Tetrahedron Letters No. 48, pp 4291 - 4294, 1975. Pergamon Press. Printed in Great Britain.

ABNORMAL OXIDATION OF SEYCHELLENE

Mohan L. Maheshwari* and Dinesh B. Saxena

Division of Agricultural Chemicals,
Indian Agricultural Research Institute,
New Delhi 110012, India

(Received in UK 1 October 1975; accepted for publication 20 October 1975)

In one of our earlier publications[1], it was reported that seychellene (I) a perfumery constituent of patchouli and jatamansi oils gave an unstable epoxide (II) with *m*-CPBA (*meta* - chloroperbenzoic acid), which on immediate reduction with LAH furnished seychelanol (III) in good yields. Now we report a novel transformation of seychellene epoxide (II) in to norseychelanone (IV, 40%). Although there is a similar report of such norketone formation from longifolene earlier, by consumption of two moles. of perbenzoic acid via Baeyer-Williger oxidation[2], this case is different as the formation of norketone (IV) took place directly from the epoxide (II) in the absence of *m*-CPBA (excess of *m*-CPBA was destroyed). The epoxide (II) remained stable with excess of *m*-CPBA at low temperature (15°C) and in dark (TLC) but when epoxide (II) alone was kept at room temperature in light and air, it soon started getting converted in to a mixture of products, the only clean product isolated and characterised was norseychelanone (IV) identical in all respects with the degradation product of seychellene[1] and natural one[3] [TLC, $(\alpha)_D$, IR, NMR and Mass].

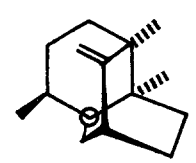
In order to follow the course of this transformation, following indirect route was adopted: The epoxide was kept at room temperature for five days in light and air and then reduced with LAH, which gave rise to a complex mixture of secondary alcohol, norseychelanol (V, 40%), a primary alcohol (VI, 25%), a small amount of a diol (2%) and an unresolvable intricate mixture of polar products.

Norseychelanol (V), a crystalline compound, m.p. 55° (reported earlier as a liquid[4]) has been found to be identical [TLC, $(\alpha)_D$, IR, NMR] with the one obtained by LAH reduction

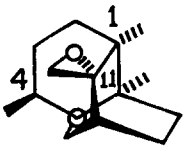
---

Contribution No. 102 from the Division of Agricultural Chemicals, IARI, New Delhi 11 0012

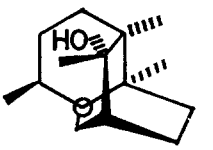
of norseychelanone (IV). The liquid primary alcohol [VI, MS : *m/e* 222.2 (M^+, 35.36%), 207.1 (42.19%), 191.1 (M^+ - CH_2OH, 76.30%), 175.11 (11.11%), 163.1 (15.96%), 149.1 (17.87%), 135.1 (36.20%), 121.1 (37.72%), 107 (57.80%), 95 (100%), 81 (86.47%), 67 (45.87%) and 41.1 (94.72%)] was compared with the primary alcohol (VII) prepared by hydroboration of seychellene (I)[4]. Though the IR spectra[5] were identical, the specific rotation was lower [VI: $(\alpha)_D$ −69° (c, 0.99); VII: $(\alpha)_D$ −80° (c, 0.4)] and NMR spectra[5] showed a little different pattern specially in the methyl region [VI: NMR - 100MHz ($CDCl_3$)[6] : 9.15 (*d*, 3H, *J* = 6.5Hz) >CH - $\underline{CH_3}$; 9.18 (*s*, 3H) >$\underline{CH_3}$; 9.26 (*s*, 3H) >$\underline{CH_3}$; 6.1 - 6.6 (*m*, 2H) - $\underline{CH_2}$OH; 7.83 (*s*, 1H) - $\underline{OH}$]. It was felt that the primary alcohol (VI) is a stereoisomer of VII having -CH_2OH group in α-orientation.



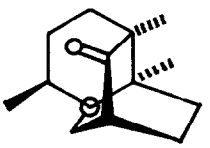
I



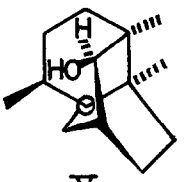
II



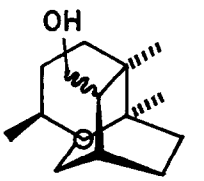
III



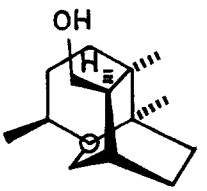
IV



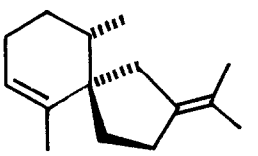
V



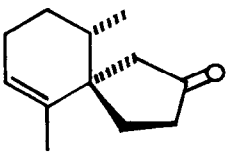
VI



VII



XI

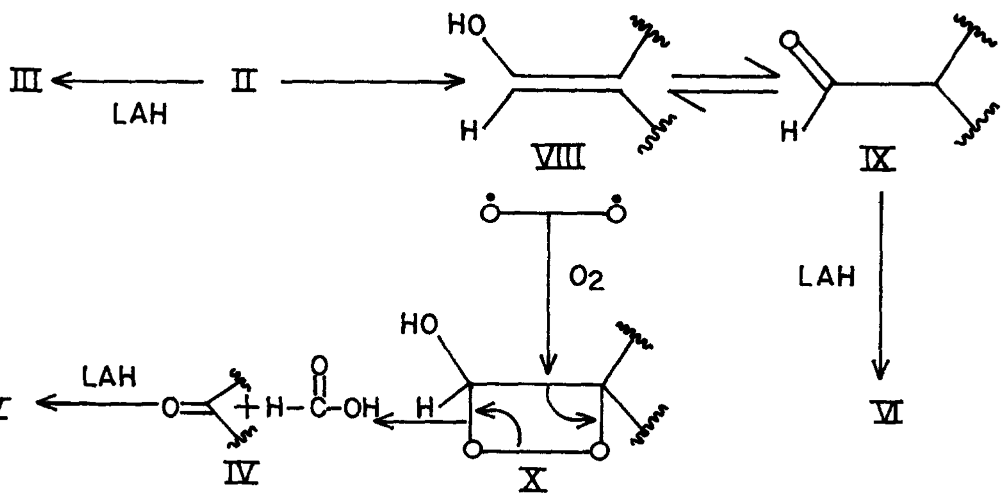


XII

The structure of minor product, diol, $C_{15}H_{26}O_2$, m.p. 185° (nonreactive to periodate) could not be established due to paucity of material [MS : *m/e* 238.3 (M^+, 26.06%), 220.3 (33.88%),

177.1 (37.56%), 163.1 (19.09%), 149.1 (22.71%), 137.1 (13.04%), 135.1 (18.18%), 125.2 (100.0%) and 109.1 (37.56%)]. Its mass spectral fragmentation pattern showed the absence of a primary alcoholic group (no $M^+ - 31$). Diol reacted smoothly with Ac_2O-Pyridine at room temperature to give a liquid diolmonoacetate [$\nu_{max.}^{CHCl_3}$: 3610, 3500, 1725 and 1250 cm^{-1}, NMR ($CDCl_3$) : 9.18 (*d*, 3H, *J* = 6Hz), $>$CH - $\underline{CH_3}$; 9.08, 8.92 (*s*, *s*, 6H) $\underline{2\ CH_3}$$-<$; 7.97 (*s*, 3H) $\underline{CH_3}$ - CO - O-; 4.98 - 4.72 (*q*, 1H) $\underline{H}$ - C - O - CO - ; MS : *m/e*, 280 (M^+, 4.1%), 220 (31.8%), 177 (28.61%), 163 (18.8%), 149 (16.67%), 135 (19.4%), 125 (45.48%), 109 (32.2%), 55 (36.4%), 43 (59.04%) and 31 (100%)]. Above information confirmed that one of the hydroxyls of diol is secondary, while the other one is probably a tertiary (no signal in NMR of acetate in the region 5.0 - 7.0). The above data also indicated that perhaps diol is formed by some skeletal rearrangement and is probably related to norseychelanone by mass spectral fragmentation (IV, *m/e* 178, 163, 149, 137 and 125).

Following mechanism may be suggested for the formation of norseychelanone (IV) from seychellene epoxide (II):



While recording the IR spectrum, it was observed that the epoxide (II) changes over to aldenol [(VIII, IX), $\nu_{max.}^{CCl_4}$: 3400, 2710 and 1720 cm^{-1}; NMR (CCl_4) : 0.15 (*m*), -CH - C = O; 4.7 (*s*), H/HO>C=C<; 7.26, 7.5 (*d*, *d*, *J* = 5.5 Hz), H/H] and hence the first step of the reaction could be epoxide opening. Since no other reagent was present except light and air,

addition of oxygen to the activated double bond of enol (VIII) followed by opening of the four membered peroxide ring (X) could be the most logical steps leading to the formation of norseychelanone (IV, relieving the strain on C_{11}). Such addition of oxygen to activated double bond was recently reported (XI to XII) but the reaction was carried out under energetic conditions (UV light, benzene, methanol)[7].

We acknowledge our sincere thanks to Drs. S.K. Mukerjee for the facilities in the division, R.C. Pandey, University of Illinois, Urbana for the 100 MHz NMR and mass spectra and R.V. Swamy for helpful discussion.

References

1. N.L. Maheshwari and D.B. Saxena, *Ind. J. Chem.* 12 (11), 1221 (1974).
2. U.R. Nayak and Sukh Dev, *Tetrahedron* 19, 2269 (1963).
3. G. Rucker, J. Tautges, N.L. Maheshwari and D.B. Saxena, Communicated to *Phytochemistry*, 1975.
4. G. Wolf and G. Ourisson, *Tetrahedron* 25, 4903 (1969).
5. We thank Dr. G. Wolf, University of Strasbourg for IR and NMR spectra of VII and its acetate.
6. Chemical shifts here and elsewhere are in τ values.
7. B. Maurer, L.G. Fracheboud and G. Ohloff, *Ger. Offen.* 2,327,370, Dec. 13, 1973. Cf. C.A. 80(13), 70441v (1974).