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# A ONE-STEP CONVERSION OF (+)- β -HIMACHALENE INTO (+)-CUPARENE

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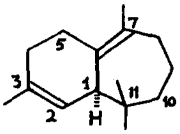
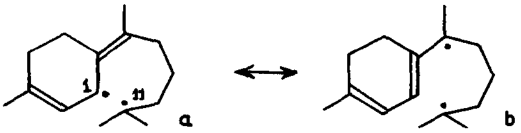
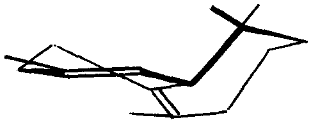
AN examination of the structure[1] of β-himachalene (I) shows that the 1,11-linkage may be especially vulnerable to thermal dissociation as the resulting $C_1$-radical (II), being biallylic, would be energetically favoured. Furthermore, a study of the molecular models for the most likely conformations (III, IV)[1] of β-himachalene reveals the $C_1$-$C_{11}$ bond to be conformationally strained, thus further lowering the energy barrier to dissociation. It may also be noted that the odd-electron at $C_{11}$ in II is also located on a tertiary carbon, a situation, which is not unfavourable. Thus, thermal rearrangement of β-himachalene may be reasonably expected to prefer a pathway involving II. One consequence of this is the possibility of collapse of II (cf. IIb) to dihydrocuparene (V). It was to study this aspect that we investigated the thermal reorganisation of β-himachalene and the results, which bear out this expectation, are briefly described below.



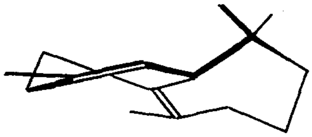
I



II



III



IV

When β-himachalene was slowly dropped ($N_2$, ~600 mm. press.) through a vertical bed of broken Pyrex glass pieces, maintained at 480-490° * (outside temp.), the product (~80% recovery) consisted of at least ten components, besides ~15% β-himachalene. The major product (35-40% by GLC) was isolated by a combination of fractional distillation and inverted-dry-column chromatography[2] over 10% $AgNO_3$-$SiO_2$ gel and was

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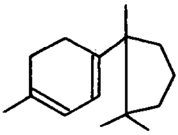
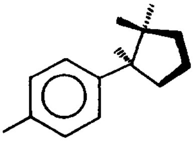
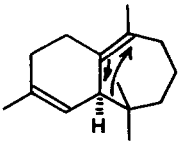
*Close to the threshold temp.; very little rearrangement occurred at ~ 460°.

identified (IR, PMR, GLC, TLC) as cuparene (VI). The isolation of cuparene, rather than dihydrocuparene, is not unexpected, in view of the known[3] facile aromatization of dihydrocuparenes by exposure to air. Cuparene obtained this way had $[\alpha]_D$ +11.6° and was over 95% pure by GLC. It was again rigorously purified and the product (~100% pure by GLC and PMR) showed $[\alpha]_D$ +12.47°. Thus, cuparene resulting from the pyrolysis of (+)-β-himachalene (I) is not completely racemised (pure cuparene has $[\alpha]_D$ +65°[4]) as would have been expected from a pathway involving completely free II. The formation of (+)-cuparene of some 20% optical purity, requires that the cleavage of the 1,11-bond and the formation of 7,11- and 1,6-bonds must be proceeding partly by a concerted mechanism*, such as VII. Formula I represents[1] the absolute stereostructure of (+)-β-himachalene and, the migration of the $C_{11}$ to $C_7$ from the β-face, leads to the R-chirality[5] at $C_7$ and, this is what has been established[4] for (+)-cuparene (VI).


V


VI


VII

The identification of other products of pyrolysis will be dealt with in the fuller publication.

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*A concerted mechanism for the above thermal rearrangement, which falls into the category of (1,3)sigmatropic transformations, is contraindicated by the selection rules of Woodward and Hoffmann[6], which predict a low probability for a (1,3) carbon shift in small to medium-sized rings.

## REFERENCES

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