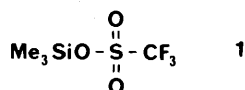




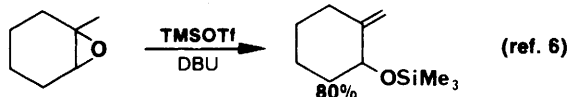
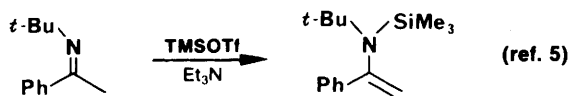
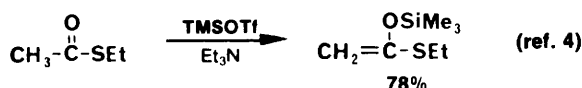
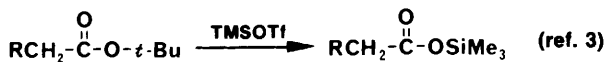
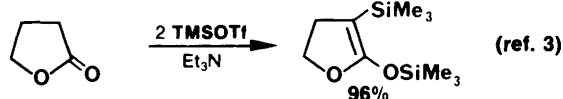
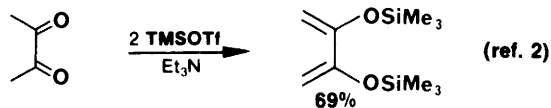
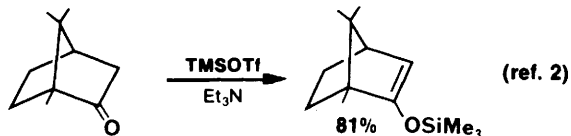
# Trimethylsilyl Trifluoromethanesulfonate

## Versatile Reagent and Catalyst

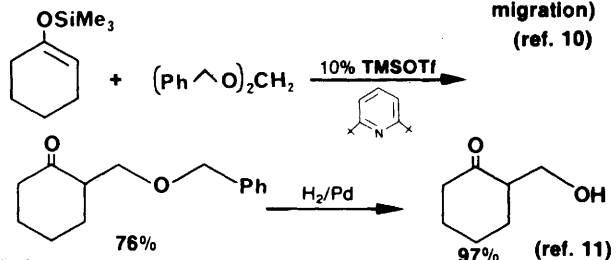
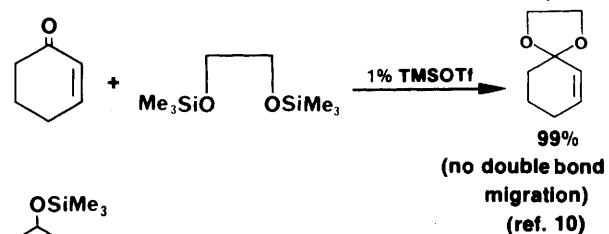
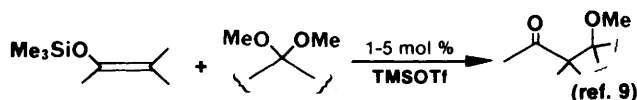
Trimethylsilyl trifluoromethanesulfonate (1, trimethylsilyl triflate, TMSOTf) is an exceptionally strong silylating



agent.<sup>1</sup> Representative reactions in which 1 is used stoichiometrically are shown below.



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.



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13,206-3	Triethylamine.....	500g \$8.75; 2kg \$22.45
13,900-9	1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)	25g \$9.45; 100g \$26.30; 500g \$87.75
20,826-4	Allyltrimethylsilane.....	10g \$13.25; 50g \$44.00
22,580-0	1,2-Bis(trimethylsilyloxy)ethane.....	10g \$7.30; 50g \$22.50
21,958-4	2,6-Di-tert-butylpyridine.....	\$g \$19.60



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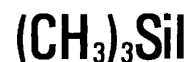
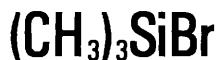
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# TRIMETHYLBROMOSILANE TRIMETHYLIODOSILANE TRIMETHYLSILYL TRIFLUOROMETHANESULFONATE



## Three Highly Reactive Silylating Agents

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

Relative rates ( $k_{\text{rel}}$ ) for the silylation of ketones by some silylating agents  $((\text{CH}_3)_3\text{SiX})$ :

X	Cl	$\text{CH}_3\text{SO}_3$	$\text{C}_6\text{H}_5\text{SO}_3$	$(\text{CH}_3)_3\text{SiOSO}_3$	Br	$\text{CF}_3\text{SO}_3$	I
$k_{\text{rel}}$	1	40	160	270	$7.9 \cdot 10^4$	$6.7 \cdot 10^8$	$7 \cdot 10^9$

Trimethylbromosilane<sup>2)</sup>, trimethylsilyl trifluoromethanesulfonate<sup>3)4)</sup> and ref in <sup>1)</sup> and trimethyliodosilane<sup>5)</sup> 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  $(\text{CH}_3)_3\text{SiBr}$  and  $(\text{CH}_3)_3\text{SiI}$  covering the literature until early 1980 was recently published by A. H. Schmidt<sup>22)</sup>]:

$(\text{CH}_3)_3\text{SiBr}$ <sup>6-8)21)22)</sup> e.g. cleavage of ethers<sup>6)</sup>, lactones<sup>8)</sup>, orthoesters<sup>6)</sup> and phosphonates<sup>7)</sup>; conversion of alcohols to bromides<sup>6)</sup>; synthesis of glycosyl bromides<sup>21)</sup>

$\text{CF}_3\text{SO}_3\text{Si}(\text{CH}_3)_3$ <sup>1)9-14)</sup> e.g. cleavage of oxiranes<sup>9)10)</sup>; catalyst for different reactions: synthesis of nucleosides, conversion of acetals to ethers<sup>11)</sup>, acetalization under aprotic conditions<sup>11)</sup>, condensation of silyl enol ethers with acetals<sup>12)13)</sup>; cleavage of tert-butylesters under non acidic conditions<sup>14)</sup>

$(\text{CH}_3)_3\text{SiI}$ <sup>8)15-22)</sup> e.g. cleavage of ethers<sup>15)</sup>, esters, lactones<sup>8)</sup>, acetals<sup>16)</sup>, phosphonates<sup>17)</sup> and carbamates; deoxygenation of sulfoxides and  $\alpha$ -ketols<sup>18)</sup>; conversion of alcohols to iodides; conversion of ketals to ketones; synthesis of allylic alcohols<sup>19)</sup>; synthesis of  $\alpha$ -iodosulfides<sup>20)</sup>

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- A. H. Schmidt, *Chemiker-Zeitung* **104**, 253 (1980)

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For other silylating agents see FLUKA-catalogue 12, 1980/81 or the new FLUKA-brochure "Silylating Agents".

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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.

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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 enquiries 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.

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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.

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## 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 monoterpene 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.