

PHOTOCHEMISTRY OF BICYCLO(3.3.1)NONENES

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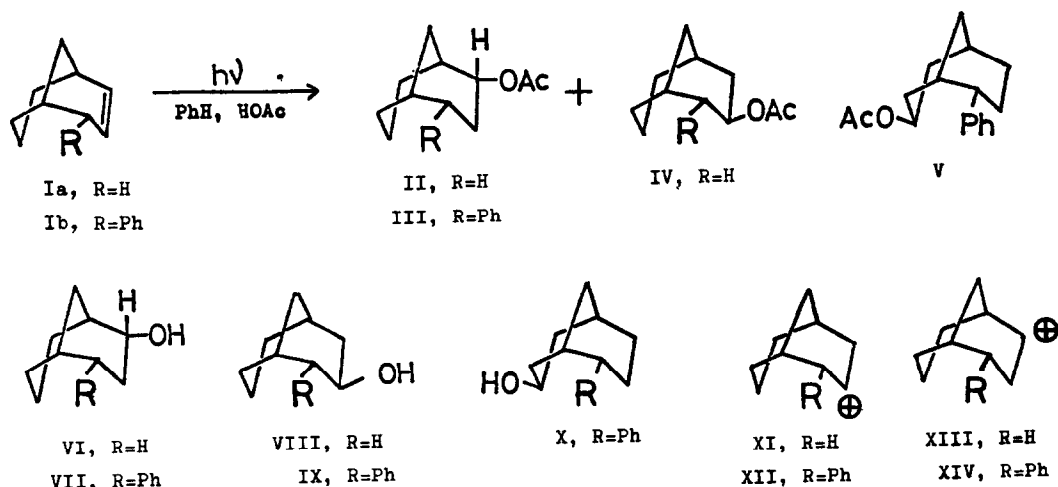
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Recent report (1) on photochemical polar addition reaction of methanol or 2-propanol to a bridged bicyclic olefin, bicyclo(3.2.1)oct-2-ene, has prompted us to report results on the polar addition of acetic acid to the similar system, bicyclo(3.3.1)non-2-ene and its derivative, possibly accompanying 3,7-hydride shift.

When a 1% acetic acid-benzene solution of I was irradiated with unfiltered high pressure mercury arc for 48 hr under atmosphere of N_2 , two isomeric adducts, II and IV, were formed in 22% and 4% yield, respectively (2). The structure of the major product, 2-endo-acetate (II), follows from an elemental analysis ($C_{11}H_{18}O_2$) (3), IR: 1740, 1380 and 1240 cm^{-1} and NMR: δ 5.00 (broad m, 1H, \underline{CH} -OAc), 2.00 (s, 3H, Me) and 1.8-1.0 (m, 14H) ppm. Additionally, hydrolysis in methanolic KOH or LAH reduction of II gave 2-endo-bicyclo(3.3.1)nonanol (VI), m.p. 170°, which was identical with an authentic sample synthesized alternatively from bicyclo(3.3.1)nonan-2-one (4). Similarly, the minor product (IV) was confirmed to be 3-exo-acetoxybicyclo(3.3.1)nonane by elemental analysis, IR and NMR and the comparison of its reduced product, 3-exo-bicyclo(3.3.1)nonanol (VIII), with an authentic sample (4).



When π,π^* triplet state of I generated by benzene sensitization is protonated, the C-2 (XIII, R=H) and C-3 (XI, R=H) carbonium ions should be formed intermediately. In such a carbonium ion at C-3 of this system, 3,7-transannular hydride shift is well-known (5). To test the possibility of this shift during the formation of IV, the photochemistry of 3-phenylbicyclo[3.3.1]non-2-ene (Ib) was investigated.

When a 1% acetic acid-benzene solution (6) of Ib was irradiated in the similar way, the isomeric acetates, III and V were formed in 28% and 34% yield, respectively (7). The minor adduct (III) was found to be 2-endo-acetoxy-4-phenylbicyclo[3.3.1]nonane by elemental analysis, IR and NMR. Further evidence for the structure of III was obtained by conversion into known 4-phenyl-2-endo-bicyclo[3.3.1]nonanol (VII), m.p. 82-84°, which was identical with an authentic specimen (8). The structure of the major adduct (V) was assigned as indicated; elemental analysis ($C_{17}H_{22}O_2$), IR: 1735, 1380 and 1235 cm^{-1} , and NMR: δ 7.10 (s, 5H, arom), 4.80 (broad m, 1H, $CH-OAc$) and 2.05 (s, 3H, Me) ppm were all consistent. LAH reduction of V gave 6-phenyl-3-exo-bicyclo[3.3.1]nonanol (X), IR: 3400, 1045 and 695 cm^{-1} , and NMR: δ 7.15 (s, 5H, arom), 3.80 (m, 1H, $CH-OH$) and 2.7 (narrow d, 1H, OH). The known isomer, 2-phenyl-3-exo-bicyclo[3.3.1]nonanol (IX), m.p. 110°, was clearly different from X (8). Tosylation of X followed by LAH reduction gave 2-phenylbicyclo[3.3.1]nonane which indicated no skeletal change being occurred in the photochemical reaction.

These results imply that the C-3 carbonium ion (XII) generated by protonation of the starting olefin in their excited state causes 3,7-transannular hydride shift in preference to a direct attack of acetoxy anion at C-3.

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REFERENCES

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2. Polymeric substance was formed, and a small amount of volatile olefin was recovered which had probably undergone skeletal rearrangement. The structure has not been determined.
3. All compounds gave correct elemental analyses.
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7. Starting material was recovered unchanged.
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