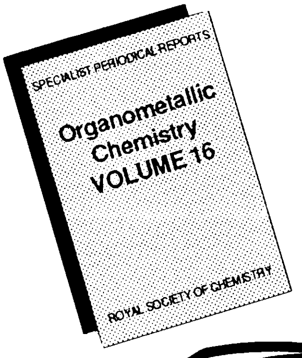
ROYAL SOCIETY OF CHEMISTRY

TWO IMPORTANT NEW BOOKS FOR INORGANIC CHEMISTS . . .



Organometallic Chemistry Vol. 16

This volume reviews the literature published during 1986.

Brief Contents:
Group I: The Alkali and Coinage Metals; Group II: Alkaline Earths and Zinc and its Congeners; Boron with the Exception of the Carbaboranes; Carbaboranes, including their Metal Derivatives; Group III: Aluminium, Gallium, Indium and Thallium; Group IV: The Silicon Group; Group V: Arsenic, Antimony and Bismuth; Metal Carbonyls; Organometallic Compounds Containing Metal – Metal Bonds; Ligand Substitution Reactions of Metal and Organometal Carbonyls with Group V and VI Donor Ligands; Complexes Containing Metal – Carbon σ-Bonds of the Groups Scandium to Manganese, Including Carbenes and Carbynes; Complexes Containing Metal – Carbon σ-Bonds of the Groups Iron, Cobalt and Nickel; Metal – Hydrocarbon π-Complexes, Other than π-Cyclopentadienyl and π-Arene Complexes; π-Cyclopentadienyl, π-Arene and Related Complexes; Homogeneous Catalysis by Transition Metal Complexes; Structures of Organometallic Compounds determined by Diffraction Methods.

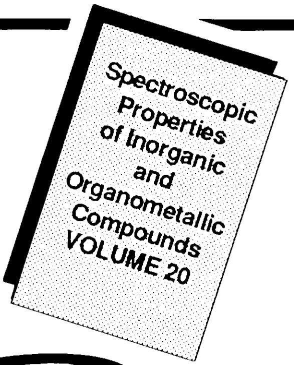
This volume contains a foreword by the senior reporter, an extensive contents list and is indexed. Each chapter includes extensive references.

NEW

Senior Reporters: E.W. Abel, *University of Exeter* and F.G.A. Stone, *University of Bristol*

Specialist Periodical Report (1987)
Hardcover 544pp
ISBN 0 85186 641 7
Price £120.00 ($236.00)

Spectroscopic Properties of Inorganic and Organometallic Compounds Vol. 20



"It should definitely be included in the library holdings of all chemistry departments which are attempting to conduct research in the areas of inorganic and organometallic chemistry." – *Journal of the American Chemical Society reviewing Vol. 17.*

This book reviews the recent literature published up to late 1986.

Brief Contents:
Nuclear Magnetic Resonance Spectroscopy; Nuclear Quadrupole Resonance Spectroscopy; Rotational Spectroscopy; Characteristic Vibrations of Compounds of Main-group Elements; Vibrational Spectra of Transition-element Compounds; Vibrational Spectra of Some Co-ordinated Ligands; Mössbauer Spectroscopy; Gas-phase Molecular Structures Determined by Electron Diffraction.

NEW

Senior Reporters: G. Davidson, *University of Nottingham*, and E.A.V. Ebsworth, *University of Edinburgh*

Specialist Periodical Report (1987)
Hardcover 494pp
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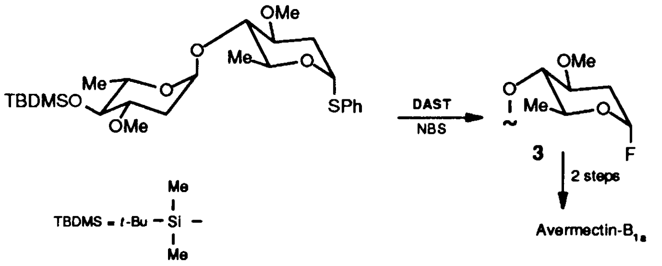
DAST and Methyl DAST

Et_2NSF_3 **1** Me_2NSF_3 **2**

Although fluorinated organic compounds find wide application in key areas of polymer chemistry, medicinal chemistry and photographic imaging (tomography), their laboratory syntheses pose challenges due to the special procedures and equipment often needed for the safe handling of many reactive fluorinating agents. **DAST** (diethylaminosulfur trifluoride, **1**) and **methyl DAST** (dimethylaminosulfur trifluoride, **2**) are stable, liquid reagents which were introduced in the mid-1970's.[1] They not only provide an effective solution to a number of handling problems, but also offer the researcher two versatile reagents possessing many desirable properties such as greater selectivity, milder reaction conditions and compatibility with a variety of functional groups, compared to conventional reagents.[1a] Not surprisingly, these reagents have found widespread utility in the fluorination of simple alcohols, aldehydes and ketones, as well as sensitive polyfunctional molecules such as cephalosporins,[2] carbohydrates,[3,4] penems,[5] glycosides[6] and peptides.[7]

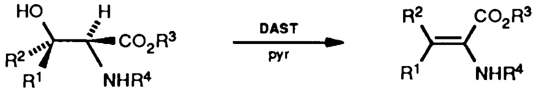
Preparation of glycosyl fluorides:[4]

Glycosyl fluorides, which are important synthetic intermediates in carbohydrate chemistry, have been prepared by treating glycosyl thioethers with **DAST**-NBS[3a] or by treating furanose or pyranose hemiacetals with **DAST.**[3b,c] The Nicolaou research group utilized the glycosyl fluoride **3**, prepared by the former method, in an interesting synthesis of Avermectin-B_{1a}.[4]



Dehydration of β-hydroxy α-amino acids:[8]

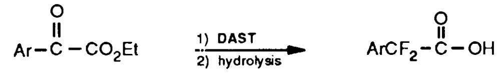
Olefin formation is sometimes observed as a side reaction in the fluorination of alcohols with **DAST**. This observation was exploited by Shanzer and Somekh, who developed a general synthesis of dehydro amino acids from β-hydroxy α-amino acids.



The dehydro amino acids, which serve as precursors for the asymmetric synthesis of amino acids and peptides, were obtained in high yield as well as high isomeric purity.

Preparation of difluoroarylacetic acids:[9]

The difluoroarylacetic acids which are of medicinal interest, were previously thought to be somewhat inaccessible due to the lack of practical preparative methods. Middleton and Bingham discovered that the reaction of aryl keto esters and amides with neat **DAST** gave the α,α-difluoro acids in high yields.



$$Ar-\overset{\overset{\displaystyle O}{\|}}{C}-CO_2Et \xrightarrow[\text{2) hydrolysis}]{\text{1) DAST}} ArCF_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

References:

(1)(a) Middleton, W.J. *J. Org. Chem.* **1975,** *40,* 574. (b) Markovskij, L.N.; Pashinnik, V.E.; Kirsanov, A.V. *Synthesis* **1973,** 787. (c) For a recent review, see Hudlický, M. *Fluorination with Diethylaminosulfur Trifluoride and Related Aminofluorosulfuranes;* Organic Reactions; John Wiley and Sons, Inc.: New York, 1988; Vol. 35, Chapter 3, p513. (2) Boswell, G.A., Jr.; Brittelli, D.R. U.S. Patent 3 919 204 ,1975; *Chem. Abstr.* **1976,** *84,* 90161g. (3)(a) Posner, G.H.; Haines, S.R. *Tetrahedron Lett.* **1985,** *26,* 5. (b) Rosenbrook, W., Jr.; Riley, D.A.; Lartey, P.A. *ibid.* **1985,** *26,* 3. (4) Nicolaou, K.C.; Dolle, R.E.; Papahatjis, D.P.; Randall, J.L. *J. Am. Chem. Soc.* **1984,** *106,* 4189. (5) Mak, C.P.; Fliri, H. Ger. Offen. DE 3 434 504, 1985; *Chem. Abstr.* **1985,** *103,* 195945n. (6) Somawardhana, C.W.; Brunngraber, E.G. *Carbohydr. Res.* **1983,** *121,* 51. (7) Sufrin, J.R.; Balsubramanian, T.M.; Vora, C.M.; Marshall, G.R. *Int. J. Pept. Protein Res.* **1982,** *20,* 438. (8) Somekh, L.; Shanzer, A. *J. Org. Chem.* **1983,** *48,* 907. (9) Middleton, W.J.; Bingham, E.M. *ibid.* **1980,** *45,* 2883.

23,525-3 Diethylaminosulfur trifluoride (DAST, **1**)
5g $40.45; 25g $124.40

24,821-5 Dimethylaminosulfur trifluoride (methyl DAST, **2**)
5g $37.55; 25g $121.40

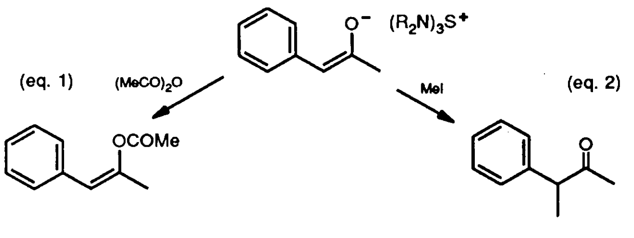
TAS-F

$(Me_2N)_3S^+ \quad Me_3SiF_2^-$

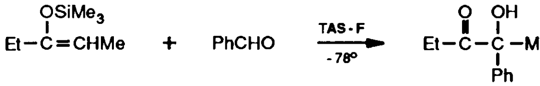
1

TAS enolates are versatile synthetic intermediates generated from silyl enol ethers and **tris(dimethylamino)sulfur (trimethylsilyl)difluoride (TAS-F, 1)** in aprotic solvents. These "naked" enolates exhibit increased nucleophilicity compared with metal-coordinated analogs and are free from the hydrogen-bonded species formed during the traditional method of enolate-ion generation (carbonyl compound/base) in aqueous or alcoholic media.

The isolated tris(dialkylamino)sulfonium enolate undergoes O-acetylation (eq. 1) as well as C-alkylation (eq. 2).[1]



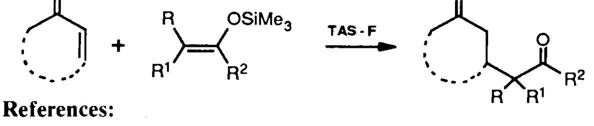
TAS enolates react with aldehyde substrates to give aldol-type adducts with predominantly *erythro* stereochemistry.[1]



$$Et-\overset{\overset{\displaystyle OSiMe_3}{|}}{C}=CHMe + PhCHO \xrightarrow[\text{-78°}]{\text{TAS-F}} Et-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}-Me$$

Michael-type additions have been reported in which **TAS-F** catalyzes the selective conjugate addition of trimethylsilylketene acetals to α,β-unsaturated ketones. High yields of only the 1,4-addition products are obtained.[2]

The chemistry of TAS-F has been reviewed recently.[3]



References:

(1) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983,** *105,* 1598. (2) RajanBabu, T.V. *J. Org. Chem.* **1984,** *49,* 2083. (3) Hudlický, M. *Fluorination with Diethylaminosulfur Trifluoride and Related Aminofluorosulfuranes;* Organic Reactions; John Wiley and Sons, Inc.: New York, 1988; Vol. 35, Chapter 3, p513.

25,060-0 Tris(dimethylamino)sulfur (trimethylsilyl)difluoride
(TAS-F, **1**) **1g $23.15; 5g $76.35**

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