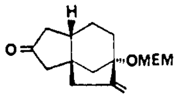
previously described[1a] to afford the keto MEM ether **22** in 53% overall yield from **20** (after chromatography on activity III basic Woelm alumina). Wittig methylenation was accomplished with 5 equiv of methylenetriphenylphosphorane in 2.5:1 THF-HMPA for 1.8 h at reflux to yield the desired olefin **23** (71% yield after chromatography on silica gel). Deketalization using 3:1 acetic acid-water for 1 h at 25 °C gave tricyclic ketone **24** quantitatively.



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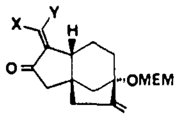
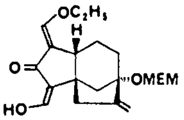


25 X = OH Y = H
26 X = H Y = OCH_3
27 X = OCH_3, Y = H



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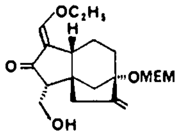

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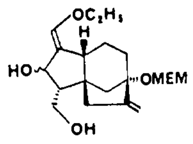

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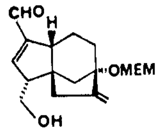

31

Conversion of tricyclic ketone **24** to target dienol **2** was accomplished by a seven-step sequence.[17] Selective formylation at the less shielded methylene α to the carbonyl in **24** was achieved in 88% yield by reaction with sodium hydride (6 equiv), ethyl formate (~30 equiv), and a trace of ethanol in 1,2-dimethoxyethane (DME) for 1 h at 0-25 °C.[18] The crude ketone **25** was immediately methylated using potassium *tert*-butoxide (2 equiv) and methyl iodide (18 equiv) in 10:1 THF-HMPA at 25 °C for 2 h to afford **26** and **27** (6:1 ratio; 60% yield overall from **24** after chromatography on silica gel). The assignment of structure is supported by ^1H NMR data and by the subsequent conversion of **26** and **27** to the known dienol **2**. Treatment of the mixture of **26** and **27** with sodium hydride (6 equiv), ethyl formate (~30 equiv), and a trace of ethanol in DME at 30 °C for 15-30 min afforded **28**. The β-dicarbonyl system was immediately reduced by conversion to the sodium enolate with sodium hydride (5 equiv) in THF at 25 °C, treatment with sodium bis(2-methoxyethoxy)aluminium hydride (5 equiv) at −20 to 0 °C for 50 min, and quenching with ammonium chloride at 0 °C to give after column chromatography a single stereoisomer **29**.[18,19] The stereochemistry of **29** was predicted from the consideration that the enolate protonation step which determines the stereochemistry of the final product should involve attack from the less shielded β face. Addition of **29** to a toluene solution containing sodium bis(2-methoxyethoxy)aluminum hydride (5 equiv) and 1,4-diazabicyclo[2.2.2]octane (5 equiv) at −20 °C followed by stirring at −20 °C for 0.5 h afforded diols **30** quantitatively.[20] An ethereal solution of the labile diols was immediately treated with a solution of aqueous oxalic acid (pH 3) at 0 °C for 2 h to afford α,β-unsaturated aldehyde **31** (60%). Treatment of **31** with 10 equiv of methylenetriphenylphosphorane in THF at 0 °C for 10 min afforded dienol **2** (65% yield after chromatography on silica gel). The spectra (IR, ^1H NMR, mass) and chromatographic behavior (TLC and high-pressure liquid chromatography) of this product were all identical with those found for a pure sample of **2** prepared by the previously described route.[1a] Further, the corresponding acetate esters were likewise demonstrated to be identical.

The synthesis of **2** reported herein demonstrates a completely different synthetic strategy from that previously utilized.[1a] In addition it illustrates a number of interesting situations in which high positional and stereoselectivity could be achieved by taking advantage of rather modest geometrical differences.[21]

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(4) Satisfactory infrared, proton magnetic resonance, and high resolution mass spectral data were obtained on purified, chromatographically homogeneous samples of all synthetic intermediates described herein. All reactions involving air- or moisture-sensitive species were carried out in an atmosphere of dry argon.

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(19) We could only detect a single isomer of intermediates **29**, **31**, and **2** by ^1H NMR and multiple development TLC analysis.

(20) We were unable to effect this type of carbonyl reduction in a similarly functionalized model system with a variety of other reducing agents including basic $NaBH_4$, $LiBH_4$, L-selectride, or 9-BBN.

(21) This work was assisted financially by a grant from the National Science Foundation and by graduate fellowships to J.G.S. from NSF and IBM Corp.

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Stereochemistry of the Reaction of Chlorine(I) Trifluoromethanesulfonate with Alkenes and Alkyl Halides

Sir:

Trifluoromethanesulfonate derivatives (triflates) are important intermediates in organic chemistry. There are many methods for the synthesis of these compounds,[1] but few are applicable to the preparation of highly halogenated esters and only one perfluoro ester, $CF_3SO_3CF_3$, has been reported.[2,3] With the discovery of CF_3SO_3Cl,[4] a variety of new halogenated esters can be obtained by the addition of CF_3SO_3Cl to alkenes and by the novel halogen displacement reaction shown in the following equation.

$$CF_3SO_3Cl + R\text{-}X \rightarrow XCl + CF_3SO_3R$$

$$X = Cl, Br; R = \text{alkyl and haloalkyl}$$

Our interest has been in the synthesis of highly fluorinated esters and in the mechanisms of the addition and displacement

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reaction. We have now established that the addition of CF_3SO_3Cl to the cis and trans isomers of CFH=CFH is stereospecific and that the displacement of Cl from a single stereoisomer of $CF_3CO_2CFH\text{-}CFHCl$ proceeds with retention of configuration. These results suggest that CF_3SO_3Cl and its bromine analogue[5] could be very useful reagents in organic chemistry, the main drawback to the latter being the control of the reactions in certain cases (*Caution! explosions can result from contact of CF_3SO_3Cl with readily oxidizable materials*).

The addition of CF_3SO_3Cl to *cis*-CFH=CFH proceeds readily in the absence of solvent at −111 to −40 °C to give an 88% (GLC) yield of $CF_3SO_3CFH\text{-}CFHCl$. Reaction of CF_3SO_3Cl with a 3:2 mixture of cis-trans CFH=CFH proceeds under the same conditions to give a 90% (GLC) yield of $CF_3SO_3CFH\text{-}CFHCl$. By ^{19}F NMR it was readily apparent that two stereoisomers are present in the latter reaction in the ratio of ~3:2 and that the more abundant isomer is the same as that formed using the pure cis olefin. Similar conclusions are arrived at by examination of the ^1H NMR spectra, but these spectra are rather extreme examples of complicated second-order spectra.[6]

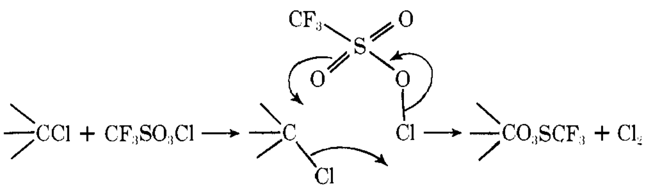
The distinction as to which stereoisomer is erythro and which is threo cannot be made with great certainty. In these compounds, one has vicinal $^3J_{HF}$, $^3J_{FF}$, and $^3J_{HH}$ couplings available as structural probes, but only the $^3J_{HH}$ coupling is completely reliable. Unfortunately, the latter is the most difficult to extricate from the observed ^1H or ^{19}F spectra. $^3J_{FF}$ is the easiest value to ascertain, but it is the least reliable. These uncertainties not withstanding, we tentatively assign the stereoisomers in the following way.

In the additions of CF_3SO_3Cl, CF_3SO_3Br[5], CF_3OCl[7], and CF_3CO_2Cl[8] to cis and trans CFH-CFH, a single stereoisomer is obtained with each geometrical isomer in every case. $^3J_{FF}$ values for these cis and trans adducts are, respectively, as follows: CF_3SO_3Cl (15.8, 20.5), CF_3SO_3Br (19.5, 25.5), CF_3OCl (14.5, 20.0), and CF_3CO_2Cl (15.4, 20.4 Hz). These values indicate an inverse dependence of $^3J_{FF}$ on the electronegativity of the substituents and a clear dependence on the dihedral angle assuming the same average rotomer populations. If one assumes that the most abundant rotomer in both erythro and threo has the R_fO group trans to Cl or Br, then the vicinal fluorines are trans for erythro and gauche for threo. For this related series of compounds only, it may then be a reasonable conclusion that the larger $^3J_{FF}$ belongs to the threo isomer and the smaller $^3J_{FF}$ to the erythro isomer, making the addition cis.[9-12]

Reaction of CF_3SO_3Cl with the stereoisomer formed by addition of CF_3CO_2Cl to cis CFH=CFH yields a single stereoisomer as indicated by ^{19}F NMR:

$$CF_3CO_2CFH\text{-}CFHCl + CF_3SO_3Cl \xrightarrow{-111 \text{ to } 22\ ^\circ C} CF_3CO_2CFH\text{-}CFHO_3SCF_3 + Cl_2$$

Because CF_3SO_3 is more electronegative than Cl, one expects $^3J_{FF}$ to be 10–15 Hz if the substitution proceeds with retention of configuration and 15–20 Hz if inversion occurs. The observed $^3J_{FF}$ value is 10.8 Hz, suggesting that the reaction proceeds with retention of configuration. We propose that the substitution proceeds by an S_Ei-type mechanism[13] like the following:



Precedent for reactions of this type are limited and we hope to provide other examples via additional reactions of CF_3SO_3Cl and reactions of CF_3SO_3Br and $BrOSO_2F$. The latter compound has previously been shown to undergo this type of reaction, but no systems were investigated that allowed any mechanistic conclusions to be made.[14]

Acknowledgment is made to the National Science Foundation for support of this research.

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(12) Additional support for this conclusion can be obtained from the ^{19}F chemical shift of the CHF groups. In a series of 2-fluoro-3-halobutanes and related compounds, the ^{19}F signal for the CHF group is at higher field for the threo isomers: G. A. Olah, M. Bollinger, and J. Brinch, *J. Am. Chem. Soc.*, **90**, 2587 (1968); R. Fields, *Annu. Rep. NMR Spectrosc.*, **5A**, 99 (1972), pp. 101, 102. For the series of compounds for which $^3J_{FF}$ values are given here, the addition product to the trans isomer has the two ^{19}F signals for the CHF groups at higher field in every case than the product with the cis isomer.
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Electrochemical Oxidation of Some Mesocyclic Dithioethers and Related Compounds

Sir:

Evidence supporting the hypothesis that suitable neighboring groups can facilitate oxidation at sulfur of substituted dialkyl sulfides has been previously presented.[1] Since all of these oxidations are irreversible, thermodynamic parameters cannot be directly secured from the data. Recently, the existence of unusually stable aliphatic cation radicals derived from certain mesocyclic dithioethers was reported.[2] Further one-electron oxidation affords the corresponding dications which have been obtained as solid salts.[3] The unusual stability of these compounds compared with ordinary alkyl sulfide cation radicals and dications has been attributed to intramolecular transannular interaction between the sulfur atoms in which an S–S bond is formed. These results suggested that reversible electrochemical oxidation might be observed with these compounds from which thermodynamic parameters could readily be obtained and that transannular participation by one sulfur atom might facilitate oxidation of the other.

This paper reports the electrochemical oxidation of some mesocyclic dithioethers and a series of other mono- and dithioethers. The most remarkable findings are that a number of the mesocyclic dithioethers studied undergo reversible oxidation with unusual ease. Further, the formal potential, $E_2°'$, for the second one-electron oxidation is equal to or less than that of the first.[4] These properties are, as far as we are aware, unprecedented in saturated aliphatic sulfide electrochemistry.

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