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STEREOCHEMICAL CONTROL ON THE PHOTOCHEMISTRY OF α-METHOXY-β, γ-CYCLOPROPYL CYCLIC KETONES REACTIONS OF EPIMERIC 3-METHOXY-4-CARANONES[+]

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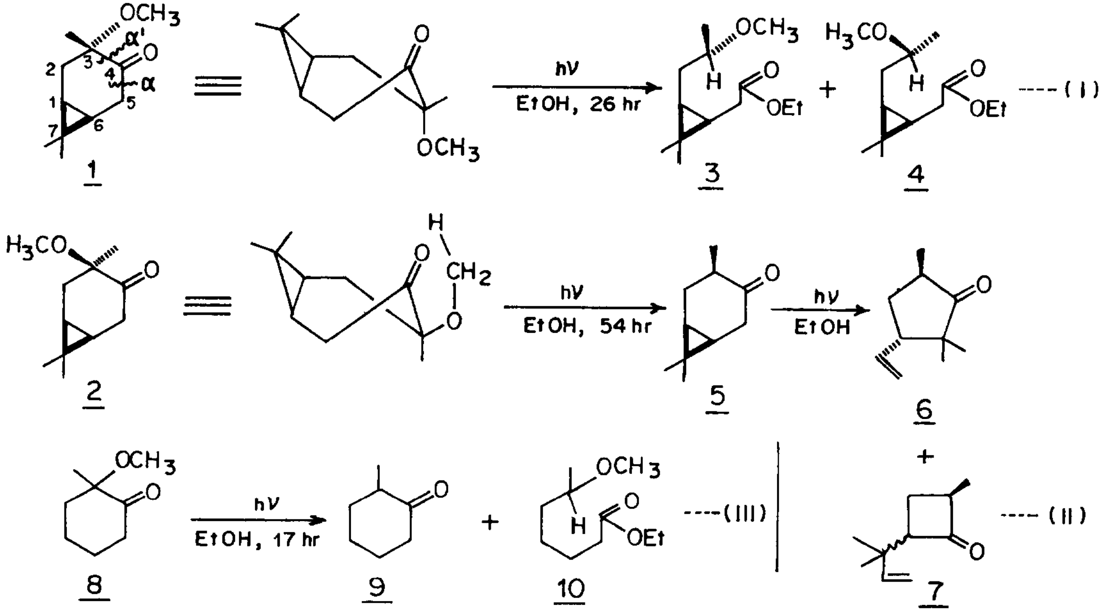
SUMMARY The two distinct photoreactions exhibited by epimeric ketones have been correlated with their stereochemistry

Typically, a β, γ-cyclopropyl cyclic ketone on photoexcitation is known to undergo α-cleavage and cyclopropyl-carbinylhomoallyl rearrangement[1] The effect of different α-substituents in this class of cycloalkanones has practically remained unexplored We report herein a remarkable stereochemical control on the photochemical behaviour of two ketones 1 and 2 bearing α-methoxy substituent at C-3 position

Ketone 1[2] on irradiation[3] in ethanol through corex afforded a photolysate (69%) which essentially was a mixture of ethyl esters[4] 3 and 4 in a 4 1 ratio and a minor amount of 5 (eqn-I) By contrast, the ketone 2[5] upon similar irradiation furnished only isocaranone 5 as the primary photoproduct which on further photodecomposition[6] finally yielded (55%) a mixture of 6 and 7 (eqn-II) During the course of irradiations, the interconversion of 1 ⇄ 2 was not detected



The unique features of these photochemical transformations are as follows (i) The ketone 1 possessing an axial methoxy group[7] favoured α'-cleavage which is rare in β,γ-cyclopropyl ketone photochemistry The parent ketone 5 is known[6] to furnish 6 and 7 by α-cleavage, 'allylic' to cyclopropane (eqn-II) A preference for α'-cleavage in 1 may be ascribed to the formation of a stabler tertiary radical (ii) A stereoselective formation of ester 3 (iii) The ketone 2 with an equatorial methoxy group underwent exclusively Norrish type II elimination to 5 The required in-plane six-membered transition state can readily occur in this ketone (cf molecular model), therefore, the other competitive process of α-cleavage is of less importance (iv) Interestingly enough, the model ketone 8[7] on similar irradiation furnished ∼1 1 mixture (75%) of 9[4] and 10[4] arising from Norrish type I α-cleavage and Norrish type II elimination respectively (eqn-III)

We believe that the selective transformation of ketone 1 to esters 3 and 4 may find application in the synthesis of pyrethroids[8]

REFERENCES AND NOTES

\+ NCL Communication No 3298

1 R K.Murray and T M Ford, J Am Chem Soc , 102, 3194 (1980) and references cited therein

2 W Cocker and D H Crayson, Tetrahedron Letters, 4451 (1969)

3 Irradiations were carried out using a 200 watt high pressure Hanovia lamp till the disappearance of the starting ketones

4 All photoproducts exhibited consistent spectral data (PMR, IR, MS) and gave satisfactory elemental analyses The structures 3 and 4 were confirmed by direct comparison with their authentic samples prepared by $NaBH_4$ reduction of ethyl-2,2-dimethyl-3-(2'-oxopropyl)-cyclopropane-cis-1 acetate [R R.Sobti and Sukh Dev, Tetrahedron, 30, 2927 (1974)] followed by methylation with $HC(OCH_3)_3$ Ester 4 was not formed when 1 was irradiated in the presence of piperylene suggesting that 3 and 4 are derived from the singlet and triplet excited states respectively Hydrogen abstraction in the singlet biradical (α'-cleavage) is expected to maintain the original configuration at C-3 to give 3 [R B Gagosian, J C Dalton and N J Turro, J Am Chem Soc , 97, 5189, (1975)]

5 Z G Isaeva and I S Andreeva, Dokl Akad Nauk SSSR, 152, 106 (1963)

6 D C Heckert and P J Kropp, J Am Chem Soc , 90, 4911 (1968), An independent irradiation of 5 under similar conditions afforded essentially a mixture of 6 and 7 (yield 48%)

7 The conformations depicted for 1 and 2 are based on the preferred conformations of 5 and it's C-3 epimer [P Teisseire, A Galfre, M Plattier, P Rouillier and B.Corbier, Recherches, 16, 119 (1967)]

8 Ketone 8 was prepared by a new route (unpublished results).

9 M Elliot and N F Janes, Chem Soc Revs , 7, 473 (1978)

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