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PHOTO-SENSITIZED ISOMERIZATION OF 4-HOMOADAMANTENE IN PROTIC MEDIA

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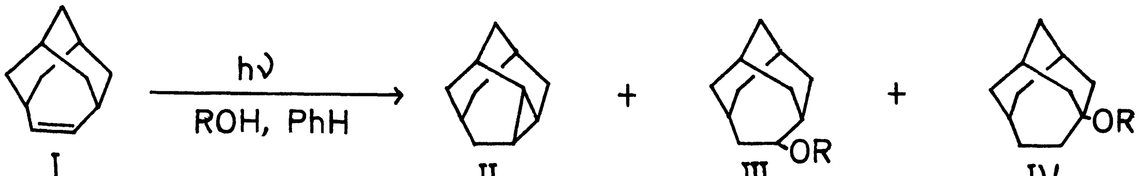
UV-irradiation of 4-homoadamantene (I) in acetic acid in the presence of BTX afforded 2,4-dehydrohomoadamantane (II), isomeric to I, together with 4-homoadamantyl and 3-homoadamantyl acetates (IIIa and IVa). Photo-isomerization of I into II was also observed with added catalytic amount of methanesulfonic acid.

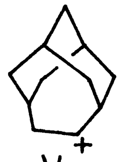
Photochemical incorporation of protic solvents to cycloalkenes in the presence of BTX (aromatic hydrocarbon sensitizer) has been investigated extensively.2) We have found a novel isomerization of 4-homoadamantene (I) into 2,4-dehydrohomoadamantane (II) in protic media.

A solution of I (500 mg)3) in acetic acid (30 ml) containing benzene (1.5 ml) as a sensitizer was irradiated in a quartz vessel by means of medium pressure Hg arc at room temp. for one week, and usual work-up gave a mixture, GLC analysis of which revealed the existence of an isomer of I which lacks vinylic proton in NMR together with two acetates. The products were separated by preparative GLC (PEG 20M, 180°) into 2,4-dehydrohomoadamantane (II),4) 4-homoadamantyl acetate (IIIa),5) and 3-homoadamantyl acetate (IVa),6) which were identical in all respects with authentic specimens. Similar reaction with pivalic acid gave products, II, IIIb, and IVb. The yields of adducts, IIIb and IVb, were slightly lower than those obtained in acetic acid probably due to the bulkiness of pivalic acid.

When the irradiation of I in xylene or benzene solution was effected without AcOH, no isomerization of I into II was observed. However, mass spectral analysis clearly demonstrated that the isomer obtained in the experiment with AcOD contained one deuterium (M^+, 149). Furthermore, the irradiation of I in xylene containing catalytic amount of methanesulfonic acid did induce isomerization of I into II (I : II = 1 : 1 after 7 days).7)



I II III IV



V

a. R=Ac-	24.7%	31.6%	5.4%
b. R= t-Bu$\overset{O}{\overset{\|}{C}}$-	28.5%	12.4%	3.3%

These results show that this novel isomerization of I into II proceeds <u>via</u> carbonium ion (V), probably due to the vibrationally excited nature of V immediately after its formation.[2] Further investigations aiming at the mechanistic details on the formation of II as well as V are in progress.

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7) The reaction did not take place in the dark. II is photostable under all the reaction conditions described herein.

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