

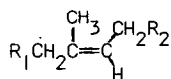
A CONVENIENT ROUTE TO CIS AND TRANS
TRISUBSTITUTED OLEFINS FROM GERANIOL AND NEROL

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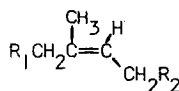
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Many naturally occurring systems have either cis or trans trisubstituted double bonds in which one of the substituents is a methyl group (cf. I and II). The importance of these systems in synthesis (e.g. of polyisoprenoids) or in mechanistic studies led to a number of

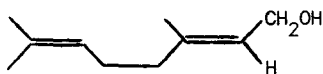


I

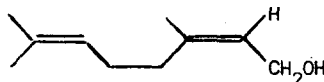


II

new methods which exhibit very high or complete stereoselectivity. (1) Our need for pure substances of types I and II has led us to develop a convenient transformation of the readily available geraniol (III) and nerol (IV) into olefins of types I and II respectively.

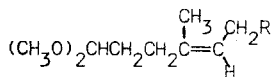


III

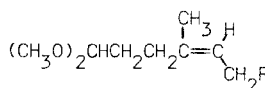


IV

We have found that it is possible to ozonize the acetates of nerol and geraniol with reasonable selectivity so as to form the aldehyde derived by cleavage at the isopropylidene terminus. For instance, treatment of neryl acetate with one equivalent of ozone in methanol at -78° , followed by decomposition with dimethyl sulfide (2), produced an aldehyde which was isolated (methanol- $CaCl_2$, room temperature) as the dimethyl acetal V, $R=OAc$, bp $85-86^\circ$ (0.35 mm), λ (film) 5.72, 8.85 μ ; δ ($CDCl_3$) 1.75 (3H,s), 3.30 (6H,s), 4.34 (1H,t,J-5), 4.60 (2H,d,J-7), 5.40 (1H,t,J-7). The overall yield from neryl acetate was 60%. The corresponding alcohol V, $R=OH$, was obtained by reduction with lithium aluminum hydride in ether (92% yield) bp $89-90^\circ$ (0.25 mm) λ (film) 2.92 μ ; δ ($CDCl_3$) 1.75 (3H,s), 3.30 (6H,s), 4.10 (2H,d,J-7), 4.35 (1H,t,J-5), 5.48 (1H,t,J-7).



VI



V

In a similar manner geranyl acetate was transformed to the acetal VI, R=OH, with essentially the same properties as V, R=OH, except for the position of the methyl group at a somewhat higher field (3) (-8 cps) in the nmr.

The masked aldehyde of V can be used to introduce a variety of functions (including, presumably, H via decarbonylation of the aldehyde), but transformation of the allylic alcohol portion of V, R=H, presents a more serious problem which is indeed a common one with all methods proceeding via allylic alcohols, however synthesized. It is clearly necessary to have a method for the transformation of such allylic alcohols into the relatively stable chlorides without any ionization or rearrangement. We have developed such a method, and illustrate it in the accompanying communication.

Acknowledgement.

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References.

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