

Two of the authors (MAS and KSR) thank CSIR, New Delhi for financial support. and AJ thanks CSIR, New Delhi for a fellowship.

8 September 1987

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OXIDATION STUDIES USING PYRIDINIUM CHLOROCHROMATE ON (+)-3-CARENE DERIVATIVES

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MATSUI *et al*¹ reported that rethronyl esters of (\pm) *cis*- and (\pm) *trans*-2,2,3-trimethylcyclopropanecarboxylic acids exhibit high insecticidal activity. Therefore, it was expected that the pure optically active isomers of 2,2,3-trimethylcyclopropanecarboxylates, with the 1*R*-*cis* configuration should show enhanced insecticidal activity. For obtaining such esters, the hydroxyaldehyde viz. 2,2-dimethyl-1-(2-methyl-2-hydroxypropyl)-*cis*-1-formylcyclopropane (II) was considered as the suitable starting material.

Pyridinium chlorochromate² (PCC) is considered as one of the best mild oxidizing agents for selective oxidation of primary alcohols to aldehydes in high yields. The diol (III), obtainable from (+)-3-carene (I) was subjected to PCC oxidation in the hope of getting the desired hydroxyaldehyde (II). Contrary to our expectation a mixture of two lactones was obtained as the major product of the reaction.

These have been separated by column chromatography over silicic acid. Fractions eluted with

petroleum ether containing 65% chloroform gave a solid, purified by crystallization from petroleum ether (36%), m.p. 82–83° [α]_D²⁵ – 78° (C, 2.0, CHCl₃) identified as (–) *cis*-dihydrochrysanthemolactone (V) by comparison of spectral properties with those reported in the literature³.

Elution of column with chloroform containing 20% ethyl acetate furnished a TLC pure liquid (18%) identified as the hydroxylactone (VII), *C₁₀H₁₈O₃, M⁺ 186, [α]_D²⁵ – 48° (C, 1.7, CHCl₃) by spectral properties described below: **IR: 3521 (OH), 1752 (γ -lactone); PMR: 1.26 (9H, *s*, methyls of hydroxyisopropyl and one of the methyls at C₄), 1.4 (5H, *s*, overlapping a multiplet, another methyl at C₄ and CH₂ at C₅), 2.2–2.5 (3H, *m*, CH₂ at C₂ and methine proton at C₃), 3.06 (1H, *brs*, exchangeable with D₂O, OH proton).

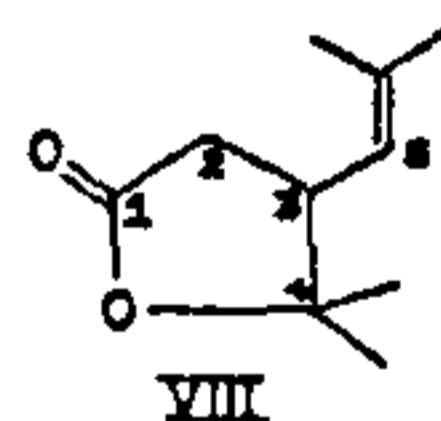
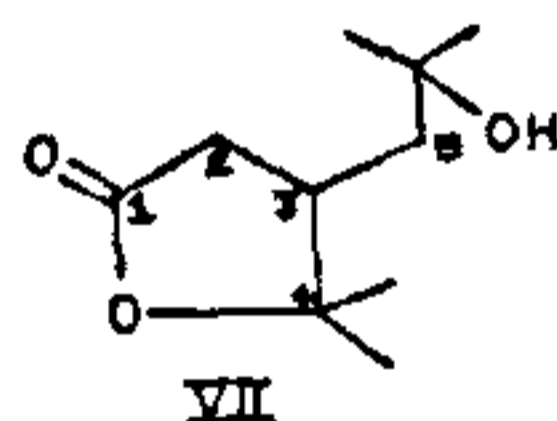
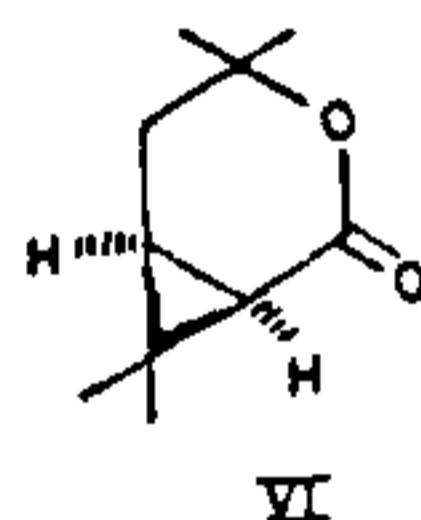
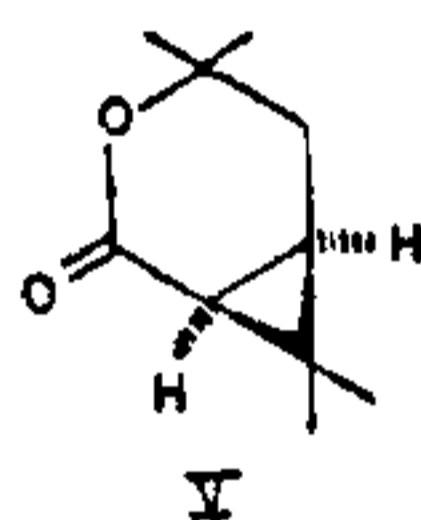
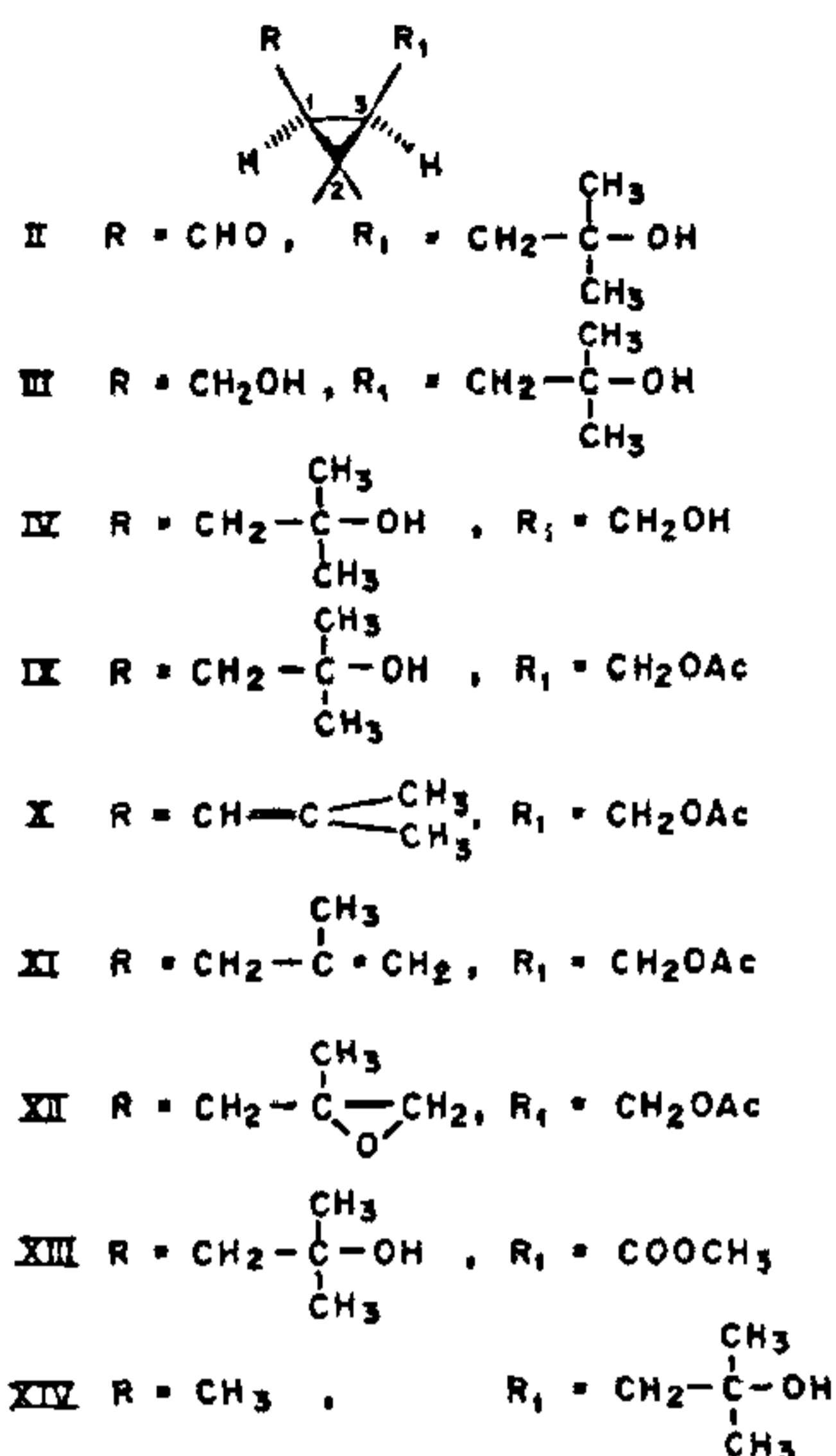
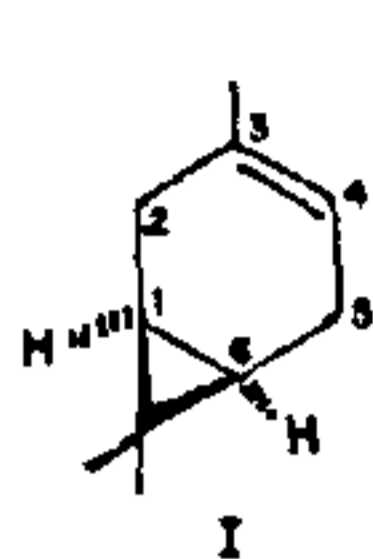
The assignment of structure to hydroxylactone (VII) was further confirmed by its conversion to the known (–) pyrocine⁴. Thus, dehydration of hydroxylactone (VII) by PTS in refluxing benzene afforded a crystalline solid (85%), C₁₀H₁₆O₂, M⁺ 168, m.p. 84–85°; [α]_D²⁶ – 66° (C, 1.8, CHCl₃) identified as (–) pyrocine (VIII) on the basis of following spectral data; IR: 1770 (γ -lactone), 840 (CH=C<); PMR: 1.21, 1.36 (3H each, *s* each, methyls at C₄), 1.7, 1.76 (3H each, *s* each, vinyl methyls), 2.26, 2.43 (1H each, *d* each, J = 5 Hz each, methylene protons at C₂), 2.96 (1H, *m*, methine proton at C₃) and 5.0 (1H, *d*, J = 9 Hz, olefinic proton).

However, PCC oxidation of diol (III) under buffer conditions (2 equivalents of sodium acetate) afforded in addition to the above two lactones (V and VII) the expected hydroxyaldehyde (II) but in low yield (13%) as a thick liquid, C₁₀H₁₈O₂, M⁺ 170, identified by spectral data; IR: 3509 (OH), 2740, 1695 (CHO); PMR: 0.75 (1H, *m*, C₃ cyclopropane proton), 1.0, 1.1 (3H each, *s* each, *gem*-dimethyl), 1.2 (8H, *brs*, methyls of hydroxy isopropyl and CH₂ at C₃), 1.6 (1H, *m*, C₁ cyclopropane proton), 2.96 (1H, *brs*, exchangeable with D₂O, OH proton) and 9.3 (1H, *d*, J = 6 Hz, aldehyde proton).

The tertiary alcohol (XIV) was considered as a suitable intermediate, since it was expected to give, on dehydration followed by oxidation of the resulting olefin, the required 2,2,3-trimethylcyclopropanecarboxylic acid. However, the Huang-Minlon reduction of (II) to (XIV) did not proceed satisfactorily.

* Satisfactory elemental analysis have been obtained for all the compounds reported.

** IR bands expressed in ν (cm⁻¹) and PMR chemical shifts in δ (ppm) scale with TMS as internal standard.



Dehydration of hydroxyacetate viz. 3-(acetoxy-methyl)-2,2-dimethyl-*cis*-1-(2-hydroxy-2-methylpropyl) cyclopropane (IX) by POCl₃/pyridine at 0° is known⁵ to yield a mixture of two isomeric unsaturated acetates (X and XI) in 60:40 ratio. Acetate (X) has been successfully converted into methyl (+)-*cis*-chrysanthemate by Bhat *et al*⁶. The isomeric unsaturated acetate (XI) which is a by-product, has now been converted into (+) *cis*-dihydrochrysanthemolactone (VI).

Thus in another sequence of reactions, acetate (XI) on epoxidation with perbenzoic acid (PBA, 2N) gave the epoxyacetate (XII, 92%), C₁₂H₂₀O₃, M⁺ 212, [α]_D²⁷-18.2° (C, 2, CHCl₃); IR:1730, 1240 (-OCOCH₃); PMR (CCl₄):0.60, 0.80 (1H each, *m*, C₁ and C₃ cyclopropane protons), 1.06, 1.16 (3H each, *s* each, *gem*-dimethyl), 1.33 (3H, *s*, tertiary methyl in the side chain), 1.56 (2H, *brm*, CH₂ at C₁), 2.03 (3H, *s*, acetate methyl), 2.48 (2H, *m*, methylene

protons attached to carbon bearing the epoxide function) and 4.0 (2H, *m*, CH₂ at C₃).

Lithium aluminium hydride reduction of epoxyacetate (XII) in ether at 0° followed by usual work-up afforded the crystalline diol (IV, 92.5%), C₁₀H₂₀O₂; m.p. 72–73°, M⁺ 172, identified by the spectral data: IR:3320, 1020 (OH); PMR (CDCl₃):0.7 (2H, *m*, C₁ and C₃ cyclopropane protons), 1, 1.12 (3H each, *s* each, *gem*-dimethyl), 1.32 (6H, *s*, hydroxy-isopropylmethyls), 1.54 (2H, *m*, CH₂ at C₁), 3.34–3.94 (2H, *m*, CH₂OH protons) and 4.76 (2H, *s*, exchangeable with D₂O, OH protons).

Jones chromic acid oxidation of the diol (IV) under controlled conditions gave a mixture of products, separated into acidic (19%) and neutral (70%) parts. The neutral part was purified by column chromatography over silicic acid and identified as (+)-*cis*-dihydrochrysanthemolactone (VI), C₁₀H₁₆O₂, m.p. 82–83° (petroleum ether), M⁺ 168 [α]_D²⁵+78° (C, 1.5, CHCl₃) by comparison of spectral properties with those reported earlier⁷. The acidic part was esterified with an ethereal solution of diazo methane and characterized as the known hydroxyester (XIII).

(+) *cis* and (-) *cis*-dihydrochrysanthemolactones are important intermediates in the synthesis of (+) 1R-*cis* and (+) 1R-*trans* chrysanthemic acids⁸, which give rise to active insecticidal esters.

21 September 1987; Revised 5 December 1987

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