## PHOTOCHEMISTRY OF ORGANIC MULTICHROMOPHORIC MOLECULES AND REACTION SELECTIVITY-I : REACTIONS OF (+) -4 a -ACETYL-2-CARENE H.R.Sonawane<sup>\*</sup>, V.G.Naik, B.S.Nanjundiah and P.C.Purohit National Chemical Laboratory, Pune 411008, India.

## SUMMARY : Selective photochemical transformations of two different bichromophores incorporated in a single molecule are reported.

The photochemistry of bichromophoric molecules<sup>1</sup>, particularly  $\beta_{\gamma}$  -enones<sup>2</sup> is the subject of many recent investigations.  $4 \propto -Acetyl-2-carene$  ] is a molecule containing not only  $\mathbf{B}, \mathbf{Y}$ -enone system but also vinyl cyclopropane system. In such a system, three reactions viz. 1,3-acylshift (1,3 AS); oxa-di- $\pi$ -methane rearrangement (ODPM, eqn-1) and vinyl cyclopropane (VCR, eqn-2) rearrangement are expected.



In the present communication we report a dramatic reaction selectivity in the title compound. On direct irradiation exclusively 1,3 AS is seen whereas in the sensitized reaction only VCR is observed. ODPM rearrangement was not observed with this substrate.

Direct irradiation<sup>3</sup> of  $1^4$  in cyclohexane for a short period (~ 45 minutes) afforded essentially 1,3-AS product 2 (32%) along with cyclobutanol<sup>5</sup> 3(10%), a product of competing 'Norrish type II cyclization' in the ketone 2. When irradiated for a longer period (2 hr) another cyclobutanol 4 (5%) was formed<sup>6</sup> from the ketone 1 (scheme-I). These products have been isolated by preparative GLC and characterized from their spectral properties<sup>6</sup> and by direct comparison with an authentic sample<sup>6</sup> in the case of 2. Irradiation of 2 under identical conditions furnished ], 3 and 4 almost in the same ratio. However, the photodecomposition of 2 was much faster than that of 1.

The involvement of singlet excited states in the formation  $\underline{1} - \underline{4}$  is shown by photolysis of  $\underline{1}$  and  $\underline{2}$  in the presence of triplet quencher, piperylene wherein the product composition essentially remained unchanged.



Acetone-sensitized irradiation<sup>3</sup> of ketone <u>1</u> through corex cleanly brought about its conversion to a~1:1 mixture of two new products (46% based on <u>1</u> consumed) having close retention times (GLC). These were separated by preparative GLC combined with column chromatography (SiO<sub>2</sub>) and identified as diastereomeric ketones <u>5</u> and <u>6</u> from their spectral properties<sup>6</sup> (scheme-II). A clear evidence in support of the bicyclo [3.2.0]heptane



skeleton was obtained by the sequence of reactions which involved the treatment of a mixture of dihydro 5 and 6 with m-chloroperbenzoic acid, alkaline hydrolysis of the resulting acetates followed by chromic acid oxidation. The ketone thus obtained displayed an intense IR band at 1775 cm<sup>-1</sup> characteristic of cyclobutanones. The distinction between 5 and 6 is made on the basis of their PMR data. Significantly, the vinylic protons in 6 appeared as a AB quartet ( $\delta$  5.20) suggesting the proximity of the  $\alpha$ -acetyl function<sup>7</sup>

(cf. molecular model). This, therefore, suggests that the substituents at the ring junction<sup>8</sup> are trans with respect to the acetyl function. This was further supported by the multiplet observed ( $\mathcal{S}$  2.73) for the C-7  $\beta$ -hydrogen due to W-coupling<sup>9</sup> with the C-5 hydrogen. In  $\underline{5}$ , the vinylic protons appeared as a singlet ( $\mathcal{S}$  5.43) and the C-7 hydrogen exhibited a doublet of a doublet ( $\mathcal{S}$  2.86) indicating the cis-geometry of the substituents at the ring junction with respect to the acetyl group. Treatment of (-)  $\underline{5}$  with CH<sub>3</sub>ONa in methanol furnished the optical antipode (-)  $\underline{6}$  of the photoproduct (+)  $\underline{6}$  suggesting the diastereomeric relationship of (-)  $\underline{5}$  and (+)  $\underline{6}$  having antipodal relationship at the ring junction. The formation of  $\underline{5}$  and  $\underline{6}$  thus clearly shows that the ketone  $\underline{1}$  under photosensitized conditions preferentially undergoes VCR reaction rather than a typical ODPM rearrangement of  $\beta$ ,  $\gamma$  -enone chromophore giving rise to the expected  $\underline{7}$ .

This observation led us to the belief that  $\mathcal{L}$ -carene <u>8</u> should also yield a VCR product on sensitized photolysis. However, direct or sensitized irradiation of (+)  $\mathcal{L}$ -carene <u>8</u><sup>10</sup> only afforded solvent insertion products<sup>11</sup>. This clearly suggested that for the compound <u>1</u>, the acetyl group is obviously involved in VCR reaction.

The potential of this selective photochemical transformation in the synthesis of (+)-Grandisol  $\frac{9}{2}$ , a major component of male Boll Weevil sex pheromone<sup>12</sup>, utilizing a suitable (+)  $\Delta^2$ -carene derivative is in progress.

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## REFERENCES AND NOTES

N.C.L. Communication No.3226.

1. H.Morrison, Accounts Chem. Res., 12, 383 (1979).

2. K.N.Houk, Chem. Rev., 76, 1 (1976).

- 3. Irradiations were carried out in an immersion well apparatus with a corex filter and 200 watt high pressure Hg Hanovia lamp using 0.5% solns. under nitrogen. The sensitized experiments were conducted in neat acetone with corex/pyrex filter. Use of pyrex filter resulted essentially in the same product composition, however, the photodecomposition was very slow.
- 4. P.J.Kropp, D.C.Heckert and T.J.Flautt, <u>Tetrahedron</u>, <u>24</u>, 1385 (1968).
- 5. Of two isomeric cyclobutanols possible differing in stereochemistry at the carbon carrying the hydroxyl in <u>3</u> and <u>4</u> only one was obtained in each case. This selectivity could probably be attributed to the singlet excited state. (R.G.Gagosian, J.C.Dalton and N.J.Turro, JACS., <u>97</u>, 5189 (1975). The stereochemistry of the hydroxyl is still to be established.
- 6. Product composition is determined by GLC, the starting ketones account for the rest.  $\underline{1} : [\alpha]_{D}^{260} + 458^{\circ} (C, 2.9\%); UV : \lambda_{max} (cyclohexane) 281 nm ( \varepsilon = 272); other spectral data were identical with those reported<sup>4</sup>. <u>2</u>: [\alpha]_{D}^{260} -280^{\circ} (C, 2.5\%), UV: \lambda_{max} (EtOH) 261 nm, ( \varepsilon = 290); IR: 1703, 1675, 840 cm<sup>-1</sup>. PMR (CCl<sub>4</sub>) : 5.40 (m, 1H, -C=C<u>H</u>-), 2.70 (br.s, 1H, -C<u>H</u>COCH<sub>3</sub>), 2.03 (s, 3H, -COC<u>H<sub>3</sub></u>), 1.53 (br.s, 3H,$

-C=C-C $\underline{H}_3$ ), 1.13, 0.90 (2s, 3H each, t-C $\underline{H}_3$ s); MS: m/e 178 (M<sup>+</sup>); An authentic sample of <u>2</u> was prepared by the acylation of (+)  $\overset{2}{\checkmark}$ -carene with (C $\underline{H}_3$ CO)<sub>2</sub>Oin the presence of anhy. ZnCl<sub>2</sub>; <u>3</u> : (>96% pure); IR: 3600, 1667, 805 and 775 cm<sup>-1</sup>; PMR : 5.43 (m, 1H, -C=C<u>H</u>), 2.95 - 2.00 (m, 7H, methylenes and methines), 1.45, 1.10, 0.73 (3s, 3H each, t-CH<sub>3</sub>s); MS: m/e 178 (M<sup>+</sup>); <u>4</u>: (~95% pure); IR: 3400, 1675, 750 cm<sup>-1</sup>; PMR: 5.76 (m, 1H, -C=C<u>H</u>), 3.00 - 2.00 (m, 7H, methylenes and methines), 1.36, 1.10, 0.86 (3s, 3H each, t-CH<sub>3</sub>s); MS: m/e 178 (M<sup>+</sup>). In addition to these, dimeric products (~15%) were formed by the combination of allylic radicals arising from *<*-cleavage. <u>5:</u>[<]<sup>26</sup><sub>D</sub> - 29<sup>o</sup> (C, 1.56%); IR: 1695, 1643, 800, 781 cm<sup>-1</sup>; PMR: 5.43 (s, 2H, -C=C<u>H</u>), 2.86 (dd, J=8 & 3Hz, 1H, -C<u>H</u> -COCH<sub>3</sub>), 2.06 (s, 3H, -COC<u>H<sub>3</sub></u>), 1.10, 1.05, 1.00 (3s, 3H each, t-CH<sub>3</sub>s); MS:m/e 178 (M<sup>+</sup>); (+) <u>6</u>: [<]<sup>26</sup><sub>D</sub> + 13<sup>o</sup> (C, 1.67%); IR: 1706, 1626, 798, 772 cm<sup>-1</sup>; PMR: 5.20 (q, J=6Hz, 2H, -C=C<u>H</u>), 2.73 (m, 1H, -C<u>H</u>COCH<sub>3</sub>), 1.96 (s, 3H, COC<u>H<sub>3</sub></u>), 1.40, 1.05, 1.00 (3s, 3H each, t-CH<sub>3</sub>s); MS: m/e 178 (M<sup>+</sup>); (-) <u>6</u>: [<]<sup>26</sup><sub>D</sub> - 10<sup>o</sup> (C, 0.13%). Spectral data and GLC were identical with those of (+) 6. All the compounds gave satisfactory elemental analysis.

- 7.  $\propto$ -Orientation of the acetyl group in both <u>5</u> and <u>6</u> is assumed, as the spectral data of the recovered ketone from the irradiation were identical with those of <u>1</u>. The structures <u>5</u> and <u>6</u> would be antipodal representations in case there is a change in the stereochemistry of the acetyl group.
- Cis-ring fusion is assumed as trans-bicyclo [3.2.0]hept-2-enes should be highly strained.
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- 10. We thank Dr.Sykh Dev, Maltichem Research Centre, Baroda, for a generous gift of pure  $(+)\Delta^2$ -carene.
- 11. The results from this experiment will be published later.
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