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Photocycloadditions of Benzophenone with 6-Methylenetricyclo[3.2.1.$0^{2,7}$]-oct-3-en-8-one and Its Related Compounds. Di-π-methane Photorearrangement of the Primary Photocycloadducts[1)]

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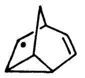
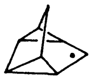
The photocycloadditions of benzophenone with constrained divinylcyclopropanes such as 1,5-dimethyl- and 1,3,5-trimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-ones, 5,8-dimethyl-9-methylenetricyclo[3.3.1.$0^{2,8}$]non-3-en-6-one, 5,8-dimethyl-9-methylenetricyclo[3.3.1.$0^{2,8}$]non-3-en-7-one, and their corresponding alcohols were investigated. In no cases, was oxetane formation observed but the formal [2+6] cycloaddition which originates from the cleavage of a cyclopropane ring was observed. In the case of the compounds which have a carbonyl function, benzophenone sensitized di-π-methane or oxadi-π-methane rearrangement of the primary photocycloadducts was observed. The mechanism of the formation of photoproducts is discussed with emphasis on (i) the nature of the intermediates having tricyclo[3.2.1.$0^{2,7}$]oct-3-en-6-yl and tricyclo[3.3.1.$0^{2,8}$]non-3-en-9-yl radicals, (ii) the regioselectivity of the di-π-methane or oxadi-π-methane rearrangement of the primary photocycloadducts.

Rearrangement of free radicals has been observed in reactions with low activation energies.[2)] Photocycloaddition of benzophenone with olefins has afforded oxetanes,[3)] while with cyclopropylethylenes, oxetanes and tetrahydrooxepins originating from the cleavage of a cyclopropane ring are obtained.[4)] An example of this class of cycloaddition reaction involving the constrained divinylcyclopropane moiety was the cycloaddition of benzophenone with barbaralone investigated by Mukai and Kuribayashi.[5)] Recently, we have reported that the cycloaddition of benzophenone with 1,5-dimethyl- and 1,3,5-trimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-ones (**1a** and **1b**) and 1,5-dimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-*endo*-ol (**1c**) afforded formal [2+6] cycloadducts originated from cleavage of the cyclopropane ring.[6)] It was recently concluded[7)] from product analysis and ESR spectroscopy that of radicals containing the bicyclo[3.2.1]octane skeleton (**A**), (**B**), and (**C**), the allyl radical (**C**) was the most stable. The radical (**A**) or (**B**) rearranges rapidly to radical (**C**). Because of the interest in clarifying the ring size effect and substituent effect[8)] of the radical rearrangement and the detailed photochemical behavior of the primary photocycloadduct, we have also investigated the photocycloaddition of benzophenone with the one-carbon ring enlarged compounds such as 5,8-dimethyl-9-methylenetricyclo[3.3.1.$0^{2,8}$]non-3-en-6-*endo*-ol (**2a**), 5,8-dimethyl-9-methylenetricyclo[3.3.1.$0^{2,8}$]non-3-en-7-ol (**2b**), 5,8-dimethyl-9-methylenetricyclo[3.3.1.$0^{2,8}$]non-3-en-6-one (**2c**), and 5,8-dimethyl-9-methylenetricyclo[3.3.1.$0^{2,8}$]non-3-en-7-one (**2d**). Through these studies, it was proven that the adduct **3a** is a rearrangement product of a primary photocycloadduct and **4a** has a different regiochemistry from that assigned in an ealier communication.[6)] We would like to report the full details of the results.


(A)


(B)

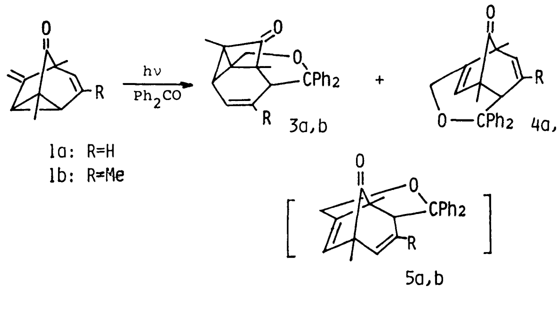

(C)


1a: X=O, R=H
1b: X=O, R=Me
1c: X=H, OH
R=H


2a: X=H₂, Y=H, OH
2b: X=H, OH, Y=H₂
2c: X=H₂, Y=O
2d: X=O, Y=H₂

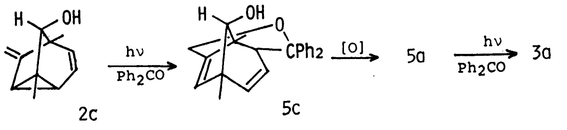
Results and Discussion

*Photocycloaddition of Benzophenone with **1a**, **1b**, and **1c**.* The photocycloaddition of benzophenone with **1a**[9)] was performed in anhydrous benzene with RPR-350 nm lamps in a nitrogen atmosphere.[6)] The major product was a cycloadduct **3a** (mp 166—167 °C, 47%) and a minor cycloadduct was **4a** (mp 270—271 °C, 15%). The photoreaction of benzophenone with **1b**[9)] afforded a similar cycloadducts **3b** and **4b** in 28% and 8% yields respectively. The adduct **3a** exhibited a parent ion peak at 342 in the mass spectrum, and a strong IR absorption band at 1763 cm^{-1} due to the cyclobutanone ring. The NMR spectrum of **3a** exhibited a proton of the cyclopropane ring at δ 2.10 (d, J=4.0 Hz), and three protons of an allylic moiety at δ 3.50 (d, J=7.8 Hz), δ 5.60 (dxd, J=8.2, 7.8 Hz), and δ 6.02 (dxd, J=8.2, 4.0 Hz), in addition to the protons of two methyl groups at δ 0.92, δ 1.56, two methylene protons at δ 4.34 (d, J=10.0 Hz), δ 4.90 (d, J=10.0 Hz), and ten protons of the phenyl groups. These chemical shifts and the coupling patterns are in good agreement with the proposed structure **3a**. Similarly the structure of **3b** was assessed by the comparison of the spectral data with those of **3a** (see Experimental). The compound **4a** exhibited a parent ion peak at 342, and a strong IR absorption band at 1752 cm^{-1} which is suggestive of a skeleton **4a**. The NMR spectrum of **4a** exhibited a



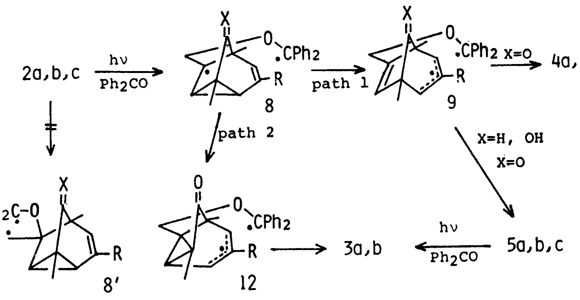
singlet vinyl proton at δ 4.90 and three protons of an allylic moiety at δ 3.78 (m), δ 5.10 (dxd, J=10.0, 4.0 Hz), δ 5.68 (dxd, J=10.0, 2.0 Hz), in addition to the two methyl signals at δ 0.68, δ 1.57, two methylene protons at δ 4.05 (d, J=13.0 Hz), δ 4.53 (d, J=13.0 Hz), and ten protons of the phenyl groups. These chemical shifts and the coupling patterns suggest the structure **4a**. In our ealier communication, we assigned the structure **5a** for these spectral data, and the structure **4a** was discarded because of the ring strain of the tetrahydrooxepin which contains a *trans* double bond.[10] The following reaction sequences, however, elucidate the correctness of the structure **4a** and **4b**.

The photocycloaddition of benzophenone with **1c**[11] was carried out in a similar manner, and **5c** (mp 74—75 °C) was obtained in 76% yield. The adduct **5c** exhibited a parent ion peak at 344 in the mass spectrum. The NMR spectrum of **5c** exhibited a vinyl proton at δ 6.15 and three protons of allylic moiety at δ 3.17 (m), δ 5.15 (dxd, J=9.5, 3.8 Hz), δ 5.74 (broad d, J=9.5 Hz), in addition to two methyl groups at δ 0.97, δ 1.09, two methylene protons at δ 4.90 (d, J=11.2 Hz), δ 4.38 (d, J=11.2 Hz), a methine proton at δ 3.49 (broad s), hydroxyl proton at δ 1.72 and ten protons of the phenyl groups. Therefore the structure **5c** was deduced as depicted in the scheme. On oxidation with pyridinium chlorochromate[12] in dichloromethane, the adduct **5c** was converted to **5a** (mp 152—153 °C) in 23% yield. The compound **5a** exhibited a parent ion peak at 342 in the mass spectrum, and a strong IR absorption band at 1750 cm^{-1} due to a cyclopentenone moiety. The NMR spectrum exhibited a singlet vinyl proton at δ 6.50, three protons of allylic moiety at δ 3.66 (m), δ 4.98 (dxd, J=9.0, 4.0 Hz), δ 6.00 (dxd, J=9.0, 2.0 Hz), in addition to two methyl signals at δ 1.00, δ 1.17, two methylene protons at δ 4.23 (d, J=10.0 Hz), δ 4.47 (d, J=10.0 Hz), and ten protons of the phenyl groups. Where the vinyl and the allylic moieties are concerned, the coupling patterns of the NMR spectra of **4a**, **b**, and **5a** are very similar to each other. Since the methyl group in **4b** occupies a position corresponding to a proton in an allylic moiety of **4a** (see Experimental), the coupling patterns of **4b** are simplified. However, the relatively high chemical shift of the vinyl proton at δ 4.90 of **4a** or at δ 4.95 of **4b** as compared to δ 6.50 of **5a** or δ 6.15 of **5c** should be ascribed to the anisotropy effect of the phenyl groups, which located very close to the singlet vinyl proton in the case of **4a**, **b**. Therefore the structure of **4a** and **4b** could be reasonably assessed to have a *trans*-tetrahydrooxepin ring.

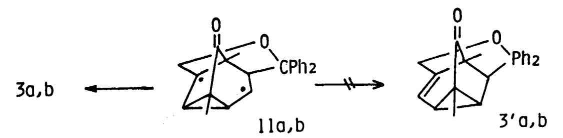


As reported previously,[6] independent irradiation of **4a**, in the presence or absence of benzophenone, did not cause rearrangement affording **3a**. The benzophenone sensitized photoreaction of **5a**, on the other hand, afforded the di-π-methane rearrangement product **3a** (70% yield), which was identical with an authentic specimen. Therefore **5a** and then **5b** should be the supportive intermediates affording **3a**, **b** in the photocycloaddition of benzophenone with **1a**, **b**.

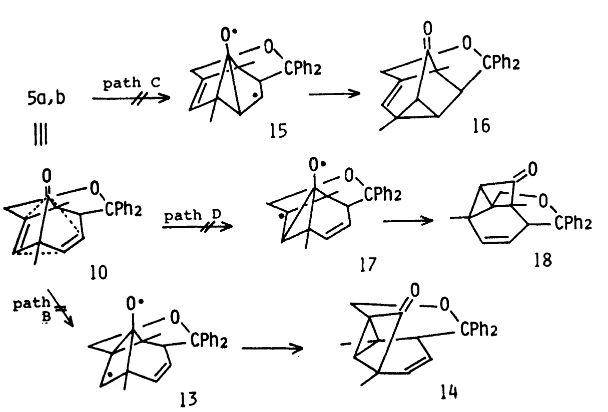
We proposed a mechanistic scheme for the formation of the photocycloadducts (Scheme 1). The diradical **8** has been considered to be the intermediate[3,4] and it may be produced either because it is more stable than **8′**, or from an initially formed complex of a prefered orientation.[13] Recently kinetic data [E_a 5.9 kcal/mol; log (A/s^{-1}) 12.48] for the cyclopropylcarbinyl→allylcarbinyl radical rearrangement have been obtained from ESR spectroscopy in the temperature range of −120 °C to −140 °C.[14] However, the type (**A**) radical [which has the same skeleton as **8**] has not been detected at −140 °C, and only the rearranged radical species has been detected.[7] These facts may suggest that the rearrangement of the constrained radical species such as **8** may be faster than that of a simple cyclopropylcarbinyl radical itself. Furthermore the combination in **8** affording oxetane should have some degree of F-strain. Therefore the tricyclic radical species **8** rearranges rapidly to the allyl radical species **9** (path 1), and the latter combines to give **4a**, **b**. The cycloadducts **4a**, **b** contains a *trans*-tetrahydrooxepin ring, which seems to be very constained. Therefore the pathway affording **4a**, **b** should be a relatively high-energy process. Another major pathway from **9** to the photocycloadducts should afford **5a**, **5b**, and **5c**, all of which have no *trans*-tetrahydrooxepin ring. However, we have no explanation for the formation of **4a**, **b** in the case of **1a**, **b** as compared to the case of **1c**. It may be impossible for the cycloadduct **5c** to absorb light in the present conditions. Furthermore a benzophenone sensitized di-π-methane rearrangement may be impossible because of its high triplet-state energy. This assumption is reminiscent of the acetone or acetophenone sensitized rearrangement of bicyclo[3.2.1]octadiene.[15] On the other hand, the energy transfer from benzophenone is possible in the case of the corresponding ketones, **5a**, **b** and results in the di-π-methane rearrangement giving **3a**, **b**. The carbonyl group seems to be indespensable for this rearrangement. In an earlier communication, the direct formation of **3a**, **b** from **8** *via* **12** (path 2) was considered.[6] However, the selective formation of **4a**, **b** seems unreasonable because of the high strain energy. In addition, the photochemical behavior of the independently prepared **5a** can contradict the path 2. This explanation is also supported by the experimental results of the similar reaction of the one-carbon ring



Scheme 1.



enlarged compounds **2** (*vide infra*). Other di-π-methane rearrangement such as **3'a, b** were not obtained *via* **11.** The examples of the directionality for migration of the vinyl group in the di-π-methane rearrangements are reported.[16] The less substituted or less conjugated double bond can migrate because the high electron density is needed for migration. However, the present selectivity affording **3a, b** might be controlled by the steric factor originated from the $-CH_2-O-CPh_2-$ bridge: In compounds **3'a, b**, an end of $-CH_2-O-CPh_2-$ moiety is attached to a double bond, therefore **3'a, b** are more constained as compared to **3a, b**.

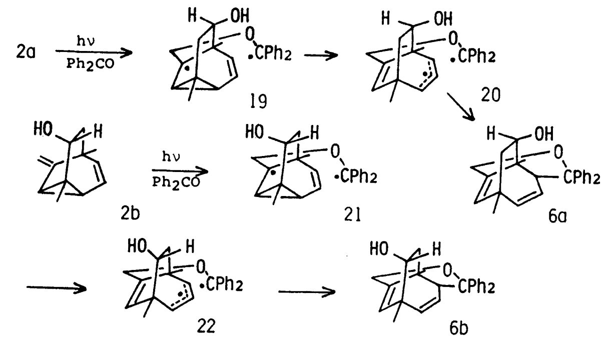


It is noticeable that the oxadi-π-methane rearrangement affording **14**, **16**, and **18** were not observed on photoreaction. We think this fact should imply the fully homoconjugated interaction of the carbonyl group with the two basal double bonds, as indicated in the structural formula **10**, and that the full interaction leads to the di-π-methane rearrangement.

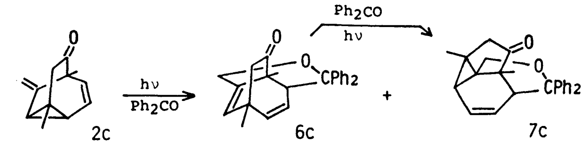
Photocycloaddition of One-carbon Ring Enlarged Compounds ***2a—d.*** In order to clarify the ring size effect on the radical rearrangement of **8** or **9** as well as on the photochemical behavior of the primary photocycloadducts such as **5**, photocycloadditions of benzophenone with **2a—d** were also investigated.

The irradiation of a benzene solution of benzophenone and **2a**[17] or **2b**[18] afforded an cycloadduct **6a** or **6b** in 78% or 73% yield, respectively. The chemical shifts and the coupling patterns of the NMR spectra of **6a, b** are very similar to those of **5a, c** (see Experimental). Especially the chemical shifts of the singlet vinyl protons at δ 6.55 of **6a** and at δ 6.17 of **6b** are similar to those of **5a** (δ 6.55) or **5c** (δ 6.50), therefore the structures **6a, b** were deduced. The adduct **6a** or **6b** could arise from the diradical species **20** or **22**, which originate from the rearrangement of the initially formed cyclopropylcarbinyl radical species **19** or **21**, respectively, as in the case of the reaction of benzophenone with **1**.

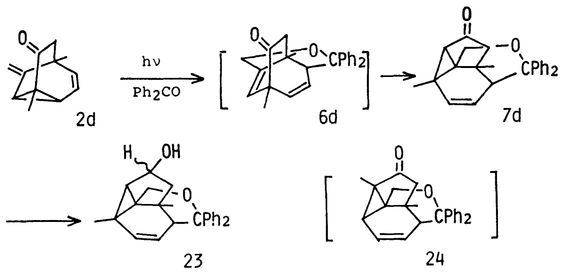
Irradiation of a benzene solution of **2c**[19] with benzophenone, on the other hand, afforded two photoproducts **6c** and **7c** in 13% and 40% yields, respectively. The mass spectral data and the analytical data of **6c** and **7c** were satisfactory for the 1 to 1 adducts of **2c** and benzophenone. The adduct **6c** exhibited a very similar NMR spectrum to those of **6a** or **6b**, and a strong absorption band at 1715 cm^{-1} in the IR spectrum; therefore the structure was attributed it. The formation of **6c** is explained by the similar reaction sequences to the case of **1** or **2a, b**. The IR spectrum of **7c** exhibited a strong absorption at 1735 cm^{-1} due to the cyclopentanone moiety. The NMR spectrum of **7c** was in full accord with the proposed structure (see Experimental). The double peak at δ 1.34 (J=4.0 Hz) was assigned to a proton on the cyclopropane ring by the help of a decoupling technique. Independent irradiation of a benzene solution of **6c** in the presence of benzophenone afforded **7c** in 80% yield. This fact indicates that **7c** originates from the benzophenone sensitized di-π-methane rearrangement of primary photocycloadduct **6c**.



On the other hand, the irradiation of a benzene solution of **2d**[19] and benzophenone in 1/5 molar ratio gave an adduct **7d** (mp 182—183 °C) in 69% yield. The adduct **7d** exhibited a parent ion peak at 356 in the mass spectrum, and a strong absorption band at 1705 cm^{-1} due to a cyclopropyl ketone. The NMR spectrum of **7d** exhibited a cyclopropane proton at δ 2.45 (1H, s) and three protons of an allylic moiety at δ 3.43 (1H, d, J=6.8 Hz), δ 5.50 (1H, dxd, J=8.0, 6.8 Hz) and δ 5.70 (1H, d, J=8.0 Hz), in addition to the protons of two methylene groups, two methyl groups, and two phenyl groups. On LAH reduction, **7a** was converted to the alcohol **23** (mp 158—160 °C)

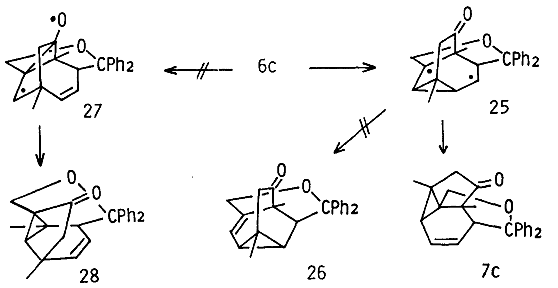


in 65% yield. The stereochemistry of the hydroxyl group of **23** was not determined, however, the NMR spectrum of **23** exhibited a doublet peak at δ 2.06 (J=4.5 Hz), which was assigned to the proton of the cyclopropane ring by the help of a decoupling technique: decoupling of the proton at δ 4.50—4.75 shows change a doublet peak at δ 2.06 to a singlet. This fact and the other spectral data (see Experimental) supported the structures **23** and **7d**, and could eliminate the other possible structure such as **24**, which is expected from the di-π-methane rearrangement on the two basal



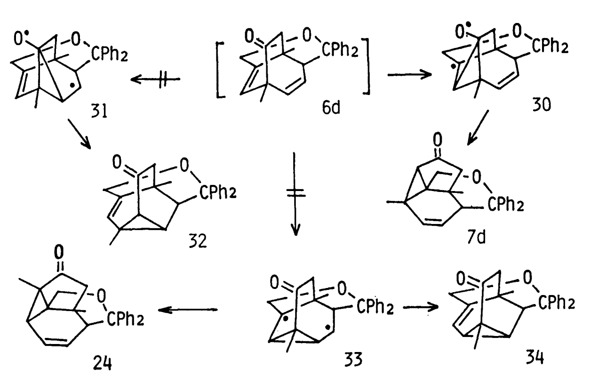
double bonds of the postulated primary photocycloadduct **6d**.

Several remarkable points are noticed here. Tricyclo-[3.2.1.0^{2,8}]non-3-en-9-yl radical species, which are derived from the addition of triplet benzophenone to **2a**—**d**, underwent cyclopropylcarbinyl-allylcarbinyl radical type rearrangement as in the case of type **A** radical or **8**. The rearrangement was independent of the presence of the carbonyl group. The reaction site of the benzophenone sensitized rearrangement of the primary photocycloadducts seemed to be dependent on the position of the carbonyl group in the similar skeleton. The cycloadduct **6c** underwent di-π-methane rearrangement on the two basal double bonds to afford **7c** *via* 1,4-diradical species **25**. This feature is similar to the rearrangement of **5a** (*vide supra*). The carbonyl group of **6c** can also interact with two basal double bonds in a fully homoconjugated manner as in the case of **5c**. Another isomer **26** should be constrained as mentioned in the case of **3'a**, **b**, therefore the pathway affording **26** should be a higher energy process than that of **7c**. The compound **26** which is a one-carbon ring enlarged derivative of **3'a** seems to be more constrained even than **3'a** judging from a molecular model. The other oxadi-π-methane rearrangement product **28**, which has a very constrained molecular geometry, could not be obtained.



Scheme 2.

On the other hand, in the postulated primary photocycloadduct **6d**, the carbonyl group and two double bonds build up a special cross homoconjugated system, unlike the case of **5a** or **6c**. The adduct **7d** was considered to be derived from **6d** by the oxadi-π-methane rearrangement *via* **30**. Another oxadi-π-methane rearrangement product **32** was expected to be derived from the interaction of the carbonyl group with another vinyl group *via* **31**, however, it was not obtained. The compound **32** has a similar skeleton to **26** and it is supposed to be constrained, therefore the pathway to **32** should be a high-energy process and **31** possibly goes back to **6d**. Other isomers such as **24** and **34** may be derived formally from a di-π-methane rearrangement of the two basal double bonds *via* **33**. Concerning the ring constraint, **34** has a similar skeleton to **26** or **32**, therefore this ring system is suggested to be unfavorable. The compound **24** has a similar skeleton to **7d**, on the other hand, it was not obtained. These observations seem to suggest that excited-state energy is localized on the homoconjugated system of the carbonyl group and a vinyl group.



Schelme 3.

In conclusion, it was clarified that tricyclo[3.2.1.0^{2,7}]-oct-3-en-6-yl or tricyclo[3.3.1.0^{2,8}]non-9-yl radical species, which were generated by an initial attack of a triplet benzophenone on **1** or **2**, could not afford oxetanes and rearranged to the less strained bicyclic allyl radical species affording formal [2+6] cycloadducts. The electron-withdrawing carbonyl group which is located to conjugate with the cyclopropane ring in **1** or **2d** could not reflect the electronic property on the radical rearrangement[8] in the present case. The regioselectivity of the subsequent benzophenone sensitized rearrangement of the primary photocycloadducts, however, was much affected by the position of the carbonyl group.

The investigation of photochemical reactions of β,γ-unsaturated carbonyl compounds has been accumulated.[20] Among these investigations, bicyclic ketones such as bicyclo[2.2.2]octenone derivatives undergo acetone sensitized 1,2-acyl migration (oxadi-π-methane rearrangement), 1,3-acyl migration and a bridge elimination.[20,21] The bicyclo[2.2.2]octa-2,5-dien-7-one derivatives are also known to eliminate ketene to afford benzene derivatives. The other noticeable example has been reported by Mukai and Kurabayashi: The triplet photorearrangement of bicyclo[4.2.1]non-2,4,7-trien-9-one, which containes a carbonyl group, a vinyl group and a butadiene moiety in a bicyclic skeleton, afford barbaralone.[23] The presented di-π-methane and oxadi-π-methane rearrangement are good examples reflecting the interactions of the carbonyl group with the two other vinyl groups in the homoconjugated manner. The explanation of the selectivity of the rearrangements is rather qualitative and the ring constraint is proposed as the reason for supressing the possible products such as **14**, **28** or **16**, and **26** and **32**. For profound confirmation of the selectivity for the rearrangement involving the interaction of the carbonyl group with the two other vinyl groups, the study of the compounds containing no $-CH_2-O-CPh_2-$ moiety in **5**, **6c**, and **6d** might be helpfull.

Experimental

IR spectra were measured on a Shimadzu IR-100 spectrometer. NMR spectra were recorded on a JEOL PS-100 high resolution NMR spectrometer. Chemical shifts were determined in carbon tetrachloride or in deuteriochloroform. The abbreviations given in the NMR data are s=singlet, d=doublet, dxd=doublets of doublet, t=triplet, and m=multiplet. VPC analysis was carried out either on Shimadzu GC-6A or on a Varian model-920 gas chromatograph using columns packed with either 5% SE-30 or 5% FFAP on Chromosorb W. The mass spectral studies were conducted using a Hitachi RMU-60 spectrometer. All melting points are uncorrected.

General Procedure of Irradiation. All photoreactions were carried out in a deoxygenated (nitrogen bubbled) benzene solution of a mixture of substrate and benzophenone. Irradiation was made with a RPR-100 photoreactor, which was fitted with RPR-350 nm lamps.

*Photoreaction of Benzophenone with **1a**.* A benzene (40 cm^3) solution of 3.64 g (20 mmol) of benzophenone and 640 mg (4 mmol) of **1a** was irradiated in a Pyrex cell at room temperature for 7 h. VPC analysis indicated that almost all of **1a** was consumed. Solvent was removed under reduced pressure. The residue was chromatographed on alumina (130 g). Elution with hexane–benzene mixture (19/1) gave a colorless solid. Recrystallization of this solid from chloroform–ethanol mixture gave colorless crystals (647 mg, 47% based on **1a** used), which were characterized as **3a**: mp 166—167 °C; IR (KBr): 3050, 1763, 1630, 1597, 1498, 1447, 1025 cm^{-1}; NMR (CDCl$_3$): δ 0.92 (3H, s), 1.56 (3H, s), 2.10 (1H, d, J=4.0 Hz), 3.50 (1H, d, J=7.8 Hz), 4.34 (1H, d, J=10.0 Hz), 4.90 (1H, d, J=10.0 Hz), 5.60 (1H, dxd, J=8.2, 7.8 Hz), 6.02 (1H, dxd, J=8.2, 4.0 Hz), 7.2—8.2 (1H, m); MS, *m/e* (rel intensity): 342 (M$^+$, 9), 132 (100). Found: C, 84.04; H, 6.49%. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47%. Further elution of the column with hexane–benzene mixture (1/1) gave a colorless solid. Recrystallization of this solid from chloroform–ethanol mixture gave colorless crystals (199 mg, 15% based on **1a** used), which were characeterized as **4a**: mp 270—272 °C; IR (KBr): 1752, 1595, 1025 cm^{-1}; NMR (CDCl$_3$): δ 0.68 (3H, s), 1.57 (3H, s), 3.87 (1H, m), 4.05 (1H, d, J=13.0 Hz), 4.53 (1H, d, J=13.0 Hz), 4.90 (1H, s), 5.10 (1H, dxd, J=10.0, 4.0 Hz), 5.68 (1H, dxd, J=10.0, 2.0 Hz), 7.2—7.8 (1H, m); MS, *m/e* (rel intensity): 342 (M$^+$, 18), 132 (100). Found: C, 84.53; H, 6.23%. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47%.

*Photoreaction of Benzophenone with **1b**.* A benzene solution (40 cm^3) of 3.64 g (20 mmol) of benzophenone and 696 mg (4 mmol) of **1b** was irradiated in a Pyrex vessel at room temperature for 12 h. VPC analysis indicated that almost all of **1b** was consumed. After solvent removal in vacuo, the resulting residue was chromatographed on alumina (60 g). Elution with hexane–benzene mixture (9/1) gave 430 mg of a colorless solid and 130 mg of the second colorless solid. Recrystallization of the first solid from chloroform–ethanol mixture gave colorless crystals (402 mg, 28% based on **1b** used), which were identified as **3b**: mp 144—145 °C; IR (KBr): 1750, 1598, 1025 cm^{-1}; NMR (CDCl$_3$): δ 0.75 (3H, s), 0.84 (3H, s), 1.54 (3H, s), 2.02 (1H, m), 2.90 (1H, s), 4.12 (1H, d, J=10.0 Hz), 4.64 (1H, d, J=10.0 Hz), 5.57 (1H, m), 7.0—7.7 (1H, m); MS, *m/e* (rel intensity): 356 (M$^+$, 5), 146 ((100). Found: C 84.02; H, 6.72%. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H. 6.79%. Recrystallization of the second solid from chloroform–ethanol mixture gave colorless crystals (110 mg, 8% based on **1b** used), which were characterized as **4b** by the following physical data: mp 290—291 °C; IR (KBr): 1748, 1600, 1035, 1023 cm^{-1}; NMR (CDCl$_3$): δ 0.50 (3H, s), 0.82 (3H, s), 1.54 (3H, broad s), 3.51 (1H, s), 3.88 (1H, d, J=10.0 Hz), 4.36 (1H, d, J=10.0 Hz), 4.95 (1H, s), 5.43 (1H, broad s), 7.2—7.8 (10H, m); MS, *m/e* (rel intensity): 356 (M$^+$, 24), 146 (100). Found: C, 83.95; H, 6.45%. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79%.

*Photoreaction of Benzophenone with **1e**.* A benzene solution (10 cm^3) of 182 mg (1 mmol) of benzophenone and 324 mg (2 mmol) of **1c** was irradiated at room temperature for 4 h. After solvent removal *in vacuo*, the residue was chromatographed on alumina (20 g). Elution with benzene–benzene–hexane (1/1) and benzene gave 260 mg (76% based on benzophenone used) of **5c** which was recrystallized from hexane as colorless crystals: mp 74—76 °C; IR (KBr): 3400, 1155, 1125 cm^{-1}; NMR (CCl$_4$): δ 0.97 (3H, s), 1.09 (3H, s), 1.72 (1H, s), 3.17 (1H, m), 3.49 (1H, broad s), 4.09 (1H, d, J=11.2 Hz), 4.38 (1H, d, J=11.2 Hz), 5.15 (1H, dxd, J=9.5, 3.8 Hz), 5.74 (1H, broad d, J=9.5 Hz), 6.15 (1H, s), 7.1—7.8 (10H, m).

*Oxidation of **5c**.* To a stirred solution of 204 mg (0.95 mmol) of pyridinium chlorochromate and 164 mg of anhydrous sodium acetate in 5 cm^3 of dichloromethane was added 218 mg (0.63 mmol) of **5c** in a nitrogen stream. Upon completion of the addition, the mixture was stirred at room temperature for 2.5 h. After addition of water, the mixture was extracted with ether (4 × 20 cm^3). The combined organic portion was dried over sodium sulfate, followed by solvent evaporation. The crude product was purified by TLC on silica gel using benzenes as the eluent to give 50 mg of **5a** (23%) as a colorless crystalline solid, which was recrystallized from ethanol: mp 152—153 °C; IR (KBr): 1750, 1600, 1040, 1007 cm^{-1}; NMR (CDCl$_3$): δ 1.00 (3H, s), 1.17 (3H, s), 3.66 (1H, m), 4.23 (1H, d, J=10.0 Hz), 4.47 (1H, d, J=10.0 Hz), 4.98 (1H, dxd, J=9.0, 4.0 Hz), 6.00 (1H, dxd, J=9.0, 2.0 Hz), 6.50 (1H, s), 7.1—7.6 (10H, m); MS, *m/e* (rel intensity): 342 (M$^+$, 1), 132 (100). Found: C, 84.01; H, 6.27%. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47%.

*Irradiation of **4a** in the Presence or Absence of Benzophenone.* Two Pyrex vessels, which containes **4a** (20 mg, 0.06 mmol) in, (a) benzene (2 cm^3), and (b) benzene (10 cm^3) containing benzophenone (22 mg, 0.12 mmol) were irradiated for 5 h. After removal of the solvent, each of the residues was purified by TLC on silica gel using benzene–dichloromethane (1/1) as the eluent to give **5a**, 90% (a), **5a**, 90% and 17 mg of benzophenone (b).

*Benzophenone-sensitized Irradiation of **5a**.* A solution containing 22 mg (0.12 mmol) of benzophenone and 20 mg (0.06 mmol) of **5a** in 2 cm^3 of benzene was irradiated in a Pyrex vessel for 3 h. After solvent removal *in vacuo* the resulting residue was separated by TLC on silica gel using benzene–dichloromethane (1/1) as the eluent. The first band isolated from the TLC plates contained 18 mg of benzophenone. The second band from the TLC plates contained 14 mg (70%) of **3a**, which was identical with the authentic specimen.

*Photoreaction of Benzophenone with **2a**.* A solution of 69 mg (0.38 mmol) of benzophenone and 134 mg (0.76 mmol) of **2a** in 8 cm^3 of benzene was irradiated at room temperature for 2 h. After evaporation of the solvent under reduced pressure, the residue was separated by TLC on alumina using chloroform as the eluent to give 61 mg of **2a** (R_f=0.43, 46%), and 106 mg of **6a** (R_f=0.69, 78% based on benzophenone used). The cycloadduct **6a** gave the following physical data: IR (film): 3450, 1600, 1040 cm^{-1}; NMR (CCl$_4$): δ 1.06 (3H, s), 1.16 (3H, s), 1.76 (1H, d, J=13.0 Hz), 2.15 (1H, dxd, J=13.0, 8.8 Hz), 3.55 (1H, dxd, J=5.0, 2.0 Hz), 3.84 (1H, broad d, J=8.8 Hz), 4.10 (1H, d, J=10.0 Hz), 5.62 (1H, d, J=10.0 Hz), 5.70 (1H, dxd, J=11.0, 5.0 Hz), 5.75 (1H, dxd, J=11.0, 2.0 Hz), 6.55 (1H, s), 7.1—8.0 (10H, m). Found: C, 83.37; H, 7.07%. Calcd for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31%.

Photoreactions of Benzophenone with **2b**. A solution of 75 mg (0.41 mmol) of benzophenone and 146 mg (0.83 mmol) of **2b** in 8 cm^3 of benzene was irradiated at room temperature for 3 h. After solvent remolval *in vacuo*, the resulting residue was separated by TLC on alumina using hexane–ethyl acetate (3/1) to give 62 mg (R_f=0.40, 42%) of **2b** and 108 mg (R_f=0.23, 73% based on benzophenone used) of **6b**. The cycloadduct **6b** gave the following physical data: IR (film): 3420, 1600, 1045 cm^{-1}; NMR (CCl_4): δ 0.94 (3H, s), 1.22 (3H, s), 1.63 (1H, d, J=15.0 Hz), 2.30 (1H, dxd, J=15.0, 9.0 Hz), 3.06 (1H, dxd, J=4.8, 2.0 Hz), 3.68 (1H, broad d, J=9.0 Hz), 4.05 (1H, d, J=11.0, 4.8 Hz), 4.57 (1H, d, J=10.0 Hz), 4.58 (1H, dxd, J=11.0, 4.8 Hz), 5.52 (1H, dxd, J=11.0, 2.0 Hz), 6.17 (1H, s), 7.7—7.8 (10H, m). Found: C, 84.28; H, 7.12%. Calcd for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31%.

Photoreaction of Benzophenone with **2c**. A solution of 150 mg (0.83 mmol) of benzophenone and 144 mg (0.83 mmol) of **2c** in 9 cm^3 of benzene was irradiated at room temperature for 3.5 h. After solvent removal *in vacuo*, the resulting residue was separated by TLC on silica gel using hexane–ethyl acetate (4/1) as the eluent to give 25 mg (R_f=0.85, 17%) of **2c**, 35 mg (R_f=0.45, 13%) of **6c**, and 119 mg (R_f=0.30, 40%) of **7c**. Recrystallization of **6c** gave colorless crystals: mp 205—206 °C: IR (KBr): 1718, 1595, 1045 cm^{-1}; NMR ($CDCl_3$): δ 1.04 (3H, s), 1.26 (3H, s), 2.50 (2H, s), 3.40 (1H, dxd, J=4.0, 2.0 Hz), 4.14 (1H, d, J=10.0 Hz), 4.53 (1H, d, J=10.0 Hz), 4.67 (1H, dxd, J=12.0, 4.0 Hz), 5.75 (1H, dxd, J=12.0, 2.0 Hz), 6.60 (1H, s), 7.00—7.70 (10H, m); MS, m/e (rel intensity); 356 (M^+, 1), 132 (100). Found: C, 84.49; H, 6.56%. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79%.

The cycloadduct **7c** was crystallized from ethanol to give colorless crystals: mp 139—140 °C; IR (KBr): 1733, 1595, 1040 cm^{-1}; NMR ($CDCl_3$): δ 0.76 (3H, s), 1.40 (3H, s), 1.34 (1H, d, J=4.0 Hz), 2.30 (1H, d, J=18.8 Hz), 2.47 (1H, d, J=18.8 Hz), 3.73 (1H, d, J=6.8 Hz), 3.88 (1H, d, J=11.0 Hz), 4.59 (1H, d, J=11.0 Hz), 5.50 (1H, dxd, J=9.0, 6.8 Hz), 5.72 (1H, dxd, J=9.0, 4.0 Hz), 7.05—7.83 (10H, m); MS, m/e (rel intensity): 356 (M^+, 1), 132 (100). Found: C, 84.00; H, 6.90%. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79%.

Photoreaction of Benzophenone with **2d**. A solution of 91 mg (0.5 mmol) of benzophenone and 87 mg (0.5 mmol) of **2d** in 5 cm^3 of benzene was irradiated at room pemperature for 8 h. After solvent removal *in vacuo*, the resulting residue was separated by TLC on silica gel using ether–hexane (1/1) as the eluent to give 10 mg (R_f=0.90, 10%) of **2d** and 95 mg (R_f=0.50, 69%) of **7d**. Recrystallization of **7d** from ethanol gave colorless crystals: mp 182—183 °C: IR (KBr): 1705, 1595, 1035 cm^{-1}; NMR ($CDCl_3$): δ 0.95 (3H, s), 1.47 (3H, s), 1.86 (1H, d, J=18.8 Hz), 2.34 (1H, d, J=18.8 Hz), 2.45 (1H, s), 3.43 (1H, d, J=6.8 Hz), 4.06 (1H, d, J=11.0 Hz), 4.62 (1H, d, J=11.0 Hz), 5.50 (1H, dxd, J=8.0, 6.8 Hz), 5.79 (1H, d, J=8.0 Hz), 7.05—7.77 (10H, m); MS, m/e (rel intensity): 356 (M^+, 1), 132 (100). Found: C, 84.72; H, 6.78%. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79%.

Reduction of **7d**. To a suspension containing 19 mg (0.5 mmol) of lithium aluminium hydride in 2 cm^3 of anhydrous tetrahydrofuran was added 89 mg (0.25 mmol) of **7d**. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then treated with water (3 cm^3) followed by aqueous ammonium chloride, and extracted with ether (10 cm^3×4). The combined organic portion was dried over sodium sulfate. The solvent was removed under reduced pressure and the resulting residue was chromatographed on alumina column using benzene as the eluent to give a colorless crystalline solid, which was recrystallized from carbon tetrachloride to give 58 mg (65%) of **7e**: mp 158—159 °C; IR (KBr): 3450, 1600, 1075, 1010 cm^{-1}; NMR ($CDCl_3$): δ 0.87 (3H, s), 1.35 (3H, s), 1.72 (1H, dxd, J=14.0, 9.6 Hz), 1.96 (1H, dxd, J=14.0, 9.6 Hz), 2.06 (1H, d, J=4.6 Hz), 3.37 (1H, d, J=6.2 Hz), 3.96 (1H, d, J=10.8 Hz), 4.53 (1H, d, J=10.8 Hz), 4.50—4.75 (1H, m), 5.26 (1H, dxd, J=9.0, 6.2 Hz), 5.94 (1H, d, J=9.0 Hz), 7.0—7.75 (1H, m). Found: C, 84.48; H, 7.38%. Calcd for $C_{25}H_{26}O_2$: C, 84.70; H, 7.39%.

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