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Photolysis of 1,1,1-Triphenyl-2-alkenes and Methyl Triphenylacetate

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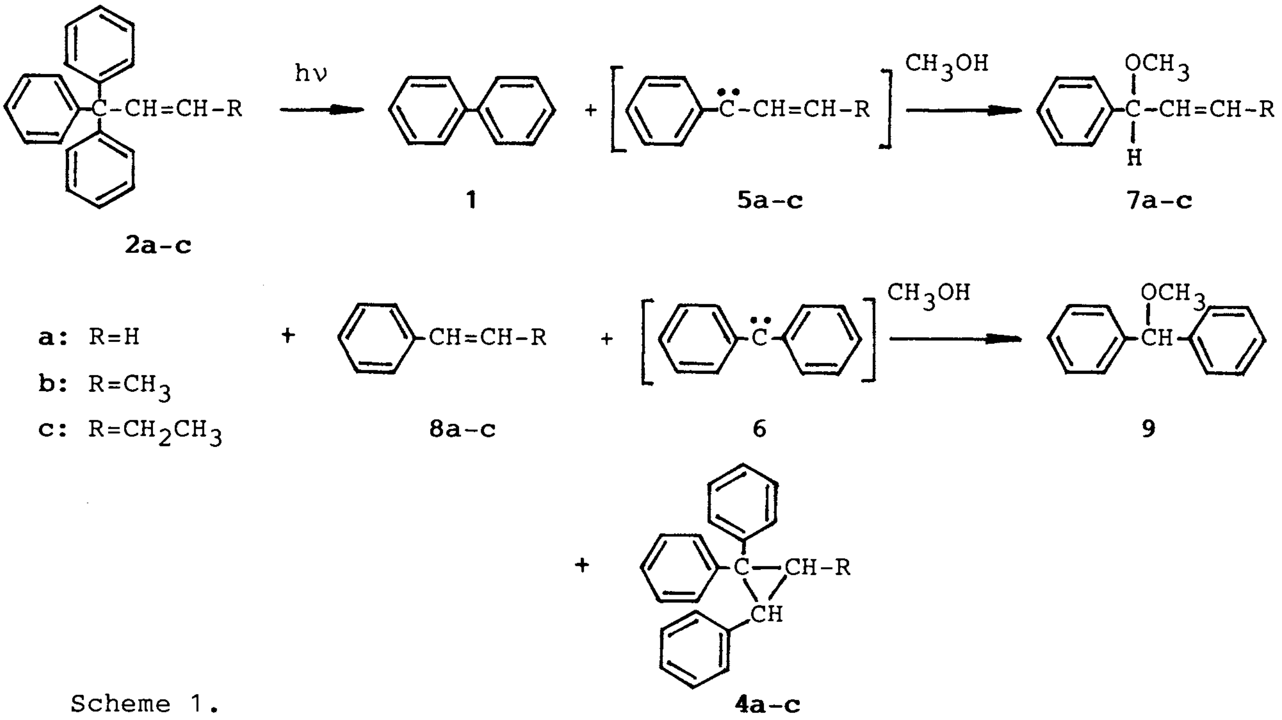
Upon UV irradiation in methanol 1,1,1-triphenyl-2-alkene or methyl triphenylacetate underwent two kinds of α,α-elimination of two phenyl groups and phenyl-alkenyl groups or phenyl-methoxycarbonyl groups to give biphenyl, 1-phenylalkene or methyl benzoate, and two kinds of corresponding carbene intermediates, which inserted into the O-H bond of methanol to afford two kinds of methyl ethers, respectively.

We have already reported that upon UV irradiation in methanol 1,1,1-triarylhept-2-yne underwent a novel α,α-elimination of two aryl groups to give biaryl (Φ =0.020-0.045) and the corresponding carbene intermediate, which inserted into the O-H bond of methanol to afford the methyl ether.[1] This interesting photochemical behavior stimulated us to study further the photolysis of 1,1,1-triphenyl-2-alkenes (**2a-c**)[2] and methyl triphenylacetate (3).

In 1965, Griffin has reported that when 1,1,1-triphenyl-2-propene (2a) was irradiated with 254-nm light in a degassed benzene solution for 50 h, the major product was 1,1,2-triphenylcyclopropane (4a), as the result of cyclization and concomitant phenyl migration. In addition a considerable amount of starting material and a number of unidentified minor products were given.[3]

In this paper, we wish to report a different type of photochemical reaction of **2a-c** from those reported by Griffin and to propose a mechanism which is consistent with both types of reactions.

Upon irradiation of a methanol solution of **2a-c** with a high pressure mercury lamp (300 W) under argon atmosphere, besides cyclization products **4a-c**, two kinds of α, α-elimination took place to give the corresponding two kinds of carbene intermediates (**5a-c**) and (**6**), respectively: one was the α,α-elimination of two phenyl groups to give biphenyl (**1**) and alkenyl(phenyl)carbene (**5a-c**), which inserted into the O-H bond of methanol to afford the methyl ether (**7a-c**); another was the α,α-elimination of an alkenyl and a phenyl group to give phenylalkene (**8a-c**) and diphenylcarbene (**6**), which similarly inserted into the O-H bond of methanol to give methoxy(diphenyl)methane (**9**) (Scheme 1). Their yields were summarized in Table 1.



Scheme 1.

Table 1. Photolysis of **2a-c**[a)]

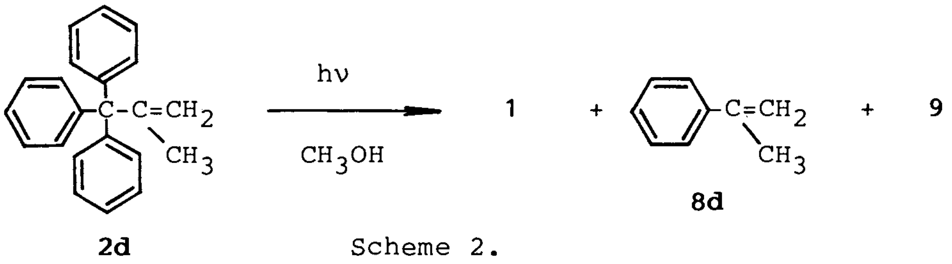
Compd.	Quantum yield	Conv./%	Product/% **1**	**7**	**8**	**9**	**4**
2a	0.006[b)]	27	8	5	trace	4	14
2b	0.01[b)]	38	22	15	trace	5	8
2c	0.01[b)]	43	24	16	trace	6	9

a) The compounds **2a-c** (10 mmol dm^{-3}) in methanol were irradiated in a quartz tube for 2 h.

b) The quantum yield of **1**.

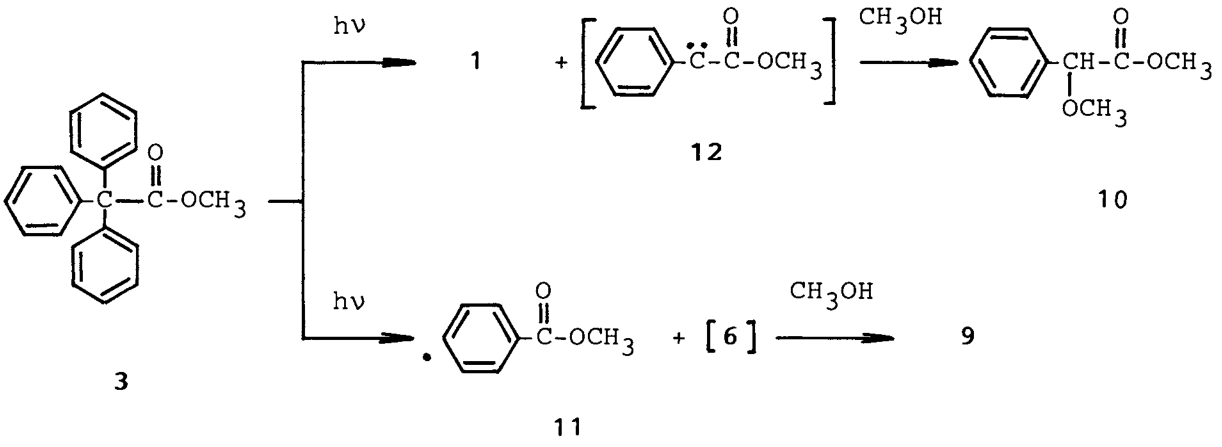
Furthermore, we have carefully checked the photochemical behaviors of **2a-c** under the similar conditions reported by Griffin (irradiated in a degassed benzene solution, 0.1 mol dm^{-3})[3)] and found that **1** and **8a-c** were also formed in the similar yields as described in Table 1, although the carbene product could not be identified.

When 2-methyl-3,3,3-triphenylpropene (**2d**)4) was used as a substrate, the formations of **1** (24%), **8d** (trace), and **9** (5%) were observed. However, a cyclization product could not be detected (Scheme 2). This result implies that the introduction of a methyl group into the position adjacent to the triphenylmethyl group hinders the 1,2-phenyl migration.



Scheme 2.

On the other hand, photolysis of a methanol solution of methyl triphenylacetate (**3**, 5 mmol dm^{-3}) under the same conditions as described above for 2 h also give four kinds of products derived from two types of α, α-elimination, respectively: **1** (10%), methyl α-methoxyphenylacetate (**10**, 10%), methyl benzoate (**11**, 11%), and **9** (11%) (Scheme 3). Yields of these products increased linearly with the lapse of irradiation time at the conversion less than 30% and the ratio of the products did not change up to the conversion of 50%. The facts indicate that all of them are primary products and two types of α,α-elimination take place at the same time. Moreover, UV irradiation of triphenylmethyl methyl ketone in methanol for 1 h also gave **1** (5%) and **9** (7%), however, the major product was triphenylmeth-



Scheme 3.

ane (12%) and methoxy(triphenyl)methane (20%) clearly derived from the homolytic α-cleavage of ketone.

Further to confirm the formation of carbene intermediates 5a-**c**, **6**, and **12** the photolyses of **2a-c** and **3** in cyclohexene were undertaken in the hope of isolating the adducts. The formation of the adducts were confirmed by GC-mass, although their structures were not yet determined.

These results reveals an unique carbene formation in the photolysis of **2a-c** in addition to the cyclization reported by Griffin. The α,α-elimination of phenyl-alkenyl groups and phenyl-methoxycarbonyl groups is a novel type and indicates that in addition to phenyl group, alkenyl group and methoxycarbonyl group can also participate the α,α-elimination. The mechanism of the elimination of two phenyl groups and phenyl-alkenyl groups can be understood in terms of photochemical di-π-methane rearrangement and the elimination of phenyl-methoxycarbonyl groups can be also similarly understood as oxa-di-π-methane rearrangement.$^{5)}$ The similar carbene formation was previously reported in the case of triptycene as a special case of di-π-methane rearrangement.$^{6)}$

The identification of these products was achieved by comparison of GLC retention times and mass spectra with those of authentic samples. The product yields were determined by means of GLC calibration with triphenylmethane as an internal standard.

References

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2) The compounds 2a-c were synthesized by Wittig reaction, involving treatment of triphenylethanal with these appropriate alkylidenetriphenylphosphoranes. **2b** and **2c** are the mixture of Z and E. **2b**, Z:E=3:2; **2c**, Z:E=9:1.

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