New method for the synthesis of α-chlorocinnamonitriles

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A novel method for the preparation of nitriles of α-chlorocinnamic acid from aldehydes and ketones was proposed. Transformation of carbonyl compounds into hydrazones followed by treatment of the reaction mixture with CCl_3CN in the presence of copper chloride(I) yields α-chlorocinnamonitriles.

Key words: catalytic olefination reaction, copper salts, trichloroacetonitrile, α-chlorocinnamonitriles, hydrazones.

Polyfunctional but still rather simple building blocks that can be involved in chemo-, regio-, and stereoselective reactions are very significant in modern organic synthesis. This type of compound can be exemplified by nitriles of α-chlorocinnamic acids, which have found wide use in organic synthesis.[1] In particular, a broad range of N-, S-, and O-containing heterocycles have been synthesized by reactions of derivatives of α-chloro- and α-bromoacrylic acid nitriles and esters with various binucleophiles.[1]

This study describes a new method for the synthesis of α-chlorocinnamonitriles on the basis of the catalytic olefination reaction (COR) of carbonyl compounds proposed in our previous studies.[2—6] This method can serve as a convenient alternative to the known methods used to prepare these substances, for example, the Wittig reaction,[7,8] the addition of chlorine to cinnamonitriles followed by elimination of HCl,[9] the reaction of alkyl α-cyanocinnamates with chlorine followed by decarboxylation,[10] and the reaction of carbonyl compounds with 1-chloro-1-cyanoketene.[11]

Results and Discussion

Previously, it was shown that *N*-unsubstituted hydrazones of aromatic aldehydes and ketones are transformed into the corresponding substituted alkenes on treatment with polyhaloalkanes in the presence of catalytic amounts of CuCl. The double carbon—carbon bond is formed stereoselectively, the thermodynamically more stable alkene isomer being formed predominantly.[12]

In this study we used trichloroacetonitrile as the polyhalogenated compound. We took 4-chlorobenzaldehyde hydrazone (**1a**) as an example to study the roles of various factors and to optimize the reaction conditions, because previously it had been shown that the natures of the solvent and the base that is complexed with the catalyst and the counter-ion have a pronounced effect on the course of the process. The effects of the natures of the base and the solvent on the yield of the target alkene were studied using an invariable amount of the CuCl catalyst (10 mol.%) and a fivefold molar excess of Cl_3CCN with respect to hydrazone. A number of solvents (DMSO, EtOH, and MeCN) and bases (aqueous NH_3, ethylene-1,2-diamine, Et_3N, TMEDA, and DBU) were tested. The highest yield of the target 2-chloro-3-(4-chlorophenyl)acrylonitrile (**2a**) (61%) was obtained using DMSO as the solvent and Et_3N as the base. It should be mentioned that with aqueous NH_3, no target product was formed. The highest yield of the product was attained with a fivefold molar excess of Cl_3CCN. When 2.5 or 1 equiv. of Cl_3CCN were used, the product yield decreased to 46 or 39%, respectively. Under standard conditions, we compared the catalytic properties of various copper salts. As shown by experiments, copper(I) chloride as the catalyst provides the highest yields of the target product.

Catalyst	CuCl	$CuCl_2$	$CuSO_4$	$Cu(OAc)_2$	$Cu(OTf)_2$
Yield (%)	61	41	59	55	53

The reaction of 4-chlorobenzaldehyde hydrazone (**1a**) with trichloroacetonitrile affords a mixture of the *E*- and *Z*-isomers of the corresponding α-chlorocinnamonitrile **2a** (Scheme 1).

To determine the configuration of the resulting product, the ^{13}C NMR spectrum without proton decoupling

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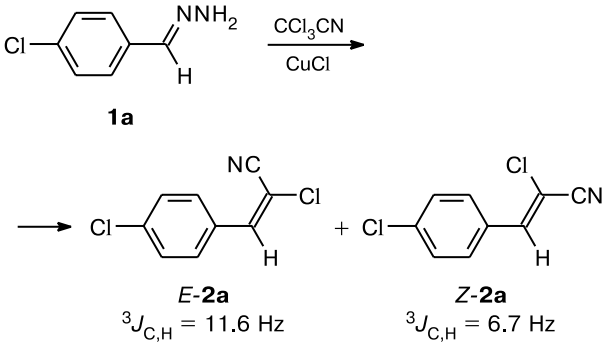
Scheme 1

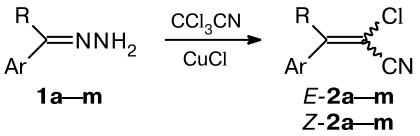


was recorded and the spin-spin coupling constant between the nitrile C atom and the proton at the double bond was measured. By comparing the results with published data,[13] we found that the reaction gives predominantly the *E*-isomer, for which the $^3J_{C,H}$ constant is 11.6 Hz; for the minor *Z*-isomer, this value is 6.7 Hz.

In the case of aromatic aldehydes, one-pot method in which the hydrazone of the carbonyl compound is prepared prior to the reaction directly in the reaction vessel and used without isolation proved to be efficient. This method has undeniable advantages, as the isolation of the hydrazone is thus bypassed. Hence, not only the reaction time and the number of steps are decreased but also the difficulties associated with the isolation of unstable hydrazones of aldehydes are eliminated.

A broad range of aromatic aldehydes both with donor and with acceptor substituents were introduced in the reaction under the conditions of choice (Scheme 2, Table 1).

Scheme 2



Note. For the description of substituents, see Table 1.

Most often, the target products **2a**—**m** are formed in satisfactory yields ranging from 26 to 78% (see Table 1). The reaction is sensitive to steric factors, the lowest product yield (26%) being obtained for sterically crowded 2,6-dichlorobenzaldehyde. In all cases, *E*-isomers are formed as the major products. It is noteworthy that the stereochemistry of this process is opposite to that observed in the reaction with ethyl trichloroacetate.[14] In our opinion, this may be due to the difference between the steric bulks of the cyano- and ethoxycarbonyl groups. Whereas the cyano group is less bulky than the Cl atom (the conformational energies are 0.17 and 0.43 kcal mol^{-1}, respectively), for the ethoxycarbonyl group, the conformational energy equals 1.2 kcal mol^{-1}.[15]

Table 1. Reactions of hydrazones **1a**—**m** with trichloroacetonitrile

Compound	Ar	R	Method	Yield (%)	(*Z* : *E*)*
2a	4-ClC_6H_4	H	*A*, *B*	61	1 : 4
2b	4-$MeOC_6H_4$	H	*B*	66	1 : 1.6
2c	2,4-$Me_2C_6H_3$	H	*B*	57	1 : 2.3
2d	4-$O_2NC_6H_4$	H	*B*	29	1 : 2.2
2e	2,6-$Cl_2C_6H_3$	H	*B*	26	1 : 2
2f	4-$Me_2NC_6H_4$	H	*B*	40	1 : 1.2
2g	3-$O_2NC_6H_4$	H	*B*	37	1 : 1.5
2h	4-ClC_6H_4	Me	*A*	74	1 : 1.6
2i	4-$O_2NC_6H_4$	Me	*A*	52	1 : 3.8
2j	4-$MeOC_6H_4$	Me	*A*	78	1 : 1.3
2k	4-BrC_6H_4	Me	*A*	63	1 : 1.75
2l	3,5-Me_2-4-$MeOC_6H_2$	Me	*A*	61	1 : 1.5
2m		Me	*A*	44	1 : 2

* Ratio of isomers.

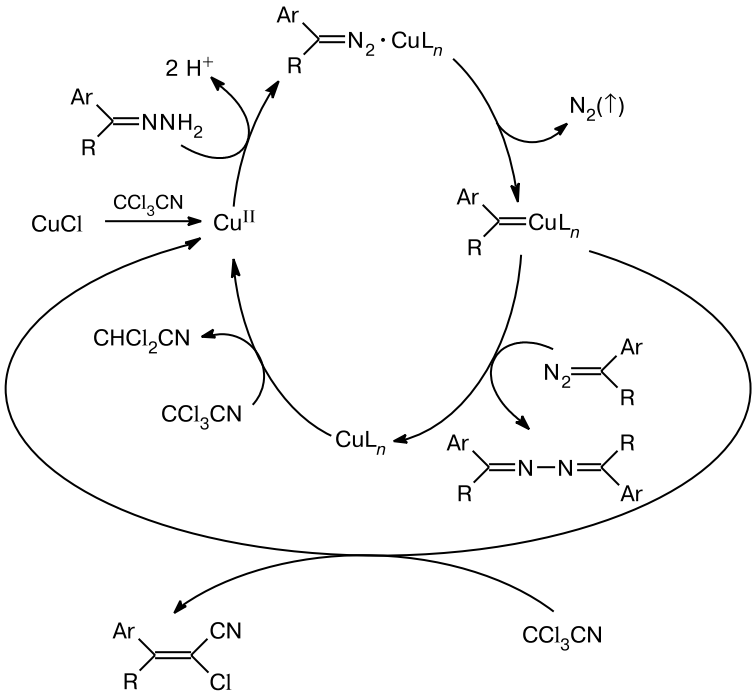
It was also shown that hydrazones of various acetophenones including heterocyclic derivatives can also be introduced in this reaction. All products were obtained in good yields; however, the process selectivity is somewhat lower with acetophenones. Nevertheless, the reaction is applicable to a broad range of substrates and gives products in good yields.

We found that the reaction follows the mechanism we proposed previously for catalytic olefination and can be described by the following catalytic cycle (Scheme 3).

The first step is oxidation of copper(I) to copper(II). Subsequently, Cu^{II} reacts with the aldehyde or ketone hydrazone to give a copper—carbene complex through the intermediate formation of the corresponding diazoalkane. The copper—carbene complex, similar to the metal—carbene complexes described in the literature,[16—18] is the key intermediate of the reaction. It reacts with CCl_3CN to give α-chlorocinnamonitrile and copper(II), the latter being involved again in the catalytic cycle. We confirmed the presence of the reduction product of CCl_3CN into $CHCl_2CN$ by mass spectrometry. The other product formed in the catalytic olefination is the corresponding azine of the carbonyl compound.

Thus, in this work, we developed a new strategy for the synthesis of α-chlorocinnamonitriles, valuable for synthetic purposes. This method appears to be a convenient alternative to the known methods for the preparation of these compounds. The advantages of this method include, apart from the ready availability of the starting compounds,

Scheme 3



R = H, Me
L = Et_3N, Cl^-

mild conditions of the reaction and simplicity of the procedure.

Experimental

IR spectra were measured on a UR-20 spectrophotometer in thin film for liquids and in mineral oil for solids. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (operating at 400 and 100 MHz, respectively) in $CDCl_3$ using Me_4Si as the internal standard. TLC was performed using plates with silica gel 60 F_{254} (Merck), and column chromatography was carried out using Merck silica gel (63—200 mesh). The hydrazones of aromatic aldehydes and ketones were prepared from commercially available aldehydes by published procedures.[19]

The synthesis of α-chlorocinnamonitriles (general procedure). ***A.*** Triethylamine (3.5 mL) and freshly purified CuCl [3] (50 mg, 0.5 mmol) were added to a solution of freshly prepared hydrazone (5 mmol) in DMSO (15 mL). A solution of CCl_3CN (2.5 mL, 25 mmol) in DMSO (5 mL) was added dropwise over a period of 2 min, the temperature being maintained at ~20 °C by water-bath cooling. The reaction mixture was stirred for 2 h and quenched with 0.1 *M* HCl (200 mL). The products were extracted with CH_2Cl_2 (3×50 mL), the combined extracts were dried over Na_2SO_4, the solvent was evaporated, and the products (a mixture of isomers) were isolated by column chromatography (elution with hexane—CH_2Cl_2, 1 : 1).

B. A solution of aldehyde (5 mmol) in DMSO (10 mL) was added dropwise with stirring to a solution of $N_2H_4 \cdot H_2O$ (0.12 mL, 5 mmol) in DMSO (5 mL). A mixture was stirred until the starting aldehyde disappeared (TLC monitoring). Then Et_3N (3.5 mL) and freshly purified CuCl (50 mg, 0.5 mmol) were added to the resulting solution of hydrazone. Then a solution of CCl_3CN (2.5 mL, 25 mmol) in DMSO (5 mL) was added dropwise at ~20 °C over a period of 2 min, the temperature being maintained at ~20 °C by water-bath cooling. The reaction mixture was stirred for 2 h and quenched with 0.1 *M* HCl (200 mL). The products were isolated as described in procedure ***A***.

2-Chloro-3-(4-chlorophenyl)acrylonitrile (2a) (isomer mixture, *E* : *Z* = 4 : 1) was formed as yellow crystals, R_f 0.54 and 0.46 for *E*- and *Z*-isomers, respectively (hexane—CH_2Cl_2, 1 : 2). ^1H NMR, δ, *E*-isomer: 7.62, 7.42 (both d, 2 H each, H arom., *J* = 8.5 Hz); 7.30 (s, 1 H, CH); *Z*-isomer: 7.67, 7.42 (both d, 2 H each, H arom., *J* = 8.8 Hz); 7.29 (s, 1 H, CH). The data of the ^1H NMR spectra correspond to those reported previously.[11] ^{13}C NMR, δ, *E*-isomer: 143.8 (CH), 137.2, 129.7, 129.6, 129.4, 114.7 (CN), 100.7 (CCl); *Z*-isomer: 140.8 (CH), 137.2, 131.4, 130.0, 129.0, 116.0 (CN), 101.8 (CCl).

2-Chloro-3-(4-methoxyphenyl)acrylonitrile (2b) (isomer mixture, *E* : *Z* = 1.6 : 1) was formed as yellow oil, R_f 0.54 and 0.42 for *E*- and *Z*-isomers, respectively (hexane—CH_2Cl_2, 1 : 2). ^1H NMR, δ, *E*-isomer: 7.59 (d, 2 H, H arom., *J* = 8.8 Hz); 7.19 (s, 1 H, CH); 6.87 (d, 2 H, H arom., *J* = 8.8 Hz); 3.78 (s, 3 H, OMe); *Z*-isomer: 7.67 (d, 2 H, H arom., *J* = 9.1 Hz); 7.18 (s, 1 H, CH); 6.89 (d, 2 H, H arom., *J* = 9.1 Hz); 3.8 (s, 3 H, OMe). The NMR data correspond to those reported previously.[11]

2-Chloro-3-(2,4-dimethylphenyl)acrylonitrile (2c) (isomer mixture, *E* : *Z* = 2.3 : 1) was formed as a colorless oil, R_f 0.62 and

0.56 for *E*- and *Z*-isomers, respectively (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 7.68 (d, 1 H, H arom., J = 7.9 Hz); 7.54 (s, 1 H, CH); 7.08 (d, 1 H, H arom., J = 7.9 Hz); 7.06 (s, 1 H, H arom.); 2.34, 2.31 (both s, 3 H each, Me); *Z*-isomer: 7.70 (d, 1 H, H arom., J = 8.5 Hz); 7.50 (s, 1 H, CH); 7.07 (s, 1 H, H arom.); 7.06 (d, 1 H, H arom., J = 8.5 Hz); 2.34, 2.31 (both s, 3 H each, Me). ^{13}C NMR, δ, *E*-isomer: 143.9, 141.4, 137.1, 131.4, 130.5, 127.4, 127.2, 128.0, 115.0 (CN), 100.4 (CCl), 21.29 (Me), 19.57 (Me). Found (%): C, 68.54; H, 5.12. $C_{11}H_{10}ClN$. Calculated (%): C, 68.93; H, 5.26.

2-Chloro-3-(4-nitrophenyl)acrylonitrile (2d) (isomer mixture, $E : Z$ = 4 : 1) was formed as yellow crystals, R_f 0.42 and 0.35 for *E*- and *Z*-isomers, respectively (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 8.30, 7.85 (both d, 2 H each, H arom., J = 8.8 Hz); 7.44 (s, 1 H, CH); *Z*-isomer: 8.29, 7.86 (both d, 2 H each, H arom., J = 8.8 Hz); 7.42 (s, 1 H, CH). The NMR data correspond to those reported previously.[11]

2-Chloro-3-(2,6-dichlorophenyl)acrylonitrile (2e) (isomer mixture, $E : Z$ = 2 : 1) was formed as a yellow oil, R_f 0.61 and 0.53 for *E*- and *Z*-isomers, respectively (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 7.35—7.30 (m, 2 H, H arom.); 7.26 (s, 1 H, CH); 7.25—7.18 (m, 1 H, H arom.). Found (%): C, 46.93; H, 6.05. $C_9H_4Cl_3N$. Calculated (%): C, 46.49; H, 6.02.

2-Chloro-3-(4-*N*,*N*-dimethylaminophenyl)acrylonitrile (2f) (isomer mixture, $E : Z$ = 1.2 : 1) was formed as yellow crystals, R_f 0.50 and 0.45 for *E*- and *Z*-isomers, respectively (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 7.59 (d, 2 H, H arom., J = 7.6 Hz); 7.16 (s, 1 H, CH); 6.66 (d, 2 H, H arom., J = 7.6 Hz); 3.03 (s, 6 H, NMe_2); *Z*-isomer: 7.60 (d, 2 H, H arom., J = 9.0 Hz); 7.05 (s, 1 H, CH); 6.60 (d, 2 H, H arom., J = 9.0 Hz); 2.99 (s, 6 H, NMe_2). The NMR data correspond to those reported previously.[11]

2-Chloro-3-(3-nitrophenyl)acrylonitrile (2g)[10] (isomer mixture, $E : Z$ = 1.5 : 1) was formed as yellow crystals, R_f 0.44 and 0.37 for *E*- and *Z*-isomers, respectively (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 8.44 (s, 1 H, H arom.); 8.30 (d, 1 H, H arom., J = 8.2 Hz); 8.09 (d, 1 H, H arom., J = 8.0 Hz); 8.30 (t, 1 H, H arom., J = 8.2 Hz); 7.45 (s, 1 H, CH); *Z*-isomer: 8.60 (s, 1 H, Ar); 8.02 (d, 1 H, H arom., J = 8.0 Hz); 7.43 (s, 1 H, CH); other proton signals are superimposed by the signals of the major isomer.

2-Chloro-3-(4-chlorophenyl)but-2-enonitrile (2h) (isomer mixture, $E : Z$ = 1.6 : 1) was formed as a yellow oil, R_f 0.60 (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 7.32, 7.20 (both d, 2 H each, H arom., J = 8.5 Hz); 2.36 (s, 3 H, Me); *Z*-isomer: 7.33, 7.28 (both d, 2 H each, H arom., J = 8.8 Hz); 2.26 (s, 3 H, Me). ^{13}C NMR, δ, *E*-isomer: 153.0, 136.0, 135.4, 129.0, 128.7, 114.8 (CN), 92.2 (CCl), 24.0 (Me). Found (%): C, 56.76; H, 3.36. $C_{10}H_7Cl_2N$. Calculated (%): C, 56.63; H, 3.33.

2-Chloro-3-(4-nitrophenyl)but-2-enonitrile (2i) (isomer mixture, $E : Z$ = 3.8 : 1) was formed as a yellow oil, R_f 0.40 (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 8.23, 7.43 (both d, 2 H each, H arom., J = 9.1 Hz); 2.42 (s, 3 H, Me); *Z*-isomer: 8.23, 7.54 (both d, 2 H each, H arom., J = 9.1 Hz); 2.33 (s, 3 H, Me). ^{13}C NMR, δ, *E*-isomer: 152.2, 148.0, 143.2, 128.3, 124.0, 114.0 (CN), 101.0 (CCl), 23.8 (Me). Found (%): C, 54.00; H, 3.33. $C_{10}H_7ClN_2O_2$. Calculated (%): C, 53.95; H, 3.17.

2-Chloro-3-(4-methoxyphenyl)but-2-enonitrile (2j) (isomer mixture, $E : Z$ = 1.3 : 1) was formed as a yellow oil, R_f 0.52 (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 7.26, 6.86 (both d, 2 H each, H arom., J = 8.8 Hz); 3.76 (s, 3 H, OMe); 2.36 (s, 3 H, Me); *Z*-isomer: 7.31, 6.86 (both d, 2 H each, H arom., J = 8.8 Hz); 3.76 (s, 3 H, OMe); 2.25 (s, 3 H, Me). ^{13}C NMR, δ, *E*-isomer: 160.4, 153.5, 129.1, 115.5 (CN), 113.7, 98.8 (CCl), 55.2 (OMe), 24.0 (Me). Found (%): C, 63.20; H, 4.60. $C_{11}H_{10}ClNO$. Calculated (%): C, 63.62; H, 4.85.

3-(4-Bromophenyl)-2-chlorobut-2-enonitrile (2k) (isomer mixture, $E : Z$ = 1.8 : 1) was formed as yellow-brown crystals, R_f 0.62 (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 7.49, 7.14 (both d, 2 H each, H arom., J = 8.5 Hz); 2.36 (s, 3 H, Me); *Z*-isomer: 7.50, 7.22 (both d, 2 H each, H arom., J = 8.5 Hz); 2.27 (s, 3 H, Me). ^{13}C NMR, δ, *E*-isomer: 153.0, 135.6, 131.7, 128.9, 123.7, 114.8 (CN), 99.2 (CCl), 24.0 (Me). Found (%): C, 46.59; H, 2.73. $C_{10}H_7BrClN$. Calculated (%): C, 46.32; H, 2.75.

2-Chloro-3-(4-methoxy-3,5-dimethylphenyl)but-2-enonitrile (2l) (isomer mixture, $E : Z$ = 1.2 : 1) was formed as a yellow oil, R_f 0.48 (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 6.99 (s, 2 H, H arom.); 3.74 (s, 3 H, OMe); 2.30 (s, 3 H, Me); 2.30 (s, 6 H, Me); *Z*-isomer: 7.07 (s, 2 H, H arom.); 3.74 (s, 3 H, OMe); 2.40 (s, 6 H, Me); 2.30 (s, 3 H, Me). ^{13}C NMR, δ, *E*-isomer: 157.8, 154.2, 132.9, 132.1, 131.4, 131.1, 127.9, 115.3 (CN), 98.0 (CCl), 59.6 (OMe), 24.2 (Me), 16.1 (Me). Found (%): C, 65.71; H, 6.13. $C_{13}H_{14}ClNO$. Calculated (%): C, 66.24; H, 5.99.

2-Chloro-3-(2-thienyl)but-2-enonitrile (2m) (isomer mixture, $E : Z$ = 1.8 : 1) was formed as a yellow oil, R_f 0.60 (hexane—CH_2Cl_2, 1 : 2). ^{1}H NMR, δ, *E*-isomer: 7.62, 7.61 (both s, 1 H each, H heteroarom.); 7.16 (t, 1 H, H heteroarom., J = 4.7 Hz); 2.59 (s, 3 H, Me); *Z*-isomer: 7.64 (dd, 1 H, H heteroarom., J = 1.2 Hz, J = 3.8 Hz); 7.48 (dd, 1 H, H heteroarom., J = 1.1 Hz, J = 5.0 Hz); 7.10 (dd, 1 H, H heteroarom., J = 3.8 Hz, J = 5.0 Hz); 2.42 (s, 3 H, Me). ^{13}C NMR, δ, *E*-isomer: 146.4, 138.0, 131.9, 129.1, 127.0, 116.0 (CN), 96.4 (CCl), 22.8 (Me). Found (%): C, 52.05; H, 3.44. C_8H_6ClNS. Calculated (%): C, 52.32; H, 3.29.

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