CHEMISTRY LETTERS, pp. 1297-1300, 1989.

Photolysis of 1,1,1-Triarylhept-2-ynes. Generation of Phenyl(hex-1-ynyl)carbene

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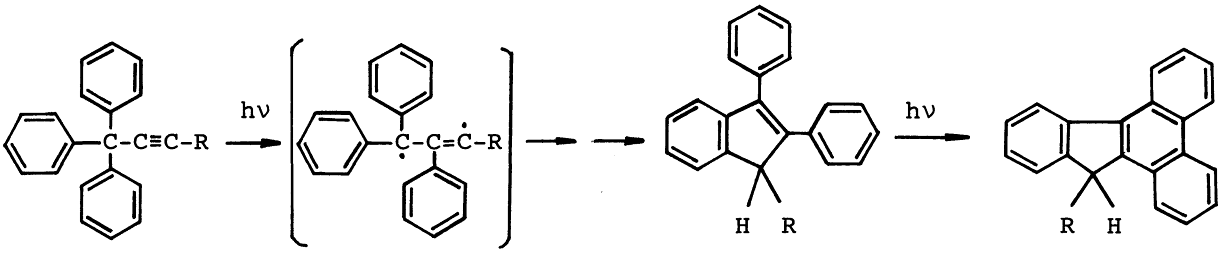
Photolysis of 1,1,1-triarylhept-2-yne in methanol gave biaryl and 1-aryl-1-methoxyhept-2-yne, which may be derived from the insertion of aryl(hex-1-ynyl)carbene into the OH bond of methanol. The carbene may be generated by photo-α,α-elimination of two aryl groups from the substrate.

In the course of studies on the photochemical carbene generation from triarylmethyl derivatives,[1,2] we have found an interesting phenomenon in photolysis of 1-substituted 3,3,3-triarylpropynes (**1**), where the reaction type is dramatically controlled by a kind of the substituent. Griffin and coworkers have reported the photochemical rearrangement of a 1-phenyl derivative (**1a**) to an indenophenanthrene derivative (**2a**).[3] In this reaction, a biradical species was proposed as a possible intermediate leading to an indene derivative which in turn undergoes subsequent dehydrocyclyzation to **2a** (Scheme 1). Wilson and Huhtanen have also presented an additional example of analogous photo-rearrangement in the case of a 1-methoxycarbonyl derivative (**1b**).[4]

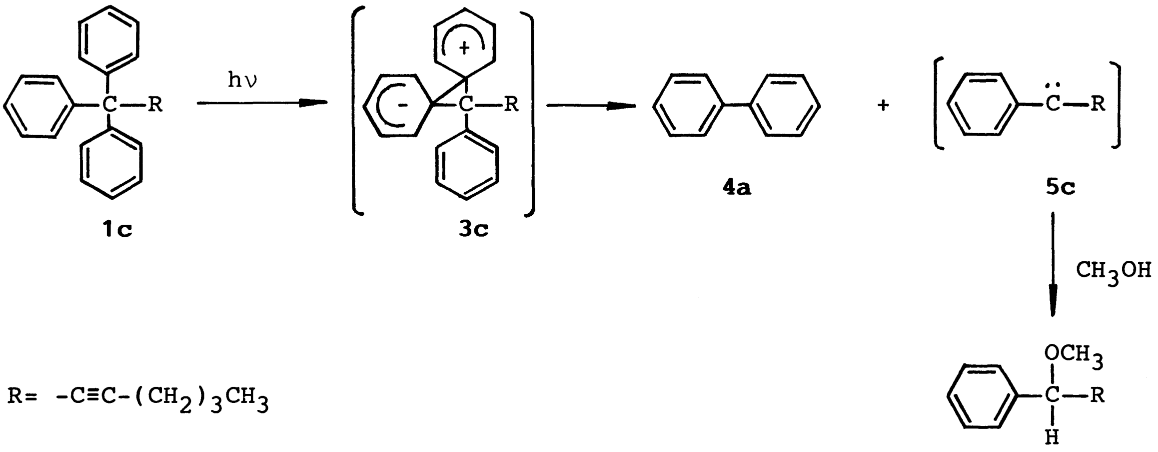


1a, b (**a**; R=C_6H_5, **b**; R=$COOCH_3$) **2a,b**

Scheme 1.

We present here a different type of photochemical reaction of 1-alkyl derivatives, 1,1,1-triarylhept-2-ynes (**1c-g**).

A methanol solution of 1,1,1-triphenylhept-2-yne[5] (**1c**, 5.0 mmol dm^{-1}) was irradiated in a quartz tube under argon atmosphere 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 analyzed with GC-MS (JMS-DX300-GLC, OV-7, 2%, Support Uniport HP, an 1-m glass column) on the base of the data of authentic samples. Biphenyl (**4a**) and 1-phenyl-1-methoxyhept-2-yne (**6c**)$^{6)}$ were obtained in 25 and 24% yields, respectively. The quantum yield of **4a** was 0.028.$^{7)}$ Upon irradiation in cyclohexene, **1c** also afforded **4a** in a comparable yield although the yield of a trapping product by cyclohexene was very low. The photo-rearranged product such as observed in photolysis of **1a** and **1b** could not be detected. From these findings, a similar reaction scheme to that in the photolysis of dimethyl (triphenylmethyl)phosphonate$^{1)}$ and methyl triphenylacetate$^{2)}$ can be postulated; **1c** undergoes an α,α-elimination of two phenyl groups to afford **4a** and a corresponding carbene intermediate (**5c**) which is transformed to **6c** by the reaction with methanol (Scheme 2).

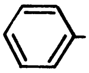
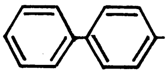
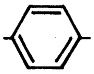
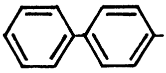
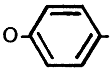
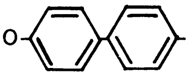


R= -C≡C-(CH$_2$)$_3$CH$_3$

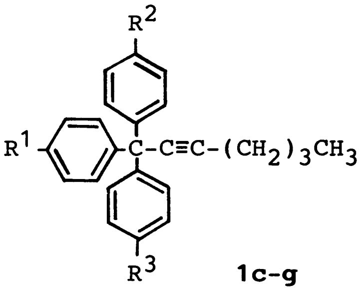
Scheme 2.

The difference of the photochemical behaviors observed between **1a** or **b** and **1c** 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 **1** should be required for the α,α-elimination of two phenyl groups. The requirement may be satisfied for **1c** since the excitation energy level of benzene is lower than that of acetylene. The introduction of a chromophore such as phenyl or methoxycarbonyl group to the acetylenic triple bond lowers the energy level of the acetylenic moiety by the conjugation effect. Therefore, in the cases of **1a** and **1b**, the excitation energy may localize to the acetylenic moiety and, consequently, **1a** and **1b** undergo a typical photochemical reaction of acetylenic derivatives.$^{3)}$ The difference of the energy levels of their excited states are also presumed from the UV absorption spectra of **1a** (λmax 328 nm) and **1c** (λmax 260 nm). In order to further clarify the underlying mechanism responsible for the α,α-elimination of two aryl groups, we have investigated the photolysis of the p-substituted derivatives (**1d-g**) under the similar conditions, and the quantum yields of biaryl (**4**) and the selectivities of the α,α-elimination of aryl groups were determined (Table 1).

Table 1. Photolysis of **1c-g** in methanol[a)]

	Compound **1**[b)]			Quantum yield of **4** X10^2	Conv.[c)] /%	Product (Yield/%)[c)]
	R^1	R^2	R^3			
1c	H	H	H	2.8	40	(**4a**, 25), -$CH(OCH_3)C\equiv C(CH_2)_3CH_3$(**6c**, 24)
1d	H	H	CH_3	3.8[d)]	60	**4a**(8.0), -CH_3(**4b**, 26), **6c**(26) CH_3--$CH(OCH_3)C\equiv C(CH_2)_3CH_3$(**6d**, 7.5)
1e	CH_3	CH_3	CH_3	3.7	58	CH_3--CH_3(**4c**, 40), **6d**(39)
1f	H	H	OCH_3	4.9[d)]	50	**4a**(7.1), -OCH_3(**4d**, 30), **6c**(29) CH_3O--$CH(OCH_3)C\equiv C(CH_2)_3CH_3$(**6e**, 6.9)
1g	OCH_3	OCH_3	OCH_3	4.4	70	CH_3O--OCH_3(**4e**, 30), **6e**(28)

a) Reaction conditions; **1c-g** 10 mmol dm^{-3}, in MeOH, under Ar, a high pressure mercury lamp for 2 h.

b) 

1c-g

c) Conversions and yields based on GC analysis, calibrated using pure authentic samples.

d) Quantum yields were calculated on the combined yields of both biaryls at low conversion (<5%). See note 7.

The quantum yields of **4** from the methyl or methoxy-substituted derivatives (**1d-g**) were larger than that of **4a** from the unsubstituted derivatives (**1c**). In photolysis of **1d** or **1f**, the elimination of different aryl groups each other to form an unsymmetric **4b** or **4d** is more favorable than that of a symmetric **4a** even after taking into account the correction of the ratio of statistical elimination of aryl groups. This fact may suggest the increasing of an inter-ring of charge-transfer interaction between the benzene ring and the substituted benzene ring (cf., **3c**).[8)] Intramolecular charge-transfer interaction was also observed among the three benzene rings of triptycene derivatives, where the similar photochemical generation of a carbene intermediate was proposed by Iwamura and Yoshimura.[9)] In photolysis of tetraphenylmethane[9)] and dibenzonorbornadiene,[10)] the analogous carbene generation have been also reported.

This work was supported by A Grant-in-Aid for Scientific Research No. 62750785 from the Ministry of Education, Science and Culture.

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5) **1c** was prepared as follows; To an etheral solution of hex-1-ynylmagnesium bromide (from 3.6 mmol hex-1-yne and 3.5 mmol ethylmagnesium bromide) was added a benzene solution of triphenylmethyl chloride (1.6 mmol) at room temperature under nitrogen atmosphere, and the resulting solution was refluxed for 3 h. Usual work-up followed by recrystalization from hexane gave **1c**, which was pure by GLC and for microanalysis; mp 44-46 ^{o}C, UV(MeOH)λmax 260 nm (ε 742). **1d-g** were synthesized in the similar manner, **1d**; mp 52-54 ^{o}C, UV(CH_3OH)λmax 260 nm (ε 1400), **1e**; mp 71-72 ^{o}C, UV(CH_3OH)λmax 266 nm (ε 1440), **1f**; mp 58-60 ^{o}C, UV(CH_3OH)λmax 276 nm (ε 1820), **1g**; mp 94-96 ^{o}C, UV(CH_3OH)λmax 277 nm (ε 4720).

6) The product **6c** was isolated by column chromatography on silica gel (hexane: benzene=8:2). ^{1}H-NMR ($CDCl_3$/TMS) δ=0.83(3H, t, J_{HH}=5.6 Hz), 1.1-1.6(4H, m), 2.2(2H, t, J_{HH}=5.9 Hz), 3.83(3H, s), 5.0(1H, s), 7.2-7.6(5H, m). The authentic samples were prepared by the known method [A. L. Kranzfelder and R. R. Vogt, J. Am. Chem. Soc., 60, 1714(1938)].

7) Determination of quantum yields of **4** in photolysis of **1c-g** was carried out as follows: A low-pressure mercury lamp (60 W) with a Vicor glass filter was used as a 254-nm radiation source. Actinometry was carried out using a ferric oxalate solution. The product formation was measured by GLC (Shimadzu GC-7A, Silicone OV-7, 2% Support; Uniport HP, an 1-m glass column). The photolysis was carried out at conversion less than 5%.

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(Received May 2, 1989)