

A NOVEL ANTIMONY TRICHLORIDE CATALYSED REARRANGEMENT ON KHUSINOLOXIDE

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In our attempts to open the epoxy ring in khusinoloxide (I) to the corresponding aldehyde we reacted it with  $\text{BF}_3\text{-Et}_2\text{O}$ . This procedure, however, afforded a complex mixture of products. Based on recent publications<sup>1,2</sup> from our laboratory reporting the  $\text{SbCl}_3$  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 communication reports this reaction and other related unusual transformations.

Reaction of khusinoloxide<sup>3</sup>(I) with  $\text{SbCl}_3\text{-Et}_2\text{O}$  for one minute at room temperature ( $29^\circ\text{C}$ ) furnished after work up a single product  $\text{C}_{15}\text{H}_{24}\text{O}_2$ , m.p.  $170^\circ\text{C}$  in quantitative yields. Its IR spectrum displayed bands for a hydroxyl group ( $3325\text{ cm}^{-1}$ ) and a trisubstituted double bond ( $1660$  and  $816\text{ cm}^{-1}$ ), while its PMR spectrum indicated apart from the isopropyl (two doublets, 3H each at 0.77 and 0.94 $\delta$   $J=7.5$  Hz) and  $\text{H}-\text{C}=\text{C}-\text{CH}_3$  (3H broad singlet at 1.7 and 1H narrow multiplet at 5.37 $\delta$ ) groupings, an additional signal (3H) at 3.92 $\delta$  which must represent a newly created hydroxy methylene ( $\text{CH}_2\text{OH}$ ) 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  $\text{C}_{17}\text{H}_{26}\text{O}_3$  m.p.  $102^\circ\text{C}$ . Its spectral features clearly require this compound to have  $=\text{C}-\text{CH}_2\text{OH}$  (IR: 3560; PMR: 1H singlet exchangeable at 3.16 and 2H singlet at 3.63 $\delta$ ),  $\text{CH}-\text{OAc}$  (IR: 1730 and  $1225\text{ cm}^{-1}$ ; PMR: 3H singlet at 2.1 and 1H multiplet at 5.03 $\delta$ ,  $\text{WH} = 18.0$  Hz),  $\text{CH}_3-\text{C}=\text{C}-\text{H}$  (IR: 1650 and  $825\text{ cm}^{-1}$ ; PMR: 3H broad singlet at 1.7 and 1H narrow multiplet at 5.40 $\delta$ ) and  $\text{Me}_2\text{CH}-$  (PMR: two doublets 3H each at 0.78 and 0.95 $\delta$ ,  $J=8$  Hz) groupings. This data not only confirms structure (II) for the diol 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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