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# LIGHT-INDUCED INCORPORATION OF PROTIC SOLVENTS TO CYCLOHEXENYL AND CYCLOHEPTENYL ESTERS

T. Okada, K. Shibata,* M. Kawanisi and H. Nozaki

Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

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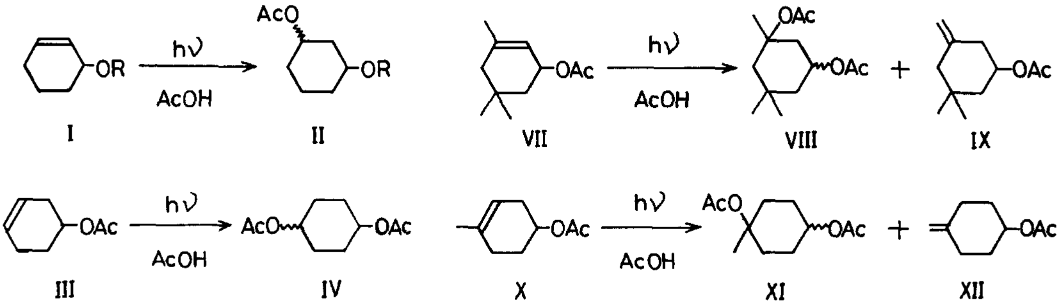
Protic solvents add photochemically to six- or seven-membered cyclic olefins in the presence of BTX sensitizers.[1] We have extended this reaction to cyclohexenes and cycloheptenes containing an acyloxy group at allylic or homoallylic position to establish an efficient method of preparing 1,3- or 1,4-cycloalkanediol derivatives.

Irradiation of a solution of 2-cyclohexenyl acetate (I: R=Ac, 5.0 g)[2] in acetic acid (300 ml) and xylene (10 ml) in a quartz vessel was effected by means of external 200 W high pressure mercury arc for 70 hr to afford a *cis*, *trans* mixture (ca. 1:1) of 1,3-diacetoxycyclohexane (II: R=Ac, 70%).[4] Irradiation of 2-cyclohexenyl benzoate (I: R=Bz)[2] in acetic acid without sensitizer[5] resulted in the formation of ca. 1:1 mixture of *cis*- and *trans*-1-acetoxy-3-benzoyloxycyclohexane (II: R=Bz, 56%).[7] Similar irradiation of 3-cyclohexenyl acetate (III)[7] as I yielded a *cis*, *trans* mixture (ca. 1:1)[8] of 1,4-diacetoxycyclohexane (IV, 95%). Methanol or higher carboxylic acids were also found to afford adducts[7] with I. Solvent (yield in %): methanol (51%), propionic acid (53%), *n*-butyric acid (61%), isobutyric acid (40%), isovaleric acid (37%), and pivalic acid (35%). In the reaction of 2-cycloheptenyl acetate (V)[7] the presence of sulfuric acid[9] was requisite for the formation of a *cis*, *trans* mixture (ca. 1:1) of 1,3-diacetoxycycloheptane (VI, 30%).[10] "Carbonium ion-stabilizing" methyl substituent yielded inferior yields of adducts. The acetate VII afforded the diacetate VIII (30%)[7] along with the exocyclic



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olefin IX (60%)[7] under identical condition. The acetate X[7] also gave the diacetate XI (25%)[7] and the exocyclic olefin XII (70%).[7] The formation of the diesters II and IV occurred in a positionally specific manner, which may suggest participation of the neighbouring acyloxy group controlling the protonation. It seems probable that initially formed carbonium ion has much more vibrational energy than the one generated by simple protonation of ground-state *cis*-olefin. The formation of exo-olefins IX and XI shows that kinetic rather than thermodynamic control prevails in the subsequent reactions of the carbonium ion.

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REFERENCES AND NOTES

(1) (a) P. J. Kropp, *J. Am. Chem. Soc.*, **91**, 5783 (1969).
(b) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969) and preceding papers.

(2) The acetates I were synthesized according to Kharasch *et al.*[3]

(3) M. S. Kharasch, G. Sosnovsky and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959).

(4) Authentic samples of 1,2-, 1,3- and 1,4-diacetoxycyclohexanes were prepared by acetylation of the corresponding cyclohexanediols and the pure isomers were isolated by preparative vpc only in the case of 1,3-diesters.

(5) In the case of I (R=Bz), both the intermolecular and the intramolecular transfer of aromatic excitation to olefinic double bond[6] could be assumed, since the direct excitation of olefinic moiety must require much higher energy than near ultraviolet region.

(6) Intramolecular energy transfer of aromatic excitation to the olefinic double bond has been recorded in the case of 1-phenyl-2-butene. See H. Morrison and R. Peiffer, *J. Am. Chem. Soc.*, **90**, 3428 (1968).

(7) All compounds analyzed correctly. The synthesis or the identification of these compounds will be described in the full paper along with other details.

(8) Although *cis*- and *trans*-mixture of 1,2- and 1,4-diacetoxycyclohexanes appeared in one peak in various conditions of vpc, only Golay column (BDS-45, Hitachi Gas Chromatograph K-23) could separate them into two peaks in both cases. The authors are indebted to Dr. T. Ando for Golay column.

(9) Without sulphuric acid, only a mixture of dimeric and polymeric products was obtained, which could not be further studied.

(10) The pure isomers were separated by preparative vpc. The structure of VI was supported by IR, NMR and elemental analyses. The IR and NMR spectra of *cis*-VI were kindly supplied by Prof. U. Schöllkopf. Authentic VI was prepared according to the literature.[11]

(11) S. Moon and B. H. Waxman, *Chem. Commun.*, 1283 (1967).