Supplementary Material Available: Listings of final atomic coordinates, anisotropic thermal parameters, and bond lengths and bond angles together with complete details of the structure determination for **9** (10 pages). Ordering information is given on any current masthead page.

Dichlorofluoromethane-*d*: A Versatile Solvent for VT-NMR Experiments

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VT-NMR experiments are often hindered or complicated by problems associated with the physical properties of the solvent being used. The most critical of these properties can be identified as follows: (1) the liquid range of the solvent (mp, bp); (2) the viscosity of the solvent at low temperatures; (3) the ability of the solvent to solvate a wide range of solutes; (4) the chemical and signal purity (spectral window); (5) the ease and expense of the solvent preparation. The solvents most commonly used today falter in a least one or more of these areas. For example, chloroform, though a good solvent for many solutes, has a relatively high melting point (–60 °C) and is rather viscous below –50 °C. Dichloromethane-d_2 and dichloromethane-d_2/pyridine-d_5 have greater liquid ranges but are expensive with the latter having additional problems, associated with the lack of chemical inertness. Dimethyl ether-d_6 has been proposed[1] because of its low melting point, but it too is very expensive.

To address this problem, we present here a simple one-step procedure for the synthesis of dichlorofluoromethane-*d* (DCFM). The solvent physical properties of DCFM are well-suited for variable temperature work: mp –135 °C, bp 10 °C;[2] low viscosity at low temperatures; solvates solutes analogously to chloroform; chemically inert; synthesized readily from commercially available chloroform-*d*.

Previously, DCFM has been reported in the literature to have been made by the action of NaOD/D_2O on chlorofluoromethane,[3] by mercuric salt catalyzed fluorination of chloroform,[4] and by a manner similar to what we report herein using antimony trifluoride to fluorinate chloroform-*d*.[5] Our method uses a stoichiometric amount of antimony trifluoride and chloroform-*d* with a catalytic amount of antimony pentachloride. It is performed at 30–35 °C in an all-glass one-pot set-up from which the product distills as it is formed and is collected in a dry ice/acetone cooled trap. The procedure is accomplished in high yield (80%) and can be run on large scale (100 mL of $CDCl_3$) conveniently.

The purity of this material has been checked by ^1H and ^{13}C NMR (Figure 1). Some chloroform-*d* and a small amount of chlorodifluoromethane-*d* (CDFM) distills over with the product.[6] These secondary components typically do not interfere with the solvent's utility but they can be removed and the product can be purified by simple distillation.

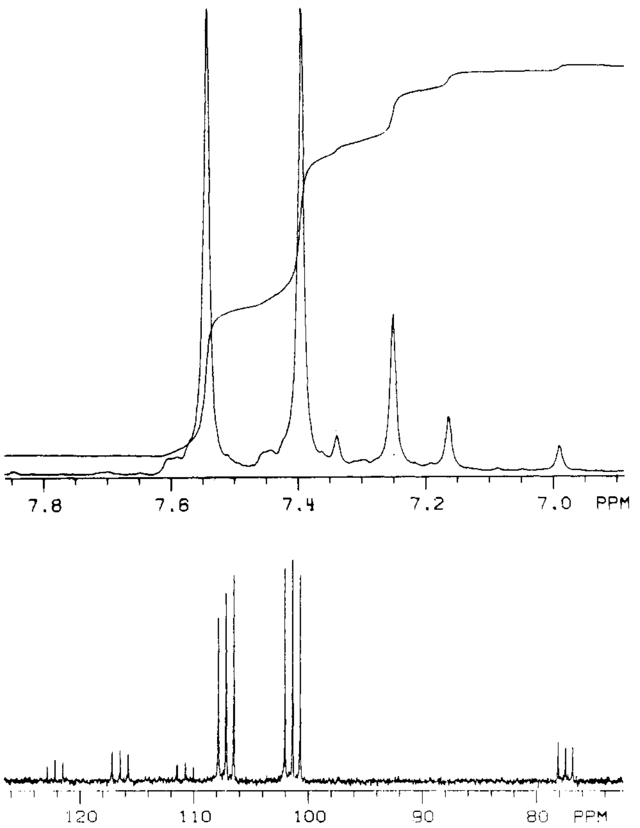

Figure 1. ^1H and ^{13}C NMR spectra of crude distillate from the halogen exchange reaction. ^1H NMR spectrum shows integration which indicated a product mixture of 80% DCFM, 13% $CDCl_3$, and 7% CDFM.

We have used this solvent successfully in a number of variable temperature studies,[7] and we anticipate its wide spread utility to many other problems of general interest.

Experimental Section

General Data. Proton NMR spectra were recorded on a ^1H NMR spectrometer equipped with a Nicolet 1180E computer interfaced with an Oxford magnet operating at 360 MHz. Carbon NMR spectra were recorded on a Nicolet NT200 spectrometer. All chemicals were used in their commercially available form (Aldrich).

Dichlorofluoromethane-*d*. A 100-mL single-neck Kjeldahl flask is charged with 50 g (0.28 mol) of antimony trifluoride from a freshly opened bottle which has been hand ground in a mortar and pestle.[8] Chloroform-*d* (100 g, 0.84 mol) plus 3 mL (6.9 g, 0.023 mol) of antimony pentachloride are added to the reaction flask. The flask is then immediately fitted to the all-glass apparatus. The reaction begins almost at once with bubbles appearing within a few minutes. The reaction is run under a static blanket of argon and is vented via the curved adaptor through the mercury bubbler which is attached to the argon manifold. A dry ice/acetone bath is brought up around the airless flask, thus submerging the greater portion of the flask. The product distills

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[1] Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

[2] DCFM can be supercooled easily to –150 °C for an hour.

[3] Hine, J.; Burske, N. W. *J. Am. Chem. Soc.* **1956**, *78*, 3337.

[4] (a) Andrews, L.; Keelan, B. W. *J. Am. Chem. Soc.* **1979**, *101*, 3500. (b) Squillacote, M. E.; Neth, J. E. *Magn. Reson. Chem.* **1987**, *25*, 53.

[5] Andrews, L.; Willner, H.; Prochaska, F. T. *J. Fluorine Chem.* **1979**, *13*, 273.

[6] From the integration of the residual ^1H NMR signals one can estimate the solvent composition as 80% DCFM, 13% chloroform, and 7% CDFM.

[7] (a) Anet, F. A. L.; Bacon, B.; Kofelevich, M., Unpublished results. (b) Kilway, K. V.; Siegel, J. S., manuscript in preparation. (c) Anet, F. A. L.; Chmurny, G. N.; Kane, J. *J. Am. Chem. Soc.* **1973**, *95*, 4423.

[8] (a) This step does not require the use of a drybox or special atmosphere but the transfer of the freshly ground material to the reaction apparatus must be expedient so as to avoid collecting too much moisture.

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over as the reaction proceeds. The reaction mixture is warmed gently by means of a heating mantle to ca. 35 °C. If rapid bubbling is seen in the exit bubbler, then the reaction is too vigorous and should be cooled until only occasional bubbles pass through the mercury exit tube. As the reaction proceeds the amount of liquid in the reaction flask diminishes and the reaction is considered complete when only a thick slurry remains in the reaction vessel; reaction time takes about 4 h in all. Roughly 70 g of DCFM is produced during this time. A yield of 80% is typical for this procedure, though yields as high as 87% have been obtained: ^{1}H NMR (neat) δ 7.47 (d, $J_{\mathrm{H-F}} = 50$ Hz); ^{13}C NMR (neat) δ 104.2 (dt, $J_{\mathrm{C-F}} = 292$ Hz, $J_{\mathrm{C-D}} = 34$ Hz).

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Registry No. DCFM, 558-19-0; CDFM, 1495-14-3; chloroform-*d*, 865-49-6.

Synthesis and Diels-Alder Reactions of 5-Alkenyl-1,3-oxathiole 3-Oxides. A New Class of Diheterosubstituted 1,3-Dienes

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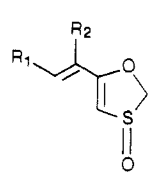
The Diels-Alder reaction remains one of the cornerstones of synthetic organic chemistry.[1] Recent years have witnessed an almost explosive development of heterosubstituted dienes as components for Diels-Alder syntheses.[2,3] The heteroatom substituent not only can control the regiochemical and stereochemical outcome of the cycloaddition but also can endow the newly formed cyclohexene with useful functionality for subsequent elaboration of the cycloadduct.[1,2]

For ongoing studies of factors which control face selectivity in Diels-Alder reactions of chiral dienes,[4] we required a series of sulfinyl dienes that incorporated an additional oxygen substituent. Although the preparation and cycloaddition chemistry of dienes containing alkoxy and sulfide substituents have been examined in some detail,[5] dienes containing sulfinyl and alkoxy substituents have not, to the best of our knowledge, received significant study.[6] In this paper, we report that one class of dienes of this general type, specifically 5-alkenyl-1,3-oxathiole 3-oxides (**1**), can be prepared by the general method of Johnson.[7] We also report[4] that the sulfinyl substituent exerts complete control of the face selectivity of Diels-Alder reactions of these dienes and surprisingly that the ring oxygen substituent has a net *deactivating* effect on cycloadditions of dienes **1** with electron-deficient dienophiles.



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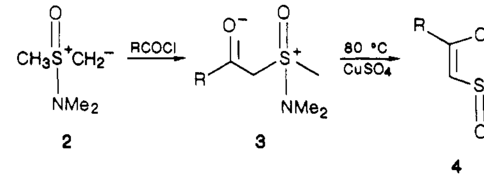
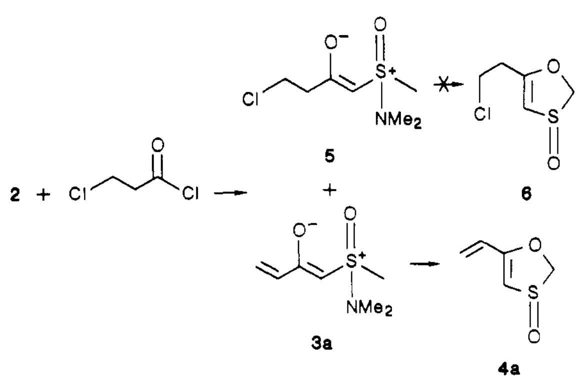
Johnson had previously demonstrated[7] that ylides **3** derived from acylation of (dimethylamino)methyloxosulfonium methylide (**2**) with acid chlorides cyclize in the presence of anhydrous $CuSO_4$ to yield 5-substituted 1,3-oxathiole-3-oxides **4** in good yield (eq 1). Although 5-alkenyl-substituted 1,3-oxathiole 3-oxides were not included in this original report,[7] we have found that the Johnson synthesis can be employed to provide ready access to this class of heterosubstituted 1,3-dienes. Our results are summarized in Table I. The reaction of **2** with α,β-unsaturated acid chlorides was instantaneous at −78 °C and yielded unsaturated ylides **3a–i** as hygroscopic oils, which, in most cases, were impossible to obtain in anhydrous form. The oxygen-substituted ylides **3e**, **3f**, and **3i** were particularly prone to decomposition during isolation, thus necessitating rapid chromatographic purification. Cyclization of the unsaturated ylides at 80 °C in the presence of anhydrous $CuSO_4$ proceeded without incident to give, after quick filtration of the crude material through alumina, the corresponding dienes **4a–i** in good yields.



(1)

Attempts to prepare the parent ylide of this class, **3a**, from acryloyl chloride and oxosulfonium methylide **2** were not successful, since reaction of these components afforded only traces of **3a** and copious amounts of polymer. Alternatively, 3-chloropropionyl chloride was found to react smoothly with **2**, giving the chloro-substituted ylide **5** in 68% yield. Initial attempts to cyclize **5** gave intractable mixtures with no trace of the expected oxathiole 3-oxide **6**. However, analysis of the reaction mixture at short reaction times did reveal the presence of **3a**, suggesting that **5** was decomposing, presumably by loss of HCl, under the reaction conditions. The known acid lability[7] of oxa-



(2)

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[1] See, e.g.: Desimoni, G.; Tacconi, G.; Bario, A.; Pollini, G. P. *Natural Product Syntheses Through Pericyclic Reactions*; ACS Monograph 180; American Chemical Society: Washington, DC, 1984; Chapter 5.

[2] For reviews, see: Petrazilka, M.; Grayson, J. I. *Synthesis* **1981**, 753. Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400.

[3] Recent leading references as well as a discussion of models for predicting regioselectivity in cycloadditions of heterosubstituted dienes can be found in Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381.

[4] See: Fisher, M. J.; Kahn, S. D.; Hehre, W. J.; Overman, L. E. *J. Am. Chem. Soc.*, in press.

[5] Cohen, T.; Mura, A. J.; Shull, D. W.; Fogel, E. R.; Ruffner, R. J.; Falck, J. R. *J. Org. Chem.* **1976**, *41*, 3218. Trost, B. M.; Ippen, J.; Vladuchick, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 8116. Trost, B. M.; Vladuchick, W. C.; Briges, A. G. *Ibid.* **1980**, *102*, 3554. Cohen, T.; Kosarych, Z. *J. Org. Chem.* **1982**, *47*, 4008.

[6] Dienes containing acylamino and sulfinyl substituents have received some attention: Overman, L. E.; Petty, C. B.; Ban, T.; Huang, G. *J. Am. Chem. Soc.* **1983**, *105*, 6335.

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