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THE REACTION OF ALLYLSILANES WITH PHENYLTHIOACETALS IN THE PRESENCE OF ALUMINIUM TRICHLORIDE

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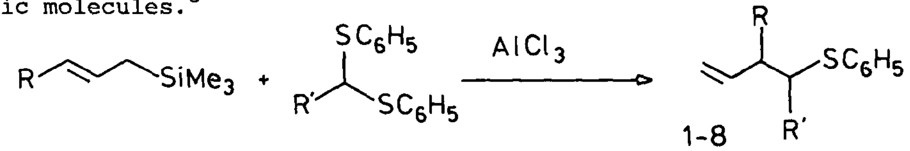
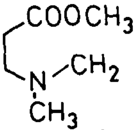
Summary. *Thionium ions, generated from phenylthioacetals and* $AlCl_3$, *react with several allylsilanes to give phenylthioethers which can be easily transformed into conjugated dienes.*

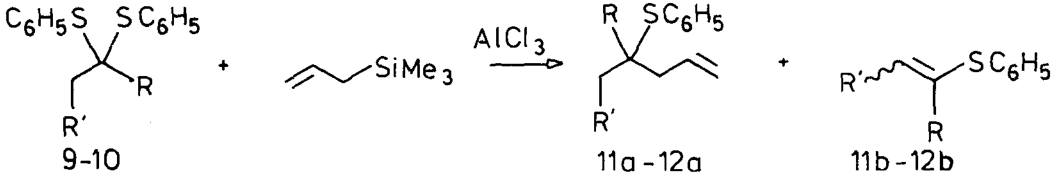
The use of thionium ions as carbon electrophiles for allylsilanes is well established, most of them derived from α-chlorosulphides[1] or other reagents.[2] Thioacetals have been also used as sources of this type of electrophiles but reactions with allylsilanes have been reported to be not so straightforward[3].. Following a brief report of Bartlett and Heathcock[4] who recently described the nucleophilic addition of allyltrimethylsilane to chiral thionium ions, we report here the reaction between allylsilanes and phenylthioacetals in the presence of $AlCl_3$, leading to unsaturated phenylthioethers which may be considered as versatile intermediates in the stereocontrolled synthesis of polyenic molecules.[5]



1-8

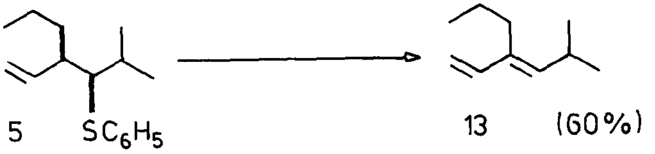
R	R'	Product	Yields
H	H	**1**	60%
C_3H_7	C_3H_7	**2**	62%
$(CH_3)(C_2H_5)CH$	C_3H_7	**3**	70%
H	$(CH_3)_2CH$	**4**	81%
C_3H_7	$(CH_3)_2CH$	**5**	63%
H	$(CH_3)_3C$	**6**	76%
$(CH_3)_2$	$(CH_3)_3C$	**7**	62%
H		**8**	49%

In a typical procedure, a mixture of the phenylthioacetal (1 mmol) and the allylsilane (1.1 mmol) in toluene (0.5 mL) was slowly added to $AlCl_3$ (1 mmol) dissolved in dry toluene (2 mL) at room temperature and subsequently cooled to 0°C. The progress of the reaction was checked by TLC and when the starting material disappeared (generally after 1-5 h), the mixture was poured into a hexane / pH 7 aqueous buffer mixture and, after vigorous stirring, the organic layer separated, dried, and the phenylthioether isolated by column chromatography on silica gel (eluant hexane). The reaction course was dramatically dependent upon the presence of toluene as solvent and by the order of the addition (the phenylthioacetal and allylsilane mixture to the Lewis acid). These factors were crucial in order to obtain the desired products in acceptable yields. Phenylthioketals **9** and **10** gave a mixture of the addition (**11a** and **12a**) and the expected elimination products (**11b** and **12b**).



R-R' = C_4H_8 9,11 R = C_6H_5 R' = H 10-12

Nevertheless working with an excess of the allylsilane, performing the addition at -78°C and quenching as soon as the temperature of the reaction mixture had reached 5°C, it was possible to obtain the desired allylation products (40-55% yields by gas cromathography) which could be purified by column chromatography and PTLC to give **11a** and **12a**, isolated in yields ranging from 30 to 40%. The chemo- and the stereoselectivity of the reaction seems also promising. Compound **8** was obtained working with one equivalent of the Lewis acid and, in the only example analyzed, **5** was isolated as a single stereoisomer, the *syn* product[6], which showed at ^{1}H NMR analysis (300 MHz) a ^{3}J (CH(3)-CH(4)) = 8 Hz, and whose structure was fully elucidated by the *syn* sulphoxide elimination[9] ($NaIO_4$, 10 : 1 MeOH : H_2O, 20°C, 50 h, 60% yield) which gave product **13** .



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