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STEREOCHEMICAL INTEGRITY OF THE TERMINUS OF THE MIGRATING CARBON IN PHOTO-BECKMANN REARRANGEMENTS [1]

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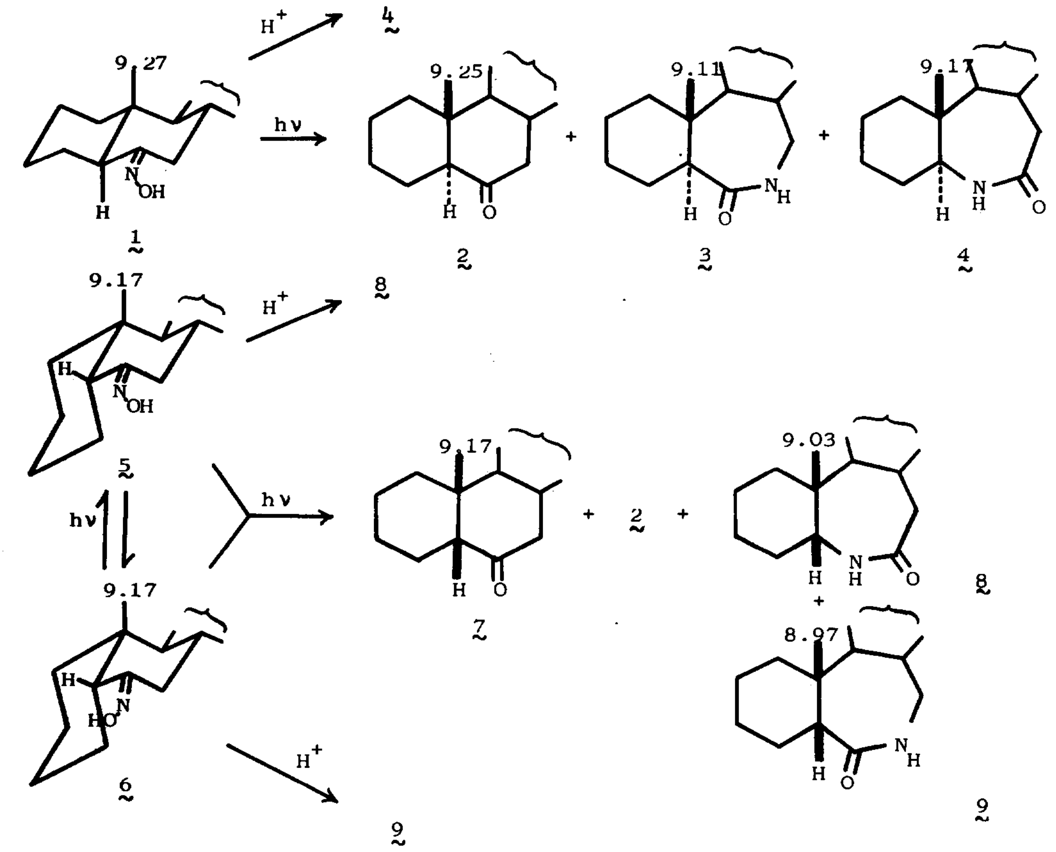
Since the first report [2] of photo-Beckmann rearrangement a number of additional examples has recently been recorded. [3,4] Oxaziridines were suggested as the intermediate species of the reaction [2,3] and this was demonstrated only recently. [4,5]

We wish to report photo-Beckmann rearrangements of 5 α-cholestan-6-one oxime (1) [6] and the isomeric 5β-cholestan-6-one oximes (5 and 6) which indicate that the photochemical bond migration [7] from intermediary oxaziridines to amides is a stereospecific process, the migration of C-5 occurring with retention of configuration.

Thus, photolysis of 1 (500 mg) in dry methanol (350 ml) by a 150 W low pressure Hg arc lamp for 27 hours afforded three products as confirmed by tlc. By preparative tlc beside the starting oxime (6%), a trace of 5α-cholestan-6-one (2) and two new compounds both having the same molecular formula $C_{27}H_{47}ON$ [8] 3, m.p. 110-114°C (11%) and 4, m.p. 174-179°C (15%), were obtained. Both 3 and 4 demonstrated carbonyl absorptions of lactams at 1656 cm^{-1} and 1669 cm^{-1}, respectively The structures of these lactams, 3 and 4 were established as 7-aza-B-homo-5α-cholestan-6-one (3) and 6-aza-B-homo-5α-cholestan-7-one (4) respectively by the nmr spectra (3, (100 Mz), CONH, τ 3.96 (1H), N-CH_2, m, τ6.90-7.03 (2H), C-5 H, q, τ7.45 (1H), J=5.0 and 11.5 Hz; after deuterium exchange, (60 Mz), N-CH_2, d, τ7.05, J= 4.3 Hz; 4, (100 Mz), CONH, d, τ4.48 (1H), J=5.5 Hz, C-5 H, q, τ6.76 (1H), J=4.0



Arabic numerals denote chemical shifts (τ) of 19 methyl protons.

and 11.0 Hz) as well as by the results of ground state Beckmann rearrangement. Beckmann rearrangement of 1 with polyphosphoric acid [9] afforded 4 as the sole product (65%), which confirmed that the configuration of the oximino-function in 1 is anti C_5-C_6 bond. [10]

In contrast to 5α-cholestan-6-one, 5β-cholestan-6-one [11] gave two isomeric oximes, amorphous 5 and crystalline 6, m.p. 144-146°, approximately in a ratio of 3:1.

Ground state Beckmann rearrangement of 5 afforded a single crystalline lactam

8, m.p. 95-100°, (80%) and that of 6 yielded amorphous lactam 9 (90%), respectively. These lactams were isomeric and had the molecular formula $C_{27}H_{47}ON$. The spectral data [8, i.r., ($CHCl_3$) lactam C=O, 1645 cm^{-1}, n.m.r., (100 Mz), after deuterium exchange, C-5 H, broad d, τ7.70, (1H), J=8.0 Hz; 9, i.r., ($CHCl_3$) lactam C=O, 1643 cm^{-1}, n.m.r., (100 Mz), $NHCH_2$, broad S, τ7.02 (2H), W_H 10 Hz] are in accord with the structures, 6-aza-B-homo-5β-cholestan-6-one (8) and 7-aza-B-homo-5β-cholestan-6-one (9). On this basis, the configurations of the oximino-groups of 5 and 6 are assigned as anti-C_5-C_6 bond and syn-C_5-C_6 bond, respectively.[10]

Irradiation of 5 or 6 (500 mg) in dry methanol (250 ml) led to a rapid syn-anti equilibration[12] and it was found that the rate of disappearance of oxime 5 or 6 was considerably faster than that in the case of oxime 1. Careful preparative tlc gave only a pair of lactams 8 and 9 in each case; 5 afforded 8 (28%), 9 (11%), 5β-cholestan-6-one (20%) and 5α-cholestan-6-one (6%). 6 afforded 8 (30%), 9 (9%), 5β-cholestan-6-one (5%) and 5α-cholestan-6-one (3%).

The foregoing observations prove the stereochemical integrity of the terminus of the migrating carbon in the photo-Beckmann rearrangement and this may be general in oximes of aliphatic ketones and aldehydes. Moreover, these results suggest that the C_5-C_6 bond of oximes described is not cleaved to give either a radical pair or an ion pair.

It is very probable that the rearrangement of oxaziridines to amides occurs either by heterolytic N-O bond cleavage followed by the formation of C=O and the migration of C-5 or C-7 to nitrogen concertedly, or through the cleavage of N-O bond and the migration of C-5 or C-7 to nitrogen in a fully concerted manner.

Faster rates observed in cis oximes 5 and 6, when compared with trans oxime 1, must be mainly attributed to the relief of steric compression due to non-bonded interactions of 2α- and 4α-axial hydrogens with 7α- and 9α-axial hydrogens in going from the oxime 5 or 6 to the lactams 8 and 9.

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