three peaks at δ 136.0, 132.1, and 127.5 corresponds to the molecular symmetry; UV(cyclohexane) λ_{max} (log ϵ) 236 (sh, 4.44), 266 (sh, 4.86), 275 (5.14), 296 (4.46), 331 (3.91), 388 (sh, 290), 403 (2.83).

The molecular structure of **3** has been determined by X-ray crystallography,[14] and Figure 1 is an ORTEP drawing[17] of **3**. The crystallographic 2-fold axis coincident with the C(1)–C(2) bond passes through the midpoints of C(12)–C(12′) and C(15)–C(15′) bonds, and this makes only half of the molecule independent. The central 7-membered ring assumes a boat conformation, and the whole molecular shape closely approximates a saddle form. The C–C bonds can be classified into four groups: (1) the central core bonds (e.g, C(1)–C(14)) with bond distances of 1.447–1.466 Å, av 1.457 Å, (2) the spoke bonds (e.g. C(1)–C(2)) with bond distanes of 1.433–1.435 Å, av 1.434 Å, (3) the next outer bonds (e.g., C(2)–C(3)) with bond distances of 1.407–1.423 Å, av 1.414 Å and (4) the outermost bonds (e.g., C(3)–C(4)) with bond distances of 1.327–1.344 Å, av 1.338 Å. The average esd for each C–C bond is 0.005 Å.

Registry No. 3, 76276-09-0; **5**, 13688-64-7; **6**, 87586-74-1; **7**, 87586-75-2; **8**, 38309-89-6; **9**, 87586-76-3; **10**, 87586-78-5; **11**, 87597-03-3; **12**, 87597-04-4; **14**, 87586-79-6; **15**, 87586-80-9; **16**, 87586-81-0; **17**, 87586-82-1; dimethoxycarbonium fluoroborate, 18346-68-4.

Supplementary Material Available: Table SI of fractional atomic coordinates of [7]circulene (1 page). Ordering information is given on any current masthead page.

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(14) Crystal data of **3**: $C_{28}H_{14}$, M_r 350.4, monoclinic, space group $C2/c$, a = 13.106 (2) Å, b = 11.664 (2) Å, c = 11.015 (3) Å, β = 95.67 (1)°, U = 1675.5 (5) Å^3, Z = 4, D_x = 1.390 g cm^{-3}. Diffraction intensities were measured on a Rigaku four-circle diffractometer with graphite monochromatized Mo Kα radiation. A total of 2449 reflections was collected up to 2θ = 60°, among which 1535 were nonzero reflections. The structure was solved by the direct method (MULTAN-78)[15] and refined by the block-diagonal least squares (HBLS-V)[16] to the R index of 0.094 for nonzero reflections (non-hydrogen atoms anisotropically, hydrogen atoms isotropically).

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A Stable Sulfenic Acid, 9-Triptycenesulfenic Acid: Its Isolation and Characterization[1]

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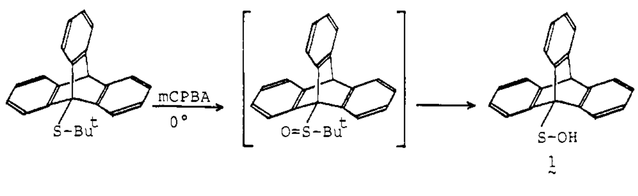
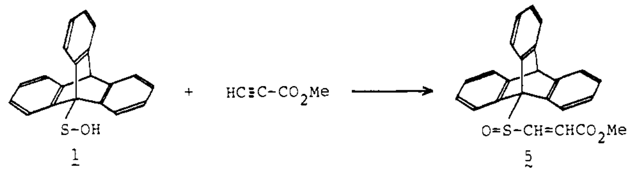
Received July 26, 1983

Although sulfenic acids are well recognized as important intermediates in organosulfur chemistry,[2] their high reactivity and the difficulty in generating them under mild conditions have precluded their isolation. Gas-phase conditions were sometimes employed for isolation and study of unstabilized sulfenic acid of short lifetimes.[2b] A few special examples known hitherto have been stabilized by their electronic properties and hydrogen bonding,[2a,c] while 2-methyl-2-propanesulfenic acid has been reported to be stable in solution[3] probably due to steric effects. Bulky groups have been used effectively to stabilize transient species such as [4]annulenes,[4] disilenes,[5] digermene,[6] and diphosphenes.[7] The steric properties of the triptycene skeleton have previously been applied to isolation of a variety of rotational[8,9] and phase isomers.[1] We now report the first isolation and characterization of a stable sulfenic acid, 9-triptycenesulfenic acid (**1**), whose stability may be attributed mainly to the steric nature of a triptycene skeleton.[10]

Scheme I



Scheme II



A solution of 9-(*tert*-butylthio)triptycene[11] (0.86 mmol) in dichloromethane (20 mL) was treated with 1 equiv of mCPBA in dichloromethane (10 mL) at 0 °C. The mixture was stirred 12 h (0–25 °C) and washed with an aqueous bicarbonate solution. The usual workup including preparative TLC (Merck, Art. 5717), using a 1:2 mixture of hexane and dichloromethane, provided single major product A (R_f 0.30) in addition to the recovered 9-(*tert*-butylthio)triptycene (R_f 0.85). Compound A, mp 204–205 °C dec, obtained in 77.5% yield, carries no *tert*-butyl group as readily confirmable by ^{1}H NMR and exhibits spectral properties[12a] completely consistent with the sulfenic acid **1** (Scheme I): (i) The conservation of the triptycene–sulfur linkage in the compound A is confirmed not only by the ^{13}C NMR signal at 65.11 ppm, which is characteristic of a triptycene bridgehead carbon bearing a divalent sulfur functionality,[13] but also by the IR band at 635 cm^{-1},

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(10) All new compounds gave satisfactory elemental analyses and/or spectral data.

(11) Obtained by the addition reaction of benzyne (generated from anthranilic acid and isopentyl nitrite in 1,2-dimethoxyethane) to 9-(*tert*-butylthio)anthracene. The detailed procedure has been submitted for publication in *Chemistry Letters*. ^{1}H NMR (CDCl$_3$) δ 1.72 (s, 9 H, *t*-Bu), 5.72 (s, 1 H, 10-H), 6.83–7.10 (m, 6 H, aromatic), 7.20–7.45 (m, 3 H, aromatic), 7.69–7.95 (m, 3 H, aromatic); ^{13}C NMR (CDCl$_3$) δ 34.25 (Me C's of *t*-Bu), 47.07 (quanternary C of *t*-Bu), 54.13 (10-C), 65.61 (9-C), 122.99, 123.85, 124.42, 125.27 (aromatic C's with H), 145.23, 146.13 (aromatic ipso-C's).

(12) (a) **1**: ^{1}H NMR (CDCl$_3$) δ 3.20 (brs, 1 H, OH), 5.37 (s, 1 H, 10-H), 6.85–7.17 (m, 6 H, aromatic), 7.27–7.57 (m, 6 H, aromatic); ^{13}C NMR (CD$_2$Cl$_2$) δ 53.42 (10-C), 65.11 (9-C), 121.80, 123.38, 124.88, 125.37 (aromatic C's with H), 143.02, 145.50 (atomatic ipso-C's); IR (Nujol) 3340, 1295, 1225, 1170, 780, 635 cm^{-1}. (b) The chemical shift of the hydroxyl proton is dependent on the sample concentration, and the signal moves to a higher field in a more dilute solution. (c) The analytical sample was dried in vacuo at room temperature to avoid possible decomposition at an elevated temperature: Anal. Calcd for $C_{20}H_{14}OS\cdot0.4H_2O$: C, 77.59; H, 4.82; S, 10.35. Found: C, 77.71; H, 4.80; S, 10.29. (d) Molecular weight. Calcd for $C_{20}H_{14}OS$: 302. Found (osmometry in benzene): 302.

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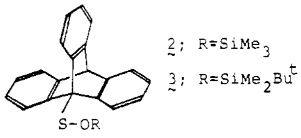
J. Am. Chem. Soc. **1983**, *105*, 7173-7175

which is within the established range for C–S bonds.[14] (ii) Compound A displays its hydroxyl group absorptions at 3340 cm^{-1} (Nujol) and δ 3.2 (readily exchangable with D_2O) in IR and NMR spectra, respectively.[12b] (iii) The absence of any IR band in a range 1120–1050 cm^{-1} clearly excludes a thiosulfinate structure [RSS(O)R] from the compound A.[14] Finally, (iv) the high-resolution mass spectrum of the compound A gives correct molecular formula $C_{20}H_{14}OS$ (found *m/e* 302.0764, calcd *m/e* 302.0764).[12c,d]

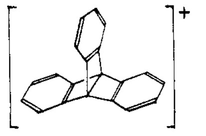
The sulfenic acid **1** (0.21 mmol), upon treatment with a twofold excess of silylating reagent such as chlorotrimethylsilane/hexamethyldisilazane and *tert*-butylchlorodimethylsilane/imidazole,[15] furnished the corresponding trimethylsilyl sulfenate **2**,[16] mp 148–149 °C, and *tert*-butyldimethylsilyl sulfenate **3**,[17] mp 139–141 °C, in 80.6% and 78.8% yield, respectively, after purification by column chromatography on silica gel. These esters are moderately stable to moisture but easily hydrolyzed back to the acid unless precautions against moisture are taken during the drying stage of the preparative TLC plates after development. The reaction shown in Scheme II and fact ii mentioned above are in good agreement with the previous result that the sulfenic acid hydrogen attaches to the oxygen atom, i.e., SOH.[2b]



2; R=SiMe$_3$

3; R=SiMe$_2$Bu^t

2, 3



4

It is of interest to note that in the mass spectrum of **1** the cleavage of the bond between the triptycene group and the sulfur atom appears to occur more easily than that of the S–O bond, as the relative intensity ratio observed for the fragments [M – SOH] (*m/e* 253) and [M – OH] (*m/e* 283) is 1:0.28, respectively. Similar trends have been also observed in the mass spectra of **2** and **3**, thus the intensity ratios of *m/e* 253 to 285 for **2** and **3** are 1:0.28 and 1:0.76, respectively. One common feature to these mass spectra of **1**, **2**, and **3** is the appearance of an intense peak at *m/e* 252, which might be equivalent to the tribenzo[2.2.2]propellatriene structure (**4**).

Addition reactions of transient sulfenic acids to carbon–carbon multiple bonds to yield sulfoxides are frequently employed to trap and characterize them.[2a,15b,18] The sulfenic acid **1** (0.25 mmol), when heated with methyl propiolate (0.5 mL) at 50 °C for 20 min, gave the expected sulfoxide, methyl *trans*-(9-triptycylsulfinyl)acrylate (**5**),[19] mp 239.5–241.5 °C, in 89.4% yield. This process can be followed by monitoring the decrease in the acetylenic proton intensity of the starting propiolate (δ 2.90) and the increase in the olefinic proton intensities of the product **5** (δ 8.48). Thus the second-order rate constant for the reaction (Scheme II) at 50 °C in chloroform-*d* has been determined as $k_2 = 1.28 \times 10^{-3}$ L·mol^{-1}·s^{-1}.

Though **1** is stable at room temperature in air for more than several weeks, it is readily converted, upon treatment with thionyl chloride at 0 °C, into a less polar compound, which is very likely to be the corresponding sulfenyl chloride on the basis of its NMR and IR spectra.[20]

The facts so far stated imply that the use of triptycene skeleton(s) may be an effective approach for stabilization of otherwise labile functional groups such as selenenic acids. Further studies are now in progress.

Acknowledgment. I acknowledge Professor Michinori Ōki, The University of Tokyo, for his generous support and Dr. Hiroshi Hirota of The University of Tokyo for taking the mass spectra.

Supplementary Material Available: IR spectra of **1** and the reaction product of 9-triptycenesulfenic acid, ^{1}H NMR spectra of **1**, and a mass spectral chart of **1** (7 pages). Ordering information is given on any current masthead page.

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(13) Some representative ^{13}C NMR δ values for the 9-C's of 9-triptycyl sulfides are 65.29 (2,3-Me$_2$-9-*t*-BuS-Trip), 65.29 (1,2,3,4-Cl$_4$-9-*t*-BuS-Trip), and 65.61 (9-*t*-BuS-Trip). The 9-C signal of a 9-triptycyl sulfoxide, 1,4-(MeO)$_2$-9-PhCH$_2$SO-Trip, appears at δ 72.00.

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(16) **2**: ^{1}H NMR (CDCl$_3$) δ 0.41 (s, 9 H, SiMe$_3$), 5.31 (s, 1 H, 10-H), 6.8–7.1 (m, 6 H, aromatic), 7.23–7.37 (m, 3 H, aromatic), 7.37–7.57 (m, 3 H, aromatic); exact mass (EI), calcd for $C_{23}H_{22}OSSi$ *m/e* 374.1151, found *m/e* 374.1150.

(17) **3**: ^{1}H NMR (CDCl$_3$) δ 0.40 (s, 6 H, SiMe$_2$), 0.97 (s, 9 H, *t*-Bu), 5.33 (s, 1 H, 10-H), 6.86–7.13 (m, 6 H, aromatic), 7.23–7.40 (m, 3 H, aromatic), 7.40–7.60 (m, 3 H, aromatic); exact mass (EI), calcd for $C_{26}H_{28}OSSi$ *m/e* 416.1628, found *m/e* 416.1582.

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(19) **5**: ^{1}H NMR (CDCl$_3$) δ 3.75 (s, 3 H, OMe), 5.34 (s, 1 H, 10-H), 6.8–7.3 (m, 7 H, aromatic), 7.24 (d, 1 H, J = 15 Hz, olefin proton β to SO group), 7.4–7.6 (m, 3 H, aromatic), 7.90–8.06 (m, 1 H, aromatic), 8.06–8.25 (m, 1 H, aromatic), 8.48 (d, 1 H, J = 15 Hz, olefin proton α to SO group); ^{13}C NMR (CDCl$_3$) δ 52.33 (OMe), 54.02 (10-C), 68.37 (9-C), 122.52 (aromatic C's with H), 122.92 (olefin C β to SO), 124.01, 125.18, 126.09 (aromatic C's with H), 140.57, 146.02 (aromatic ipso-C's), 148.43 (olefin C α to SO), 166.88 (C=O); IR (Nujol) 1715 (C=O), 1065 cm^{-1} (S=O). Anal. Calcd for $C_{24}H_{18}O_3S$: C, 74.59; H, 4.69; S, 8.30. Found: C, 74.49; H, 4.65; S, 8.25.

(20) ^{1}H NMR (CDCl$_3$) δ 5.32 (s, 1 H, 10-H), 6.90–7.20 (m, 6 H, aromatic), 7.20–7.46 (m, 3 H, aromatic), 7.46–7.75 (m, 3 H, aromatic); ^{13}C NMR (CDCl$_3$) δ 53.82 (10-C), 65.22 (9-C), 122.62, 123.54, 125.11, 125.87 (aromatic C's with H), 142.61, 145.50 (aromatic ipso-C's); IR (CH$_2$Cl$_2$) 1155, 1090, 960, 635, 605, 530 cm^{-1}; exact mass (EI), calcd for $C_{20}H_{13}ClS$ *m/e* 320.0426, found *m/e* 320.0413.

(21) **Note Added in Proof**: In the mass spectrum of 9-(*tert*-butylthio)triptycene-*10-d*$_1$ (D content ≥95%), the intense peaks appeared at *m/e* 253 and 254. This fact indicates that the deuterium atom is retained in these peaks and argues against the formation of structure **4**. Cf.: Schwartz, L. H. *J. Org. Chem.* **1968**, *33*, 3977. Klanderman, B. H.; Criswell, T. R. *Ibid.* **1969**, *34*, 3426.

Palladium-Catalyzed Cross-Coupling of Allyl Halides with Organotins

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The cross-coupling of an organometallic with an organic halide catalyzed by a transition metal is an important, versatile method of stereo- and regiospecific carbon–carbon bond formation. Various organometals have been utilized in this reaction with disparate success. The copper-promoted coupling of different vinyl or aryl groups is slow and often results in extensive homocoupling.[1] Similarly, cross-coupling reactions involving Grignard reagents catalyzed by various transition metals can lead to homocoupling. The inability of many organometallic partners, such as organolithium, Grignard reagents, and organoaluminums, to tolerate more reactive functional groups, either on the organic halide or on the organometallic partner, limits the functionality that can be brought into the coupled product.[2] Other organometallic partners containing a more electropositive metal, such as boron, zinc, or zirconium, often are not conveniently synthesized, or the methods of synthesis are limited to the extent that a wide variety of structures and functional groups are not available in the organic framework of the organometallic reagent.[3] Although organo-

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