A NOVEL ANTIMONY TRICHLORIDE CATALYSED REARRANGEMENT ON KHUSINOLOXIDE R.S. Dhillon, B.R. Chhabra, M.S. Wadia and P.S. Kalsi Department of Chemistry and Biochemistry Punjab Agricultural University, Luthiana (India)

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In our attempts to open the epoxy ring in khusinoloxide (I) to the corresponding aldehyde we reacted it with BF3-Et20. This procedure, however, afforded a complex mixture of products. Based on recent publications^{1,2} from our laboratory reporting the SDCl₃ catalysed reactions of methanol, acetic and formic acid to the methylenic double bond of khusinol, we reacted khusinoloxide with antimony trichloride. Interestingly, this reaction followed an unexpected path, the present communication reports this reaction and other related unusual transformations.

Reaction of khusinoloxide 3(I) with SbCl₂-Et₂O for one minute at room temperature (29°C) furnished after work up a single product $C_{15}H_{2L}O_2$, m.p. $170^{\circ}C$ in quantitative yields. Its IR spectrum displayed bands for a hydroxyl group (3325 cm⁻¹) and a trisubstituted double bond (1660 and 816 cm⁻¹), while its PMR spectrum indicated apart from the isopropyl (two doublets, 3H each at 0.77 and 0.946 J=7.5 Hz) and H - C = C - CH_2 (3H broad singlet at 1.7 and 1H narrow multiplet at 5.376) groupings, an additional signal (3H) at 3.926 which must represent a newly created hydroxy methylene (CH,OH) function. The broadening at the base of this signal should represent the C-5 proton. This spectral data along with the mode of formation makes structure (II) an attractive possibility. Acetylation of (II) with acetic anhydride and pyridine at room temperature afforded an acetate C₁₇H₂₆O₃ m.p. 102°C. Its spectral features clearly require this compound to have = C - CH_OH (IR: 3560; PMR: 1H singlet exchangeable at 3.16 and 2H singlet at 3.636), CH-OAc (IR: 1730 and 1225 cm⁻¹; PMR: 3H singlet at 2.1 and 1H multiplet at 5.036, WH = 18.0 Hz), CH₃ - C = C - H (IR: 1650 and 825 cm⁻¹; PMR: 3H broad singlet at 1.7 and 1H narrow multiplet at 5.406) and Me $_2$ CH- (FMR: two doublets 3H each at 0.78 and 0.956, J=8 Hz) groupings. This data not only confirms structure (II) for the diel but requires the acetate to be represented by (III).

Two other reactions of the diol (II) are of interest. Reduction of (II) with lithium aluminium hydride follows an unusual path to afford a mixture of products from which a compound

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m.p.130°C, identified (IR, TIC, m m p, NMR) as the known^{4,5} khusinodicl (IV) was isolated. This reduction involves cyclisation to (T) followed by its reduction to (IV). The presence of (I) in the reduction mixture has been confirmed by comparative TLC and mixed melting point determination with an authentic sample. Shaking (II) with Al₂0₃ for five minutes at room temperature affords quantitatively a product m.p. 113°C identified by usual means (TLC, IR, m m p) as khusinoloxide (I).

The cis elimination observed in the conversion of (I to II) can be rationalized by assuming an E_1 mechanism. Loss of C-6 proton being more favoured as compared to the loss of C-8 proton because of the difference in stability of the two olefins. The cis addition observed in the reverse reaction is, however, more difficult to explain. A probable mechanism depicted in Eq. (i) involves transfer of the proton to afford a stable transfusion as shown in (V). Attack by the oxygen on the carbonium ion (V) then takes place from that conformation in which oxygen is β -placed since this is stabilized by hydrogen bonding. In support of such a mechanism the hydroxy acetate (III) remained unchanged on contact with alumina even after a long time.

- 1. J.C. Kohli, M.S. Wadia and P.S. Kalsi. Experientia. 26, 131 (1972)
- 2. J.C. Kohli, M.S. Wadia and P.S. Kalsi. Indian J. Chem. 10, 1130 (1972)
- 3 R. Seshadri, F.S.Kalsi, K.K. Chakravarti and S.C. Bhattacharyya. Tetrahadron 23, 1267(1967)
- 4 C.K.Trivedi, A.D. Wagh, S.K. Paknikar, K.K.Chakravarti and S.C. Ehattacharyya. Tetrahedron 22, 1641 (1966)
- 5 S.V. Tirodkar, S.K. Pakuikar and K.K. Chakravarti. Sci. Cult. (India) 35, 27 (1969)