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A NEW SYNTHESIS OF ALLYL ETHERS
VIA ALLYLDIALKYLTELLURONIUM SALTS

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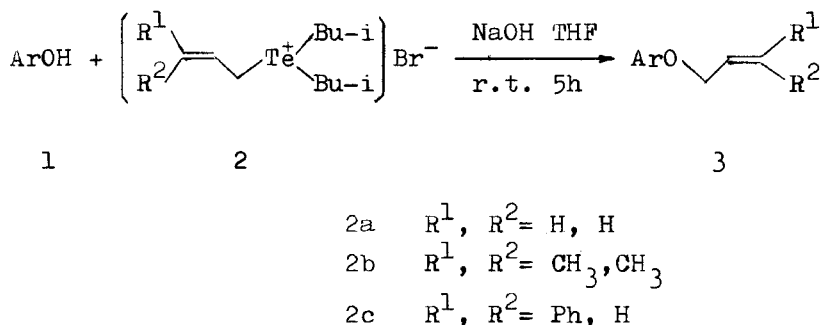
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ABSTRACT: Allyldialkyltelluronium bromides were treated with phenols in the presence of NaOH at room temperature, readily giving allyl aromatic ethers in excellent yields. This procedure represents an efficient means for synthesis of allyl aromatic 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 compounds². Due to the lower energy and higher polarity 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 aldehydes⁴. However, there is no report on allyltelluronium salt, precursor 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 solid 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.).



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 compounds⁵, but they are available by a relatively limited number of procedures⁶. 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

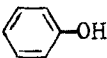
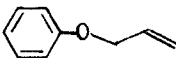
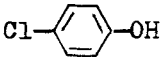
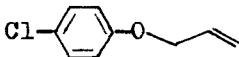
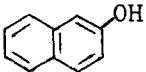
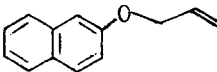
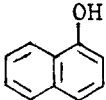
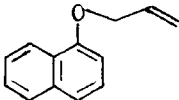
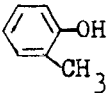
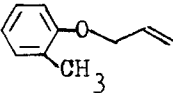
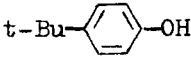
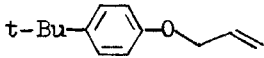
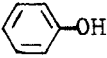
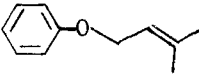

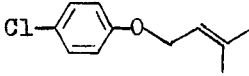
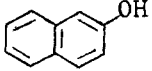
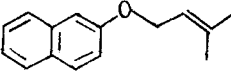
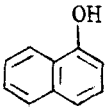
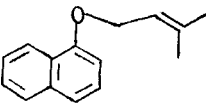
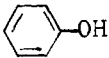
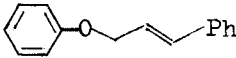
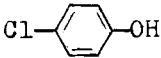
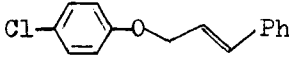
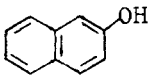
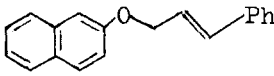
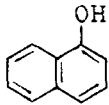
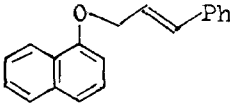
Phenol	Te salt	Product	Yield, %
	2a		85
	2a		86
	2a		88
	2a		81
	2a		85
	2a		93
	2b		86
	2b		87
	2b		92
	2b		82

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 ¹H-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 NaHCO₃ solution was added and extracted with CH₂Cl₂. The extract was dried over anhyd.MgSO₄ 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%).

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