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*}

^aDepartment of Chemical Sciences, Tezpur University, Napaam, Tezpur, Assam, Pin-784028

^bLaboratory 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

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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.

| Entry | Experimental Procedure | Remarks |
|-------|--|--|
| 1 | CAN (1.5 equiv., 0.4117 g), 4-Iodoanisole (1a, 0.5 | |
| | mmol. 0.117 g) and K_2CO_3 (1 equiv., 0.068 g) were | The cvanated product. 3 <i>a</i> was not |
| | taken in 2 mL DMF. After 24 h, TLC of the | observed in the developed TLC of the |
| | reaction was developed in 20% ethyl acetate/hexane | reaction mixture. |
| | system. | |
| | | |
| 2 | Pd(OAc) ₂ (30 mol%, 0.15 mmol, 0.034 g), CAN | The reaction mixture was extracted in |
| | (1.5 equiv., 0.75 mmol, 0.411 g), 4-Iodoanisole (1a, | ethyl acetate, dried over anhydrous |
| | 0.5 mmol, 0.117 g) and K_2CO_3 (1 equiv., 0.068 g) | Na_2SO_4 and concentrated in a rotary |
| | were taken in 2 mL DMF. After 24 h, TLC of the | evaporator. The product was purified |
| | reaction was developed in 20% ethyl acetate/hexane | through column chromatography and |
| | system. | isolated in 50% yield |
| 3 | Ni(OAc) ₂ ·4H ₂ O (30 mol%, 0.15 mmol, 0.039 g), | The reaction mixture was extracted in |
| | CAN (1.5 equiv., 0.75 mmol, 0.411 g), 4- | ethyl acetate, dried over anhydrous |
| | Iodoanisole (1a, 0.5 mmol, 0.117 g) and K_2CO_3 (1 | Na ₂ SO ₄ and concentrated in a rotary |
| | equiv., 0.068 g) were taken in 2 mL DMF. After 24 | evaporator. The product was purified |
| | h, TLC of the reaction was developed in 20% ethyl | through column chromatography and |
| | acetate/hexane system. | isolated in 35% yield |
| | $C_{-}(OTE) = (20 - m_{2})(0.15 - m_{2})(0.054 - c)$ | |
| 4 | $Cu(O11)_2$ (30 mol%, 0.15 mmol, 0.054 g), | The cyanated product was not observed in |
| | CeC_{13}/H_2O (1.5 equiv., 0.75 mmol, 0.411 g), 4- | the developed TLC of the reaction |
| | Indoanisole (1a, 0.5 mmol, 0.117 g) and K_2CO_3 (1 | mixture. |
| | b TLC of the reaction was developed in 20% athul | |
| | n, The of the reaction was developed in 20% emyr | |
| | acetate/nexane system. | |
| 5 | Cu(OTf) ₂ (30 mol%, 0.15 mmol, 0.054 g), | The reaction mixture was extracted in |
| | NH ₄ (SO ₄) ₂ (1.5 equiv., 0.75 mmol, 0.098 g), 4- | ethyl acetate, dried over anhydrous |
| | Iodoanisole (1a, 0.5 mmol, 0.117 g) and K_2CO_3 (1 | Na_2SO_4 and concentrated in a rotary |
| | equiv., 0.068 g) were taken in 2 mL DMF. After 24 | evaporator. The product was purified |
| | h, TLC of the reaction was developed in 20% ethyl | through column chromatography and |
| | acetate/hexane system. | isolated in 55% yield. |
| | | |

| 6 | Cu(OTf) ₂ (30 mol%, 0.15 mmol, 0.054 g), 4- | The cyanated product was not observed in | |
|---|---|--|--|
| | Iodoanisole (1a, 0.5 mmol, 0.117 g) and K_2CO_3 (1 | the developed TLC of the reaction | |
| | equiv., 0.068 g) were taken in 2 mL DMF. After 24 | mixture. | |
| | h, TLC of the reaction was developed in 20% ethyl | | |
| | acetate/hexane system. | | |
| 7 | Cu(OTf) ₂ (30 mol%, 0.15 mmol, 0.054 g), CAN | The reaction mixture was extracted in | |
| | (1.5 equiv., 0.4117 g), 4-Iodoanisole (1a, 0.5 mmol, | ethyl acetate, dried over anhydrous | |
| | 0.117 g) and K_2CO_3 (1 equiv., 0.068 g) were taken | Na ₂ SO ₄ and concentrated in a rotary | |
| | in 2 mL DMF and stirred under nitrogen | evaporator. The product was purified | |
| | atmosphere. After 24 h, TLC of the reaction was | through column chromatography and | |
| | developed in 20% ethyl acetate/hexane system. | isolated in 85% yield. | |
| | | | |
| | | | |
| 8 | Cu(OTf) ₂ (30 mol%, 0.15 mmol, 0.054 g), CAN | The cyanated product was not observed in | |
| | (1.5 equiv., 0.4117 g), 4-Iodoanisole (1a, 0.5 mmol, | the developed TLC of the reaction | |
| | 0.117 g) and KCl (1 equiv., 0.037 g) were taken in 2 | mixture. | |
| | mL DMF. After 24 h, TLC of the reaction was | | |
| | developed in 20% ethyl acetate/hexane system. | | |
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4. Copies of ¹H and ¹³C NMR spectra of the aryl nitrile derivatives











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