# A NOVEL ANITMONY TRICHLORIDE CATALYSED RBARRANGZMENT ON KHUSINOLOXIDE <br> R.S. Dhillon, B.R. Ghhabra, M.S.Wadia* and P.S.Kalai <br> Department of Chemistry and Biochendstry <br> Pumjab Agricultural Oniversity, Ludhiana (India) <br> (Received in UK 11 December 1973; accepted for publication 28 December 1973) 

In our atterqte to open the epoxy ring in khusinoloxide (I) to the corresponding aldehyde we reacted it with $\mathrm{BF}_{3}-\mathrm{Et}_{2} \mathrm{O}$. This procedure, however, afforded a complex mixture of products. Based on recent publications ${ }^{1,2}$ from our laboratory reporting the $\mathrm{SbCl}_{3}$ 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 commuication reports this reaction and other related unusual transformations.

Reaction of chusinoloxide ${ }^{3}(\mathrm{I})$ with $\mathrm{SbCl}_{3}-\mathrm{Et}_{2} \mathrm{O}$ for one minute at room temperature $\left(29^{\circ} \mathrm{C}\right)$ furnished after work up a single product $\mathrm{C}_{15} \mathrm{H}_{24} \mathrm{O}_{2}, \mathrm{~m} \cdot \mathrm{p} \cdot 170^{\circ} \mathrm{C}$ in quantitative yields. Its IR spectrum displayed bands for a hyiroxyl group ( $3325 \mathrm{~cm}^{-1}$ ) and a trisubstituted double bond ( 1660 and $816 \mathrm{~cm}^{-1}$ ), while its PMR spectrum indicated apart from the isopropyl (two drublets, 3 H each at 0.77 and $0.946 \mathrm{~J}=7.5 \mathrm{~Hz}$ ) and $\mathrm{H}-\mathrm{C}=\mathrm{C}-\mathrm{CH}_{3}$ ( 311 broad singlet at 1.7 and 1 H narrow multiplet at 5.378 ) groupings, an additional signal (3世) at 3.926 which must represent a newly created hyriroxy methylene $\left(\mathrm{CH}_{2} \mathrm{OH}\right)$ function. The broadening at the base of this signal should represent the C-5 proton. This spectral data along with the morle of formation makes structure (II) an attractive possibility. Acetylation of (II) with acetic anhyiride and pyridine at room temperature afforded an acetate $\mathrm{C}_{17} 7^{\mathrm{H}} 26^{\mathrm{O}} 3^{\mathrm{mop}} \mathrm{p} \cdot 102^{\circ} \mathrm{C}$. Its spectral features clearly require this compound to have $=\mathrm{C}-\mathrm{CH}_{2} \mathrm{OH}$ (IR: 3560; PMR: 1H singlet exchangeable at 3.16 and 2 F singlet at 3.536 ), $\mathrm{CH}-\mathrm{OAC}$ (IR: 1730 and $1225 \mathrm{~cm}^{-1}$; PMR: 3 H singlet at 2.1 and 1 H multiplot at 5.036 , $W H=18.0 \mathrm{Kz}$ ), $\mathrm{CH}_{3}-\mathrm{C}=\mathrm{C}-\mathrm{H}$ (IR: 1650 and $825 \mathrm{~cm}^{-1}$; PMR: 3 H broad sinclet at 1.7 and 1 H narrow multiplet at 5.408 ) and $\mathrm{Me}_{2} \mathrm{CH}$ (FNR : two doublets 3 H each at 0.78 and $0.958, \mathrm{~T}=8 \mathrm{~Hz}$ ) groupings. This data not only confirms structure (II) for the diol but requires the acotate to be represented by (III).

Two other reactions of the diol (II) are of interest. Reduction of (I) with lithiua aluminium hydride follows an unsual path to afford a nixture of products from which a compound

[^0]m.p. $130^{\circ} \mathrm{C}$, identified (IR, TLC, $m \mathrm{~m} \mathrm{p}, \mathrm{NR}$ ) as the known ${ }^{4,5}$ khusinodiol. (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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ for five minutes at room temperature affords quantitatively a proruct m.p. $113^{\circ} \mathrm{C}$ identified by usual means (TLC, IR, mmp) as khusinoloxide (I).


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II $R=H$
III $R=\mathrm{COCH}_{3}$

iv

The cis elimination observed in the corversion 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-B proton because of the difference in stabji]ity of the two olefing. 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 $\beta$-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.


- J.C. Kohli, M.S. Tadia and P.S. Kalsi. Fixperientia. ふ, 131 (1972)

2. J.C. Kohli, v.S. Wadia and P.S. Kalsi. Indian J. Chem. 10, 1130 (1972)

3 P. Seshariri, F.S.Kaisi, K.K. Chakravarti and S.C. Shattacharyya.Tetrahadron 23, 1267(1967)
4 G.K.Trivedi, A.D. Wagh, S.K. Paknikar, K.K.Chakravarti and S.C.Shattacharyya. Tetrahedron 22, 1641 (1966)

5
S.V. Tirodkar, S.K. Paknikar and K. K. Chakravarti. Sci. Cult.(India) 35, 27 (1969)


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