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AROMATIZATION OF CYCLOALKENES WITH TRIFLUOROACETIC ACID

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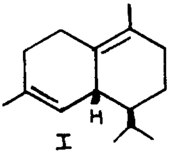
In our studies of the acid-catalyzed rearrangements of sesquiterpenes[1] we have frequently encountered dehydrogenated materials among the products of these reactions (see as an example the preceding communication). In those examples using HCO_2H, H_2SO_4-HOAc, $HClO_4$-HOAc, or H_3PO_4 as the acid these products result from air oxidation as their production can be effectively reduced by careful exclusion of atmospheric oxygen. However when trifluoracetic acid (TFA) is employed the exclusion of other oxidizing agents does not prevent the reaction.[2] We report here the use of this novel dehydrogenation for the partial aromatization of sesquiterpenes.

The reaction appears to be particularly suited for the production of tetralins. Thus cadinane hydrocarbons I → IV are each converted in a few minutes to calamenene (V) in good yield when a 1-5% n-decane solution of the olefin is treated with excess TFA at room temperature with stirring. Limonene (VI) on the other hand, requires hours for complete conversion to cymene (VIII) even though the equilibrium mixture of terpinenes (VII) is established rapidly. The equivalent reaction in the sesquiterpene case takes a different course, α-curcumene (IX) is not produced from either β- or γ-curcumene (X and XI). Instead, the product observed (75% of total hydrocarbons) is (+)-dihydro-α-curcumene (XII, 13% optical purity).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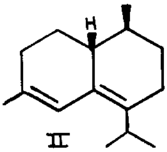
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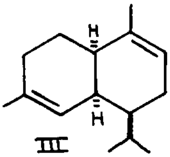
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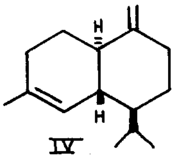
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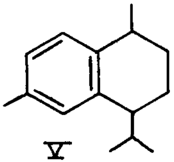
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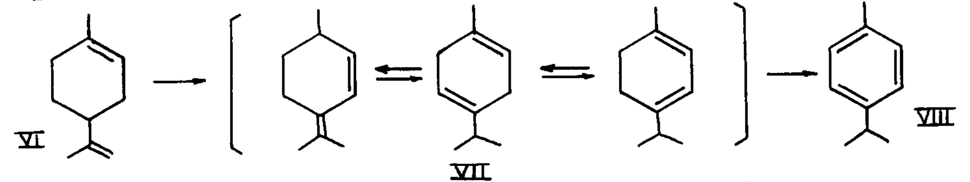

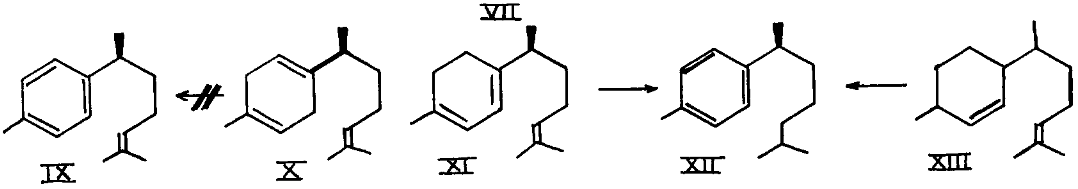

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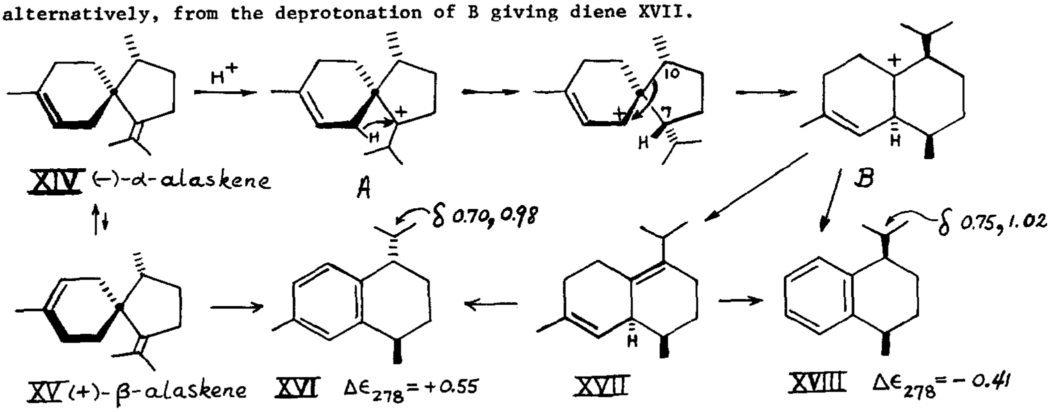
The retention of optical activity suggests protonation at the isopropylidene followed by hydride abstraction (either intra- or intermolecular) to form an intermediate cyclohexadienyl cation. Thus dehydrogenation occurs only when aromatics cannot be obtained by other routes, as in the case of XIII $\rightarrow$ XII which occurs slowly but in excellent yield.

In other cases rearrangement must occur prior to aromatization. The alaskenes (XIV and XV) afford mixtures of isocalamenenes XVI and XVIII in high yield[3] on exposure to TFA. The isocalamenene structure was assigned on the basis of a compatible mass spectrum and NMR, and by dehydrogenation (S, triglyme) to the known naphthalene.[4] The diastereomer ratio, determined by NMR (note the different chemical shifts for the i-Pr signals), XVIII:XVI, was 2:3 from β-alaskene and 3:1 from α-alaskene.[5] The only pathway, of the many considered, that offered an explanation for this stereoselectivity is shown below (in the case α-alaskene) — the hydride shift in intermediate A establishes the cis relationship. The smaller amount of XVI produced is probably due to some prior equilibration between α- and β-alaskene, or alternatively, from the deprotonation of B giving diene XVII.



Dehydrogenations have also been observed using trichloroacetic acid with catalysis by sulfuric acid. In this case reduction products are observed, $CHCl_3$ and HCO_2H; and $CHCl_3$ has been shown to be produced at the same rate as cymene in the reaction with limonene.

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REFERENCES

1. N. H. Andersen, Tetrahedron Letters, 1755 (1970); N. H. Andersen and D. D. Syrdal, ibid, 2277 (1970); N. H. Andersen and M. S. Falcone, Chem. Ind., 62 (1971).

2. TFA does not appear to promote disproportionation. We have not been able to demonstrate the presence of dihydrosesquiterpenes in any of these reactions.

3. The absence of calamene (V) in the products from the alaskenes is apparently a reflection of the axial disposition of C-10 which facilitates the migration of C-10 in preference to C-7.

4. The authentic naphthalene (=isocadalene) was prepared from acorone by a slight modification of the reported sequence - V. Sykora, V. Herout, J. Pliva, and F. Sorm, Coll. Czech. Chem. Comm., **23**, 1072 (1958).

5. The Δε-values are calculated assuming no epimerization at the methyl substituent. The cis/trans assignment was made by NMR comparison with the calamenenes.