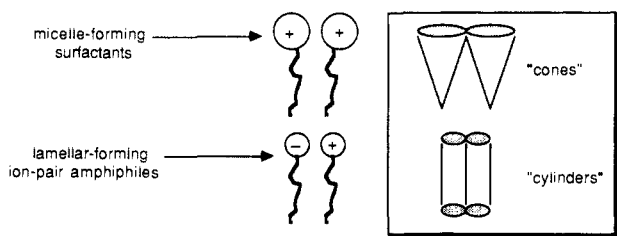


Figure 3. Surface pressure–area isotherms for (a) **1b** and (b) an equal molar mixture of cetyltrimethylammonium bromide plus palmitic acid (spread as one solution) at 20 °C. Monolayers were spread from benzene/ethanol (9:1, v/v) on a pure water subphase. Limiting areas, estimated by extrapolation to zero surface pressure, are 36 and 50 Å² for a and b, respectively.

Scheme I



surement of turbidity and fluorescence intensity, demonstrated that these microspheres contained an internal aqueous compartment. From such experiments, the captured volume was estimated to be 1.6 L/mol.⁵

Attempted vesicle formation by direct mixing of an equal molar mixture of cetyltrimethylammonium bromide and sodium palmitate in pure water (3 mg/mL) afforded a translucent dispersion that exhibited an apparent T_c of 41.0 °C. In sharp contrast to **1b**, however, its gel filtration profile was very broad, affording a 51% recovery in the void volume (fractions 7–11) and a 31% recovery in fractions 12–20 (Figure 2). These results infer the presence of both a vesicular and a micellar phase and also highlight the influence that salts and ion-exchange equilibria can exert on such systems. Comparison of the surface pressure–area isotherms measured for **1b** and for an equal molar mixture of cetyltrimethylammonium bromide plus palmitic acid also illustrates incomplete IPA formation at the air–water interface (Figure 3). The lower compressibility and smaller limiting area of **1b** are a likely consequence of tight ion pairing.

Ion-pair amphiphiles represent a new and unique class of vesicle-forming surfactants that warrant a detailed examination from both a theoretical and practical standpoint. Unlike conventional double-chain surfactants, however, special attention will have to be paid to the nature and concentration of all ionic species present in solution and to the appropriate ion-exchange equilibria. Studies that are now in progress are aimed at defining the full scope of IPAs and at the preparation of polymerizable analogues.

Acknowledgment. We are grateful to Michael Markowitz and Olga Shaffer (Lehigh) for valuable technical assistance.

(5) The entrapment value given in the text has been corrected for an apparent adsorption of ca. 0.4 L/mol.

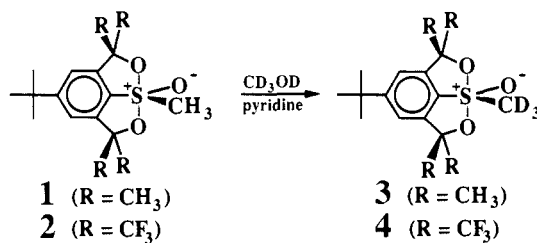
Replacing Apical-Substituent Methyl Groups by Trifluoromethyl Groups in 10-S-5 Hypervalent Sulfur Species Provides Less Acidic C–H Bonds on Equatorial Methyls^{1,2}

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The substitution of a trifluoromethyl group for a methyl group has been found to increase the acidity of a labile proton of many acidic compounds.³ The replacement of five methyl groups of pentamethylcyclopentadiene by trifluoromethyl groups was found by Laganis and Lemal^{3c} to strongly stabilize the cyclopentadienyl anion, making the C–H proton of the cyclopentadiene more acidic than nitric acid. We find, however, that protons of the equatorial *S*-methyl group of a 10-S-5² sulfurane oxide are much reduced in acidity when the four methyl groups (R) adjacent to the apical oxygens (**1**) are replaced by trifluoromethyl groups (**2**).⁴



It was found earlier⁶ that the equatorial methyl group of **1** was rapidly deuterated in CD₃OD at 25 °C. A solution of **1** and **2** in CD₃OD/pyridine at 25 °C showed within a few seconds, by NMR spectroscopy, complete deuteration of the equatorial methyl group of **1**, but no observable exchange for the fluorinated analogue **2** at that time. A much slower reaction (12 days at 25 °C) provided substantial deuteration of **2**. Deuterium exchange rates⁷ are faster for **1** than for CF₃-substituted **2** by a factor of ca. 86 000 at 25 °C.

Deuteration of either **1** or **2** was catalyzed by an appropriate base, increasing the rate linearly relative to the base concentration. Easily measurable catalysis for **2** required a strong base such as sodium methoxide-*d*₃ ($pK_a = 15.5$)^{3a} in a solvent made of equal volumes of tetrahydrofuran-*d*₈ (THF-*d*₈) and CD₃OD. For sulfurane oxide **1**, in an equal volume mixture of CD₂Cl₂ and CD₃OD, the much weaker base with $pK_a = 10.7$, potassium hexafluoro-2-phenyl-2-propoxide^{8,9} [KOC(CF₃)₂Ph], provided

(1) Rongione, J. C.; Martin, J. C. Presented in part at the 194th National Meeting of the American Chemical Society, New Orleans, LA, Sept 1987; paper ORGN 270.

(2) An *N*-X-*L* system formally involves *N* electrons in bonding *L* ligands to atom X. Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(3) (a) Serjeant, E. P.; Dempsey, B. *Ionization Constants of Organic Acids in Aqueous Solutions*; Pergamon Press: Oxford, 1979; Vol. 19, pp 23, 78, 10. (b) Kortur, G.; Vogel, W.; Andrusson, K. *Dissociation Constants of Organic Acids in Aqueous Solutions*; Butterworth: London, 1961; p 297. (c) Laganis, E. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 6633.

(4) 2,6-Bis(1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl)-4-*tert*-butylbenzenethiol was methylated at sulfur with dimethyl sulfate and aqueous KOH.⁵ Oxidation by *tert*-butyl hypochlorite provided 10-S-4 methylsulfurane in quantitative yield. Further oxidation to **2** (98%) used RuO₂/NaIO₄ in 1:1 v/v CCl₄/H₂O for 12 h at 25 °C. Although KMnO₄ is the oxidant used to form **1**, it does not oxidize the sulfurane precursor of the more electron deficient **2**.

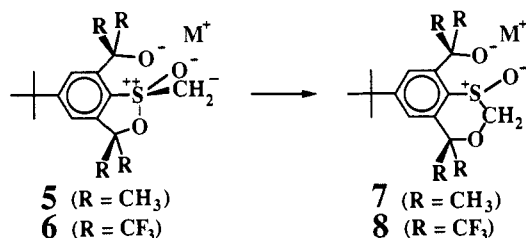
(5) Perkins, C. W.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 3209.

(6) Lau, P. H.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5490.

(7) Rates were determined in a 1:9 v/v CD₂Cl₂/CD₃OD solvent without added base. For **1**, rates were measured at –65 °C ($2.17 \times 10^{-4} \text{ s}^{-1}$), –55 °C ($6.73 \times 10^{-4} \text{ s}^{-1}$), and –39 °C ($2.43 \times 10^{-3} \text{ s}^{-1}$) ($\Delta H^\ddagger = 8.36 \text{ kcal/mol}$; $\Delta S^\ddagger = 34.2 \text{ eu}$). The rate at 25 °C was then calculated to be 0.151 s^{-1} for **1**. The rate of deuterium exchange for **2** ($1.75 \times 10^{-6} \text{ s}^{-1}$) was measured in the same solvent at 25 °C.

easily measured catalyzed kinetics. Exchange was much slower for **2** than for **1**, with catalysis by this weak base. It is clear that trifluoromethylated **2** is much less kinetically acidic than methylated **1**.

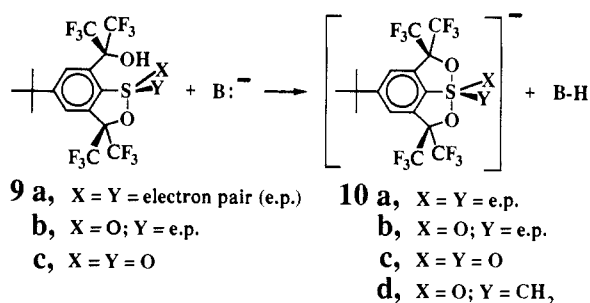
The two fluorine apical ligands of the 10-F-2 trifluoride anion (F_3^-) have a calculated¹⁰ total negative charge of -1.03 , more than the negative charge (-1.00) on the same two atoms of the precursor species (F_2 and F^-). It is clear for a wide range of hypervalent species, with center atoms more electropositive than the central F of F_3^- , that the trifluoromethyl groups of the tridentate ligands of **2**, more than the methyl groups of **1**, strongly stabilize the symmetrical species, relative to an unsymmetrical species obtained by cleaving one of the apical bonds. If the anions of the sulfurane oxides are unsymmetrical as **5** and **6**, there could be less total negative charge on the two alkoxy centers of the unsymmetrical anions than on both of the alkoxy centers of the symmetrical neutral sulfurane oxides. Stabilization of anions **5** or **6** would therefore be provided more by CH_3 groups than by CF_3 groups, since there is thought to be less total negative charge on the two alkoxy centers of unsymmetrical anion **5** (or **6**) than is expected on the same two alkoxy centers of the symmetrical hypervalent species **1** (or **2**).



The observation (by ¹H and ¹⁹F NMR) of anions **5** and **6** revealed their unsymmetrical geometry.¹¹ It was necessary to use a stronger base to convert **2** to **6** (KO-*t*-Bu/CH₃Li, $pK_a > 58$)^{12,13} than to convert **1** to **5** (lithium tetramethylpiperidine, LiTMP, $pK_a = 37.3$).¹⁴ The weaker base (LiTMP) did not completely form **6** from **2**, providing evidence for the lower equilibrium acidity of **2** relative to **1**. Both **5** and **6** rearrange by transfer of an alkoxy oxygen from S to C to form **7** and **8**.¹¹

It was established⁵ (by low-temperature NMR and X-ray crystallography) that anions **10a-c** are symmetrical hypervalent anions (10-S-3, 10-S-4, and 10-S-5), while protonated species **9a-c** are unsymmetrical (8-S-2, 8-S-3, and 8-S-4). The destabilization of anions **10** by introduction of π -donor equatorial oxygens is seen by the acidities of **9a** ($pK_a = 4.4$), **9b** (5.0), and **9c** (7.2). The sulfurane dioxide anion (**10c**) is stable (2.6 kcal/mol), relative to the unsymmetrical anion formed by cleaving one of the apical S-O bonds, but considerably less stable than the sulfurane anion **10a** (7.5 kcal/mol).⁵ Replacement of one of the oxygens of **10c**

by a more electropositive CH_2^- ligand makes unsymmetrical 8-S-4 **6** more stable than **10d**, which is not seen.¹⁵ While equatorial π -donor ligands have usually been found¹⁶ to have their electron-pair orbitals perpendicular to the 3c-4e bond, it is probable that the repulsive interaction between the equatorial CH_2^- and O⁻ ligands of **10d** would make the CH_2^- electron pair parallel to the 3c-4e bond. This would allow electron donation to the antibonding unoccupied hypervalent orbital of the 3c-4e bond, destabilizing **10d** to make it rearrange to **6**. Although **6** is an anion, its unsymmetrical geometry sufficiently reduces the negative charge on the two alkoxy oxygens, relative to the apical oxygens of symmetrical **2**. The CF_3 substituent effects, therefore, make **2** less acidic than **1**.



Further work on the reactions of **1** and **2**, as well as on the analogous species formed by replacing sulfur with selenium, is underway.

Acknowledgment. This research was supported in part by National Science Foundation Grant CHE-8910896.

(15) Although **6** is unsymmetrical, there may be a small bonding interaction between the alkoxide oxygen and the adjacent sulfur.

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Activation Parameters for a 1,2 Carbon Shift in a Carbene Rearrangement[†]

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Laser flash photolysis (LFP) has been extensively employed to determine the absolute rate constants and associated activation parameters for *intermolecular* carbene reactions.¹ Previously obscure aspects of these processes have thereby been highlighted. For example, the activation energies of certain carbene/alkene cycloadditions were found to be very low, or even negative, whereas the free energy barriers were controlled by highly unfavorable activation entropies.²

Less is known about the absolute rate constants and activation parameters of *intramolecular* carbene reactions. Experimental

[†] Dedicated to Professor Wolfgang Kirmse on his 60th birthday.

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(8) The potassium salt was dried at 100 °C at 0.5 mmHg for 12 h prior to its use in a glove box. The CD₂OD was distilled from Mg, THF-*d*₄ from Na and benzophenone, and CD₂Cl₂ from CaH₂. A CD₂OD solution of base was added to a sulfurane oxide solution in CD₂Cl₂ or THF-*d*₄ frozen in liquid nitrogen. Samples thawed at -78 °C immediately prior to use were placed in a precooled NMR probe for kinetic studies.

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(11) The ¹H aromatic singlet of **1** (7.49 ppm), upon the addition of lithium tetramethylpiperidine (LiTMP), became two singlets (7.43 and 7.58 ppm) at -60 °C in THF-*d*₈. A stronger base (KO-*t*-Bu/CH₃Li)¹² at -43 °C was needed to convert **2** (8.24 ppm) to **6** (8.06 and 7.48 ppm). Further evidence for this conversion was found in the ¹⁹F NMR spectrum; the two quartets of **2** (-75.67 and -76.05 ppm) became the four equal-size quartets appropriate for **6** (-66.72, -71.03, -73.32, and -74.35 ppm). Quenching **5** and **6** by water reformed **1** (82%) and **2** (6%), together with sulfoxides **7** and **8**. (The rearrangement of **6** to **8** was fast enough to reduce the amount of **2** observed.)

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