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PRELIMINARY NOTE

2-(Trifluoromethyl)-1-(Phenylsulfenyl)Vinyltrimethylsilane. A Useful Building Block for Trifluoromethylated Organic Molecules [1]

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SUMMARY

The title compound was allowed to react with various aldehydes in the presence of catalytic amounts of fluoride ion to afford adducts in moderate to excellent yields with perfect retention of its geometry stereospecifically. These adducts were also subjected to the conditions of [3,3] sigmatropic rearrangements to give esters or aldehydes in moderate yields.

Recently, fluorine-containing organic molecules have been paid much attention, especially those bearing a trifluoromethyl group, due to their possible unique biological activities [2]. We have been studying the preparation of building blocks as a tool for the introduction of this group

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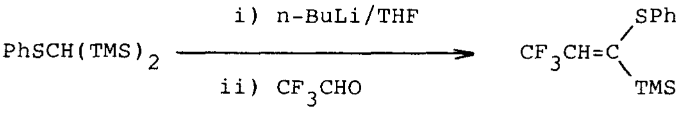
into organic molecules, because the direct methods with regio- and/or chemoselectivity often prove to be difficult, and also the available starting materials are quite limited.

In our programme of work for the preparation of building blocks containing a trifluoromethyl group [3], we wish here to report the synthesis of 2-(trifluoromethyl)-1-(phenylsulfenyl)vinyltrimethylsilane (I) and its reactions with aldehydes.

For the preparation of building blocks, trifluoroacetic acid or its derivatives, for example, ethyl trifluoroacetate [4] or trifluoroacetaldehyde [5], are among the best starting materials because of low cost, and being safe and easy to handle. This applies also to our new building block, 2-(trifluoromethyl)-1-(phenylsulfenyl)vinyltrimethylsilane (I) was prepared as follows. To a solution of 26.9 g (100 mmol) of (phenylthio)bis(trimethylsilyl)methane in 150 ml of THF was added 68.8 ml (110 mmol) of n-BuLi in n-hexane at -78 °C and stirring was continued for 2 h at ambient temperature [6]. To this solution was introduced 11.8 g (120 mmol) of trifluoroacetaldehyde at -78 °C and further 2 h stirring at room temperature gave vinylsilane (I) in 68 % yield as an *E*,*Z* mixture (*E*/*Z* = 72/28) which could be easily separated by column chromatography on silica gel.



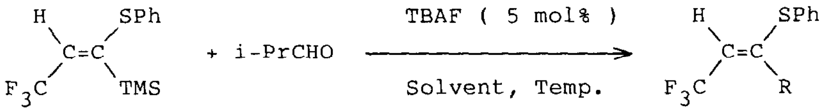
$$PhSCH(TMS)_2 \xrightarrow[\text{ii) } CF_3CHO]{\text{i) n-BuLi/THF}} CF_3CH{=}C\begin{matrix} \diagup SPh \\ \diagdown TMS \end{matrix}$$

(I)

Non-fluorinated vinylsilanes, having been actively studied recently, are known to react readily with a wide range of electrophiles in the presence of Lewis acids. On the contrary, only a few compounds which contain an electron withdrawing group to stabilize the labile vinyl anions are known to have their reactions promoted by fluoride ion [7].

TABLE 1

Reaction of (I) with various conditions



(I)

(II):R=i-PrCH(OH)-

(III):R=H

Run[a]	Solvent (ml)	Temperature (°C)	Yield (%)[b]
1	THF (5)	-78	65 / 35
2	THF (5)	-18	52 / 48
3	THF (5)	rt	31 / 69
4	THF (20)	-78	55 / 45
5	THF (2)	-78	54 / 46
6	Et_2O (5)	-78	41 / 59
7	DMF (5)	-18	62 / 38
8	DMF (5)	-60	83 / 17

a) 2 mmol of (I) and 3 mmol of i-PrCHO were employed in each case.

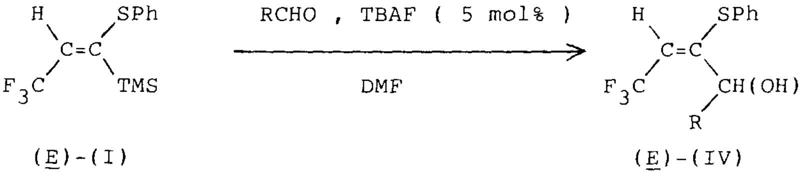
b) Ratio of (II)/(III) was determined by ^{19}F NMR using $PhCF_3$ as an internal standard and combined yields were more than 95 % in each case.

Our vinylsilane (I) was subjected to both conditions, but no product was obtained in the former case, presumably due to the low nucleophilic nature of (I) caused by the strongly electron withdrawing trifluoromethyl group. However, using the latter conditions, this effect seemed to promote reaction in an effective manner. The process using fluoride ion was therefore studied in more detail.

In the earlier work [7], more than 1 equiv. of tetra-n-butylammonium fluoride (TBAF) was used for the generation of the vinyl anions, but from the analogy of the similar procedures used with allylsilanes [8], it was thought that even catalytic amounts of TBAF would be enough. This idea was supported by our preliminary experiments, and employing either catalytic or excess amounts of TBAF did not give any significant influence on product distributions, whereas solvents and temperature were found to affect them considerably (see Table 1).

TABLE 2

Reaction of (I) with various aldehydes



Run	R	Isolated yield (%)	Chemical shift of CF_3 (δ ppm)[a)]
1	Me	69	-23.0 (d, 8.8)
2	Et	83	-23.6 (d, 8.3)
3	i-Pr	71	-24.2 (d, 8.6)
4[b)]	i-Pr	72	-21.3 (dd, 8.0, 1.2)
5	n-Bu	76	-23.4 (d, 8.9)
6	t-Bu	36	-23.8 (d, 8.7)
7	$CH_3CH=CH$-	34	-23.5 (d, 8.9)
8	Ph	90	-23.8 (d, 8.8)
9[b)]	Ph	71	-21.3 (dd, 8.0, 1.9)
10	$PhCH_2CH_2$-	70	-23.3 (d, 9.1)

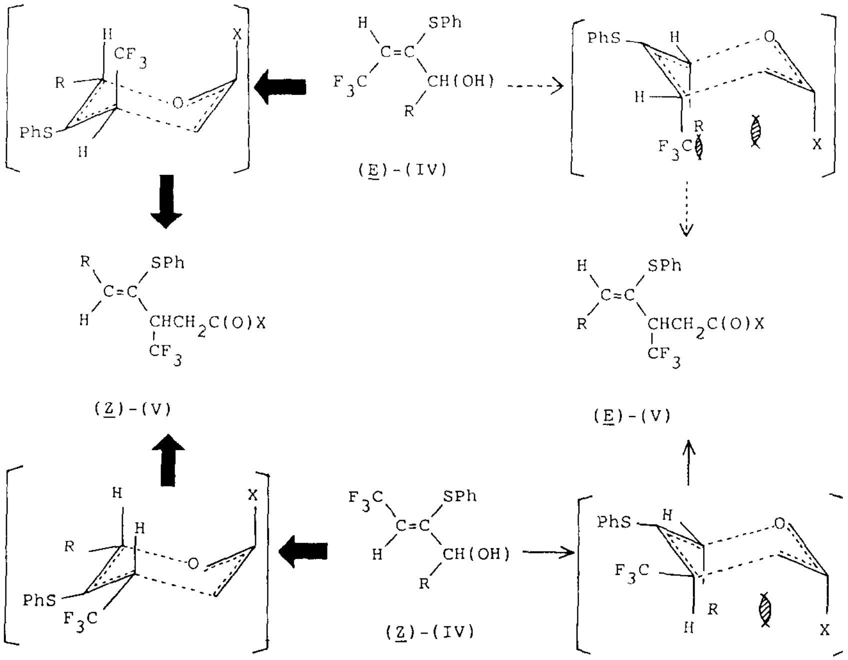
a) Calculated from external CF_3CO_2H and in the parentheses were given the coupling constants (Hz).

b) Z-(I) was employed instead of E isomer, affording Z-(IV) stereospecifically.

The conditions having been optimized, the reaction of (I) with various aldehydes was carried out as for Run 8 of Table 1, to afford the adducts in good to excellent yields accompanied by only small amounts (about 10% yield) of protodesilylated compound. These reactions proceeded with

TABLE 3

[3,3] Sigmatropic Rearrangements of (IV)



X : H in method (A), OEt in method (B)

R	Method	Isolated yield (%)	(Z)/(E) ratio
i-Pr (E)	(A)	50	>97:<3
i-Pr (Z)	(A)	53	57:43
Et (E)	(B)	55	>97:<3
Et (Z)	(B)	69	95: 5

the complete retention of its geometry stereospecifically [7b]. On the other hand, employing ketones as electrophiles gave only protodesilylated material such as (III), probably due to their lower reactivity, the resulting vinyl anion picking up proton from the solvent. Since these compounds can be easily converted to synthetically useful allylic alcohols using various methods, we attempted thier [3,3] sigmatropic rearrangement (Claisen and Johnson-Claisen rearrangement) [9]. (IV) was treated with (A) ethyl vinyl ether and 30 mol% of $Hg(OAc)_2$ or (B) triethyl orthoacetate in the presence of 10 mol% of propionic acid, to afford rearranged aldehydes or esters respectively in moderate yields. In three cases, substrates gave (Z) geometry at the newly formed C-C double bond with high stereoselectivity.* Only (Z)-(IV) (R=i-Pr) using method (A) afforded an E, Z mixture in almost equal amount, which could be explained by a chair-like transition state model [9].

These rearrangements with other substrates and desulfinylation are on progress.

REFERENCES

1 This preliminary report should be regarded as the Part IV of a series of ' Building Blocks for Trifluoromethylated Organic Molecules '. For the Part III, see ref. 3.

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* The geometry was decided by the transition state model and their ratio was determined by ^{19}F NMR.

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