

The Putative Structure of Albene; X-Ray Structure of an Analogue

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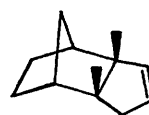
Summary As a result of the X-ray analysis on the thioenolether (4) the proposed structure of the tricyclic natural hydrocarbon albene has to be revised; furthermore the relative configuration of the *endo* Diels-Alder adduct (3) is secured.

PLANTS of the genera *petasites* and *adenostyles* contain an optically active crystalline hydrocarbon first isolated and named 'albene' by Novotný and his co-workers.¹ In 1972 Šorm² substituted earlier structure assignments by formula (1) for albene, and correlated at the same time its absolute configuration to (+)-camphene. Lansbury³ later published several synthetic efforts apparently directed towards the synthesis of albene. He reported an elegant route to a compound considered to be represented by formula (2). This ketone of Lansbury was shown to be identical with a degradation product of natural albene, thus seemingly confirming the previous assigned structure of the latter.

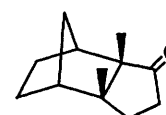
Meanwhile we had started an independent synthesis of albene, the first step of which comprised a Diels-Alder reaction⁴ between cyclopentadiene and dimethylmaleic acid anhydride⁵ leading to (3). Transformation of (3) *via*

the thioenolether (4) to the tricyclocene (1) was achieved in the conventional manner.

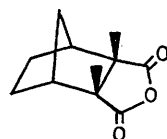
Surprisingly our synthetic racemic material, m.p. 150—154 °C, differed from natural albene not only in the reported m.p. (110—115 °C) but also in its ¹H n.m.r. spectrum.†



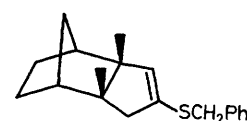
(1)



(2)



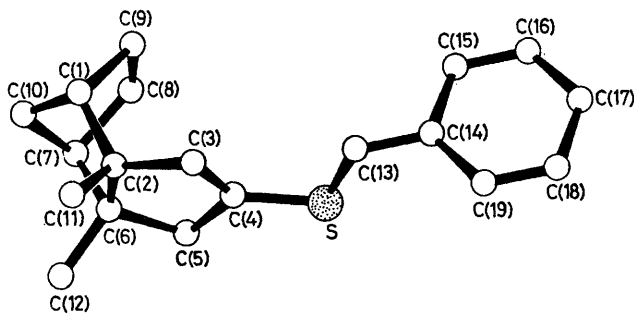
(3)



(4)

† All m.p.s were measured in sealed tubes.

Hydrogenation of our product afforded a substance, m.p. 182—186 °C, with inner symmetry as indicated by its ^{13}C n.m.r. spectra, whereas the quoted m.p. for the likewise achiral dihydro albene is 125—130 °C. In view of the fact that the two olefinic compounds are clearly not identical, we wondered which one was actually represented by formula (1). The relative configuration of our own molecule was initially based on the assignment⁶ analogous to that of the demethyl derivative of (3).



FIGURE

This problem has now been solved by X-ray analysis. As the hydrocarbon itself proved too volatile, the thioenol-ether (4) was chosen as the most closely related derivative. The structure is shown in the Figure. Crystals of (4) (m.p.

66—68 °C) are monoclinic, space group $P2_1/c$ with $a = 18.081(13)$, $b = 10.881(6)$, $c = 8.153(5)$ Å, $\beta = 93.41(9)^\circ$, $Z = 4$. The structure was solved by direct methods and refined to $R = 0.058$ for 2492 unique reflections with $F \geq 3.0\sigma(F)$. Hydrogen atoms were located and refined with individual isotropic temperature factors. A very long annular C(2)—C(6) bond distance of 1.584(4) Å is observed. Evidence for π -delocalisation over the S—C=C system is provided by the shortness of S—C(4) [1.750(3)] bond in comparison to S—C(13) [1.813(3) Å]. All other bond distances lie within the expected ranges. The C(1)—C(10)—C(7) angle is $93.8(2)^\circ$ ‡

As a result, the assignment of Diels and Alder⁴ for (3) was confirmed and the structure given by Šorm² to natural albene is shown to be no longer valid. By an additional synthesis of natural albene⁷ we have now obtained evidence, that the compound in fact corresponds to the omitted formula (1a) in Šorm's paper.² Its absolute configuration requires a new interpretation of the experimental data given therein.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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

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⁷ W. Kreiser and L. Janitschke, unpublished results.