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ELECTROPHILIC SUBSTITUTION OF ALLYLSILANES: SYNTHESIS OF β,γ-UNSATURATED 1,3-DITHIANES

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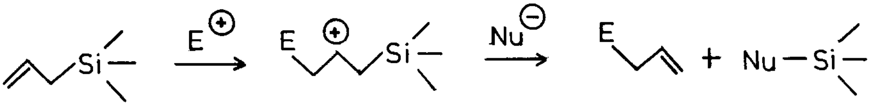
Abstract: *Regiospecific substitution of some allylsilanes using 1,3-dithienium tetrafluoroborate as a formyl cation equivalent is described.*

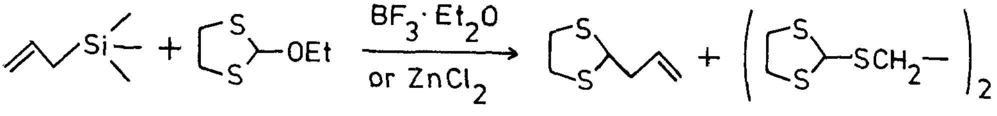
Allylsilanes are very useful intermediates in organic synthesis,[1] primarily perhaps because of their regiospecific substitution reactions with different electrophiles.[2]



Although many electrophiles have been used, there seems to be no example in the literature of the utilization of a formyl cation equivalent in this type of reaction.

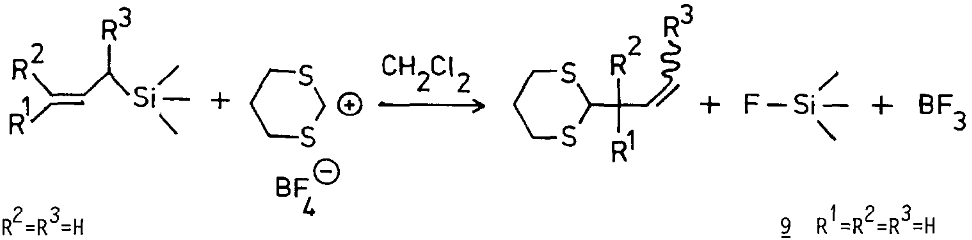
It is known that acetals and monothioacetals react with allylsilanes in the presence of Lewis acids,[3] iodotrimethylsilane[4] or trimethylsilyl trifluoromethanesulfonate[5] giving homoallyl ethers and homoallyl thioethers. Similar results have also been obtained using trialkyl orthoformates. Thus, treatment of allyltrimethylsilane (1) with triethyl orthoformate/$TiCl_4$ gave only bishomoallyl ether and no homoallyl acetal.[3a] Apparently the reaction of 1 with the resulting acetal is faster than the monoallylation of the orthoformate.

Since thioacetals in general are more stable to Lewis acids than their corresponding O-analogs, 2-ethoxy-1,3-dithiolane (2) was initially chosen as a suitable formyl cation equivalent. This reagent, which can be prepared from 1,2-ethandithiol and triethyl orthoformate,[6] has previously been used by Tanimoto et al. for the preparation of ketene-S,S-acetals,[7] half-protected 1,3-dicarbonyl compounds[8] and for aromatic formylation.[9] Treatment of 2 with 1 in the presence of $BF_3 \cdot Et_2O$ gave the expected product (3), although in a rather low yield (30-40%). The main product was instead the bis-1,3-dithiolane 4, a compound which is usually formed when handling 2.[8,9] Similar yields were also obtained using $ZnCl_2$ as a catalyst.[10]



1 2 3 4

In view of these low yields and the general instability of 2,[11] other potential formyl cation equivalents containing the thioacetal moiety were considered. The most promising one seemed to be the relatively stable, easily handled 1,3-dithienium tetrafluoroborate (5). This compound, which can readily be prepared by hydride abstraction from 1,3-dithiane by trityl tetrafluoroborate,[12] has found some recent use in the allylation of O-silyl enolates and dienolates.[12b,13] Treatment of 5 with different allylsilanes gave the expected β,γ-unsaturated dithianes in good yields (see Table).



1 $R^1=R^2=R^3=H$
6 $R^1=H$, $R^2/R^3=(CH_2)_3$
7 $R^1=R^2=CH_3$, $R^3=H$
8 $R^1=Ph$, $R^2=R^3=H$

5

9 $R^1=R^2=R^3=H$
10 $R^1=H$, $R^2/R^3=(CH_2)_3$
11 $R^1=R^2=CH_3$, $R^3=H$
12 $R^1=Ph$, $R^2=R^3=H$

Table: Reaction of allylsilanes with 5

Entry	Allylsilane	React. cond.	Product (yield)[a]	^{1}H NMR data δ ($CDCl_3$)
1	1	1 h, r.t.	9 (78%)	1.6-3.0(m,8H); 4.1(t,1H,J=6.6 Hz, -SCHS-); 4.9-6.7(m,3H,$-CH=CH_2$)
2	6[14]	0.5 h, reflux 2.5 h, r.t.	10 (72%)	1.5-3.9(m,13H); 4.2(t,1H,J=6.0 Hz, -SCHS-); 5.8(bs,2H,-CH=CH-)
3	7[15]	4 h, r.t.	11 (79%)	1.0(s,6H,CH_3); 1.6-3.4(m,6H); 4.0(s,1H,-SCHS-); 4.9-6.1(m,3H,$-CH=CH_2$)
4	8[16]	18 h, reflux	12 (60%)	1.6-3.7(m,7H); 4.4(d,1H,J=8.2 Hz, -SCHS-); 4.9-6.3(m,3H,$-CH=CH_2$); 7.2(bs,5H,ArH)

a) isolated, not optimized yields.

The reaction of allyltrimethylsilane (1) with 5 occurred rapidly and somewhat exothermically with evolution of BF_3. Substitution of the double bond (entries 2-4) resulted, as expected on steric grounds, in a decrease of reactivity. In the case of entry 4, this lowered reactivity can also be partly rationalized by invoking conjugative stabilization of the double bond. As can be seen from entries 3 and 4, the substitution occurred regiospecifically, giving only products resulting from γ-attack. None of the possible isomeric products could be detected. In regard to entry 4, this shows that in this type of reaction, benzylic stabilization of a carbocation is worth less than stabilization by a β-situated silicon atom.

In all four cases (entries 1-4), small amounts of aldehydic compounds were detected by ^1H NMR of the crude reaction products. These byproducts could however be removed using the method of Ohta et al.[17]

General experimental procedure: A mixture of the allylsilane (10 mmol) of 1,3-dithienium tetrafluoroborate, 5, (12 mmol) in 25 ml of CH_2Cl_2 was stirred at room temperature or at reflux (see Table). The reaction was monitored by GLC (OV101, 3%, 2.5 m), and when all of the allylsilane had been consumed, the mixture was poured into a saturated $NaHCO_3$-solution. After ethereal work-up and shaking twice with an aqueous 1.2 N solution of sodium ε-amino-n-caproate in order to remove aldehydic byproducts,[17] the β,γ-unsaturated dithiane was obtained as a pale yellow oil, which could be further purified by flash chromatography on silica gel.[18] For yields and ^1H NMR data, see Table.

In conclusion, a very useful method for the regiospecific preparation of otherwise hardly accessible β,γ-unsaturated dithianes has been developed.[19] This method offers rich synthetic possibilities since a 1,3-dithiane substituent may, if desired, be hydrolyzed to a formyl group,[20] converted into a methyl group by reductive desulfurization or, perhaps more important, be utilized for further synthetic elaborations via the well-established formyl anion equivalent chemistry.[21]

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