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Preliminary communication

THE SYNTHESIS OF FUNCTIONALISED SILYLTRIFLATES*

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Summary

The cleavage of R_2SiXY (R = alkyl, phenyl; X = H, Cl, Y = α-Np, Ph, Cl, H) by triflic acid is selective, leading to new difunctional silyltriflates, $R_2SiXOTf$, with the relative ease of cleavage of Si—Y being, $\alpha\text{-Np} > \text{Ph} > \text{Cl} > \text{H} \gg \text{Me, Et, Bu}$

The highly reactive silyltriflates, R_3SiOTf and $R_2Si(OTf)_2$ are proving extremely valuable reagents in organic chemistry [1—3]. Only a limited number of such compounds have been synthesised, and only those with R = alkyl, or aryl have been reported [1—4]. This paper describes the simple synthesis of a variety of functionalised silyltriflates.

The most common route to silyltriflates involves the direct reaction of R_3SiX with triflic acid [5].

$$R_3SiX + CF_3SO_3H \longrightarrow R_3SiOSO_2CF_3 + HX$$

(X = Cl [5], H [6], Ph [6], $CH_2CH{=}CH_2$ [6], CH_3 [6])

We chose to investigate the reaction of R_2SiXY with triflic acid for its specifici

$$R_2SiXY + CF_3SO_3H \longrightarrow R_2SiXOSO_2CF_3 + HY$$

(X, Y = α-Np, Ph, Cl, H; R = Me, Et, Bu^t)

This reaction has the twin advantages of avoiding expensive reagents, such as silver triflate [7], and using readily available starting materials. Prior to this study, no information was available concerning the relative ease of cleavage of various groups from silicon by triflic acid, except for the inference that alkyl groups are least likely to be removed [6]. The results and reaction conditions

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are given in Table 1, and show that compounds $R_2SiXOTf$ can be synthesised readily by highly selective cleavages. It can be inferred from the table that the ease of replacement of Si—Y by Si—OTf decreases in the order, α-Np>Ph>Cl> H>>Me, Et, Bu^{t}. In no cases were competitive cleavages of Si—X or Si—R observed.

TABLE 1

THE SYNTHESIS OF NEW SILYLTRIFLATES, $R_2SiXOTf$, FROM R_2SiXY AND TRIFLIC ACID

R_2SiXY	$R_2SiXOTf$	Isolated yield (%) [a]	B.p. (°/mmHg)	Reaction conditions [b]
Me_2SiHCl	$Me_2SiHOTf$ [c]	95	123/760	stirred 5 min
Me_2SiHPh	$Me_2SiHOTf$ [c]	86	123/760	stirred 5 min
H_3SiPh	H_3SiOTf	see ref. 9		immediate reaction
Bu^{t}PhSiClPh	Bu^{t}PhSiClOTf [c]	92	70/0.01	stirred 30 min
Ph_3SiBu^t	Ph_2SiBu^tOTf [c]	73	115/0.02	silane dissolved in $CHCl_3$, 30 min reflux
Cl_3SiPh	Cl_3SiOTf [c]	85	35/25	60° for 3 h
(±)-α-NpPhMeSiH	PhMeSiHOTf	[d]		silane dissolved in $CHCl_3$, stirred 10 min
Ph_2MeSiH	PhMeSiHOTf [c]	93	67/0.8	stirred 5 min

[a] All reactions essentially quantitative by ^{1}H NMR. [b] Unless otherwise stated, equimolar quantities of reagents used, triflic acid added dropwise to neat silane at ambient temperature, distilled after stirring. All reactions and atmospheric pressure distillations carried out under a blanket of dry nitrogen. [c] Satisfactory microanalytical data were obtained. [d] All spectral properties identical to the product obtained from Ph_2MeSiH, not isolated.

For characterisation, we isolated the products by distillation, or crystallisation, but for use in synthesis the reagents can be used in situ.

Some comment is necessary on some of the individual compounds. Preliminary studies indicate that $HSiMe_2OTf$ may be a very useful reagent as it is significantly more reactive than the more common Me_3SiOTf. Similarly, the highly hindered Ph_2Bu^tSiOTf provides an attractive, alternative route to hydrolytically stable protected alcohols etc. [8].

We have opened up a possible route to simple, chiral, bifunctional, organosilicon compounds, through the selective cleavage of (±)-α-NpPhMeSiH to give PhMeSiHOTf. If the reaction is stereoselective this could have important applications in chiral syntheses. Further studies are in progress.

The first silyltriflate containing no organic groups, Cl_3SiOTf, was prepared from $PhSiCl_3$,,and isolated as a pure compound. This compound apparently shows little promise as a reagent as it forms insoluble, unreactive complexes with amines, such as pyridine [9].

Silyltriflate H_3SiOTf is readily formed from $PhSiH_3$, and was characterised by its NMR spectra. *Caution.* Silyltriflate cannot be isolated pure by distillation at atmospheric pressure as the explosive silane, SiH_4, is formed by disproportionation [9]. H_3SiOTf with Et_3N can be used to form silyl enol ether in the same manner as other silyltriflates.

There is some evidence from our work that the cleavage of phenyl groups from silicon by triflic acid involves radicals, at least as a competitive route. Cleavage of Ph_3SiBu^t with carefully purified triflic acid, and in all glass apparatus, produced a persistent red colour giving a strong, unresolved ESR signal and biphenyl was obtained in approximately 25% yield from the reaction mixture.

Table 2 gives ^{1}H and ^{29}Si NMR spectra for a variety of silyltriflates which should be of use to workers using the reagents in situ.

TABLE 2

^{1}H AND ^{29}Si NMR DATA FOR SILYLTRIFLATES

Silyltriflate	^{1}H NMR ^{a}	^{29}Si NMR ^{a}
$Me_2SiHOTf$ ^{b}	δ 0.57d, J 2.9 Hz, 6H, CH_3; δ 4.98q, J 2.90 Hz, 1H, SiH	δ 24.8, J(SiH) 233 Hz
H_3SiOTf ^{b}	δ 4.2s, SiH	δ −23.2, J(SiH) 254 Hz
Cl_3SiOTf ^{c}	—	δ −18.3
Ph_2Bu^tSiOTf ^{b}	δ 7.3—7.8m, 10H, Ph; δ 1.21s, 9H, CH_3	δ 12.7
Me_3SiOTf ^{b}	δ 0.48s, CH_3	δ 43.4
Et_3SiOTf ^{c}	δ 1.01—1.06m	δ 45.1
Bu^tMe_2SiOTf ^{c}	δ 0.48s, 6H, CH_3; δ 1.0s, 9H, $(CH_3)_3C$	δ 45.6
$Bu^tPhSiClOTf$ ^{b}	δ 1.14s, 9H, CH_3; δ 7.5—7.77m, 5H, Ph	δ 10.2
PhMeSiHOTf ^{b}	δ 0.77d, J 2.9 Hz, 3H, CH_3; δ 5.34q, J 2.9H, 1H, SiH; δ 7.3—7.7m, 5H, Ph	δ 11.9

^{a} Chemical shifts, δ(ppm) referenced to internal TMS. ^{b} 5—10% in $CDCl_3$. ^{c} 5—10% in CD_3CN.

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