Rapid and Quantitative Aromatization of Non-conjugated Cyclohexadienes by Potassium Permanganate in Benzene

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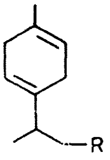
Summary γ-Terpinene (**1**; R = H) and other non-conjugated cyclohexadienes are quantitatively aromatized with $KMnO_4$ dissolved in benzene by complexing with the macrocyclic polyether dicyclohexyl-18-crown-6, whereas the conjugated analogues do not react under identical conditions.

POTASSIUM PERMANGANATE, when solubilized in benzene by complexing with dicyclohexyl-18-crown-6, is a very efficient oxidant for water-insoluble compounds under mild neutral conditions, as illustrated by the oxidation of several olefins, primary alcohols, and aldehydes.[1] However, there has been no report of an oxidative aromatization utilizing this reagent.

When 0·22 mmol of γ-terpinene (**1**; R = H) was stirred with 0·33 mmol of $KMnO_4$ dissolved with an equimolar amount of dicyclohexyl-18-crown-6 (Aldrich) in 5 ml of benzene at 25 °C for 10 min, 88% of (**1**; R = H) was converted into *p*-cymene (**4**; R = H),† and conversion was quantitative after 30 min. Further extension of the reaction time resulted in somewhat lower yields of *p*-cymene, presumably from the further oxidation of this product to the corresponding benzoic acid.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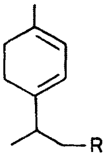
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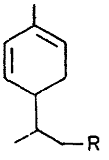
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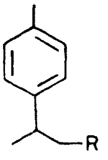
(4)

Activated MnO_2 (excess) oxidatively dehydrogenates certain cyclohexene aldehydes, ketones, and Schiff bases,[2] and certain cyclohexadienes,[3] to the corresponding aromatic derivatives, but attempts to aromatize γ-terpinene with ordinary MnO_2 or activated MnO_2[4] were unsuccessful under the same conditions as those used for $KMnO_4$. Thus, the present aromatization could not be attributed to MnO_2 that may have been generated in the reaction mixture by a slow rate of oxidative cleavage of the cyclohexadiene to keto acids. The close agreement of the observed stoicheiometry (0·73) with theoretical (0·67) also argues against the involvement of MnO_2.

Under conditions where γ-terpinene was quantitatively aromatized, the conjugated analogues α-terpinene (**2**; R = H) and α-phellandrene (**3**; R = H) were not aromatized. Furthermore, over 80% of these starting materials could be recovered from the reaction mixture because oxidative cleavage of the conjugated dienes was very limited under these conditions. Comparable differences in reactivity were also observed between cyclohexa-1,4-diene and cyclohexa-1,3-diene, and between the sesquiterpene β-curcumene (**1**; R = dimethylallyl) and its conjugated analogues γ-curcumene (**2**; R = dimethylallyl) and α-zingiberene (**3**; R = dimethylallyl),‡ thus suggesting the synthetic utility of this reaction for the selective aromatization of non-conjugated cyclohexadienes in the presence of conjugated cyclohexadienes. The reaction also provides a useful aid in the purification of conjugated cyclohexadienes from mixtures containing the non-conjugated isomers, since the separation of a conjugated diene from an aromatic compound is generally simpler than the separation of conjugated from non-conjugated diene isomers. Application of the described technique to a mixture containing 0·5 mmol each of α-terpinene and γ-terpinene (0·75 mmol $KMnO_4$), followed by backwashing with water, concentration of the solvent, and t.l.c.,§ afforded pure α-terpinine (by g.l.c.) in 82% yield. When the method was applied to a 1 : 1 mixture of β-curcumene and γ-curcumene, recovery§ of the pure conjugated derivative (as the methyl ester) was nearly quantitative.

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† This and subsequent reactions were monitored by g.l.c. (SE-30) and the products were identified by combined g.l.c.–m.s.

‡ In the presence of three-fold excess of $KMnO_4$ under the conditions described, β-curcumene was quantitatively aromatized and the side-chain cleaved (**4**; R = carboxymethyl). The side-chains of γ-curcumene and α-zingiberene were also cleaved under these conditions, but no aromatized product was detected.

§ The monoterpenes were chromatographed on silica gel G containing 8% $AgNO_3$ with benzene–hexane–ether (50 : 50 : 1), while t.l.c. of the sesquiterpene derivatives was performed on silica gel G with hexane–ethyl acetate (7 : 3).

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