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INTRODUCTION OF AN ARYLTHIO(TRIMETHYLSILYL)METHYL GROUP INTO ARENES BY FRIEDEL-CRAFTS REACTION: SYNTHESIS OF ARYLMETHYLTRIMETHYLSILANES

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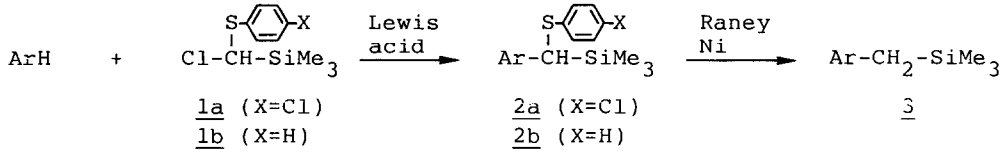
Summary: Friedel-Crafts reactions of [arylthio(chloro)methyl]trimethylsilanes (1a,b) with arenes gave [aryl(arylthio)methyl]trimethylsilanes (2a,b), which were converted into arylmethyltrimethylsilanes (3) by reduction with Raney nickel.

Arylmethyltrimethylsilanes (3) are versatile intermediates in organic synthesis.[1] These compounds are generally prepared by the reaction of arylmethylmagnesium halides with chlorotrimethylsilane. Here we wish to report an alternative simple method for the preparation of 3, which involves a Friedel-Crafts reaction of [arylthio(chloro)methyl]trimethylsilanes (1a,b) with arenes and subsequent desulfurization of the resultant products (2a,b).



1a (X=Cl)
1b (X=H)

2a (X=Cl)
2b (X=H)

3

The chlorides (1a: bp 126°C/4 mmHg)[2] and (1b: bp 101°C/5 mmHg)[3] were prepared from the corresponding (arylthiomethyl)trimethylsilanes in quantitative yields by treating with N-chlorosuccinimide in CCl_4.

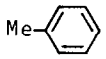
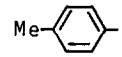
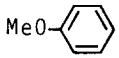
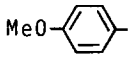
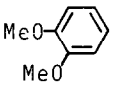
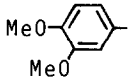
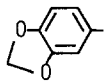
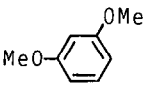
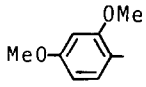
The typical experimental procedure is as follows. To a solution of 1a (530 mg, 2 mmol) and anisole (216 mg, 2 mmol) in CH_2Cl_2 (10 ml) was added $TiCl_4$ (379 mg, 2 mmol)[4] at -20°C and the mixture was stirred at the same temperature for 30 min. The reaction was quenched with water and the organic layer was separated. After removal of the solvent, the residue was chromatographed on silica gel (n-hexane) to give the product (2a: Ar=4-$MeOC_6H_4$) (605 mg, 90%). High yields were obtained with other arenes (Table).[5] These reactions afforded neither positional isomers nor poly-alkylated products. The chloride (1b) can also be used for this reaction, although the yields of the

products (2b) were slightly lower (Table).

The compounds (2a,b) were converted in high yields (88-98%) into the arylmethyltrimethylsilanes (3) by reductive desulfurization with Raney nickel.

It is difficult to introduce directly the trimethylsilylmethyl group into aromatic rings by means of the Friedel-Crafts method using chloromethyltrimethylsilane.[6] Our studies have revealed that the chlorides (1a,b) can act as equivalents of trimethylsilylmethyl cation ($Me_3SiCH_2^+$) in the Friedel-Crafts reaction.

Table. Preparation of [Aryl(arylthio)methyl]trimethylsilanes (2a,b)[2]

ArH	Chloride	1/ArH	Lewis acid	Reaction temp./time	Product 2 Ar	X	%Yield	mp
	1a	2(1)	$SnCl_4$	-20°C/30min		Cl	95 (47)	oil
	1a	1	$TiCl_4$	-20°C/30min		Cl	90	oil
	1b	1	$TiCl_4$	-20°C/30min		H	82	oil
	1a	1	$SnCl_4$	0°C/30min		Cl	98	74.5-75°C
	1b	1	$SnCl_4$	0°C/30min		H	79	oil
	1a	1	$SnCl_4$	-20°C/30min		Cl	91	65.5-66°C
	1a	1	$TiCl_4$	-20°C/30min		Cl	72	77-78°C

References and Notes

1) For recent uses of arylmethyltrimethylsilanes in organic synthesis, see: K. Atsumi and I. Kuwajima, Chem. Lett., 1978, 387; D. J. Coughlin and R. G. Salomon, J. Org. Chem., 44, 3784 (1979); S. Takano, H. Numata, and K. Ogasawara, J. Chem. Soc., Chem. Commun., 1982, 769; S. Takano, S. Otaki, and K. Ogasawara, ibid., 1985, 485; Y. Ito, Y. Amino, M. Nakatsuka and T. Saegusa, J. Am. Chem. Soc., 105, 1586 (1983); H. Vorbrueggen and K. Krolikiewicz, Tetrahedron Lett., 24, 889 (1983); B. Bennetau and J. Dunogues, ibid., 24, 4271 (1983) and references cited therein
2) All new compounds gave satisfactory elemental and spectral analyses.
3) I. Fleming and S. K. Patel, Tetrahedron Lett., 22, 2321 (1981).
4) The use of an equimolar amount of Lewis acid afforded an optimum yield.
5) The reaction with benzene or chlorobenzene gave unsatisfactory results.
6) P. D. George, J. Am. Chem. Soc., 26, 4235 (1961).

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