A New Synthetic Method for Sulphenimines. Fluoride-catalysed Reaction of *N,N*-Bis(trimethylsilyl)sulphenamides with Aldehydes and Ketones

Toshiaki Morimoto,* Yoshitaka Nezu, Kazuo Achiwa, and Minoru Sekiya
Shizuoka College of Pharmacy, Oshika, Shizuoka 422, Japan

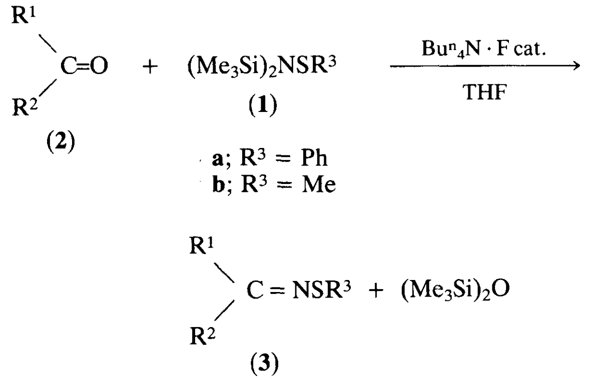
A convenient, general method for the preparation of sulphenimines by the reaction of aldehydes and ketones with *N,N*-bis(trimethylsilyl)sulphenamides in the presence of tetrabutylammonium fluoride catalyst is described.

In spite of the fascinating structure of sulphenimines possessing both the imine function and a sulphur–nitrogen bond, their chemistry[1,2] has not yet been widely explored. This is probably because of the lack of sufficient and practical methods for their preparation.[2] The existing procedure involves the condensation of aldehydes or ketones with *N*-unsubstituted sulphenamides which are stable only as aromatic analogues, H_2NSAr, possessing electron-withdrawing groups in the ring.[2a] *N*-

Table 1. Preparation[a] of sulphenimines (**3**) from carbonyl compounds (**2**) and *N,N*-bis(silyl)sulphenamides (**1a,b**).

				Sulphenimines (**3**)	
R^1	R^2	R^3	Cat. (mol %)	Yield (%)	M.p. (°C) or b.p.[b] (°C/mmHg)
Ph	H	Ph	1	100	45—46
PhCH=CH	H	Ph	5	96[c]	60—61
Ph	Ph	Ph	10	95	71—72
Ph	Me	Ph	5	82[c,d]	190/2
$-[CH_2]_5-$		Ph	5	92	170/1
Me	H	Ph	5	83[d,e]	120/2
Ph	H	Me	1	92	140/5
p-ClC_6H_4	H	Me	5	90	38—39
m-$O_2NC_6H_4$	H	Me	5	88	67—68
PhCO	Ph	Me	5	84	220/1.5
cyclohexyl	H	Me	5	89[d]	130/14

[a] Molar ratio, (**1a,b**):(**2**) = 1:1; THF; room temp.; 1—2 h; cat., Bu_4NF. [b] Bath temp. of a 'Kugelrohr' apparatus. [c] *anti*:*syn* = 5:1. [d] Crude yield. [e] *anti*:*syn* = 2:1.



Unsubstituted aliphatic sulphenamides are unstable and not available except the stable *S*-tritylsulphenamide.[2b] An alternative method reported Davis *et al.* is the one-step synthesis from aryl disulphides, silver nitrite, ammonia, and aldehydes or ketones.[2c]. Unfortunately, the method has limited utility, because of low yields or no reaction for ketones and for alkane disulphides, and other drawbacks such as the necessity of using a large excess of aldehydes or ketones and a stoicheiometric amount of silver nitrite.

Our continuing interest in the use of organosilicon compounds in organic synthesis led us to use *N,N*-bis(silyl)sulphenamide (**1**) as a stable *N*-unsubstituted sulphenamide synthon for the synthesis of sulphenimines (**3**). *N,N*-Bis(trimethylsilyl)benzenesulphenamide (**1a**)[3] and *N,N*-bis(trimethylsilyl)methanesulphenamide (**1b**)[4] were prepared in good yields by the reactions of lithium bis(trimethylsilyl)-amide with benzenesulphenyl chloride and dimethyl disulphide, respectively, in tetrahydrofuran (THF) under similar conditions to those reported previously.[5] The reaction of (**1a,b**) with carbonyl compounds (**2**) was found to be catalysed by fluoride in THF. No reaction occurred with the use of trimethylsilyl trifluoromethanesulphonate† or other Lewis acids as catalysts. As a typical example, the reaction of (**1a**) with benzaldehyde proceeded exothermically at room temperature in the presence of a catalytic amount of tetrabutylammonium fluoride to give *N*-(benzylidene)benzenesulphenamide quantitatively. Other fluoride catalysts such as potassium fluoride-18-crown and caesium fluoride were less effective under similar conditions. Preparations of a variety of sulphenimines (**3**) from the corresponding carbonyl compounds (**2**) and *N,N*-bis(trimethylsilyl)sulphenamides (**1a,b**) are summarized in Table 1.

Major advantages of the present method are; (i) the reagents (**1**) are readily available and stable over long storage times, (ii) the reaction proceeds smoothly under mild conditions, (iii) the procedures are simple, (iv) yields are generally high, and (v) the reaction solution, if necessary, may be used *in situ* as a sulphenimine solution, since hexamethyldisiloxane formed simultaneously is inert to common reagents.

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† In a preceding communication,[6] we reported that trimethylsilyl trifluoromethanesulphonate is an excellent catalyst for the reaction of *N,N*-bis(silyl)amines with aldehydes or ketones yielding Schiff bases.