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PHOTOLYSIS OF 1,1,1-TRIPHENYLALKANES

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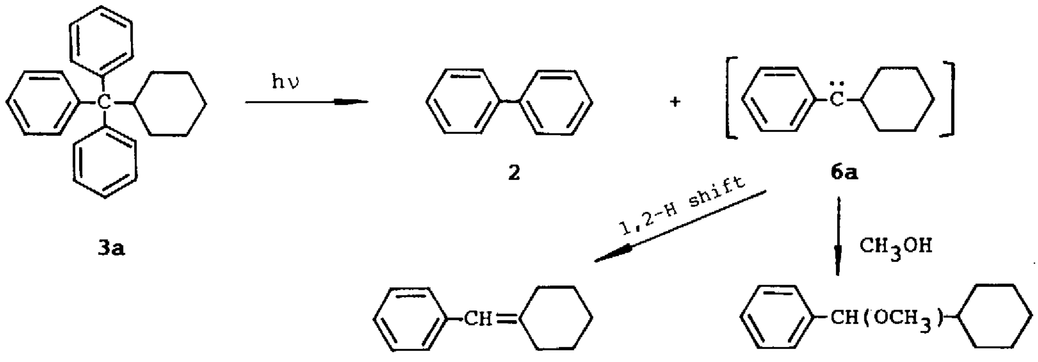
Summary: Photolysis of 1,1,1-triphenylalkane in methanol gave biphenyl, 1-methoxy-1-phenylalkane, and 1-phenylalkene. The generation of the carbene intermediate by photo α,α-elimination of two phenyl groups was presumed.

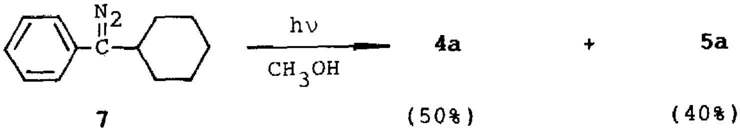
We have recently reported that upon UV-irradiation, the dimethyl triphenylmethylphosphonate(**1**) underwent a novel α,α-elimination of two phenyl groups to afford biphenyl (**2**) and dimethoxyphosphinyl(phenyl)carbene.[1] During our further clarification of the scope and limitation of this photolysis, we found that some 1,1,1-triphenylalkanes (**3**)[2] having a secondary alkyl group also readily underwent a similar photochemical reaction.

Irradiation of a methanol solution of (triphenylmethyl)cyclohexane (**3a**) (10 mM) in a quartz tube under argon atmosphere with a high pressure mercury lamp (300 W) for 2 h(conversion 55%) gave **2** (27%), cyclohexyl-(methoxy)phenylmethane (**4a**, 16%), and benzylidenecyclohexane (**5a**, 10%) (Scheme 1). The products **4a** and **5a** may be derived from the insertion of the carbene **6a** into the O-H bond of methanol and from the 1,2-hydrogen shift in the carbene **6a**, respectively. It is known that the carbene



Scheme 1

intermediate undergoes 1,2-hydrogen shift to give olefin. For example, Overberger showed that methyl(phenyl)carbene underwent hydrogen shift to give styrene,[3] and Robson further reported the hydrogen migratory aptitude in detail.[4] In order to further verify this reaction scheme, the photolysis of a corresponding carbene-precursor, cyclohexyl(phenyl)diazomethane (**7**)[5] was carried out. After complete photo-bleaching of the red color of **7** in methanol, the products **4a** and **5a** were obtained in 50 and 40% yields, respectively (Scheme 2). On sensitized photolysis of **7** with Michler's ketone in methanol using a $BiCl_3$/HCl filter (>350 nm), 2-cyclohexyl-2-phenylethanol was obtained as an additional product.



(Scheme 2)

Moreover, photolysis of **3a** in cyclohexane, acetonitrile, or tetrahydrofuran (THF) (10 mM) for 2 h also led to the formation of **2** and **5a** in comparable amounts. Their yields are summarized in Table 1, together with the results in methanol.

Table 1. Photolysis of **3a**

Solvent	$\Phi^{b)}$	Conv./%$^{a)}$	Product, Yield/%		
			2	**4a**	**5a**
cyclohexane	0.015	40	24	-	23
acetonitrile	0.014	56	21	-	18
THF	0.024	50	36	-	35
methanol	0.016	55	27	16	10

a) These photo-products **2**, **4a**, and **5a** were identified by comparison of the GLC, GC-MS, and ^1H and ^{13}C-NMR spectral data with those of authentic samples.[7,8] The yields and conversions were determined by GLC (Shimadzu GC-7A, Silicone OV-7, 2% Uniport HP, 1-m glass column) using triphenylmethane as an internal standard. b) Quantum yield of **2** (see ref. 6).

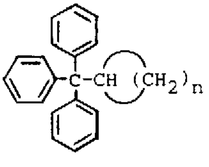
It should be noted that the product resulted from hydrogen abstraction from the solvent by the triplet state species (triplet carbene) could not be detected. Furthermore, upon irradiation of the oxygen-saturated methanol solution, the yields of **2**, **4a** and the intramolecular rearranged product **5a** were unchanged. Therefore, these results suggest that the photo-decomposition of **3a** would proceed via a singlet excited state to give **2** and the singlet carbene **6a**, which reacts with methanol to afford **4a** and/or undergoes a 1,2-H shift to give **5a**.

Upon irradiation of other (triphenylmethyl)cycloalkanes; (triphenylmethyl)cyclopropane (**3b**), (triphenylmethyl)cyclopentane (**3c**), and (triphenylmethyl)cycloheptane (**3d**) in methanol under the same conditions, we found that the yields of **2** are highly dependent upon the size of ring in the order of **3a**=**3d**>**3c**>**3b**. The compounds **3b** and **3c** did not give the product arising from 1,2-H shift of the carbene intermediate (Table 2).

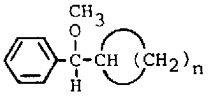
Table 2. Photolysis of **3b**-**3d** in methanol

		Product[a] (yield/%)		
3	Conv./%	**2**	**4**	**5**
3b	38	5	**4b**(4)	**5b**(0)
3c	50	21	**4c**(19)	**5c**(0)
3d	60	25	**4d**(10)	**5d**(13)

a) The spectral and analytical data of all compounds produced were in satisfactory agreement with those of authentic samples.



3b - d

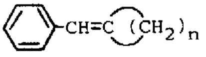


4b - d

b; n= 2

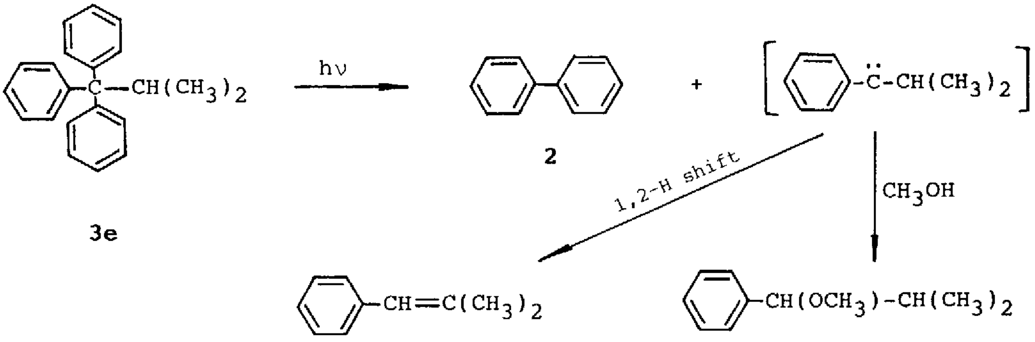
c; n= 4

d; n= 6



5b - d

On the other hand, photolysis of acyclic triphenylalkanes; 1,1,1-triphenyl-2-methylpropane (**3e**) in methanol for 2 h also provide **2** (25%), 1-methoxy-1-phenyl-2-methylpropane (**4e**, 10%), and 1-phenyl-2-methylpropene (**5e**, 15%) (Scheme 3). However, upon irradiation of triphenylmethane (**3f**), 1,1,1-triphenylethane (**3g**) or 1,1,1-triphenyl-2,2-dimethylpropane (**3h**) in methanol, only trace amount of **2** could be detected by GLC.



Scheme 3

5e

4e

These results imply that the structure of the alkyl groups bonding with triphenylmethyl group would play an important role in their photolysis process; a moderate bulkiness of an alkyl group seems to be favorable for this photolytic decomposition. The similar formation processes of **2** and the carbene intermediate have been reported in photolysis of tetraphenylmethane,[9] dibenzonorbornadiene,[10] and triptycene.[11]

References and Notes

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

2) The compounds (**3**) were prepared by the reaction of triphenylmethyl chloride with the corresponding alkylmagnesium bromides in a mixture of ethyl ether and benzene under a nitrogen atmosphere according to the method reported (T. Petrow, Izv. Akad. SSSR Otd. Chim., **1961**, 2209). After usual work-up, the residue was purified by flash chromatography with n-hexane as an eluant, followed by recrystalization from hexane gave **3**. **3a**; mp 143-145 °C, UV(MeOH)λmax=260 nm(ε 980 $M^{-1}cm^{-1}$), **3b**; mp 80-81 °C, UV(MeOH)λmax=260 nm(ε 723 $M^{-1}cm^{-1}$), **3c**; mp 68-70°C, UV(MeOH) λmax=260 nm(ε 972 $M^{-1}cm^{-1}$), **3d**; mp 112-114 °C, UV(MeOH)λ max=260 nm (ε 800 $M^{-1}cm^{-1}$), **3e**; mp 91-92 °C, UV(MeOH)λmax=260 nm(ε 850 $M^{-1}cm^{-1}$) **3f**; mp 92-94 °C, UV(MeOH)λmax=260 nm(ε 260 $M^{-1}cm^{-1}$) **3g**; 94-95 °C, UV(MeOH)λmax=260 nm(ε 785 $M^{-1}cm^{-1}$) **3h**; mp 184-185 °C, UV(MeOH)λmax=260 nm(ε 800 $M^{-1}cm^{-1}$).

3) C. G. Overberger and J. -P. Anselme, J. Org. Chem., **29**, 1188 (1964).

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6) Determination of quantum yields of **2** was carried out 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 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%.

7) **4a** was prepared by the methylation of cyclohexyl(phenyl)methanol, which was derived from the reaction of benzaldehyde with cyclohexylmagnesium bromide, with dimethyl sulfate. bp 108-109 °C(0.1 mmHg), ^{1}H NMR δ=0.80-2.10(11H, m, cyclohexyl), 3.17(3H, s, CH_3O), 3.78(1H, d, J_{HH}=7.3 Hz), 7.2-7.4(5H, m, Ph).

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