



Green Syntheses of N-Alkyl-2-styrylbenzimidazoles

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(Received: 2 January 2013;

Accepted: 4 October 2013)

AJC-14231

Simple and green methodologies for the syntheses of 2-styrylbenzimidazoles (**3a-c**) and its N-alkyl derivatives (**7a-i**) have been developed. *o*-Phenylenediamine (**1**) was condensed with cinnamic acids (**2a-c**) resulting in 2-styrylbenzimidazoles (**3a-c**) using glycerol as a green and efficient solvent. **3** were also prepared alternatively by the condensation of 2-methylbenzimidazole (**4**) with benzaldehydes (**5a-c**) using glycerol as solvent. 2-Styrylbenzimidazoles (**3a-c**) and 2-methylbenzimidazole (**4**) were alkylated independently to obtain N-alkyl-2-styrylbenzimidazole (**7a-i**) and N-alkyl-2-methylbenzimidazole (**6a-c**), respectively using DMS/DES/PhCH₂Cl applying green methods such as simple physical grinding of reactants in solid phase, treating reactants in PEG-600 as a solvent in solution phase and using microwave irradiation of reactants respectively. Compounds **7a-i** could also be prepared, alternatively, by heating **6a-c** with **5a-c** in glycerol at 180 °C for 3-4 h.

Key Words: 2-Styrylbenzimidazoles, Glycerol, Alkylations, Physical grinding, Microwave irradiation, PEG-600.

INTRODUCTION

The development of green methods for syntheses of target compounds from easily available starting materials is a major challenge to the present day organic chemist. In this category, glycerol mediated¹⁻³ reactions are very useful for the synthesis of important heterocycles such as benzimidazoles which are known to possess a range of biological activities such as anti-hypertensive⁴, antiviral⁴ and anticancer types⁵. Compounds that contain benzimidazole skeleton exhibit significant activity against several viruses such as HIV⁶, herpes simplex virus Type-1 (HSV-1)⁷, influenza⁸ and human cytomegalovirus (HCMV)⁶.

Although many methods are available for the synthesis of 2-substituted benzimidazoles⁹⁻¹⁶, not much work seems to have been done to develop green synthetic methods to prepare these types of compounds. Among the most notable green methods used in synthesis, solid phase synthesis^{17,18}, solution phase synthesis using green solvents¹⁹ and microwave techniques²⁰ are very important. In continuation of our earlier work on synthesis of 2-styrylbenzimidazoles²¹⁻²⁴, we now wish to report our studies on preparation and N-alkylation of 2-styrylbenzimidazoles using green methodologies.

EXPERIMENTAL

All the reagents used in this work were obtained from commercial suppliers. Solvents were freshly distilled before

being used. Melting points were determined using a Buchi Melting Point B-545 apparatus and are uncorrected. TLC analyses were done on glass plates coated with silica gel GF-254 and spotting was done using iodine/UV lamp. IR spectra were recorded on a Perkin-Elmer model 446 instrument in KBr phase. ¹H NMR were recorded in CDCl₃/DMSO using 400 MHz Varian Gemini spectrometer and mass spectra were recorded on LC-MS spectrometer, model HP-5989A.

Preparation of 2-styrylbenzimidazoles (3a-c) from *o*-phenylenediamine (1): An intimate mixture of **1** (1.08 g, 10 mM), cinnamic acids (**2a-c**) (10 mM) and glycerol (10 mL) was heated at 170-180 °C for 1 h. At the end of this period, the reaction mixture was poured into ice cold water. The separated solid was filtered, washed with water and dried. The crude products were recrystallized from suitable solvent to get pure **3a-c**.

Alternative preparation of 2-styrylbenzimidazoles (3a-c) from 2-methylbenzimidazole (4): A mixture of **4** (1.32 g, 10 mM), aromatic aldehydes (**5a-c**) (10 mM) and glycerol (10 mL) was heated at 170-180 °C for 3 h in an oil bath. At the end of this period, the reaction mixture was cooled to room temperature, dissolved in isopropanol (25 mL) and treated with a solution of oxalic acid (1.5 g) in isopropanol (10 mL). Each of the oxalate salts of (**3a-c**) obtained were filtered and neutralized, independently, with aqueous NH₃ to pH of 8-10. The products were filtered, washed with water, dried and recrystallized using suitable solvent to obtain **3a-c**.

Preparation of N-alkyl-2-styrylbenzimidazoles (7a-i) from N-alkyl-2-methylbenzimidazoles [6(a-c)]: The procedure is same as mentioned above for the synthesis of **3a-c** from **4**.

Preparation of N-alkyl-2-styrylbenzimidazoles (7a-i) & N-alkyl-2-methylbenzimidazoles [6(a-c)]: In solid phase (Physical grinding method). A mixture of **3a-c** or **4** (10 mM), K₂CO₃ (20 mM), tetrabutylammonium bromide (1 mM) and alkylating agent (10 mM) were ground together independently for about 10-15 min in a mortar with a pestle at room temperature to obtain a homogeneous mixture. The latter was then treated with ice-cold water (30-40 mL). The separated solid was filtered, washed with water (2 × 10 mL) and dried to obtain crude **6a-c** or **7a-i** respectively, which were recrystallized from a suitable solvent to obtain pure **7a-i** or **6a-c** respectively. For yields (Table-2).

In solution phase (In PEG-600): A mixture of **3a-c** or **4** (10 mM), alkylating agent (10 mM) and PEG-600 (20 mL) were taken to heat at 100 °C on water bath for 2 h. At the end of this period, the reaction mixture was poured into ice-cold water. The separated solid was filtered, washed with water and dried. The crude products were recrystallized from suitable solvent to obtain pure **7a-i** or **6a-c** respectively. For yields (Table-3).

Under microwave irradiation condition: A mixture of **3a-c** or **4** (10 mM) dissolved in PEG-600 (10 mL) and alkylating agent (10 mM) was added and taken in a 10 mL CEM-reaction tube sealed by rubber stopper and subjected to microwave irradiation for 5 min at 130 °C in the commercial micro-wave reactor. After that, the tube was cooled and the completion of reaction was checked by TLC then poured into ice-cold water. The separated solid was filtered, washed with water and dried. The crude product was recrystallized from a suitable solvent to obtain pure **7a-i** or **6a-c** respectively. For yields (Table-4).

Physical and spectral data of the obtained compounds are given below.

1-Methyl-2-styryl-1H-benzimidazole (7a) (Table-1, entry 4): Yield (1.6g, 70 %), m.p. 114-115 °C (Lit. m.p.²⁴ 112-114), IR (KBr, $\nu_{\max}$, cm⁻¹): 3010 (-CH=CH), 1624 (C=N), ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.6 (3H, s, -N-CH), δ 6.9-7.0 (2H, dd, *trans*-CH=CH), δ 7.1-7.3 (5H, m, aromatic) δ 7.2-7.7 (4H, m, aromatic); MS: *m/z* 249.13 (M⁺). Anal. calcd. (%) for C₁₆H₁₄N₂: C, 82.02; H, 6.02; N, 11.96; Found C, 82.12; H, 6.10; N, 11.99.

1-Ethyl-2-styryl-1H-benzimidazole (7b) (Table-1, entry 5): Yield (1.6 g, 68 %), m.p. 158-160 °C (Lit. m.p.²⁴ 160-161 °C), IR (KBr, $\nu_{\max}$, cm⁻¹): 3010 (-CH=CH), 1625 (C=N), ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.5 (3H, t, N-C-CH), δ 3.7-3.8 (2H, q, N-CH), δ 6.9-7.0 (2H, dd, *trans*-CH=CH), δ 7.1-7.3 (5H, m, aromatic), δ 7.3-7.7 (4H, m, aromatic); MS: *m/z* 249.13 (M⁺). Anal. calcd. (%) for C₁₇H₁₆N₂: C, 82.22; H, 6.49; N, 11.28; Found C, 82.42; H, 6.56; N, 11.30.

1-Benzyl-2-styryl-1H-benzimidazole (7c) (Table-1, entry 6): Yield (2.1 g, 70 %), m.p. 120-121 °C (Lit. m.p. 120 °C), IR (KBr, $\nu_{\max}$, cm⁻¹): 3020 (-CH=CH), 1624 (C=N), ¹H NMR (400 MHz, DMSO-*d*₆): δ 4.9-5.0 (2H, s, N-CH), δ 6.9-7.0 (2H, dd, *trans*-CH=CH), δ 7.0-7.4 (5H, m, aromatic), δ 7.1-7.3 (5H, m, aromatic), δ 7.3-7.8 (4H, m, aromatic); MS: *m/z* 311.15 (M⁺). Anal. calcd. (%) for C₂₂H₁₈N₂: C, 85.13; H, 5.85; N, 9.03; Found C, 85.16; H, 5.92; N, 9.79.

1-Methyl-2-(2-*p*-tolyl-vinyl)-1H-benzimidazole (7d) (Table-1, entry 7): Yield (1.8 g, 72 %), m.p. 129-130 °C (Lit. m.p.²⁴ 128-130), IR (KBr, $\nu_{\max}$, cm⁻¹): 3010 (-CH=CH), 1625 (C=N), ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.3 (3H, s, -CH), δ 3.6 (3H, s, N-CH), δ 6.9-7.0 (2H, dd, *trans*-CH=CH), δ 7.0-7.2 (4H, q, aromatic), δ 7.3-7.7 (4H, m, aromatic); MS: *m/z* 249.13 (M⁺). Anal. calcd. (%) for C₁₇H₁₆N₂: C, 82.22; H, 6.49; N, 11.28; Found C, 82.30; H, 6.55; N, 11.30.

1-Ethyl-2-(2-*p*-tolyl-vinyl)-1H-benzimidazole (7e) (Table-1, entry 8): Yield (1.8 g, 70 %), m.p. 108-110 °C, IR (KBr, $\nu_{\max}$, cm⁻¹): 3010 (-CH=CH), 1625 (C=N), ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.5 (3H, t, N-C-CH), δ 2.3-2.5 (3H, s, -CH), δ 3.7-3.8 (2H, q, N-CH), δ 6.9-7.0 (2H, dd, *trans*-CH=CH), δ 7.0-7.2 (4H, q, aromatic) δ 7.3-7.7 (4H, m, aromatic); MS: *m/z* 263.35 (M⁺). Anal. calcd. (%) for C₁₈H₁₈N₂: C, 82.41; H, 6.92; N, 10.68; Found C, 82.44; H, 6.98; N, 10.80.

N-Benzyl-2-(2-*p*-tolyl-vinyl)-1H-benzimidazole (7f) (Table-1, entry 9): Yield (2.1 g, 65 %), m.p. 210-212 °C, IR (KBr, $\nu_{\max}$, cm⁻¹): 3020 (-CH=CH), 1624 (C=N), ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.3-2.5 (3H, s, -CH), δ 4.9-5.0 (2H, s, N-CH), δ 6.9-7.0 (2H, dd, *trans*-CH=CH), δ 7.0-7.2 (9H, m, aromatic), δ 7.3-7.7 (4H, m, aromatic); MS: *m/z* 325.12 (M⁺). Anal. calcd. (%) for C₂₃H₂₀N₂: C, 85.15; H, 6.21; N, 8.63; Found C, 85.24; H, 6.28; N, 8.72.

2-[2-(4-Chloro-phenyl)-vinyl]-1-methyl-1H-benzimidazole (7g) (Table-1, entry 10): Yield (1.9 g, 73 %), m.p. 143-145 °C (Lit. m.p.²⁴ 142-143 °C), IR (KBr, $\nu_{\max}$, cm⁻¹): 3010 (-CH=CH), 1625 (C=N), ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.6 (3H, s, N-CH), δ 6.9-7.0 (dd, 2H, *trans*-CH=CH), δ 7.3-7.8 (8H, m, aromatic); MS: *m/z* 269 (M⁺). Anal. calcd. (%) for C₁₆H₁₃N₂Cl: C, 71.51; H, 4.88; Cl, 13.19; N, 10.42; Found C, 71.60; H, 4.92; Cl, 13.30; N, 10.55.

2-[2-(4-Chloro-phenyl)-vinyl]-1-ethyl-1H-benzimidazole (7h) (Table-1, entry 11): Yield (1.9 g, 70 %), m.p. 136-138 °C, IR (KBr, $\nu_{\max}$, cm⁻¹): 3010 (-CH=CH), 1624 (C=N), ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.5 (3H, t, N-C-CH), δ 3.7-3.8 (2H, q, N-CH), δ 6.9-7.0 (2H, dd, *trans*-CH=CH), δ 7.2-7.8 (8H, m, aromatic); MS: *m/z* 283.7 (M⁺). Anal. calcd. (%) for C₁₇H₁₅N₂Cl: C, 72.21; H, 5.35; Cl, 12.54; N, 9.91; Found C, 72.30; H, 5.42; N, 9.99.

N-Benzyl-2-[(E)-2-(4-chlorophenyl)ethenyl]-1H-1,3-benzimidazole (7i). (Table-1, entry 12): Yield (2.4 g, 72 %), m.p. > 230 °C, IR (KBr, $\nu_{\max}$, cm⁻¹): 3020 (-CH=CH), 1625 (C=N), ¹H NMR (400 MHz, DMSO-*d*₆): δ 4.9-5.0 (2H, s, N-CH), δ 6.9-7.0 (2H, dd, *trans*-CH=CH), δ 7.0-7.2 (5H, m, aromatic), δ 7.3-7.8 (8H, m, aromatic); MS: *m/z* 345.42 (M⁺). Anal. calcd. (%) for C₂₂H₁₇N₂Cl: C, 76.63; H, 4.97; Cl, 10.28; N, 8.12; Found C, 76.70; H, 4.99; Cl, 10.35; N, 8.26.

RESULTS AND DISCUSSION

Reaction of *o*-phenylenediamine (**1**) with cinnamic acids (**2a-c**) in glycerol at 180 °C resulted in 2-styrylbenzimidazoles (**3a-c**) (*i.e.*, **3a**, Ar = C₆H₅), (**3b**, Ar = C₆H₄-*p*-Cl) and (**3c**, Ar = C₆H₄-*p*-CH₃) in good yields (Table-1) and the products were identical with the ones reported in earlier methods^{25,26} in all respects (m.p. m.m.p and co-TLC analysis). 2-Methylbenzimidazole (**4**), which was prepared by Philip's condensation²⁷, condensation of **1** with acetic acid using 4 N HCl, on reacting with substituted benzaldehydes (**5a-c**) (*i.e.*, **5a**, Ar = C₆H₅),

TABLE-1
 SYNTHESIS OF COMPOUNDS **3a-c** AND **7a-i** FROM **1**, **4** AND **6a-c** RESPECTIVELY

S. No.	^a Product	R ₁	Time (h)	Temp. (°C)	^b Yield (%)	m.p. (°C)
1	3a (Ar = C ₆ H ₅)	–	1	100	75	205
2	3b (Ar = C ₆ H ₄ - <i>p</i> -CH ₃)	–	1	100	70	216-217
3	3c (Ar = C ₆ H ₄ - <i>p</i> -Cl)	–	1	100	73	222
4	7a (Ar = C ₆ H ₅)	CH ₃	3	160	70	114-115
5	7b (Ar = C ₆ H ₅)	C ₂ H ₅	3	170	68	158-160
6	7c (Ar = C ₆ H ₅)	CH ₂ Ph	3	170	70	120-121
7	7d (Ar = C ₆ H ₄ - <i>p</i> -CH ₃)	CH ₃	3	170	72	129-130
8	7e (Ar = C ₆ H ₄ - <i>p</i> -CH ₃)	C ₂ H ₅	3	170	70	108-110
9	7f (Ar = C ₆ H ₄ - <i>p</i> -CH ₃)	CH ₂ Ph	3	180	65	210-212
10	7g (Ar = C ₆ H ₄ - <i>p</i> -Cl)	CH ₃	3	175	73	143-145
11	7h (Ar = C ₆ H ₄ - <i>p</i> -Cl)	C ₂ H ₅	3	175	70	171-172
12	7i (Ar = C ₆ H ₄ - <i>p</i> -Cl)	CH ₂ Ph	3	180	72	>230

^aAll the products were characterized by ¹H NMR, IR and mass spectral data and comparison with the authentic samples available or prepared according to reported methods.

^bYields refers to isolated yields.

(**5b**, Ar = C₆H₄-*p*-Cl) and (**5c**, Ar = C₆H₄-*p*-CH₃) in glycerol at 170-180 °C for 1 h, resulted in **3a-c** (*i.e.*, **3a**, Ar = C₆H₅), (**3b**, Ar = C₆H₄-*p*-Cl) and (**3c**, Ar = C₆H₄-*p*-CH₃) in good yields (Table-1) also identical with the products obtained above in all respects (m.p. m.m.p. and co-TLC analysis).

The N-alkylation of (**3a-c**) and (**4**) and with alkylating agents such as dimethyl sulphate (DMS), diethyl sulphate (DES) and benzyl chloride (PhCH₂Cl) in the presence of K₂CO₃ as a mild base and tetrabutylammonium bromide (TBAB) as phase transfer catalyst, by a simple physical grinding of the reactants in a mortar with a pestle under solvent-free conditions for 5 min at room temperature, gave respectively, N-methyl-2-styrylbenzimidazole (**7a**, *i.e.*, R₁ = CH₃, Ar = C₆H₅), N-ethyl-2-styrylbenzimidazole (**7b**, *i.e.*, R₁ = C₂H₅, Ar = C₆H₅), N-benzyl-2-styrylbenzimidazole (**7c**, *i.e.*, R₁ = PhCH₂Cl, Ar = C₆H₅), N-methyl-2-[(E)-2-(4-methylphenyl)ethenyl]-1*H*-1,3-benzimidazole (**7d**, *i.e.*, R₁ = CH₃, Ar = C₆H₄-*p*-CH₃), N-ethyl-2-[(E)-2-(4-methylphenyl)ethenyl]-1*H*-1,3-benzimidazole (**7e**, *i.e.*, R₁ = C₂H₅, Ar = C₆H₄-*p*-CH₃), N-benzyl-2-[(E)-2-(4-methylphenyl)ethenyl]-1*H*-1,3-benzimidazole (**7f**, *i.e.*, R₁ = PhCH₂Cl, Ar = C₆H₄-*p*-CH₃), N-methyl-2-[(E)-2-(4-chlorophenyl)ethenyl]-1*H*-1,3-benzimidazole (**7g**, *i.e.*, R₁ = CH₃, Ar = C₆H₄-*p*-Cl), N-ethyl-2-[(E)-2-(4-chlorophenyl)ethenyl]-1*H*-1,3-benzimidazole (**7h**, *i.e.*, R₁ = C₂H₅, Ar = C₆H₄-*p*-Cl) and N-benzyl-2-[(E)-2-(4-chlorophenyl)ethenyl]-1*H*-1,3-benzimidazole (**7i**, *i.e.*, R₁ = PhCH₂Cl, Ar = C₆H₄-*p*-Cl) respectively (Table-2).

Compound **4** on treatment with alkylating agents in the presence of K₂CO₃ and TBAB under physical grinding conditions in a mortar with pestle gave the products N-methyl-2-methylbenzimidazole (**6a**, *i.e.*, R = CH₃), N-ethyl-2-methylbenzimidazole (**6b**, *i.e.*, R = C₂H₅) and N-benzyl-2-methylbenzimidazole (**6c**, *i.e.*, R = PhCH₂Cl) respectively and these products were identical with the ones prepared earlier^{22,25} using conventional methods in all respects (m.p. m.m.p and co-TLC analysis) (Table-2).

The N-alkylation reactions of **3a-c** and **4** were also carried out in PEG-600 as a solvent, both by heating at 100 °C on a water bath and in microwave method. Thus the treatment of **3a-c** and **4**, independently, with each of dimethyl sulphate (DMS), diethyl sulphate (DES) and benzyl chloride (PhCH₂Cl)

 TABLE-2
 N-ALKYL/ARALKYLATIONS OF COMPOUNDS **3a-c** AND **4** USING SOLID PHASE SYNTHESIS (BY SIMPLE PHYSICAL GRINDING)

S. No.	Substrate	Reagent	Product ^a	Solid-phase (simple physical grinding)		
				Time (min)	Temp. (°C)	Yield ^b (%)
1	3a (R=CH ₃)	DMS	7a	5	RT	80
		DES	7b	5	RT	78
		Ph-CH ₂ Cl	7c	10	RT	90
2	3b (R=OH)	DMS	7d	5	RT	80
		DES	7e	8	RT	75
		Ph-CH ₂ Cl	7f	10	RT	78
3	3c (R=Cl)	DMS	7g	6	RT	90
		DES	7h	10	RT	80
		Ph-CH ₂ Cl	7i	10	RT	78
4	4	DMS	6a	5	RT	80
		DES	6b	10	RT	78
		PhCH ₂ Cl	6c	10	RT	80

^aAll the products were characterized by ¹H NMR, IR and mass spectral data and comparison with the authentic samples available or prepared according to reported methods.

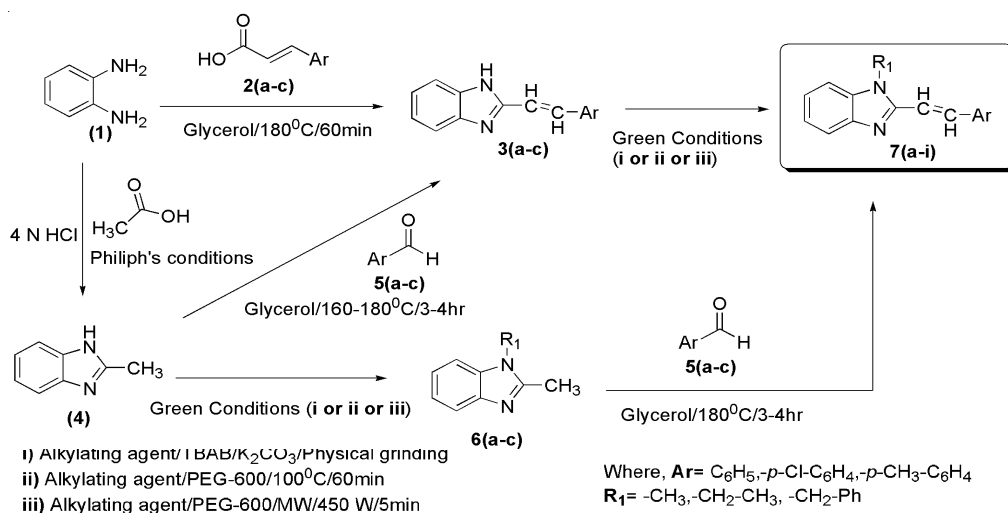
^bYields refers to the isolated yields

in PEG-600 at 100 °C about 1 h without the use of any base, followed by simple processing, gave respectively, **7a-i** and **6a-c** (Table-3).

Compounds **7a-i**) and **6a-c** were also be prepared by an alternative method. Thus, **3a-c** and **4** on reactions, independently, with each of dimethyl sulphate (DMS), diethyl sulphate (DES) and benzyl chloride (PhCH₂Cl) under microwave irradiation conditions for 5-10 min and subsequent processing, gave **7a-i** and **6a-c** (Table-4).

Conclusion

In conclusion, green and simple syntheses of 2-styrylbenzimidazoles (**3a-c**) and their N-alkyl/aralkyl derivatives **7a-i** were described. It appears from this study that green syntheses using solvents such as glycerol and PEG-600 and eco-friendly methods like solid phase synthesis (physical grinding) and microwave irradiation gives better yields, quality and in less reaction time the products over conventional methods. The entire sequence of reactions shown in **Scheme-I** has been carried out using eco-friendly solvents and green conditions.



Scheme-I: Synthesis & N-alkylation studies of 2-styrylbenzimidazoles 7a-i

TABLE-3 N-ALKYL/ARALKYLATIONS OF COMPOUNDS 3a-c AND 4 USING PEG-600 AS SOLVENT (SOLUTION PHASE)						
S.No	Substrate	Reagent	Product ^a	Green solvent (solution phase) in PEG-600		
				Time (min)	Temp (°C)	Yield ^b (%)
1.	3a (R=CH ₃)	DMS	7a	60	100	82
		DES	7b	80	100	75
		PhCH ₂ Cl	7c	130	100	72
2.	3b (R=OH)	DMS	7d	60	100	80
		DES	7e	60	100	70
		PhCH ₂ Cl	7f	130	100	75
3.	3c (R=Cl)	DMS	7g	60	100	83
		DES	7h	60	100	76
		PhCH ₂ Cl	7i	120	100	78
4.	4	DES	6b	80	100	75
		PhCH ₂ Cl	6c	120	100	68

^aAll the products were characterized by ¹H-NMR, IR and Mass spectral data and comparison with the authentic samples available or prepared according to reported methods.
^bYields refers to the isolated yields.

TABLE-4 N-ALKYL/ARALKYLATIONS OF COMPOUNDS 3a-c AND 4 USING MICROWAVE						
S.No	Substrate	Reagent	Product ^a	Microwave irradiation		
				Time (min)	Temp (°C)/ Watt	Yield ^b (%)
1.	3a (R=CH ₃)	DMS	7a	3	100/450	88
		DES	7b	5	100/450	80
		PhCH ₂ Cl	7c	5	100/450	75
2.	3b (R=OH)	DMS	7d	5	100/450	80
		DES	7e	5	100/450	78
		PhCH ₂ Cl	7f	5	100/450	75
3.	3c (R=Cl)	DMS	7g	5	100/450	88
		DES	7h	5	100/450	78
		PhCH ₂ Cl	7i	5	100/450	75
4.	4	DES	6b	5	100/450	85
		PhCH ₂ Cl	6c	5	100/450	82

^aAll the products were characterized by ¹H-NMR, IR and Mass spectral data and comparison with the authentic samples available or prepared according to reported methods.
^bYields refers to the isolated yields

ACKNOWLEDGEMENTS

The authors are thankful to the authorities of Jawaharlal Nehru Technological University Hyderabad, for providing financial support and laboratory facilities.

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