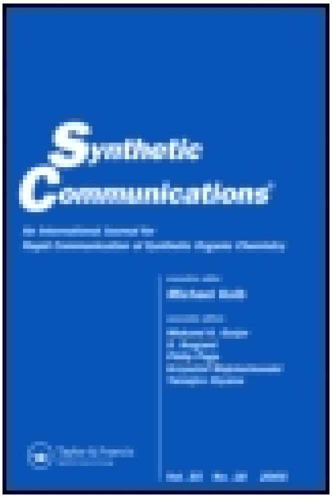

# Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

# Stereoselecive Synthesis of 3-Alkylcinnamic Esters via Coupling Reaction of (2Z)-3-(Aryltelluro)cinnamic Esters in Presence of CuI

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SYNTHETIC COMMUNICATIONS, 27(2), 237–241 (1997)

# STEREOSELECIVE SYNTHESIS OF 3-ALKYLCINNAMIC ESTERS *VIA* COUPLING REACTION OF (2Z)-3-(ARYLTELLURO)CINNAMIC ESTERS IN PRESENCE OF CuI

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**Abstract:** Coupling reaction of (2Z)-3-(aryltelluro)cinnamic esters with Grignard reagents in presence of CuI produced trisubstituted alkenes containing ester groups with retention of configuration.

The synthesis of trisubstituted alkenes has attracted the attention of chemists in recent years because many biologically active compounds have the structures of trisubstituted alkenes[1,2]. Vinyl tellurides, because of various reactivity of their telluro groups, become important precursors of alkenes. There have been several reports about synthesis of alkenes utilizing vinyl tellurides[3,4]. But the synthesis of alkenes containing ester groups from vinyl tellurides is scarcely reported[5]. Using (2Z)-3-(aryltelluro)cinnamic esters and coupling them with Grignard reagents in presence of CuI, we successfully syn-

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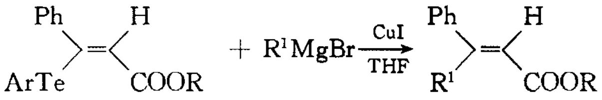
thesized the trisubstituted alkenes containing ester groups with high stereoselectivity.

We have used cat. amount Ni(PPh$_3$)$_2$Cl$_2$ to catalyse the coupling reaction, but have not isolated the trisubstituted $\alpha,\beta$-unsaturated esters. So we used equal amount of CuI. The coupling reaction of (2Z)-3-(aryltelluro)cinnamates **1** with 2eq. Grignard reagents **2** proceeded in anhydrous THF in presence of 1eq. CuI. When the Grignard reagents **2** were added to the mixtures of **1** and CuI in THF, the ester groups were not affected, producing the retention products **3** which have small space hinderation. We did not isolated the conversion products[6] (Table 1).



**1** **2** **3**

**Table 1** Coupling reaction of (2Z)-3-(aryltelluro)cinnamic esters with Grignard reagents

| Products | R$^1$ | R | Ar | Yield % |
|---|---|---|---|---|
| **3a** | $CH_3$ | $C_2H_5$ | Ph | 79 |
| **3b** | $C_2H_5$ | $C_2H_5$ | Ph | 94 |
| **3c** | $C_2H_5$ | $CH_3$ | p-$CH_3OC_6H_4$ | 88 |
| **3d** | n-$C_4H_9$ | $C_2H_5$ | Ph | 91 |
| **3e** | i-$C_4H_9$ | $C_2H_5$ | Ph | 84 |
| **3f** | Ph | $C_2H_5$ | Ph | 91 |

Most of the reported methods for the synthesis of alkenes from coupling reaction of vinyl tellurides used active organometallic reagents and used Ni$^{II}$ as catalyst[3,4]. Our procedure is the first report of coupling reaction of vinyl tellurides in presence of CuI. Because the active organometallic reagents may affect to the sensitive ester groups, our method is very valuable for synthesis of alkenes containing ester groups, in which the ester groups are unchanged.

## Experimental

$^1$H-NMR spectra were run on PMR-60MHz instrument. IR spectra were recorded on a Perkin-Elmer 683 spectrophotometer.

**Coupling reaction of (2Z)-3-(aryltelluro)cinnamates with Grignard reagents in presence of CuI. Typical procedure.**

Under $N_2$, CuI (0.19g, 1mmole) was stirred in 10ml anhy. THF then added several drops of Grignard reagent. **1** (1mmole) was added and stirred for 5min. The Grignard reagent (2mmole, ~1M soln. in THF) was added slowly in drops at 10℃. The mixture was stirred for 2h. Filtered away the solid and washed it with $Et_2O$. The combined organic phase was washed with $NH_4Cl$ solution and then with water. Dried with $Na_2SO_4$, evaporated the solvent and the residue was purificated by prepared TLC on silica gel. (AcOEt/n-Hexane=1 : 8).

**Ethyl (E)-3-phenyl-2-butenoate (3a)**

$^1$H-NMR ($CCl_4$/TMS), δ(ppm) 1.20(t, 3H), 2.35(s, 1H), 4.01(q, 2H), 5.90(s, 1H), 7.00-736(m, 5H).

IR(neat)(cm$^{-1}$) 1730, 1642, 1505, 1458, 1280, 1175, 1048, 872, 766, 694.

**Ethyl (E)-3-phenyl-2-pentenoate (3b)**

$^1$H-NMR ($CCl_4$/TMS), δ(ppm) 0.96-1.06(m, 6H), 2.96(q, 2H), 4.03(q, 2H), 5.83(s, 1H), 7.06-7.43(m, 5H).

IR(neat)(cm$^{-1}$) 1726, 1640, 1465, 1375, 1298, 1075, 1044, 875, 770, 696.

**Methyl (E)-3-phenyl-2-butenoate (3c)**

$^1$H-NMR ($CCl_4$/TMS), δ(ppm) 0.98(t, 3H), 3.00(q, 2H), 3.56(s, 3H), 5.85(s, 1H), 7.10-7.35(m, 5H).

IR(neat)(cm$^{-1}$) 1732, 1640, 1502, 1455, 1362, 1296, 1250, 1170, 1042, 872, 770, 695.

**Ethyl (E)-3-phenyl-2-heptenoate (3d)**

$^1$H-NMR ($CCl_4$/TMS), δ(ppm) 1.03-1.53(m, 7H), 2.83-3.16(m, 2H), 4.03(q,2H), 5.83(s,1H), 7.06-7.31(m,5H).

IR(neat)($cm^{-1}$) 1730, 1635, 1502, 1460, 1376, 1270, 1175, 1050, 876, 770, 694.

**Ethyl (E)-3-phenyl-5-methyl-2-hexenoate (3e)**

$^1$H-NMR ($CCl_4$/TMS),δ(ppm) 1.03-1.66(m,7H), 2.96(d,2H), 4.03(q, 2H), 5.90(s,1H), 7.05-7.33(m,5H).

IR(neat)($cm^{-1}$) 1730, 1638, 1588, 1502, 1475, 1452, 1375, 1320, 1270, 1175, 1050, 880, 765, 695.

**Ethyl 3,3-diphenyl-2-propenoate (3f)**

$^1$H-NMR ($CCl_4$/TMS),δ(ppm) 0.98(t,3H), 3.85(q,2H), 6.12(s,1H), 6.83-7.13(m,10H).

IR(neat)($cm^{-1}$) 1738, 1630, 1502, 1458, 1375, 1270, 1170, 1040, 875, 770, 696.

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5. In lit. 4, Uemura have used cat. amount $Ni(PPh_3)_2Cl_2$ to catalysize the coupling reaction of ethyl (Z)-3-phenyltelluropropenoate with phenyl Grignard rengent, but he obtained the coupling product only in 28% yield.
6. For 3,3-disubstituted propenoates, see (a) Jalander, L. and Broms, M., *Acta. Chem. Scand. B.*, **1983**, *B(37)*, 173. (b) Jones,G. and Maisey,

R. F., *Chem. Commun.*, **1968**, 543. (c) Texier-Boulet, F. and Foucaud, A., *Synthesis*, **1979**, 884. Our products **3** have the same spetra data with E-type products of above references.

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