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PHOTOCHEMICAL GENERATION OF AN ORTHO-XYLYLENE FROM AN ORTHO-ALKYLSTYRENE

Joseph M. Hornback

Department of Chemistry, University of Denver, Denver, Colorado 80210, U.S.A.

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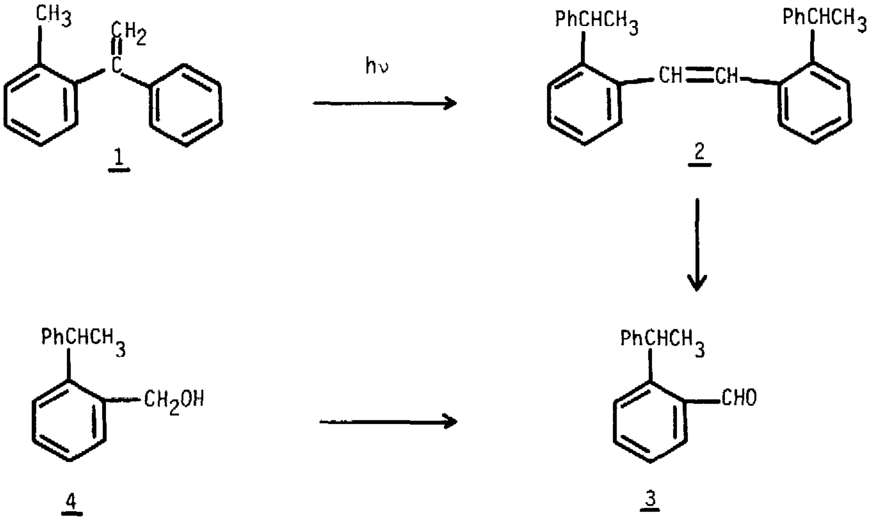
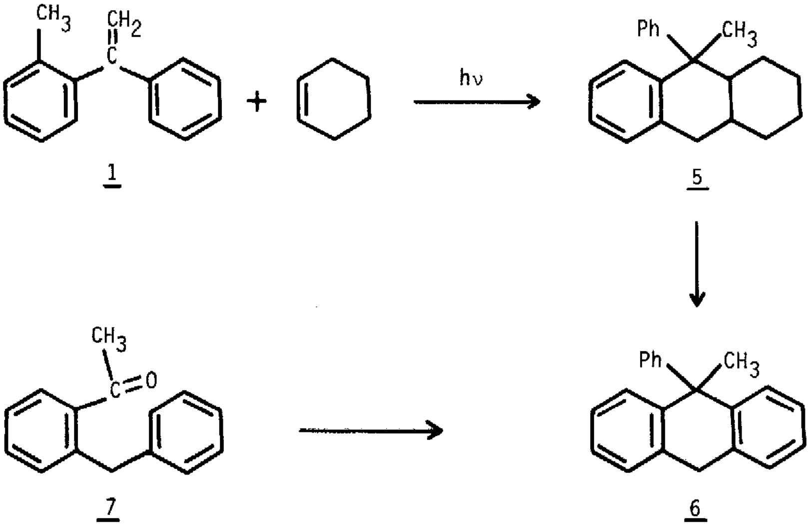
Many photochemical reactions of the carbonyl group are initiated by hydrogen transfer to the oxygen of the excited carbonyl. There is now evidence that similar hydrogen transfer reactions occur in the photochemistry of alkenes. Thus, both intermolecular photoreduction[1] and intramolecular hydrogen transfer[2] similar to the Type II photoelimination of ketones have recently been reported for alkenes. We wish to describe the photochemical behavior of 1-phenyl-1-(2-methylphenyl)ethylene (1)[3] and present evidence that the initial reaction upon irradiation of 1 is a 1,5-hydrogen migration to produce an ortho-xylylene.



Upon irradiation through quartz with a 450-W Hanovia immersion apparatus, a benzene solution of 1 gave a single product[4] in quantitative yield based on unrecovered 1. The mass spectrum of the photoproduct showed a molecular ion at 388, indicating that it was a dimer of 1. In addition to a multiplet for the aromatic protons, the nmr spectrum showed a broad singlet integrating for two protons at δ6.64, a quartet integrating for two protons at δ4.36, and a doublet integrating for six protons at δ1.56. The latter two signals indicated the presence of a $CHCH_3$ group, while the first suggested the presence of the vinyl protons of a stilbene derivative. This information together with mechanistic considerations suggested that the photoproduct was 2,2'-bis-(1-phenylethyl)stilbene (2), of unknown stereochemistry. To confirm this structural assignment oxidative cleavage of the ethylene double bond was attempted. Both Lemieux von Rudloff[5] oxidation and "purple benzene"[6] oxidation of 2 failed to give an isolable product, probably because the double bond of 2 is quite sterically hindered. However, oxidation with ruthenium tetroxide and sodium periodate[7] gave 2-(1-phenylethyl)benzaldehyde (3)[4]. The sample of 3 thus obtained was identical to a sample prepared by oxidation of 2-(1-phenylethyl)-benzyl alcohol (4)[8] with chromium trioxide-pyridine complex.

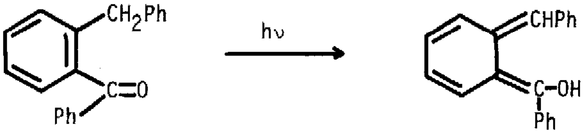
Irradiation of a solution of 1 in a mixture of benzene and cyclohexene gave a 94% yield of



1 5 7 6

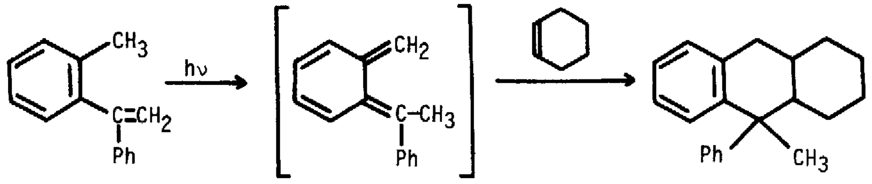
a new photoproduct[4]. The mass spectrum of this product showed a molecular ion at 276 indicating that it was a 1:1 adduct of 1 and cyclohexene. The nmr spectrum showed a multiplet at δ7.1 integrating for nine protons and assigned as the aromatic protons, a multiplet at δ2.7 integrating for two protons, and a broad multiplet at δ0.8-2.1 with two singlets superimposed at δ1.73 and δ1.50, integrating for 13 protons. This data supports 5 as the structure of the adduct. If 5 resulted from a Diels-Alder reaction of an o-xylylene (see below) and cyclohexene, it would be expected to be a mixture of stereoisomers. The reaction should occur cis on the cyclohexene ring, but the methyl may be cis or trans to the hydrogens of the ring junctions, thus giving rise to two signals for the methyl in the nmr. To confirm this structural assignment, 5 was dehydrogenated by heating with sulfur to produce 9-methyl-9-phenyl-9,10-dihydroanthracene (6)[4]. This material was identical in all respects to a sample of 6 prepared by a Grignard reaction of o-benzylacetophenone (7)[9] and phenylmagnesium bromide followed by an intramolecular Friedel-Crafts alkylation of the resulting crude alcohol in the presence of 85% sulfuric acid.

Deuterium labeling and trapping studies have shown that o-alkylbenzophenones, such as 8, produce photoenols, such as 9, upon irradiation[10]. We propose that the photochemical reactions

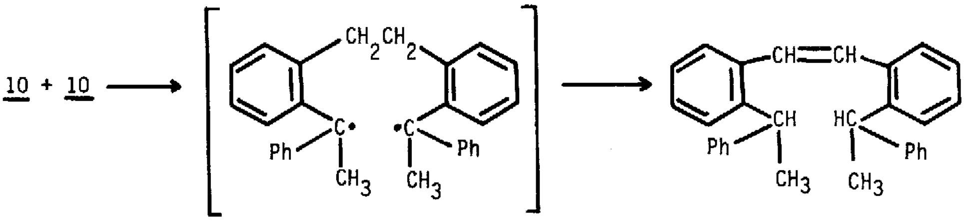


8 9

of 1 proceed through a similar intermediate, the substituted o-xylylene derivative 10. Thus, upon irradiation of 1, hydrogen transfer produces 10. In the presence of excess cyclohexene, 10 is trapped as its Diels-Alder adduct 5. In the absence of cyclohexene, 2 is produced by dimerization of 10, possibly via initial formation of biradical 11. A similar biradical may be involved in the formation of dibenzocyclooctadiene from the parent unsubstituted o-xylylene[11]. In the present case, however, steric hindrance slows the formation of the eight-membered ring, and intramolecular hydrogen migration to produce 2 occurs instead. It is interesting to note that photoenols such as 9 have only been trapped with very reactive dienophiles such as dimethyl acetylenedicarboxylate, while less reactive dienophiles, such as cyclohexene, failed to give an adduct[12]. A possible explanation of the fact that 10 is readily trapped with cyclohexene is that 10 has a longer lifetime than 9.



1 10 5



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References

1. H. M. Rosenberg and P. Serve, J. Amer. Chem. Soc., 92, 4746 (1970).
2. J. M. Hornback, J. Amer. Chem. Soc., 96, 6773 (1974).
3. E. Bergmann and A. Bondi, Ber., 66, 286 (1933).
4. Satisfactory elemental analyses were obtained on all new compounds.
5. R. U. Lemieux and E. von Rudloff, Can. J. Chem., 33, 1710 (1955).
6. D. J. Sam and H. E. Simmons, J. Amer. Chem. Soc., 94, 4024 (1972).
7. L. M. Berkowitz and P. N. Rylander, J. Amer. Chem. Soc., 80, 6682 (1958).
8. N. J. Lenord, A. J. Kresge, and M. Oki, J. Amer. Chem. Soc., 77, 5078 (1955).
9. C. K. Bradsher and S. T. Webster, J. Amer. Chem. Soc., 79, 393 (1957).
10. N. C. Yang and C. Rivas, J. Amer. Chem. Soc., 83, 2213 (1961). See also K. R. Huffman, M. Loy, and E.F. Ullman, J. Amer. Chem. Soc., 87, 5417 (1965) and references contained therein.
11. M. P. Cava and A. A. Deana, J. Amer. Chem. Soc., 81, 4266 (1959).
12. N. D. Heindel, E. W. Sarver, and M. A. Pfau, Tetrahedron Lett., 3579 (1968).