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FURTHER REARRANGEMENT OF ISOLONGIFOLENE

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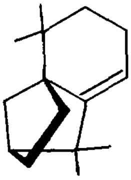
ISOLONGIFOLENE (I)[1] on being refluxed (5 hr) with Amberlyst-15[2] or acid-treated silica gel yields, besides a polymer (25-30%) a mixture consisting essentially of an aromatic hydrocarbon (~ 55%) and mono-olefins (~ 45%; at least four components, with one predominating to the extent of over 60%). The same reaction products can be reached by using longifolene (II) instead, and its exposure to these reagents under milder conditions (36 hr at 95°) results in over 95% yield of isolongifolene (α_D -22.6). The transformation of longifolene (or isolongifolene) to these new products can be effected more conveniently with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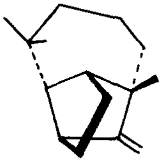
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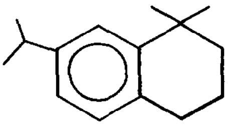
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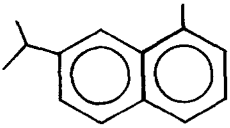
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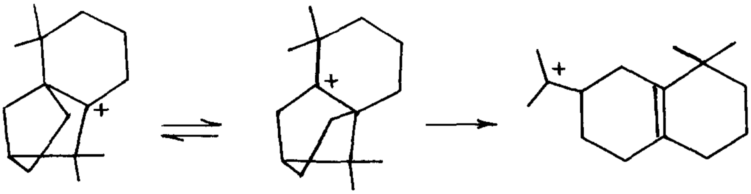
V VI VII

$BF_3.Et_2O$; for example, addition of this reagent (3%) to longifolene (neat) at room temp. (~ 27°) results in an exothermic reaction leading to a product (after 14 hr at room temp.) essentially identical with that described earlier.

The aromatic hydrocarbon from the above reactions was isolated either by preparative GLC or by treatment of the monomeric hydrocarbon mixture with perbenzoic acid, followed by chromatography over Al_2O_3/I. This compound (colorless liquid, b.p. 90-92°/1 mm) analyses for $C_{15}H_{22}$ (M^+, m/e = 202) and is clearly a benzene derivative $[\lambda_{max}^{EtOH}$ 277 mμ, ε 630; 267 mμ, ε 606. IR (smear): Aromatic absorption 1612, 1575, 900 and 825 cm^{-1}, possibly 1,2,4-trisubstituted.[3] PMR (CCl_4): three aromatic protons, 2H, partly overlapping singlets centred at 409 c/s and, 1H broadened singlet at 421 c/s $]$. The PMR spectrum further shows signals assignable to two quaternary methyls and an isopropyl group (6H singlet at 76 c/s; 6H doublet centred at 72.5 c/s, J = 7 c/s) and three benzylic protons (3H envelope centred at ~160 c/s, essentially a triplet overlapping a septet). These data, considered along with mechanistic reasoning for its genesis from isolongifolene, suggest its formulation as III. This was readily confirmed by its Se dehydrogenation to eudalene (IV) in good yield.

Conceivably, the transformation of I to III can be visualised as proceeding through V to VI to the bicyclic cation (VII), which by elimination followed by isomerisation - disproportionation results in the tetralin III and the so-far uncharacterised mono-olefins. Obviously, conjugated diene(s) generated by VII, should be capable of interception, before disproportionation, by a suitable dienophile. When isomerisation of isolongifolene was carried out in presence of maleic anhydride, though considerable yield of adducted product (isolated as acids, after hydrolysis) was obtained, no pure component could be isolated.

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