SOLUTION PHOTOCHEMISTRY. XI. IRRADIATION OF SOME SUBSTITUTED BUTADIENE-METHYL VINYL KETONE DIELS-ALDER ADDUCTS.

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We have recently embarked upon a study of the photochemistry of a variety of enonediene Diels-Alder adducts (2,3). For example we have found that irradiation of the 2,3-dimethylbutadiene-benzoquinone adduct I leads, very likely <u>via</u> an intramolecular allylic ß-hydrogen abstraction, to the products II-IV whose relative amounts are strongly solvent dependent (3).



In this paper we report an attempt to extend this type of reaction to three monocyclic Diels-Alder adducts analogous to I, namely those formed between methyl vinyl ketone and 2,3-dimethylbutadiene (V) and <u>trans,trans</u>-2,4-hexadiene (VII and IX)(4). Among other things, these adducts appeared to possess the possibility for γ as well as β allylic hydrogen abstraction due to their greater conformational mobility compared to I. However, as is often the case, neither of the anticipated hydrogen abstraction processes was observed, and the major course of photochemical reaction for these systems appears to consist of addition of the excited carbonyl oxygen to C₃ followed, where stereochemically feasible, by a novel intramolecular hydrogen atom transfer.

Thus photolysis (5) of 3,4-dimethyl-3-cyclohexenyl methyl ketone (Va) gave VIa, a colorless liquid, as the only volatile product (6). Distinguishing spectral features which permitted this structure assignment are the following: no ir carbonyl absorption, ultraviolet end absorption only, and particularly informative, the nmr spectrum (CDCl₃) τ 4.7 (m, 1, vinyl)

6.1 (quartet, 1, J = 6 Hz, C_3 methine), 7.9 (m, 3, C_5 methylene and C_4 methine), 8.3 (m, 5, vinyl methyl and C_8 methylene), 8.6 (s, 3, C_1 methyl), and 8.9 (doublet, 3, J = 6 Hz, C_3 methyl)(7).

The structure of VI as well as the mechanism of its formation was further indicated by the photolysis of the tetra-deutero analogue Vb (8) which gave VIb with no loss in overall deuterium content (mass spectrum). The nmr spectrum of VIb showed no vinyl hydrogen signal, no quartet due to the C_3 methine, and a triplet (J = 1 Hz) due to the C_3 methyl, all of which are consistent with the proposed structure.

Photolysis of Diels-Alder adduct VII (4) as above led to the formation of two volatile products which could be separated and isolated in low yield by preparative glpc. The major product was deduced to have the structure VIII (6) in analogy to VI and on the basis of the following nmr spectrum (CCl₄): τ 4.4 (m, 1, vinyl), 6.0 (m, 2, C₁ and C₃ methines), 7.7-8.3 (m, 4, C₅ methylene and C₄ and C₈ methines), 8.3 (s, 3, vinyl methyl), 8.8 (d, 3, J = 6 Hz, C₃ or C₈ methyl), and 9.0 (d, 3, J = 6 Hz, C₃ or C₈ methyl). The minor photoproduct, very likely a double bond isomer of VII, has not yet been fully characterized.

Finally, photolysis of the all <u>cis</u> Diels-Alder adduct IX (4) led to two major volatile photoproducts, X and XI, neither of which possess the 2-oxabicyclo[3.2.1]oct-6-ene ring system previously observed. The structures of X and XI were assigned on the basis of their spectra (6,9) and represent the more familiar photochemical processes of cyclobutanol and intramolecular oxetane formation.

The formation of photoproducts VI and VIII from V and VII, the deuterium labeling results, and the different course of reaction in the case of IX can be well accomodated by the following mechanistic interpretation: Photolysis of V and VII leads to biradical intermediates XII and XIII respectively (10) which possess the requisite stereochemistry to undergo the intramolecular hydrogen atom transfer leading to VI and VIII (11). Biradical XIV however, formed from IX, is stereochemically incapable of this process and as a result bonding occurs between the radical centers giving oxetane X. That γ -hydrogen abstraction leading to cyclobutanol XI is competitive in the case of IX is not unexpected.



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- 3. J.R. Scheffer, K.S. Bhandari, R.E. Gayler, and R.H. Wiekenkamp, ibid., 94, 285 (1972).
- 4. A.A. Pettov and N.P. Sopov, J. <u>Gen. Chem. Russia</u>, <u>22</u>, 653 (1952). The relative stereochemistries of VII and IX were assigned on the basis of epimerization studies assuming the all <u>cis</u> isomer IX to be the less stable. Thus thermolysis (180° for 21 hrs) or base treatment of either VII or IX gave an equilibrium mixture of VII:IX = 2:1.
- 5. Photolyses (450 W Hanovia lamp fitted with a Corex filter sleeve) were carried out in pentane or hexane solution at a concentration of 1-2 mg/ml. All samples were thoroughly degassed prior to photolysis.
- 6. All compounds described gave satisfactory analyses and mass spectral parent ion peaks.
- 7. The stereochemistry at C₃ (<u>exo</u>-methyl) follows from the lack of coupling between the C₃ and C₄ methines. For a discussion of this point in a system very similar to VI see W.C. Agosta and A.B. Smith, III, <u>J. Amer. Chem. Soc.</u>, <u>93</u>, 5513 (1971).
- This material was prepared using 2,3-dimethylbutadiene-1,1,4,4-d₄ which was in turn prepared by the general procedure of A.C. Cope, G.A. Berchtold, and D.L. Ross, <u>J. Amer. Chem. Soc.</u>, <u>83</u>, 3859 (1961).
- 9. Photoproduct X showed the following: ir (film) no OH or C=O absorption; nmr (CDCl₃) τ 5.8 (d, 1, J = 4 Hz, C₂ methine), 7.5-8.4 (m, 6, methines at C₁, C₃, C₄ and C₆ plus methylene at C₅), 8.5 (s, 3, C₇ methyl), 9.0 (d, 3, J = 11 Hz, C₃ or C₆ methyl), and 9.1 (d, 3, J = 10 Hz, C₃ or C₆ methyl). This data does not unequivocally rule out the less likely oxetane structure resulting from oxygen addition to C₄. Photoisomer XI exhibited the following: ir (film) 3375 cm⁻¹ (OH), no C=O; nmr (CDCl₃) τ 4.4 (m, 2, vinyls), 6.8-8.4 (m, 7), 8.8 (s, 3, C₇ methyl), and 9.0 (d, 3, J = 7 Hz, C₄ methyl).
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