Brief Communications

A new method for the synthesis of cinnamonitriles by catalytic olefination

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Catalytic olefination of hydrazones of aromatic aldehydes with dibromoacetonitrile affords cinnamonitriles.

Key words: cinnamonitriles, dibromoacetonitrile, catalytic olefination, catalysis, copper salts.

Earlier,[1] we proposed a new copper-catalyzed olefination of hydrazones of carbonyl compounds with polyhaloalkanes for the preparation of alkenes. Recently,[2] we have found that trichloroacetonitrile reacts with hydrazones to give α-chlorocinnamonitriles. The goal of the present work was to further study the potential of catalytic olefination of hydrazones of aromatic aldehydes. Dibromoacetonitrile was used as an olefinating reagent. The known syntheses of cinnamonitriles involve the Wittig[3] and Wittig—Horner[4] reactions and condensation reactions of aldehydes with cyanoacetic acid followed by decarboxylation of the condensation products.[5]

We studied the effects of the solvent and the base in the reaction of 4-chlorobenzaldehyde hydrazone with Br_2CHCN (Scheme 1). In ethanol in the presence of ethylenediamine, 4-chlorocinnamonitrile (**1a**) was obtained in the highest yield (85%). According to GC-MS data, the reaction mixture contained bromoacetonitrile (reduction product of Br_2CHCN) and the corresponding symmetrical azine (1,4-bis(4-chlorophenyl)-2,3-diaza-buta-1,3-diene); this suggests that the reaction follows the previously proposed mechanism.[2]

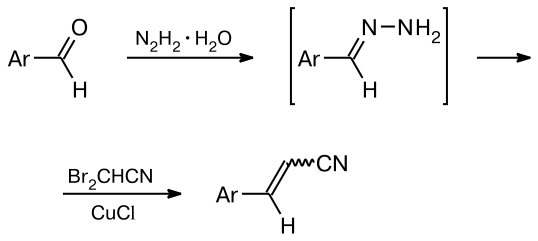
Syntheses of hydrazones of aromatic aldehydes and their subsequent reactions with Br_2CHCN can be effected as a "*one-pot*" process. Nitriles **1a**—**g** thus obtained were mixtures of *E*- and *Z*-isomers (see Scheme 1).

The reaction of 4-chloroacetophenone hydrazone with Br_2CHCN gave the symmetrical azine of 4-chloroacetophenone as the major product and 3-(4-chlorophenyl)-3-methylacrylonitrile in trace amounts. The use

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 247—249, January, 2005.

1066-5285/05/5401-0252

Scheme 1



1a—g

Compound	Ar	Yield (%)	*E* : *Z*
1a	4-ClC_6H_4	85	5 : 1
1b	4-$MeOC_6H_4$	64	6 : 1
1c	4-$Me_2NC_6H_4$	27	4 : 1
1d	4-$NO_2C_6H_4$	46	2.5 : 1
1e	2,4-$Me_2C_6H_3$	71	4.8 : 1
1f	2-Naphthyl	40	2 : 1
1g	4-BrC_6H_4	77	5 : 1

of aqueous NH_3, Et_3N, or TMEDA instead of ethylenediamine did not increase the yield of the target product.

The results of these studies demonstrate that Br_2CHCN ensures generally higher yields of the products than does CCl_3CN[2] and the reaction is significantly more stereoselective. Apparently, this difference is due to steric factors. The reactions with Br_2CHCN predominantly give *E*-nitriles, while unsaturated nitriles with *cis*-arrangement of the cyano and aryl fragments are obtained by the reactions with CCl_3CN.

It is worth noting that the described reactions of aromatic aldehydes with Br_2CHCN are the first example of catalytic olefination yielding olefins containing no halogen at the double bond.

Thus, catalytic olefination affords cinnamonitriles from aromatic aldehydes and dibromoacetonitrile. Mild reaction conditions, accessible starting reagents, and the possibility of varying substituents are its essential advantages over the known methods.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer (thin film for liquids and Nujol for solids). ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$ with Me_4Si as the internal standard. TLC analysis was carried out on Merck 60 F_{254} plates; Merck silica gel (63—200 mesh) was used for column chromatography.

Synthesis of cinnamonitriles 1a—g (general procedure). A solution of an aldehyde (5 mmol) in ethanol (10 mL) was added dropwise to a stirred solution of hydrazine hydrate (0.25 g, 0.24 mL, 5 mmol) in ethanol (5 mL). The reaction mixture was stirred until the starting aromatic aldehyde was completely consumed (TLC). Then ethylenediamine (1 mL, 15 mmol) and freshly purified CuCl (50 mg, 0.5 mmol) were added to the resulting solution of hydrazone. Dibromoacetonitrile (1.26 mL, 15 mmol) was added dropwise for 2 min, the temperature being maintained at ~20 °C. The reaction mixture was stirred for 6 h and neutralized with 0.1 *M* HCl (200 mL). The reaction products were extracted with CH_2Cl_2 (3×50 mL), the combined extracts dried with Na_2SO_4, and the reaction products isolated by column chromatography in CH_2Cl_2.

4-Chlorocinnamonitrile (1a), yellow crystals, m.p. 85—86 °C (*cf.* Ref. 6: m.p. 84—86 °C). R_f 0.62. ^1H NMR ($CDCl_3$), δ, *E*-isomer: 7.46—7.37 (m, 4 H, H_{arom}); 7.36 (d, 1 H, ArCH=, J = 16.4 Hz); 5.87 (d, 1 H, =CHCN, J = 16.4 Hz); *Z*-isomer: 7.75 (d, 2 H, H_{arom}, J = 8.0 Hz); 7.45 (d, 2 H, H_{arom}, J = 8.0 Hz); 7.08 (d, 1 H, J = 11.8 Hz); 5.48 (d, 1 H).

4-Methoxycinnamonitrile (1b), yellow crystals, m.p. 61—64 °C (*cf.* Ref. 7: m.p. 62—63 °C). R_f 0.58. ^1H NMR ($CDCl_3$), δ, *E*-isomer: 7.37 (d, 2 H, H_{arom}, J = 8.7 Hz); 7.30 (d, 1 H, J = 16.7 Hz); 6.89 (d, 2 H, H_{arom}, J = 8.7 Hz); 5.69 (d, 1 H, J = 16.7 Hz); 3.83 (s, 3 H, Me); *Z*-isomer: 7.01 (d, 1 H, J = 12.0 Hz); 5.27 (d, 1 H, J = 12.0 Hz); 3.84 (s, 3 H, Me); the other signals are masked by the signals of the major isomer.

4-(*N*,*N*-Dimethylamino)cinnamonitrile (1c), yellow crystals, m.p. 154—156 °C (*cf.* Ref. 7: m.p. 158—160 °C). R_f 0.58. ^1H NMR ($CDCl_3$), δ, *E*-isomer: 7.34 (d, 2 H, H_{arom}, J = 9.1 Hz); 7.30 (d, 1 H, J = 17.6 Hz); 6.68 (d, 2 H, H_{arom}, J = 9.1 Hz); 5.60 (d, 1 H, J = 17.6 Hz); 3.05 (s, 6 H, Me); *Z*-isomer: 7.78 (d, 2 H, H_{arom}, J = 9.1 Hz); 6.96 (d, 1 H, J = 12.1 Hz); 6.70 (d, 2 H, H_{arom}, J = 9.1 Hz); 5.11 (d, 1 H, J = 12.1 Hz); 3.06 (s, 6 H, Me).

4-Nitrocinnamonitrile (1d), yellow crystals, m.p. 200—201 °C (*cf.* Ref. 6: m.p. 200—202 °C). R_f 0.54. ^1H NMR ($CDCl_3$), δ, *E*-isomer: 8.26 (d, 2 H, H_{arom}, J = 8.8 Hz); 7.62 (d, 2 H, H_{arom}, J = 8.8 Hz); 7.46 (d, 1 H, J = 16.7 Hz); 6.04 (d, 1 H); *Z*-isomer: 8.32 (d, 2 H, H_{arom}, J = 8.5 Hz); 7.95 (d, 2 H, H_{arom}, J = 8.5 Hz); 7.22 (d, 1 H, J = 12.0 Hz); 5.69 (d, 1 H, J = 12.0 Hz).

2,4-Dimethylcinnamonitrile (1e), a colorless oil. R_f 0.6. ^1H NMR ($CDCl_3$), δ, *E*-isomer: 7.95 (d, 2 H, H_{arom}, J = 8.2 Hz); 7.65 (d, 1 H, J = 16.7 Hz); 7.10—7.05 (m, 2 H, H_{arom}); 5.74 (d, 2 H, J = 16.7 Hz); 2.51 (s, 3 H, Me); 2.35 (s, 3 H, Me); *Z*-isomer: 5.44 (d, 1 H, J = 12.0 Hz); the other signals are masked by the signals of the major isomer.

3-(2-Naphthyl)acrylonitrile (1f), yellow crystals, m.p. 124—126 °C (*cf.* Ref. 8: m.p. 123—126 °C). R_f 0.6. ^1H NMR ($CDCl_3$), δ, *E*-isomer: 7.31—7.67 (m, 8 H, H_{arom} and CH); 5.63 (d, 1 H, J = 16.0 Hz); *Z*-isomer: 5.39 (d, 1 H, J = 12.1 Hz); the other signals are masked by the signals of the major isomer.

4-Bromocinnamonitrile (1g), yellow crystals, m.p. 104—105 °C (*cf.* Ref. 9: m.p. 106—107 °C). R_f 0.62. ^1H NMR ($CDCl_3$), δ, *E*-isomer: 7.53 (d, 2 H, H_{arom}, J = 8.5 Hz); 7.32 (d, 1 H, J = 16.7 Hz); 7.30 (d, 2 H, H_{arom}, J = 8.5 Hz); 5.87 (d, 1 H, J = 16.7 Hz); *Z*-isomer: 7.06 (d, 1 H, J = 12.3 Hz); 5.48 (d, 1 H, J = 12.3 Hz); the other signals are masked by the signals of the major isomer.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32052a).

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Received July 16, 2004;
in revised form October 7, 2004