Heteroatom Chemistry
Volume 5, Number 1, 1994

The Reaction of Allyldialkyltelluronium Bromides with Anilines

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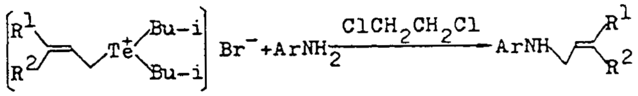
Received 8 April 1993; revised 9 August 1993

ABSTRACT

Allyldialkyltelluronium bromides were treated with aromatic amines in 1,2-dichloroethane, readily giving allyl aryl amines in excellent yields.

In recent years, there has been a remarkable development of new synthetic methods using organotellurium compounds [1]. It was found that telluronium ylides especially have many interesting applications in carbon–carbon bond formation [2]. Among them, dialkyltelluronium allylides were used for the synthesis of α,β-unsaturated epoxides [3]. However, there are no reports on the use of allyldialkyltelluronium salts as allylation reagents.

Ogura and co-workers [4] have reported that benzenetellurinyl trifluoroacetate, when treated with allyltrimethylsilane in the presence of boron trifluoride etherate, gave allyl phenyl telluroxide. The latter was then treated in situ with an alkylamine to give the corresponding allylamine. We thought that the dialkyltelluronium group would be a better leaving group than the benzenetellurinyl group. Therefore, we studied the allylation reactions of aromatic amines with allyldialkyltelluronium bromides. Experimental results showed that aromatic allylamines can be obtained conveniently in excellent yields.



1 2 3

a R^1, R^2=H,H
b R^1, R^2=CH_3,CH_3
c R^1, R^2=Ph ,H

Substituted allyltelluronium salts also underwent similar reactions. As shown in Table 1, when they were reacted with arylamines, only α-substituted products were found, with no γ-substituted ones. Monoallylation products were obtained except with p-methoxyaniline which gave mono- and diallylation products because of its greater nucleophilicity (Table 2).

When the mechanism of the reaction of **1** with anilines was considered, we thought it might be an S_N2-type of process. Due to the weak C–Te bond, anilines would undergo reaction as nucleophilic reagents with the telluronium salt to give allylamines, with the departing group being diisobutyl telluride. However, the possibility of a ligand coupling process involving a tellurane intermediate cannot be ruled out on the basis of the present evidence.

Allylic amines are both useful synthetic intermediates and common structural elements in natural products, but they are available only by a relatively limited number of procedures [5]. The present method provides a convenient one-pot reaction for the synthesis of allylic amines.

EXPERIMENTAL

Preparation of Telluronium Salts (1a–1c)

Telluronium salts (**1a–1c**) are readily available as colorless crystals by reactions of diisobutyltellu-

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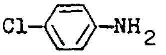
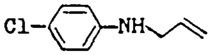
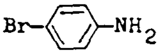
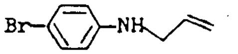
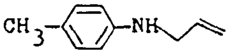
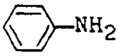
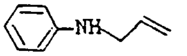
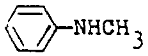
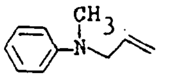
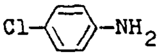
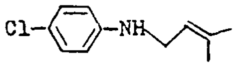
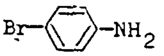
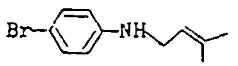
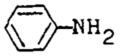
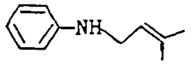
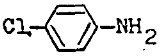
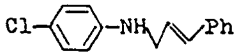
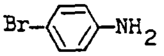
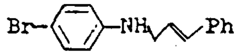
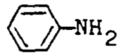
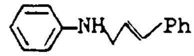
1042-7163/94/$5.00 + .25

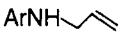
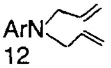
TABLE 1 Allylation of Aromaticamines via Allyldialkyltelluronium Bromides

Amine	*Te Salt*	*Product*[a]	*Yield, %*
	1a		86
	1a		87
	1a		85
	1a		86
	1a		95
	1b		83
	1b		82
	1b		85
	1c		90
	1c		89
	1c		91

[a] All the products were characterized by ^{1}H NMR spectroscopic comparison with known compounds and by elemental analyses.

ride with allyl bromide, 3, 3-dimethylallyl bromide, and cinnamyl bromide, respectively, without solvent for 2 hours at room temperature. Salt **1a**, yield 86%, mp 95.5–96.5°C (94.5–95.5°C [3]); **1b**, yield 84%, mp 69–70°C; and **1c**, yield 91%, mp 89.5–90.5°C.

TABLE 2 Allylation of *p*-Methoxyaniline with **1a**

Reactant[a] *(mmol)*		*Product*[a] *(Yield, %)*	
$ArNH_2$	**1a**		
2.5 mmol	1 mmol	81	12
1 mmol	1 mmol	54	40
1 mmol	2.5 mmol	15	78

[a] Ar = 4–$CH_3OC_6H_4$–.

Synthesis of Allylamines from Telluronium Salts

A typical procedure is as follows. A mixture of allyldiisobutyltelluronium bromide (1 mmol), *p*-chloroaniline (2.5 mmol), and 1,2-dichloroethane (10 mL) was heated at 60°C with stirring for 6 hours under nitrogen. Aqueous saturated $NaHCO_3$ solution was added, and the mixture was extracted with CH_2Cl_2. The extract was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel with 95:5 hexane-ethyl acetate as an eluent to give a pale yellow oil of *N*-allyl-*p*-chloroaniline (144 mg, 86% yield).

ACKNOWLEDGMENT

Financial support from the National Science Foundation of China is gratefully acknowledged.

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