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A NOVEL REARRANGEMENT OF GUAIOL TO CADALANE TYPE SKELETON IN STRONG ACID MEDIUM[1]

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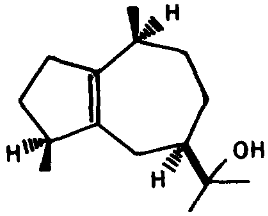
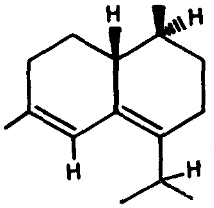
In earlier communications, we have described[2] some novel and interesting rearrangements of terpenoids in strong acid medium. Continuation of efforts in this area have led to the discovery of a new and efficient rearrangement of guaiol (I) to 10-epi-Zonarene (II), a bicyclic heteroannular diene of cadalane type, which has been recently shown[3] to occur widely in nature. Reactions of guaiol (I) with various acidic reagents have been previously studied by many workers[4] and shown to lead to the formation of an equilibrium mixture of various guaienes and guaioxide without any skeletal rearrangement. However, the reaction of (I) with conc. sulphuric acid, under the conditions that are salubrious to the formation of stable carbocations, takes an entirely different course and highlights the role of this technique as a source of unusual and fascinating molecular rearrangements.



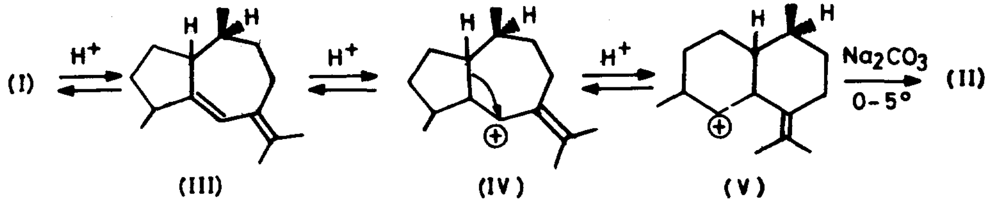
(I)



(II)

When a solution of guaiol (I) in CH_2Cl_2 was rapidly dispersed in conc. H_2SO_4 (97-99%, BDH) at 0-5°C, a clear orange solution ($\lambda_{max}^{H_2SO_4}$ 330 nm) was obtained. Quenching of this solution (1hr) in iced aq. Na_2CO_3 led to 80-90% recovery of an olefinic mixture from which the major component (II) was obtained pure ($AgNO_3$-SiO_2 column) in 40% yield. The rest of the olefinic mixture consisted of various guaienes. The structure of (II) was evident from the following data: $C_{15}H_{24}$, λ_{max}^{MeOH} 249 nm (ϵ = 13,000), δ 0.97 (9 H, d, J=7 Hz), 1.76 (3H,br. S), 3.04 (1H, septet, J=7 Hz) and 6.14 (1H,br S). A direct spectral comparison established the mutual identity of (II) and naturally occurring 10-epi-Zonarene.[3]

Scheme 1



A reasonable interpretation of the (I)→(II) rearrangement is depicted in Scheme 1, and involves initial isomerisation of guaiol (I) to the guaiene isomer (III) followed by protonation to (IV), alkyl migration to (V) and isomerisation to (II). Since the guaiane and cadalane type skeletons are abundantly distributed in nature and are derived from farnesyl pyrophosphate by independent pathways, we consider this facile conversion of (I)→(II) as biogenetically significant.

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References

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