Intramolecular Photocycloaddition of 3-Allyloxy- and 3-Allylamino-cyclohex-2-enones: Formation of Oxa- and Aza-bicyclo[2,1,1]hexanes

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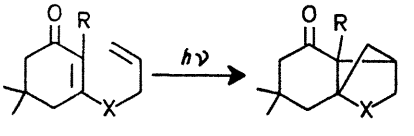
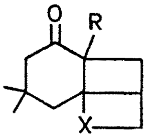
Summary Photo-irradiation of 3-allyloxy- and 3-allylamino-cyclohex-2-enones results in an intramolecular cycloaddition to produce oxa- and aza-bicyclo[2,1,1]hexane derivatives.

3-ALLYLOXY-5,5-DIMETHYLCYCLOHEX-2-ENONE (Ia) undergoes a Claisen rearrangement on heating.[1] We have now investigated the photochemical behaviour of (Ia) and its aza-analogues (Ib, d) and found that a photo-induced Claisen rearrangement[2] did not occur, but instead an intramolecular cycloaddition involving two double bonds took place, leading to the formation of the oxabicyclo[2,1,1]hexane derivative (IIa) from (Ia) and the azabicyclo[2,1,1]hexanes (IIb, d) from (Ib, d).

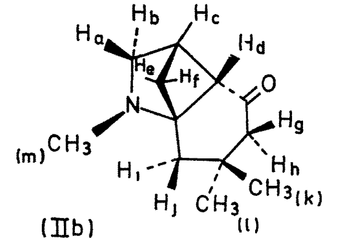


(I) (II)



(III)

a, X = O, R = H, b, X = NMe, R = H,
c, X = NMe, R = D, d, X = NCH$_2$CH=CH$_2$, R = H



(IIb)

A 0·02 M cyclohexane solution of (Ia) was irradiated with a 450w high-pressure mercury lamp in a Pyrex vessel for 10 h. Distillation of the reaction mixture afforded a colourless liquid in yields of greater than 70%, b.p. 65—70° (bath temp.) at 0·18 mm Hg, which has the molecular formula $C_{11}H_{16}O_2$ (M 180 by mass spec.). Its n.m.r. spectrum clearly showed it to be a mixture of two compounds in a ratio of *ca.* 4:1, although the t.l.c. and g.l.c. failed to separate the components. On the other hand, irradiation of a cyclohexane solution† of (Ib, d) gave a single product (IIb, d) [(IIb) 50—60% yield, m.p. 48·5—49·5°, $C_{12}H_{19}ON$, *m/e* 193 (M^+), (IId) 60% yield, m.p. 44—44·5°, $C_{14}H_{21}ON$, *m/e* 219(M^+)].

The elemental analysis and molecular weight of (IIb) indicate that it is an isomer of (Ib). The i.r. (1710 cm^{-1}, six-membered C=O, no OH or NH absorption), u.v., and n.m.r. spectra show no unsaturation, and hence it must be tricyclic. The compound (IIb) formed its hydrochloride, m.p. 139—140·5°, only under anhydrous conditions. Reduction of (IIb) with $LiAlH_4$ in ether at room temperature provided an oily secondary alcohol, $C_{12}H_{21}ON$ [*m/e* 195 (M^+)], which could be acetylated by treatment with acetic anhydride and pyridine to give an oily acetate (i.r., 1720 cm^{-1}).

The results presented below are consistent with the structure (IIb) rather than the alternative one (IIIb). The n.m.r. spectrum (100 MHz in $CDCl_3$) of (IIb) exhibits signals at τ 6·60 (1H, dd, *J* 8 and 1·5 Hz, H_b), 7·10 (1H, br, H_c), 7·53 (1H, br, H_d), 7·70 (3H, s, H_m), 7·81 (1H, d, *J* 8 Hz, H_a), 7·86 (2H, s, H_g and H_h), 8·12 (2H, AB quartet, ‡*J* 14 Hz, H_i and H_j), 8·29 (1H, dd, *J* 7 and 1·5 Hz, H_e), 8·47 (1H, ddd, *J* 7, 2·6 and 1·5 Hz, H_f), 8·66 and 8·86 (2 × 3H, s, H_k and H_l). These assignments were supported by decoupling experiments, deuterium labelling experiments, and experiments using a shift reagent, Eu(DPM)$_3$.[3] (i) Irradiation of H_b at τ 6·60 caused the doublet (H_a) at τ 7·81 to collapse to a singlet, and irradiation of H_c at τ 7·10 transformed the broad signal (H_d) at τ 7·53 to a sharp singlet and the signal (H_f) at τ 8·47 to a doublet-doublet (*J* 7·0 and 1·5 Hz). (ii) Deuterium labelling§ at H_d (IIc) resulted in disappearance of the signal at τ 7·53 and sharpening of a broad signal (H_c) at τ 7·10. (iii) Signals due to H_b, H_d, H_g, and H_h were strongly affected by addition of Eu(DPM)$_3$. Coupling constants (J_{ef} 7 Hz, J_{cf} 2·6 Hz, J_{ce} 1·5 Hz) are in good agreement with those reported for bicyclo[2,1,1]hexanes.[4]

The structures of (IIa) [the major product from (Ia)] and (IId) are suggested as such on the basis of their n.m.r. spectra which are very similar to that of (IIb) except for signals ascribed to H_a and H_b in that of (IIa) (shifted downfield) and to the *N*-substituent in that of (IId).

The formation of (II) may be visualized as analogous to the photocycloaddition reaction of hepta-2,6-dienones, in which a radical mechanism has been suggested.[5]

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† It is interesting to note that (IIb) was not formed when the solvent was changed from aprotic solvents such as cyclohexane, ether, methylene chloride, and benzene to a protic solvent such as methanol.

‡ Appeared as a singlet at 60 Mc.

§ This compound (IIc) was prepared by irradiation of (Ic) which was readily obtained by shaking a methylene chloride solution of (Ib) with D_2O for 3 min.

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