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THE REAL STRUCTURE OF "ALBENE" AND ITS TOTAL SYNTHESIS

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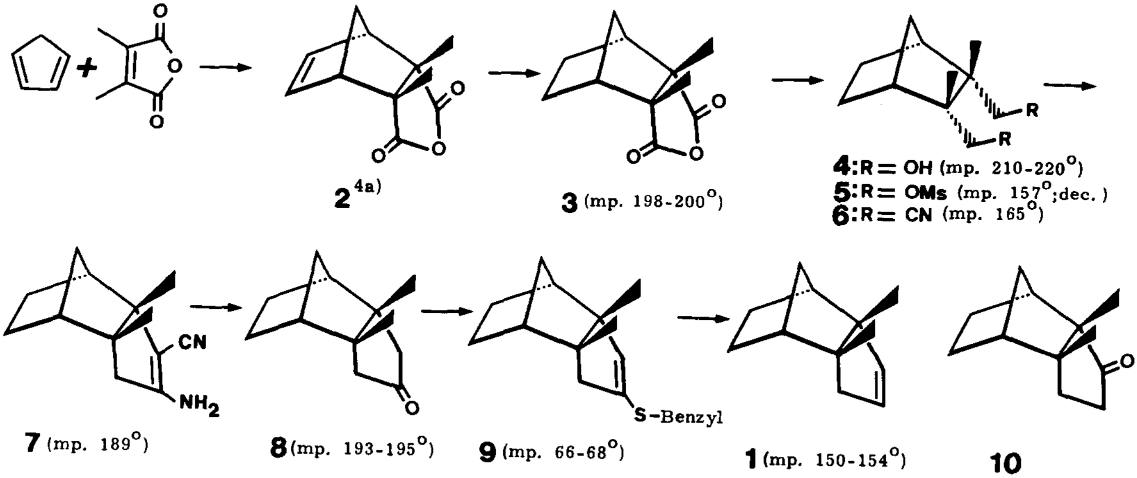
Ten years after the first isolation[1)] of the optically active crystalline hydrocarbon "albene" from petasites albus; its constitution and absolute configuration were elucidated in 1972 by Šorm et al.[2)] as formula **1** . According to the following scheme I we have synthesized that compound **1** .

Scheme I:

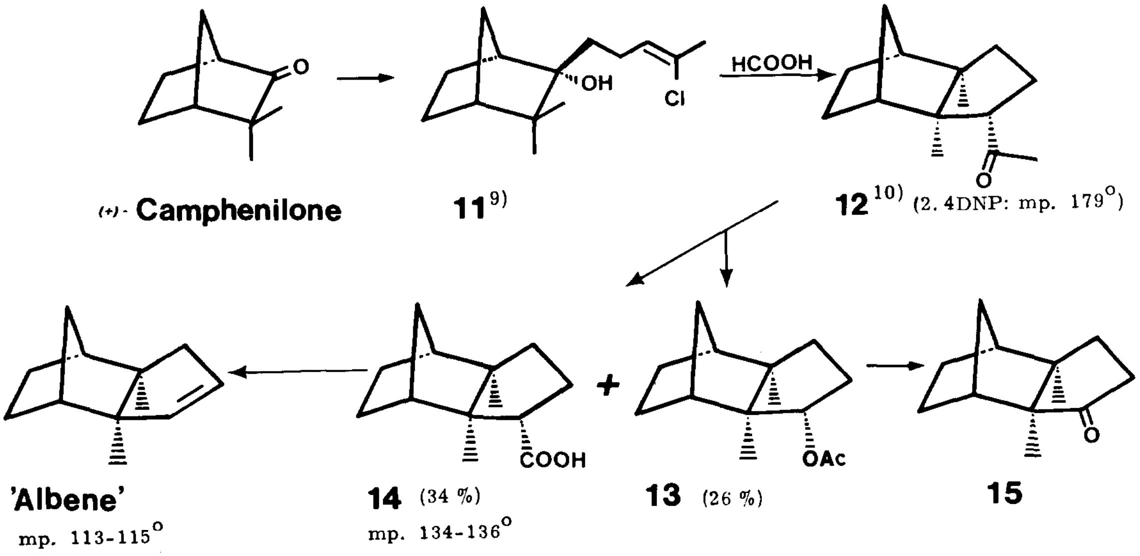


Surprisingly the material produced in this way as a racemate (mp. 150 - 154°) markedly differed in melting point[3)] (reported 110 - 115°) and ^{1}H NMR spectral properties from the data published[2)] for natural "albene". The relative configuration of our synthetic substance **1** was originally based on general considerations[4)] for the Diels-Alder adduct **2** ; but very recently[5)] we established its structure definitely by an X-ray analysis of **9** . Since our synthetic hydrocarbon **1** proved not to be identical to natural "albene" , the structure of the latter had to be revised and due to this fact further investigations remained necessary to disclose its real constitution.

In the meantime Lansbury[6)], in contrast to our findings, seemingly secured Šorm's statement by synthesizing a ketone, claimed to present a regioisomer of **8** and to possess formula **10**. Actually this unsymmetrical endo-tricyclodecanone derivative of Lansbury's has been identified by direct comparison with degradation material of "albene" from a natural source.

An X-ray analysis having confirmed the stereochemical outcome of our first synthesis as **1** (which is therefore named "isoalbene"), we took advantage of Lansbury's identification and repeated his reaction sequence. Starting with the optically pure (+)-enantiomer of camphenilone we easily produced the homogeneous acetyl compound **12** of Lansbury's, which still displayed a significant optical rotation. In order to achieve the corresponding tricyclic olefin via conversion of **15** into a thioenolether we followed scheme II . (The relative configuration of all intermediates given within scheme II deviates from that of Lansbury in accordance with the stereochemistry which is actually observed.)

Scheme II:



Treatment of **12** with trifluoroacetic acid anhydride, hydrogenperoxide (80 %) and catalytic amounts of sulfuric acid in acetic acid as a solvent leads to a 26 % yield of **13**, which in turn was saponified and consequently submitted to Collins oxidation, thereby affording Lansbury's ketone **15**. - Wrongly assigned by him as **10**. - The tricyclodecanone **15** formed a 2.4-dinitrophenylhydrazone, melting at 167 - 168°.

Surprisingly enough, the Baeyer-Villiger cleavage of **12** was accompanied by a homogeneous (deduced from the ^{13}C NMR spectrum) crystalline carboxylic acid **14** in 34 % yield. Oxidative decarboxylation of the latter in the presence of lead tetraacetate[7)] resulted in the desired 2.6-dimethyl-*exo*-tricyclo$[5.2.1.0^{2,6}]$dec-3-ene (mp. 113 - 115°) being formed.

The material thus gained, proved to be identical to natural "albene" in every respect, with the exception of lower optical purity, probably on account of partial racemisation during carbocation rearrangement.

Furthermore, by using the above synthetic route the absolute configuration of natural "albene" can be related to (+)-camphenilone. A detailed ^{13}C NMR study[8)] on "albene", "isoalbene" and the corresponding dihydroproducts confirmed the respective assignments of relative configuration, as well.

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2) K. Vokáč, Z. Samek, V. Herout and F. Šorm, *Tetrahedron Lett.*, 1665 (1972).

3) All melting point determinations made on samples in sealed capillaries, since the compounds especially the tricyclic olefins are, even at room temperature, extremely volatile.

4) (a) O. Diels and K. Alder, *Ber. dtsch. Chem. Ges.* 62, 557 (1929).
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6) P. T. Lansbury and R. M. Boden, *Tetrahedron Lett.*, 5017 (1973).

7) R. A. Sheldon and J. K. Kochi, *Organic Reactions* **19**, 279 (1972).

8) W. Kreiser, L. Janitschke and L. Ernst, Tetrahedron 33, (1977).

9) In fact a mixture of **11** was used, containing 5 % impurity resulting from endo-attack on camphenilone. Moreover the reaction sequence was started with 2-chloro-5-iodopent-2-ene as a mixture of geometric isomers.

10) Whereas all intermediates of scheme I are nicely crystalline compounds, scheme II deals with oils only (with the exceptions of **14** and "albene" itself).

11) Just these days T. Ross Kelly, Boston College informed us, that he has followed a similar route directed to the synthesis of "isoalbene". (Vid.: T. R. Kelly, H. M. Dali and W. G. Tsang, Tetrahedron Lett., 3859 (1977).