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CONFORMATION-SPECIFIC PHOTOCHEMISTRY IN ISOTROPIC LIQUID MEDIA: NORRISH TYPE II REACTIONS OF EPIMERIC 2-ACETYL-3,3-DIMETHYL NORBORNANES

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SUMMARY: The epimeric ketones 1 and 2 have been shown to display conformation-specific photobehaviour, especially in liquid media.

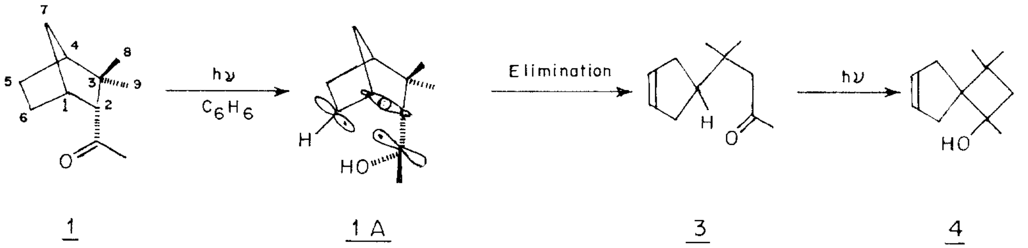
The Norrish type II reaction of ketones possessing favourably oriented γ-hydrogen atoms is one of the most extensively studied photoreactions and still remains the object of current mechanistic and synthetic interest[1]. The intermediacy of 1,4-biradical in the formation of elimination and/or cyclization products as well as ground state ketone is now well established[2]. An examination of the effects of solvent polarity[3], temperature[4] and the different substituents in the ketone[5] has greatly increased the understanding of the competition between elimination and cyclization reactions in 1,4-biradicals[3]. The literature reports indicate that in liquid media, it is extremely difficult to achieve reaction selectivity due to the high mobility of the 1,4-biradical conformers[6]. Therefore, the photochemistry of ketones in ordered media viz. smectic and solid phases has currently gained importance[7] as environmental factors are known to greatly influence the conformational flexibility of organic molecules[8].

It is, therefore, apparent that in isotropic liquid phase, the immobilization of the conformations of 1,4-biradicals to the point to effect their specific reactions still remains a goal to be achieved. In this communication, we wish to disclose for the first time, the conformation-specific photochemistry displayed by the epimeric ketones 1 and 2 especially in liquid media. The design of these ketones primarily rests on two main considerations; firstly, the choice of norbornane skeleton is supposed to freeze the free rotations of bonds C_2-C_3/C_1-C_6 between the carbonyl group and γ-C hydrogens, available to the flexible acyclic analogues and secondly, the introduction of gem-dimethyl groups at C-3 is crucial in further immobilizing the conformations not only in the ground states but as well in the corresponding 1,4-biradicals (vide infra). The results described below amply demonstrate the above surmise.

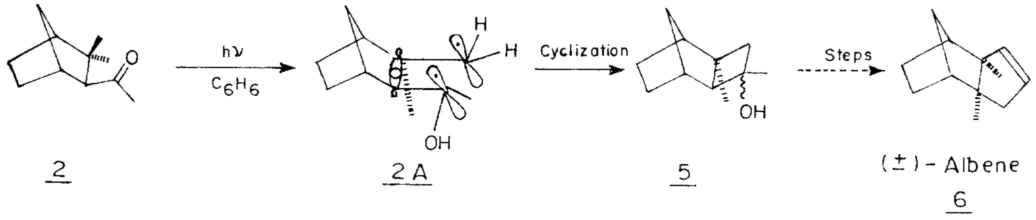
endo-Ketone 1[9] when irradiated[11] in benzene afforded essentially a single primary photoproduct which was found to change readily into a secondary major photoproduct alongwith some minor ones (65% conversion, 20 hr). The former and the latter products were isolated by chromatographing the total photolysate over SiO_2 and were characterized as 3 and 4 respectively (eqn-1) on the basis of their spectral data[12]. The structural assignment of 3 for the primary photoproduct was further corroborated by its hydrogenation and its direct comparison with an authentic sample[13] of the dihydro 3. Between the primary C-9 and the secondary C-6 γ-hydrogens in 1, selective hydrogen abstraction from C-6 by the carbonyl group can be attributed to the energetics of the reactions.

On the other hand, the exo-ketone 2 exhibited a highly contrasting photobehaviour by undergoing cyclization to furnish the cyclobutanol 5[12] (80% conversion, 20 hr) to the exclusion of type II elimination (eqn-2).

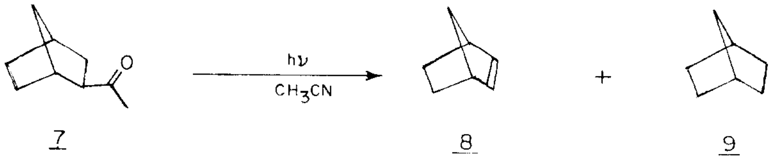
The reaction selectivity observed in the photobehaviour of the two epimeric ketones can be understood on the basis of widely accepted rationale of orbital overlap[1]. Owing to the rigid framework of the molecules 1 and 2, it is reasonable to assume that the intermediate 1,4-hydroxy



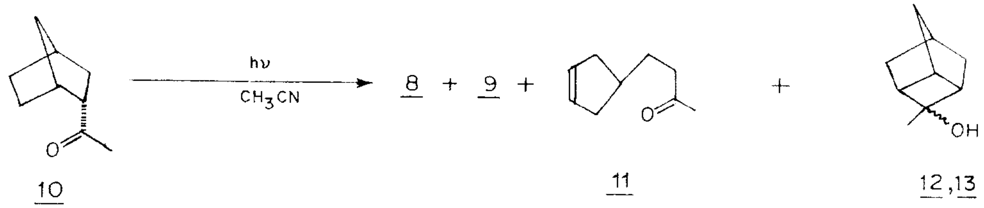
[Eqn. 1.]



[Eqn. 2.]



[Eqn. 3.]



[Eqn. 4.]

radicals involved in the present reactions have the same basic conformation as their ketonic precursors. An examination of the molecular model of 1 indicated that 1,4-hydroxy biradical generated by the abstraction of endo- C_6 hydrogen is found to assume the most favourable conformation (1A) wherein both singly occupied p-orbitals overlap significantly with the central bond (C_1-C_2), thus resulting in a facile elimination. This situation is naturally the consequence of the fact that the singly occupied p-orbitabl at C_6 incorporated in the rigid norbornane skeleton is almost parallel with C_1-C_2 bond and the ketyl radical has undergone a rotation (~90°) from its original geometry. In the exo-isomer 2, however, the conformation of the 1,4-hydroxy biradical (2A) generated by the abstraction of the γC-H at C_8 is poorly alligned for the cleavage; in fact, the only available conformation free from any non-bonded interactions (cf. molecular models) appears to involve a good overlap of 1,4-hydroxy radicals thus favouring cyclization. This notably constitutes a unique cisoid-locked 1,4-biradical conformation wherein the inborn geometry of the ketyl radical seems to play an important role.

When compared with the known reports on the photochemistry of similar kind of ketones, the importance of the conformational factors involved in the present results become more prominent. For example, Moron and Roussi[14] observed that exo-1-acetylnorbornane 7 undergoes a Type I reaction (α-cleavage) leading to a mixture of norbornene 8 and norbornane 9 (eqn-3), whereas its endo-epimer 10 affords both elimination 11 and cyclization products 12 and 13 respectively along with the products of α-cleavage (eqn.4). Therefore, the present results reveal the importance of the immobilizing effect of C_3 gem-dimethyl groups on the conformations of 1,4-hydroxybiradicals (1A and 1B).

In summary, the present epimeric ketones 1 and 2 provide an example of unique photobehaviour in liquid media wherein the conformational factors have been shown to play a dominant role in furnishing reaction selectivity. The potential of the selective transformation (eqn. 2) is being utilized in the synthesis of (±)albene, a cyclopentanoid natural product of current synthetic interest[15].

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9. We have developed a new method to prepare essentially the endo-1. It involves the hydroboration/H_2O_2 oxidation of ω-methyl camphene[10], followed by chromic acid oxidation of the resulting secondary alcohol; epimerization of 1 with CH_3ONa in CH_3OH readily furnished 2.
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11. A typical experiment consisted of the irradiation of a solution of 0.012 M ketone in 250 ml of benzene with a 200 Watt medium pressure Hanovia lamp using a Vycor filter in an immersion well apparatus.
12. 3: IR 1710 cm^{-1}; PMR 0.94 (s, 6H, t-CH_3), 2.13 (s, 3H, $COCH_3$) 2.33 (s, 2H, -CH_2CO) and 5.66 (s, 2H, HC=CH); Mass m/e 166 (M^+ 15%), 108 (48%), 93 (100%) and 66 (90%);
    4: IR 3695 cm^{-1}; PMR: 1.04, 1.07 (2s, 3H each, t-CH_3), 1.35 (s, 3H, C(OH)CH_3) and 5.77 (m, 2H, -CH=CH); Mass m/e 166 (M^+ 50%), 151 (49%), 108(94%) and 93 (100%);
    5: IR 3355 cm^{-1}; PMR 1.10 (s, 3H, t-CH_3), 1.30 (s, 3H, -C(OH)CH_3) and 2.05 (6s, 2H bridgehead protons); Mass m/e 166 (M^+, 49%), 148 (50%) and 123 (100%), 108(85%), 80(82%) and 66 (58%).
    The compounds 3 - 5 gave satisfactory elemental analysis.
13. The details of the synthesis of dihydro 3 will be described separately.
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