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PHOTOCHEMICAL REACTION OF 2,7-CYCLOOCTADIENONE IN PROTIC SOLVENTS

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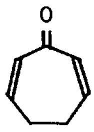
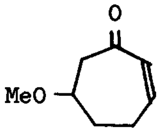
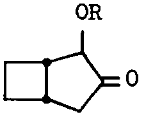
In our earlier work on the photochemistry of 2,6-cycloheptadienone (I), we had shown that the course of the reaction is markedly influenced by the nucleophilicity of the solvent employed (1). Irradiation of I in methyl alcohol gives a monocyclic ether II as the major primary product. On the other hand, reaction in less nucleophilic media such as acetic acid or t-butyl alcohol containing a trace amount of sulfuric acid affords bicyclic polar addition products III. We now wish to describe the photochemical polar addition of the homologous dienone, 2,7-cyclooctadienone (IV).



I

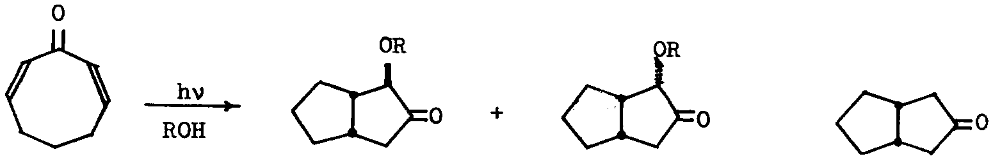


II



III R = Ac or t-Bu

Irradiation of the dienone IV (2) in acetic acid for 20 min (3) gave a stereoisomeric mixture of exo- and endo-2-acetoxy-cis-bicyclo[3.3.0]octan-3-one (V and VI in a 4:1 ratio), b.p. 100-110° (3 mm), in a 70% yield (4). Reduction with zinc dust in acetic acid yielded known bicyclooctanone VII, 2,4-dinitrophenylhydrazone m.p. 115-116° (5). The stereochemistry of each adduct was determined



IV

V R = Ac
VIII R = Me

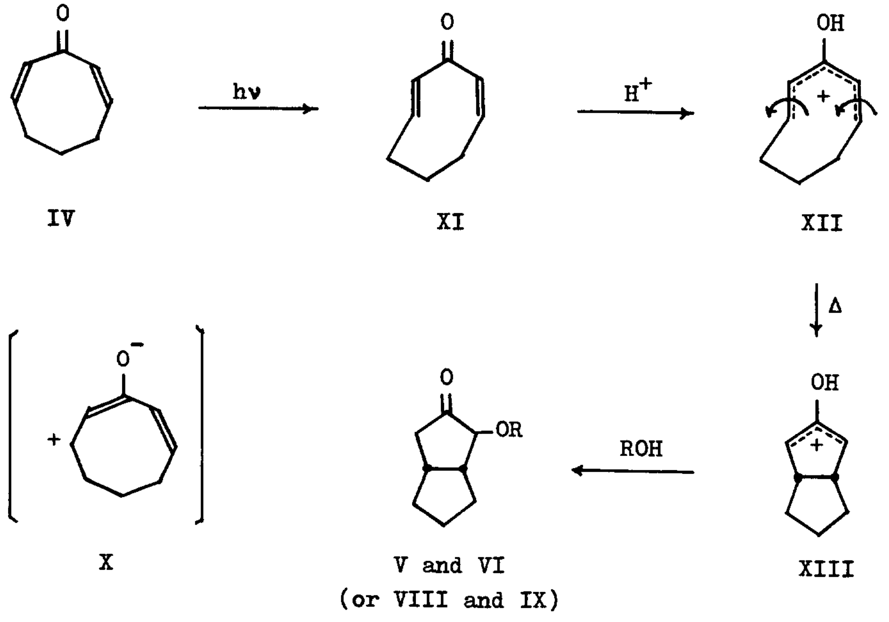
VI R = Ac
IX R = Me

VII

on the basis of the nmr data (6). The *endo* isomer VI showed the C_2 methine proton as a doublet at δ 5.32 ppm (J = 9.8 Hz), whereas the signal of the *exo* isomer V occurred at a higher field, δ 4.74 ppm (doublet with J = 7.5 Hz), due to shielding effect of the C_1-C_8 bond.

In contrast to the behavior of I, exposure of IV in methyl alcohol (1 hr) also led to formation of bicyclic adducts, *exo*- and *endo*-2-methoxy-*cis*-bicyclo[3.3.0]octan-3-one (VIII and IX, 8:1 ratio), b.p. 80-84° (4 mm), as the major products (60% yield) (7). Treatment with acetic anhydride in the presence of boron trifluoride afforded the acetoxy ketone V in a 30% yield. *endo* Adduct IX gave an nmr doublet arising from the C_2 proton at δ 3.72 ppm (J = *ca*. 5 Hz), while the *exo* isomer VIII at δ 3.18 ppm (doublet, J = 3.6 Hz).

The overall transformations of the dienone IV would be accounted for as follows. Photoirradiation of IV would give rise to the *polar state* X as proposed previously (1). Such a formulation, however, does not necessarily mean a polarized excited molecule, but a *chemically* reactive species which rationarizes the photochemical reaction in terms of ionic processes. In this case, highly strained *cis*,*trans*-cyclooctadienone (XI) seems to be the more exact representation. The



fact that transformation into the bicyclic system was readily attained even in methyl alcohol, would imply the diminished electrophilicity of the dienone XI. This might be ascribed to that the imposed constraint is reduced to some extent in comparison with the case of the seven-membered homolog. Then XI is amenable to protonation yielding strained "U-shaped" pentadienyl cation XII (8), and this is followed by thermal conrotatory cyclization into bicyclic allyl cation XIII (9), in which the ring fusion is cis. Finally, solvent attack affords the corresponding polar addition products V and VI (or VIII and IX) (10).

Experiments designed to characterize the cis,trans dienone XI are now in progress.

REFERENCES AND FOOTNOTES

1. H. Nozaki, M. Kurita and R. Noyori, Tetrahedron Letters 3635 (1968).
2. E. W. Garbisch, Jr., J. Org. Chem. **30**, 2109 (1965).
3. All photolyses were carried out in 0.1 M solution placed in a Pyrex tube (1 x 8 cm) using a 200W high-pressure mercury arc at room temperature under nitrogen atmosphere.
4. All the new compounds were characterized by ir, nmr and mass spectrometry as well as elemental analyses.
5. J. D. Roberts and W. F. Gorham, J. Am. Chem. Soc. **74**, 2278 (1952).
6. All nmr spectra were taken in 10% carbon tetrachloride solution using tetramethylsilane as an internal standard.
7. A variety of minor compornents were produced. The structure determination is open to research in the future.
8. Nmr spectrum of IV in acetic acid showed no signs of protonation in the dark.
9. R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc. **87**, 395 (1965).
10. Behavior of 2,6-cycloheptadienone (1) could be interpreted in a similar manner.

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