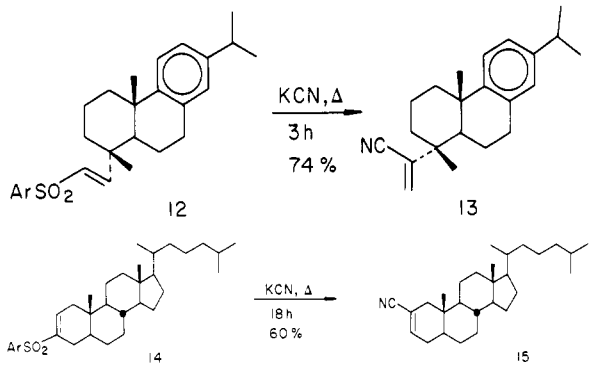
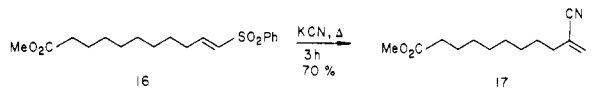


Finally, as exemplified by ester **16**, the reaction conditions are compatible with base-labile functionality.[18a]



Given the variety of established routes to vinyl sulfones,[19] we expect this method for carbon–carbon bond formation to be of general application. We also expect that reversal of olefin polarization, especially with concomitant carbon–carbon bond formation, will be an increasingly important concept in carbon skeleton assembly.

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Registry No. 1, 43208-94-2; 2, 16212-05-8; 3, 79328-72-6; 4, 79328-73-7; 5, 79328-74-8; 7, 18744-24-6; 8, 112-54-9; 9, 40137-12-0; 10, 79328-75-9; 11, 79328-76-0; 12, 79328-77-1; 13, 79328-78-2; 14, 79356-96-0; 15, 79356-97-1; 16, 79328-79-3; 17, 79328-80-6; dehydroabietinal, 13601-88-2.

(19) For recent advances in sulfone chemistry, see: (a) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979. (b) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.

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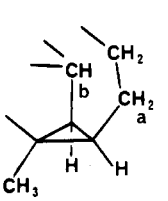
Cycloseychellene: A Structural Revision

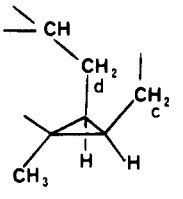
Summary: Investigation of the 400-MHz proton NMR spectra of the original structure **1** reported for cycloseychellene as well as the natural product leads to the conclusion that the actual carbon skeleton for natural cycloseychellene is represented as structure **2**.

Sir: Unequivocal synthesis of the molecule having the structure reported for cycloseychellene[1] produced a hydrocarbon, $C_{15}H_{24}$, the spectral properties and chromatographic behavior of which were unlike those of the natural product.[2] Since the synthesis was straightforward, we elected to remove this ambiguity by first interpreting the 400-MHz NMR spectrum of our synthetic material to ascertain that it is structure **1** and then interpreting the high-field NMR spectrum of natural cycloseychellene[3] as that of structure **2**.

The 400-MHz proton NMR spectra of **1** and **2** are shown in Figure 1. The synthetic and natural hydrocarbons are clearly distinct entities. The reasoning which distinguishes compound **1** from **2** is as follows. The synthesis of **1**[1] and the equilibration of **2** with seychellene,[1,2,4] a substance of certain structure, allows us to specify the essential carbon framework of compounds **1** and **2**. The difference between these two structures is localized with respect to the cyclopropyl ring. Appropriate partial structures which identify these compounds are **1A** and **2A**.



1A



2A

The assignments of the spectra are reduced to identifying the methylene and methine hydrogen atoms (a–d) adjacent to the cyclopropyl ring and determining whether there are three or four such protons in each structure. This seemingly trivial task is complicated by the fact that the cyclopropyl carbinyl protons exhibit unusual coupling patterns. The cyclopropyl resonances in structure **1** occur at δ 0.55 (a doublet of triplets) and 0.85 (a doublet). The doublet of triplets in the upfield resonance is collapsed to a doublet by decoupling a methylene group (a) at δ 1.87 to establish the cyclopropyl–methylene connectivity. The downfield cyclopropyl doublet is collapsed to a singlet by irradiation at δ 0.55. The coupling of ~0 Hz between the cyclopropyl and bridgehead proton (b) in structure **1** is the result of a 75° dihedral angle.[5] We point out that this geometrical decoupling can occur only if the adjacent group is a methine. An adjacent methylene group would have at least one significant J coupling into the cyclopropyl ring.

The spectrum of natural cycloseychellene features cyclopropyl resonances at δ 0.59 and 0.88. The fine structure in both cases is a four-line doublet of doublets. Decoupling the low-field cyclopropyl proton at δ 0.88 simplified the high-field cyclopropyl proton at δ 0.59 to a doublet and located the resonance at δ 1.656 as the last portion of an ABX spin system. The diastereotopic methylene protons (c) at δ 1.656 and 1.442 have dihedral angles of 40° and 80°, respectively, and show J couplings to the cyclopropyl resonance of 4 and 0 Hz.[5] Decoupling of the resonance at δ 1.442 and examination of the unperturbed pattern located another diastereotopic methylene group (d, δ 1.693 and 1.753). Decoupling the cyclopropyl resonance at δ 0.59 also confirms this assignment. The assessment of partial structure **1A** for natural cycloseychellene is completed when dihedral angles of 100° and 20° are found in a

(1) Welch, S. C.; Gruber, J. M.; Chou, C.-Y.; Willcott, M. R.; Inners, R. *J. Org. Chem.*, preceding paper in this issue.

(2) Terhune, S. J.; Hogg, J. W.; Lawrence, B. M. *Tetrahedron Lett.* **1973**, 4705.

(3) Natural cycloseychellene (**2**, 0.0397 g) was reisolated from West Indian Patchouli Oil (7.857 g), Bruce Starke and Co., according to ref 2. This essential oil was obtained from Dr. B. M. Lawrence, R. J. Reynolds Tobacco Co. We thank Dr. Lawrence for this generous gift and copies of his spectra.

(4) Wolff, G.; Ourisson, G. *Tetrahedron Lett.* **1968**, 3849; *Tetrahedron* **196.**, *25*, 4903.

(5) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

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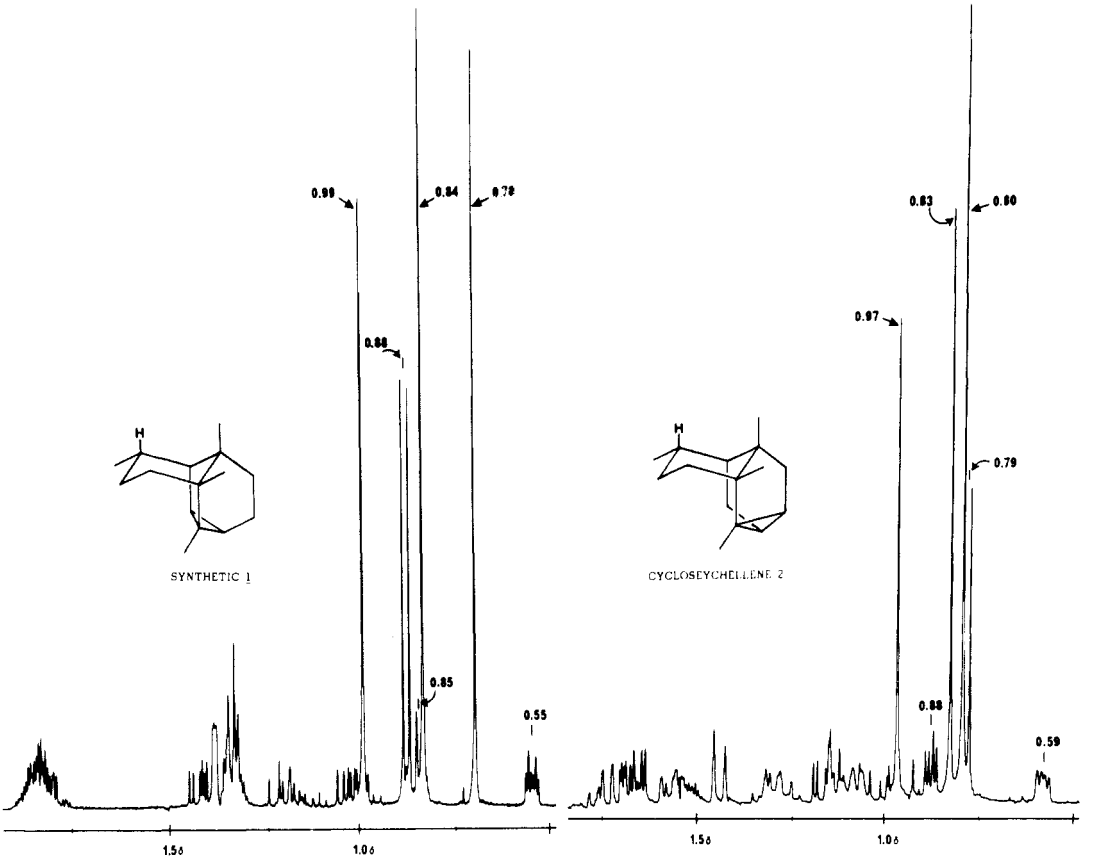

Figure 1. 400-MHz proton NMR spectra (C_6D_6).

Drieding stereomodel for these methylene protons and the cyclopropyl hydrogen. These lead to the small coupling and a 6-Hz coupling seen in the upfield cyclopropyl resonance.

An alternative interpretation can be made from a simple heuristic. Cyclopropyl carbinyl hydrogens are shifted to low field usually in the range of δ 1.44–2.0. Of course methine hydrogens also resonate in this region. We predict that structure **1** has four low-field resonances while structure **2** has six such low-field resonances. Indeed, the number of resonances in each of the δ 1.44–2.0 windows bears out those assignments.

In summary, we have shown that interpretation of the 400-MHz proton NMR spectra in Figure 1 verifies structure **1** for ur synthetic material.[1] We have also shown that it is necessary to revise the structure of natural cycloseychellene to that of **2**.

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