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1,5-FUNCTIONALIZATION OF 1,3-CYCLOHEXADIENE ON SbF_5-PROMOTED SO_2 ADDITION

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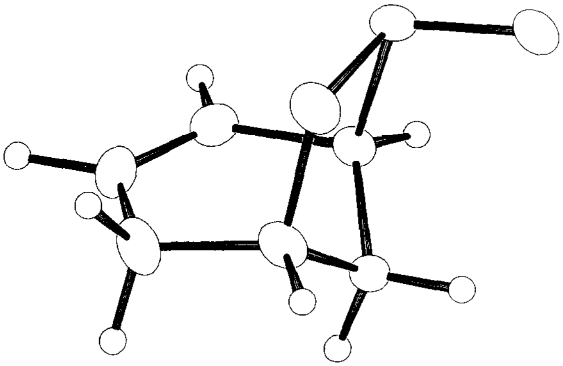
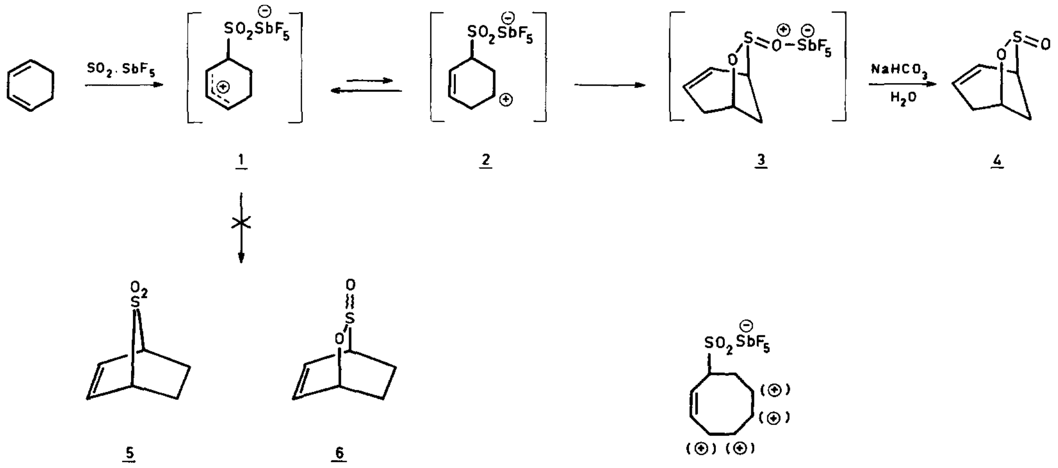
Addition of sulfur dioxide to conjugated dienes has been known for many years.[1,2] Usually 2,5-dihydrothiophene-1,1-dioxides (sulfones) are formed. Recently[3,4] however, two highly reactive 1,3-dienes have been reported to yield 3,6-dihydro-1,2-oxathiin-2-oxides (sultines). Cyclic dienes such as cyclopentadiene, 1,3-cyclohexadiene and 1,3-cyclooctadiene[5] fail to react with sulfur dioxide to the corresponding sulfones or sultines.

Also a cycloaddition reaction of sulfur dioxide complexed[6] to antimony pentafluoride has recently been reported to occur with cyclooctatetraene[7a-c] and hexamethyl dewarbenzene[7d] yielding sulfones. In these reactions - in which SO_2 has been made strongly electrophilic - intermediate ions have been observed, e.g. a homotropylium ion in the case of cyclooctatetraene.

In this communication we wish to report a new type of antimony pentafluoride promoted reaction, in which bicyclic sultines are formed on cycloaddition of sulfur dioxide to some cyclic 1,3-dienes. In a specific example, sulfur dioxide (50 ml) was condensed below -80^0 into a bottle containing antimony pentafluoride (3.76 g, 17.3 mmol). The white crystalline $SO_2.SbF_5$ complex formed, dissolved upon warming to -20^0, after which the solution was cooled again to -55^0. Over a period of 10 min. a cooled solution (-78^0, dry ice) of 1,3-cyclohexadiene (470 mg, 5.87 mmol) in SO_2ClF (4 ml) was added through a syringe and the resulting reddish-brown solution stirred for an additional hour at -55^0. The reaction mixture was quenched by pouring it portionwise into an aqueous $NaHCO_3$ solution. After extraction of the latter with methylene chloride (2x150 ml), the combined organic layers were dried over $MgSO_4$ and the solvent was evaporated, leaving almost pure compound 4 (344 mg, 2.39 mmol, 40%). Spectroscopic and analytical data[8] were in agreement with the presence of a sultine moiety, but were insufficient to assign the structure of the compound unambiguously. An X-ray analysis[9] proved the structure to be 6-oxa-7-thia-bicyclo|3.2.1|oct-2-ene 7-*exo*-oxide, as shown below. Remarkably, neither the epimeric sultine (with the S=0 group in *endo* position), nor 1,4-addition products such as 5 or 6 have been isolated in this reaction.



A possible mechanism which explains the formation of 4, involves the occurrence of a 1,2-H shift in the initially generated allylic intermediate 1 to afford 2 (SCHEME), which rapidly ring-closes to 3. Intermediate ions, e.g. 1 and 2 have not been detected by low temperature (-75^{0}) ^{1}H-NMR spectroscopic measurements performed immediately after preparation of the reaction mixture. These spectra[10] were almost identical to those obtained from samples in which antimony pentafluoride was added to authentic material 4 in SO_2ClF solution. It is of interest to note



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that the 1,2-H shift in the reaction 1 → 2 has recently been studied in the parent cyclohexenyl ion,[11] which can undergo a ring contraction to the methylcyclopentenyl ion. In the presently described reaction no ring-contracted products have been isolated.

The cycloaddition of sulfur dioxide to 1,3-cyclooctadiene has been carried out in a similar way.[12] Spectroscopic data of the isolated product do not distinguish, however, between the various possible structures of the sultine, which can arise from a 1,4, 1,5, 1,6, or 1,7 ring-closure of intermediate ions 7. In contrast to sultine 4 this product is rather unstable and dissociates at room temperature into 1,3-cyclooctadiene and sulfur dioxide.

Although the applicability of the SbF_5-promoted addition of SO_2 to cyclic dienes may well be limited to certain special cases,[13] the reaction constitutes in principle a novel way for preparing bicyclic sultines.[14] Moreover a 1,5-functionalization of 1,3-cyclohexadiene can be accomplished in this manner.

References and Notes:

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8. 6-oxa-7-thia-bicyclo|3.2.1|oct-2-ene-7-exo-oxide (4): ^{1}H-NMR ($CDCl_3$): 5.7 (m, 2H), 5.2 (m, 1H),

3.6 (m, 1H), 2.8 (m, 1H), 2.2 (m, 3H); ^{13}C-NMR ($CDCl_3$): 129.7 (sp^2CH), 120.3 (sp^2CH), 83.6 (sp^3CH), 64.3 (sp^3CH), 33.5 (sp^3CH_2), 28.9 (sp^3CH_2); IR: 1115 cm^{-1} (S=0); MS: M^+ found at m/e 144.020, calc. m/e 144.024; Analysis: Found % C 50.18, 50.07, % H 5.75, 5.69, % S 22.47, 22.28, 22.07, Calc. % C 49.98, % H 5.59, % S 22.23; mp: 45-47^o(from methyl cyclohexane/methylene chloride at -30^o).

9. Dr. A.L. Spek, Laboratory of General Chemistry, University of Utrecht, The Netherlands.
10. ^{1}H-NMR data of 1,3-cyclohexadiene with $SO_2.SbF_5$ (SO_2/SO_2ClF): 6.0 (m, 3H), 4.8 (m, 1H), 3.0-2.6 (m, 4H).
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12. 1,3-Cyclooctadiene (490 mg, 4.54 mmol) in SO_2ClF (3.5 ml) was added to SbF_5 (2.74 g, 12.63 mmol) in SO_2 (60 ml) at -75^o. After stirring for 45 min at -65^o and usual work-up 350 mg (2.04 mmol, 45%) of almost pure $C_8H_{12}O_2S$ was obtained. ^{1}H-NMR ($CDCl_3$): 6.25 (m, 2H), 5.05 (m, 1H), 3.55 (m, 1H), 2.2-1.7 (m, 8H); ^{13}C-NMR ($CDCl_3$): 129.4 (sp^2CH), 122.7 (sp^2CH), 75.3 (sp^3CH), 57.1 (sp^3CH), 33.2 (sp^3CH_2), 28.8 (sp^3CH_2), 23.3 (sp^3CH_2), 22.3 (sp^3CH_2); IR: 1130 cm^{-1} (S=0); MS: M^+ found at m/e 172.056, calc. m/e 172.056; Correct elemental analysis could not be obtained due to decomposition.
13. Reaction of 1,3-cycloheptadiene with the $SO_2.SbF_5$ complex yielded a mixture of compounds (in the decoupled ^{13}C-NMR spectrum 21 absorptions are found at positions similar to those of 4 and $C_8H_{12}O_2S$) which has not been separated. The IR spectrum indicates the presence of sultines (abs. at 1130 cm^{-1}, no abs. at 1300 cm^{-1}). Attempts to prepare a sultine from cyclopentadiene were unsuccessful however.
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