

SUPPORTING INFORMATION

FOR

Revisiting the Synthesis of Aryl Nitriles: A pivotal role of CAN

Rakhee Saikia,^a Kwihwan Park,^b Hayato Masuda,^b Miki Itoh,^b Tsuyoshi Yamada,^b Hironao Sajiki,^b
Sanjeev P Mahanta, Ashim J Thakur,^a Utpal Bora^{a*}

^a*Department of Chemical Sciences, Tezpur University, Napaam, Tezpur, Assam, Pin-784028*

^b*Laboratory of Organic Chemistry, Gifu Pharmaceutical University, 1-25-4 Daigaku-nishi, Gifu 501-1196, Japan*

E-mail: utbora@yahoo.co.in, ubora@tezu.ernet.in

CONTENTS

<i>S. No.</i>		<i>Page No.</i>
1	XPS analysis of the reaction mixture	S2
2	Picrate paper test	S2
3	Experimental procedures for controlled reactions	S2-S4
4	Copies of ¹ H and ¹³ C NMR spectra of the aryl nitrile derivatives	S5-S29

1. XPS ANALYSIS OF THE REACTION MIXTURE

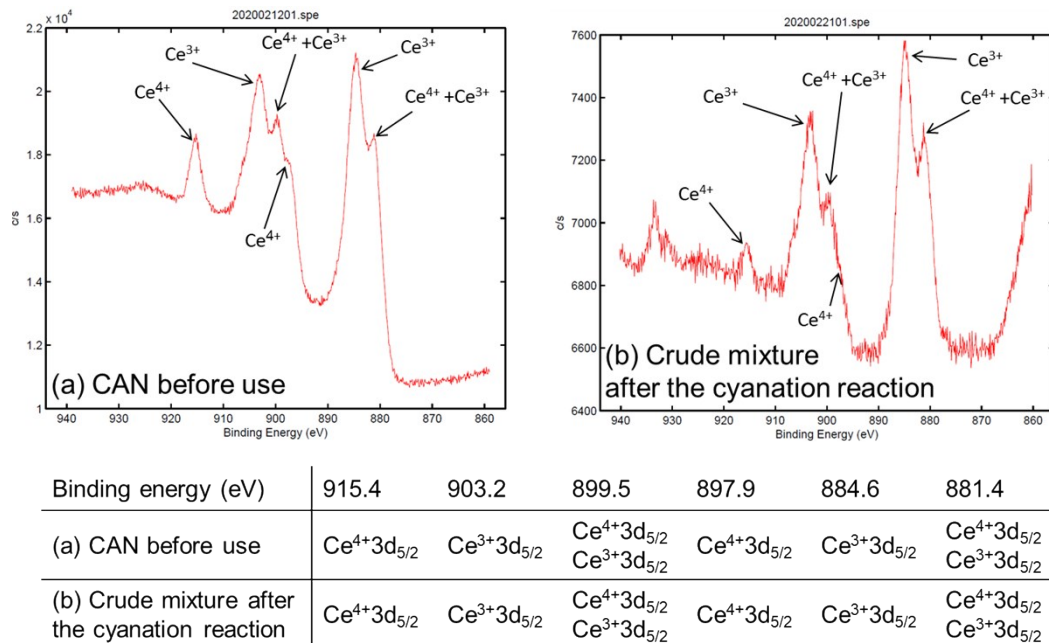


Figure 1 XPS spectra of (a) CAN before use and (b) crude mixture after cyanation reaction.

2. PICRATE PAPER TEST

Picrate paper is prepared by dipping a filter paper in a 0.5% w/v solution of moist picric acid in 2.5% w/v NaHCO₃, allowing the paper to dry in air and then cutting to the required strip size.

A picrate paper strip was inserted into the reaction flask under reflux conditions in a pre-heated oil bath at 130 °C, containing CAN, Cu(OTf)₂, K₂CO₃ and DMF. The colour of the picrate paper strip changed from yellow to red. This indicates the generation of CN⁻ in the reaction medium.

3. EXPERIMENTAL PROCEDURE FOR CONTROLLED REACTIONS

All the reactions were carried out in a 50 ml round-bottomed flask with a magnetic stirring bead fitted to a condenser (filled with water) and stirred at 130 °C in a pre-heated oil bath under reflux conditions for 24 hours.

<i>Entry</i>	<i>Experimental Procedure</i>	<i>Remarks</i>
1	CAN (1.5 equiv., 0.4117 g), 4-Iodoanisole (1a , 0.5 mmol, 0.117 g) and K ₂ CO ₃ (1 equiv., 0.068 g) were taken in 2 mL DMF. After 24 h, TLC of the reaction was developed in 20% ethyl acetate/hexane system.	The cyanated product, 3a was not observed in the developed TLC of the reaction mixture.
2	Pd(OAc) ₂ (30 mol%, 0.15 mmol, 0.034 g), CAN (1.5 equiv., 0.75 mmol, 0.411 g), 4-Iodoanisole (1a , 0.5 mmol, 0.117 g) and K ₂ CO ₃ (1 equiv., 0.068 g) were taken in 2 mL DMF. After 24 h, TLC of the reaction was developed in 20% ethyl acetate/hexane system.	The reaction mixture was extracted in ethyl acetate, dried over anhydrous Na ₂ SO ₄ and concentrated in a rotary evaporator. The product was purified through column chromatography and isolated in 50% yield
3	Ni(OAc) ₂ ·4H ₂ O (30 mol%, 0.15 mmol, 0.039 g), CAN (1.5 equiv., 0.75 mmol, 0.411 g), 4-Iodoanisole (1a , 0.5 mmol, 0.117 g) and K ₂ CO ₃ (1 equiv., 0.068 g) were taken in 2 mL DMF. After 24 h, TLC of the reaction was developed in 20% ethyl acetate/hexane system.	The reaction mixture was extracted in ethyl acetate, dried over anhydrous Na ₂ SO ₄ and concentrated in a rotary evaporator. The product was purified through column chromatography and isolated in 35% yield
4	Cu(OTf) ₂ (30 mol%, 0.15 mmol, 0.054 g), CeCl ₃ ·7H ₂ O (1.5 equiv., 0.75 mmol, 0.411 g), 4-Iodoanisole (1a , 0.5 mmol, 0.117 g) and K ₂ CO ₃ (1 equiv., 0.068 g) were taken in 2 mL DMF. After 24 h, TLC of the reaction was developed in 20% ethyl acetate/hexane system.	The cyanated product was not observed in the developed TLC of the reaction mixture.
5	Cu(OTf) ₂ (30 mol%, 0.15 mmol, 0.054 g), NH ₄ (SO ₄) ₂ (1.5 equiv., 0.75 mmol, 0.098 g), 4-Iodoanisole (1a , 0.5 mmol, 0.117 g) and K ₂ CO ₃ (1 equiv., 0.068 g) were taken in 2 mL DMF. After 24 h, TLC of the reaction was developed in 20% ethyl acetate/hexane system.	The reaction mixture was extracted in ethyl acetate, dried over anhydrous Na ₂ SO ₄ and concentrated in a rotary evaporator. The product was purified through column chromatography and isolated in 55% yield.

6	Cu(OTf) ₂ (30 mol%, 0.15 mmol, 0.054 g), 4-Iodoanisole (1a , 0.5 mmol, 0.117 g) and K ₂ CO ₃ (1 equiv., 0.068 g) were taken in 2 mL DMF. After 24 h, TLC of the reaction was developed in 20% ethyl acetate/hexane system.	The cyanated product was not observed in the developed TLC of the reaction mixture.
7	Cu(OTf) ₂ (30 mol%, 0.15 mmol, 0.054 g), CAN (1.5 equiv., 0.4117 g), 4-Iodoanisole (1a , 0.5 mmol, 0.117 g) and K ₂ CO ₃ (1 equiv., 0.068 g) were taken in 2 mL DMF and stirred under nitrogen atmosphere. After 24 h, TLC of the reaction was developed in 20% ethyl acetate/hexane system.	The reaction mixture was extracted in ethyl acetate, dried over anhydrous Na ₂ SO ₄ and concentrated in a rotary evaporator. The product was purified through column chromatography and isolated in 85% yield.
8	Cu(OTf) ₂ (30 mol%, 0.15 mmol, 0.054 g), CAN (1.5 equiv., 0.4117 g), 4-Iodoanisole (1a , 0.5 mmol, 0.117 g) and KCl (1 equiv., 0.037 g) were taken in 2 mL DMF. After 24 h, TLC of the reaction was developed in 20% ethyl acetate/hexane system.	The cyanated product was not observed in the developed TLC of the reaction mixture.

4. Copies of ^1H and ^{13}C NMR spectra of the aryl nitrile derivatives

