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PHOTO-INDUCED POLAR ADDITION OF PROTIC SOLVENTS TO cis-CYCLOOCTENE

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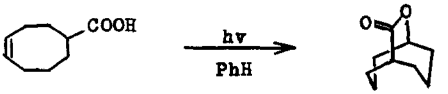
Recent reports mentioned that photochemical reactions of protic solvents with *cis*-cyclooctene did not give any volatile adduct in the presence of BTX sensitizers.[1] We have now found that protonated MeOH as well as other protic solvents actually add to excited *cis*-cyclooctene by means of aromatic sensitization.

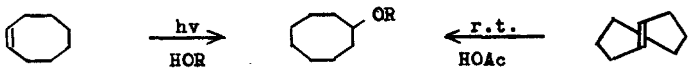
When a 1% PhH solution of 4-cyclooctenecarboxylic acid (I) with unfiltered Hg arc for 48 hr under atmosphere of N_2, a bicyclic lactone (II), m.p. 140.2-143.5°, was obtained in 20% yield and characterized by comparison with the authentic specimen.[2]



I II

Formation of II can be interpreted in terms of an intramolecular photochemical polar addition and this result prompted us to reinvestigate the photochemistry of *cis*-cyclooctene (III) in protic media in the presence of BTX sensitizers.

When a 1% AcOH-PhH (40:1) solution of III was irradiated with unfiltered high pressure mercury arc for 50 hr under N_2 atmosphere, cyclooctyl acetate (IVa) was formed in 18% yield.[3] The structure of the product follows from an elemental analysis[4], IR and NMR and the comparison with the authentic sample synthesized by acetylation of cyclooctanol in the conventional manner. Incidentally, *trans*-cyclooctene (V) was also found to afford IV in 65% yield when treated with acetic acid *in the dark* at room temperature.[5]



III IV V

a. R=Ac, b. R=HCO
c. R=Ph, d. R=Me

Formic acid also gave IVb (11%) under similar photochemical condition. In addition, irradiation of a PhH solution of equimolar mixture of III and PhOH resulted in the formation of IVc in 12% yield.

When a 1% MeOH-PhH (10:1) solution of III containing a few drops of 12N H_2SO_4[6] was irradiated similarly, an ether (IVd) was secured in 10% yield,[7] and the structure was confirmed by its elemental analysis, IR, NMR and the comparison with an authentic sample obtained by solvomercuration-demercuration[8] of III.

These observations clearly demonstrated that III is by no means reluctant to the photo-induced polar addition in contradiction to the description in the literature.[1] The reactive species in the photochemical polar addition of 6- or 7-membered cyclic olefins have been argued by assuming a transoid olefin[1a] or an orthogonal triplet state of the olefin.[1b] The fact that V gave IVa in the dark could be taken as a support to the intermediacy of the transoid olefin in the present case, since Swenton has found that III can be isomerized to V photochemically.[9] However, we feel that the final decision should be postponed until more conclusive evidences are accumlated.

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2. A. C. Cope and D. M. Gade, J. Am. Chem. Soc., **85**, 3743 (1963).
3. Counter-parts in the dark to this and other photochemical reactions were equally not observed.
4. All compounds described herein gave correct elemental analyses.
5. For the addition of naphthalene sulphonic acid to V, see K. Ziegler and H. Wilms, Ann., **567** , 1 (1950).
6. Without H_2SO_4 no appreciable change was observed.
7. Another product also had MeO group revealed by IR and NMR, but structure is unknown at present.
8. H. C. Brown and M.-H. Rei, J. Am. Chem. Soc., **91**, 5646 (1969).
9. J. S. Swenton, J. Org. Chem., **34**, 3217 (1969).