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Photolysis of Tetraarylmethanes and 3-(Triarylmethyl)pyridines

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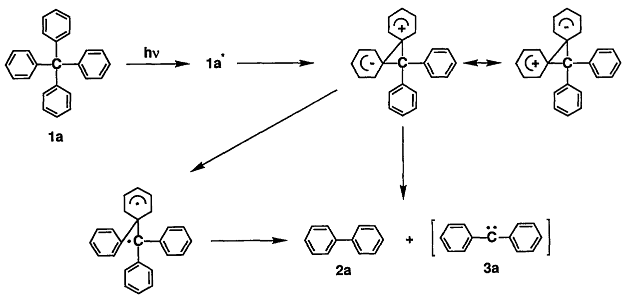
Synopsis. Upon UV irradiation in benzene–methanol (1:2) tetraarylmethanes or 3-(triarylmethyl)pyridines underwent an α,α-elimination of two aryl groups to give biaryls or 3-arylpyridine, and two corresponding carbene intermediates. The latters afforded methyl ethers by the O–H insertion to methanol.

It has been reported that upon UV irradiation in cyclohexane tetraphenylmethane (**1a**) undergoes an α,α-elimination of two phenyl groups to give biphenyl (**2a**) and diphenylcarbene (**3a**), which reacts with cyclohexane to afford diphenylmethane and diphenyl (cyclohexyl)methane.[1] However, its quantum yield is very small $(\phi=7.1\times10^{-4})$.[2] The mechanism of this reaction can be explained as follows[3,4]: in an excited state, an intramolecular interaction among the four benzene rings occurs, and two phenyl groups are eliminated via an initial bonding between their C-1 positions (ipso coupling), yielding the carbene **3a** (Scheme 1). An analogous photochemical generation of carbene has also been proposed in triptycene derivatives.[5]



Scheme 1.

Since the interaction among the aryl rings might be more enhanced by the increase of their polarizability by introducing substituents, we prepared and examined some substituted tetraarylmethanes (**1b**—**i**).

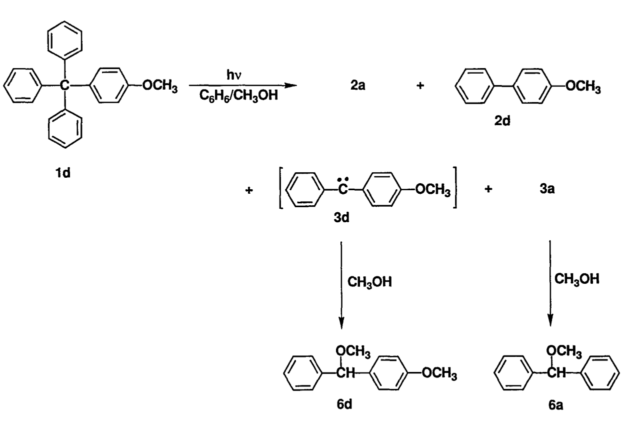
In order to clarify the scope and limitation of this carbene generation, we also prepared 3-(triarylmethyl) pyridines (**4a**—**e**) and 2-(triphenylmethyl)thiophene (**5**) and studied their photochemical behaviors.[6]

Results and Discussion

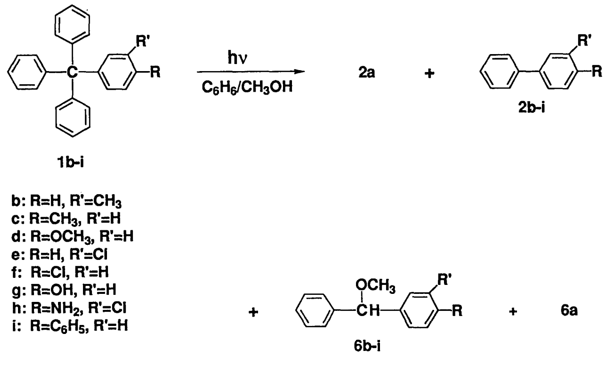
Upon UV irradiation of a benzene–methanol (1:2) solution of (4-methoxyphenyl)triphenylmethane (**1d**) (5 mmol dm^{-3}) for 1 h in a quartz tube using a high-pressure mercury lamp (300 W) under argon atmosphere, **2a** and 4-methoxybiphenyl (**2d**) were obtained in the yields of 6 and 18% (total quantum yield=0.018), respectively. A mixture of benzene and methanol was used to solubilize **1** and to trap the carbenes **3a** and **3d**. The elimination of **2a** and **2d** from **1d** resulted in the generation of two kinds of carbenes **3a** and **3d**, affording corresponding methyl ethers **6a** and **6d**[7] in the yields comparable to those of **2a** and **2d**, respectively (Scheme 2). After 4 h irradiation, the compound (**1d**) was consumed completely and the combined yield of **2a** and **2d** was 50%.

The photolyses of other tetraarylmethanes (**1b**, **c**, **f**—**i**) were carried out under the same conditions. The results are summarized in Table 1 and Scheme 3. These results indicate that the introduction of substituents into the benzene ring causes the preferential formation of the unsymmetric biaryl and the significant increase in total quantum yields of **2**, regardless of the nature of substituent, electron releasing or withdrawing. This suggests that the interaction between the benzene rings in electronically excited state is much enhanced by the introduction of substituents.

However, the introduction of a hydroxyl, an amino, or a phenyl group into the benzene ring depressed the yield of **2a**. For example, even upon a prolonged irradiation of triphenyl(4-hydroxyphenyl)methane (**1g**)



Scheme 2.



Scheme 3.

Table 1. Photolysis of Tetraarylmethane (**1b—i**) in Benzene-Methanol (1:2)

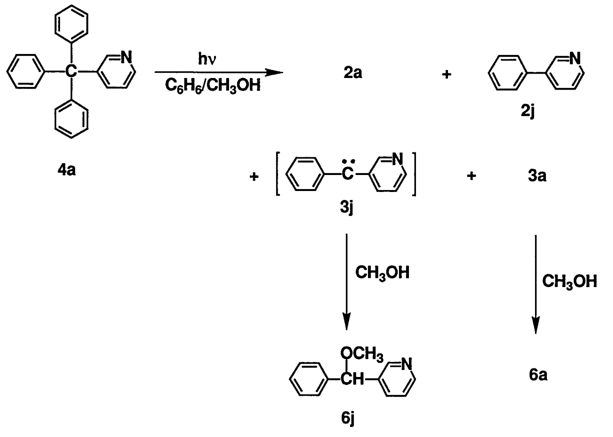
Compd			Conv./%[a]	Φ[b]	Product (yield/%)			
1	R	R′			**2a**	**6b—i**	**2b—i**	**6a**
1b	H	CH_3	40	0.014	(6)	**6b**(6)	**2b**(17)	(18)
1c	CH_3	H	44	0.015	(7)	**6c**(6)	**2c**(18)	(18)
1d	OCH_3	H	46	0.018	(6)	**6d**(6)	**2d**(18)	(18)
1e	H	Cl	42	0.014	(6)	**6e**(3)	**2e**(16)	(17)
1f	Cl	H	43	0.014	(6)	**6f** (3)	**2f** (17)	(17)
1g	OH	H	20	—	(3)	**6g**(0)	**2g**(0)	(0)
1h	NH_2	Cl	25	—	(2)	**6h**(2)	**2h**(0)	(0)
1i	C_6H_5	H	10	—	(2)	**6i** (0)	**2i** (0)	(0)

a) Irradiated in a quartz tube for 1 h. b) The total quantum yields of 2.

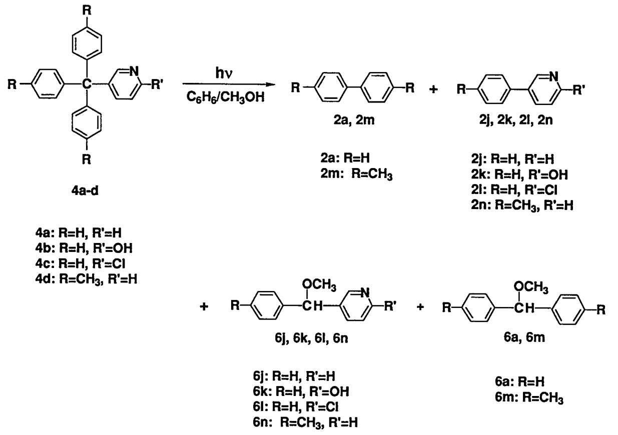
Table 2. Photolysis of 3-(Triarylmethyl)pyridine (**4a—d**) in Benzene-Methanol (1:2)

Compd			Conv./%[a]	Φ[b]	Product (yield/%)	
4	R	R′			**2**	**6**
4a	H	H	30	0.01	**2a** (6), **2j** (11)	**6a** (12), **6j** (5)
4b	H	OH	5	0	**2a** (0), **2k**(0)	**6a** (0), **6k**(0)
4c	H	Cl	40	0.014	**2a** (6), **2l** (17)	**6a** (17), **6l** (5)
4d	CH_3	H	40	0.012	**2m**(8), **2n**(10)	**6m**(10), **6n**(7)

a) Irradiated in a quartz tube for 1 h. b) The total quantum yields of 2.



Scheme 4.



Scheme 5.

or triphenyl(3-methyl-4-aminophenyl)methane (**1h**) in benzene-methanol (1:2), **2a** was obtained only in 2—3% yields, respectively (Table 1). These facts can be interpreted as follows: in an electronically excited singlet state, the hydroxyl group of the phenol derivatives **1g** is apt to dissociate due to the increase of positive charge on oxygen atom.[8] Therefore, the α,α-elimination of aryl groups of **1g** hardly occurs. In the case of **1h**, the similar interpretation can be also applied. *p*-Biphenylyl(triphenyl)methane (**1i**) was also stable upon irradiation. The biphenylyl group possesses a lowest T_1 (π,π^*) state, so that an intramolecular energy transfer takes place from the highest (π,π^*) state localized on phenyl group to the lowest state localized on the biphenylyl group. As the results, the α,α-elimination of aryl groups of **1i** may be also depressed.

In order to examine the competitive elimination of a heteroaromatic ring, the photolysis of 3-(triphenylmethyl)pyridine (**4a**) was carried out under the same conditions. The two products, **2a** and 3-phenylpyridine (**2j**), were obtained. The yield of **2j** (11.0%) was higher than that of **2a** (6.0%) (total quantum yield=0.01). The methyl ethers **6a** and **6j** derived from the corresponding carbenes **3a** and **3j** were likewise obtained (Scheme 4). The substituent effect on the photolysis of **4** was also studied. Upon UV-irradiation of 2-chloro-5-(triphenyl)pyridine (**4c**) or 3-(tri-*p*-tolylmethyl)pyridine (**4d**), the yield of 2-chloro-3-phenylpyridine (**2l**) or 3-*p*-tolylpyridine (**2n**) was larger than that of **2a** or 4,4′-dimethylbiphenyl (**2m**), respectively (Scheme 5, Table 2). These results indicate that the interaction between a phenyl and pyridyl groups is larger than that between phenyl ones.

2-Hydroxy-5-(triphenylmethyl)pyridine (**4b**) and 3-[(4-biphenylyl)diphenylmethyl]pyridine (**4e**) were found to be stable upon irradiation. These photo-stability were explained by the same reason described above.

2-Triphenylmethylthiophene (**5**) was also stable upon UV-irradiation in methanol. This may be due to its lower photo-excited energy level of **5** (UV$_{max}$=300 nm) compared to that of **1** or **4** (UV$_{max}$=260—270 nm).

Experimental

The compounds **1b—i** and **4a—e** were prepared according to the literature.[9—13]

Triphenyl(*m*-tolyl)methane (1b).[9] Mp 162—164 °C; UV (CH_3OH)$_{max}$=265 nm (ε 980 dm^{3}mol^{-1}cm^{-1}).

Triphenyl(*p*-tolyl)methane (1c).[9] Mp 206—208 °C; UV (CH_3OH)$_{max}$=265 nm (ε 1100 dm^{3}mol^{-1} cm^{-1}).

Triphenyl(4-methoxyphenyl)methane (1d). Mp 200—202 °C; UV(CH_3OH)$_{max}$=272 nm (ε 2000 dm^3 mol^{-1} cm^{-1}); Found: C, 89.08; H, 6.40%. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33%.

Triphenyl(3-chlorophenyl)methane (1e).[9] Mp 190—192 °C; UV(CH_3OH)$_{max}$=266 nm (ε 1000 dm^3 mol^{-1} cm^{-1}).

Triphenyl(4-chlorophenyl)methane (1f).[11] Mp 216—218 °C; UV(CH_3OH)$_{max}$=270 nm (ε 1300 dm^3 mol^{-1} cm^{-1}).

Triphenyl(4-hydroxyphenyl)methane (1g).[10] Mp 281—282 °C; UV(CH_3OH)$_{max}$=274 nm (ε 2000 dm^3 mol^{-1} cm^{-1}).

Triphenyl(3-chloro-4-aminophenyl)methane (1h).[9] Mp 246—248 °C; UV(CH_3OH)$_{max}$=300 nm (ε 1500 dm^3 mol^{-1} cm^{-1}).

***p*-Biphenylyl(triphenyl)methane (1i).**[12] Mp 197—199 °C; UV(CH_3OH)$_{max}$=263 nm (ε 20000 dm^3 mol^{-1} cm^{-1}).

3-(Triphenylmethyl)pyridine (4a).[13] Mp 269—270 °C; UV (CH_3OH)$_{max}$=263 nm (ε 1000 dm^3 mol^{-1} cm^{-1}).

2-Hydroxy-5-(triphenylmethyl)pyridine (4b).[13] Mp >300 °C; UV$_{max}$=262 nm (ε 980 dm^3 mol^{-1} cm^{-1}).

2-Chloro-5-(triphenylmethyl)pyridine (4c).[13] Mp 256—260 °C; UV(CH_3OH)$_{max}$=263 nm (ε 1100 dm^3 mol^{-1} cm^{-1}).

3-(Tri-*p*-tolylmethyl)pyridine (4d).[13] Mp 256—260 °C; UV (CH_3OH)$_{max}$=270 nm (ε 1600 dm^3 mol^{-1} cm^{-1}); Found: C, 89.10; H, 7.01; N, 3.76%. Calcd for $C_{27}H_{25}N$: C, 89.22; H, 6.93; N, 3.85%.

3-[(4-Bibphenylyl)diphenylmethyl]pyridine (4e).[13] Mp 190—192 °C; UV(CH_3OH)$_{max}$=260 nm (ε 20000 dm^3 mol^{-1} cm^{-1}).

2-(Triphenylmethyl)thiophene (5). The compound **5** was prepared by the reaction of triphenylmethyl chloride with 2-thienylmagnesium bromide. Mp 194—196 °C (decomp); UV(CH_3OH)$_{max}$=300 nm (ε 400 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR ($CDCl_3$) δ=6.76 (1H, dd, J=3.6, 1.2 Hz), 6.95 (1H, dd, J=5.2, 3.6 Hz), 7.0—7.50 (16H, m, Ar and -CH=C-); MS (70 eV) m/z (rel intensity) 326 (M^+; 80), 249 (100), and 78 (70); Found; C, 84.58; H, 5.60%. Calcd for $C_{23}H_{18}S$: C, 84.62, H, 5.56%.

Preparation of Some Authentic Samples. Diphenylmethyl Methyl Ether (6a): Diphenylmethyl methyl ether was prepared by the methylation of diphenylmethanol with dimethyl sulfate.[14] ^{1}H NMR ($CDCl_3$) δ=3.24 (3H, s, OCH_3), 5.10 (1H, s, -CH-), 7.0—7.40 (10H, m, Ar); Found: m/z 198.1040. Calcd for $C_{14}H_{14}O$: M, 198.1044.

(3-Methylphenyl)phenylmethyl Methyl Ether (6b): Colorless oil. ^{1}H NMR ($CDCl_3$) δ=2.20 (3H, s, CH_3), 3.20 (3H, s, OCH_3), 5.12 (1H, s, -CH-), 7.0—7.40 (9H, m, Ar); Found: m/z 212.1202. Calcd for $C_{15}H_{16}O$: M, 212.1200.

(4-Methylphenyl)phenylmethyl Methyl Ether (6c): Colorless oil. ^{1}H NMR ($CDCl_3$) δ=2.21 (3H, s, CH_3), 3.22 (3H, s, OCH_3), 5.12 (1H, s, -CH-), 7.0—7.40 (9H, m, Ar); Found: m/z 212.1200. Calcd for $C_{15}H_{16}O$: M, 212.1200.

(4-Methoxyphenyl)phenylmethyl Methyl Ether (6d): Mp 64—66 °C. ^{1}H NMR ($CDCl_3$) δ=3.24 (3H, s, OCH_3), 3.64 (6H, s, OCH_3), 5.10 (1H, s, -CH-), 7.0—7.40 (9H, m, Ar); Found: m/z 228.1148. Calcd for $C_{15}H_{16}O_2$: M, 228.1150.

(3-Chlorophenyl)phenylmethyl Methyl Ether (6e): Colorless oil. ^{1}H NMR ($CDCl_3$) δ=3.22 (3H, s, OCH_3), 5.12 (1H, s, -CH-), 7.0—7.50 (9H, m, Ar); Found: m/z 232.0650, 234.0622. Calcd for $C_{14}H_{13}OCl$: M, 232.0655, 234.0625.

(4-Chlorophenyl)phenylmethyl Methyl Ether (6f): Colorless oil. ^{1}H NMR ($CDCl_3$) δ=3.24 (3H, s, OCH_3), 5.10 (1H, s, -CH-), 7.0—7.50 (9H, m, Ar); Found: m/z 232.0648, 234.0620. Calcd for $C_{14}H_{13}OCl$: M, 232.0655, 234.0652.

The compounds (**6j**, **6l**, and **6n**) were identified by use of high GC-MS measurement, because these compounds were too difficult to prepare by usual methods.

3-(α-Methoxybenzyl)pyridine (6j) Found: m/z 199.0994. Calcd for $C_{13}H_{13}NO$: M, 199.0996.

2-Chloro-5-(α-methoxybenzyl)pyridine (6l) Found: m/z 233.0606, 235.0577. Calcd for $C_{13}H_{12}NOCl$: M, 233.0607, 235.0577.

Di-*p*-tolylmethyl Methyl Ether (6m): Colorless oil. ^{1}H NMR ($CDCl_3$) δ=2.20 (6H, s, CH_3), 5.10 (1H, s, -CH-), 7.0—7.50 (8H, m, Ar); Found; m/z 210.1406. Calcd for $C_{16}H_{18}O$: M, 210.1408.

3-(α-Methoxy-4-methylbenzyl)pyridine (6n): Found: m/z 213.1150. Calcd for $C_{14}H_{15}NO$: M, 213.1153.

A General Procedure of Photolysis. Irradiation and analysis of **1** or **4** were carried out in the same manner as reported previously.[4]

Measurement of the Quantum Yields. The quantum yields were measured on the base of **2** in the same manner as reported previously.[4]

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