

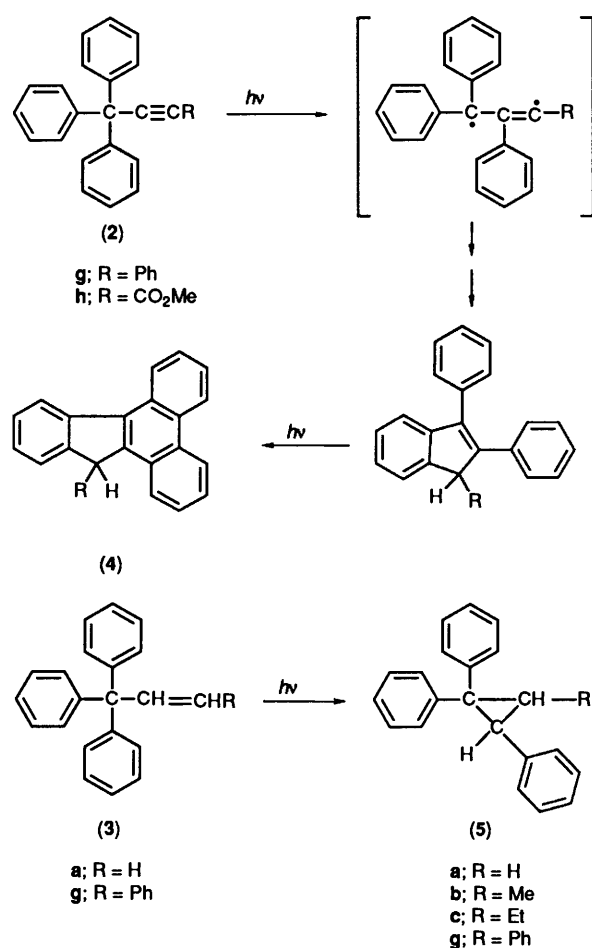
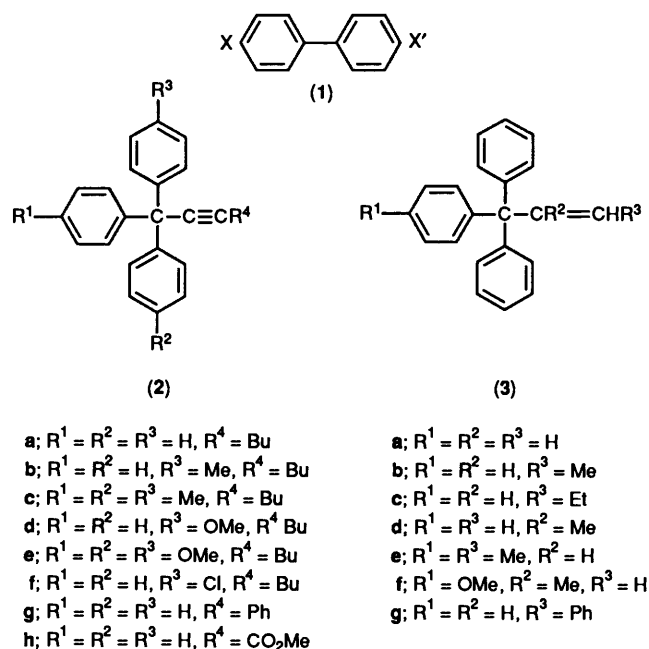
## Photolysis of 1,1,1-Triarylalk-2-enes and 1,1,1-Triarylhept-2-ynes. A Novel Generation of Aryl(alk-1-enyl)carbenes and Aryl(alk-1-ynyl)carbenes

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Upon UV irradiation in methanol, 1,1,1-triarylhept-2-ynes underwent an  $\alpha,\alpha$ -elimination of two aryl groups to give a biaryl and the corresponding carbene which reacted with methanol to give a 1-aryl-1-methoxyhept-2-yne. 1,1,1-Triphenylalk-2-enes underwent  $\alpha,\alpha$ -elimination of two phenyl groups and also elimination of an alkene and a phenyl group to give biphenyl and a 1-phenylalkene respectively. In both cases, the corresponding carbenes were formed and were isolated as methanol insertion products (a 1-methoxy-1-phenylalk-2-ene and diphenylmethyl methyl ether, respectively). A rearrangement product, a 1,1,2-triphenylcyclopropane, was also formed.

Recently, we found that, upon UV irradiation in methanol, dimethyl (triarylmethyl)phosphonates underwent an  $\alpha,\alpha$ -elimination of two aryl groups to give biaryl (1) and a dimethoxyphosphoryl(aryl)carbene intermediate, which reacted with methanol to afford a dimethyl methoxy(aryl)methylphosphonate.<sup>1</sup> In the course of studies on the photochemical carbene generation from other triarylmethyl derivatives,<sup>2</sup> we have found interesting phenomena in the photolysis of 1,1,1-triarylhept-2-ynes (2a-f) and 1,1,1-triarylalk-2-enes (3a-f), in which the reaction course is dramatically controlled by the nature of the substituent.<sup>3</sup>

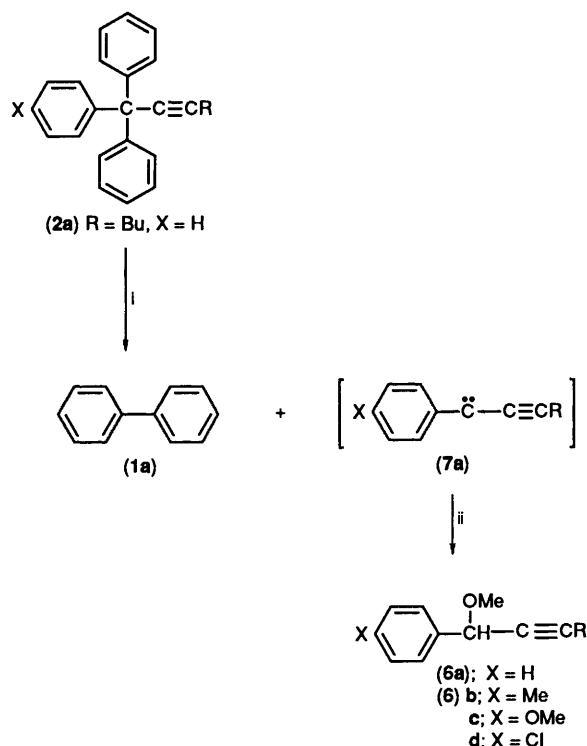


Scheme 1.

Griffin and co-workers have reported that when 1-phenyl-3,3,3-triphenylpropyne (2g) was irradiated with 254 nm light in degassed benzene solution for 50 h, an indenophenanthrene derivative (4) was obtained (Scheme 1).<sup>4</sup> Wilson and Huhtanen have also presented an additional example of analogous photorearrangement in the case of 1-methoxycarbonyl-3,3,3-triphenylpropyne (2h) (Scheme 1).<sup>5</sup> Furthermore, in 1965, Griffin revealed that upon irradiation of 3,3,3-triphenylpropene (3a) and 1,3,3,3-tetraphenylpropene (3g) under similar con-

ditions as described above, the major products were 1,1,2-triphenylcyclopropane (5a) and 1,1,2,3-tetraphenylcyclopropane (5g), respectively, the result of cyclization and concomitant phenyl migration; in addition considerable starting material and a number of unidentified minor products were observed (Scheme 1).<sup>6</sup>

In this paper, we present a different type of photochemical behaviour of compounds (2a-f) and (3a-f).



Scheme 2. Reagents and conditions: i,  $h\nu$ , 2 h; ii, MeOH.

## Results and Discussion

A methanolic solution of 1,1,1-triphenylhept-2-yne (**2a**) ( $10 \text{ mmol dm}^{-3}$ ) was irradiated in a quartz tube under argon by use of a merry-go-round apparatus for 2 h with a high-pressure mercury lamp (300 W). After irradiation (conversion 40%), the products were analysed with GC-MS by comparison with authentic samples. Biphenyl (**1a**) and 1-phenyl-1-methoxyhept-2-yne (**6a**) were obtained in 25 and 24% yield, respectively. The quantum yield of biphenyl (**1a**) was 0.028. The photorearranged product such as that observed in the photolysis of compounds (**2g**) and (**2h**) could not be detected. From these findings, a similar reaction scheme to that for the photolysis of dimethyl (triphenylmethyl)phosphonate can be postulated; upon UV excitation, alkyne (**2a**) undergoes an  $\alpha,\alpha$ -elimination of two phenyl groups to afford biphenyl (**1a**) and the corresponding carbene intermediate (**7a**) which is transformed to (**6a**) by reaction with methanol (Scheme 2).

In order to verify further these photochemical results reported by Griffin and others, we re-examined carefully the photochemical behaviour of compound (**2g**) under the same conditions as for photolysis of compound (**2a**). We found that even upon prolonged UV irradiation only a trace amount of biphenyl (**1a**), besides the pentacycle (**4**), could be detected.

The difference in the photochemical behaviour observed between alkynes (**2a**) and (**2g**) or (**2h**) can be accounted for by the difference of the energy levels of their excited states. Localization of the excitation energy in three phenyl groups of alkynes (**2**) should be required for the  $\alpha,\alpha$ -elimination of two phenyl groups. The requirement may be satisfied for compound (**2a**) since the excitation energy level of benzene is lower than that of acetylene. The introduction of a chromophore such as a phenyl or a methoxycarbonyl group to the acetylenic triple bond lowers the energy level of the acetylenic moiety by the conjugation effect. Therefore, in the cases of compounds (**2g**) and (**2h**) the excitation energy of the triphenylmethyl group may transfer to the acetylenic moiety in a lower excited state

and, consequently, compounds (**2g**) and (**2h**) undergo typical photolysis of acetylenic derivatives. The difference of the energy levels of their excited states can also be estimated from the UV absorption spectra of compounds (**2g**) ( $\lambda_{\text{max}}$  260, 280, and 328 nm) and (**2a**) ( $\lambda_{\text{max}}$  260 nm). In order to clarify further the underlying mechanism responsible for  $\alpha,\alpha$ -elimination of two aryl groups, we have investigated the photolysis of the *p*-substituted derivatives (**2b-f**) under the similar conditions. The quantum yields of biphenyl (**1**) and the selectivities of the  $\alpha,\alpha$ -elimination of aryl groups were determined (Table 1). The yields and quantum yields of 4,4'-dimethylbiphenyl (**1c**) from 1,1,1-tritolyhept-2-yne (**2c**) were also dependent on the solvent used (Table 2).

The quantum yields of biphenyls (**1**) from the *p*-substituted derivatives (**2b-f**) were larger than that of the unsubstituted derivative (**2a**), so the introduction of a substituent, regardless of its electron-donating or -withdrawing properties, facilitates the  $\alpha,\alpha$ -elimination of aryl groups. In the photolysis of 1,1-diphenyl-1-tolylhept-2-yne (**2b**), 1-(4-methoxyphenyl)-1,1-diphenylhept-2-yne (**2d**), or 1-(4-chlorophenyl)-1,1-diphenylhept-2-yne (**2f**), the  $\alpha,\alpha$ -elimination of different aryl groups to form an unsymmetric biaryl, 4-methylbiphenyl (**1b**), 4-methoxybiphenyl (**1d**), and 4-chlorobiphenyl (**1f**) were more favourable than that to form a symmetrical biaryl such as (**1a**) even after taking into account the correction ratio of the statistical elimination of aryl groups. This fact may suggest an increasing inter-ring charge-transfer interaction between the benzene ring and the substituted benzene ring.<sup>7</sup> The solvent effect in the photolysis of compound (**2c**) also supports this postulate, because in more highly polar solvents, the quantum yield of compound (**1c**) was larger than that on irradiation in non-polar solvents (Table 2).

Intramolecular charge-transfer interaction was also observed among the three benzene rings of the triptycene derivatives, in which a similar photochemical generation of a carbene intermediate was proposed by Iwamura and Yoshimura.<sup>8</sup>

On the other hand, upon UV irradiation of 3,3,3-triphenylpropene (**3a**), 1,1,1-triphenylbut-2-ene (**3b**), and 1,1,1-triphenylpent-2-ene (**3c**) with a high-pressure mercury lamp (300 W) under argon besides cyclization products (**5a**), 2-methyl-1,1,3-triphenylcyclopropane (**5b**), and 2-ethyl-1,1,3-triphenylcyclopropane (**5c**), two kinds of  $\alpha,\alpha$ -elimination took place to give two kinds of carbene intermediate. One was the  $\alpha,\alpha$ -elimination of two phenyl groups to give biphenyl (**1a**) and an alkenyl(phenyl)carbene intermediate (**8**), which inserted into the O-H bond of methanol to afford the methyl ether (**9**); another was the  $\alpha,\alpha$ -elimination of an alkene group and a phenyl group to give a 1-phenylalkene (**10**) and diphenylcarbene (**11**), which similarly inserted into the O-H bond of methanol to give diphenylmethyl methyl ether (**12**) (Scheme 3). Their yields are summarized in Table 3.

We further checked the photochemical behaviour of compounds (**3a**), (**3b**), and (**3c**) under similar conditions to those reported by Griffin (under irradiation with 254 nm light in a degassed benzene solution;  $0.1 \text{ mol dm}^{-3}$ ) and found that compound (**1a**) and (**10**) were also formed, although the carbene products could not be detected.

These results revealed a unique photochemical behaviour of compound (**3**) under UV irradiation, which is very different from that of alkynes (**2**) described previously.

When 2-methyl-3,3,3-triphenylpropene (**3d**)\* was used as a substrate, upon UV irradiation in methanol compounds (**1a**), (**12**), and 2-phenylpropene were obtained in 24% and trace yields respectively, but the product derived from cyclization could not be detected (Scheme 4). This result implies that the

\* Compounds (**3d**) and (**3f**) were prepared according to the literature procedure.

**Table 1.** Photolysis of alkynes (**2a–f**).<sup>a</sup>

	Compound ( <b>2</b> )			$10^2 \Phi^c$	Conversion (%) <sup>c</sup>	Product (Yield/%) <sup>c</sup>
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>			
( <b>2a</b> )	H	H	H	2.8	40	( <b>1a</b> ) (25) ( <b>6a</b> ) (24)
( <b>2b</b> )	H	H	Me	3.8	60	( <b>1a</b> ) (8);  ( <b>1b</b> ) (26); ( <b>6a</b> ) (26) ( <b>6b</b> ) (7)
( <b>2c</b> )	Me	Me	Me	3.7	58	( <b>1c</b> ) (40); ( <b>6b</b> ) (39)
( <b>2d</b> )	H	H	OMe	4.9	50	( <b>1a</b> ) (7);  ( <b>1d</b> ) (30); ( <b>6a</b> ) (29);  ( <b>6c</b> ) (7)
( <b>2e</b> )	OMe	OMe	OMe	4.4	70	( <b>1e</b> ) (30); ( <b>6c</b> ) (28)
( <b>2f</b> )	H	H	Cl	4.5	60	( <b>1a</b> ) (7);  ( <b>1f</b> ) (36); ( <b>6a</b> ) (35) ( <b>6d</b> ) (6)

<sup>a</sup> Reaction conditions: (**2a–f**) (10 mmol dm<sup>-3</sup>), MeOH, Ar, high-pressure mercury lamp, 2 h. <sup>c</sup> Conversions and yields were based on GC analysis; calibration using pure authentic samples. <sup>b</sup> Quantum yields were calculated on the combined yields of both biaryls at low conversion (< 5%).

**Table 2.** Photolysis of alkyne (**2c**) in various solvents for 2 h.

Solvent	$10^2 \Phi$	Conversion (%)	Product ( <b>1c</b> ) (%)
Methanol	3.7	58	40
Acetonitrile	2.7	54	32
Tetrahydrofuran (THF)	2.6	52	32
Cyclohexane	1.8	49	28
Cyclohexene	1.6	48	26

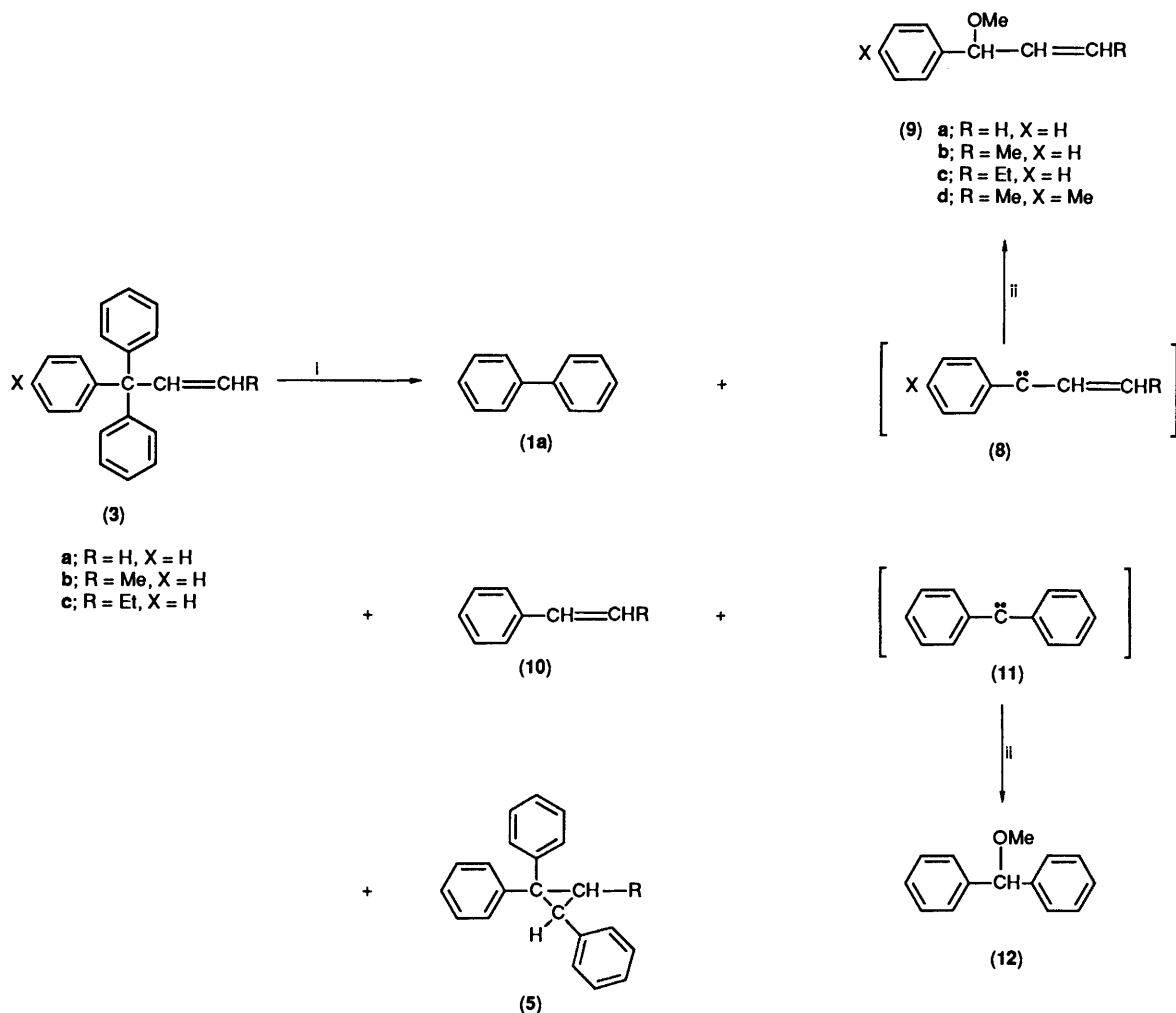
introduction of a methyl group into the position adjacent to the triphenylmethyl group hinders the 1,2-phenyl migration and the  $\alpha,\alpha$ -elimination of an alkene and a phenyl group. Furthermore, when an electron-donating substituent was introduced into the phenyl group, for example, 1,1-diphenyl-1-tolyl-but-2-ene (**3e**) or 3-(4-methoxyphenyl)-2-methyl-3,3-diphenylpropene (**3f**),<sup>9</sup> only unsymmetrical biaryls were obtained, in 15 and 20% yield, respectively. This result also indicated the existence of a more intense inter-ring charge-transfer interaction between the substituted and unsubstituted benzene rings.

In order to gain insight about the excited species, the effect of oxygen was examined. Upon UV irradiation in an oxygen-saturated methanol solution of alkyne (**2a**) the yield of biphenyl (**1a**) was unchanged. On the other hand, upon triplet-sensitized

irradiation of alkyne (**2c**) using benzophenone in methanol, biphenyl (**1a**) could not be detected by GLC. Moreover, in the photolysis of an oxygen-saturated methanolic solution of alkene (**3c**), the yield of biphenyl (**1a**) was also unchanged. Consequently, the formation of the carbene as an intermediate from alkyne (**2a**) can be postulated as occurring as shown in Scheme 5.

In the photo-excited state of substrates (**2**) and (**3**), probably a singlet excited state, there is an intramolecular charge-transfer interaction among the three aryl rings and, subsequently, two aryl groups are eliminated *via* the initial bonding between C-1 positions of two aryl groups (*ipso* coupling). The elimination of the biaryl may proceed in a stepwise or in a concerted manner. The mechanism of this reaction is understood in terms of a photochemical di- $\pi$ -methane rearrangement.<sup>10</sup> The carbene intermediate was thus formed, and was then converted into final products by the reaction with solvent, *i.e.* insertion into the O–H bond of an alcohol.

In addition, in the case of irradiation of alkenes (**3**) in methanol, the mechanism of the formation of cyclization products can be explained as a usual 1,2-phenyl migration *via* a biradical intermediate (**13**). The mechanism of the formation of products (**1a**), (**10**), and the carbene intermediates (**8**) and (**11**) can be formulated as an alternative degradation path of compounds (**3**) through the intermediates (**14**) and (**15**),



Scheme 3. Reagents and conditions: i, hv; ii, MeOH.

Table 3. Yields of photolysis products of alkenes (3a), (3b), and (3c).

Alkene	Conversion (%) <sup>a</sup>	10 <sup>2</sup> $\Phi^b$	Product (%)				
			(1a)	(9)	(10)	(12)	(5)
(3a)	27	0.6	8	5	trace	4	14
(3b)	38	1.0	22	15	trace	5	8
(3c)	43	1.0	24	16	trace	6	9

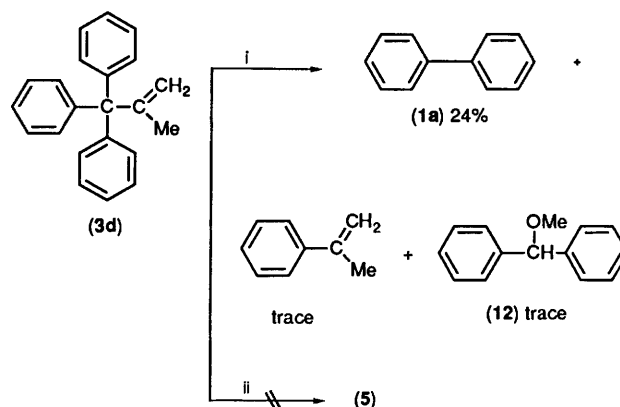
<sup>a</sup> Irradiated in a quartz tube for 2 h. <sup>b</sup> Quantum yields of biphenyl (1a).

respectively (Scheme 6), similar to the special case of the di-methane rearrangement as described in Scheme 5.

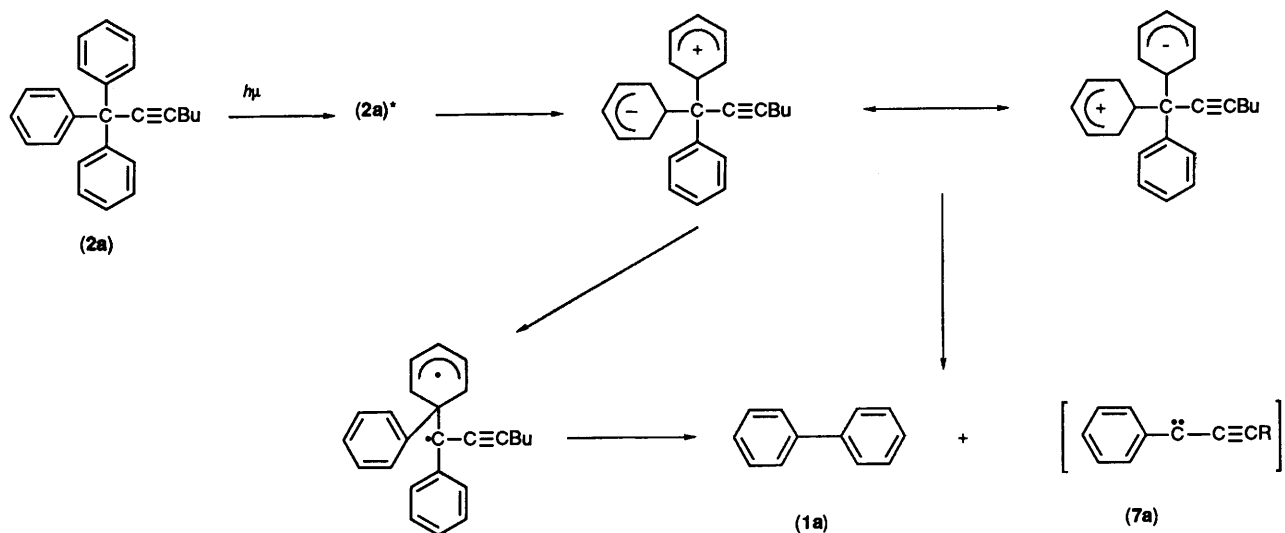
In photolysis of triptycene,<sup>11</sup> tetraphenylmethane,<sup>12</sup> and dibenzonorbbornadiene,<sup>13</sup> analogous generation of carbene intermediates has been reported. Geminal photochemical elimination of two aryl groups to give biaryls (1) has previously been reported for reactions catalysed on elements such as Zn,<sup>14</sup> Al,<sup>15</sup> B,<sup>16</sup> and Sn.<sup>17</sup>

### Experimental

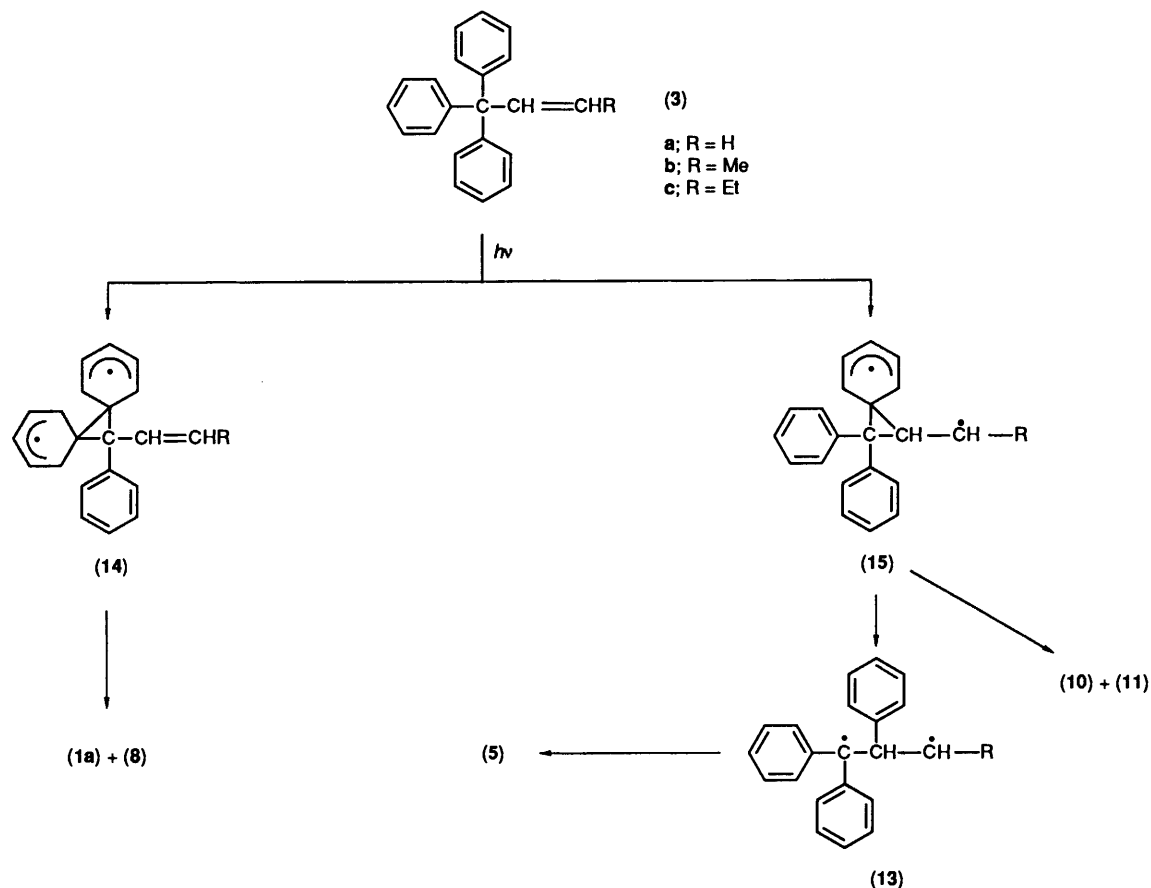
M.p.s and b.p.s were obtained with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. UV-visible spectra were recorded with a Hitachi 150-20 spectrometer with methanol as solvent. IR spectra were measured as KBr disks on



Scheme 4. Reagents and conditions: i, hv, MeOH, 2 h; ii, hv, MeOH.



Scheme 5.



Scheme 6.

a Hitachi Model 345 spectrometer.  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra were determined for solutions in  $\text{CDCl}_3$  with tetramethylsilane as internal standard on a JNM-GSX400 spectrometer. GLC analyses were carried out on a 2% Silicone OV-17 on Chrom. WAW DMCS (60/80 mesh) column with a Shimadzu Model 7A chromatography. Quantitative determination of yields was carried out by use of GLC calibration with triphenylmethane as internal standard. GC-MS spectra were recorded with a JMS-

DX300 instrument. All compounds reported in this paper gave satisfactory CHN microanalyses with a Perkin-Elmer Model 240 analyser.

*Preparation of 1,1,1-Triphenylhept-2-yne (2a).*—To an ethereal solution of hex-1-ynylmagnesium bromide [prepared from hex-1-yne (36.0 mmol) and ethylmagnesium bromide (35.0 mmol)] at room temperature was added a benzene solution of

trityl chloride (16.0 mmol) under nitrogen, and the resulting solution was refluxed for 3 h. After usual work-up, the residue was recrystallized from hexane to give *compound* (**2a**) (4.15 g, 80%), m.p. 44–46 °C;  $\lambda_{\max}(\text{MeOH})$  260 nm ( $\epsilon$  742 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>);  $\nu_{\max}$  2 200 cm<sup>-1</sup> (C≡C);  $\delta_{\text{H}}(400 \text{ MHz})$  0.91 (3 H, t, *J* 7.3 Hz), 1.40–1.70 (4 H, m), 2.34 (2 H, t, *J* 7.3 Hz), and 7.20–7.30 (15 H, m, Ph);  $\delta_{\text{C}}(400 \text{ MHz})$  13.62, 18.75, 22.07, 31.00, 55.56, 85.52, 86.07, 126.55, 127.82, 129.14, and 145.99 (Found: C, 92.5; H, 7.4. C<sub>25</sub>H<sub>24</sub> requires C, 92.54; H, 7.46%).

The other 1,1,1-triarylhept-2-yne (**2b–f**) were prepared similarly.

1,1-Diphenyl-1-(*p*-tolyl)hept-2-yne (**2b**) (4.32 g, 80%), m.p. 52–54 °C;  $\lambda_{\max}(\text{MeOH})$  260 nm (1 400);  $\nu_{\max}$  2 200 cm<sup>-1</sup> (C≡C);  $\delta_{\text{H}}(400 \text{ MHz})$  0.89 (3 H, t, *J* 7.3 Hz), 1.38–1.62 (4 H, m), 2.31 (3 H, s), 2.33 (2 H, t, *J* 7.3 Hz), and 6.95–7.40 (14 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  13.63, 18.76, 20.94, 22.07, 31.03, 55.24, 85.31, 86.22, 126.49, 127.79, 128.55, 129.02, 129.11, 136.13, 143.11, and 146.18 (Found: C, 92.2; H, 8.0. C<sub>26</sub>H<sub>26</sub> requires C, 92.26; H, 7.74%).

1,1,1-Tri(*p*-tolyl)hept-2-yne (**2c**) (4.69 g, 80%), m.p. 71–72 °C;  $\lambda_{\max}(\text{MeOH})$  266 nm (1 440);  $\nu_{\max}$  2 180 cm<sup>-1</sup> (C≡C);  $\delta_{\text{H}}(400 \text{ MHz})$  0.90 (3 H, t, *J* 7.3 Hz), 1.38–1.60 (4 H, m), 2.31 (2 H, t, *J* 7.3 Hz), 2.30 (9 H, s), and 7.00–7.40 (12 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  13.63, 18.76, 20.94, 22.07, 31.06, 54.52, 84.93, 86.41, 128.48, 128.95, 135.96, and 143.43 (Found: C, 91.8; H, 8.4. C<sub>28</sub>H<sub>30</sub> requires C, 91.75; H, 8.25%).

1-(4-Methoxyphenyl)-1,1-diphenylhept-2-yne (**2d**) (3.84 g, 70%), m.p. 58–60 °C;  $\lambda_{\max}(\text{MeOH})$  276 nm (1 820);  $\nu_{\max}$  2 185 cm<sup>-1</sup> (C≡C);  $\delta_{\text{H}}(400 \text{ MHz})$  0.91 (3 H, t, *J* 7.3 Hz), 1.38–1.65 (4 H, m), 2.33 (2 H, t, *J* 7.3 Hz), 3.77 (3 H, s, OMe), and 6.70–7.35 (14 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  13.63, 18.75, 22.07, 31.03, 54.87, 55.21, 85.28, 86.26, 113.13, 126.50, 127.79, 129.07, 130.18, 138.19, 146.30, and 158.17 (Found: C, 87.9; H, 7.7. C<sub>25</sub>H<sub>26</sub>O requires C, 87.68; H, 7.65%).

1,1,1-Tris(4-methoxyphenyl)hept-2-yne (**2e**) (5.60 g, 85%), m.p. 94–96 °C;  $\lambda_{\max}(\text{MeOH})$  277 nm (4 720);  $\nu_{\max}$  2 200 cm<sup>-1</sup> (C≡C);  $\delta_{\text{H}}(400 \text{ MHz})$  0.91 (3 H, t, *J* 7.3 Hz), 1.40–1.65 (4 H, m), 2.32 (2 H, t, *J* 7.3 Hz), 3.77 (9 H, s, OMe), and 6.75–7.20 (12 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  13.63, 18.75, 22.08, 31.08, 53.05, 55.22, 84.81, 86.59, 113.08, 130.02, 138.79, and 158.10 (Found: C, 81.0; H, 7.2. C<sub>28</sub>H<sub>30</sub>O<sub>3</sub> requires C, 81.13; H, 7.20%).

1-(4-Chlorophenyl)-1,1-diphenylhept-2-yne (**2f**) (3.46 g, 60%), m.p. 45–46 °C;  $\lambda_{\max}(\text{MeOH})$  260 nm (1 160);  $\nu_{\max}$  2 180 cm<sup>-1</sup> (C≡C);  $\delta_{\text{H}}(400 \text{ MHz})$  0.89 (3 H, t, *J* 7.3 Hz), 1.40–1.64 (4 H, m), 2.33 (2 H, t, *J* 7.3 Hz), and 7.14–7.40 (14 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  13.62, 18.72, 22.07, 30.95, 55.15, 85.66, 85.93, 126.78, 127.96, 129.02, 130.56, 132.51, 144.69, and 145.52 (Found: C, 83.8; H, 6.4. C<sub>25</sub>H<sub>23</sub>Cl requires C, 83.66; H, 6.46%).

**Preparation of 1,3,3,3-tetraphenylpropyne (2g).**—To an ethereal solution of phenylethynylmagnesium bromide [prepared from phenylacetylene (36.0 mmol) and ethylmagnesium bromide (35.0 mmol)] at room temperature was added a benzene solution of trityl chloride (16.0 mmol) under nitrogen, and the resulting solution was refluxed for 3 h. After usual work-up, the residue was recrystallized from benzene to give *compound* (**2g**) (5.22 g, 95%), m.p. 138–141 °C;  $\lambda_{\max}(\text{MeOH})$  260, 280, and 320 nm (2 000, 620, and 200);  $\nu_{\max}$  2 300 cm<sup>-1</sup> (C≡C);  $\delta_{\text{H}}(400 \text{ MHz})$  7.16–7.60 (m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  56.09, 85.14, 95.64, 123.59, 126.81, 128.00, 128.22, 129.18, 131.61, and 145.34 (Found: C, 94.2; H, 5.6. C<sub>27</sub>H<sub>20</sub> requires C, 94.15; H, 5.85%).

**Preparation of 3,3,3-Triphenylpropene (3a).**—Wittig reaction involving treatment of triphenylacetaldehyde (26.0 mmol) with the appropriate alkylidetriphenylphosphorane [from methyltriphenylphosphonium iodide (30 mmol) and BuLi (30 mmol)] gave the triphenylpropene (**3a**), which was purified by column

chromatography (eluant hexane) to afford the *title compound* (**3a**) (2.73 g, 32%), m.p. 78–79 °C;  $\lambda_{\max}(\text{MeOH})$  260 nm (680);  $\nu_{\max}$  1 650 cm<sup>-1</sup> (C=C);  $\delta_{\text{H}}(400 \text{ MHz})$  4.86 (1 H, dd, *J* 17.6 and 1.6 Hz), 5.40 (1 H, dd, *J* 11.2 and 1.6 Hz), 6.86 (1 H, dd, *J* 17.6 and 11.2 Hz), and 7.00–7.30 (15 H, m, Ph);  $\delta_{\text{C}}(400 \text{ MHz})$  61.43, 116.40, 126.28, 127.65, 130.14, 144.75, and 145.66 (Found: C, 93.3; H, 6.5. C<sub>21</sub>H<sub>18</sub> requires C, 93.33; H, 6.67%).

The other 1,1,1-triarylalk-2-enes (**3b**), (**3c**), and (**3e**) were prepared similarly.

1,1,1-Triphenylbut-2-ene (**3b**) (3.00 g, 40%) [(*Z*):(*E*) 3:2], m.p. 55–60 °C;  $\lambda_{\max}(\text{MeOH})$  260 nm (900);  $\nu_{\max}$  1 660 cm<sup>-1</sup> (C=C); (*Z*)-(**3b**)  $\delta_{\text{H}}(400 \text{ MHz})$  1.07 (3 H, dd, *J* 7.9 and 2.0 Hz, Me), 5.81 (1 H, dq, *J* 12.0 and 7.9 Hz), 6.45 (1 H, dq, *J* 12.0 and 2.0 Hz), and 6.90–7.45 (15 H, m, Ph);  $\delta_{\text{C}}(400 \text{ MHz})$  15.64, 60.39, 125.90, 127.05, 127.57, 138.23, 130.04, and 146.55. (*E*)-(**3b**)  $\delta_{\text{H}}(400 \text{ MHz})$  1.79 (3 H, dd, *J* 7.2 and 2.0 Hz, Me), 5.23 (1 H, dq, *J* 16.0 and 7.2 Hz), 6.48 (1 H, dq, *J* 16.0 and 2.0 Hz), and 6.90–7.40 (15 H, m, Ph);  $\delta_{\text{C}}(400 \text{ MHz})$  18.30, 60.67, 126.12, 127.71, 128.47, 130.25, 139.35, and 147.63 (Found: C, 92.9; H, 7.0. C<sub>22</sub>H<sub>20</sub> requires C, 92.96; H, 7.04%).

1,1,1-Triphenylpent-2-ene (**3c**) (2.80 g, 36%) [(*Z*):(*E*) 5:1], m.p. 50–54 °C;  $\lambda_{\max}(\text{MeOH})$  261 nm (600);  $\nu_{\max}$  1 660 cm<sup>-1</sup> (C=C); (*Z*)-(**3c**)  $\delta_{\text{H}}(400 \text{ MHz})$  0.64 (3 H, t, *J* 7.3 Hz, Me), 1.40 (2 H, qdd, *J* 7.3, 7.3, and 2.0 Hz, CH<sub>2</sub>), 5.63 (1 H, dt, *J* 12.0 and 7.3 Hz), 6.39 (1 H, dt, *J* 12.0 and 2.0 Hz), and 6.90–7.50 (15 H, m, Ph);  $\delta_{\text{C}}(400 \text{ MHz})$  13.04, 23.01, 60.45, 125.86, 127.55, 130.04, 136.09, 137.55, and 147.74; (*E*)-(**3c**)  $\delta_{\text{H}}(400 \text{ MHz})$  1.01 (3 H, t, *J* 7.3 Hz, Me), 2.13 (2 H, qdd, *J* 7.3, 7.3, and 2.0 Hz), 5.28 (1 H, dt, *J* 16.0 and 7.3 Hz), 6.56 (1 H, dt, *J* 16.0 and 2.0 Hz), and 6.90–7.40 (15 H, m, Ph);  $\delta_{\text{C}}(400 \text{ MHz})$  13.10, 24.65, 60.60, 126.09, 128.11, 130.25, 134.20, 136.19, and 146.59 (Found: C, 92.5; H, 7.45. C<sub>23</sub>H<sub>22</sub> requires C, 92.62; H, 7.38%).

1,1-Diphenyl-1-(*p*-tolyl)but-2-ene (**3e**) (2.85 g, 34%) [(*Z*):(*E*)], oil;  $\lambda_{\max}(\text{MeOH})$  264 nm (1 000);  $\nu_{\max}$  1 660 cm<sup>-1</sup> (C=C); (*Z*)-(**3e**)  $\delta_{\text{H}}(400 \text{ MHz})$  1.09 (3 H, dd, *J* 7.9 and 2.0 Hz, Me), 2.29 (3 H, s, Me), 5.81 (1 H, dq, *J* 12.0 and 7.9 Hz), 6.45 (1 H, dq, *J* 12.0 and 2.0 Hz), and 6.90–7.45 (14 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  15.64, 21.01, 60.39, 125.90, 127.10, 127.60, 130.06, 138.23, and 146.56. (*E*)-(**3e**)  $\delta_{\text{H}}(400 \text{ MHz})$  1.80 (3 H, dd, *J* 7.2 and 2.0 Hz, Me), 2.30 (3 H, s, Me), 5.23 (1 H, dq, *J* 16.0 and 7.2 Hz), 6.48 (1 H, dq, *J* 16.0 and 2.0 Hz), and 6.90–7.40 (14 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  18.32, 22.66, 60.70, 126.12, 127.72, 128.50, 130.30, 139.35 and 147.63 (Found: C, 92.6; H, 7.35. C<sub>23</sub>H<sub>22</sub> requires C, 92.62; H, 7.38%).

2-Methyl-3,3,3-triphenylpropene (**3d**) was prepared according to the literature method<sup>9</sup> (5.80 g, 50%), m.p. 92–95 °C.

3-(4-Methoxyphenyl)-2-methyl-3,3-diphenylpropene (**3f**) was prepared according to the literature method<sup>9</sup> (4.00 g, 30%), m.p. 110–112 °C.

**Preparation of Authentic Samples.**—The cyclopropanes (**5a**), (**5b**), and (**5c**) were identified by comparison (GC-MS and retention time) with authentic samples prepared by heating diphenyldiazomethane with styrene, 1-phenylpropene, and 1-phenylbutene.<sup>6</sup>

1-Phenyl-1-methoxyhept-2-yne (**6a**) was prepared by the reaction of hex-1-ynylmagnesium bromide (30 mmol) with benzaldehyde dimethyl acetal (30 mmol) in diethyl ether under reflux.<sup>18</sup> After usual work-up, the product (**6a**) was isolated by column chromatography on silica gel (eluant hexane–benzene 8:2) (2.43 g, 40%),  $\delta_{\text{H}}(400 \text{ MHz})$  0.83 (3 H, t, *J* 7.6 Hz), 1.10–1.60 (4 H, m), 2.20 (2 H, t, *J* 7.6 Hz), 3.83 (3 H, s, OMe), 5.0 (1 H, s), 7.20–7.60 (5 H, m, ArH) (Found: *M*<sup>+</sup>, 202.1356. C<sub>14</sub>H<sub>18</sub>O requires *M*, 202.1357).

The other authentic samples (**6b–d**) were prepared similarly.

1-Methoxy-1-(*p*-tolyl)hept-2-yne (**6b**) (2.20 g, 34%),  $\delta_{\text{H}}(400 \text{ MHz})$  0.83 (3 H, t, *J* 7.6 Hz), 1.10–1.62 (4 H, m), 2.20 (2 H, t, *J* 7.6 Hz), 2.30 (3 H, s, Me), 3.83 (3 H, s, OMe), 5.06 (1 H, s), and 7.10–

7.60 (4 H, m, ArH) (Found:  $M^+$ , 216.1510.  $C_{15}H_{20}O$  requires  $M$ , 216.1513).

1-Methoxy-1-(4-methoxyphenyl)hept-2-yne (**6c**) (2.50 g, 36%),  $\delta_H$ (400 MHz) 0.83 (3 H, t,  $J$  7.6 Hz), 1.10–1.64 (4 H, m), 2.20 (2 H, t,  $J$  7.6 Hz), 3.75 (3 H, s, OMe), 3.85 (3 H, s, OMe), 4.98 (1 H, s), and 7.10–7.60 (4 H, m, ArH) (Found:  $M^+$ , 232.1460.  $C_{15}H_{20}O_2$  requires  $M$ , 232.1462).

1-(4-Chlorophenyl)-1-methoxyhept-2-yne (**6d**) (2.12 g, 30%),  $\delta_H$ (400 MHz) 0.80 (3 H, t,  $J$  7.6 Hz), 1.10–1.60 (4 H, m), 2.20 (2 H, t,  $J$  7.6 Hz), 3.85 (3 H, s, OMe), 5.05 (1 H, s), 7.0–7.60 (4 H, m, ArH) (Found:  $M^+$ , 236.0964.  $C_{14}H_{17}ClO$  requires  $M$ , 236.0968).

**Preparation of 1-Methoxy-1-phenylalk-2-enes (9).**—Methylation of 1-hydroxy-1-phenylpropene [prepared from phenylmagnesium bromide (30.0 mmol) and propenal (32.0 mmol)<sup>19</sup>] with methyl iodide (80 mmol) in alkaline media followed by the usual work-up, gave the product (**9a**), isolated by column chromatography on silica gel (eluant hexane–chloroform 3:1) (2.66 g, 65%),  $\delta_H$ (400 MHz) 3.24 (3 H, s, OMe), 5.10 (1 H, dd,  $J$  11.1 and 1.6 Hz), 5.31 (1 H, dd,  $J$  22.1 and 1.6 Hz), 5.99 (1 H, ddd,  $J$  22.1, 11.1, and 11.0 Hz), 6.19 (1 H, d,  $J$  11.2 Hz), and 7.0–7.40 (5 H, m, ArH) (Found:  $M^+$ , 148.2040.  $C_{10}H_{12}O$  requires  $M$ , 148.2042).

The other compounds (**9b**), (**9c**), and (**9d**) were prepared similarly.

1-Methoxy-1-phenylbut-2-ene (**9b**) (3.89 g, 80%) as isolated was a mixture of *E/Z* isomers; (*Z*)-(**9b**)  $\delta_H$ (400 MHz) 1.31 (3 H, d,  $J$  6.4 Hz, Me), 3.29 (3 H, s, OMe), 3.86 (1 H, qd,  $J$  7.3 and 6.4 Hz), 6.07 (1 H, dd,  $J$  15.6 and 7.3 Hz), 6.50 (1 H, d,  $J$  15.6 Hz), and 7.14–7.60 (5 H, m, Ph); (*E*)-(**9b**)  $\delta_H$ (400 MHz) 1.68 (3 H, d,  $J$  7.3 Hz, Me), 3.27 (3 H, s, OMe), 4.54 (1 H, d,  $J$  7.3 Hz), 5.55 (1 H, dd,  $J$  16.0 and 7.3 Hz), 5.65 (1 H, dq,  $J$  16.0 and 7.3 Hz), and 7.14–7.60 (5 H, m, Ph) (Found:  $M^+$ , 162.2313.  $C_{11}H_{14}O$  requires  $M$ , 162.2310).

1-Methoxy-1-phenylpent-2-ene (**9c**) (3.16 g, 60%); (*Z*)-(**9c**)  $\delta_H$ (400 MHz) 0.60 (3 H, t,  $J$  7.3 Hz, Me), 1.38 (2 H, qd,  $J$  7.3 and 7.3 Hz,  $CH_2$ ), 3.28 (3 H, s, OMe), 3.90 (1 H, dt,  $J$  7.3 and 7.3 Hz), 6.0 (1 H, dd,  $J$  15.6 and 7.3 Hz), 6.60 (1 H, d,  $J$  15.6 Hz), and 7.10–7.60 (5 H, m, Ph); (*E*)-(**9c**)  $\delta_H$ (400 MHz) 1.02 (3 H,  $J$  7.3 Hz, Me), 2.15 (2 H, dt,  $J$  7.3 and 7.3 Hz,  $CH_2$ ), 3.28 (3 H, s, OMe), 4.60 (1 H, d,  $J$  7.3 Hz), 5.58 (1 H, dd,  $J$  16.0 and 7.3 Hz), 5.68 (1 H, dt,  $J$  16.0 and 7.3 Hz), and 7.10–7.60 (5 H, m, Ph) (Found:  $M^+$ , 176.2574.  $C_{12}H_{16}O$  requires  $M$ , 176.2578).

1-Methoxy-1-tolylbut-2-ene (**9d**) (3.70 g, 70%); (*Z*)-(**9d**)  $\delta_H$ (400 MHz) 1.31 (3 H, d,  $J$  6.4 Hz, Me), 2.29 (3 H, s, Me), 3.29 (3 H, s, OMe), 3.86 (1 H, qd,  $J$  7.3 and 6.4 Hz), 6.07 (1 H, dd,  $J$  15.6 and 7.3 Hz), 6.50 (1 H, d,  $J$  15.6 Hz), and 7.14–7.60 (4 H, m, ArH); (*E*)-(**9d**)  $\delta_H$ (400 MHz) 1.68 (3 H, d,  $J$  7.3 Hz, Me), 2.30 (3 H, s, Me), 3.27 (3 H, s, OMe), 4.54 (1 H, d,  $J$  7.3 Hz), 5.55 (1 H, dd,  $J$  16.0 and 7.3 Hz), 5.65 (1 H, dq,  $J$  16.0 and 7.3 Hz), and 7.14–7.60 (4 H, m, ArH) (Found:  $M^+$ , 176.2576.  $C_{12}H_{16}O$  requires  $M$ , 176.2578).

**Preparation of Diphenylmethyl Methyl Ether (12).**—Methylation of diphenylmethyl alcohol (30 mmol) with methyl iodide (80 mmol) in alkaline media (pH > 11), and the usual work-up, gave the title product (**12**), isolated by distillation under reduced pressure (4.75 g, 80%), b.p. 153–155 °C/14.5 mmHg;  $\delta_H$ (400 MHz) 3.24 (3 H, s, OMe), 5.10 (1 H, s), and 7.0–7.40 (10 H, m, Ph).

**General Procedure for Photolysis.**—An MeOH solution (3 ml) of an alkyne (**2**) or alkyne (**3**) ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>) was placed in a quartz tube ( $\phi$  10 mm) and purged of dissolved air by bubbling with argon. Subsequently, the solution was irradiated by a high-pressure mercury lamp (300 W) at ambient temperature for 3 h. The photolysate was analysed by GLC on a

2-m OV-17 glass column, employing a temperature gradient: start at 120 °C (2 min); increase at 8 °C min<sup>-1</sup> to 250 °C. The detector temperature was 280 °C and a carrier gas (N<sub>2</sub>) flow of 50 ml min<sup>-1</sup> was used.

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 triphenylmethane as internal standard.

The photolysis of alkyne (**2c**) in other solvents, *viz.* cyclohexene, cyclohexane, tetrahydrofuran (THF), and acetonitrile, was carried out similarly.

**Photolysis of Alkyne (2c) in the Presence of Molecular Oxygen.**—Three separate methanolic solutions (3 ml) of compound (**2c**) ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>) were placed in quartz tubes ( $\phi$  10 mm). Argon, air, or oxygen was bubbled into the solutions at 20 °C for 10 min while they were irradiated, on a merry-go-round apparatus, in a similar manner to that described above. The yields of compound (**1c**) in these cases were determined by GLC.

**Photolysis of Alkyne (2c) in the Presence of Benzophenone.**—Sensitized photolysis of alkyne (**2c**) (10 mmol dm<sup>-3</sup>) was performed in a methanolic solution of benzophenone (30 mmol dm<sup>-3</sup>) in a Pyrex tube. After irradiation for 1 h by a high-pressure mercury lamp, the reaction mixture was analysed by GLC.

**Photolysis of Alkyne (2c) (Preparative Scale).**—A methanolic solution (100 ml) (**2c**) ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>) was purged of dissolved air by bubbling with argon. It was then 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 off, the residue was chromatographed on silica gel with benzene–CHCl<sub>3</sub> (2:1) as eluant to give compounds (**1c**) and (**6c**), the pressure of which was confirmed by comparison of spectral data with those of authentic samples.

**Measurement of the Quantum Yield.**—The quantum yields of biaryls (**1**) in the photolysis of compounds (**2c–h**) or (**3**) were measured as follows: A low-pressure mercury lamp (60 W) with a Vycor glass filter was used as a 254-nm radiation source. Actinometry was carried out by use of a potassium trioxalatoferate(III) solution. The yields of products were determined by GLC. Photolysis was carried out at a conversion of <5%.

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