November, 1990] NOTES *Bull. Chem. Soc. Jpn.*, *63*, *3345—3347 (1990)* 3345

Photolysis of Triphenylacetic Acid and Its Methyl Ester: A Novel Photochemical Generation of Carbene Intermediates

Min Shi, Yoshiki Okamoto,* and Setsuo Takamuku
The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567
(Received April 13, 1990)

Synopsis. The photolysis of methyl triphenylacetate in methanol gave biphenyl, methyl α-methoxyphenylacetate, methyl benzoate, and methoxydiphenylmethane. The formation of these products suggests that two types of α,α-elimination take place: One is the elimination of two phenyl groups leaving $Ph-\ddot{C}-CO_2Me$ (type **a**), and the other is the elimination of the phenyl and methoxycarbonyl groups generating Ph_2C: (type **b**). Only type **a** elimination was efficiently quenched by oxygen.

Carbene intermediates have been of interest in connection with both synthetic and spectroscopic investigations in recent years.[1)] In these studies the photolysis of the corresponding diazo compounds has been used for the generation of carbene. Our recent study[2)] concerning on the photolysis of dimethyl (triphenylmethyl)phosphonic acid (**1**) has revealed that it undergoes a photochemical α,α-elimination of two phenyl groups to afford biphenyl (**2**) and dihydroxy(phenyl)carbene. This finding prompted us to further study the details of this photochemical generation of carbene. We have found that in the photolysis of triphenylacetic acid (**3**) and its methyl ester (**4**) another type α,α-elimination of the phenyl and methoxycarbonyl groups also takes place to give methyl benzoate (**5**) and another product.

Results and Discussion

Photolysis of Triphenylacetic Acid (3). The photochemical behavior of **3** was dependent upon the pH of the solution. Upon irradiation in an alkaline solution (pH>8), **3** gave only triphenylmethane (**6**). The photo-decarboxylation of triarylacetic acids at pH 7—11 is known.[3)] An analogous photo-dephosphorylation has been also observed in the photolysis of **1**.[2)]

With lowering the pH of the ethanol solution of **3**, the yield of **6** decreased, while the yields of **2** and ethoxydiphenylmethane (**7**) increased (Fig. 1 and Scheme 1).

Photolysis of Methyl Triphenylacetate (4). The photolysis of a methanol solution of **4** (5 mmol dm^{-3}) for 2 h (conversion 55%) gave four kinds of products: **2** (yield 9.8%), **5** (11.0%), methoxydiphenylmethane (**8**, 11.3%), and methyl α-methoxyphenylacetate (**9**, 10.5%). These yields increased linearly with a constant proportion with the lapse of irradiation time at a conversion of less than 30%. These facts indicate that all of the products are primary and two types of α,α-elimination (type **a** and **b**) took place concurrently. The formation of two kinds of carbene intermediates (**10** and **11**) can be illustrated as shown in Scheme 2.

The quantum yield of **2** or **9** (0.017) was nearly the same as that of **5** or **8**, respectively, indicating that type **a** and **b** eliminations took place to the same extent. The type **a** elimination is quite similar to that of **1**, in which two phenyl groups are eliminated via the initial bonding between the C-1 positions of two phenyl

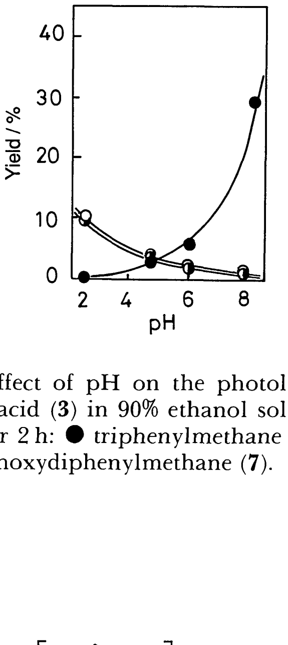
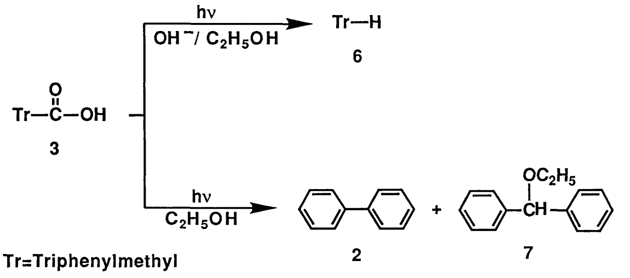
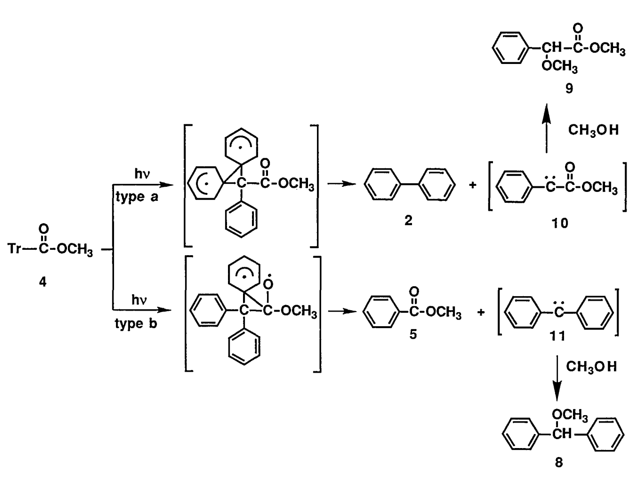


Fig. 1. Effect of pH on the photolysis of triphenylacetic acid (**3**) in 90% ethanol solution (10 mmol dm^{-3}) for 2 h: ● triphenylmethane (**6**); ○ biphenyl (**2**); ◑ ethoxydiphenylmethane (**7**).



Scheme 1.



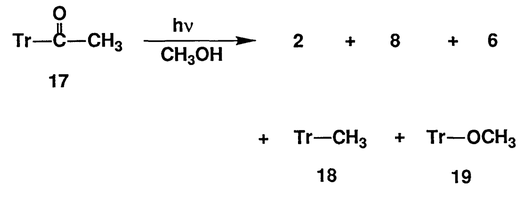
Scheme 2.

groups (ipso coupling). Similar carbene formations were previously reported in the cases of tetraphenyl methane,[4] dibenzonorbornadiene,[5] and triptycene[6] as a special case of di-π-methane rearrangement,[7] in which the fragmentation occurs from biradical intermediates instead of cyclization to cyclopropane derivatives. In the present type **a** elimination, a similar mechanism can be presumed.

On the other hand, the type **b** elimination proceeds via an α,α-elimination of phenyl and methoxycarbonyl groups to provide **5** and diphenylcarbene (**11**). This novel carbene formation indicates that a methoxycarbonyl group can also participate in the α,α-elimination. The reaction may be regarded as being an oxa-di-π-methane rearrangement.[7,8] In the photochemical reaction of **4**, bond formation between the carbonyl carbon and the C-1 carbon of the phenyl group is followed by fragmentation to form the carbene **11**. Reports concerning the oxa-di-π-methane rearrangement of ester have been very few.[9] Moreover, upon the photolysis of methyl tris(4-methoxyphenyl)acetate (**12**) in methanol, the formation of 4,4′-dimethoxybiphenyl (**13**, 10.6%), methyl α-methoxy(4-methoxyphenyl)acetate (**14**, 10.8%), methyl 4-methoxybenzoate (**15**, 12.2%), and methoxybis(4-methoxyphenyl)methane (**16**, 11.8%) were observed; this also supports the coupling process.

There is no fundamental difference between the photolysis of **3** and **4**, although the isolation of benzoic acid, derived from type **b** elimination from **3**, has not yet been carried out.

UV irradiation of triphenylmethyl methyl ketone (**17**)[10] in methanol for 1 h also gave **2** (5%) and **8** (7%). However, in this case, the major products were **6** (12%), 1,1,1-triphenylethane (**18**, 10%), and methoxytriphenylmethane (**19**, 20%) derived from the homolytic α-cleavage of ketone (Scheme 3).



Scheme 3.

In order to obtain further information concerning the reaction mechanism, the effects of oxygen and *cis*-1,3-pentadidene on the photolysis of **4** were examined. The results shown in Table 1 indicate that the yields of products **2** and **9** via the type **a** elimination were efficiently quenched by oxygen or *cis*-1,3-pentadiene, while the products **5** and **8** via the type **b** elimination were not affected. These results can be explained by assuming the presence of two excited states of **4** having different lifetimes. An exited species with a longer lifetime participates in the type **a** elimination. This might be a triplet excited state, since the photolysis of **4** under acetone (E_T=334—377 kJ mol^{-1}) sensitization in methanol provided only **2**, although under benzophenone (E_T=287 kJ mol^{-1}) or acetophenone (E_T=310 kJ mol^{-1}) it did not give **2**.

The product derived from the triplet carbene could not be detected. This may be explained by supposing that there is a rapid equilibrium established between the singlet and the triplet carbenes at ambient temperature, and that the reactivity of the singlet carbene with methanol is much larger compared with that of the triplet carbene.[11,12]

A photochemical geminal elimination of two aryl groups to give biaryl has been previously reported concerning carbon[4] as well as other elements such as zinc,[13] aluminum,[14] boron,[15] and tin.[16] However, the formation of carbene via a geminal photo-elimination of phenyl and methoxycarbonyl groups was unknown to the best of our knowledge. Therefore, emphasis should be placed on the novel photochemical generation of carbenes from alkyl triarylacetates. These results also suggest the possibility that other groups than phenyl and methoxycarbonyl participate in geminal elimination.

Experimental

GC-MS spectrometry data were obtained on a Shimadzu Model GCMS-QP 1000 (1-m glass column, 2% Silicone OV-7 on Uniport HP). GLC analyses were carried out using 2% Silicone OV-17 on Chrom. WAW DMCS (60/80 mesh) with a Shimadzu Model 7A instrument. The yields of photoproducts were determined using methyl diphenylacetate or triphenylmethane (**6**) as internal references.

Materials. Triphenylacetic acid (**3**) was commercially available. Methyl triphenylacetate (**4**),[18] methyl tris(4-methoxyphenyl)acetate (**12**),[19] and triphenylmethyl methyl

Table 1. The Effects of Quencher on the Photolysis of **4**[a)]

Additives	mmol dm^{-3}	Conv. of **4**	Product (Yield/%)[b)]				
		%	**2**	**9**	**5**	**8**	**20**[c)]
None[d)]	—	55	9.8	10.5	11.0	11.3	—
Oxygen	2.12[e)]	53	8.2	7.8	10.7	10.8	—
	9.57[f)]	50	3.2	3.0	12.0	10.0	2.0
cis-1,3-Pentadiene	2.0	42	6.6	5.9	10.1	10.0	—
	5.0	45	4.0	3.6	10.5	10.2	—
	10	40	2.0	1.2	10.7	10.4	—
	20	38	0.2	0	10.6	10.1	—

a) Photolysis of a methanol solution of **4** (5 mmol dm^{-3}) was carried out with a high pressure Hg lamp for 2 h in a quartz cell. b) The product yields were determined by GLC on the basis of the initial amount of **4**. c) **20** is benzophenone. d) Argon saturated. e) Air saturated. f) Oxygen saturated.

ketone (**17**)[10] were prepared according methods described in the literature.

Preparation of Authentic Sample. Biphenyl (**2**), triphenylacetic acid (**3**),[14] 4,4′-dimethoxybiphenyl (**13**), triphenylmethane (**6**), methyl benzoate (**5**), and methyl 4-methoxybenzoate (**15**) used for authentic samples were commercially available.

Methoxydiphenylmethane (**8**),[20] methyl methoxyphenylacetate (**9**),[21] 1,1,1-triphenylethane (**18**),[22] methoxytriphenylmethane (**19**)[23] were prepared according to the literatures.

Methoxybis(4-methoxyphenyl)methane (16). Bp 161.0—161.5 °C (14.5 mmHg, 1 mmHg≈133.322 Pa); mp 30.4—31.0 °C; ^{1}H NMR (CDCl$_3$) δ=3.22 (s, 3H, OCH$_3$) 3.78 (s, 6H, PhOCH$_3$), 5.08 (s, 1H), 7.0—7.4 (m, 8H, Ph).

Methyl α-Methoxy(4-methoxyphenyl)acetate (14). Bp 140—142 °C (18 mmHg); ^{1}H NMR (CDCl$_3$) δ=3.40 (s, 3H, OCH$_3$), 3.62 (s, 3H, C(O)OCH$_3$), 3.76 (s, 3H, PhOCH$_3$), 4.70 (s, 1H), 7.0—7.4 (m, 4H, Ph).

Photolysis of 3 in Ethanol. A 5-ml EtOH solution (pH 3.0) of **3** (10 mmol dm^{-3}) was purged of dissolved air by flushing argon gas and irradiated in a quartz tube(ϕ=10 mm) in a merry-go-round apparatus with a high-pressure Hg lamp (300 W) for 2 h. After irradiation the products were analyzed with GC-MS. These data were identified with those of authentic samples. Products **2** and **7** were obtained in 11.0 and 9.8% yields, respectively.

The pH's of the solutions were adjusted to 4.8, 5.0, and 8.0 with an 1 equiv NaOH aqueous solution, respectively, and they were irradiated in a similar manner to that described above.

Photolysis of 4 in Methanol. A 5-ml MeOH solution of **4** (5 mmol dm^{-3}) was irradiated for 2 h in a similar manner as that described above. Products **2**, **5**, **8**, and **9** were obtained in yields of 9.8, 11.0, 11.3, and 10.5%, respectively; the conversion of **4** was 42%.

Photolysis of 12 in Methanol. A 5-ml MeOH solution of **12** (5 mmol dm^{-3}) was irradiated for 2 h in a similar manner as that described above. Products **13**, **14**, **15**, and **16** were obtained in yields of 10.6, 10.8, 12.2, and 11.8%, respectively; the conversion of **12** was 54%.

Sensitized Photolysis of 4. A 3-ml acetone solution of **4** (5 mmol dm^{-3}) was irradiated for 3 h by the use of a low-pressure Hg lamp (60 W) (conv. 50%). Only **2** was obtained in a 10% yield. However, the photolysis of **4** in methanol (5 mmol dm^{-3}) using benzophenone or acetophenone (20 mmol dm^{-3}) as a sensitizer in a Pyrex tube was performed. After irradiation for 2 h using a high-pressure Hg lamp, the product could not be detected.

Photolysis of 4 in the Presence of Quencher[Q]. Oxygen: Three 3-ml MeOH solutions of **4** (10 mmol dm^{-3}) were charged in three separate quartz tubes (ϕ=10 mm). Argon, air or oxygen was bubbled into the solutions at 20 °C for 10 min, respectively, and irradiated using a high-pressure Hg lamp at the same time with a merry-go-round apparatus.

cis-1,3-Pentadiene: Five 3-ml MeOH solutions of **4** (10 mmol dm^{-3}) were charged in five separate quartz tubes (ϕ=10 mm). After purging any dissolved air by bubbling argon, *cis*-1,3-pentadiene [Q] was added. The concentrations of [Q] in these tubes were adjusted to 0, 2, 5, 10, and 20 mmol dm^{-3}, respectively. They were irradiated in a similar manner as that described above. These obtained results are shown in Table 1.

Determination of Quantum Yield. The quantum yields were measured in the same manner as reported previously.[2]

References

1) T. Sugawara, H. Iwamura, H. Hayashi, A. Sekiguchi, W. Ando, and M. T. H. Liu, *Chem. Lett.*, **1983**, 1261; L. M. Hadel, M. S. Platz, and J. C. Scaiano, *J. Am. Chem. Soc.*, **106**, 283 (1984); H. L. Casal, M. Tanner, N. H. Werstiuk, and J. C. Acaiano, *J. Am. Chem. Soc.*, **107**, 4616 (1985); Y. Fujiwara, Y. Tanimoto, M. Itoh, K. Hirai, and H. Tomioka, *J. Am. Chem. Soc.*, **109**, 1942 (1987).

2) M. Shi, Y. Okamoto, and S. Takamuku, *J. Chem. Soc., Chem. Commun.*, **1989**, 151.

3) J. L. Faria and S. Steenken, *J. Am. Chem. Soc.*, **112**, 1277 (1990).

4) T. D. Walsh and D. R. Powers, *Tetrahedron Lett.*, **1970**, 3855.

5) J. Ipaktshi, *Chem. Ber.*, **105**, 1989 (1972).

6) H. Iwamura and K. Yoshimura, *J. Am. Chem. Soc.*, **96**, 2652 (1974).

7) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

8) K. N. Houk, *Chem. Rev.*, **76**, 1 (1976).

9) J. S. Swenton and D. M. Madigan, *Tetrahedron*, **28**, 2703 (1972).

10) J. L. Greene and H. D. Zook, *J. Am. Chem. Soc.*, **80**, 3629 (1958).

11) K. B. Eisenthal, N. J. Turro, M. Aikawa, J. A. Butcher, Jr., C. Dupuy, G. Hefferon, W. Hetherington, G. M. Korenowski, and M. J. McAuliffe, *J. Am. Chem. Soc.*, **102**, 6563 (1980).

12) H. Tomioka, H. Okuno, and Y. Izawa, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 1636.

13) R. W. Hoffmann and W. Sieber, *Justus Liebigs Ann. Chem.*, **703**, 96 (1967).

14) J. Meinwald, S. Knapp, S. K. Obendorf, and R. E. J. Hughes, *J. Am. Chem. Soc.*, **98**, 6643 (1976).

15) G. C. Chalhoun and G. B. Schuster, *J. Org. Chem.*, **49**, 1295 (1984).

16) J. Meinwald, S. Knapp, and T. Tatsuoka, *Tetrahedron Lett.*, **1970**, 2247.

17) H. H. Lewis, M. Nierenstein, and E. M. Rich, *J. Am. Chem. Soc.*, **47**, 1731 (1925).

18) H. Meyer, *Monatsh. Chem.*, **27**, 1094 (1906).

19) A. Bistrzycki and S. Jabionski, *Helv. Chim. Acta*, **15**, 890 (1932).

20) C. M. Welch and H. A. Smith, *J. Am. Chem. Soc.*, **72**, 4748 (1950).

21) R. G. Ault, W. N. Haworth, and E. L. Hirst, *J. Chem. Soc.*, **1934**, 1722.

22) M. Gomberg and L. H. Cone, *Chem. Ber.*, **34**, 1466 (1906).

23) M. F. Hawthorne and D. J. Cram, *J. Am. Chem. Soc.*, **76**, 3451 (1954).