Tetrahedron Letters No.40, pp. 3557-3558, 1969. Pergamon Press. Printed in Great Britain.

PHOTOCHEMISTRY OF CYCLIC OLEFINS IN ACIDIC MEDIA.
UNUSUAL SENSITIZATION AND DECARBOXYLATIVE ALKYLATION

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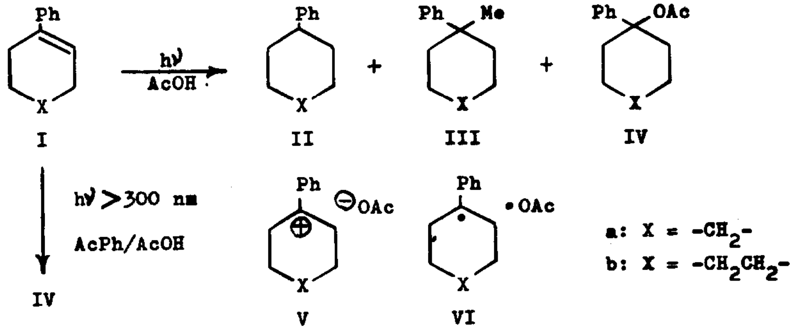
(Received in Japan 14 July 1969; received in UK for publication 31 July 1969)

Photosensitized ionic addition to cycloolefins has been the subject of current interest.[1] The present communication is concerned with the photochemical addition of acetic acid to cycloalkenes having conjugated benzene chromophore in the absence of added BTX sensitizers and, incidentally, with the polar addition induced by low energy sensitizers such as acetophenone, for which no precedent example appears to have been published.

Irradiation[2] of 1-phenylcyclohexene (Ia) was performed in acetic acid (conversion, 72%) and the resulting photoproducts were separated by preparative-scale TLC. Two hydrocarbons isolated were analyzed by GC and identified as phenylcyclohexane (IIa, 2%)[3] and 1-methyl-1-phenylcyclohexane (IIIa, 3%),[4] respectively, by comparison with authentic samples. The main product isolated by TLC was characterized as 1-acetoxy-1-phenylcyclohexane (IVa, 31%. Anal. Found: C, 77.3; H, 8.4%) on the basis of its IR (1740 cm^{-1}) and NMR spectra (δ 1.93, OAc). The acetate IVa decomposed into Ia on GC and on column chromatography.

Similarly, irradiation[2] of 1-phenylcycloheptene (Ib) in acetic acid (conversion, 93%) gave phenylcycloheptane (IIb, 5%),[5] 1-methyl-1-phenylcycloheptane (IIIb, 4%)[6] and 1-acetoxy-1-phenylcycloheptane (IVb, 41%. Anal. Found: C, 77.8; H, 8.7%. IR: 1735 cm^{-1}. NMR: δ 1.92 (OAc)).

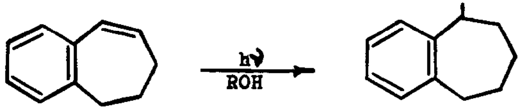
Rather unexpectedly, acetophenone-sensitized reaction[7] of Ia and Ib in acetic acid



smoothly occurred to afford IVa (42%) and IVb (56%), respectively, as a sole isolable product in each case.[8]

The formation of the acetates IVa and IVb appears to be ionic in nature, as the addition involves the O-H bond fission of acetic acid and protonation occurs on β-carbon to yield stable benzylic cations (V). The protonation may proceed through the cycloalkene triplet or a highly strained *trans* olefin derived from it.[1] On the other hand, however, a radical pair VI seems to be the most likely intermediate in the novel methylation giving III in view of the simultaneous formation of II.[9] The requisite step of decarboxylation would probably occur through the radical pair VI rather than the ion pair V.[10]

Simple irradiation[2] of 1,2-benzo-1,3-cycloheptadiene (VII) in acetic acid gave 3-acetoxy-1,2-benzocycloheptene (VIIIa)[11] in a 22% yield. Acetophenone-sensitized reaction[7] of VII in acetic acid also gave VIIIa in a 32% yield. Finally, methanol addition to VII proceeded in the presence of 0.5% sulphuric acid under unsensitized[2] and acetophenone-sensitized condition[7] to produce 3-methoxy-1,2-benzocycloheptene (VIIIb, Anal. Found: C, 82.0; H, 9.1%. NMR: δ 3.27 (OMe)) in 8 and 14% yields, respectively.



a: R = Ac

b: R = Me

VII VIII

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2. Irradiation was effected on 0.04 M solutions placed in quartz tubes with an external 200 W high-pressure Hg arc under N_2 atmosphere at room temperature.
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7. Irradiation was effected by means of an external 200 W high-pressure Hg arc and a 1.5 cm thick 9% $CuSO_4$ solution as a filter on 0.05 M solutions in Pyrex tubes containing *ca.* equimolar amount of acetophenone.
8. Considerable amount of polymeric product(s) was obtained with 79-89% recovery of unchanged acetophenone.
9. Photochemical reductions of cyclic olefins have been recorded and explained on the basis of radical mechanism. See P. J. Kropp, *J. Am. Chem. Soc.*, 89, 3650 (1967); R. R. Sauers, W. Schinski and M. M. Mason, *Tetrahedron Letters*, 4763 (1967).
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