glass was dissolved in dichloromethane and filtered through a small amount of activated charcoal. The dichloromethane was removed under reduced pressure and the remaining material fractionally sublimed. Sublimation gave 1,2,3,4-tetrafluoronaphthalene (152 mg, 0.76 mmol, 87%). Anthracene (44 mg, 0.25 mmol) and a trace of dibenzobarrelene were next recovered (60° C, 0.1 mmHg), and finally, pure janusene[12] (269 mg, 0.70 mmol, 74%) was collected (140 °C, 0.1 mmHg). ^{13}C NMR at 20 MHz not previously recorded: 145.6, 140.4, 125.6, 125.5, 125.3, 123.8, 49.1, 45.1 ppm.

Registry No. 1, 5162-34-5; 2, 2734-13-6; 3, 14707-22-3; anthracene, 120-12-7.

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[12] Spectral and physical properties, including melting point (236–7 °C), were identical with those of an authentic sample of janusene graciously supplied to us by Prof. Stanley Cristol.

Epoxidation of 3-Cyclohexenemethanol. A Correction

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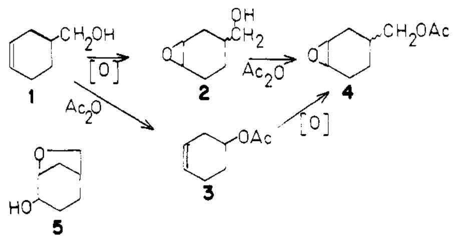
The presence of an alcohol or other hydrogen-bonding substituent in a position spatially proximate to a carbon–carbon double bond is well-known to accelerate the rate of epoxidation reactions and to strongly favor epoxidation from the side cis to the substituent.[1] These effects are evident in both peracid and catalyzed *tert*-butyl hydroperoxide (TBHP) reactions.[2] In the course of his pioneering experiments which elucidated this phenomenon, Henbest[3] reported that 3-cyclohexenemethanol (1) and its corresponding acetate (3) afforded predominantly the trans epoxides upon reaction with peracids. The evidence for this was chemical in nature. For accommodation of these results, the reacting conformations of 1 and 3 must be such that the side chain adopts a position capable of sterically shielding one side of the molecule without causing the mentioned cis epoxidation.

In the course of other work, we had occasion to examine the epoxidation of 1 and its derived acetate 3 using both MCPBA and TBHP. We can now report that, in both cases, epoxidation of 1 leads to a 1:1 mixture of cis and trans epoxy alcohols 2. The evidence upon which this conclusion is based includes the ^{13}C NMR spectrum of the acetate 4 which, at 100 MHz, shows a doubling of seven of the nine absorptions and the 60-MHz ^1H NMR which shows two apparent doublets for the acetoxymethyl group. The acetate was chosen for the NMR experiments to increase the shift of the oxygenated methylene group and to eliminate any unusual conformational effects caused by intramolecular hydrogen bonding. The fact that exactly the same results are obtained from the epoxidation of acetate 3 as from epoxidation of alcohol 1 followed by acetylation using either MCPBA or TBHP insures that no rearrangement of 1 to the bicyclic alcohol 5 has occurred (Scheme I).[4]

Scheme I



For further analysis of the mixture, the 400-MHz ^1H NMR of 4 was obtained. As expected, the spectrum was quite complex in the δ 1.0–2.5 region, suggesting that geminally situated protons on the ring carbons have substantially different chemical shifts in many cases. The epoxide hydrogens occur as a broadened multiplet centered at δ 3.17. The acetoxymethyl group appears as two discrete signals of equal integrated intensity: a doublet (J = 6.1 Hz) at δ 3.85 and a doublet of doublets (J = 3.6 and 2.9 Hz) centered at δ 3.89. Decoupling studies confirm that the two absorptions arise from different spin systems since the signal at δ 3.89 was collapsed to a singlet by irradiation at δ 1.89 while the signal at δ 3.85 is unaffected. Inspection of molecular models does not suggest an obvious reason why only one diastereomer should possess nonequivalent protons. Nevertheless, these results confirm the formation of two diastereomers from the epoxidation of 1 or 3.

Experimental Section

MCPBA Epoxidations of 1 and 3. In a typical experiment, 0.06 mol of 85% MCPBA was dissolved in 60 mL of methylene chloride and filtered. This solution was cooled in an ice-bath during the dropwise addition of 0.035 mol of 3-cyclohexenemethanol (1)[5] or its acetate (3).[6] The reaction mixture was stirred for 15 h at ambient temperature, filtered, and washed with aqueous sodium bicarbonate until the washings were basic. The dried ($MgSO_4$) solution was evaporated and distilled under reduced pressure to give pure epoxy alcohol 2 in 36% yield: bp 65–68 °C (0.15 mm).

Acetate 3 afforded epoxy acetate 4 in 95% yield: bp 135 °C (17 mm) (lit.[7] bp 119–120 °C (9 mm)). Acetylation of 2 using acetic anhydride in pyridine gave 4 which was identical with the product of epoxidation of 3: ^{13}C NMR ($CDCl_3$) 171.1, 68.6, 68.4, 52.5, 52.4, 51.6, 51.1, 32.2, 29.4, 28.2, 27.1, 24.6, 23.7, 22.9, 21.1, 20.9; ^1H NMR ($CDCl_3$) (60 MHz) 3.85 (dd, 3 H, J = 3, 3Hz), 3.1 (m, 2 H), 0.5–2.5 (m, 10 H); (400 MHz) (CH_2O-protons) 3.85 (d, J = 6.1 Hz), 3.98 (dd, J = 3.6, 2.9 Hz).

Hydroperoxide Epoxidation of 1 and 3. In a typical procedure, 0.02 mol of alkene, 0.02 g of $Mo(CO)_6$, 0.02 g of Na_2HPO_4 were combined, dissolved in 20 mL of dichloroethane, and brought to reflux. Anhydrous TBHP–dichloroethane solution[2,8] (10 mL, 4.5 M) was added dropwise. The resulting solution was refluxed for 2 h. To the cooled solution was added 50 mL of 40% Na_2SO_3 solution and the mixture was stirred for 15 h at which time a negative starch–iodide test was obtained. The organic layer was separated and washed with water and brine. The dried solution was evaporated and the oil obtained was distilled to give pure epoxy acetate 4[9] in 56% yield. This material was identical with that obtained from the peracid oxidation.

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[1] Berti, G. *Top. Stereochem.* **1973**, *7*, 93.

[2] Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63.

[3] Henbest, H. B.; Nicholls, B. *J. Chem. Soc.* **1959**, 221.

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[5] Klein, J. *Isr. J. Chem.* **1963**, *1*, 385.

[6] Blömquist, A. T.; Meinwald, Y. C. *J. Am. Chem. Soc.* **1959**, *81*, 667.

[7] Phillips, B.; Starcher, P. S. US Patent 2794028; Chem. *Abstr.* **1957**, *51*, 16555*h*.

[8] Sharpless has recently reported that an anhydrous TBHP/toluene solution is now the system of choice for such oxidations: Hill, G. H.; Rossiter, B. E.; Sharpless, K. B. *J.Org. Chem.* **1983**, *48*, 3607.

[9] The epoxy alcohol 2 decomposed on distillation. ^1H NMR of the crude product confirms the presence of the expected product. In order to obtain a pure product, the acetate was made in situ by using acetic anhydride in pyridine.

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Registry No. 1, 1679-51-2; *cis*-2, 91108-45-1; *trans*-2, 91108-46-2; 3, 10437-78-2; *cis*-4, 81370-42-5; *trans*-4, 81370-41-4; MCPBA, 937-14-4; tBHP, 75-91-2.

New Developments in Heterocyclic Silyl Enol Ether Chemistry: Synthesis and Lewis Acid Mediated Reactions with Carbon Electrophiles of 2,5-Bis(trimethylsiloxy)thiophene and 1-Methyl-2,5-bis(trimethylsiloxy)pyrrole

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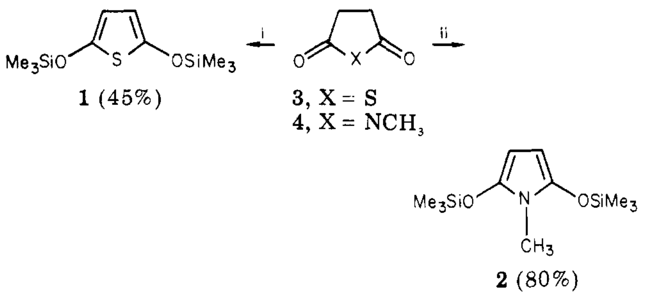
Although heterocyclic mono silyl enol ethers such as 2-(trimethylsiloxy)furan,[1a,b] -thiophene,[2] and -pyrrole[2] show reactivity with electrophiles, in acidic[1b,2] or basic[1a] conditions, predictable on the grounds of the behavior of aliphatic and aromatic silyl enol ethers,[3] the recently reported 2,5-bis(trimethylsiloxy)furan (6)[4a] exhibits several unexpected features with electrophiles and TiCl$_4$.[4b]

We now report the synthesis of the new compounds 2,5-bis(trimethylsiloxy)thiophene (1) and 1-methyl-2,5-bis(trimethylsiloxy)pyrrole (2) and a study of their regioselective functionalization with electrophiles in the presence of a Lewis acid, which shows how electrophilic addition in 2,5-bis(trimthylsiloxy) five-membered heterocyclic compounds changes with the nature of the ring heteroatom, leading to different reaction products of potential interest in synthetic organic chemistry.

The preparation of the title compounds, starting from the corresponding dicarbonyl compounds 3 and 4 is outlined in Scheme I. Product 1 was synthesized in satisfactory yields (45%) from the thioanhydride 3 by using Et$_3$N/Me$_3$SiCl/ZnCl$_2$ as silylating agent, whereas under the same reaction conditions the succinimide 4 did not react. 2 was obtained in very good yields by treatment of 4 with 2 equiv of LDA at −78 °C, followed by Me$_3$SiCl, and was purified by fractional distillation.[5]

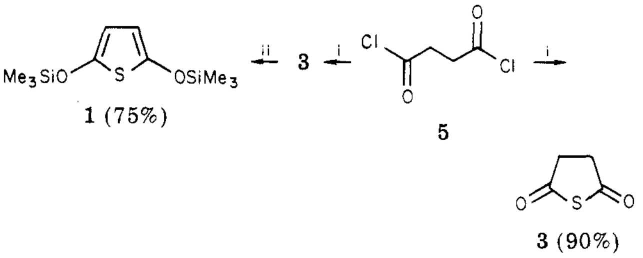
Serious limits to the synthetic approach for compound 1 lay in the low yields and the difficulties in the previously reported preparation of 3.[6] We have developed a new method for the synthesis of this thioanhydride; starting from succinyl chloride 5 and (Me$_2$Si)$_2$S in the presence of ZnCl$_2$, 3 was obtained in high yields (90%) almost pure. A further advantage of this procedure is that, by simply adding Et$_3$N to the reaction mixture, the bis-siloxy derivative 1 was obtained directly, in a one-pot reaction besides minor amounts of 3 (Scheme II).

Scheme I[a]



[a] (i) ZnCl$_2$, Et$_3$N, Me$_3$SiCl; (ii) LDA, Me$_3$SiCl.

Scheme II[a]



[a] (i) (Me$_3$Si)$_2$S, ZnCl$_2$; (ii) Et$_3$N.

Compounds 1 and 2 are yellow oils that could be kept indefinitely at room temperature under inert atmosphere; 2 solidifies at 0 °C.

Compounds 1 and 2, as well as the oxygen analogue 2,5-bis(trimethylsiloxy)furan (6),[4b] present two reactive sites at C(3) and C(4) and undergo regioselective functionalization with carbon electrophiles (Scheme III).

When 2 equiv of SnCl$_4$ were added to a mixture of 6 and of acetone (7a), butyraldehyde (7b), or benzaldehyde (7c) as electrophiles in CH$_2$Cl$_2$ at −78 °C, after quenching with 10% NH$_4$Cl at room temperature, dilactones 8a–c (entry 1 in Scheme III), analogues of naturally occurring lignans, were obtained in good yields, probably through intramolecular rearrangement of the products of electrophilic addition. This reaction had been previously described[4b] and occurred with the same features even though we used SnCl$_4$ instead of TiCl$_4$ as Lewis acid.

Under the same reaction conditions, 2,5-bis(trimethylsiloxy)thiophene (1) afforded a mixture containing comparable yields of the lignans 8a–c and of the 3,4-disubstituted thioanhydrides 9a–c (entry 2 in Scheme III), probably formed from the same intermediate,[4b] easily separated by column chromatography on silica gel.

1-Methyl-2,5-bis(trimethylsiloxy)pyrrole (2) on the other hand, gave only products 10a–c coming from an electrophilic attack at C(3) and C(4) (entry 3 in Scheme III); the lower reactivity of the imidic carbonyl center in this case prevents intramolecular attack leading to the dilactone system.

2 undergoes also regioselective monofunctionalization with 1 equiv of the electrophile and of SnCl$_4$; compound 11 was thus obtained in high yields by employing 7a as an electrophile. A *differential functionalization* at C(3) and C(4) was also performed in a one-pot reaction by simply adding to 2 a mixture of 1 equiv of acetone (7a) and of SnCl$_4$ in CH$_2$Cl$_2$ at −78 °C, followed by addition of 1 equiv

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[1] (a) Fiorenza, M.; Ricci, A.; Romanelli, M. N.; Taddei, M.; Dembech, P.; Seconi, G. *Heterocycles* **1982**, *19*, 2327. (b) Asaoka, M.; Yanagida, N.; Ishibashi, K.; Takei, M. *Tetrahedron Lett.* **1981**, *22*, 4269.

[2] Fiorenza, M.; Reginato, G.; Ricci, A.; Taddei, M.; Dembech, P. *J. Org. Chem.* **1984**, *49*, 551.

[3] For a complete review on the argument, see: Brownbridge, P. *Synthesis* **1983**, 1.

[4] (a) Brownbridge, P.; Chan, T. H. *Tetrahedron Lett.* **1980**, *21*, 3423. (b) Brownbridge, P.; Chan, T. H. *Ibid.* **1980**, *21*, 3427.

[5] Attempts to use other silylating reagents such as Me$_3$SiNEt$_2$, DBU/Me$_3$SiI, *n*-BuLi/Me$_3$SiCl, or NaN(SiMe$_3$)$_2$/Me$_3$SiCl did not give the same good results.

[6] To our knowledge a simple preparation of 3 is reported only in "Beilstein Handbuch der Organischen Chemie", Vol. 17, p 421, but we obtained only unsatisfactory yields by following it. On the other hand the more recent syntheses outline a tedious series of lithiations of halogenated thiophenes [Jakobsen, H. J.; Larsen, E. H.; Lawesson, S. O. *Tetrahedron* **1963**, *19*, 1867] or photochemical pathways [Saito, K.; Sato, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3601].

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