

New Synthetic Approach to α -Chlorocinnamates: First Example of Synthesis of Functionally Substituted Alkenes Using Catalytic Olefination Reaction

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Received 24 September 2003; revised 17 December 2003

Abstract: A new simple and efficient transformation of carbonyl compounds to α -chlorocinnamates is described. Catalytic olefination reaction with ethyl trichloroacetate gives target alkenes in moderate to good yields. The reaction with aromatic aldehydes proceeds stereoselectively to form preferably *Z*-isomers.

Key words: catalytic olefination, α -chlorocinnamates, catalysis, alkenes, ethyl trichloroacetate

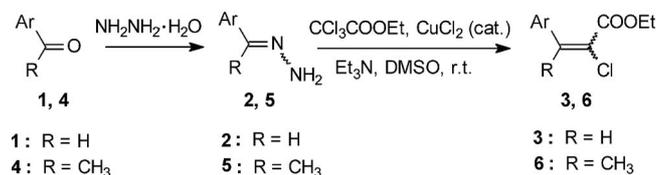
Conversion of carbonyl compounds to the corresponding alkenes is a very important functional group transformation in organic synthesis.¹ In addition to this, many natural products possess various trisubstituted alkene moieties, and a highly stereoselective construction of trisubstituted alkenes is one of the most challenging problems in synthetic organic chemistry.² Although many skillful and selective synthetic methods for the preparation of this important functional group have been devised for decades, there is still the need for a general and stereoselective method for the efficient synthesis of trisubstituted alkenes.

Recently, we have elaborated a novel approach to alkene synthesis – catalytic olefination reaction (COR) of aromatic aldehydes and ketones. It was found that *N*-unsubstituted hydrazones of aromatic carbonyl compounds could be smoothly converted to various substituted alkenes by treatment with polyhalogenalkanes in the presence of catalytic amounts of CuCl. Based on COR we elaborated novel methods of synthesis of dichloroalkenes, dibromoalkenes, vinyl bromides, vinyl iodides and fluoro-containing alkenes from aromatic and heteroaromatic carbonyl precursors. A possible mechanism of olefination was discussed and a catalytic cycle of COR was reported earlier.³

This article is devoted to the synthesis of functionally substituted alkenes using catalytic olefination. We tried to use ethyl trichloroacetate as a polyhalogenated synthon in COR to prepare the corresponding α -chlorocinnamates which can be used as valuable building blocks for the synthesis of aziridines, optically active α -haloesters, amino acids, and some other heterocyclic systems.⁴ Previously such compounds have been prepared using: Wittig and

Wittig–Horner approach,⁵ Knoevenagel-type condensation of aldehydes with halogen substituted CH-acids,⁶ Reformatsky-type addition of methyl trichloroacetate to aldehydes in the presence of Fe(CO)₅,⁷ transition-metal promoted carbonylation of vinyl halogenides,⁸ chlorination of corresponding cinnamates,⁹ solvolytic rearrangement of trichloroallyl alcohols,¹⁰ electrochemical synthesis,¹¹ Zn metal-promoted olefination of aldehydes and ketones with gem-dihalo compounds,¹² and triphenylphosphine-mediated deoxygenation of 3-phenyl-3-chloroketopropionic acid methyl ester.¹³

The procedure of COR was applied to the hydrazone of 4-chlorobenzaldehyde as a model substrate, but we had to do some optimization of reaction conditions because bases previously used in COR such as ammonia and ethylenediamine effected conversion of ethyl trichloroacetate to the corresponding amides. Use of variation of bases (TMEDA, triethylamine, diisopropylamine, ethyldiisopropylamine) in DMSO and ethanol as solvents show that the optimal condition is triethylamine in DMSO. We investigated also some copper salts as catalysts [CuSO₄·5H₂O, CuCl, CuCl₂, CuCl₂·2H₂O, Cu(OAc)₂] and found higher yield of product in the case of 1% of CuCl₂·2H₂O as a catalyst. Having found the optimal reaction conditions we tried to explore a one-pot technique for the preparation of α -chlorocinnamates to avoid preliminary preparation of hydrazones. We found that generally the yield of target product prepared from aldehyde was almost the same as for hydrazone, but one-pot synthesis is more simple (Scheme 1). In the case of olefination of ketones it was found necessary to use previously prepared hydrazones because an attempt to carry out the reaction in situ failed due to lower reactivity of carbonyl group of ketones.



Scheme 1

Therefore, we investigated the conversion of wide range of aromatic aldehydes and acetophenones bearing various substituents in the aromatic ring to the corresponding α -

chlorocinnamates. In general, the reaction proceeded smoothly to give the target products **3,6** in moderate yield (Table 1). We succeeded also in the preparation of condensed **3k** and heterocyclic (pyridine and thiophene) derivatives **3l,m** of 1-chloroacrylic acid. The reaction with aldehydes proceeds stereoselectively with preferable formation of *Z*-isomers. It is interesting to note, that the isomer composition is very similar to those observed for Wittig olefination. The configuration of alkene **3i** was unambiguously determined using the $^3J_{C-H}$ coupling between carbonyl carbon atom and alkene proton. The major *Z*-isomer has a $^3J_{C-H}$ coupling 4.8 Hz whereas the minor *E*-isomer has a coupling of 10.8 Hz.¹⁴

Besides the formation of alkenes that is accompanied with nitrogen evolution, another reaction product is *sym*-azine. General yield of two products is almost quantitative.

In the case of reaction with acetophenones the stereoselectivity of olefination is very low. Both isomers are formed in almost equal amounts. Similar selectivity have also been observed previously for Wittig-type synthesis.⁵

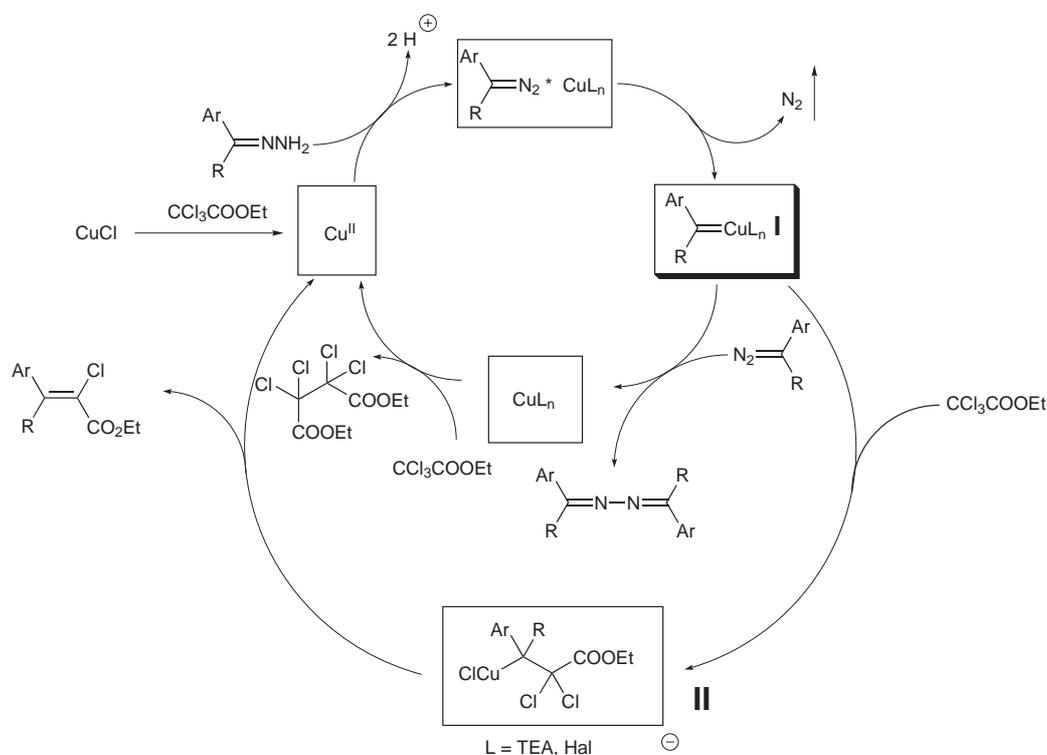
We found that the reaction of hydrazones with CCl_3CO_2Et is in a good agreement with previously proposed general mechanism of COR.³ At the first step of catalytic cycle hydrazone **2,5** is oxidized by Cu(II) to give the corresponding diazoalkane (Scheme 2). Subsequent copper-catalyzed decomposition of diazoalkane leads to formation of copper-carbene complex **I**. Complex **I** is the key intermediate of the reaction. Two competitive routes of subsequent transformation of **I** are possible. Complex **I** reacts with CCl_3CO_2Et to give the target alkene **3,6** and to

Table 1 α -Chlorocinnamates **3** and **6** Prepared

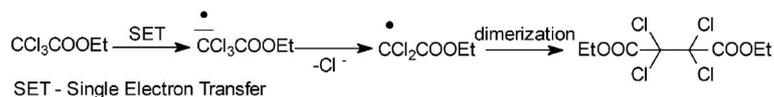
Product	Aryl	R	<i>Z/E</i>	Yield (%) ^a
3a	C ₆ H ₅	H	5.7:1	58
3b	4-MeC ₆ H ₄	H	7.3:1	49
3c	2-ClC ₆ H ₄	H	4.6:1	41
3d	4-ClC ₆ H ₄	H	7.3:1	60
3e	4-MeOC ₆ H ₄	H	9:1	53
3f	3-NO ₂ C ₆ H ₄	H	4.6:1	60
3g	4-NO ₂ C ₆ H ₄	H	5.7:1	49
3h	4-Me ₂ NC ₆ H ₄	H	5.3:1	40
3i	4-IC ₆ H ₄	H	4.6:1	42
3j	4-FC ₆ H ₄	H	5.7:1	53
3k	2-naphthyl	H	5.7:1	41
3l	3-pyridyl	H	4.6:1	57
3m	2-thienyl	H	1:0	21
6a	C ₆ H ₅	CH ₃	1.04:1 ^b	44
6b	4-MeOC ₆ H ₄	CH ₃	1.1:1 ^b	45
6c	4-NO ₂ C ₆ H ₄	CH ₃	0.4:1 ^b	30

^a Isolated yields by chromatography over silica gel.

^b The configuration have not been established.



Scheme 2



Scheme 3

regenerate the catalyst (outside the cycle). Addition of ethyl trichloroacetate to copper-carbene complex **I** proceeds via organocopper intermediate **II**.³ Another type of transformation of complex **I** is its reaction with diazoalkane to form the *sym*-azine (inside the cycle).

Recently we have investigated in detail the transformations of various polyhalogenalkanes $\text{C}(\text{Hal})_2\text{XY}$ and found that such compounds are partially reduced under COR conditions by SET mechanism (inside cycle). In the case of reaction with ethyl trichloroacetate another type of transformation is observed. No formation of ethyl dichloroacetate takes place but dimerization of radicals leading, according to GC and mass spectra analyses, to the formation of diethyl tetrachlorosuccinate (Scheme 3).¹⁵

In summary, we have elaborated a new non-Wittig approach to α -chlorocinnamates. First example of synthesis of functionalized alkenes using catalytic olefination reaction was demonstrated. Mild conditions, simplicity of the experimental technique and purification of products are remarkable advantages of the presented method.

Melting points are uncorrected. The IR spectra were recorded with UR-20 spectrometer. NMR spectra were recorded on Varian VXR-400 spectrometer in CDCl_3 with TMS as an internal standard. GC-MS analyses were performed with an Finnigan SSQ 7000 Mass Spectrometer connected to a Varian 3400 GC, equipped with a DB-5MS column (30 m, 0.2 mm of internal diameter), electron impact (EI) at 70 eV and He was used as the carrier gas. Merck 60F₂₅₄ plates were used for analytical (TLC) chromatography. Column chromatography was performed on silica gel (63–200 mesh, Merck). All starting materials are commercially available.

The known compounds were identified by the comparison of the spectral data with those described in the literature **3a,c,e**,¹⁶ **3b**,¹⁷ **3d,f**,⁹ **3g**,¹¹ **3j,m**,¹⁸ **6a**.¹⁹

α -Chlorocinnamates **3**; General One-Pot Procedure

A solution of aromatic aldehyde **1** (5 mmol) in DMSO (5 mL) was added dropwise to 100% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (0.25 mL, 5 mmol) and the mixture was stirred until the aldehyde had disappeared (TLC monitoring). Then $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (9 mg, 0.05 mmol) and Et_3N (2.1 mL, 0.015 mmol) were added. After 5 min, ethyl trichloroacetate (2.1 mL, 0.015 mmol) was added dropwise at 20 °C. The reaction mixture was stirred for 24 h, then quenched with aq 5% HCl (300 mL) and extracted with CH_2Cl_2 (3 \times 50 mL). The combined extracts were dried (Na_2SO_4), the CH_2Cl_2 was evaporated in vacuo and the residue was purified by column chromatography (hexane– CH_2Cl_2). In the case of aromatic aldehydes, the major *Z*-isomer can be separated by column chromatography (Table 1).

Ethyl 2-Chloro-3-(4-*N,N*-dimethylaminophenyl)acrylate (**3h**)

Yellow solid; mixture of *Z/E*-isomers (5.3:1); R_f 0.52 (hexane– CH_2Cl_2 , 1:2); mp 65–69 °C.

IR (Nujol): 1705 (C=O), 1600 cm^{-1} .

¹H NMR (400 MHz, CDCl_3): δ (major isomer) = 7.83 (d, J = 9.1 Hz, 2 H), 7.81 (s, 1 H), 6.68 (d, J = 9.1 Hz, 2 H), 4.32 (q, J = 7.0 Hz, 2 H), 3.02 (s, 6 H), 1.36 (t, J = 7.0 Hz, 3 H).

¹³C NMR (100 MHz, CDCl_3): δ (major isomer) = 164.1 (C=O), 151.4, 137.1 (C=), 132.8, 131.0, 120.6 (C=C), 111.3, 62.0 (CH_2), 40.0 [$(\text{CH}_3)_2\text{N}$], 14.3 (CH_3).

MS: m/z (%) = 255 (30), 253 (100), 225 (20), 189 (30), 145 (45), 128 (6), 73 (8).

Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{ClNO}_2$: C, 61.54; H, 6.36. Found: C, 61.37; H, 6.32.

Ethyl 2-Chloro-3-(4-iodophenyl)acrylate (**3i**)

Pale yellow oil; mixture of *Z/E*-isomers (4.6:1); R_f 0.67 (hexane– CH_2Cl_2 , 1:2).

IR (CHCl_3): 1740 (C=O), 1625 cm^{-1} .

¹H NMR (400 MHz, CDCl_3): δ (major isomer) = 7.81 (s, 1 H), 7.76 (d, J = 8.5 Hz, 2 H), 7.55 (d, J = 8.5 Hz, 2 H), 4.35 (q, J = 7.1 Hz, 2 H), 1.38 (t, J = 7.1 Hz, 3 H).

¹³C NMR (100 MHz, CDCl_3): δ (major isomer) = 163.0 (C=O), 137.7 (C=), 135.7, 130.1, 131.9, 123.0 (C=C), 96.6, 62.6 (CH_2), 14.2 (CH_3).

MS: m/z (%) = 338 (33), 336 (100), 301 (15), 273 (33), 228 (48), 164 (24), 136 (22), 101 (30).

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{ClIO}_2$: C, 39.26; H, 2.99. Found: C, 39.19; H, 2.73.

Ethyl 2-Chloro-3-(2-naphthyl)acrylate (**3k**)

White solid; mixture of isomers (5.7:1); R_f 0.61 (hexane– CH_2Cl_2 , 1:2); mp 53–57 °C.

IR (Nujol): 1720 (C=O), 1620 cm^{-1} .

¹H NMR (400 MHz, CDCl_3): δ (major isomer) = 8.33 (s, 1 H), 8.06 (s, 1 H), 7.95 (dd, J = 2.0, 8.5 Hz, 1 H), 7.89–7.82 (m, 3 H), 7.56–7.49 (m, 2 H), 4.38 (q, J = 7.0 Hz, 2 H), 1.41 (t, J = 7.0 Hz, 3 H).

¹³C NMR (100 MHz, CDCl_3): δ (major isomer) = 163.4 (C=O), 136.9 (C=), 133.8, 132.9, 131.4, 130.4, 128.7, 128.0, 127.6, 127.5, 126.9, 126.5, 122.2 (C=C), 62.6 (CH_2), 14.2 (CH_3).

MS: m/z (%) = 262 (10), 260 (24), 197 (13), 179 (11), 152 (100), 76 (22), 44 (18).

Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{ClO}_2$: C, 69.10; H, 5.03. Found: C, 69.17; H, 5.03.

Ethyl 2-Chloro-3-pyridin-3-ylacrylate (**3m**)

Brown oil, mixture of *Z/E*-isomers (4.6:1); R_f 0.2 (CH_2Cl_2).

IR (CHCl_3): 1740 (C=O), 1630 cm^{-1} .

¹H NMR (400 MHz, CDCl_3): δ (major isomer) = 8.90 (s, 1 H), 8.62 (d, J = 4.8 Hz, 1 H), 8.31 (dt, J = 2.0, 8.2 Hz, 1 H), 7.89 (s, 1 H), 7.38 (dd, 4.8, 8.0, 1 H), 4.37 (q, J = 7.0 Hz, 2 H), 1.40 (t, J = 7.0 Hz, 3 H).

¹³C NMR (100 MHz, CDCl_3): δ (major isomer) = 162.5 (C=O), 151.3, 150.4, 136.5 (C=), 133.1, 129.0, 124.6, 123.2 (C=C), 62.6 (CH_2), 14.0 (CH_3).

MS: m/z (%) = 211 (25), 182 (17), 176 (45), 167 (59), 148 (100), 138 (24), 130 (28), 102 (57), 75 (40).

Anal. Calcd for $C_{10}H_{10}ClNO_2$: C, 56.75; H, 4.76. Found: C, 56.69; H, 4.96.

Hydrazones 5a–c; General Procedure

The hydrazones **5a–c** were prepared by refluxing for several hours the ketone (1 equiv) and 100% hydrazine hydrate (3 equiv) dissolved in a minimum amount of EtOH to achieve homogeneity at boiling point. In the case of **5b,c**, the reaction mixture was poured into H_2O (300 mL) and filtered. The crude hydrazones were washed with H_2O (3×100 mL) and dried in vacuo. In the case of **5a**, EtOH, H_2O and excess of hydrazine were removed in vacuo, the crude hydrazone was dissolved in Et_2O and washed with brine. The solvent was removed under reduced pressure and the hydrazone was crystallized by cooling.

1-Phenylethanone Hydrazone (5a)

Yield: 70%; colorless crystals; mp 23–24 °C (Lit.²⁰ mp 22–26 °C).

1-(4-Methoxyphenyl)ethanone Hydrazone (5b)

Yield: 93%; colorless crystals; mp 119–120 °C (Lit.²¹ mp 122–123 °C).

1-(4-Nitrophenyl)ethanone Hydrazone (5c)

Yield: 92%; orange crystals; mp 148–149 °C (Lit.²² mp 149–151 °C).

α -Chlorocinnamates **6** from Hydrazones; General Procedure

To a solution of hydrazone **5** (5 mmol) in DMSO (5 mL) were added $CuCl_2 \cdot 2H_2O$ (9 mg, 0.05 mmol) and Et_3N (2.1 mL, 0.015 mmol). After 5 min, ethyl trichloroacetate (2.1 mL, 0.015 mmol) was added dropwise keeping the reaction temperature at 20 °C. The reaction mixture was stirred for 24 h, then quenched with aq 5% HCl (300 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined extracts were dried (Na_2SO_4), the CH_2Cl_2 was evaporated in vacuo and the residue was purified by column chromatography (hexane– CH_2Cl_2) (Table 1).

Ethyl 2-Chloro-3-(4-methoxyphenyl)but-2-enoate (6b)

Pale yellow oil mixture of isomers (1.1:1); R_f 0.61 (hexane– CH_2Cl_2 , 1:2).

IR ($CHCl_3$): 1730 (C=O), 1620 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): δ (first isomer) = 7.11 (d, J = 9.0 Hz, 2 H), 6.86 (d, J = 9.0 Hz, 2 H), 4.01 (q, J = 7.2 Hz, 2 H, CH_2O), 3.81 (s, 3 H, CH_3O), 2.27 (s, 3 H, CH_3), 0.99 (t, J = 7.2 Hz, 3 H, CH_3CH_2); δ (second isomer) = 7.23 (d, J = 9.0 Hz, 2 H), 6.92 (d, J = 9.0 Hz, 2 H), 4.33 (q, J = 7.2 Hz, 2 H, CH_2O), 3.83 (s, 3 H, CH_3O), 2.39 (s, 3 H, CH_3), 1.38 (t, J = 7.2 Hz, 3 H, CH_3CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ (first isomer) = 164.3 (C=O), 159.2, 144.8 (CCH_3), 133.1, 128.2, 113.6, 118.4 (C=C), 61.5 (OCH_2), 55.2 (CH_3O), 23.4 (CH_3), 13.6 (CH_3CH_2); δ (second isomer) = 164.4 (C=O), 159.4, 147.1 (CCH_3), 133.7, 128.7, 113.6, 119.8 (C=C), 61.9 (OCH_2), 55.2 (CH_3O), 23.4 (CH_3), 14.1 (CH_3CH_2).

MS: m/z (%) for the first isomer = 256 (15), 254 (46), 208 (100), 145 (50), 131 (21), 115 (19), 108 (96), 102 (13), 77 (23); for the second isomer = 256 (13), 254 (39), 208 (92), 145 (51), 131 (19), 115 (18), 108 (100), 103 (28), 77 (23).

Anal. Calcd for $C_{13}H_{15}ClO_3$: C, 61.30; H, 5.94. Found: C, 61.12; H, 6.09.

Ethyl 2-Chloro-3-(4-nitrophenyl)but-2-enoate (6c)

Pale yellow oil mixture of isomers (0.4:1); R_f 0.61 (hexane– CH_2Cl_2 , 1:2).

IR ($CHCl_3$): 1720 (C=O), 1600 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): δ (major isomer) = 8.20 (d, J = 8.8 Hz, 2 H), 7.32 (d, J = 8.8 Hz, 2 H), 4.00 (q, J = 7.3 Hz, 2 H, CH_2), 2.30 (s, 3 H, CH_3), 0.99 (t, J = 7.3 Hz, 3 H, CH_3CH_2); δ (minor isomer) = 8.25 (d, J = 8.8 Hz, 2 H), 7.41 (d, J = 8.8 Hz, 2 H), 4.34 (q, J = 7.3 Hz, 2 H, CH_2), 2.40 (s, 3 H, CH_3), 1.38 (t, J = 7.3 Hz, 3 H, CH_3CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ (major isomer) = 162.8 (C=O), 148.0 (CCH_3), 145.1, 144.3, 127.8, 123.6, 121.8 (C=C), 62.1 (OCH_2), 22.9 (CH_3), 13.6 (CH_3CH_2); δ (signals of minor isomer) = 163.3 (C=O), 148.0 (CCH_3), 145.1, 144.3, 128.2, 123.8, 122.1 (C=C), 62.3 (OCH_2), 23.8 (CH_3), 14.1 (CH_3CH_2).

MS: m/z (%) for major isomer = 271 (3), 269 (10), 252 (22), 224 (100), 194 (50), 178 (15), 149 (20), 131 (11), 115 (70), 103 (11), 89 (12), 78 (27), 44 (78); for minor isomer = 271 (1), 269 (3), 252 (5), 224 (39), 194 (11), 178 (3), 149 (6), 115 (19), 78 (43), 44 (100).

Anal. Calcd for $C_{12}H_{12}ClNO_4$: C, 53.44; H, 4.49. Found: C, 53.77; H, 4.30.

Acknowledgment

Financial support from Russian Fundamental Investigation Foundation (Grant 03-03-32052a) is gratefully acknowledged.

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