

The Regio- and Stereo-controlled Synthesis of *cis-p*-Menth-3-ene-1,2-diol by means of a 1,2,4-Trioxane Intermediate

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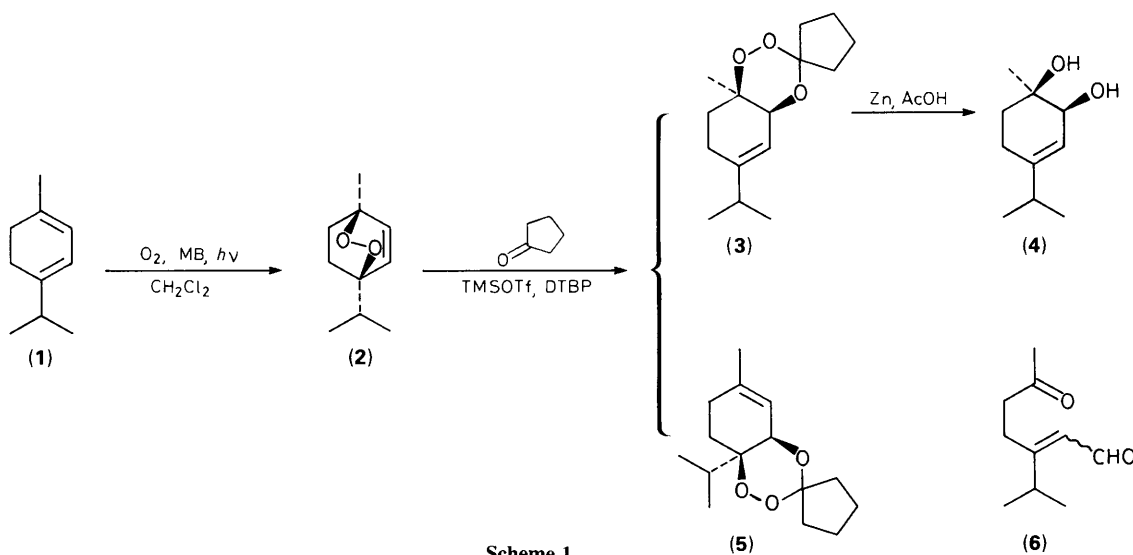
A concise synthesis of (\pm)-*cis-p*-menth-3-ene-1,2-diol from α -terpinene is described which relies on the regio- and stereo-controlled construction of a 1,2,4-trioxane intermediate; structures proposed for two aroma constituents of *Ferula jaeschkeana* oil are revised.

1,2,4-Trioxanes, like certain cyclic peroxides,¹ have potential in organic synthesis.² So far they have been virtually unexploited owing to their limited availability and the belief that they might be unstable. Now that 1,2,4-trioxanes can be prepared conveniently from a variety of electron-rich alkenes and dienes *via* hydroperoxides, 1,2-dioxetanes, and endoperoxides,³ they provide an opportunity for further chemical elaboration. Preliminary studies have shown that the 1,2,4-trioxane ring is sufficiently robust to undergo chemical reaction,⁴ and can also be deployed as an entity of masked, dual functionality.⁵

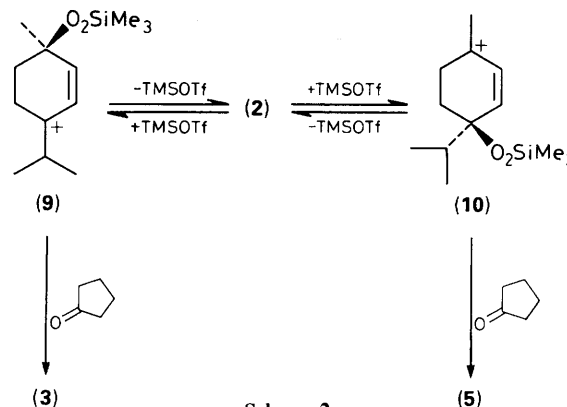
We now describe an application of the aforementioned

chemistry to the synthesis of *cis-p*-menth-3-ene-1,2-diol (**4**), the structure proposed for a recently isolated constituent of the essential oil of the rhizomes of *Ferula jaeschkeana*.⁶ This plant is abundant in the north-west Himalayas and its oil, which contains many oxygenated monoterpenoids, is of importance in Indian perfumery. Interestingly, the diol (**4**) is thought to be one of the components responsible for the exotic aroma of the oil.⁷

Our scheme starts with the commercially available α -terpinene (**1**), which was converted to ascaridole (**2**) by methylene blue (MB)-sensitized photo-oxygenation⁸ in CH_2Cl_2 at -10°C for 14 h. Under these conditions (**2**) was obtained in



Scheme 1



(grant No. 20-5380.87) for financial support of this work. We thank Dr. S. K. Agarwal of the Central Institute of Medicinal and Aromatic Plants, Lucknow, India, for providing the spectra of the constituents of *F. jaeschkeana* oil.

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The mechanism by which (2) is converted into (3) and (5) requires comment. Silylation-desilylation undoubtedly generates the isomeric peroxy allylic cations (9) and (10) which are in fast equilibrium through (2).¹² Capture of either by cyclopentanone to produce the *cis*-fused trioxane ring is probably dictated by steric considerations, thereby accounting for the preferred formation of (3) over (5) (Scheme 2).

In conclusion, the synthesis is easy to perform and novel in conception. It demonstrates how an unsymmetrical 1,3-diene can be functionalized in a regio- and stereo-controlled manner.¹³ Formally, a 1,4-endoperoxide is converted to an allylic *cis*-1,2-diol¹⁴ through the agency of the selective formation and reduction of a *cis*-fused 1,2,4-trioxane intermediate.

We are indebted to the Swiss National Science Foundation

† New trioxanes (**3**) and (**5**) were characterized by their ^1H - and ^{13}C -NMR and IR spectra and by elemental analyses.

‡ Our structural assignments refer to relative configurations.