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Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Solvent free Cannizzaro reaction applying grindstone technique

A.F.M. Motiur Rahman *, Adnan A. Kadi

Department of Pharmaceutical Chemistry, College of Pharmacy, King Saud University, P.O. Box 2457, Riyadh 11451, Saudi Arabia

Received 2 October 2011; accepted 28 February 2012

KEYWORDS

Cannizzaro reaction;
Grindstone technique;
Solvent free

Abstract Cannizzaro reaction of various aryl aldehydes employing solvent free grindstone technique using solid sodium hydroxide was examined and obtained excellent yields (94–99%) with 97–100% conversion rate.

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1. Introduction

The redox disproportionation of non-enolizable aldehydes to carboxylic acids and alcohols was conducted in potassium carbonate by Cannizzaro in 1853, known as Cannizzaro reaction (Cannizzaro, 1853; Geissman, 1944; List and Limpricht, 1854; Phonchaiya et al., 2009). The Cannizzaro reaction is one of the oldest and interesting organic reactions that depends on solvent and requires heating in the presence of base, usually concentrated aqueous base. Even though Cannizzaro reaction is the oldest and uses the known reaction method, it continues to attract the attention of chemists due to its interesting synthetic and mechanistic challenges (Abaee et al., 2005; Curini

et al., 2005; Vida et al., 2005). The development of the Cannizzaro reaction has been made in the past several years. Strong bases, such as NaOH, KOH, Ba(OH)₂ and LiOH (Cannizzaro, 1853; Geissman, 1944; List and Limpricht, 1854; Phonchaiya et al., 2009; Antonio et al., 2008), LiBr with Et₃N (Mojtahedi et al., 2007), cation templates (Vida et al., 2005) with NaOH, solvent-free conditions (Yoshizawa et al., 2001) with KOH at 100 °C, ruthenium-catalyzed transfer hydrogenation (Vida et al., 2005; Kim et al., 2003), in the presence of KOH, NaOH, microwave irradiation (Sharifi et al., 1999; Varma et al., 1998) with Al₂O₃(basic), NaOH, and Ba(OH)₂, ultrasound mediation (Entezari and Shameili, 2000) in KOH have been introduced for the methodology development of the reaction. Lewis acid (Russell et al., 2000; Yang et al., 2005) catalysts such as, Cu(OTf)₂ and Ln(OH)₃, Organo-base (Basavaiah et al., 2006), magnesium bromide ethyl etherate and triethylamine in room-temperature (Abaee et al., 2005), aqueous solid–liquid biphasic reaction in presence of cyclodextrins (Canipelle et al., 2011), solid-supported reagents (Reddy et al., 2002) with KF–Al₂O₃, gas-phase process (Sheldon et al., 1997), photo induction (Kagan, 1996) and chiral Lewis acid (Ishihara et al., 2008) have also been applied for the development of the methodology. In addition, crossed Cannizzaro version (Curini et al., 2005) of the reaction with Yb(OTf)₃, intramolecular Cannizzaro reaction in the presence of tetraethyl ammonium hydroxide have (Akhigbe et al., 2009)

* Corresponding author. Tel.: +966 146 70237; fax: +966 146 76220.

E-mail address: afmrahman@ksu.edu.sa (A.F.M. Motiur Rahman).

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Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2012.02.010



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recently been used. Nevertheless, up to this point the development of procedures for the Cannizzaro reaction relied on the use of strong base, solvent and hazard workup condition, which led continuing interests to develop an efficient procedure and/or catalyst. We herein describe a simple, efficient, inexpensive, time saving, solvent free procedure for the Cannizzaro reaction applying grindstone technique in the presence of solid sodium hydroxide.

2. Experimental

2.1. General

Melting points were determined on a Fisher–Jones melting-point apparatus and are uncorrected. Infrared spectra were recorded using KBr pellets for solids and neat for liquids on a Perkin–Elmer 1330 grating spectrometer. NMR spectra were obtained using a Bruker-250 spectrometer (250 MHz for ^1H NMR and 62.5 MHz for ^{13}C NMR) and 500 MHz Avance Bruker Ultra Shield™ spectrometer and are reported as parts per million (ppm) from the internal standard of tetramethylsilane. Column chromatography was carried out on 60–120-mesh Merck silica gel. Chemicals and solvents were of commercial reagent grade and were used without further purifications.

2.2. General Procedure for the Cannizzaro Reaction

A mixture of aryl aldehyde (**1**, 0.1 mmol) and NaOH (0.1 mmol) was ground together in a mortar using pestle for 10 min. The reaction proceeds exothermically (indicated by rise in temperature of 25–100 °C). The reaction progress was monitored by TLC, after observing no aldehyde presence in the reaction mixture, the whole mass of the reaction mixture was then poured into stirring ice-cold water, neutralized with 2 M HCl and the precipitate formed was filtered, aryl acid was obtained (**2**). The filtrate was then extracted with ethyl acetate, dried over MgSO_4 , the organic solvent was evaporated, and aryl alcohol was obtained (**3**). Isolated products were characterized by melting points, NMR and mass spectrometric data and were compared with the literature and/or with authentic samples.

2.3. Benzoic acid (**2a**)

^1H NMR (CDCl_3 , 500 MHz) δ 8.13 (dd, $J = 8.0, 1.3$ Hz, 2H), 7.64 (t, $J = 7.0$ Hz, 2H), 7.50 (t, $J = 8.0$ Hz, 1H) ppm. ESI-MS (m/z): 121.4 [$\text{M}-\text{H}$] $^-$.

2.4. 2-Chlorobenzoic acid (**2b**)

^1H NMR (CDCl_3 , 250 MHz) δ 8.00 (d, $J = 8.3$ Hz, 1H), 7.48–7.43 (m, 2H), 7.37–7.31 (m, 1H) ppm. ^{13}C NMR (CDCl_3 , 62.5 MHz) δ 170.56, 134.76, 133.60, 132.49, 131.51, 128.33, 126.71 ppm. ESI-MS (m/z): 154.2 (100%) [M (^{35}Cl)- H] $^-$, 156.2 (30%) [M (^{37}Cl)- H] $^-$.

2.5. 2-Fluorobenzoic acid (**2c**)

^1H NMR (CDCl_3 , 250 MHz) δ 8.03 (t, $^3J_{\text{H-H}} = 7.7$ Hz, 1H), 7.58 (q, $^3J_{\text{H-H}} = 5.0$ Hz, 1H), 7.26–7.13 (m, 2H) ppm. ^{13}C NMR (CDCl_3 , 62.5 MHz) δ 169.37, 162.63 (d, $^1J_{\text{C-F}} = 260.4$ Hz),

135.62 (d, $^3J_{\text{C-F}} = 9.1$ Hz), 132.77, 124.11 (d, $^3J_{\text{C-F}} = 2.25$ Hz), 117.46 (d, $^2J_{\text{C-F}} = 10.25$ Hz), 117.17 (d, $^2J_{\text{C-F}} = 22.12$ Hz) ppm. ESI-MS (m/z): 138.7 (100%) [M (^{18}F)- H] $^-$, 139.3 (37%) [M (^{19}F)- H] $^-$.

2.6. 3-Chlorobenzoic acid (**2d**)

^1H NMR (CDCl_3 , 250 MHz) δ 8.07 (s, 1H), 7.98 (d, $J = 7.7$ Hz, 1H), 7.98 (d, $J = 7.7$ Hz, 1H), 7.57 (d, $J = 8.10$ Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H) ppm. ^{13}C NMR (CDCl_3 , 62.5 MHz) δ 170.93, 134.68, 133.89, 130.96, 130.24, 129.83, 128.30 ppm. ESI-MS (m/z): 154.2 (100%) [M (^{35}Cl)- H] $^-$, 155.9 (33%) [M (^{37}Cl)- H] $^-$.

2.7. 3-Methoxybenzoic acid (**2e**)

^1H NMR (CDCl_3 , 250 MHz) δ 7.71 (d, $J = 7.6$ Hz, 1H), 7.61 (s, 1H), 7.36 (t, $J = 7.9$ Hz, 1H), 7.14 (dd, $J = 8.2, 2.5$ Hz, 1H), 3.85 (s, 3H) ppm. ^{13}C NMR (CDCl_3 , 62.5 MHz) δ 171.98, 159.54, 130.55, 129.51, 122.66, 120.44, 114.33, 55.43 ppm. ESI-MS (m/z): 150.1 [$\text{M}-\text{H}$] $^-$.

2.8. 4-Bromobenzoic acid (**2f**)

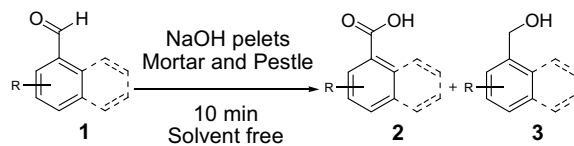
^1H NMR (CDCl_3 , 250 MHz) δ 7.94 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H) ppm. ^{13}C NMR ($\text{CDCl}_3 + \text{CD}_3\text{OD}$, 62.5 MHz) δ 167.69, 131.21, 130.94, 129.15, 127.49 ppm. ESI-MS (m/z): 198.9 (95%) [M (^{79}Br)- H] $^-$, 199.7 (100%), 200.8 (10%) [M (^{81}Br)- H] $^-$.

2.9. 4-Chlorobenzoic acid (**2g**)

^1H NMR (CDCl_3 , 250 MHz) δ 8.02 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H) ppm. ^{13}C NMR ($\text{CDCl}_3 + \text{CD}_3\text{OD}$, 62.5 MHz) δ 167.29, 138.62, 130.57, 128.56, 127.95 ppm. ESI-MS (m/z): 154.3 (100%) [M (^{35}Cl)- H] $^-$, 156.1 (40%) [M (^{37}Cl)- H] $^-$.

2.10. 4-Fluorobenzoic acid (**2h**)

^1H NMR (CDCl_3 , 250 MHz) δ 8.11 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 2H), 7.13 (d, $^2J_{\text{H-H}} = 8.3$ Hz, 2H) ppm. ^{13}C NMR (CDCl_3 , 62.5 MHz) δ 170.91, 166.30 (d, $^1J_{\text{C-F}} = 253.4$ Hz), 132.85 (d, $^3J_{\text{C-F}} = 9.5$ Hz), 125.50 (d, $^4J_{\text{C-F}} = 3.1$ Hz), 115.46 (d, $^2J_{\text{C-F}} = 22.06$ Hz) ppm. ESI-MS (m/z): 138.6 (100%) [M (^{18}F)- H] $^-$, 139.2 (30%) [M (^{19}F)- H] $^-$.



Scheme 1 Cannizzaro reaction of various aryl aldehydes using solid NaOH pellets.

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