

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**.

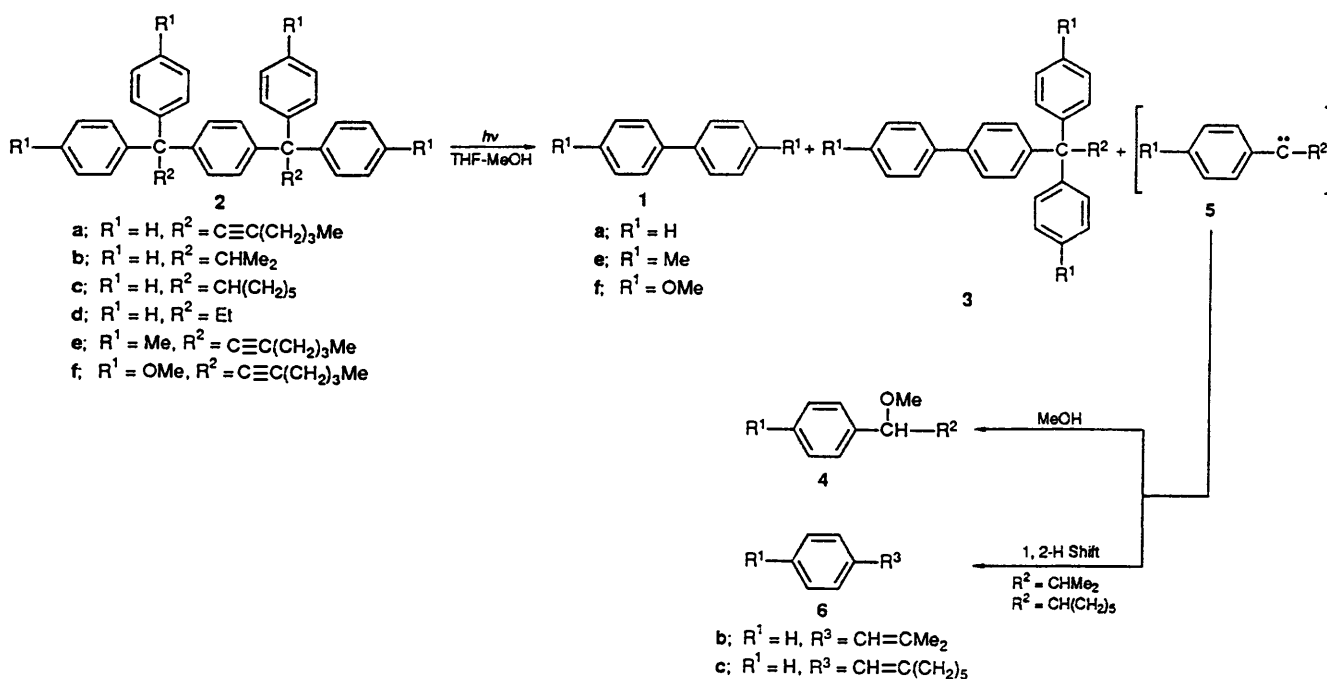
Results and Discussion

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 biphenyl 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 biphenyl 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. ¹H and ¹³C NMR spectra were recorded on a JEOL FX-90Q spectrometer, with CDCl₃ 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. C₄₄H₄₂ requires C, 92.58; H, 7.42%; λ_{\max} (MeOH)/nm 261 (ϵ 880); ν_{\max} (KBr)/cm⁻¹ 2180 (C≡C); δ_{H} (CDCl₃; 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. C₃₈H₃₈ requires C, 92.26; H, 7.7%; λ_{\max} (MeOH)/nm 262 (ϵ 1000); ν_{\max} (KBr)/cm⁻¹ 1620 (C=C); δ_{H} (CDCl₃) 0.87 (12 H, d, *J* 6.3, CH₃), 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. C₄₄H₄₈ 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} (CDCl₃) 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. C₃₆H₃₄ requires C, 92.66; H, 7.34%; λ_{\max} (MeOH)/nm 261 (ϵ 1000); ν_{\max} (KBr)/cm⁻¹ 1620 (C=C); δ_{H} (CDCl₃) 1.10 (6 H, t, *J* 6.4, CH₃), 1.23 (4 H, q, *J* 6.4, CH₂) 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. C₄₈H₅₀ requires C, 91.96; H, 8.04%; λ_{\max} (MeOH)/nm 266 (ϵ 1400); ν_{\max} (neat)/cm⁻¹ 2182 (C≡C); δ_{H} (CDCl₃) 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, CH₃) 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. C₄₈H₅₀O₄ requires C, 83.44; H, 7.29%; λ_{\max} (MeOH)/nm 275 (ϵ 2300); ν_{\max} (KBr)/cm⁻¹ 2182 (C≡C); δ_{H} (CDCl₃) 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, OCH₃) 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-ynyl-magnesium 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. C₃₁H₂₈ 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} (CDCl₃) 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. C₂₈H₂₆ 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} (CDCl₃) 0.87 (6 H, d, *J* 6.3, CH₃), 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. C₃₁H₃₀ 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} (CDCl₃) 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. C₃₄H₃₄

requires C, 92.26; H, 7.74%); $\lambda_{\max}(\text{MeOH})/\text{nm}$ 265 (ϵ 26 000); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2186 ($\text{C}\equiv\text{C}$); $\delta_{\text{H}}(\text{CDCl}_3)$ 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. $\text{C}_{34}\text{H}_{34}\text{PO}_3$ requires C, 83.23; H, 6.99%); $\lambda_{\max}(\text{MeOH})/\text{nm}$ 275 (ϵ 32 000); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2182 ($\text{C}\equiv\text{C}$); $\delta_{\text{H}}(\text{CDCl}_3)$ 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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