Tetrahedron Letters,Vol.24,No.11,pp 1107-1110,1983 0040-4039/83/111107-04$03.00/0
Printed in Great Britain

CUMULENE PHOTOCHEMISTRY: PHOTOADDITION OF NEUTRAL METHANOL TO PHENYLALLENES

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ABSTRACT: Ultraviolet irradiation of tetra-, tri-, or diphenylallene in methanol leads to allylic methyl ethers. A mechanism is proposed with intermediacy of a strongly polarized planar allene excited state, initially protonated at C_2.

Photoaddition of protic solvents to alkenes has been widely studied during the past 15 years.[1,2] A notable exception is allenes and higher cumulenes, for which only one example has been described.[3] Fujita and co-workers reported vinyl acetates from irradiation of linear allenes in acetic acid. A triplet mechanism was proposed. In contrast to these observations, we report here that di-, tri-, and tetraphenylallene undergo facile singlet excited state methanol addition in the absence of acid catalyst, yielding allylic methyl ethers.

Our interest in allene photoreactions derived from our prediction[4] that π bond twisting in allene singlet excited states can lead to two "suddenly polarized"[5,6] geometries. Alcohol photoadditions have been suggested in some cases to involve strongly polarized states[7] and, in allenes, offered the potential to distinguish the two possible polarizations (vide infra).

Irradiation (Corex or Pyrex filter) of tetraphenylallene (**1**; ca. 10^{-2} M)[8] in methanol gave allylic ether **2** as major photoproduct, with **3** and **4** minor (ratio 10:1:1). All products were isolated by chromatography (mass balance >95%) and proved identical to authentic samples.[9]

To verify the absence of adventitious acid catalysis, methanol solutions of pure **1** (6×10^{-3} M), and **1** plus $NaOCH_3$, (0.16 M) were irradiated simultaneously to low conversion at 254 nm in a merry-go-round apparatus. Within experimental error, no difference was observed either in reaction rate or product distribution. Dark reaction of **1** in slightly acidic methanol (10^{-3} M HCl) at ambient temperature gave no reaction. Heating, or use of stronger acid yielded 1,1,3-triphenylindene , consistent with previous reports.[10]

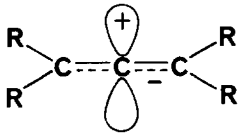
The photoreaction multiplicity was established as singlet through triplet sensitization experiments with triphenylene and 4-phenylbenzophenone. Prolonged irradiation of **1** (10^{-2} M) and sensitizers (10^{-1} M) in methanol at $\lambda > 330$ nm led to recovery of unreacted **1** and sensitizer. Energy transfer from triphenylene ($E_T = 67.2$ kcal/mol) or 4-phenylbenzophenone ($E_T = 60.7$) to **1** ($E_T = 57.4$)[11] should be efficient. Interestingly, attempted triplet sensitization with xanthone afforded only vinyl ether **6** in >80% yield.[12] This is undoubtedly an electron transfer process;[13] sensitization with 9,10-dicyanoanthracene produced identical results.[12b] Xanthone was also used as sensitizer by Fujita *et al.*,[3] and we speculate that their sensitized results might be due to electron transfer, rather than triplet energy transfer.

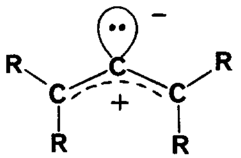
Irradiation of triphenyl- and 1,3-diphenylallene in methanol yielded allylic ethers, with no products comparable to **3** or **4**. Authentic samples of **8**, **9**, and **11** were prepared independently.[14] The **8**:**9** ratio was *ca.* 5:1, with **9** undergoing rapid secondary di-π-methane reaction.[14a] Reactivity decreased in the sequence **1** > **7** > **10** >> **12**; phenylallene yielded no ether photoproduct upon prolonged irradiation (28 h; Corex filter) in methanol.

In contrast to the high reactivity of **1**, its higher homolog, tetraphenylbutatriene, (**13**) was recovered unchanged after prolonged irradiation of dilute methanol solutions. Experiments with tetraphenylpentatetraene are in progress.

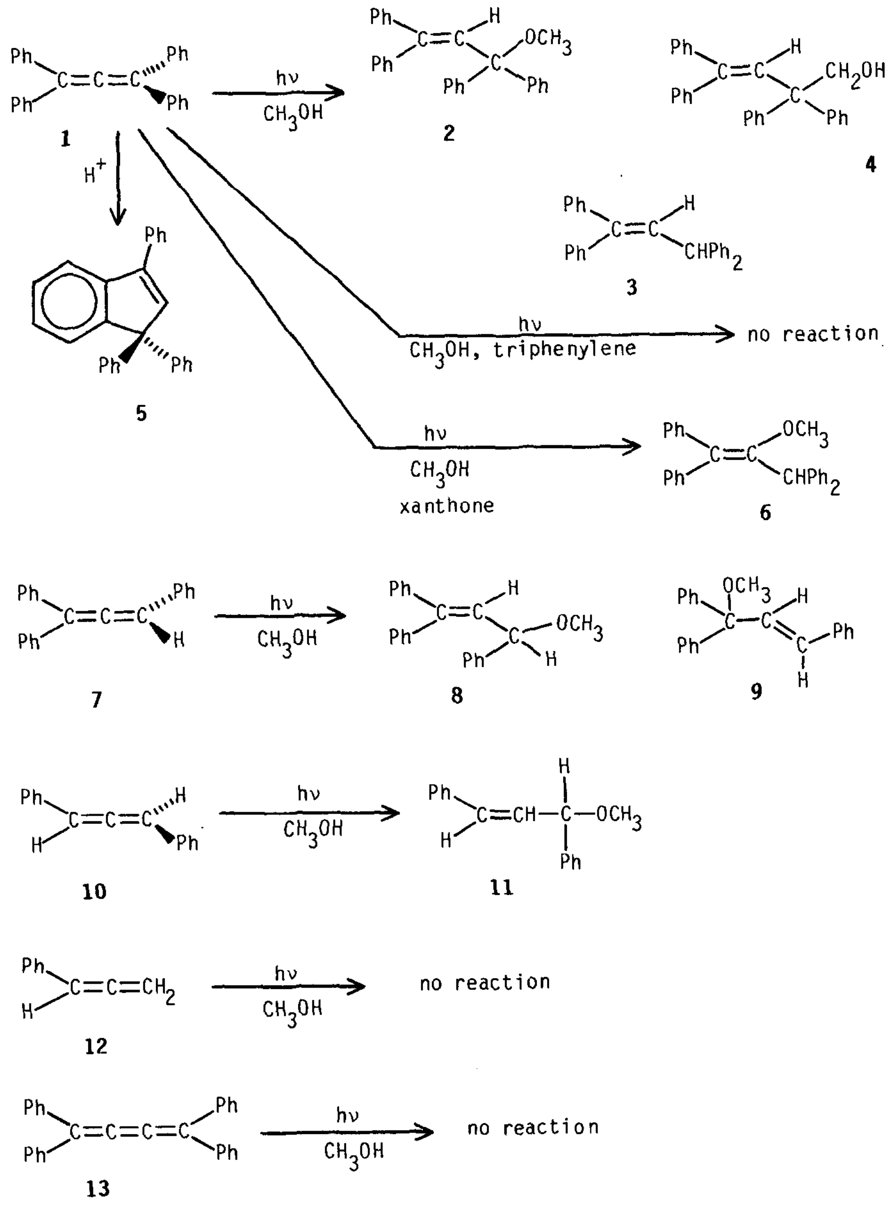
Based on *ab initio* MC-SCF calculations, we have concluded that two energetically proximate minima corresponding to I and II should exist on the allene excited state surface.[4] Both are "suddenly polarized", but in opposite directions. Phenylallenes might be expected to favor the C_{2v} geometry. Highly substituted allenes typically undergo ground state protonation at C_2, which presumably precedes twisting to the more stable allyl cation.[15] In the singlet excited state, we suggest that initial twisting to highly polarized II will permit protonation by even weak acids such as methanol, yielding directly a ground state allyl cation. Decreasing reactivity with fewer phenyl groups may reflect a decrease in stability of species II or the resultant allyl cation. Minor products **3** and **4** result from a competitive homolytic hydrogen abstraction from solvent.

I





II


1
hν
CH3OH
2
4
3
H+
5
hν
CH3OH, triphenylene
no reaction
hν
CH3OH
xanthone
6
7
hν
CH3OH
8
9
10
hν
CH3OH
11
12
hν
CH3OH
no reaction
13
hν
CH3OH
no reaction

More detailed mechanistic studies of these and related reactions are in progress.

ACKNOWLEDGEMENT is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES AND NOTES

(1) Reviews: (a) J. A. Marshall, Acc. Chem. Res. **2**, 33 (1969); (b) G. Sosnovsky and D. J. Rawlinson, Houben-Weyl, Methoden der Organischen Chemie, Band IV/5a, Photochemie I, 1975; (c) J. D. Coyle, in "The Chemistry of the C-C Triple Bond," S. Patai, Editor, John Wiley & Sons, 1978, Part II, Chpt. 12, p. 523; (d) P. J. Kropp, Org. Photochem., **4**, 1 (1979).

(2) Recent references: (a) P. Wan, S. Culshaw and K. Yates, J. Am. Chem. Soc., **104**, 2509 (1982); (b) W. G. Dauben, H. C. H. A. van Riel, J. D. Robbins and G. J. Wagner, J. Am. Chem. Soc., **101**, 6383 (1979); (c) P. J. Baldry, J. Chem. Soc., Perkin II 805 (1980); (d) P. J. Kropp and F. P. Tise, J. Am. Chem. Soc., **103**, 7293 (1981).

(3) K. Fujita, K. Matsui and T. Shono, J. Am. Chem. Soc., **97**, 6256 (1975).

(4) B. Lam and R. P. Johnson, J. Am. Chem. Soc., submitted for publication.

(5) L. Salem, Acc. Chem. Res., **12**, 87 (1979); J.-P. Malrieu, Theoret. Chim. Acta, **59**, 251 (1981).

(6) R. P. Johnson and M. W. Schmidt, J. Am. Chem. Soc., **103**, 3244 (1981).

(7) (a) W. G. Dauben, L. Salem and N. J. Turro, Acc. Chem. Res., **8**, 41 (1975); (b) C. M. Meerman-van Benthem, H. J. C. Jacobs and J. J. C. Mulder, Nouv. J. Chim., **2**, 123 (1978); (c) N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings Publishing, 1978.

(8) Preparative irradiations were conducted using a 450W medium pressure Hg lamp and immersion well apparatus. Irradiation of **1** and **5** in aprotic solvents led to isomerization reactions, which will be reported elsewhere.

(9) (a) **2**: J. J. Brophy and G. W. Griffin, Tetrahedron Lett. 493 (1970); (b) **3**: W. Tadros, A. B. Sakla and A. A. A. Helmy, J. Chem. Soc., 2688 (1961); (c) **4**: H. E. Zimmerman, R. J. Boettcher and W. Braig, J. Am. Chem. Soc., **95**, 2155 (1973).

(10) D. Vorander and C. Siebert, Chem. Ber., **39**, 1024 (1906).

(11) E. F. Ullman and W. A. Henderson, Jr., J. Am. Chem. Soc., **89**, 4390 (1967).

(12) (a) The structure of **6** is based on spectral data [^1H NMR ($CDCl_3$) δ 3.14 (s, 3H), 5.06 (s,1H), 7.26 (narrow m, 20H); UV(C_6H_{12}) λ_{max} 258 nm (26,500)] and on hydrolysis with HCl/EtOH to tetraphenylacetone. (b) We are grateful to Professor David Kurtz for performing the dicyanoanthracene sensitized experiments.

(13) A. J. Maroulis, Y. Shigemitsu and D. R. Arnold, J. Am. Chem. Soc. **100**, 535 (1978); S. L. Mattes and S. Farid, Acc. Chem. Rec. **15**, 80 (1982), and references therein.

(14) (a) **9**: J. J. Brophy, Australian J. Chem., **29**, 2445 (1976); (b) **11**: E. Bergman and T. Ukai, Ber. **66B**, 54 (1933); **8**: prepared from the alcohol by treatment with NaH/CH_3I: ^1H NMR ($CDCl_3$) δ 3.24 (s, 3H, CH_3), 4.72 (d, J=4.5 Hz, 1H), 6.26 (d, 1H), 7.0-7.5 (m, 15H).

(15) P. Blake, in "The Chemistry of Ketenes, Allenes and Related Compounds", S. Patai, Ed., Part 1, John Wiley & Sons, 1980, Chpt. 9, p. 310, and references therein.

(Received in USA 29 November 1982)