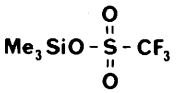
Trimethylsilyl Trifluoromethanesulfonate

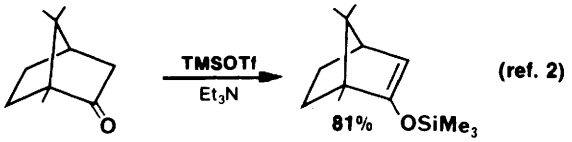
Versatile Reagent and Catalyst

Trimethylsilyl trifluoromethanesulfonate (**1**, trimethylsilyl triflate, TMSOTf) is an exceptionally strong silylating



1

agent.[1] Representative reactions in which **1** is used stoichiometrically are shown below.



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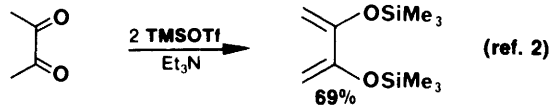

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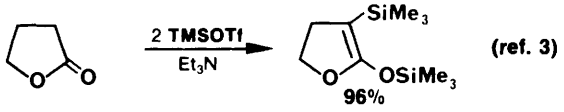

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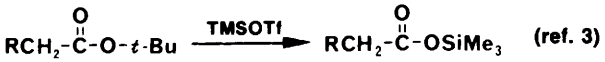

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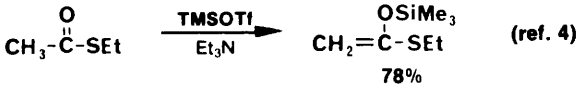

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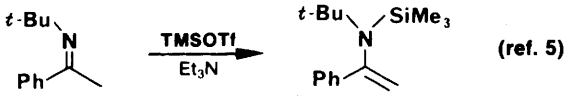

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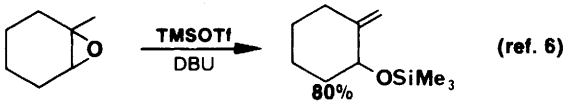
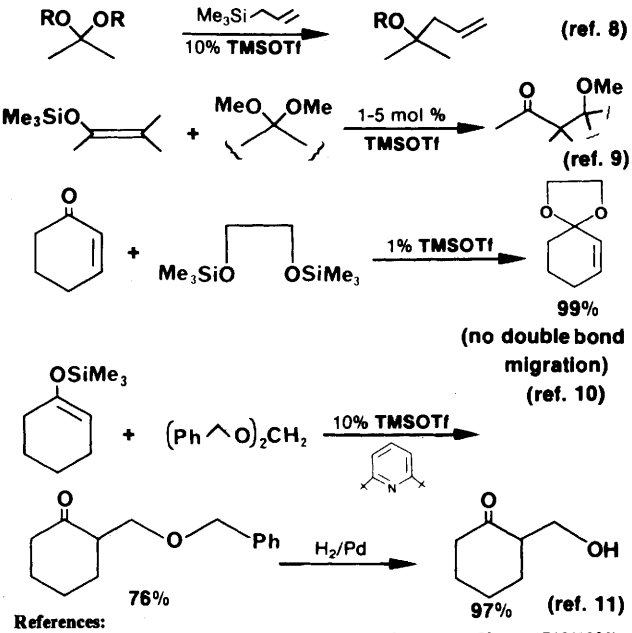


(ref. 6)

Trimethylsilyl trifluoromethanesulfonate also functions as a catalyst for a variety of transformations of importance in organic synthesis. The versatility of **1** in this regard is illustrated below.

(ref. 7)



References:

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TRIMETHYLBROMOSILANE
TRIMETHYLIODOSILANE
TRIMETHYLSILYL TRIFLUOROMETHANESULFONATE

$(CH_3)_3SiBr$	$CF_3SO_3Si(CH_3)_3$	$(CH_3)_3SiI$

Three Highly Reactive Silylating Agents

The silylating rates of ten different silylating agents were investigated by H.H. Hergott and G. Simchen[1]: trimethylbromosilane, trimethylsilyl trifluoromethanesulfonate and trimethyliodosilane gave by far the highest reaction rates.

Relative rates (k_{rel}) for the silylation of ketones by some silylating agents [$(CH_3)_3SiX$]:

X	Cl	CH_3SO_3	$C_6H_5SO_3$	$(CH_3)_3SiOSO_3$	Br	CF_3SO_3	I
k_{rel}	1	40	160	270	$7.9.10^4$	$6.7.10^8$	7.10^9

Trimethylbromosilane[2], trimethylsilyl trifluoromethanesulfonate[3][4] and ref in [1] and trimethyliodosilane[5] were also described by other authors as reagents for silylating reactions. For further synthetic uses of these highly reactive reagents note the following references and the references cited therein [a comprehensive review on $(CH_3)_3SiBr$ and $(CH_3)_3SiI$ covering the literature until early 1980 was recently published by A.H. Schmidt[22]]:

$(CH_3)_3SiBr$[6-8][21][22] e.g cleavage of ethers[6], lactones[8], orthoesters[6] and phosphonates[7]; conversion of alcohols to bromides[6]; synthesis of glycosyl bromides[21]

$CF_3SO_3Si(CH_3)_3$[1][9-14] e.g. cleavage of oxiranes[9][10]; catalyst for different reactions: synthesis of nucleosides, conversion of acetals to ethers[11], acetalization under aprotic conditions[11], condensation of silyl enol ethers with acetals[12][13]; cleavage of tert-butylesters under non acidic conditions[14]

$(CH_3)_3SiI$[8][15-22] e.g. cleavage of ethers[15], esters, lactones[8], acetals[16], phosphonates[17] and carbamates; deoxygenation of sulfoxides and α-ketols[18]; conversion of alcohols to iodides; conversion of ketals to ketones; synthesis of allylic alcohols[19]; synthesis of α-iodosulfides[20]

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CLASSIFIED ADVERTISEMENTS

UNIVERSITY OF SOUTHAMPTON

CHEMISTRY DEPARTMENT

Postdoctoral Research Fellowship in N.M.R. Spectroscopy of Liquid Crystals.

Applications are invited for an S.R.C. supported Fellowship to work on the development of spin echo and multiple quantum experiments and their applications to the study of liquid crystals.

The appointment can begin on 1 June or at a later date and will be for a period of one year with possible renewal for a second.

The salary will be on the 1A scale up to a maximum of £6880 per annum, depending on age and experience.

Applications, with the names of two referees should be sent to Dr. J. W. Emsley, Department of Chemistry, University of Southampton, Southampton SO9 5NH.

BIRKBECK COLLEGE
(University of London)

DEPARTMENT OF CHEMISTRY

POSTDOCTORAL RESEARCH OFFICER IN ORGANIC CHEMISTRY

Applications are invited for the above post, supported by the S.R.C., to work with Dr. H. A. J. Carless on photochemical reactions in the synthesis of the thromboxane A_2 ring system. Experience in synthetic organic chemistry or photochemistry is desirable. The appointment is tenable for up to 2 years, commencing 1st October 1981. Initial salary in the range £7037 – £7847 p.a. (including London Weighting). Applications, including a curriculum vitae and the names of two referees, should be sent to the Assistant Secretary (Personnel), (C.C.) Birkbeck College, Malet Street, London, WC1E 7HX.

UNIVERSITY OF EXETER

DEPARTMENT OF CHEMISTRY

Applications are invited for an SRC Postdoctoral Research Fellowship, tenable from 1 October 1981, for work in collaboration with Dr. W. Carruthers on the synthesis of the sesquiterpene quadrone and related compounds of potential physiological interest. Experience in synthetic work is essential.

The appointment will be for one year in the first instance, with possible extension to a second year. Salary: in the range £6070 – £6475 p.a., plus superannuation.

Applications with curriculum vitae and the names and addresses of two referees should be sent to Dr. W. Carruthers, Chemistry Department, University of Exeter, Exeter EX4 4QD, as soon as possible.

THE UNIVERSITY OF LEEDS

DEPARTMENT OF INORGANIC AND STRUCTURAL CHEMISTRY

Applications are invited for a post of Postdoctoral RESEARCH FELLOW in the Department of Inorganic and Structural Chemistry for work with Professor N. N. Greenwood and Dr. J. D. Kennedy on synthetic and structural aspects of metalloborane chemistry involving the use of the techniques of modern organometallic transition metal chemistry.

A good honours degree in chemistry and a higher degree or research experience in main-group or transition metal chemistry are required.

The post is available from 1 October 1981 for a period of up to 3 years.

Salary on the IA Scale for Research and Analogous Staff (£6070 – £10,575) according to age, qualifications and experience.

Informal enquires may be made to Professor N. N. Greenwood (telephone Leeds (0532) 31751 ext. 6060).

Application forms and further particulars may be obtained from the Registrar, The University, Leeds LS2 9JT, quoting reference number 44/12/AD. Closing date for applications 22 June 1981.

UNIVERSITY OF SALFORD

DEPARTMENT OF CHEMISTRY AND APPLIED CHEMISTRY

POSTDOCTORAL RESEARCH FELLOW

To collaborate with Dr. T. W. Wallace in research on new synthetic applications of organocopper reagents.

The appointment is SRC sponsored and tenable for two years from 1 September, 1981. Initial salary within the range of £6070 - £6880. USS benefits.

Application forms obtainable from the Registrar, University of Salford, Salford M5 4WT (tel: 061-736 5843 ext. 215) to whom completed applications should be returned by 26 June 1981 quoting reference number CH/282/CC.

UNIVERSITY OF LIVERPOOL

Department of Organic Chemistry

Applications are invited for the post of Postdoctoral Senior Research Assistant for work on a project entitled 'Mechanistic Studies of One-Electron Reactions of Diazo-compounds and Azides'. The project is financed for two years from 1st October, 1981, by the Science Research Council.The work will be carried out in collaboration with Professor V. D. Parker, (Norwegian Institute of Technology, Trondheim) and the person appointed may be required to make short visits to Norway.

Initial salary in the range £6070 – £6880 per annum.

Applications should be received as soon as possible by The Registrar, The University, P.O. Box 147, Liverpool L69 3BX.

Quote Ref: RV/792/CC.

UNIVERSITY OF LIVERPOOL

Department of Organic Chemistry

Postdoctoral Senior Research Assistant

Applications are invited for the post of Postdoctoral Senior Research Assistant to work with Professor I. O. Sutherland on macropolycyclic compounds as analogues of receptors and enzymes. The project is financed for two years from 1st October, 1981 by the Science Research Council.

Initial salary within the range £6070 – £6880 per annum.

Applications, together with the names of three referees, should be received not later than 19th June, 1981, by The Registrar, The University, P.O. Box 147, Liverpool, L69 3BX, from whom further particulars may be obtained.

Quote Ref: RV/789/CC.

'Two postdoctoral associateships are available in Nucleic acid synthesis from July 1, 1981 for three years in the Department of Microbiology, Biomedical Centre, University of Uppsala, Box 581, S-751 23 Uppsala, Sweden. The appointee will assist with research in developing influenza virus polymerase inhibitors under the supervision of Dr. J. B. Chattopadhyaya. Applications should be sent directly to Dr. J. B. Chattopadhyaya to the above address.'

The Polytehnic of North London
DEPARTMENT OF CHEMISTRY

Post-doctoral Fellowship in X-Ray Crystallography

Applications are invited for a post-doctoral research appointment, supported by the SRC, to work with Dr. M. McPartlin on X-RAY DIFFRACTION STUDIES OF HIGH NUCLEARITY METAL CARBONYL CLUSTER COMPOUNDS.

The research will be in collaboration with Professor J. Lewis of the University of Cambridge. The fellowship is available immediately and the appointment is tenable for two years. The initial salary will be in the range of £7221 to £8019 per annum.

Applications should be sent as soon as possible to the Head of Department of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB.

KING'S COLLEGE LONDON
(University of London)

DEPARTMENT OF CHEMISTRY

Applications are invited for an SRC POSTDOCTORAL RESEARCH ASSISTANTSHIP to study the synthesis of reduced porphyrin systems in collaboration with Dr. K. Jones. Applicants should have a good background in synthetic organic chemistry coupled with an interest in heterocyclic chemistry. The successful applicant will be expected to take up the post on 1st October, 1981. Salary £6070 – £6880 p.a. plus £967 London Allowance. Applications with curriculum vitae and names of two referees to Dr. K. Jones, Department of Chemistry, King's College London, Strand, London, WC2R 2LS from whom further details may be obtained.

THE UNIVERSITY OF MANCHESTER

DEPARTMENT OF CHEMISTRY

Applications are invited for the post of Research Associate in the above department to work with Dr. R. T. Brown on novel biomimetic and partial syntheses of monoterpenoid indole alkaloids. Appointment is tenable for three years from 1st October, 1981. Salary up to £6,880 per annum. Applications, including the names of two referees should be sent to Dr. R. T. Brown, Department of Chemistry, The University, Manchester M13 9PL.