Photolyses of 1,4-Bis(1,1-diarylhept-2-ynyl)benzenes and 1,4-Bis(1,1-diarylalkyl)benzenes

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Photolyses of 1,4-bis(1,1-diarylhept-2-ynyl)benzenes or 1,4-bis(1,1-diarylalkyl)benzenes **2** in a tetrahydrofuran–methanol mixture gave 1-biphenyl-4-yl-1,1-diarylhept-2-ynes or 1-biphenyl-4-yl-1,1-diarylalkanes **3** as major products and biaryls **1** as minor products. The products **3** were obtained with quantum yields of 0.010–0.020, respectively.

Our recent studies on the photochemical reactions of triphenylmethane derivative such as dimethyl triphenylmethylphosphonate, 1,1,1-triphenylhept-2-yne, and triphenylalk-2-ene in methanol have shown that they undergo a photochemical α,α-elimination of two phenyl groups to afford biphenyl **1a** and the corresponding carbene intermediates, with quantum yields of 0.010–0.020.[1a–c]

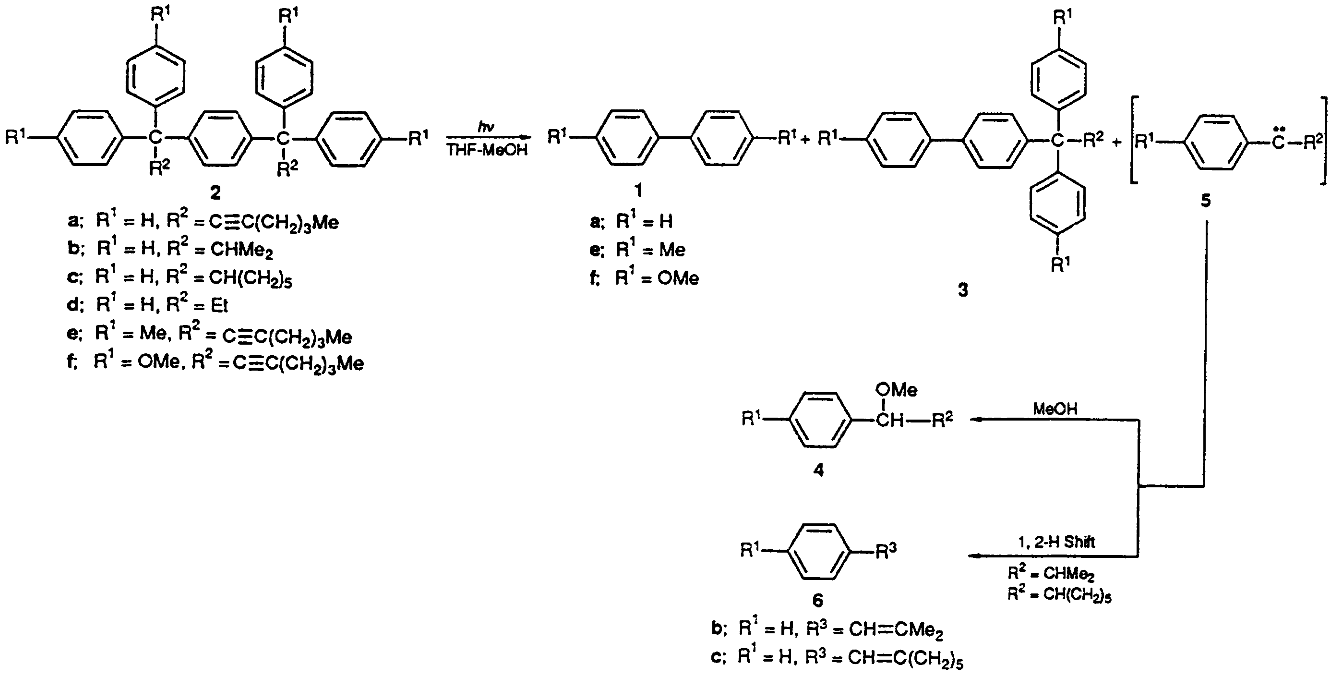
This finding prompted us to study further the photochemical reaction of other triphenylmethane derivatives. Here, we report the photolyses of some 1,4-bis(1,1-diarylhept-2-ynyl)benzene **2a, e, f** and 1,4-bis(1,1-diphenylalkyl)benzenes **2b–d**.

Results and Discussion

Photolysis of 1,4-bis(1,1-diphenylhept-2-ynyl)benzene **2a** in tetrahydrofuran (THF)–methanol under an argon atmosphere with a high pressure mercury lamp (300 W) for 2 h gave 1-biphenyl-4-yl-1,1-diphenylhept-2-yne **3a** and 1-methoxy-1-phenylhept-2-yne **4a** in 30 and 28% yields, respectively. Compound **4a** was derived from the insertion of the carbene **5a** into the O–H bond of methanol. Biphenyl **1a** was also obtained in a yield of only 2.2% (Scheme 1). The quantum yield of **3a** was 0.022. Photolysis of 1,4-bis(2-methyl-1,1-diphenylpropyl)benzene **2b** or 1,4-bis(cyclohexyldiphenylmethyl)benzene **2c** under the same conditions gave, similarly, 1-biphenyl-4-yl-2-methyl-1,1-diphenylpropane **3b** or biphenyl-4-yl(cyclohexyl)diphenylmethane **3c**, 1-methoxy-2-methyl-1-phenylpropane **4b** or cyclohexyl(methoxy)phenylmethane **4c**, and 2-methyl-1-phenylpropene **6b** or α-cyclohexylidenetoluene **6c**, respectively. The products **4b** or **4c** and **6b** or **6c** must be derived from the insertion of the carbene intermediate **5b** or **5c** into the O–H bond of methanol or from the 1,2-hydrogen shift in **5b** or **5c**, respectively (Scheme 1). In contrast, 1,4-bis(1,1-diphenylpropyl)benzene **2d** underwent little photolysis, only a trace of a complex and unidentified mixture, being obtained. This result is similar to those for the photolysis of 2-methyl-1,1,1-triphenylpropane, which gave **1a** in a quantum yield of 0.013, and 1,1,1-triphenylethane which failed to give any **1a**.[1c] The yields of products are summarized in Table 1.

Previously, and in a similar fashion, it was postulated that photochemical formation of the carbene intermediate **5** from 1,1,1-triphenylhept-2-yne occurred as a result of α,α-elimination of the two phenyl groups.[1b] Upon UV irradiation, there is intramolecular charge transfer interaction between the three aryl groups of the triphenylmethyl substituent and, subsequently, the biphenyl **1a** is formed *via* initial bonding between the C-1 positions of two phenyl groups (ipso coupling) followed by α,α-elimination. This photoinduced intramolecular elimination of **1a** may proceed *via* an excited singlet state (S_1).[1c,2–5]

In the photolysis of **2a–d**, a similar mechanism is thought to



Scheme 1

Table 1 Photolysis of **2a**–**c** in THF and MeOH

Compd.	% Conversion[b]	φ[c]	Product [yield (%)][a]			
			1a	**3**	**4**	**6**
2a	55	0.022	**1a** (2.2)	**3a** (30)	**4a** (28)	—
2b	50	0.018	**1a** (2.4)	**3b** (26)	**4b** (15)	**6b** (10)
2c	51	0.016	**1a** (2.0)	**3c** (24)	**4c** (10)	**6c** (14)
2e	60	0.029	**1e** (3.0)	**3e** (35)	**4e** (34)	—
2f	70	0.040	**1f** (1.3)	**3f** (44)	**4f** (41)	—

[a] The yield was based on the starting material used. [b] Concentration; 1.0 × 10^{-2} mol dm^{-3}, irradiated in a quartz tube for 2 h. [c] The quantum yield of **3**.

occur, although the yield of **3a** (30%) was much larger than that of **1a** (2.2%). This selective elimination of aryl groups indicates that coupling between the phenyl and the 1,4-phenylene groups predominates; the phenyl group may have a stronger interaction with a 1,4-phenylene group than another phenyl group.

Terphenyl, which may be derived by coupling of the phenyl and the biphenylyl groups of **3a**–**c** upon further irradiation, could not be detected. Attempted photolysis of **3a**–**c**, prepared by an alternative method, showed the compounds to be quite stable even upon a prolonged irradiation. Although the absorption maxima of **2a**–**c** and **3a**–**c** look very similar, the latter absorb well into the long-wavelength region. This suggests that introduction of a biphenylyl group into the molecule might result in a lowering of its excited energy level.[6] As the result, α,α-elimination of these aryl groups cannot occur.

We have further studied the photolysis of other *para*-substituted compounds, **2e** or **2f**, under similar conditions, and obtained similar results (Scheme 1). The product **3e** or **3f** was formed in 35 or 44% yield respectively, after irradiation for 2 h. The counter products, **4e** or **4f**, which were similarly derived from insertion of the corresponding carbene intermediate **5e**–**f** into the O–H bond of methanol, were obtained in an almost equivalent yields to those of **3e** and **3f**, respectively. The biaryls **1e**–**f** were also obtained in very small yield. The quantum yields of **3e** and **3f** were 0.029 and 0.040, respectively, which were larger than that of **3a** in the photolysis of the unsubstituted derivative **2a**. These facts also suggest that by introducing a substituent into the benzene ring, an inter-ring charge-transfer interaction between the benzene ring and the 1,4-phenylene ring might be increased and, subsequently, the efficiency of the biaryl elimination is enhanced.

Experimental

M.p.s and b.p.s are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer, with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard, *J* values are given in Hz.

Preparation of **2a**–**f**. *General Procedure.*—Compounds **2a**–**f** were prepared by the reaction of 1,4-bis(chlorodiarylmethyl)-benzene (5 g, 10.5 mmol) with an ethereal solution of the corresponding alkyl- or alkynyl-magnesium bromide (30.0 mmol), respectively.[7] After work-up, the crude products were recrystallized from benzene–methanol to give crystalline products.

1,4-*Bis*(1,1-*diphenylhept*-2-*ynyl*)*benzene* **2a**. (4.0 g, 70%), m.p. 120–122 °C (Found: C, 92.6; H, 7.5. $C_{44}H_{42}$ requires C, 92.58; H, 7.42%); λ_{max}(MeOH)/nm 261 (ε 880); ν_{max}(KBr)/cm^{-1} 2180 (C≡C); δ_H($CDCl_3$; TMS) 0.91 (6 H, t, *J* 7.3), 1.40–1.70 (8 H, m), 2.34 (4 H, t, *J* 7.3) and 7.0–7.50 (24 H, m, Ar).

1,4-*Bis*(2-*methyl*-1,1-*diphenylpropyl*)*benzene* **2b**. (3.9 g, 80%), m.p. 166–168 °C (Found: C, 92.1; H, 7.75. $C_{38}H_{38}$ requires C, 92.26; H, 7.7%); λ_{max}(MeOH)/nm 262 (ε 1000); ν_{max}(KBr)/cm^{-1} 1620 (C=C); δ_H($CDCl_3$) 0.87 (12 H, d, *J* 6.3, CH_3), 3.56 (2 H, sept, *J* 6.3 and 6.90–7.50 (24 H, m, Ar).

1,4-*Bis*(*cyclohexyldiphenylmethyl*)*benzene* **2c**. (3.4 g, 60%), m.p. 180–182 °C (Found: C, 91.65; H, 8.2. $C_{44}H_{48}$ requires C, 91.61.34; H, 8.39%); λ_{max}(MeOH)/nm 261 (ε 890); ν_{max}(KBr)/cm^{-1} 1620 (C=C); δ_H($CDCl_3$) 0.45–2.10 (20 H, m), 3.04 (2 H, t, *J* 11.2) and 6.90–7.50 (24 H, m, Ar).

1,4-*Bis*(1,1-*diphenylpropyl*)*benzene* **2d**. (3.7 g, 80%), m.p. 201–203 °C (Found: C, 92.8; H, 7.3. $C_{36}H_{34}$ requires C, 92.66; H, 7.34%); λ_{max}(MeOH)/nm 261 (ε 1000); ν_{max}(KBr)/cm^{-1} 1620 (C=C); δ_H($CDCl_3$) 1.10 (6 H, t, *J* 6.4, CH_3), 1.23 (4 H, q, *J* 6.4, CH_2) and 6.90–7.50 (24 H, m, Ar).

1,4-*Bis*[1,1-*di*(p-*tolyl*)*hept*-2-*ynyl*]*benzene* **2e**. (4.4 g, 70%), m.p. 145–148 °C (Found: C, 91.9; H, 8.1. $C_{48}H_{50}$ requires C, 91.96; H, 8.04%); λ_{max}(MeOH)/nm 266 (ε 1400); ν_{max}(neat)/cm^{-1} 2182 (C≡C); δ_H($CDCl_3$) 0.91 (6 H, t, *J* 7.3), 1.40–1.70 (8 H, m), 2.34 (4 H, t, *J* 7.3), 2.26 (12 H, s, CH_3) and 7.0–7.50 (20 H, m).

1,4-*Bis*[1,1-*bis*(p-*methoxyphenyl*)*hept*-2-*ynyl*]*benzene* **2f**. (4.8 g, 71%), m.p. 187–188 °C (Found: C, 83.35; H, 7.4. $C_{48}H_{50}O_4$ requires C, 83.44; H, 7.29%); λ_{max}(MeOH)/nm 275 (ε 2300); ν_{max}(KBr)/cm^{-1} 2182 (C≡C); δ_H($CDCl_3$) 0.91 (6 H, t, *J* 7.3), 1.40–1.70 (8 H, m), 2.34 (4 H, t, *J* 7.3), 3.76 (12 H, s, OCH_3) and 7.0–7.50 (20 H, m).

General Procedure for Photolyses.—Photolyses were carried out in the same manner as described previously.[1] A mixture of THF and methanol (1:1) was used as solvent, because of low solubilities of compounds **2a**–**f** and **4a**–**f** in pure methanol.

The methyl ethers **4a**–**f** and benzylidene derivatives **6b**,**c** were prepared in the same manner as described previously.[1c]

Preparation of **3a**–**f**. *General Procedure.*—Compounds **3a**–**f** were prepared by the reaction of biphenyl-4-yl(diphenyl)methyl-4′-methylbiphenyl-4-yl-1,1-di(*p*-tolyl)methyl-, or 4-methoxybiphenyl-4-yl-1,1-bis(*p*-methoxyphenyl)methyl chloride (6.0 g, 17.2 mmol) with ethyl-, isopropyl-, cyclohexyl-, or hex-1-ynylmagnesium bromide, respectively. After work-up, the crude products were recrystallized from benzene–methanol.

1-Biphenyl-4-yl-1,1-diphenylhept-2-yne **3a**. (2.4 g, 60%), m.p. 124–126 °C (Found: C, 92.75; H, 7.1. $C_{31}H_{28}$ requires C, 92.95; H, 7.05%); ν_{max}(KBr)/cm^{-1} 2184 (C≡C); λ_{max}(MeOH)/nm 258 (ε 24 500); δ_H($CDCl_3$) 0.91 (3 H, t, *J* 7.3), 1.40–1.70 (4 H, m), 2.34 (2 H, t, *J* 7.3) and 7.0–7.50 (19 H, m, Ar).

1-Biphenyl-4-yl-1,1-diphenyl-2-methylpropane **3b**. (3.0 g, 65%), m.p. 168–170 °C (Found: C, 92.65; H, 7.4. $C_{28}H_{26}$ requires C, 92.77; H, 7.23%); λ_{max}(MeOH)/nm 260 (ε 23 500); ν_{max}(KBr)/cm^{-1} 1620 (C=C), δ_H($CDCl_3$) 0.87 (6 H, d, *J* 6.3, CH_3), 3.56 (1 H, sept, *J* 6.3) and 6.90–7.50 (12 H, m, Ar).

[*Biphenyl*-4-*yl*(*diphenyl*)*methyl*]*cyclohexane* **3c**. (2.6 g, 60%), m.p. 174–176 °C (Found: C, 92.65; H, 7.4. $C_{31}H_{30}$ requires C, 92.49; H, 7.51%); λ_{max}(MeOH)/nm 260 (ε 25 000); ν_{max}(KBr)/cm^{-1} 1620 (C=C); δ_H($CDCl_3$) 0.45–2.10 (10 H, m), 3.04 (1 H, t, *J* 11.2) and 6.90–7.50 (12 H, m, Ar).

1-(4′-*Methylbiphenyl*-4-*yl*)-1,1-*di*(p-*tolyl*)*hept*-2-*yne* **3e**. (2.7 g, 61%), m.p. 123–124 °C (Found: C, 92.35; H, 7.65. $C_{34}H_{34}$

requires C, 92.26; H, 7.74%); λ_{max}(MeOH)/nm 265 (ε 26 000); ν_{max}(KBr)/cm^{-1} 2186 (C≡C); δ_H($CDCl_3$) 0.91 (3 H, t, *J* 7.3), 1.40–1.70 (4 H, m), 2.34 (2 H, t, *J* 7.3), 2.26 (9 H, s, CH_3) and 7.0–7.50 (16 H, m).

1-(4′-*Methoxybiphenyl*-4-*yl*)-1,1-*bis*(p-*methoxyphenyl*)*hept*-2-*yne* **3f**. (2.4 g, 60%) m.p. 144–146 °C (Found: C, 83.1; H, 7.0. $C_{34}H_{34}PO_3$ requires C, 83.23; H, 6.99%); λ_{max}(MeOH)/nm 275 (ε 32 000); ν_{max}(KBr)/cm^{-1} 2182 (C≡C); δ_H($CDCl_3$) 0.91 (3 H, t, *J* 7.3), 1.40–1.70 (4 H, m), 2.34 (2 H, t, *J* 7.3), 3.76 (9 H, s, OCH_3) and 7.0–7.50 (16 H, m, Ar).

Measurement of the Quantum Yield.—The quantum yields were determined in a similar manner to that described previously.[1,8]

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