Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 24 Sep 2006.

To cite this article: Caiding Xu , Shoumao Lu & Xian Huang (1993) A New Synthesis of Allyl Ethers Via Allyldialkyltelluronium Salts, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:18, 2527-2531, DOI: 10.1080/00397919308012585

To link to this article: http://dx.doi.org/10.1080/00397919308012585

SYNTHETIC COMMUNICATIONS, 23(18), 2527-2531 (1993)

A NEW SYNTHESIS OF ALLYL ETHERS VIA ALLYLDIALKYLTELLURONIUM SALTS

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ABSTRACT: Allyldialkyltelluronium bromides were treated with phenols in the presence of NaOH at room temperature, readily giving allyl aromatic ethers in excellent yields. This procedure represents an efficient means for synthesis of allyl aromatic ether.

Recently, there has been a remarkable interest in the synthetic applications of organotellurium reagents.[1] Among them, telluronium ylides condense easily with a variety of carbonyl compounds, giving α,β-unsaturated compounds[2]. Due to the lower energy and higher polality of Te-C bond, telluronium salts can also condense with carbonyl compounds to give the expected products.[3] Allyltelluronium ylide gave epoxidized products when it reacted with aldehydes[4]. However, there is no report on allyltelluronium salt, procursor of telluronium allylide, to react as an allylation reagent.

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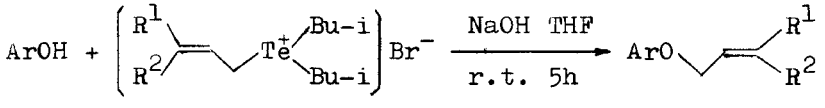
We thought that the dialkyltelluronium group would be a good leaving group, when allyltelluronium salts react with nucleophilic reagents, allylation products may be obtained. Therefore, we studied the reactions of allyltelluronium salts with phenols. Experimental results show that, in the presence of solide sodium hydrate, allyltelluronium salts can react with phenols in THF at room temperature to give excellent yields of aryl allyl ethers(Table I. and Table II.).



1 2 3

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

Allylic ethers are both useful synthetic intermediates and common structural elements in natural products, allylic ethers can also take place the Claisen rearrangement to obtain a variety of compounds[5], but they are available by a relatively limited number of procedures[6]. The present method has the advantages of easy availability of reagents,simplicity of procedure and excellent yields.

Telluronium salts(2a-2c) are readily available as colorless crystals by reactions of diisobutyltelluride with allyl bromide, 3,3-dimethylallyl bromide, and cinnamyl bromide respectively without solvent for two hours at room temperature.

Table I. Synthesis of Aryl Allyl Ether

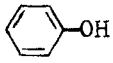
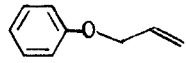
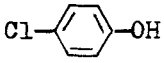
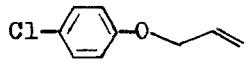
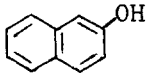
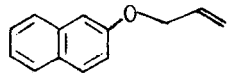
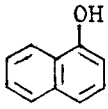
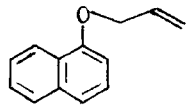
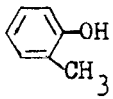
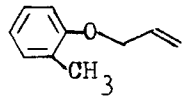
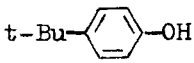
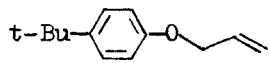
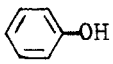
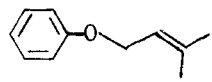
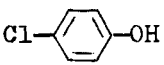
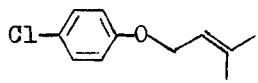
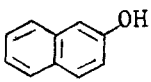
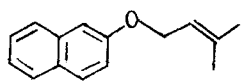
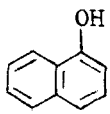
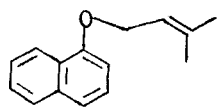
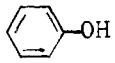
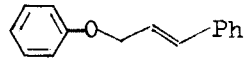
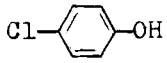
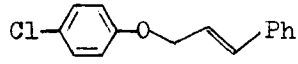
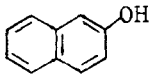
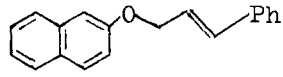
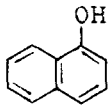
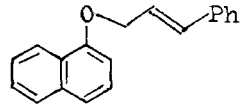
Phenol	Te salt	Product	Yield,%
	2a		85
	2a		86
	2a		88
	2a		81
	2a		85
	2a		93
	2b		86
	2b		87
	2b		92
	2b		82

Table II. Synthesis of Aryl Allyl Ether

Phenol	Te salt	[a]Product	[b]Yield,%
	2c		86
	2c		90
	2c		95
	2c		83

a All the products were characterized by ^{1}H-NMR and elemental analyses.

b Isolated yield.

Typical procedure:

A mixture of p-chlorophenol(128mg,1mmol), NaOH (40mg,1mmol), and THF(10ml) was stirred for ten min., allyldiisobutyltelluronium bromide(360mg,1mmol) was then added. The reaction mixture was stirred for another 5h at room temperature under nitrogen. Aqueous saturated $NaHCO_3$ solution was added 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 colorless oil of allyl p-chlorophenyl ether (145mg, 86%).

Acknowledgement:

This research was supported by National Science Foundation of China and Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry.

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(Received in the UK 08 March 1993)