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A NOVEL ROUTE FOR THE SYNTHESIS OF α,β-UNSATURATED ESTERS, KETONES AND NITRILES USING DIBUTYL TELLURIDE

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Summary: In the presence of dibutyl telluride, α-halo-ester, nitrile, and ketone were found to condense easily with aromatic aldehydes to afford α,β-unsaturated esters, nitriles and ketones in high yields as one-pot reaction. A possible reaction machanism was proposed.

With the development of organotellurium chemistry[1], some attention has been paid on the use of telluronium ylides in organic synthesis[2-3]. Recently, Osuka furnished a new synthetic method for α,β-unsaturated carboxylic esters by reacting dialkyl telluronium carbethoxymethylide with carbonyl compounds[3]. In view of the lower energy and higher polarity of C-Te bond in organotellurium compounds, we investigated the condensation of the telluronium salts with the carbonyl compounds in neutral medium, and found two excellent alternative procedures for the synthesis of α,β-unsaturated esters, ketones and nitriles.

Method A: In a typical reaction, an equimolar mixture of p-nitrobenzaldehyde and carbethoxy dibutyl telluronium bromide was refluxed in THF for 6 hours. Standard work-up procedure afforded methyl 3-(4'-nitrophenyl)-propenoate in 95% yield. The results with various telluronium salts and aromatic aldehydes are listed in Table 1.

Table 1. Synthesis of α,β-Unsaturated Esters, Ketones and Nitriles Using Corresponding Telluronium Salts[a]

$$R\text{-}C_6H_4CHO + n\text{-}Bu_2\overset{+}{T}eCH_2YX^- \xrightarrow[\text{reflux}]{THF} R\text{-}C_6H_4CH{=}CHY$$

R	X	Y	Yield (%)[b]
p-NO_2	Br	$COOCH_3$	95
m-NO_2	Br	$COOCH_3$	97
m-NO_2	Br	COPh	97
p-NO_2	Br	COPh	95
p-Cl	Br	COPh	97
p-Br	Br	COPh	96
p-NO_2	Cl	CN	88

a. All reactions were performed as described in detail in the text. All products were found to be the E-isomer by their m.p., I.R. and NMR spectra.
b. Isolated yields.

Method B: Because the telluronium salts can easily be prepared from dibutyl telluride and α-halo-ester, -ketone or nitrile, the formation of the salts and their condensation with carbonyl compounds can be carried out as one-pot reaction. Thus, a mixture of 3-nitrobenzaldehyde, methyl bromoacetate and dibutyl telluride was refluxed in THF. After six hours, methyl 3-(3'-nitrophenyl) -propenoate was obtained in 89% yield.

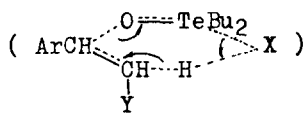
Table 2. One-pot Synthesis of α,β-Unsaturated Esters, Ketones and Nitriles Using Dibutyl Telluride[a]

$$R\text{-}C_6H_4CHO + Bu_2Te + XCH_2Y \xrightarrow[\text{reflux}]{THF} R\text{-}C_6H_4CH{=}CHY$$

R	X	Y	Yield (%)
p-NO_2	Br	$COOCH_3$	85
m-NO_2	Br	$COOCH_3$	89
p-Br	Br	$COOCH_3$	76
p-NO_2	Br	$COOC_2H_5$	93
p-NO_2	Br	COPh	92
m-NO_2	Br	COPh	90
p-Cl	Br	COPh	89
p-Br	Br	COPh	86
p-NO_2	Cl	CN	83

a. All products were found to be the E-isomer by their m.p., I.R. and NMR spectra. b. Isolated yields.

Although the mechanism of these reactions is not established, it is likely to proceed through a 6-membered cyclic transition state A.



(A)

Thus, we have found two simple methods to prepare cinnamate derivatives using organotellurium compounds under neutral conditions. Because of the simplicity of manupulation and milder reaction conditions, they should be suitable for the synthesis of cinnamate derivatives with base-sensitive functional groups

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