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Superacid-Assisted Chemistry of Tetramethylhexathiaadamantane: Formation and Trapping of a Sulfur-Stabilized Carbodication

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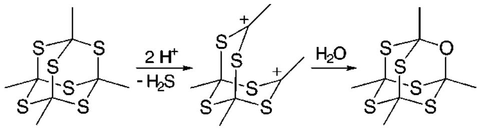
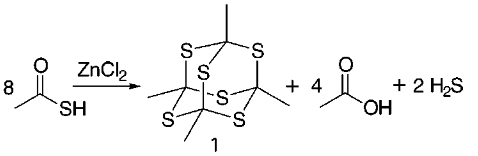
ABSTRACT



1,3,5,7-Tetramethyl-2,4,6,8,9,10-hexathiatricyclo[3.3.1.1^{3,7}]decane is quantitatively converted to a long-lived bicyclic carbodication, 1,3,5,7-tetramethyl-2,4,6,8,9-pentathiabicyclo[3.3.1]nonane-3,7-diylium dication, in superacid solution. Trapping with H_2O gives a new oxapentathia-adamantane, 1,3,5,7-tetramethyl-2-oxa-4,6,8,9,10-pentathiatricyclo[3.3.1.1^{3,7}]decane, in modest yield.

1,3,5,7-Tetramethyl-2,4,6,8,9,10-hexathiaadamantane, **1**, was first prepared, albeit without proper structural assignment, by Bongartz[1] in 1886 according to eq 1. Some 60 years later,



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[1]

Fredga surmised[2] the appropriate tricyclo[3.3.1.1^{3,7}] (adamantane-like) cage structure for **1**. Despite the early synthesis and pleasing T_d symmetry of **1**, hexathiaadamantanes (HTAs) have remained a largely unexplored class of molecules. The lack of interest is surprising given that HTAs are air stable, thermally robust, odorless molecules that generally possess good solubility in a host of organic solvents. An X-ray structure analysis has been published for **1**.[3] More recently, the molecular structure and vibrations of **1** were studied by a joint computational, gas-phase electron diffraction and spectroscopic investigation.[4] Interested in exploiting HTAs for a variety of purposes, we have begun a systematic study of HTA formation and subsequent chemistry. Accordingly, we now report our initial findings concerning the superacid-assisted chemistry of **1**,[5] namely, the formation, spectroscopic characterization, and trapping of bicyclic carbodication **2**, 1,3,5,7-tetramethyl-2,4,6,8,9-pentathiabicyclo[3.3.1]nonane-3,7-diylium dication.

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(1) Bongartz, J. *Ber.* **1886**, *19*, 2182.

(2) Fredga, A. *Arkiv Kemi, Mineral. Geol.* **1947**, *25 B*, nr 8.

(3) Pickardt, J.; Rautenberg, N. *Z. Naturforsch. B* **1986**, *41*, 409.

(4) Szász, G.; Kovács, A.; Hargittai, I.; Jeon, I.; Miller, G. P. *J. Phys. Chem. A* **1998**, *102*, 484.

(5) Synthesis of **1**: 53.25 g of thiolacetic acid (699.6 mmol) is placed into a round-bottom flask with 300 mL of chloroform and 19.49 g of dry $ZnCl_2$ (143.0 mmol). The solution is heated to reflux for 24 h and poured into an ice−water bath. Methanol is added until a homogeneous liquid layer is achieved. Off-white colored solids precipitate during the methanol addition and are collected by suction filtration. The crude solids are washed with distilled water and left to dry under vacuum. (Crude yield: 9.71 g, 36.4% theoretical; uncorrected mp 220−3 °C.); 0.9995 g of the crude solids is sublimed at 135−50 °C under reduced pressure (~5 mmHg) yielding 0.9295 g of pure **1** (93.37%, uncorrected mp 224−5 °C). Spectroscopic data for **1**: ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 2.18 (s); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ (ppm) 29.2, 58.5; EI-MS *m/z* 300 (M^+), 209, 150, 118, 59; IR (KBr) ν/cm^{-1} 2966.4, 2910.2, 2846.9, 2713.3, 1433.6, 1363.3, 1342.2, 1089.1, 1025.8, 716.4. Other published syntheses of **1** from thiolacetic acid utilize BF_3 (see: Giam, C. S.; Tabor, R. L.; Goodwin, T. E. *Org. Prep. Proced. Int.* **1981**, *13*, 134) and $TiCl_4$ (see: Ashkinazi, L. A.; Porai-Koshits, A. B.; Foshkin, V. G. U. S. S. R. Patent SU 1,641,822, 1991; *Chem. Abstr.* **1991**, *115*, 280071s) as catalyst. In our hands, $ZnCl_2$ is the superior catalyst.

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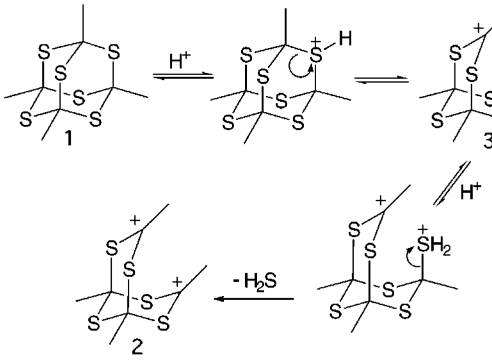
Formation of dication **2** has been accomplished in three unique superacid solutions: trifluoromethanesulfonic (triflic) acid, fuming sulfuric acid (30% free SO_3), and 25% Magic Acid (4:1 FSO_3H-SbF_5). When **1** is placed in triflic acid at rt, H_2S gas slowly evolves and a yellow-orange slurry develops. Immediate quenching of the slurry with ice−water results in the recovery of 70−80% of the starting hexasulfide, indicating the slurry to consist largely of unreacted solid **1**. Upon warming a solution of **1** in triflic acid to 45 °C, dissolution is complete, concurrent with increased H_2S evolution. A ^{13}C NMR spectrum of the triflic acid solution reveals quantitative conversion to dication **2** (Scheme 1).

Scheme 1



Excluding the triflic acid quartet, only four signals are observed at 23.1, 29.7, 64.8, and 230.0 ppm. Assignments are shown in Figure 1. The ^{13}C NMR δ values are similar to those reported[6] for the 2-methyl-1,3-dithian-2-ylium tetrafluoroborate (Figure 1), a good model cation for comparison to dication **2**.

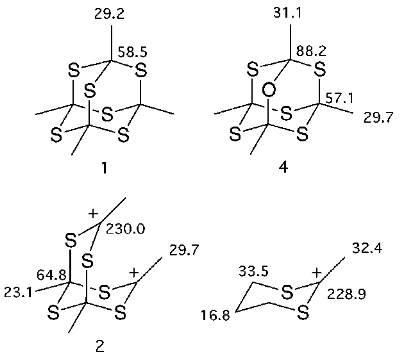
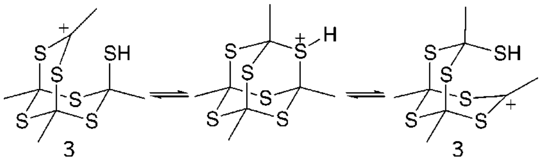


Figure 1. ^{13}C NMR shifts (ppm) for **1**, **2**, and 2-methyl-1,3-dithian-2-ylium tetrafluoroborate.[6]

1 dissolves instantly and completely in both fuming sulfuric acid and 25% Magic Acid at rt. In each case, the corresponding ^{13}C NMR spectra reveal formation of **2** with δ values identical to those obtained in triflic acid. There are differences, however, between the reactions as H_2S does not evolve from Magic Acid solution. In Magic Acid, H_2S is oxidized upon its formation to S_8^{2+}. S_8^{2+} is a known[7] polychalcogen dication with a characteristically deep blue color (λ_{max} 595 nm). It is typically generated by dissolving elemental sulfur, not H_2S, in an oxidizing superacid. Nonetheless, we have independently verified formation of S_8^{2+} from H_2S by bubbling the gas directly into 25% Magic Acid. Although we have made no attempt to verify, formation of lesser amounts of other polyatomic cations of sulfur (e.g., S_4^{2+} and S_{16}^{2+}) is likely under these conditions.[7]

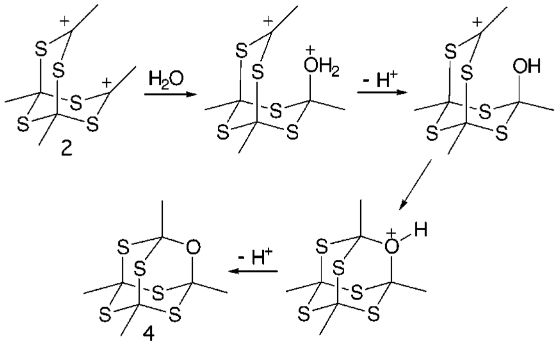
All attempts to grow crystals of **2** have failed. Without a crystal structure in hand, we have considered the possibility that the cationic species we observe is the rapidly exchanging 7-mercapto-1,3,5,7-tetramethyl-2,4,6,8,9-pentathiabicyclo-[3.3.1]nonan-3-ylium cation, **3**, rather than dication **2**.



However, the evidence in favor of dication **2** is compelling: (1) the detection of H_2S and S_8^{2+} is unmistakable; (2) ^{13}C NMR spectra of **1** dissolved in Magic Acid with SO_2ClF added as freezing point depressant show no changes to −80 °C; (3) identical ^{13}C NMR spectra are obtained in fuming sulfuric acid ($H_o \sim -13$), triflic acid ($H_o \sim -13.5$), and 25% Magic Acid ($H_o \sim -21$), seemingly inconsistent with the expectation that mercaptan protonation and ionization in **3** should increase with increasing acidity; (4) the 230 ppm ^{13}C NMR shift for C3 and C6 of dication **2** closely matches the 229 ppm shift for C2 of 2-methyl-1,3-dithian-2-ylium cation (Figure 1) and seems incompatible with a species and time-averaged C3/C6 of **3**.

Moreover, we observe that upon quenching superacid solutions of **1** with ice−water, heretofore unknown oxapentathiaadamantane **4**, 1,3,5,7-tetramethyl-2-oxa-4,6,8,9,10-pentathiatricyclo[3.3.1.1^{3,7}]decane, forms in modest yield (Scheme 2). Dissolution of **1** in a minimal quantity of fuming

Scheme 2



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(6) (a) Klaveness, J.; Undheim, K. *Acta Chem. Scand. B* **1983**, *37*, 687. (b) Kalinowski, H.-O.; Stahl, I. *Z. Naturforsch.* **1997**, *52b*, 757.

sulfuric acid followed by an ice−water quench represents the most convenient and cost-effective synthesis of **4** (30% isolated yield following flash silica column chromatography with $CHCl_3$ as eluant).

The two bridgehead carbons of **4** attached directly to oxygen exhibit the expected downfield shift in the ^{13}C NMR spectrum (Figure 1). The ^{1}H NMR spectrum of **4** consists of two singlets present in a 1:1 ratio and in the expected region (δ (ppm, $CDCl_3$) **1**, s, 2.18; **4**, s, 2.03; s, 2.15). The EI mass spectrum shows a strong parent ion at *m*/*z* 284.

Successful trapping of dication **2** with H_2O leads us to consider other trapping agents and the possibility of preparing a range of novel tricyclic structures. Those studies are now underway. Indeed, AM1 calculations (gas phase) suggest an open clam shell structure for **2** with a 3.88 Å internuclear distance between cationic carbons (Figure 2). To the extent that the AM1 structure mimics that observed in superacid solution, the inclusion of a wide range of nucleophilic traps seems reasonable. Interestingly, the charges in **2** are maintained in separate, nearly orthogonal planes, each containing two sulfur atoms adjacent to a cationic carbon and its corresponding methyl group. These two planes intersect each other at the bridgehead carbons with an interplanar angle of 114°.

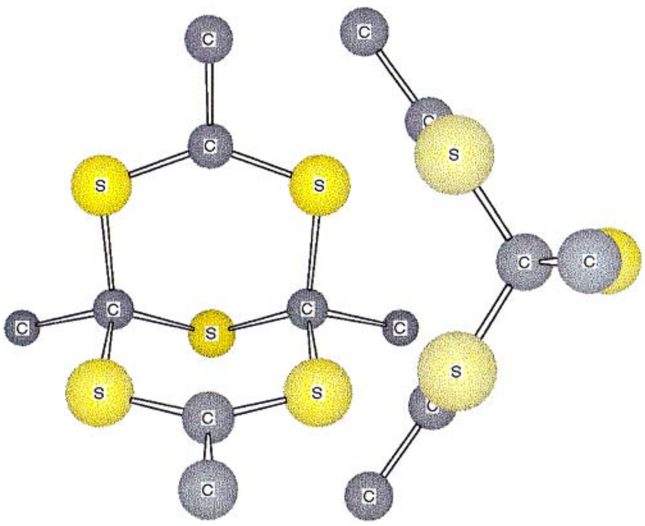
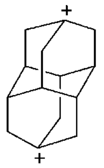


Figure 2. Front and side views of AM1 calculated **2**.

Although studies on carbodications[8] are more limited than those on carbocations,[8b] there are numerous examples of interesting dication systems including several based on adamantane.[8b−d] Olah and co-workers have successfully prepared the diadamantane-4,9-diylium dication, **5**,[8c] as well as several 2,6-disubstituted adamantane-2,6-diylium dications, **6**,[8d] in SbF_5-based superacid solution. These and other studies indicate that carbodication stability increases with increasing charge separation and/or when strong electron-donating substituents are present. Thus, persistent adamantane dications are observable in SbF_5-based superacids only when the charges are separated by at least three carbon atoms, as in **6**.[8b] Even with the charge separation, **6** is only stable when R is phenyl or cyclopropyl, but not methyl.[8b] Conversely, methyl-substituted dication **2** forms and persists at room temperature in much weaker superacid solutions. It appears that the stabilization afforded **2** by adjacent sulfur heteroatoms is greater than that afforded hydrocarbon dications by traditional strongly electron donating substituents.



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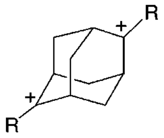

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In conclusion, hexathiaadamantane **1** is quantitatively converted to the long-lived, sulfur-stabilized carbodication **2** in superacid solution. **2** may be quenched with water to produce the previously unknown oxapentathiaadamantane **4** in modest yield.

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Supporting Information Available: Select spectroscopic data and detailed experimental procedures for the formation of dication **2** and oxapentathiaadamantane **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[7] (a) Barr, J.; Gillespie, R. J.; Ummat, P. K. *Chem. Commun.* **1970**, 264. (b) Gillespie, R. J.; Ummat, P. K. *Inorg. Chem.* **1972**, *11*, 1674. (c) Davies, C. G.; Gillespie, R. J.; Park, J. J.; Passmore, J. *Inorg. Chem.* **1971**, *10*, 2781.

[8] (a) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390. (b) Heagy, M. D.; Wang, Q.; Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1995**, *60*, 7351. (c) Olah, G. A.; Prakash, G. K. S.; Shih, J. G.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2764. (d) Prakash, G. K. S.; Krishnamurthy, V. V.; Arvanaghi, M.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 3985.