

An Accidental Synthesis of ($\pm$)-Herbertene

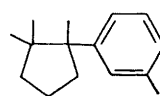
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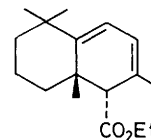
($\pm$)-Herbertene (**1**) was synthesized by acid-catalysed rearrangement of the alcohol (**3**) with a drimane skeleton.

(–)-Herbertene, a new aromatic sesquiterpene from the liverwort *Herberta aduna*, was recently described by Matsuo *et al.*¹ It has the 1,2,2-trimethyl-1-*m*-tolylcyclopentane structure while the well known cuparene-type sesquiterpenes contain a *p*-tolyl-residue (*e.g.* ref. 2).

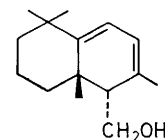
This communication describes a serendipitous synthesis of (**1**). Some years ago we reported³ the preparation of the



(1)



(2)



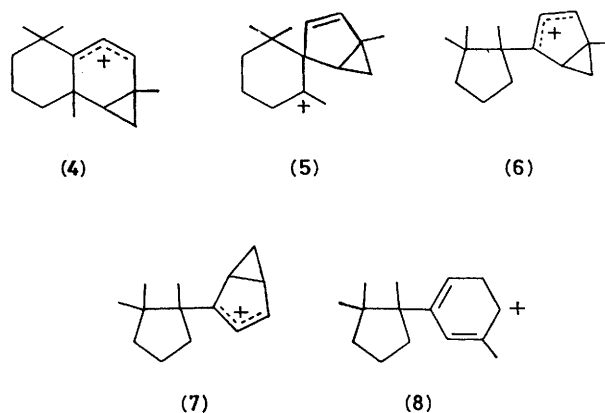
(3)

bicyclic ester (2) with a drimane skeleton, reduction of which with LiAlH_4 in ether yielded (3) (80% yield). We wanted to transform (3) into a bicyclo[5.4.0]-framework by ring-enlargement. Treatment of (3) with acid (0.02 M perchloric acid in formic acid, 10 min at reflux) gave rise to a mixture of volatile hydrocarbons (43% yield; the residue of the distillation was a hard, resinous material). About 95% of this mixture consisted of only two components in a 3:1 ratio;† they were isolated by preparative g.l.c. and the main product turned out to be identical in every respect (g.l.c. i.r., and ^1H n.m.r.) with herbertene.‡

The mechanistic interpretation of the unexpectedly specific rearrangement of (3) to (1) is uncertain. Especially remarkable is the lack of formation of cuparene.† The following explanation is suggested. After formation of (4), two successive 1,2-migrations lead to (5) and (6), respectively. Intermediate (6) is in equilibrium with four other cyclopropylcarbinyl ions resulting from cyclopropane migrations.⁴ Three of these can open to give a cyclohexadienyl ion with the required *meta*-substitution, and two a cyclohexadienyl ion with *para*-substitution. The $\Delta\Delta G^\ddagger$ value for the cyclopropane rearrangement and the formation of the cyclohexadienyl ions is probably small⁴ (≤ 4 kcal/mol) compared with the overall $\Delta G^\ddagger$ for these reactions. Therefore the relative stability of (6) and its four isomers could be of importance in the outcome of the reaction. *E.g.* collapse of (7) which we suppose to be the most stable among these isomers, would lead to (8) and thus to (1).⁵ There are other possible formal ways to convert (3) into (1).

† There is less than 0.5% of cuparene, if any, in the reaction-mixture (g.l.c.-mass spectrometry). Cuparene is stable under the reaction conditions.

‡ The mass spectra of cuparene and herbertene are nearly identical with one small but reproducible difference: the ratio of the intensities of the peaks at m/z 119 and 120 is *ca.* 2 in cuparene and *ca.* 0.5 in herbertene.



I thank Professor A. Matsuo for comparing our spectra (i.r., ^1H n.m.r.) with those of herbertene and for g.l.c. co-injection of our sample with an authentic material. I also thank Professor D. Arigoni for discussion and Dr. J. Schmid for the mass spectra.

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References

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- 4 R. F. Childs, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, 1968, **90**, 7144; R. F. Childs and S. Winstein, *ibid.*, p. 7146.
- 5 For similar homoallyl-cyclopropylcarbinyl cation rearrangements see *e.g.* Y. Hikino and P. de Mayo, *Chem. Commun.*, 1965, 550; S. W. Pelletier, S. Nakamura, and Y. Shimizu, *ibid.*, 1966, 727.