J. Chem. Sci. Vol. 123, No. 5, September 2011, pp. 609–614.

Simple and efficient Knoevenagel synthesis of (*E*)-2-((1H-indol-3-yl) methylene)-3-oxoindolylnitrile catalysed by PPh_3

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MS received 17 November 2010; revised 31 July 2011; accepted 1 August 2011

Abstract. Triphenylphosphine (TPP) is found to be an efficient catalyst for the Knoevenagel condensation of indole-3-carboxyaldehydes **1**(**a**–**e**) and their *N*-substituted derivatives **4**(**a**–**e**) with the active methylene compound, i.e., 3-cyanoacetylindole (**2**), affording novel substituted olefins **3**(**a**–**e**) and **5**(**a**–**e**) respectively. The latter products reacted with DMS in the presence of PEG-600 to afford the corresponding N, N^1 dimethylated derivatives **6**(**a**–**e**).

Keywords. Indole-3-aldehydes; 3-cyanoacetylindole; PPh_3; Ethanol; PEG-600; DMS.

1. Introduction

Knoevenagel condensation is an important carbon–carbon bond-forming reaction in organic synthesis.[1] Ever since its discovery, the Knoevenagel reaction has been widely used in organic synthesis to prepare coumarins and their derivatives, which are known to be important intermediates in the synthesis of cosmetics, perfumes and pharmaceuticals.[2] In recent times, there has been a growing interest in Knoevenagel products because many of them have significant biological activity.

The Knoevenagel reaction is generally carried out in the presence of weak bases such as ethylenediamine, piperidine or corresponding piperidinium salts, potassium fluroiodide, etc.[3–5] In contrast, there are only a few acid catalysts that are known to promote this reaction.[6] Recently many efforts have been made to prepare olefinic compounds via the Knoevenagel reaction under heterogeneous conditions employing aluminum chloride, xonotlite/tert-butoxide, cation-exchanged zeolites, alkali containing MCM-41, SiO_2, calcite or fluorite and NP/KF as heterogeneous catalysts.[7–10] More recently, ionic liquids have also been employed to accomplish this reaction.[11]

Earlier, PPh_3 has been used in different reactions like preparation of 3-acetylindoles and 3-*bis*-indolylmethane derivatives,[12] Diels–Alder synthesis of Azabicyclo[2.2.2]octan-5-ones,[13] mono- and *bis*-intramolecular imino Diels–Alder reactions for synthesis of tetrahydrochromanoquinolines[14] and Diels–Alder synthesis of Pyranoquinoline, furoquninoline, phenanthridine derivatives,[15] and other different catalytic applications.[16–17]

2. Experimental

Melting points were determined using a Buchi melting point B-545 apparatus and are uncorrected. TLC checking was done on glass plates coated with Silica Gel –G and spotting was done using iodine or UV lamp. IR spectra were recorded using Perkin Elmer model-446 FTIR in KBr. ^{1}H-NMR spectra were recorded on a Gemini-200 and AV-400 instruments operating at 200 and 400 MHz respectively.

2.1 *General procedure for the preparation of* ***3***

A mixture **1** (5 mmol), **2** (5 mmol, 0.91 g) and PPh_3 40% (1.2 mmol, 412 mg) in ethanol (15 mL) was stirred at RT for a specified period of time (table 1). After completion of reaction (as shown by TLC checking), the mixture was poured into ice-cold water. The separated solid was filtered, washed with water and dried to obtain the crude product **3**. The latter were then recrystallized from ethyl acetate to afford pure **3**.

*For correspondence

Table 1. Synthesis of Novel (*E*)-2-((1H-indol-3-yl)methylene)-3-oxoindolylnitrile products by using PPh_3 as an efficient catalyst.[a,b]

Sl. no.	Reactants		Product	Time (hrs.)	Yield (%)	M.P (°C)
1.	**1a**(R=H, R^1=H)	2	**3a**(R=H, R^1=H)	1.5	88	281–282
2.	**1b**(R=OMe, R^1=H)	2	**3b**(R=OMe, R^1=H)	2	89	211–213
3.	**1c**(R=H, R^1=OMe)	2	**3c**(R=H, R^1=OMe)	2	86	195–197
4.	**1d**(R=Br, R^1=H)	2	**3d**(R=Br, R^1=H)	2	84	187
5.	**1e**(R=NO_2, R^1=H)	2	**3e**(R=NO_2, R^1=H)	1.6	90	193–194
6.	**4a**(R=H, R^1=H)	2	**5a**(R=H, R^1=H)	1	87	179–181
7.	**4b**(R=OMe, R^1=H)	2	**5b**(R=OMe, R^1=H)	1	89	261–263
8.	**4c**(R=H, R^1=OMe)	2	**5c**(R=H, R^1=OMe)	1	90	165
9.	**4d**(R=Br, R^1=H)	2	**5d**(R=Br, R^1=H)	1	85	> 285
10.	**4e**(R=NO_2, R^1=H)	2	**5e**(R=NO_2, R^1=H)	1	87	169–170
11.	**3a/5a** (R=H, R^1=H)	DMS	**6a**(R=H, R^1=H)	1	90	248–250
12	**3b/5b** (R=OMe, R^1=H)	DMS	**6b**(R=OMe, R^1=H)	1	89	231–232
13.	**3c/5c** (R=H, R^1=OMe)	DMS	**6c**(R=H, R^1=OMe)	1	90	190
14.	**3d/5d** (R=Br, R^1=H)	DMS	**6d**(R=Br, R^1=H)	1	88	285
15.	**3e/5e** (R=NO_2, R^1=H)	DMS	**6e**(R=NO_2, R^1=H)	1	85	291

[a]**Reaction conditions**: indole-3-aldehyde, 3-cyanoacetylindole, PPh_3, EtOH, and RT
[b]**Reaction conditions**: Knoevenagel Products, PEG-600, DMS (dimethylsulphate) and Δ

*2.1a Characterization of **3a**:* Yellow solid; Yield: 1.36 gms (88%); m.p. 281–282°C; IR(KBr): 3263 cm^{-1} (due to –NH), 2203 cm^{-1} (due to –CN) and 1611 cm^{-1} (due to –CO); ^{1}H-NMR spectrum (DMSO/d_6/TMS): δ 7.28–7.98 (m, 8**H**, aryl protons of the two indole rings), δ 8.04–8.55 (m, 2**H**, α-protons of the two indole rings), δ 9.15 (vinylic proton of the indole ring), δ 12.13–12.49 (br s, 2**H**, D_2O exchangeable, two –N**H** protons of the indole ring); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 110.7, 112.7, 113.1, 114.7, 118.9, 121.0, 121.9, 122.1, 122.3, 123.6, 123.8, 126.8, 127.7, 131.6, 134.2, 136.5, 136.7, 145.5, 181.1; MS m/z = 312 (M+1).

*2.1b Characterization of **3b**:* Yellow solid; Yield: 1.51 gms (89%); m.p. 211–213°C; IR(KBr): 3263 cm^{-1} (medium, –NH stretching), 2203 cm^{-1} (sharp, –CN stretching) and 1639 (very strong, carbonyl –C=O); ^{1}H-NMR (DMSO d_6/TMS): δ 3.23–3.26 (s, 3H, $-OCH_3$), 7.14–7.96 (m, 7**H**, aryl protons of the indole rings), 8.04–8.29 (m, 2**H**, α-protons of the indole rings), 9.23 (s, 1**H**, vinyl proton of the indole ring), 12.21 –12.29 (br, s, 2H, –N**H** protons of the indole rings); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 54.9, 112.3, 113.1, 113.9, 115.3, 117.5, 121.6, 122.6, 122.8, 123.5, 123.7, 123.9, 126.8, 127.1, 130.6, 133.6, 135.5, 136.7, 151.3, 186.1; MS m/z = 342 (M+1).

*2.1c Characterization of **3c**:* Red solid; Yield: 1.46 gms (86%); m.p. 195–197°C; IR (KBr): 3218 cm^{-1} (broad, –NH stretching), 2204 cm^{-1} (sharp, –CN stretching) and 1637 (very strong, carbonyl –C=O); ^{1}H-NMR (DMSO d_6/TMS): δ 3.45–3.46 (s, 3H, $-OCH_3$), 7.29–7.86 (m, 7**H**, aryl protons of the indole rings), 8.21–8.42 (m, 2**H**, α-protons of the indole rings), 9.54 (s, 1**H**, vinyl proton of the indole ring), 12.29–12.31 (br, s, 2H, –N**H** protons of the indole rings); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 55.3, 111.1, 112.4, 113.1, 114.5, 118.4, 121.6, 122.8, 123.8, 124.0, 125.1, 125.9, 126.5, 127.6, 130.6, 134.6, 135.3, 136.9, 150.3, 185.9; MS m/z = 342 (M+1).

*2.1d Characterization of **3d**:* Yellow solid; Yield: 1.62 gms (84%); m.p. 187°C; IR (KBr): 3218 cm^{-1} (broad, –NH stretching), 2206 cm^{-1} (sharp, –CN stretching) and 1611 (very strong, highly conjugated carbonyl –C=O); ^{1}H-NMR (DMSO d_6/TMS): δ 7.26–7.91 (m, 7**H**, aryl protons of the indole rings), 8.24–8.30 (m, 2**H**, α-protons of the indole rings), 9.87–9.89 (s, 1**H**, vinyl proton of the indole ring), 12.18–12.21 (br, s, 2H, −N**H** protons of the indole rings); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 110.7, 111.8, 113.4, 114.5, 117.6, 121.6, 123.2, 123.6, 124.2, 125.3, 125.8, 126.6, 128.3, 131.6, 133.5, 134.9, 136.9, 136.3, 185.2; MS m/z = 390 (M+1).

*2.1e Characterization of **3e**:* Yellow solid; Yield: 1.60 gms (90%); m.p. 193–194°C; IR (KBr): 3120 cm^{-1} (very broad, –NH stretching), 2208 cm^{-1} (sharp, –CN

stretching) and 1615 (very strong, highly conjugated carbonyl –C=O); ^{1}H-NMR (DMSO d_6/TMS): δ 7.12–8.01 (m, 7**H**, aryl protons of the indole rings), 8.31–8.36 (m, 2**H**,-α protons of the indole rings), 9.99–10.01 (s, 1**H**, vinyl proton of the indole ring), 12.34–12.36 (br, s, 2H, –N**H** protons of the indole rings); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 110.0, 110.1, 111.0, 112.2, 114.5, 116.1, 117.5, 118.0, 119.3, 121.1, 123.3, 123.7, 125.6, 126.3, 127.0, 132.3, 133.1, 136.0, 186.3. MS m/z = 357 (M+1).

2.2 *General procedure for the preparation of **5***

A mixture of **4** (10 mmol), **2** (10 mmol, 1.82 g) and PPh_3 40% (1.2 mmol, 412 mg) in ethanol (15 mL) was stirred at RT for a specified period of time (table 1). After completion of reaction (as shown by TLC checking), the mixture was poured into ice-cold water. The separated solid was filtered, washed with water and dried to obtain the crude product. The latter were then recrystallized from ethyl acetate to afford pure **5**.

*2.2a Characterization of **5a**:* Yellow solid; Yield: 1.38 gms (87%); m.p. 172–181°C; IR (KBr): 3242 cm^{-1} (due to –NH), 2212 cm^{-1} (due to –CN) and 1621 cm^{-1} (due to –CO); ^{1}H-NMR spectrum (DMSO/d_6/TMS): δ 3.81 (s, 3H, -N-C**H**$_3$), 7.21–8.1 (m, 8**H**, aryl protons of the two indole rings), δ 8.21–8.61 (m, 2**H**, α-protons of the two indole rings), δ 9.21 (vinylic proton of the indole ring), δ 12.14 (br s, 1**H**, D_2O exchangeable, –N**H** proton of the indole ring); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 34.5, 110.1, 112.1, 113.9, 115.1, 118.5, 121.7, 121.6, 122.1, 122.3, 123.3, 123.1, 126.5, 127.7, 131.9, 134.4, 136.3, 136.7, 145.3, 183.7 MS m/z: 326 (M+1).

*2.2b Characterization of **5b**:* Yellow solid; Yield: 1.68 gms (89%); m.p: 261–263°C; IR(KBr): 3231 cm^{-1} (medium, –NH stretching), 2208 cm^{-1} (sharp, –CN stretching) and 1624 (very strong, carbonyl –CO); ^{1}H-NMR (DMSO d_6/TMS): δ 3.23–3.26 (s, 3H, –O**C**H$_3$), 4.01 (s, 3H, N-**H**$_3$), 7.11–7.89 (m, 7**H**, aryl protons of the indole rings), 8.14–8.31 (m, 2**H**, α-protons of the indole rings), 9.32 (s, 1**H**, vinyl proton of the indole ring), 12.14 (br, s, 1H, –N**H** proton of the indole ring); δ 34.9, 53.1, 112.1, 113.5, 113.7, 115.5, 116.5, 121.5, 122.3, 122.7, 123.8, 123.9, 124,2, 126.8, 127.2, 130.1, 132.6, 135.4, 137.7, 151.5, 186.5 MS m/z = 356 (M+1).

*2.2c Characterization of **5c**:* Yellow solid; Yield: 1.70 gms (90%); m.p. 165°C; IR (KBr): 3229 cm^{-1} (broad, –NH stretching), 2209 cm^{-1} (sharp, –CN stretching) and 1631 (very strong, carbonyl –CO); ^{1}H-NMR (DMSO d_6/TMS): δ 3.45–3.46 (s, 3H, –O**C**H$_3$), 3.98 (s, 3H, N-C**H**$_3$), 7.31–7.91 (m, 7**H**, aryl protons of the indole rings), 8.16–8.52 (m, 2**H**, α-protons of the indole rings), 9.61 (s, 1**H**, vinyl proton of the indole ring), 12.31 (br, s, 1H, –N**H** proton of the indole ring); ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 34.8, 55.1, 111.0, 112.8, 113.1, 114.0, 118.4, 121.0, 123.0, 123.8, 124.3, 125.3, 125.4, 126.0, 127.1, 131.6, 133.6, 135.9, 136.9, 151.3, 186.9; MS m/z = 356 (M+1).

*2.2d Characterization of **5d**:* Yellow solid; Yield: 2.01 gms (85%); m.p. >285°C; IR (KBr): 3215 cm^{-1} (broad, –NH stretching), 2211 cm^{-1} (sharp, –CN stretching) and 1615 (very strong, highly conjugated carbonyl –CO); ^{1}H-NMR (DMSO d_6/TMS): δ 4.01 (s, 3H, -N-C**H**$_3$ 7.21–7.98 (m, 7**H**, aryl protons of the indole rings), 8.21–8.34 (m, 2**H**, α-protons of the indole rings), 9.89 (s, 1**H**, vinyl proton of the indole ring), 12.19 (br, s, 1H, –N**H** proton of the indole ring); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 34.1, 110.9, 111.0, 113.1, 114.5, 117.6, 121.5, 123.1, 123.5, 124.8, 125.0, 125.8, 126.5, 128.3, 130.6, 132.5, 134.9, 135.9, 136.3, 185.0. MS m/z = 403 (M+1).

*2.2e Characterization of **5e**:* Yellow solid; Yield: 1.78 gms (87%); m.p. 169–170°C; IR (KBr): 3199 cm^{-1} (very broad, –NH stretching), 2211 cm^{-1} (sharp, –CN stretching) and 1621 (very strong, highly conjugated carbonyl –CO); ^{1}H-NMR (DMSO d_6/TMS): δ 3.99 (s, 3H, N-C**H**$_3$), 7.19–8.16 (m, 7**H**, aryl protons of the indole rings), 8.41–8.54 (m, 2**H**,-α protons of the indole rings), 10.06 (s, 1**H**, vinyl proton of the indole ring), 12.41 (br, s, 1H, –N**H** proton of the indole ring); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 36.1, 110.3, 110.4, 111.0, 112.3, 114.4, 116.3, 117.9, 118.4, 119.2, 121.2, 123.5, 123.9, 124.6, 126.3, 129.1, 132.3, 133, 135.2, 186.1. MS m/z = 372 (M+1).

2.3 *General procedure for the preparation of 6 from 3*

A mixture of **3** (5 mM), dimethyl sulphate (DMS) (10 mM, 10.8 mL) and PEG-600 (20 ml) was heated at $\approx$ 60°C for 1 h. At the end of this period, the mixture was poured into ice-cold water and neutralized with 5% aq. NaOH. The separated solid was filtered, washed

with water and dried to obtain crude product. The latter were then recrystallized from ethyl acetate to afford pure **6**.

*2.3a Characterization of **6a**:* Yellow solid**;** Yield: 1.52 gms (90%); m.p. 248–250°C; IR(KBr): 2201 cm^{-1} (medium, due to –CN stretching), 1621 cm^{-1} (strong, due to –CO stretching); ^{1}H-NMR spectrum (DMSO/d_6/TMS): δ 3.94–4.02 (s, 6**H**, 2 N-CH_3), 7.30–7.99 (m, 8**H**, aryl protons of the two indole rings), 8.22–8.24 (s, 2**H**, two α-protons of the two indole rings), 8.592–8.597 (s, 1**H**, vinylic proton of the indole ring); δ 33.5, 34.8, 110.0, 111.2, 113.1, 114.1, 118.5, 121.7, 121.4, 122.8, 123.0, 123.3, 123.8, 126.5, 127.1, 131.6, 134.2, 136.1, 136.5, 145.2, 182.1 MS m/z = 340 (M+1).

*2.3b Characterization of **6b**:* Yellow solid; Yield: 1.63 gms (89%); m.p. 231–232°C; IR (KBr): 2167 cm^{-1} (sharp, –CN stretching) and 1616 (very strong, highly conjugated carbonyl –C=O); ^{1}H-NMR (DMSO d_6/TMS): δ 3.24–3.25 (s, 3H, -Oa-C**H**$_3$), 3.98–3.99 (s, 3H, -N-C**H**$_3$), 4.06–4.08 (s, 3**H**, -N-C**H**$_3$), 7.31–7.88 (m, 7**H**, aryl protons of the indole rings), 8.24–8.39 (m, 2**H**, α-protons of the indole rings), 9.21 (s, 1**H**, vinyl proton of the indole ring); δ 33.9, 34.6, 53.5, 112.0, 113.1, 113.5, 115.0, 116.2, 121.7, 122.3, 122.7, 123.9, 124.1, 124.4, 126.8, 127.0, 130.0, 132.0, 135.4, 137.5, 151.6, 185.5 MS m/z = 370 (M+1).

*2.3c Characterization of **6c**:* Yellow solid; Yield: 1.65 gms (90%); m.p. 196°C; IR (KBr): 2197 cm^{-1} (sharp, –CN stretching) and 1612 (very strong, highly conjugated carbonyl –C=O); ^{1}H-NMR (DMSO d_6/TMS): δ 3.21–3.22 (s, 3H, -O-C**H**$_3$), 3.96–3.99 (s, 3H, -N-C**H**$_3$), 4.08–4.10 (s, 3**H**, -N-C**H**$_3$), 7.31–7.98 (m, 7**H**, aryl protons of the indole rings), 8.22–8.46 (m, 2**H**, α-protons of the indole rings), 9.23 (s, 1**H**, vinyl proton of the indole ring); ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 34.0, 35.1, 53.5, 111.2, 112.5, 113.2, 114.0, 118.5, 121.1, 123.1, 123.8, 124.5, 125.5, 125.8, 126.5, 127.8, 132.6, 133.7, 135.9, 136.6, 152.3, 184.9; MS m/z = 370 (M+1).

*2.3d Characterization of **6d**:* Parrot green colour solid; Yield: 1.83 gms (88%); m.p. 285°C; IR (KBr): 2212 cm^{-1} (sharp, –CN stretching) and 1616 (very strong, highly conjugated carbonyl –C=O); ^{1}H-NMR (DMSO d_6/TMS): δ 3.18–3.19 (s, 3H, -O-C**H**$_3$), 3.86–3.88 (s, 3H, -N-C**H**$_3$), 4.1–4.12 (s, 3**H**, -N-C**H**$_3$), 7.29–7.99 (m, 7**H**, aryl protons of the indole rings), 8.31–8.45 (m, 2**H**, α-protons of the indole rings), 9.12 (s, 1**H**, vinyl proton of the indole ring); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 33.9, 34.5, 111.9, 111.0, 113.5, 114.3, 118.5, 120.5, 122.1, 123.5, 124.1, 125.2, 125.6, 126.5, 128.8, 130.3, 132.7, 134.9, 135.9, 136.5, 185.1 MS m/z = 418 (M+1).

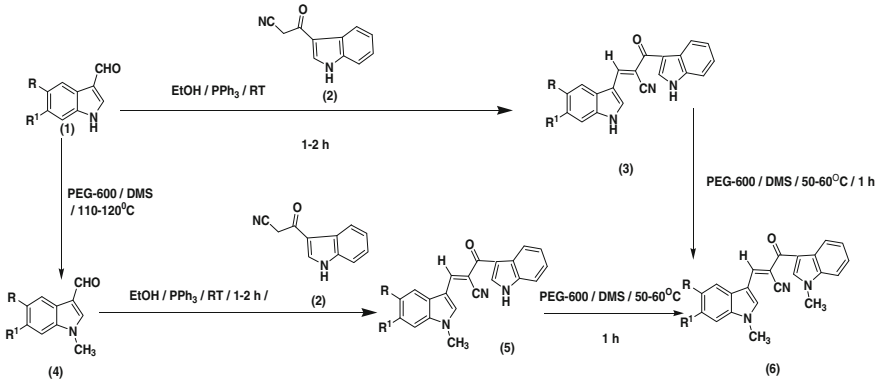
*2.3e Characterization of **6e**:* Yellow solid; Yield: 1.63 gms (85%); m.p. 291°C; IR (KBr): 2222 cm^{-1} (sharp, –CN stretching) and 1618 (very strong, highly conjugated carbonyl –C=O); ^{1}H-NMR (DMSO d_6/TMS): δ 3.18–3.20 (s, 3H, -O-C**H**$_3$), 3.91–3.92 (s, 3H, -N-C**H**$_3$), 4.12–4.13 (s, 3**H**, -N-C**H**$_3$), 7.32–7.96 (m, 7**H**, aryl protons of the indole rings), 8.36–8.43 (m, 2**H**, α-protons of the indole rings), 9.98 (s, 1**H**, vinyl proton of the indole ring); Its ^{13}C-NMR spectrum (DMSO/d_6/TMS): δ 34.5, 34.9, 110.0, 110.6, 111.0, 112.3, 114.4, 116.3, 117.9, 118.4, 119.2, 121.0, 123.6, 123.8, 124.6, 126.5, 129.2, 132.3, 133.7, 135.2, 186.0. MS m/z = 386 (M+1).

3. Results and discussion

Treatment of indole-3-carboxyldehydes **1(a–e)** and **4(a–e)** with 3-cyanoacetylindole (**2**) in the presence of

Table 2. Rate of reaction in different solvent mediums.

Entry	Solvent	Time (Hrs)	Temp (°C)	Yield (%)
1	PPh_3/ EtOH	1–2	RT	85-90
2	PPh_3/ CH_3CN	6	RT	20-30
3	PPh_3/ DMF	5–8	RT	44-50
4	Without catalyst / EtOH	24	RT / Δ	NIL
5	PPh_3/ DMSO	4–6	RT	30-40
6	PPh_3/ Benzene	15	RT	10-15
7	PPh_3/ $CHCl_3$	20	RT	NIL



Scheme 1. TPP Catalysed Knoevenagel reaction.

PPh_3 in ethanol at RT, for 1–1.5 h, resulted in the formation of novel (*E*)-2-((1H-indol-3-yl)methylene)-3-oxoindolylnitrile products **3(a–e)** and their corresponding N-methyl derivatives of **5(a–e)** in 85–90% yields (table 1) (scheme 1).

This method is very facile and convenient for the preparation of large amount of Knoevenagel adducts with high yields in less time. TPP acts as a mild Lewis base to induce the reaction. In the absence of TPP, the reaction does not proceed even after refluxing the reactants in ethanol for ≈ 24 h. The use of TPP as a catalyst helps to avoid the use of environmentally unfavourable organic solvents (DMF, C_6H_6, Toluene, DMSO, etc....,) as reaction medium. It is inexpensive, readily available and found to retain its activity even in the presence of water and other active functional groups such as CHO, −CO, NO_2, and CN present in the substrates. In all cases, the reaction proceeded smoothly with 40 mol% of TPP to give products of good purity.

In the above reaction, the product has been assigned *E*-configuration (first and second priority groups i.e., indolyl and 3-cyanoacetylindol respectively are *trans* to each other) on the basis of the assumption that the groups with maximum stereochemical bulk would be more stable in a *trans* configuration.

In order to compare the rate of the reaction in the presence of PPh_3 in EtOH, we carried out the reaction in different solvent media (table 2).

Treatment of **3(a–e)** each with DMS independently, in the presence of PEG-600[18–20] as a facile and versatile reaction medium, at ≈ 60°C for 1 h, without using any base, gave N, N-disubstituted olefins **6(a–e)** respectively in 85–90% yields (scheme 1). Alternatively, treatment of **5(a–e)** each with DMS, independently in the presence of PEG-600, gave the corresponding **6(a–e)** respectively. Each of the compounds **5(a–e)** were obtained from the respective **4(a–e)** by condensation with **2**. The compounds **4(a–e)** were obtained from **1(a–e)** by methylation with DMS in PEG-600 using our earlier described[21] green method. All the above reactions are summarized in scheme 1.

It is obvious from the above results that PEG-600 is a very effective solvent for methylations of **1(a–e), 3(a–e)** and **5(a–e)** resulting in **4(a–e)** and **6(a–e)** respectively. Mechanistic explanation of these results is that, probably, PEG-600 dissolves the substrate [i.e., olefins **3(a–e)** and **5**(**a**–**e**)] and the reagent (i.e., alkylating agent DMS) bringing them together thereby providing an effective means for chemical reaction to occur. Furthermore, use of PEG-600 negates the use of base in these reactions because PEG-600 is able to extract the hydrogen from

Table 3. The rate of reaction in different polyethylene glycol mediums.

Sl. no.	Starting material used	Reagent used	Product	Reaction time (Δ/ 60 °C)/Yield (%)
1.	3a (R=R^1=H)	PEG-600/DMS	6a (R=R^1=H)	1 h/90
2.	3a (R=R^1=H)	PEG-400/DMS	6a (R=R^1=H)	8 h/66
3.	3a (R=R^1=H)	PEG-200/DMS	6a (R=R^1=H)	12 h/59

the –NH of the substrates (**1** or **3** or **5**) able to retain it by chelation through several lone pairs of electrons in its oxygen containing chain. This role of PEG-600 is very similar to that of the crown ethers or that of the proton sponge (i.e., 1, 8-dimethylaminonaphthalene). Proton sponge (–NH or –OH) which is a very strong base due to its ability to extract hydrogen from an acidic substrate and then retain it in its claws by chelation through lone pair of electrons on the two nitrogen atoms of proton sponge.

Reaction of **3a** (i.e., $R^1 = R^2 = H$) with DMS in the presence of PEG-600 gave N, N-disubstituted olefins with high yields compare to in the presence of PEG-400 and PEG-200, the reason is due to its higher viscosity of PEG-600[22] will help reacting partners to overcome entropy barriers. The rate of the reaction in different solvent mediums described in table 3.

4. Conclusion

In summary, PPh_3 has been employed as an efficient catalyst for the preparation of novel indolo olefinic compounds by a Knoevenagel reaction in ethanol. This method is applicable to a wide range of indole-3-carboxyldehydes **1(a–e)** including N-substituted indole-3-carboxyldehydes **4(a–e)**. The attractive features of this procedure are the mild reaction conditions, high conversions, operational simplicity and inexpensive and ready availability of the catalyst, all of which make it a useful and attractive strategy for the preparation of olefins.

Acknowledgements

The authors are thankful to the University Grants Commission (UGC), Govt. of India, New Delhi, for providing financial support and to the authorities of Jawaharlal Nehru Technological University, Hyderabad, for providing laboratory facilities.

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