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SYNTHESIS OF 5-THIABICYCLO[2.1.1]HEXANE

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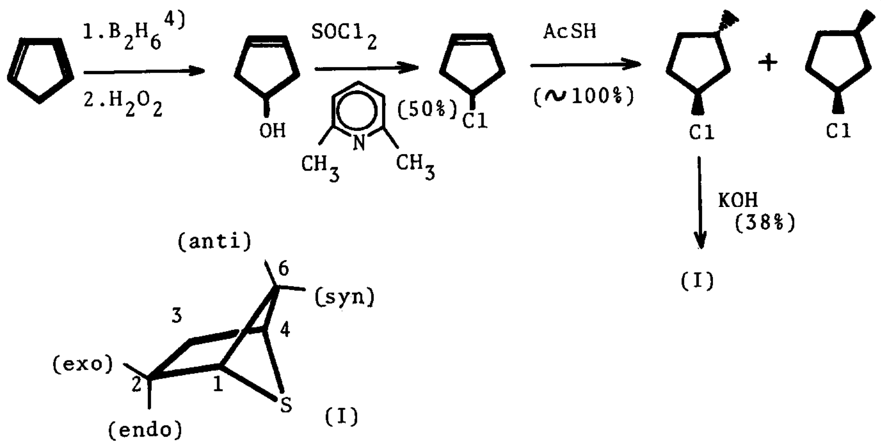
Despite their structural similarity to the carbon analogues, strained sulfur-bridged polycyclics have been much less studied. And except episulfide, the smallest member of the sulfur-bridged bicyclics ever reported was 2- or 7-thiabicyclo[2.2.1]heptane.[1] With expectation of applying thiapolycyclics to the heteroatom participation problem in carbonium ion[2] or free radical chemistry,[3] we have been trying to prepare new sulfur bridged polycyclics of partial symmetry which have substituents on an appropriate position.
Now we wish to report the successful synthesis of the parent compound of a new skelton of the series, 5-thiabicyclo[2.1.1]hexane, I, which would promise future success of syntheses of the series and development of the mechanism of heteroatom participation.

Synthetic route to I is shown in Chart I.

Chart I



4-Hydroxycyclopentene was prepared according to the reported procedure.[4] Chlorine substitution of the alcohol with thionyl chloride in methylene chloride in the presence of a small amount of 2,6-lutidine gave 4-chlorocyclopentene in ca. 50 % yield. Addition of freshly distilled thioacetic acid to the chloride gave cis- and trans-3-chlorocyclopentyl thioacetate in approximately equal amount.[5] The mixture of isomeric thioacetates was added dropweise to refluxing aqueous ethanol solution of potassium hydroxide and I was obtained in 38 % yield based on the trans isomer. I was a colorless, highly sublimable crystal and was purified by preparative VPC separation.

IR spectrum of I (CCl_4); 2995, 2925, 2900, 2865, 1440, 1293, 1280, 1235, 1210-1180, 1110-1070, 957-850, 575 cm^{-1}. Massspectrum; m/e 100 (molecular peak, relative intensity 100), 85 (84), 72(72) and 67 (95). NMR spectrum ($CDCl_3$, TMS); 3.84δ (thin multiplet, H_1, H_4), 2.89δ (double quintet, H_{6s},J_{gem} = 6.8 H_z $J_{6s,1}$ = $J_{6s,2n}$ = 2.3 H_z), 2.44-2.52δ (multiplet, H_{2x},H_{2n},H_{3x},H_{3n}), 1.72δ (doublet, H_{6a},J_{gem} = 6.8 H_z).

Of most interesting to note is that remarkably large chemical shift difference, $\Delta\delta_6 = \delta_{6s} - \delta_{6a}$, was observed for C_6-H, while that for C_2-H ($\Delta\delta_2 = \left|\delta_{2x} - \delta_{2n}\right|$) was observed to be very small. This may indicate that the present bicyclic compound is considerably deformed. In order to gain further insights, electron diffraction study is scheduled.

Oxidation of I with hydrogen peroxide in acetic acid gave the corresponding sulfone quantitatively. IR characteristic absorptions were observed at 1278 and 1140 cm^{-1}. Its m.p. was 151-152° (with subliming) after sublimation and recrystallization (ethyl acetate and hexane).

Analysis, calc'd for C_5H_8 SO_2; C; 45.55, H: 6.10, S: 24.26; found, C: 45.29, H: 6.23, S: 23.96.

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(2) Carbonium ion participation: eq. G. M. Bennett, and A. L. Hock, J. Chem. Soc., 477 (1927). A large o-acceleration was observed for the solvolysis of o- and p-(2,5-dithiacyclopentyl)benzyl chloride; M. Hojo, T. Ichi, Y. Tamaru and Z. Yoshida, J. Am. Chem. Soc., 91, 231 (1969).

These model systems for the sulfur-participation to carbonium ion, however, have ambiguity on (steric or spatial) requirement because allowed internal rotation of sulfur containning group and/or carbonium ion containning group does not fix the S-C^+ geometry. 7-Thiabicyclo[2.2.1] system seems to be a better model for the purpose than those and in our preliminary experiment, a considerably great acceleration (more than 10^3) was observed for the solvolysis of the 2-endo chloride compared with that of the corresponding carbon analogue. The results will be published soon. To estimate the angular contribution of effective overlap to the participation, we should prepare [2.1.1] or [1.1.1] skelton having sulfur atom on the 1-bridge. This work deals with the first successful attempt along the line.

(3) Free radical participation: eg., W. G. Bentrude and J. C. Martin, J. Am. Chem. Soc., 84, 1561 (1962).

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(5) The procedure is practically the same as reported for the preparation of 4-chlorocyclohexyl thioacetate; 1a).