Photolysis of 1,1,1-Triarylalkane. A New Photochemical Carbene Generation Process

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Upon UV irradiation in methanol, some 1,1,1-triarylalkanes underwent an α,α-elimination of two aryl groups to give biaryls and the corresponding carbene intermediates, which inserted into the OH bond of the methanol to afford methyl ethers and/or underwent a 1,2-H shift to afford olefins. Furthermore, the efficiency of this elimination was highly dependent upon the bulkiness of the alkyl groups.

Introduction

The methods of carbene generation have already been investigated in detail.[1] Recently we found that upon UV irradiation, dimethyl triarylmethylphosphonates undergo a novel α,α-elimination of the two aryl groups to afford biaryls (**1**) and the corresponding dialkoxyphosphinyl(aryl)carbenes.[2] In order to understand better this carbene generation process, we further studied the photochemical behavior of some other triarylmethyl derivatives. We found that upon irradiation in methanol purged with argon (triarylmethyl)cycloalkanes (**2a–h**) or 1,1,1-triphenyl-2-methylpropane (**2i**) and 3-(triphenylmethyl)heptane (**2j**) also undergo this novel α,α-elimination of two aryl groups to afford **1** and the corresponding carbene intermediates (**3**), which inserted into the O–H bond of methanol to afford the methyl ethers and/or underwent a 1,2-H shift to afford the olefins, respectively.[3]

Our aim in this report is to demonstrate the photochemical behavior of 1,1,1-triarylalkanes in detail and to elucidate the mechanism of this photodecomposition.

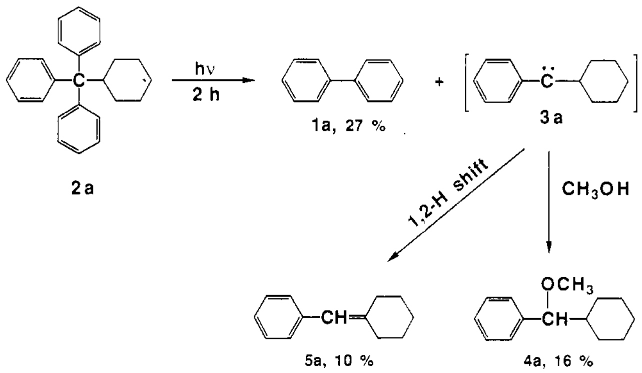
Results and Discussion

After irradiation of a methanol solution of (triphenylmethyl)cyclohexane (**2a**) (10 mM) in a quartz tube under argon atmosphere with a high-pressure mercury lamp (300 W) for 2 h, the reaction mixture was analyzed by GLC, and biphenyl (**1a**, 27%), cyclohexylmethoxyphenylmethane (**4a**, 16%), and benzylidenecyclohexane (**5a**, 10%) were obtained. The products **4a** and **5a** may be derived from the insertion of the carbene **3a** into the O–H bond of methanol and from the 1,2-hydrogen shift in **3a**, respectively (Scheme I). It is well-known that carbene intermediates undergo a 1,2-hydrogen shift to give olefins. For example, Overberger showed that methyl(phenyl)carbene underwent a hydrogen shift to give styrene,[4] and Schechter further reported the hydrogen migratory aptitude in detail.[5]

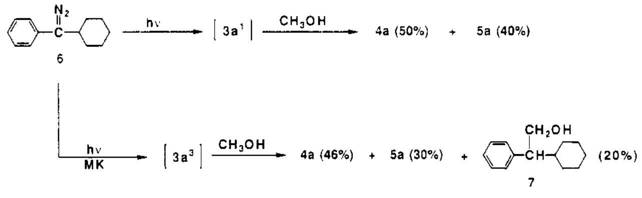
In order to verify further this reaction scheme, the photolysis of the corresponding carbene precursor, cyclohexylphenyldiazomethane (**6**),[6] was carried out. After complete photobleaching of the red color of **6** in methanol, products **4a** (50%) and **5a** (40%) were obtained as shown in Scheme II. The ratio of products (**4a**/**5a**) was almost identical with that obtained in the photolysis of **2a**.

Moreover, photolysis of **2a** (10 mM) in cyclohexane, acetonitrile, or tetrahydrofuran (THF) for 2 h also led to the formation of **1a** and **5a**. Their yields are summarized in Table I, together with the results in methanol.

Scheme I



Scheme II[a]



[a] MK = 4,4′-bis(dimethylamino)benzophenone.

Table I. Results of Photolysis of 2a in Various Solvents

solvent	Φ[a]	convn, %[b]	product (yield, %) **1a**	**4a**	**5a**
cyclohexane	0.015	40	24		23
acetonitrile	0.014	56	21		18
THF	0.024	50	36		35
methanol	0.016	55	27	16	10

[a] Quantum yield of **1a**. [b] Irradiated in a quartz tube for 2 h.

It should be noted that the product expected from hydrogen abstraction from the solvent by the triplet state species (triplet carbene) could not be detected. Furthermore, upon irradiation of the oxygen-saturated methanol solution, the yields of **1a**, **4a**, and **5a** were unchanged. On the other hand, upon sensitized photolysis of **6** with 4,4′-bis(dimethylamino)benzophenone (MK) in methanol using a $BiCl_3/HCl$ filter (>350 nm), besides products **4a** (46%) and **5a** (30%), 2-cyclohexyl-2-phenylethanol (**7**) was obtained in a yield of 20% as an additional product, which was apparently derived from the triplet carbene of **3a** (Scheme II).[7] Therefore, these results suggest that the photodecomposition of **2a** would proceed via a singlet

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(1) Moss, R. A.; Jones, M., Jr. *Carbenes*; Wiley-Interscience: New York, 1973.

(2) Shi, M.; Okamoto, Y.; Takamuku, S. *J. Chem. Soc., Chem. Commun.* **1989**, 151.

(3) Shi, M.; Okamoto, Y.; Takamuku, S. *Tetrahedron Lett.* **1989**, *30*, 6709.

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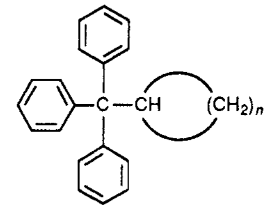
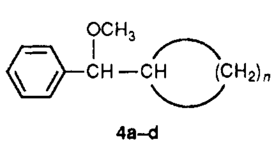
0022-3263/90/1955-3821$02.50/0

Table II. Results of Photolysis of 2b–d in Methanol

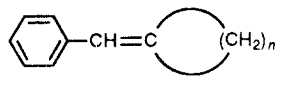


2a–d

a, n = 5; **b**, n = 2; **c**, n = 4; **d**, n = 6



4a–d

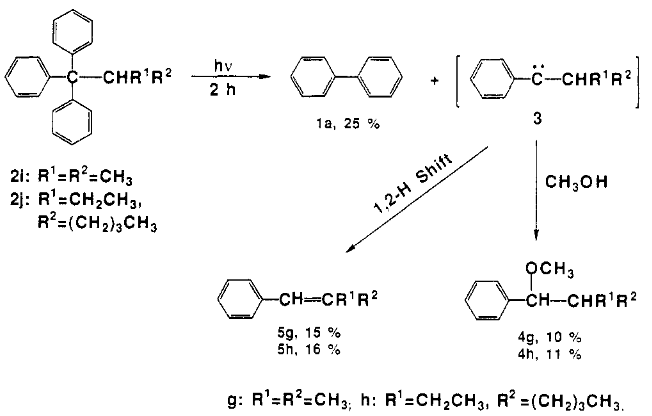


5a–d

2	convn, %^{a}	product (yield, %)		
		1a	4	5
2a	55	27	**4a** (16)	**5a** (10)
2b	38	5	**4b** (4)	**5b** (0)
2c	50	21	**4c** (19)	**5c** (0)
2d	60	25	**4d** (10)	**5d** (13)

[a] 10 mM, irradiated in a quartz tube for 2 h.

Scheme III

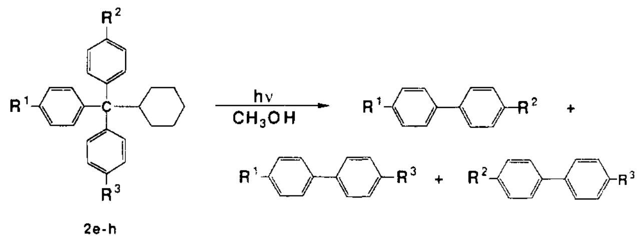


excited state to give **1a** and the singlet carbene **3a**, which reacts with methanol to afford **4a** and/or undergoes a 1,2-hydrogen shift to give **5a**.

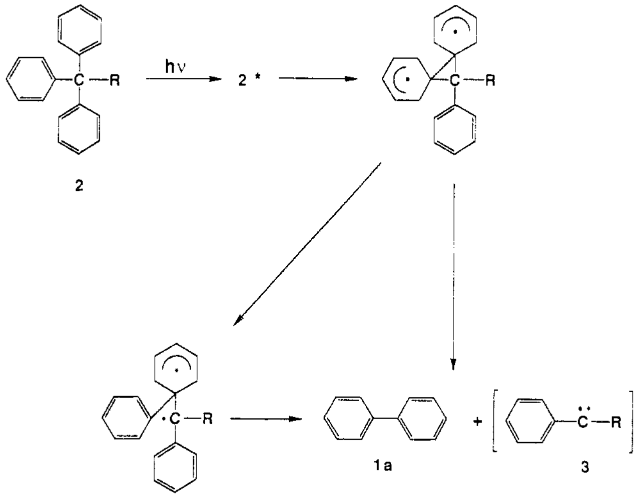
Upon irradiation of other (triphenylmethyl)cycloalkanes [(triphenylmethyl)cyclopropane (**2b**), (triphenylmethyl)cyclopentane (**2c**), and (triphenylmethyl)cycloheptane (**2d**)] in methanol under similar conditions, we found that (1) the yields of **1a** are highly dependent upon the size of the ring in the order of **2a** = **2d** > **2c** ≫ **2b** and (2) the products derived from the carbene intermediates **3** vary with the size of the ring (Table II). Thus, **2b** and **2c** did not give the products arising from the 1,2-H shift of carbene intermediates. Griffin has reported that photolysis of phenylcyclopropyldiazomethane in methanol gave only cyclopropylmethoxyphenylmethane.[8] Moreover, in the case of photolysis of **2d** in methanol, the yield of the product **5d** derived from the 1,2-H shift of the carbene was greater than that of the insertion product **4d**. These interesting results suggest that the carbene having a larger cycloalkyl group favors the intramolecular 1,2-H shift.

On the other hand, photolysis of acyclic 1,1,1-triphenylalkanes, 1,1,1-triphenyl-2-methylpropane (**2i**) or 3-(triphenylmethyl)heptane (**2j**), in methanol also provided **1a**, the corresponding methyl ether (**4g** or **4h**), and olefin (**5g** or **5h**), respectively (Scheme III). However, upon irradiation of triphenylmethane (**2m**), 1,1,1-triphenylethane (**2k**), or 1,1,1-triphenyl-2,2-dimethylpropane (**2l**) in methanol, only trace amounts of **1a** could be detected by GLC. These results imply that a bulky alkyl group seems to favor biphenyl formation. The photoinduced elimination for **2** having electron-donating substituents on the phenyl rings was also examined, and it was found that the introduction of the electron-donating substituents appears to favor slightly the elimination of two aryl groups (Scheme IV, Table III).

Scheme IV



Scheme V



The ratios of unsymmetric and symmetric **1** obtained from monosubstituted **2e** and **2g** did not deviate much from the value (2.0) expected if the aryls coupled randomly.

Consequently, the mechanism proposed for this photochemical reaction (Scheme V) is quite similar to that described earlier for the photochemical reaction of dimethyl triphenylmethylphosphonate[2] and 1,1,1-triarylhept-2-ynes.[9]

In a photoexcited state of this alkane, probably the singlet excited state (**2***), the intramolecular interaction among the three aromatic rings arises, and subsequently, two aryl groups are eliminated via the initial bonding between C-1 positions of two aryl groups (ipso coupling). The elimination of biaryl may be stepwise or concerted to produce the carbene (**3**). The mechanism of this reaction is understood in terms of photochemical di-π-methane rearrangement.[10] The final products result from reaction with solvent and/or intramolecular rearrangement of **3**.

Similar intramolecular interaction was also observed among the three benzene rings of triptycene derivatives, where a similar photochemical generation of a carbene intermediate was proposed by Iwamura and Yoshimura,[11] as a special case of di-π-methane rearrangement,[10] in which

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[9] Shi, M.; Okamoto, Y.; Takamuku, S. *Chem. Lett.* **1989**, 1299.

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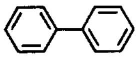
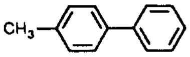
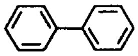
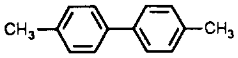
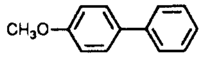
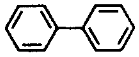
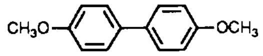
Table III. Results of the Photolysis of 2e–h in Methanol

no.	R^1	R^2	R^3	convn, %[a]	product (yield, %)[b]	(yield, %)[b]	ratio[c]
2a	H	H	H	55		(27)	
2e	H	H	CH_3	60		(20)	3
						(7)	
2f	CH_3	CH_3	CH_3	58		(24)	
2g	H	H	OCH_3	50		(20)	2
						(10)	
2h	OCH_3	OCH_3	OCH_3	70		(30)	

[a] 10 mM, irradiated in a quartz tube for 2 h. [b] Ratios of products (4/5) were almost identical with that obtained in the photolysis of **2a**, regardless of the introduction of electron-donating substituents into the aromatic rings. [c] Unsymmetric biaryl/symmetric biaryl.

the fragmentation occurs from biradical intermediates instead of cyclization to cyclopropane derivatives. In the photolysis of tetraphenylmethane[12] and dibenzonorbornadiene,[13] analogous carbene generation has been reported.

Geminal photochemical elimination of two aryl groups to give **1** has been reported on other elements such as Zn,[14] Al,[15] B,[16] and Sn.[17]

Experimental Section

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. UV-visible spectra were recorded with a Hitachi 150-20 spectrometer (MeOH solvent). ^1H NMR were recorded on a JNM-GSX400 spectrometer with tetramethylsilane (TMS) as an internal standard. Photolyses were carried out with a 300-W high-pressure mercury lamp, EHBW-300, or a 60-W low-pressure mercury lamp, ELJ-60 (Eikosha Co., Ltd.). Gas chromatography (GLC) analyses were carried out by use of a 2% Silicone OV-17 on Chrom-WAW DMCS (60/80 mesh) with a Shimadzu Model 7A. GC-MS spectra were recorded with a JMS-DX300; high-resolution mass spectra were also obtained on the JMS-DX300 instrument. Some authentic samples were commercially available, and the others were prepared by the known method (see below).

(Triphenylmethyl)cyclohexane (2a). 2a was prepared by the reaction of cyclohexylmagnesium bromide with triphenylmethyl chloride in anhydrous ether[18] and purified by use of a column chromatography (hexane was used as an eluant): mp 143–145 °C; UV (MeOH) λ_{max} 260 nm (ϵ 980 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 0.45–2.0 (m, 10 H), 3.04 (t, 1 H, J = 11.2 Hz), 6.80–7.20 (m, 15 H); HRMS (EI) m/z 326.2043 (M^+) ($C_{25}H_{26}$ requires 326.2033).

Other triarylmethylalkanes (**2b–l**) were prepared by a similar procedure as described in the preparation of **2a**.

(Triphenylmethyl)cyclopropane (2b): mp 80–81 °C; UV (MeOH) λ_{max} 260 nm (ϵ 723 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 0.026–0.066 (m, 2 H), 0.63–0.67 (m, 2 H), 2.06–2.18 (m, 1 H), 7.10–7.31 (m, 15 H); HRMS (EI) m/z 284.1561 (M^+) ($C_{22}H_{20}$ requires 284.1564).

(Triphenylmethyl)cyclopentane (2c): mp 68–70 °C; UV (MeOH) λ_{max} 260 nm (ϵ 972 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 1.0–2.0 (m, 8 H), 3.66 (quintet, 1 H), 7.0–7.40 (m, 5 H); HRMS (EI) m/z 312.1874 (M^+) ($C_{24}H_{24}$ requires 312.1877).

(Triphenylmethyl)cycloheptane (2d): mp 112–114 °C; UV (MeOH) λ_{max} 260 nm (ϵ 800 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 1.0–2.0 (m, 12 H), 3.19 (t, 1 H, J = 9.6 Hz), 6.80–7.40 (m, 15 H); HRMS (EI) m/z 340.2187 (M^+) ($C_{26}H_{28}$ requires 340.2190).

[(4-Methylphenyl)diphenylmethyl]cyclohexane (2e): mp 132–134 °C; UV (MeOH) λ_{max} 260 nm (ϵ 1118 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 0.45–2.0 (m, 10 H), 2.27 (s, 3 H), 3.03 (t, 1 H, J = 11.2 Hz), 6.90–7.42 (m, 14 H); HRMS (EI) m/z 340.2186 (M^+) ($C_{26}H_{28}$ requires 340.2190).

[Tris(4-methylphenyl)methyl]cyclohexane (2f): mp 135–137 °C; UV (MeOH) λ_{max} 264 nm (ϵ 1400 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 0.45–2.0 (m, 10 H), 2.28 (s, 9 H), 3.0 (t, 1 H, J = 11.2 Hz), 6.90–7.30 (m, 12 H); HRMS (EI) m/z 368.2501 (M^+) ($C_{28}H_{32}$ requires 368.2503).

[(4-Methoxyphenyl)diphenylmethyl]cyclohexane (2g): mp 146–148 °C; UV (MeOH) λ_{max} 273 nm (ϵ 2400 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 0.45–2.0 (m, 10 H), 3.76 (s, 3 H), 3.02 (t, 1 H, J = 11.2 Hz), 6.90–7.50 (m, 14 H); HRMS (EI) m/z 356.2138 (M^+) ($C_{26}H_{28}O$ requires 356.2139).

[Tris(4-methoxyphenyl)methyl]cyclohexane (2h): mp 156–158 °C; UV (MeOH) λ_{max} 275 nm (ϵ 3780 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 0.45–2.0 (m, 10 H), 3.76 (s, 9 H), 6.70–7.20 (m, 12 H); HRMS (EI) m/z 416.2346 (M^+) ($C_{28}H_{32}O_3$ requires 416.2349).

1,1,1-Triphenyl-2-methylpropane (2i): mp 92–94 °C; UV (MeOH) λ_{max} 260 nm (ϵ 850 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 0.82 (d, 6 H, J = 6.3 Hz), 3.57 (sept, 1 H, J = 6.4 Hz); HRMS (EI) m/z 286.1718 (M^+) ($C_{22}H_{22}$ requires 286.1720).

3-(Triphenylmethyl)heptane (2j): mp 102–104 °C; UV (MeOH) λ_{max} 260 nm (ϵ 900 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 0.80 (t, 3 H, J = 7.4 Hz), 0.98 (t, 3 H, J = 7.4 Hz), 0.65–2.0 (m, 8 H), 2.96 (quint., 1 H, J = 8.7 Hz); HRMS (EI) m/z 342.2344 (M^+) ($C_{26}H_{30}$ requires 342.2346).

1,1,1-Triphenylethane (2k): mp 94–95 °C; UV (MeOH) λ_{max} 260 nm (ϵ 785 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 2.03 (s, 3 H), 6.90 (s, 15 H); HRMS (EI) m/z 258.1404 (M^+) ($C_{20}H_{18}$ requires 258.1408).

1,1,1-Triphenyl-2,2-dimethylpropane (2l): mp 184–185 °C; UV (MeOH) λ_{max} 260 nm (ϵ 800 dm^3 mol^{-1} cm^{-1}); ^1H NMR δ 1.32 (s, 9 H), 7.22 (s, 15 H); HRMS (EI) m/z 300.1874 (M^+) ($C_{23}H_{24}$ requires 300.1877).

Preparation of Authentic Samples. Cyclohexylmethoxyphenylmethane (4a). The compound **4a** was prepared by the methylation of cyclohexylphenylmethanol, which was derived from the reaction of benzaldehyde with cyclohexylmagnesium bromide, with dimethyl sulfate in alkaline media. After reaction, the mixture was washed with water. The organic layer was extracted with benzene and dried over anhydrous magnesium sulfate. The solvent was removed by a rotary evaporator and the residue was purified by use of a column chromatography (eluant: hexane). This compound was very stable to UV irradiation and the GLC analysis conditions: bp 108–109 °C (0.1 mmHg); ^1H NMR δ 0.80–2.10 (m, 11 H), 3.17 (s, 3 H), 3.78 (d, 1 H, J = 7.3 Hz),

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7.20–7.40 (m, 5 H); HRMS (EI) *m/z* 204.1510 (M^+) ($C_{14}H_{20}O$ requires 204.1513).

Authentic samples (**4b–h**) were prepared by a similar procedure as described in the preparation of **4a**.

Cyclopropylmethoxyphenylmethane (4b): ^{1}H NMR δ 0.026–0.066 (m, 2 H), 0.63–0.67 (m, 2 H), 3.17 (s, 3 H), 3.75 (d, 1 H, $J = 7.3$ Hz), 7.0–7.40 (m, 5 H); HRMS (EI) *m/z* 162.1040 (M^+) ($C_{11}H_{14}O$ requires 162.1044).

Cyclopentylmethoxyphenylmethane (4c): ^{1}H NMR δ 1.0–2.30 (m, 9 H), 3.17 (s, 3 H), 3.70 (d, 1 H, $J = 7.3$ Hz), 7.10–7.30 (m, 5 H); HRMS (EI) *m/z* 190.1354 (M^+) ($C_{13}H_{18}O$ 190.1357).

Cycloheptylmethoxyphenylmethane (4d): ^{1}H NMR δ 0.80–2.20 (m, 13 H), 3.17 (s, 3 H), 3.76 (d, 1 H, $J = 7.3$ Hz), 7.0–7.40 (m, 5 H); HRMS (EI) *m/z* 218.1665 (M^+) ($C_{15}H_{22}O$ 218.1670).

Cyclohexylmethoxytolylmethane (4e): ^{1}H NMR δ 0.80–2.10 (m, 11 H), 2.27 (s, 3 H), 3.17 (s, 3 H), 3.78 (d, 1 H, $J = 7.3$ Hz), 7.0–7.30 (m, 4 H); HRMS (EI) *m/z* 218.1666 (M^+) ($C_{15}H_{22}O$ requires 218.1670).

Cyclohexyl(4-methoxyphenyl)methoxymethane (4f): ^{1}H NMR δ 0.80–2.10 (m, 11 H), 3.17 (s, 3 H), 3.77 (d, 1 H, $J = 7.3$ Hz), 3.78 (s, 3 H), 7.0–7.40 (m, 4 H); HRMS (EI) *m/z* 234.1618 (M^+) ($C_{15}H_{22}O_2$ requires 234.1619).

1-Methoxy-1-phenyl-2-methylpropane (4g): ^{1}H NMR δ 0.84 (d, 6 H, $J = 7.4$ Hz), 3.17 (s, 3 H), 3.77 (d, 1 H, $J = 7.0$ Hz), 7.0–7.40 (m, 5 H); HRMS (EI) *m/z* 164.1202 (M^+) ($C_{11}H_{16}O$ requires 164.1200).

3-(Methoxyphenylmethyl)heptane (4h): ^{1}H NMR δ 0.90 (t, 3 H, $J = 7.4$ Hz), 1.0 (t, 3 H, $J = 7.4$ Hz), 0.50–2.40 (m, 8 H), 3.17 (s, 3 H), 3.77 (d, 1 H, $J = 7.4$ Hz), 7.0–7.40 (m, 5 H); HRMS (EI) *m/z* 220.1824 (M^+) ($C_{15}H_{24}O$ requires 220.1826).

Benzylidenecyclohexane (5a). Diethyl benzylphosphonate (11.2 g, 0.05 mol), 50% sodium hydride in mineral oil (2.4 g, 0.05 mol), and cyclohexanone (4.9 g, 0.05 mol) were added to 100 mL of dried 1,2-dimethoxyethane. The mixture was heated slowly to 85 °C with stirring.[19] The solution was refluxed for 30 min, cooled, and then taken up in a large excess of water. The organic layer was extracted with benzene and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was separated by use of a column chromatography (eluant: hexane) to give **5a** as a colorless oil: ^{1}H NMR δ 1.40–1.80 (m, 6 H), 2.20–2.27 (m, 2 H), 2.32–2.39 (m, 2 H), 6.22 (s, 1 H), 7.0–7.40 (m, 5 H); HRMS (EI) *m/z* 172.1248 (M^+) ($C_{13}H_{16}$ requires 172.1251).

Authentic samples (**5d–h**) were prepared by a similar procedure as described in the preparation of **5a**.

Benzylidenecycloheptane (5d): ^{1}H NMR δ 1.40–2.0 (m, 8 H), 2.30–2.40 (m, 2 H), 6.20 (s, 1 H), 7.0–7.50 (m, 5 H); HRMS (EI) *m/z* 186.1406 (M^+) ($C_{14}H_{18}$ requires 186.1408).

(4-Methylbenzylidene)cyclohexane (5e): ^{1}H NMR δ 1.40–1.80 (m, 6 H), 2.20–2.27 (m, 2 H), 2.28 (s, 3 H), 2.32–2.39 (m, 2 H), 6.22 (s, 1 H), 7.0–7.40 (m, 4 H); HRMS (EI) *m/z* 186.1406 (M^+) ($C_{14}H_{18}$ requires 186.1408).

(4-Methoxybenzylidene)cyclohexane (5f): ^{1}H NMR δ 1.40–1.80 (m, 6 H), 2.20–2.27 (m, 2 H), 2.32–2.39 (m, 2 H), 3.76 (s, 3 H), 6.23 (s, 1 H), 7.0–7.40 (m, 4 H); HRMS (EI) *m/z* 202.1354 (M^+) ($C_{14}H_{18}O$ requires 202.1358).

1-Phenyl-2-methylpropene (5g): ^{1}H NMR δ 1.26 (s, 6 H), 6.23 (s, 1 H), 7.0–7.40 (m, 5 H); HRMS (EI) *m/z* 132.0934 (M^+) ($C_{10}H_{12}$ requires 132.0938).

3-Benzylideneheptane (5h): ^{1}H NMR δ 0.80 (t, 3 H, $J = 7.4$ Hz), 1.0 (t, 3 H, $J = 7.4$ Hz), 0.60–2.30 (m, 8 H), 6.20 (s, 1 H), 7.0–7.50 (m, 5 H); HRMS (EI) *m/z* 188.1562 (M^+) ($C_{14}H_{20}$ requires 188.1564).

General Procedure for Photolysis. A methanol solution (3 mL) of **2** (1.0×10^{-2} mol dm^{-3}) in a quartz tube was purged of dissolved oxygen by bubbling with argon. It was irradiated with a high-pressure mercury lamp (300 W) in a merry-go-round apparatus at ambient temperature. After irradiation for the desired time, the mixture was analyzed by GLC. The yields of **1**, **4**, and **5** were determined using methyl diphenylacetate as an internal standard.

The photolyses of **2** in other solvents (cyclohexane, acetonitrile, and THF) were carried out in a similar manner as described above.

The identification of the photoproducts was achieved by comparison of GLC retention times and mass spectra (GC/MS) with those of authentic samples. The product yields were determined by means of GLC calibration with methyl diphenylacetate as an internal standard.

Photolysis of 2a in the Presence of Molecular Oxygen. Three 3-mL methanol solutions of **2a** (1.0×10^{-2} mol dm^{-3}) were placed in separate quartz tubes (ϕ = 10 mm). Argon, air, or oxygen was bubbled into the solutions at 20 °C for 10 min, respectively. They were irradiated at the same time with a merry-go-round apparatus, in a similar manner as described above. In these cases, the yields of **1a**, **4**, and **5** were almost unchanged.

Photolysis of 2a (in a Preparative Scale). A methanol solution (100-mL) of **2a** (10×10^{-3} mol dm^{-3}) was purged of dissolved oxygen by bubbling with argon. It was irradiated in a quartz doughnut-type cell (10 mm thick) with a high-pressure mercury lamp (300 W) at ambient temperature for 3 h. After the solvent was evaporated, the residue was separated by means of chromatography on silica gel using hexane and chloroform as eluants to give **1a**, **4a**, and **5a**, which were confirmed with spectra data of authentic samples.

Photolysis of Cyclohexylphenyldiazomethane (6) in Methanol. The diazomethane (**6**) was prepared by the known method.[6] A 200-mL degassed methanol solution of **6** (40×10^{-3} mol dm^{-3}) was irradiated in a quartz tube with a high-pressure mercury lamp for 30 min. The products **4a** and **5a** were isolated by means of a column chromatography (eluant: hexane/chloroform 5:2) in the yields of 50 and 40%, respectively.

Sensitized Photolysis of 6 in Methanol. The sensitized photolysis of **6** (40×10^{-3} mol dm^{-3}) was performed using a saturated methanol solution of MK as a solvent in a Pyrex tube with a $BiCl_3$/HCl filter (>350 nm). After irradiation for 0.5 h by use of a high-pressure mercury lamp, the reaction mixture was analyzed by GLC.

Measurement of the Quantum Yield. The quantum yields were based on the formation of **1**. A low-pressure mercury lamp (60 W) with a Vycor glass filter was used as a 254-nm radiation source. A 3-mL methanol solution of **2** (10×10^{-3} mol dm^{-3}) in a quartz cell (10 mm × 10 mm) was irradiated. As an actinometry a potassium trioxalatoferrate(III) solution was used.[20] The yields of the products were measured by GLC (Shimadzu GC-7A, Silicone OV-17, 2%, support, Uniport HP, 1-m glass column). Methyl diphenylacetate was used as an internal standard. The photolyses were carried out at a conversion of <5%.

Registry No. **1a**, 92-52-4; **2a**, 13619-64-2; **2b**, 126979-53-1; **2c**, 126979-54-2; **2d**, 126979-55-3; **2e**, 126979-56-4; **2f**, 126979-57-5; **2g**, 126979-58-6; **2h**, 126979-59-7; **2i**, 29379-48-4; **2j**, 126979-60-0; **2k**, 5271-39-6; **2l**, 24523-60-2; **4a**, 126979-61-1; **4b**, 5558-08-7; **4c**, 126979-62-2; **4d**, 126979-63-3; **4e**, 126979-64-4; **4f**, 126979-65-5; **4g**, 52067-39-7; **4h**, 126979-66-6; **5a**, 1608-31-7; **5d**, 15537-53-8; **5e**, 7577-03-9; **5f**, 7577-08-4; **5g**, 768-49-0; **5h**, 126979-67-7; **6**, 82517-30-4; **7**, 4442-83-5; *p*-$MeC_6H_4C(Ph)_2Cl$, 23429-44-9; $ClC(p\text{-}C_6H_4Me)_3$, 971-93-7; *p*-$MeOC_6H_4C(Ph)_2Cl$, 14470-28-1; $ClC(p\text{-}C_6H_4OMe)_3$, 49757-42-8; $Me_2CHMgBr$, 920-39-8; $H_3C(CH_2)_3CH(CH_2CH_3)MgBr$, 126979-68-8; Me_3CMgBr, 2259-30-5; 4,4′-bis(dimethylamino)benzophenone, 90-94-8; triphenylmethyl chloride, 76-83-5; cyclohexylmagnesium bromide, 931-50-0; cyclopropylmagnesium bromide, 23719-80-4; cyclopentylmagnesium bromide, 33240-34-5; cycloheptylmagnesium bromide, 78378-12-8.

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