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TRANSFORMATION OF ALLYLSILANES INTO ALLYLAMINES VIA PHENYLTELLURINYLATION[1]

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Abstract: Allylsilanes were treated with benzenetellurinyl trifluoroacetate below room temperature followed by amines at 65°C in 1,2-dichloroethane in the presence of boron trifluoride etherate, readily giving allylamines.

Organic syntheses on tellurium-based methodology have become increasingly important.[2] We have recently reported that benzenetellurinyl trifluoroacetate (**1**) acts as an effective electrophile for additions of alkenes involving novel cyclofunctionalizations[3] and, in addition, the introduced phenyltellurinyl group has a good leaving ability for an intramolecular nucleophilic substitution, simply forming heterocycles.[4] Phenyltellurinyl function might have thus a synthetic potential in a functional transformation accompanied by the inversion of polarity of the attached bond. As one example, we here like to present a transformation of allylsilane into allylamine via phenyltellurinylation.

Benzenetellurinyl trifluoroacetate (**1**) was treated with allyltrimethylsilane (**2**) in the presence of boron trifluoride etherate in 1,2-dichloroethane at room temperature for 1 h, giving almost quantitatively allyl phenyl telluroxide (**3**) (Scheme 1). Telluroxide **3**, though detected by NMR spectroscopy,[5] was very unstable and characterized as allyl phenyl telluride after reduction with hydrazine hydrate. It was then treated in situ with alkylamine at 65°C for 3 h to give the corresponding allylamine (**4**) in a high yield.[6] Arylamine required a longer reaction time (6 h) due to its less nucleophilicity. A variety of examples are summarized in Table 1.

Substituted allylsilanes also underwent similar two-step reactions, in which the initial reaction was run at a lower temperature (-15°C) because of lability of the product and the second reaction was completed in a shorter time (1 h for alkylamine and 3 h for arylamine). This transformation is characteristic of high regioselectivity. As shown in Table 2, γ-substituted allylsilane (**5**) with arylamine gave trans γ-substituted allylamine (**9**),[7] but with alkylamine gave α-substituted one (**10**). In more detail, this selectivity

Scheme 1

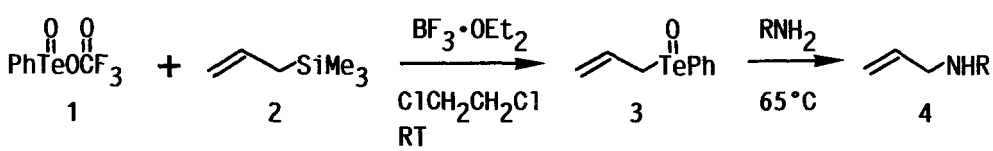
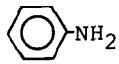
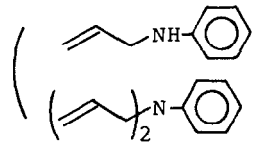
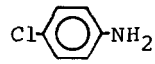
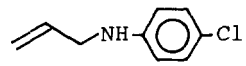
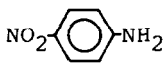
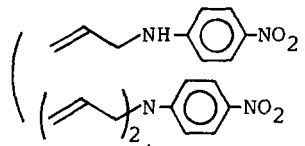
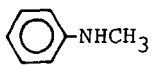
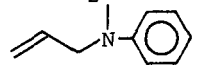
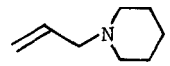
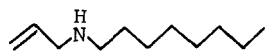
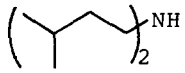
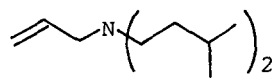


Table 1. Amination of allyl phenyl telluroxide (3), in situ generated from phenytellurinylation of allyltrimethylsilane (2)

Run	Amine	Time/h	Product	Yield/%
1		6		82 15
2		6		90
3		6		72 21
4		6		96
5		3		84
6		3		86
7		3		75

does not depend on the cis and trans geometry or α- and γ-allylic isomerism of the starting allylsilane because 2-nonenyltrimethylsilane (Runs 1-6) and 2-butenyltrimethylsilane (Runs 10 and 11) are used as these isomeric mixtures.

A more likely reaction mechanism of **5** to **9** or **10** is shown in Scheme 2. It is well known that allylsilane undergoes a regio-controlled electrophilic attack at the γ-carbon, resulting in a substitution product with a net shift of the double bond.[8] Therefore, the initial product from γ-substituted allylsilane (**5**) should be α-substituted allyl telluroxide (**6**). The NMR analysis of the products from phenyltellurinylation of 2-nonenyltrimethylsilane and 2-butenyltrimethylsilane, however, demonstrated the predominant formation of γ-substituted allyl telluroxide (**8**).[5] This indicates that the tautomerization between **6** and **8** readily occurs and the equilibrium

Scheme 2

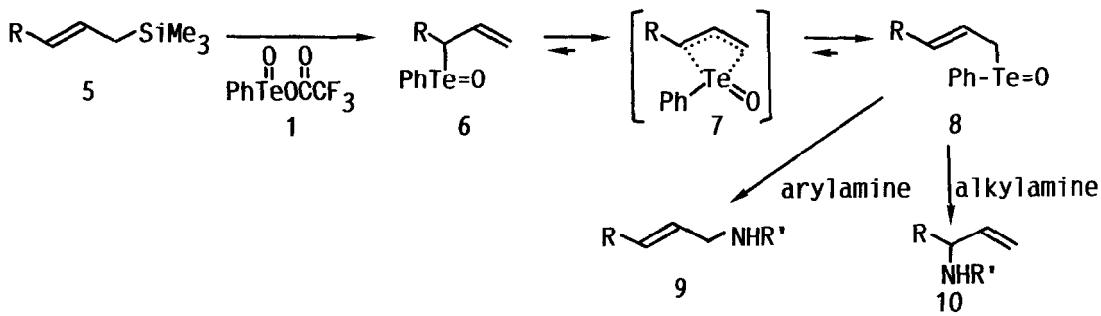
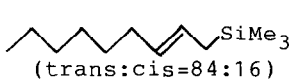
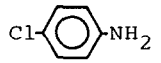
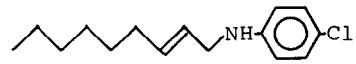
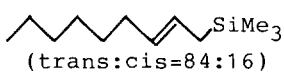
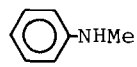
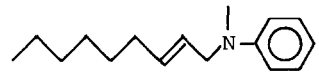
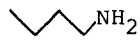
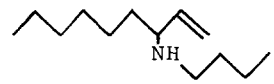
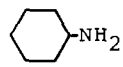
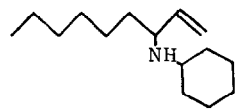
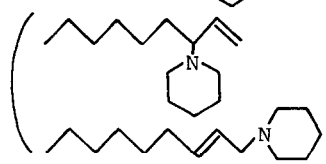
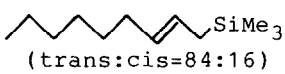
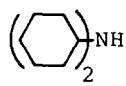
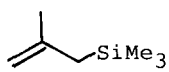
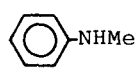
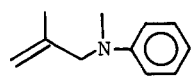
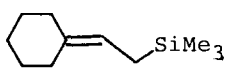
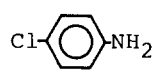
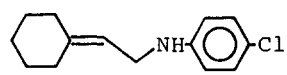
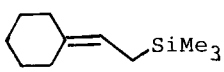
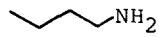
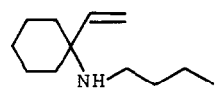
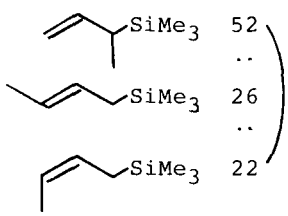
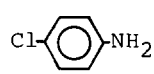
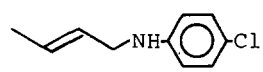
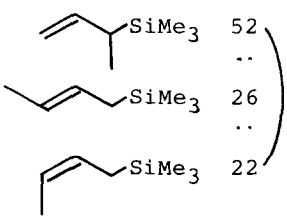
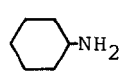
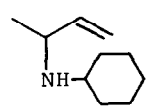


Table 2. Transformation of allylsilanes into allylamines via phenyltellurinylation

Run	Allylsilane	Amine	Product	Yield/%
1	 (trans:cis=84:16)			71
2	 (trans:cis=84:16)			89
3	 (trans:cis=84:16)			69
4	 (trans:cis=84:16)			75
5	 (trans:cis=84:16)			71 20
6	 (trans:cis=84:16)			15
7				60
8				57
9				59
10	 52 : 26 : 22			95
11	 52 : 26 : 22			58

favors isomer (**8**). The following treatment with amine gives allylamine **9** or **10**, whose regioselectivity probably depends on nucleophilicity of the amine. The less nucleophilic arylamine attacks the terminal carbon, giving the thermodynamically controlled product (**9**). On the other hand, the more nucleophilic alkylamine attacks the central carbon, giving the rearrangement product (**10**). However, bulky secondary alkylamines tend to avoid the latter reaction as piperidine gave some amount of **9** together with the main rearrangement product (Run 5) and dicyclohexylamine produced only **9** in a low yield (Run 6).

Allylic amines are both useful synthetic intermediates and a common structural element in natural products, but they are available by a relatively limited number of procedures.[9] The present method provides a convenient one-pot access from allylsilanes.

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2. For recent reviews on organotellurium chemistry see: L. Engman, Acc. Chem. Res.,**18**, 274 (1985); N. Petragnani and J. V. Comasseto, Synthesis, **1986**, 1.
3. N. X. Hu, Y. Aso, T. Otsubo, and F. Ogura, Tetrahedron Lett., **28**, 1281 (1987); Chem. Lett., **1987**, 1327.
4. (a) N. X. Hu, Y. Aso, T. Otsubo, and F. Ogura, Chem. Commun., **1987**, 1447; (b) Tetrahedron Lett., **29**, 1049 (1988).
5. NMR data (60 MHz); **3**: δ 4.32(d, J=7 Hz, 2H, CH_2), 5.2-6.5(m, 3H, vinyl H), 7.3-7.6(m, 3H, ArH), 7.9-8.2(m, 2H, ArH); **8**(R=n-C_6H_{13}): δ 0.87(bt,3H, CH_3), 1.0-1.25(bs, 8H, CH_2), 2.1(m, 2H, CH_2), 4.28(d, J=7 Hz, 2H, CH_2), 5.4-6.15(m, 2H, olefinic H), 7.3-7.6(m, 3H, ArH), 7.9-8.2(m, 2H, ArH) in $CDCl_3$.
6. A typical experimental procedure is as follows: To a solution of **1** (1 mmol) in $ClCH_2CH_2Cl$ (4 ml), generated from benzenetellurinic anhydride (0.229 g, 0.5 mmol) and trifluoroacetic anhydride (0.120 g, 0.55 mmol), were added $BF_3{\cdot}OEt_2$ (0.156 g, 1.1 mmol) and then allyltrimethylsilane (0.156 g, 1.1 mmol) in $ClCH_2CH_2Cl$ (2 ml). The solution was stirred at RT for 1 h. p-Chloroaniline (0.32 g, 2.5 mmol) was then added and the mixture was heated at 65°C with stirring for 6 h. The reddish black mixture was poured into aq. saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The extract was dried over anhyd. $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel with 95:5 hexane-ethyl acetate as eluent to give a pale yellow oil of N-allyl-p-chloroaniline (0.151 g, 90% yield).
7. The ^1H and ^{13}C NMR spectra of allylamine **9** showed that it consisted of one component with a trans olefinic coupling constant of 14-16 Hz.
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