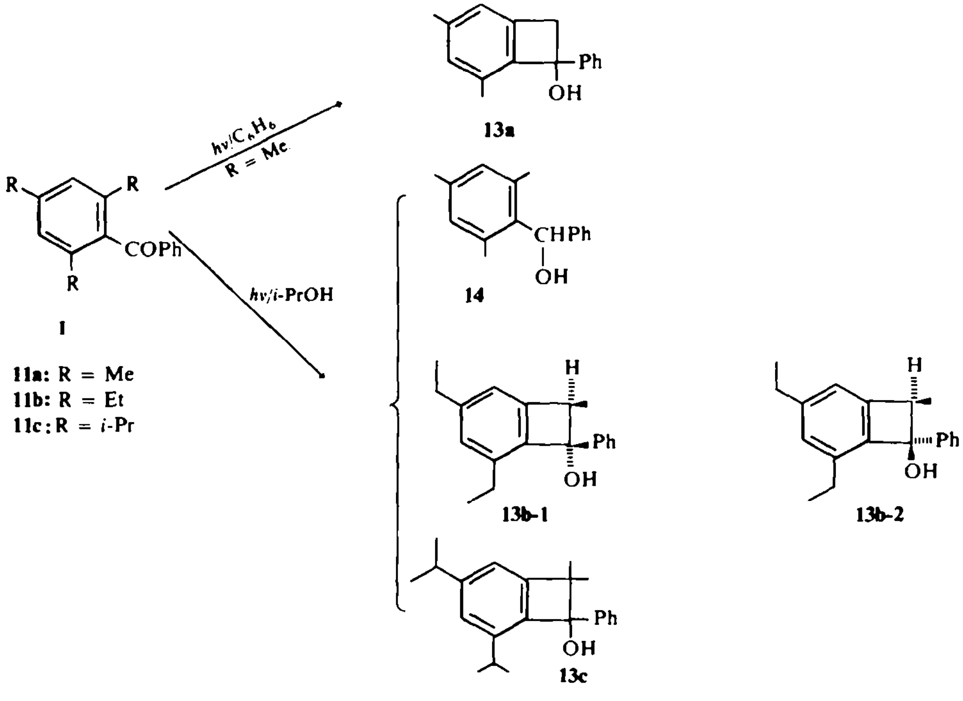
Under the similar conditions, 2.4.6-triisopropylacetophenone (**10c**) afforded the corresponding benzocyclobutenol **12c** in quantitative yield, whose chemical and spectral properties are analogous to those of **12a** and **12b**.



Irradiation of 2.4.6-trialkylbenzophenones **11**. Irradiation of 2.4.6-triethylbenzophenone (**11b**) in isopropyl alcohol under similar conditions resulted in the formation of an inseparable mixture of two isomeric products **13b-1** and **13b-2** (2:8) in 40% yield. The ratio of the products depended upon the solvent employed, as seen in Table 1. In cyclohexane, the isomer **13b-1** was exclusively obtained. The IR spectrum of **13b-1** shows an OH band at 3400 cm^{-1} and no CO absorption. The NMR spectrum exhibits three singlets at δ 7·23 (five aromatic protons), 6·95 (one aromatic proton) and 6·86 (one aromatic proton), three quartets at δ 3·58 (one benzyl proton, $J = 7$ Hz), 2·65 (two benzyl protons, $J = 7$ Hz) and 2·50 (two benzyl protons, $J = 7$ Hz), two triplets at δ 1·25 (Me proton, $J = 7$ Hz) and 1·15 (a Me proton, $J = 7$ Hz) and 1·15 (Me proton, $J = 7$ Hz) and a doublet at δ 0·81 (Me proton, $J = 7$ Hz). On pyrolysis at 200°, the product **13b-1** reverted to the starting material **11b** in essentially quantitative yield.

The other isomer **13b-2** exhibits an NMR spectrum similar to that of **13b-1**. The chemical shifts of methyl and methine hydrogens on the cyclobutene ring of the isomers provide compelling evidence for the stereochemical assignments. The resonances of methine and methyl hydrogens of **13b-2** appear at δ 2·43 and 1·33 ppm, respectively, while the corresponding resonances of **13b-1** at δ 3·58 and 0·81 ppm, respectively. The unusually high field shifts of methyl hydrogen of **13b-1** and of methine hydrogen of **13b-2** are postulated to arise from anisotropic shielding by the adjacent *cis*-phenyl ring. The results led us to assign structures **13b-1** and **13b-2** for these isomers.

Under similar conditions, 2,4,6-triisopropylbenzophenone (**11c**) afforded in quantitative yield the corresponding benzocyclobutenol **13c** whose chemical and spectral properties are analogous to those of **13b**. It has been previously shown that irradiation of 2,4,6-trimethylbenzophenone (**11a**) under the similar conditions



afforded 2,4,6-trimethylphenylbenzhydrol (**14**) in 50% yield instead of the corresponding benzocyclobutenol **13a**.[7] However, photolysis of **11a** in benzene was found to give, in 40% yield, the corresponding benzocyclobutenol **13a** whose structure was assigned from its chemical and spectral properties.

Photochemical deuterium exchange reaction of **10** *and* **11** *in monodeuteriomethanol.* The occurrence of the photoenolization in *o*-methylbenzophenone (**1**) was demonstrated by incorporation of deuterium into **1** during irradiation in MeOD.[2a] In view of the stereoelectronic requirement for hydrogen abstraction *via* the n,π* triplet state of alkyl ketones,[7, 8] the photoenolization of **10** and **11** can proceed efficiently when the C—H bond axis on α-carbon atom is directed toward the half-vacant n-orbital of the carbonyl oxygen atom. In the ground state conformation of **10a**, the twist angle between the plane of phenyl ring and CO group is about 80°,[9] and the plane of CO group of **11a** in solution is almost at right angles to that of mesityl ring and 40° to the plane of the phenyl ring.[10] Thus, it is of interest to see whether photoenolization of **10** and **11** bearing sterically a hindered CO group occurs or not.

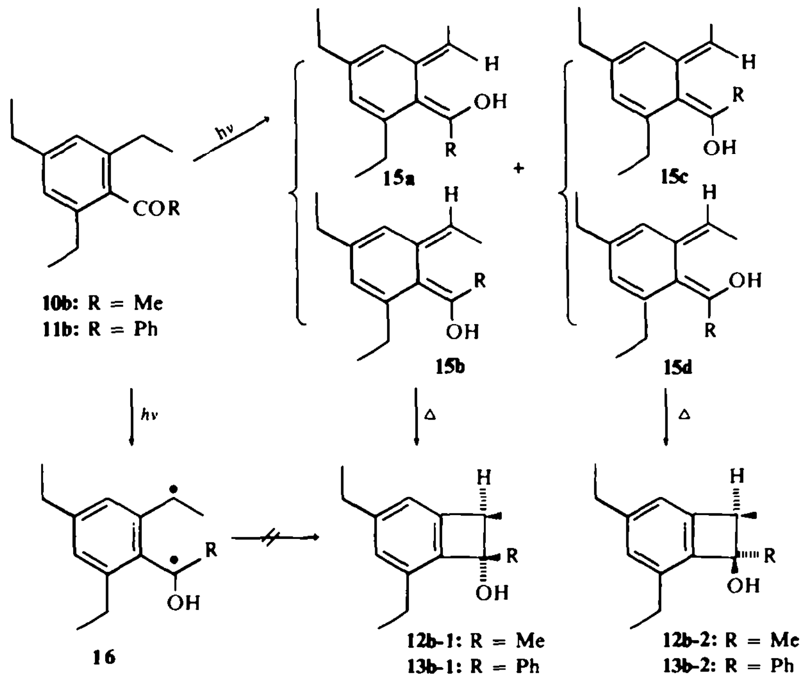
A 2×10^{-3} M solution of **10** and **11** in MeOD was irradiated under nitrogen in a merry-go-round apparatus. The deuterium enrichment in the recovered starting material was estimated by a mass spectroscopic analysis. The results are summarized in Table 2. The relative rates for the disappearance of **10** and **11** in benzene were also determined and the results are summarized in Table 2.

The excited state nature of **10** *and* **11**. The above results indicate that, in the case of acetophenone derivatives **10**, the efficiency of photoenolization and the rate of benzocyclobutenol formation are not apparently affected by the steric environment of the CO group. Although most of aromatic CO compounds with a low-lying π,π* state are not so reactive for photochemical reaction,[11] methylated acetophenones having low-lying π,π* triplet state show considerably photochemical reactivity.[12] Acetophenone itself exhibits a π,π* triplet state slightly above low-lying n,π* triplet state.[13] The energy level of π,π* triplets state falls and that of n,π* triplet state rises by introducing an electron donating Me substituent to the phenyl ring.[14] For example, *p*-methyl- and 3,4-dimethylacetophenones exhibit a n,π* triplet state slightly above the low-lying π,π* triplet state,[12] and the variation of n,π* character in the π,π* state of these compounds is thus attributed to the vibronic coupling of the π,π* triplet state with corresponding n,π* triplet state.[13, 15] Since the extent of the coupling between two states depends on the energy gap between them, the coupling increases as the energy gap decreases. Thus, as the electron donating property of 2,4,6-trialkyl substituents of **10** becomes stronger, the extent of the coupling between n,π* triplet state and π,π* triplet state may be more suppressed and the low-lying π,π* triplet may be less mixed with n,π* triplet state. The stereoelectronic requirement postulated by Turro[8] need not exist in the photochemical reaction occurring *via* π,π* excited state. From the above mentioned consideration, it can be understood that the steric orientation of the half vacant n-orbital of the excited (n,π*) carbonyl cannot play an important role in the photocyclization of **10** having a strong π,π* character in their triplet state.

On the contrary, the remarkable steric effect was observed in the formation of photoenols and the rate of cyclization in the case of benzophenone derivatives **11**.

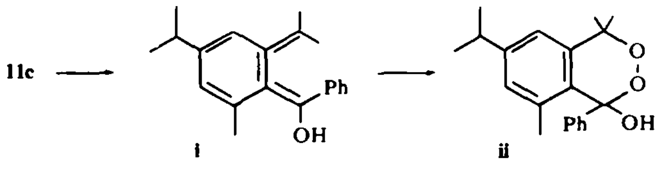
As the CO group becomes sterically more hindered, the formation of the photoenol takes place more readily and the rate of cyclization increases to a large extent.* This tendency is opposite to that required for the internal abstraction of a hydrogen on α-carbon atom of an alkyl side chain, in view of the stereoelectronic requirement for the hydrogen abstraction of carbonyl compounds occurring *via* n,π^* triplet state.[8] It has been suggested that the nonplanarity of the CO group and the phenyl ring in benzophenone introduces the possibility of strong vibronic coupling between π,π^* singlet state and σ,π^* singlet state which has strong spin-orbital coupling with n,π^* triplet state, and that the net effect is the increase of the π,π^* singlet character.[16]

Thus, the strong steric effect in the case of **11** may be rationalized by the following explanation: the more sterically hindered the CO group the more the excited state character responsible for the photoenol formation followed by cyclization decreases in the n,π^* triplet character, which requires a stereoelectronic factor, and the more the π,π^* singlet character increases which results in accelerating the rate of cyclization of **11**.



---

* Although the deuterium exchange of **11c** could not be observed because of its rapid cyclization (Table 2), the intermediate formation of photoenol **i** was confirmed by finding that **11c**, on irradiation in the presence of oxygen, gave an oxygen adduct **ii** in addition to **13c** (Experimental)



Stereochemistry of the photocyclization of **10b** *and* **11b**. As already mentioned, the photocyclization of **10b** proceeds stereospecifically to give a single benzocyclobutenol **12b-1** or **12b-2**, whereas that of **11b** is solvent dependent giving two stereoisomeric benzocyclobutenols **13b-1** and **13b-2** in various product ratios (Table 1). Considering the facile photochemical deuterium exchange reaction of **10b** and **11b** and their stereospecific photocyclization, the benzocyclobutenols must form *via* photoenol intermediate **15** but not *via* a radical intermediate **16** which may cyclize nonstereospecificically.[17] Four geometrically isomeric structures **15a**, **15b**, **15c** and **15d** can be written for such photoenol intermediates.

The Woodward-Hoffmann rule[17] predicts that, if the cyclization of **15** to benzocyclobutenols **12** proceeds *via* a thermal electrocyclic reaction, **15a** and **15b** will give **12b-1** or **13b-1** and **15c** and **15d** will give **12b-2** or **13b-2** (both conrotatory) and that, if the cyclization proceeds photochemically, **15a** and **15b** will give **12b-2** or **13b-2** and **15c** and **15d** will give **12b-1** or **13b-1** (both disrotatory). Although the available experimental data cannot distinguish between these two processes, it appears that the cyclization of photoenols **15** may proceed thermally inferring the analogous thermal cyclization of a 5,6-bismethylenecyclohexadiene.[19] The solvent dependence of the ratios of the stereoisomeric cyclobutenols **13b-1** and **13-2** may be due to the solvent effect on the distribution of geometrical isomers of photoenol **15**.

TABLE 1. SOLVENT EFFECT ON THE RATIO OF STEREOISOMERS OBTAINED FROM **11b**

Solvent	13b-1	13b-2
Cyclohexane	1·0	~0
Benzene	0·5	0·5
Acetonitrile	0·5	0·5
Isopropyl alcohol	0·2	0·8

TABLE 2. RELATIVE RATES FOR THE DISAPPEARANCE OF **10** AND **11** AND DEUTERIUM EXCHANGE DURING IRRADIATION

(Experimental)

Compound	Relative rate	Deuterium enrichment %
10a	1	11
10b	0·7	9
10c	0·7	4
11a	0·6	0[a]
11b	15	9
11c	180	--[b]

[a] See ref 7.

[b] The reaction was so fast that the starting material could not be recovered under the conditions.

EXPERIMENTAL

All m.ps were uncorrected. IR spectra were obtained on a Japan Spectroscopic Co., Model IRS spectrometer, 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, Faculty of Pharmaceutical Science, Kyoto University. All irradiations were made with a 450-W. high-pressure Hg vapour lamp (Ushio Type UM 450) surrounded by a Pyrex water-cooling jacket under bubbling N_2 unless otherwise indicated.

Irradiation of 2,4,6-triethylacetophenone (**10b**)

A. In isopropyl alcohol. A soln of **10b**[20] (1·500 g) in 400 ml isopropyl alcohol was irradiated for 40 hr. Evaporation of the solvent under reduced press gave a colourless oily residue which was dissolved in benzene and chromatographed on a silica gel column (60 g). Elution with benzene yielded the recovered **10b** (716 mg) as a colourless oil which was identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. Further elution with benzene afforded **12b** (612 mg, 78%) as a colourless oil which on distillation gave a colourless oil; b.p. 70° (10^{-3} mm); IR (neat) 3350 cm^{-1} (OH). (Found: C, 82·10; H, 10·16. Calcd. for $C_{14}H_{20}O$: C, 82·30; H, 9·87%).

B. In cyclohexane. A soln of **10b** (1·500 g) in 400 ml cyclohexane was irradiated for 29 hr. The mixture was evaporated under reduced press to give a slightly yellow oil which was dissolved in benzene and chromatographed on a silica gel column (60 g). Elution with benzene gave the unreacted **10b** (1013 mg) as a colourless oil which was identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. Further elution with benzene afforded **12b** (370 mg, 78%) as a colourless oil which was identified by a comparison of its IR spectrum with that of **12b** obtained above and by TLC analysis.

C. In benzene. A soln of **10b** (1·000 g) in 400 ml benzene was irradiated for 20 hr. Evaporation of the solvent under reduced press gave a brownish oily residue which was dissolved in light petroleum benzene (1:1) and chromatographed on a silica gel column (60 g). Elution with light petroleum benzene (1:1) gave the unreacted **10b** (600 mg) as a colourless oil which was identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. Further elution with benzene afforded **12b** (165 mg, 41%) as a colourless oil which was identified by a comparison of its IR spectrum with that of **12b** obtained above and by TLC analysis.

The product **12b** was placed in a test-tube and maintained at 200° in an oil bath for 15 min. The resulting slightly yellow oil was identified as **10b** by a comparison of its IR spectrum with that of an authentic sample and by GLPC analysis.

Irradiation of 2,4,6-triisopropylacetophenone (**10c**)

A soln of **10c**[21] (2·00 g) in 400 ml isopropyl alcohol was irradiated for 22 hr. The resulting mixture was evaporated under reduced press to give a crystalline residue which was dissolved in light petroleum benzene (1:1) and chromatographed on a silica gel column (60 g). Elution with light petroleum benzene (1:1) gave the unreacted **10c** (1·465 g) as colourless fine needles which were identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. Elution with benzene gave **12c** 245 mg, 46%) as colourless crystals which on recrystallization from aqueous MeOH gave colourless prisms: mp 73–75°: IR (Nujol) 3350 cm^{-1} (OH); NMR ($CDCl_3$) δ 6·91 (s, 1, aromatic proton), 6·80 (s, 1, aromatic proton), 3·05 (sept, 1, $J = 7$ Hz, $C\underline{H}Me_2$), 3·00 (sept, 1, $J = 7$ Hz, $C\underline{H}Me_2$), 2·00 (s, 1, $-O\underline{H}$), 1·56 (s, 3, $C\underline{H}_3$), 1·30 (d, 6, $CHMe_2$), and 1·25 (d, 6, $J = 7$ Hz, $CHMe_2$). (Found: C, 83·04; H, 10·68. Calc. for $C_{17}H_{26}O$: C, 82·87; H, 10·63%).

In the reaction mixture **12c** was detected as the sole product and no other product was detected by TLC analysis.

Irradiation of 2,4,6-triethylbenzophenone (**11b**)

A. In benzene. A soln of **11b**[22] (1·100 g) in 400 ml benzene was irradiated for 2 hr. The colourless soln immediately turned yellow and the yellow colour faded after 1 hr. The mixture was evaporated under reduced press to give a colourless viscous oily residue which was dissolved in light petroleum-benzene (1:1) and chromatographed on a silica gel column (60 g). Elution with light petroleum-benzene (1:1) was afforded a 1:1 mixture of **13b-1** and **13b-2** (945 mg, 86%) as a colourless oil which on distillation gave a colourless viscous oil: b.p. 92° (10^{-3} mm); IR (neat) 3400 cm^{-1}(OH). The product ratio was estimated by NMR analysis. (Found: C, 85·38; H, 8·36. Calc. for $C_{19}H_{22}O$: C, 85·67; H, 8·33%).

B. In cyclohexane. A soln of **11b** (1·000 g) in 400 ml cyclohexane was irradiated for 5 hr. The mixture was worked up as in A to give pure **13b-1** (910 mg) as a colourless viscous oil. The product **13b-1** (50 mg) was placed in a test-tube and maintained at 200° in an oil bath for 5 min. The resulting pale yellow oil was identified for **11b** by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis.

C. In acetonitrile. A soln of **11b** (1·00 g) in 400 ml acetonitrile was irradiated for 3 hr. A 1:1 mixture of **13b-1** and **13b-2** (980 mg, 98%) was obtained as a colourless viscous oil.

D. In isopropyl alcohol. A soln of **11b** (1·100 g) in 400 ml isopropyl alcohol was irradiated for 19 hr. A 1:4 mixture of **13b-1** and **13b-2** (440 mg, 40%) was obtained as a colourless viscous oil.

Irradiation of 2.4.6-*triisopropylbenzophenone* (**11c**)

A. In benzene. A soln of **11c**[22] (2·000 g) in 400 ml benzene was irradiated for 3 hr. The colourless soln immediately turned pale yellow and the colour faded after 30 min. Evaporation of the solvent under reduced press afforded **13c** (1·980 g, 99%) as a white solid which on recrystallization from light petroleum gave colourless fine needles; mp 100°; IR (Nujol) 3450 cm^{-1} (OH); NMR ($CDCl_3$) δ 7·25 (s, 5, aromatic protons), 7·05 (s, 1, aromatic proton), 6·85 (s, 1, aromatic proton), 2·97 (sept, 1, J = 7 Hz, $CHMe_2$), 2·85 (sept, 1, J = 7 Hz, $CHMe_2$), 2·35 (s, 1, $-O\underline{H}$), 1·45 (s, 3, $C\underline{H}_3$), 1·27 (d, 6, J = 7 Hz, $CH(C\underline{H}_3)_2$), 1·23 (d, 3, J = 7 Hz, $CH(C\underline{H}_3)_2$), 1·17 (d, 3, J = 7 Hz, $CH(C\underline{H}_3)_2$), and 0·82 ppm (s, 3, $C\underline{H}_3$). (Found: C, 85·41; H, 9·42. Calc. for $C_{21}H_{18}O$: C, 85·66; H, 9·15%).

The product **13c** (50 mg) was placed in a test-tube and maintained at 200° in an oil bath for 5 min. The resulting slightly yellow crystals were identified by a comparison of IR spectrum with that of an authentic sample and by TLC analysis.

B. In isopropyl alcohol. A soln of **11c** (2·000 g) in 400 ml isopropyl alcohol was irradiated for 10 hr. Evaporation of the solvent under reduced press gave a white solid which was dissolved in light petroleum-benzene (1:1) and chromatographed on a silica gel column (60 g). Elution with light petroleum-benzene (1:1) gave **13c** (1·943 g, 97%) as colourless crystals which were identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis.

C. In benzene under oxygen atmosphere. A soln of **11c** (2·000 g) in 400 ml benzene was irradiated under O_2 stream for 3 hr. Evaporation of the solvent under reduced press gave a pale yellow viscous oily residue which was dissolved in benzene and chromatographed on a silica gel column (60 g). Elution with benzene gave **13c** (1·710 g, 85%) as a white solid which was identified by a comparison of its IR spectrum. Elution with benzene gave an oxygen adduct (320 mg, 14%) as a white solid which on recrystallization from light petroleum gave colourless needles: mp 135–137°; IR (Nujol) 3450 cm^{-1} (OH); NMR ($CDCl_3$) δ 7·33 (s, 5, aromatic protons), 7·03 (d, 1, J = 2 Hz, aromatic proton), 6·97 (d, 1, J = 2 Hz, aromatic proton), 3·90 (broad s, 1, $O\underline{H}$), 3·25–2·55 (obscure sept, 2, J = 7 Hz $CHMe_2$), 1·75 (s, 3, $C\underline{H}_3$), 1·55 (s, 3, $C\underline{H}_3$), 1·27 (d, 6, J = 7 Hz, $CH(C\underline{H}_3)_2$), 1·07 (d, 3, J = 7 Hz, $CH(C\underline{H}_3)_2$) and 0·50 ppm (d, 3, J = 7 Hz, $CH(C\underline{H}_3)_2$). These spectral data are similar to that of an oxygen adduct obtained from 2,4,6-trimethylpropiophenone.[7] (Found: C, 77·48; H, 8·29. Calc. for $C_{22}H_{28}O_3$: C, 77·61; H, 8·29%).

Photochemical deuterium exchange reaction of **10** *and* **11** *in monodeuteriomethanol*

A 2 × 10^{-3} M soln of **10** and **11** in 2 ml monodeuteriomethanol (99% grade) was placed in a 20 ml Pyrex tube. N_2 gas was bubbled for 30 min before irradiation and the tube was sealed with a glass stopper. The tube was irradiated externally with a 450-W. high-pressure mercury vapour lamp (Ushio Type UM 450) in a merry-go-round apparatus for 20 hr. The mixture was evaporated and the residue was chromatographed on a silica gel column to give the unreacted **10** and **11** deuterium enrichment of which were estimated by mass spectroscopic analysis. The results obtained are summarized in Table 1.

Determination of the relative rate for the disappearance of **10** *and* **11** *in benzene*

A 2 × 10^{-3} M soln of **10** and **11** in 3 ml benzene 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 tube was irradiated externally with a 450-W. high-pressure mercury vapour lamp (Ushio Type UM 450) in a merry-go-round apparatus for 10 hr. GLPC analysis could not be applied for the estimation of the unreacted **10** and **11** due to the thermal decomposition of the photoproduct **12** and **13** to the starting material during analysis. The amount of the unreacted **10** and **11** was determined by the isolation using direct chromatography of the reaction mixture on a silica gel column. The results obtained are summarized in Table 1.

Irradiation of 2.4.6-*trimethylbenzophenone* (**11a**)

A soln of **11a** (1·00 g)[23] in 400 ml benzene was irradiated for 15 h. The resulting yellow soln was evaporated under reduced press to give a yellow brown oily residue which was dissolved in light petroleum ether (1 :1) and chromatographed on a silica gel column (60 g). Elution with benzene afforded **13a** (400 mg, 40%) as a colourless oil which on distillation gave a colourless viscous oil: b.p. 90° (10^{-3} mm); IR (neat) 3400 cm^{-1} (OH); NMR ($CDCl_3$) δ 2·65 (s, 5, aromatic protons), 3·20 (s, 2, aromatic protons), 6·53 (s, 2, benzyl proton), 7·50 (s, 1, $--\mathrm{O\underline{H}}$), 7·63 (s, 3, $--\mathrm{C\underline{H}_3}$), and 7·86 (s, 3, $-\mathrm{C\underline{H}_3}$). (Found: C, 85·31; H, 7·10. Calcd. $C_{16}H_{16}O$: C, 85·68; H, 7·19%).

The product **13a** was placed in a test tube and maintained at 200° in an oil bath for 15 min. The resulting slightly yellow oil was identified as **11a** by a comparison of its IR spectrum with that of an authentic sample and TLC analysis.

REFERENCES

[1] Part XLVII; T. Matsuura, Y. Hiromoto, A. Okada and K. Ogura, *Tetrahedron Letters* 3727 (1970)

[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] N. D. Heindel, E. W. Sarver and M. Pfau, *Tetrahedron Letters* 3579 (1968)

[3] A. Beckett and G. Porter, *Trans. Faraday Soc.* **59**, 2051 (1963)

[4] E. F. Ullman and K. R. Huffman, *Tetrahedron Letters* 1863 (1965)

[5] F. Nerdel and W. Brodowski, *Chem. Ber.* **101**, 1398 (1968)

[6] [a] K. R. Huffman, M. Loy and E. F. Ullman, *J. Am. Chem. Soc.* **87**, 5417 (1965);
[b] W. A. Henderson Jr., and E. F. Ullman, *Ibid.* **87**, 5424 (1965)

[7] T. Matsuura and Y. Kitaura, *Tetrahedron* **25**, 4487 (1969)

[8] N. J. Turro and D. S. Weiss, *J. Am. Chem. Soc.* **90**, 2185 (1968)

[9] [a] E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature, Lond.* **173**, 117 (1965);
[b] E. A. Braude and E. S. Waight, *Progr. Stereochem.* **1**, 126 (1954)

[10] P. H. Gore, *J. Chem. Soc.* (B) 714 (1967)

[11] [a] W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.* **83**, 2789 (1961);
[b] J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962);
[c] G. Porter and P. Suppan, *Trans. Faraday Soc.* **61**, 1664 (1965);
[d] E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr., *J. Am. Chem. Soc.* **88**, 2652 (1966)

[12] [a] N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser and R. Dusenbery, *Ibid.*, **89**, 5468 (1967);
[b] N. C. Yang and R. Dusenbery, *Ibid.* **90**, 5899 (1968)

[13] [a] D. R. Kearns and W. A. Case, *Ibid.* **88**, 5087 (1966);
[b] A. A. Lamola, *J. Chem. Phys.* **47**, 4810 (1967).

[15] M. A. El-Sayed, *Ibid.* **36**, 573 (1962); **38**, 2834, 3032 (1963)

[16] S. Dym, R. M. Hochstrasser and M. Schafer, *Ibid.* **48**, 646 (1968)

[17] S. P. Pappas, B. C. Pappas and J. E. Blackwell, Jr., *J. Org. Chem.* **32**, 3066 (1967)

[18] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, pp. 38. Verlag Chemie GmbH and Academic Press (1970)

[19] G. Quinkert, W. W. Wiersdorff, M. Finke, K. Opitz and F. G. von der Haar, *Chem. Ber.* **101**, 2302 (1968)

[20] R. C. Fuson and J. Corse, *J. Am. Chem. Soc.* **60**, 2063 (1938)

[21] A. Newton, *Ibid.* **65**, 2444 (1943)

[22] R. C. Fuson, E. M. Bottort, R. E. Foster and S. B. Speck, *Ibid.* **64**, 2573 (1942)

[23] M. S. Kharasch, R. Morrison and W. H. Urry, *Ibid.* **66**, 368 (1944)