

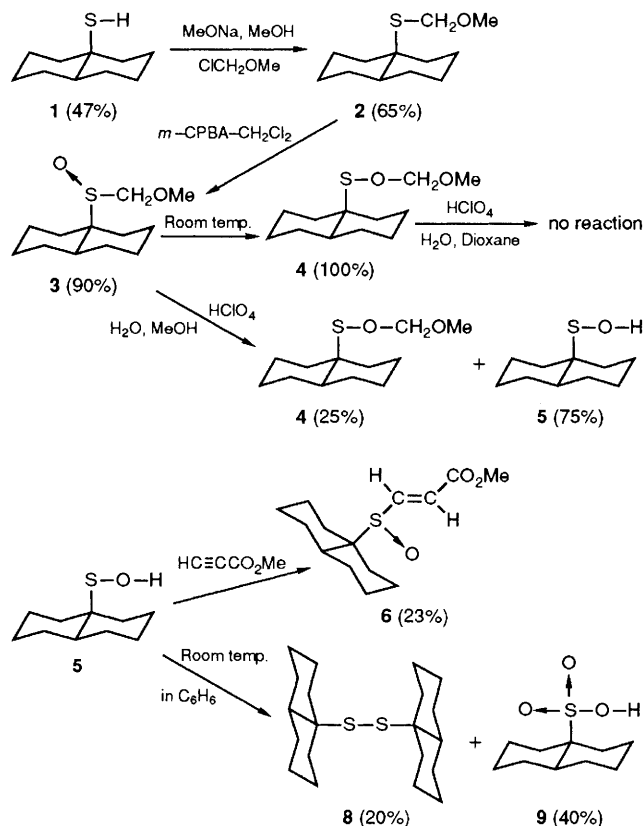
Synthesis of a Stable Sulfenic Acid, *trans*-Decalin-9-sulfenic Acid†

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Hydrolysis of *trans*-9-decalyl methoxymethyl sulfoxide with 7% perchloric acid in MeOH–H₂O (2 : 1) gave crystalline *trans*-decalin-9-sulfenic acid whose structure was confirmed by IR, NMR and mass spectrometry; addition to methyl propiolate affording methyl *trans*-3-(*trans*-9-decalylsulfinyl)acrylate.

Since the first synthesis of anthraquinone-1-sulfenic acid by Fries in 1912,¹ sulfenic acids have been interesting as important intermediates in organosulfur chemistry.² Because of their instability, despite numerous efforts to prepare sulfenic acids,^{2d-f} there are only nine isolated examples^{1,3-8} and their chemistry has not yet been explored. The sulfenic acids isolated to date have either a heteroatom or an unsaturated bond and they have been considered to be stabilized by electronic effects, intramolecular hydrogen bonding^{2f} or steric inhibition of dimerization. 2-Methylpropane-2-sulfenic acid is an example of a sterically hindered aliphatic sulfenic acid, although it is observed only in solution.⁹ It is interesting to examine how bulk stabilizes and protects sulfenic acids and their derivatives towards dimerization and nucleophilic attack at the sulfur atom. We thought that the *trans*-9-decalyl group which has four axial protons would protect the sulfenic acid functional group, and now describe the first synthesis of a bulky aliphatic sulfenic acid, *trans*-decalin-9-sulfenic acid.



Scheme 1 Synthesis and reactions of *trans*-decalin-9-sulfenic acid and its derivatives

trans-Decalin-9-thiol **1** was prepared by hydrolysis of *trans*-9-decalyl thioacetate produced by the addition of thioacetic acid to Δ^9 -octalin,¹⁰ and then separated from the *cis*-isomer by repeated column chromatography. Treatment of the thiol **1** with methoxymethyl chloride gave the corresponding methoxymethyl sulfide **2** (60%). The sulfide **2** was oxidized with *m*-chloroperbenzoic acid (mCPBA) in CH₂Cl₂ affording *trans*-9-decalyl methoxymethyl sulfoxide **3** (90%). Recently, it was reported that acidic hydrolysis of methoxymethyl phenyl sulfoxide involves benzenesulfenic acid as an intermediate.¹¹ Therefore, acidic hydrolysis of the sulfoxide **3** was attempted. The sulfoxide **3** readily underwent rearrangement to the corresponding sulfenate **4** quantitatively after 8 hours at room temperature. Unlike methoxymethyl benzenesulfenate,¹¹ the sulfenate **4** was not hydrolysed with 7% perchloric acid in dioxane–water (2 : 1) after 2 hours at room temperature. Direct acidic hydrolysis of the sulfoxide **3** with 7% perchloric acid in MeOH–H₂O (2 : 1) at room temperature for 10 min gave **4** (25%) and another product **5** (75%) after separation by column chromatography (silica gel–benzene). The product **5** is a crystalline solid, m.p. 52–54 °C, *m/z* 137 (100%) (decalyl cation) and 186 (*M*⁺, 10.2%) (HRMS, found: *m/z* 186.1075; calc. for C₁₀H₁₈OS 186.1074). An OH stretching band at 3200 cm⁻¹, and a strong band at 760 cm⁻¹ were observed in its IR spectrum. The ¹H NMR (CDCl₃) spectrum showed δ 3.29 (1H, s, OH, readily exchangeable with D₂O) and 0.6–2.6 (17H, m, decalyl CH₂ and CH). The UV spectrum showed λ_{max} /nm 210 (ϵ 1010 dm³ mol⁻¹ cm⁻¹) and 270.5 (ϵ 210) in acetonitrile. These data support the structure of **5** as *trans*-decalin-9-sulfenic acid.

Trapping reactions of transient sulfenic acids with carbon–carbon multiple bonds to yield sulfoxides are frequently employed for their characterization.^{2d-f,7,9} The structure of **5** was further confirmed by reaction with methyl propiolate at room temperature for 1 min in CDCl₃. The product, methyl *trans*-3-(*trans*-9-decalylsulfinyl)acrylate **6**,‡ was obtained in 23% yield, although it was further converted at room temperature for 1 h to methyl *trans*-3-(*trans*-9-decalylsulfonyl)acrylate **7** in 60% yield. This sulfenic acid **5** undergoes disproportionation in benzene after 30 min at 30 °C to give the corresponding disulfide **8** and sulfonic acid **9**, whereas it is stable in acetonitrile for 1 day at room temperature. Compound **5** is the first example of a sulfenic acid bearing neither an unsaturated bond nor a heteroatom, and its stability is probably due mainly to the steric inhibition of the approach of the SOH groups of two molecules of the sulfenic acid to one another by the four axial protons of the *trans*-9-decalyl group.

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† The common name *trans*-decalin is used in this paper instead of bicyclo[4.4.0]decane.

‡ Selected spectroscopic data for **6**: ¹H NMR δ (CDCl₃) 7.70 (d, 1H, *J* 14 Hz, CH), 6.65 (d, 1H, *J* 14 Hz, CH), 3.72 (s, 3H, OCH₃) and 0.8–2.5 (m, 17H, decalyl CH₂ and CH); IR (neat) ν_{max} /cm⁻¹ 1730 and 1060 cm⁻¹.

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