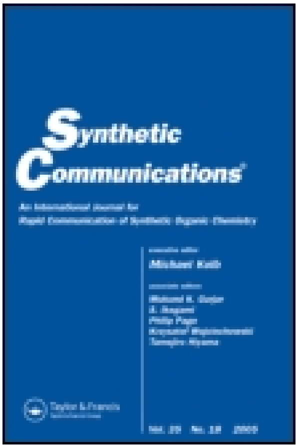

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SYNTHESIS OF α,β-UNSATURATED NITRILES FROM THE IODINE CATALYZED REACTION OF CHLOROACETONITRILE WITH ALDEHYDES PROMOTED BY TRI-n-BUTYLARSINE AND MAGNESIUM

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Abstract: α,β–Unsaturated nitriles were synthesized from the iodine catalyzed reaction of chloro- acetonitrile with aldehydes promoted by tri-n-butylarsine and magnesium.

α,β-Unsaturated nitriles are useful intermediates in organic synthesis since they could undergo many organic transformations and convert to aldehydes, ketones, carboxylic acids , esters as well as amides. Some methods for their preparation[1] have been reported , such as Wittig[2] and Wittig-Horner

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reactions[3], but multiple steps and strong base were necessary to be employed. Recently we found that α,β-unsaturated nitrile could be synthsized by the reaction of aldehydes with bromoacetonitrile promoted by tri-n-butylphosphine and zinc.[4] However bromoacetonitrile had to be used and the chloro compound is not active enough for that reaction. As an extension of that study we now wish to report by using iodine catalyzed reaction of chloroacetonitrile with aldehydes promoted by tri-n-butylarsine and magnesium the chloroacetonitrile could be employed in the synthesis of α,β-unsaturated nitrile in 69-81% yields.

$$\underset{1}{\mathrm{RCHO}} + \mathrm{ClCH_2CN} \xrightarrow[\mathrm{THF}]{n\text{-}\mathrm{Bu_3As/Mg/Cat.I_2}} \underset{2}{\mathrm{RCH{=}CHCN}}$$

Treatment of aldehyde and chloroacetonitrile with equivalent amount of tri-n-butylarsine and 0.1 equivalent amount of iodine. After being stirred and heated, for certain time (^{1}H NMR or TLC moniter, see Table 1), the products were obtained by column chromatography of the reaction mixture on silica gel. The ratios of E- and Z-isomer were estimated on the basis of NMR data.

The results are summarized in Table 1

Experimental

All melting and boiling points were uncorrected. The infrared spectra of

Table 1. Preparation of α,β-unsaturated nitrile

Compound	R	Reaction Condition Temp(°C)	Reaction Condition Time(h)	Yield[a] (%)	Ratio[b] E:Z
2a	C_6H_5	80	6	76	78:22
2b	$4\text{-}CH_3C_6H_4$	80	6	73	75:25
2c	$4\text{-}BrC_6H_4$	80	4	75	77:23
2d	$4\text{-}ClC_6H_4$	80	4	81	67:33
2e	$4\text{-}NO_2C_6H_4$	80	1.5	80	80:20
2f	$2\text{-}ClC_6H_4$	80	5	76	73:27
2g	2-Pyridyl	80	3	81	100:0

[a] Isolated yields. [b] On the basis of ^1H NMR data.

liquid products were determined as films while the solid products were determined as KCl disks on a Shimadzu IR-440 spectrometer. ^1H NMR spectra were recorded on Varian EM 360-A or Varian XL-200 instrument in CCl_4 or $CDCl_3$ solution with Me_4Si as external references and reported in δ unites (J value with Hz).

General Procedure:

Aldehydes (2.0mmol) was injected to a mixture of chloroacetonitrile (300mg, 4.0mmol), tri-n-butylarsine (490mg, 2.0mmol), magnesium (24mg, 1.0mmol), iodine (25mg) and THF (1ml) under nitrogen. The reaction mixture was stirred at 80°C for several hours (see **Table 1**) in a capped flask and monitored the disappearance of the starting material and the complete formation of the product by NMR. Then the product was separated by column chromatography on silica gel eluting with petroleum ether (60-90°C)-ethyl acetate (9:1).

3-Phenyl-prop-2-enyl nitrile (**2a**): Yield 76%; b.p. 89-92°C/2mmHg (Lit. E,97-98°C/2mmHg; Z, 88-89°C/2mmHg[5]); IR(film) υ 2200(m), 1730(s), 1620(s), 1260(s), 965(s). ^{1}H NMR (CCl_4/TMS) δ: 5.40(d, 0.22H, J=12Hz, Z); 5.82(d, 0.78H, J=16Hz, E); 7.05(d, 0.22H, J=12Hz, Z); 7.30(d, 0.78H, J=16Hz, E); 7.35(m, 5H) ppm.

3-(4-Methylphenyl)-prop-2-enyl nitrile (**2b**): Yield 73%; m.p. 55-58°C (Lit. E, m.p. 72-73°C[6]); IR(KCl) υ 2200(m), 1605(s), 1260(s), 965(s). ^{1}H NMR(CCl_4/TMS) δ: 2.33(s,3H); 5.23(d, 0.25H, J=12Hz, Z); 5.68(d, 0.75H, J=16Hz, E); 6.93(d, 0.25H, J=12Hz, Z); 7.40(d, 0.75H, J=16Hz, E); 7.18(m,4H) ppm.

3-(4-Bromophenyl)-prop-2-enyl nitrile (**2c**): Yield 75%, m.p. 84-88°C (Lit. E, 104-105°C[6]). IR(KCl) υ 2200(m), 1615(s), 1585(s), 960(s). ^{1}H NMR (CCl_4/ TMS) δ: 5.43(d, 0.23H, J=12Hz, Z); 5.83(d, 0.77H, J=16Hz, E); 7.00(d, 0.23H, J=12Hz, Z); 7.30(d, 0.77H, J=16Hz, E);7.30-7.60(m,4H) ppm.

3-(4-Chlorophenyl)-prop-2-enyl nitrile (**2d**): Yield 81%, m.p. 62-66°C (Lit. E, 83-84°C[6]). IR(KCl) υ 2200(m), 1620(s), 1590(s), 960(s). ^{1}H NMR(CCl_4/TMS) δ: 5.35(d, 0.33H, J=12Hz, Z); 5.76(d, 0.67H, J=16Hz, E); 6.97(d, 0.33H, J=12Hz, Z); 7.23(d, 0.67H, J=16Hz, E); 7.33(m,4H) ppm.

3-(4-Nitrophenyl)-prop-2-enyl nitrile (**2e**): Yield 80%, m.p. 190-194°C (Lit. E, 200°C[6]). IR(KCl) υ 2200(m), 1600(s), 1515(s), 970(s). ^{1}H NMR($CDCl_3$/TMS) δ: 5.43(d, 0.2H, J=12Hz, Z); 5.97(d, 0.8H, J=16Hz, E); 7.00(d, 0.2H, J=12Hz, Z); 7.13(d, 0.8H, J=16Hz, E); 7.37-7.70(m,4H) ppm.

3-(2-Chlorophenyl)-prop-2-enyl nitrile (**2f**): Yield 76%, b.p. 95-105°C/1mmHg (Lit. E, m.p. 41-42°C; Z, 14.3-14.8°C[7]). IR(film) υ 2200(m), 1615(s), 1590(s), 1050(s). ^{1}H NMR(CCl_4/TMS) δ: 5.50(d, 0.27H, J=12Hz, Z); 5.80(d, 0.73H, J=16Hz, E); 7.52(d, 0.27H, J=12Hz, Z); 7.90(d, 0.73H, J=16Hz, E); 7.20(m,4H) ppm.

3-(2-Pyridyl)-prop-2-enyl nitrile (**2g**): Yield 81%, m.p. 82-85°C (Lit. E, 83.5°C[8]). IR(KCl) υ 2200(m), 1620(s), 1585(s), 970(s). ^{1}H NMR($CDCl_3$/TMS) δ: 6.60(d, 1H, J=16Hz); 7.37(d, 1H, J=16Hz); 7.35-8.60(m, 4H) ppm.

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