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Synthesis and characterization of 2-(4-bromophenyl)-1H- benzimidazole and 2-(6-bromochroman-2-yl)-1H- benzimidazole compounds

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ABSTRACT

N-alkyl, N-carboxylate and N-sulfonyl compounds of 2-(4-bromophenyl)-1H-benzimidazole and 2-(6-bromochroman-2-yl)-1H-benzimidazole, using alkyl halides, alkyl chloroformates and sulfonyl chlorides, respectively have been synthesized in high yields using different polymer-supports and different solvents. The advantages of this simple and rapid method are extremely mild conditions, easy work-up and clean reaction without undesired byproducts.

KEYWORDS

Benzimidazoles;
Polymer-supported reactions;
Solvents.

INTRODUCTION

Today, there are a vast number of pharmacologically active heterocyclic compounds, which are in regular clinical use. Among the wide variety of heterocyclic compounds known, the nitrogen heteocycles are of great importance. The benzimidazole is one of such great important nitrogen heterocyclic species because of its synthetic utility and wide spectrum of pharmacological activity[1,2]. The benzimidazole nucleus is an important heterocyclic ring system, since several of its derivatives have been marketed as commercial products. Recently, bisbenzimidazoles are being developed as DNA minor-groove binding agent with antitumor activity[3] and can act as ligands to transition metals for modeling biological systems[4].

Conventional synthesis of benzimidazoles involve refluxing the reactants in aqueous hydrochloric acid for 30 min[5a]. or in a slurry of the dehydrating agent, such as polyphosphoric acid, at 250^{0}C for 4 h[5b] that result in the generation of abundant harmful waste to the environment. New methods have been recently applied for the preparation of this type of compounds. These include solid phase[6] methods, a rapid microwave assisted liquid-phase combinatorial approach[7], the strategy of palladium-catalysed intramolecular aryl-amination chemistry[8,9] using high-temperature water[10] as the medium and montmorrilonite KSF or K10[11]. As a new type of strong water-compatible Lewis acid, they have been applied in a wide variety of reactions[12]. They have been prepared from o-diaminobenzene derivatives and ortho-esters using Yb $(OTf)_3$ under solvent-free conditions[13].

Numerous catalysts have been developed for the selective synthesis of benzimidazoles from *o*-aryldiamines, such as Lead tetraacetate[14], $SOCl_2$/SiO_2[15], Dacro K13[16] and Zeolite material[17].

Various substituted benzimidazoles are known to have varied biological activity and among them 2-substituted benzimidazoles are found to be more potent[18]. Benzimidazole nucleus constitutes a special moiety found in a several therapeutic agents such as antitubercular, anticancer, anthelmintic, antiallergic, antioxidant, antihistaminic and antimicrobial, and this heterocyclic

system provides an interesting theme for the synthesis of various biological active compounds[19].

The polymer supported methodology adopted in the work could be very simple due to ease of operation and workup and also economic because of higher yield and purity of products. Our work is more centered on the structural modification[20-24]. Keeping in view the bioactivity of benzimidazole compounds, we report a simple and efficient method for the preparation of N-alkyl, N-acyl and N-sulfonyl compounds of benzimidazole in higher yields and purity under mild reaction conditions.

EXPERIMENTAL

All chemicals were of AR grade, and solvents were distilled before use. Melting points are uncorrected. Commercial Amberlite IRA 400 (chloride form) and Indion 820 (chloride form) were activated by treating with dil. HCl solution and Amberlyst A26 (hydroxide form) was activated by treating with dil. NaOH.

General procedure for supporting anion of 2-(4-bromophenyl)-1H-benzimidazole and 2-(6-bromochroman-2-yl) 1H-benzimidazole on polymer supports

2-(4 bromophenyl) 1H-benzimidazole (100 mmol) was dissolved in methanol (200 ml) and aqueous solution of sodium hydroxide (4 g, 100 mmol) was added to it. The activated Amberlite IRA 400 (chloride form) (100 gm) was packed in a column and was eluted slowly dropwise (about 1.5 ml/min) with the above solution of sodium salt of 2-(4-bromophenyl)-1H-benzimidazole. Thereafter, the resin was washed with distilled water until complete removal of hydroxide ions and excess of 2-(4-bromophenyl)-1H-benzimidazole anion. It was then washed with ethanol followed by acetone and dried in *vacuo* at 50 ^{0}C for 5 hr. The same procedure was used for supporting anion of 2-(4 bromophenyl) 1H-benzimidazole and 2-(6-bromochroman-2-yl) 1H-benzimidazole on Amberlite IRA 400 (chloride form), Amberlyst A 26 and Indion 820 (chloride form). The exchange capacity[25] of different supported resins was determined by passing 1 M KCl solution (100 ml) through supported resin (1 gm) packed in a column. The supported anions in the eluent were titrated with 0.01 N HCl using methyl orange as an indicator.

The exchange capacity of the resin was found to be 1.2 mmol 2-(4 bromophenyl) 1H-benzimidazole anion per gram of dry resin for Amberlyst A26 (hydroxide form) and 1.0 mmol for Amberlite IRA 400 (chloride form) and Indion 820 (chloride form). The exchange capacity of the resin was found to be 1.1 mmol 2-(6-bromochroman-2-yl) 1H-benzimidazole anion per gram of dry resin for Amberlite IRA-400 (chloride form) and 1.0 for Indion 820 (chloride form) and Amberlyst A26 (hydroxide form).

Synthesis of N-alkyl compounds

A mixture of anion supported resin (10 mmol) and alkyl halide (10 mmol) in dry solvent (25 ml) was stirred until the completion of reaction (30-50 min). The progress of reaction was monitored by silica-gel thin-layer chromatography (TLC) (hexane: acetone, 9:1) mixture. Melting points were determined by open capillary method and are uncorrected. The products were characterized by physical constants and spectroscopic (^{1}H NMR and IR) methods. After separation of resin by filtration and removal of solvent, the corresponding N-alkyl compounds (1, 3) were obtained as products (TABLE 1-6)

TABLE 1 : Yield (%) using Amberlite IRA 400, (chloride form), as support.

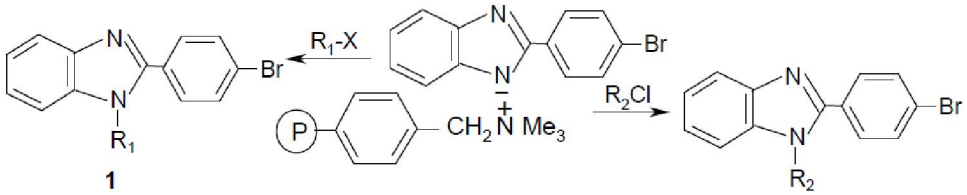
Compd. No.	Time (min)	Solvent				Mp[Lit. mp][26] (^{0}C)
		Acetone	Acetonitrile	DCM	Ethanol	
1a	40	82	92	89	78	115-116
1b	40	84	94	88	80	137-138
1c	35	85	91	87	81	92-93
2a	15	84	90	87	79	114-116
2b	10	83	93	89	80	97-99
2c	15	84	94	90	78	115-116

TABLE 2 : Yield (%) using Amberlyst A26 (hydroxide form), as support.

Compd. No.	Time (min)	Solvent			
		Acetone	Acetonitrile	DCM	Ethanol
1a	35	94	88	85	83
1b	35	92	85	82	79
1c	40	91	86	80	81
2a	10	88	84	81	78
2b	15	90	88	83	84
2c	10	93	90	85	76

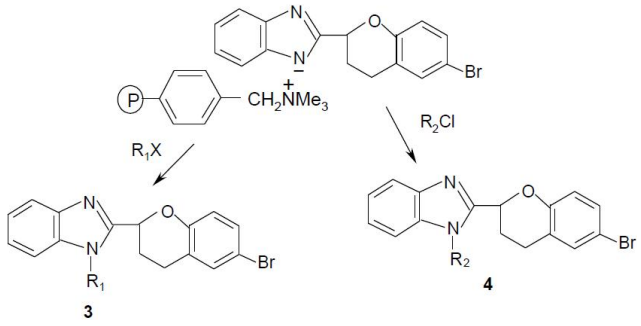
Synthesis of N-carboxylate and N-sulfonyl compounds

N-carboxylate derivatives (2, 4) were prepared by the above procedure using alkyl chloroformates and N-sulfonyl (10 mmol) instead of alkyl halides. Depending on reactivity of the alkyl chloroformates, these reactions were completed within 10 to 20 min. The products are listed in TABLE 1-6.



(1a) R_1 = -CH_3; (1b) R_1 = -CH_2CH_3 1;(1c) R_1 = -$CH_2CH_2CH_3$;
(2a) R_2 = - $COOCH_2CH_3$; (2b) R_2 = - $COO(CH_2)_3CH_3$; (2c) R_2 = - SO_2CF_3

Scheme 1 : Synthesis of 2-(4-bromophenyl)-1H-benzimidazole compounds. Solvent: acetone, acetonitrile, dichloromethane, ethanol.

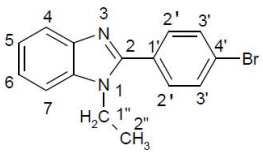


(3a) R_1 = -CH_3; (3b) R_1 = -CH_2CH_3; (4a) R_2 = -$COOCH_3$; (4b) R_2=-$COOCH_2CH_3$; (4c) R_2 = -$COO(C_6H_4)CH_3$; (4d) R_2 = -$COOCH_2C_6H_5$; (4e) R_2= -SO_2CH_3; (4f) R_2 = -$SO_2(C_6H_4)CH_3$

Scheme 2 : Synthesis of 2-(6-bromochroman-2-yl)-1H-benzimidazole. Solvent: acetone, acetonitrile, dichloromethane, ethanol.

Spectral data of compounds synthesized

The following numbering has been followed to interpret ^{1}H NMR spectra.



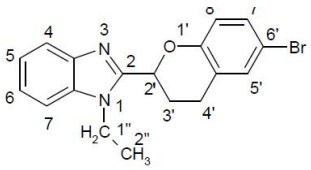


TABLE 3 : Yield (%) using Indion 820 (chloride form), as support.

Compd. No.	Time (min)	Solvent			
		Acetone	Acetonitrile	DCM	Ethanol
1a	40	90	87	93	84
1b	25	87	85	89	81
1c	30	85	86	90	80
2a	15	85	83	86	79
2b	15	87	90	87	84
2c	10	84	88	84	77

(a) 2- (4- Bromophenyl)-1-methyl-1-H-benzimidazole (1a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.87 (s, 3H, 1"-CH_3), 7.30-7.42 (m, 3H, 4, 5 & 6 Ar-H), 7.63-7.70 (m, 4H, 2' & 3' Ar-H), 7.81-7.84 (m, 1H, 7-Ar-H); IR (KBr): 2975, 1460, 1399, 1326, 1069, 1008, 833 and 816 cm^{-1}.

(b) 2- (4- Bromophenyl)-1-ethyl-1-H-benzimidazole (1b)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.46 (t, 3H, 2" –CH_3), 4.26 (q, 2H, 1" -CH_2), 7.30- 7.44 (m, 3H, 4, 5 & 6 Ar-H), 7.58-7.68 (m, 4H, 2' & 3' Ar-H), 7.81-7.84 (m, 1H, 7- Ar-H); IR (KBr): 2982, 1447, 1408, 1327, 1178, 1068, 1004, 956 and 923 cm^{-1}.

(c) 2-(4-Bromophenyl)-1-propyl-1-H-benzimidazole (1c)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.86 (t, 3H, 3" –CH_3), 1.80-1.88 (m, 2H,-2" –CH_2), 4.17 (t, 2H, 1" –CH_2), 7.28-7.34 (m, 2H, 5 & 6 Ar-H), 7.40-7.43 (m, 1H, 4- Ar-H), 7.57-7.68 (m, 4H, 2' & 3'-Ar-H), 7.80-7.83 (m, 1H, 7-Ar-H); IR (KBr): 2971, 2876, 1611, 1446, 1410, 1326, 1249, 1182, 1074, 1008 and 899 cm^{-1}.

(d) 2- (4- Bromophenyl) benzimidazole-1-carboxylic acid ethyl ester (2a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.31 (t, 3H, 4" –CH_3), 4.41 (q, 2H, 3" –CH_2), 7.39- 7.43 (m, 2H, 5 & 6 Ar-H), 7.53-7.63 (m, 4H, 2' & 3'-Ar-H), 7.78-7.82 (m, 1H, 4- Ar-H), 8.01-8.04 (m, 1H, 7-Ar-H); IR (KBr): 2978, 1750, 1480, 1450, 1372, 1335, 1264, 1205, 1147, 1069 and 1011 cm^{-1}.

Full Paper

(e) 2-(4-Bromophenyl) benzimidazole-1-carboxylic acid butyl ester (2b)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.89 (t, 3H, 6" –CH_3), 1.17-1.30 (m, 2H,-5" –CH_2), 1.55-1.65 (m, 2H, 4" –CH_2), 4.32 (t, 2H, 3" –CH_2), 7.38-7.45 (m, 2H, 5 & 6 Ar-H), 7.52-7.63 (m, 4H, 2' & 3'-Ar-H), 7.78-7.81 (m, 1H, 4-Ar-H), 8.02-8.05 (m, 1H, 7- Ar-H); IR (KBr):2960,1776, 1454, 1448,1394, 1321, 1209, 1060,1012 and 911 cm^{-1}.

(f) 2-(4-Bromophenyl)-1-trifluoromethane sulfonyl-1H-benzimidazole (2c)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48-7.58 (m, 4H, 5, 6 & 2'- Ar-H), 7.63-7.66 (m, 2H, 3' Ar-H), 7.84-7.95 (m, 2H, 4 & 7-Ar-H); IR (KBr): 3063, 1590, 1554, 1484, 1421, 1212, 1134, 1074, 1048, 1022 and 1010 cm^{-1}.

(g) 2-(6-bromochroman-2-yl)-1-methyl-1H-benzimidazole (3a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.40-2.46 (m, 2H, 3'-CH_2), 2.97-3.01 (m, 2H 4'-CH_2), 3.91 (s, 3H, 1"-CH_3), 5.54 (dd, 1H, 2'-H), 6.79-6.82 (d, 1H, 8'- Ar-H), 7.2-7.35 (m, 4H, 7', 5', 5 & 6 Ar-H), 7.59-7.66 (d, 2H, 4 and 7Ar-H); IR (KBr): 2948, 1474, 1403, 1320, 1231, 1182, 1119, 1080, 1041,997 and 744 cm^{-1}.

(h) 2-(6-bromochroman-2-yl)-1-ethyl-1H-brenzimidazole (3b)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38-1.43 (t,3H, 2"), 2.42-2.5 (m, 2H, 3'-CH_2), 3.03- 3.07 (m, 2H 4'-CH_2), 4.41 (q, 2H, 1" –CH_2), 5.62 (dd, 1H, 2'-H), 6.76-6.79 (d, 1H, 8'- Ar-H), 7.24-7.36 (m, 4H, 7', 5', 5 & 6 Ar-H), 7.61-7.67 (d, 2H, 4 & 7 Ar-H); IR (KBr): 2983, 2934, 1473, 1234, 1222, 1041, 996 and 816 cm^{-1}.

(i) Methyl-2-(6-bromochroman-2-yl)-1H-benzimidazole-1-carboxylate (4a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.48 (m, 2H, 3'-CH_2), 2.95 (m, 2H 4'-CH_2), 4.13 (s, 3H, 3" –CH_3), 5.88 (dd, 1H, 2'-H) 6.81-6.84 (d, 1H, 8'-Ar-H), 7.19-7.4 (m, 4H, 7', 5', 5 & 6 Ar-H), 7.80-7.95 (d, 2H, 4 & 7 Ar-H); IR (KBr): 2926, 1573, 1544, 1481, 1438, 1357, 1336, 1231, 1200, 1126, 1082, 1033 and 786 cm^{-1}.

(j) Ethyl-2-(6-bromochroman-2-yl)-1H-benzimidazole-1-carboxylate (4b)

^{1}HNMR ($CDCl_3$, 300 MHz): δ 1.49-1.56 (t, 3H, 4"), 2.49 (m, 2H, 3'-CH_2), 2.94-3.02 (m, 2H 4'-CH_2), 4.57-4.59 (q, 2H, 3" –CH_2), 5.88 (dd, 1H,3'-H), 6.8-6.83 (d, 1H, 8' Ar-H), 7.19-7.39 (m, 4H, 7', 5', 5 and 6Ar-H), 7.81-7.97 (d, 2H, 4 and 7Ar-H); IR (KBr): 2945, 1745, 1480, 1379, 1330, 1232, 1195, 1132, 1082, 1070, 1014 and 762 cm^{-1}.

(k) p-toluene 2-(6-bromochroman-2-yl)-1H-benzimidazole-1-carboxylate (4c)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.32 (s, 3H, -CH_3), 2.55 (m, 2H, 3'-CH_2), 3.00 (m, 2H 4'-CH_2), 5.41 (dd, 1H, 2'-H), 5.56 (s, 2H, 1"-CH_2), 6.53-6.56 (d, 1H, 5' Ar-H), 6.98- 6.70 (m, 2H, 7'& 8'Ar-H), 7.09-7.16 (m, 4H, Ar-H), 7.22-7.29 (s, 3H, Ar-H), 7.84- 7.87 (d, 1H, Ar-H).

(l) Benzyl 2-(6-bromochroman-2-yl)-1H-benzimidazole-1-carboxylate (4d)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.55 (m, 2H, 3'-CH_2), 3.01 (m, 2H 4'-CH_2), 5.38 (dd, 1H, 2'-H), 5.60 (s, 2H, 1"-CH_2), 6.46-6.49 (d, 1H, 5'Ar-H), 7.11 (m, 2H, Ar- H), 7.21 (m, 2H, Ar-H),7.26-7.28 (m, 6H,Ar-H),7.86-7.90 (m, 1H, Ar-H); IR (KBr): 2926, 1482, 1462, 1370, 1291, 1234, 1187, 1122, 1082, 1015, 938, 805 and 744 cm^{-1}.

(m) 2-(6-bromochroman-2-yl)-1-methanesulfonyl-1H-benzimidazole (4e)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.58-2.66 (m, 2H, 3'-CH_2), 3.04 (m, 2H 4'-CH_2), 3.52 (s 3H, 2" –CH_3), 5.8 (dd, 1H, 2'-H), 6.81-6.64-6.67 (d, 1H, 8'- Ar-H), 7.18- 7.44 (m, 4H, 7', 5', 5 & 6Ar-H), 7.82-7.97 (d, 2H, 4 & 7 Ar-H).

TABLE 4 : Yield (%) using Amberlite IRA-400 (chloride form), as support.

Compd. No.	Time (min)	Solvent				Mp[Lit. mp][26] (^{0}C)
		Acetone	Acetonitrile	DCM	Ethanol	
3a	45	92	90	87	86	140-141
3b	45	90	87	85	84	128-130
4a	15	93	90	88	83	142-144
4b	20	91	87	84	80	150-152
4c	20	90	86	82	81	225-226
4d	15	87	84	80	77	170-172
4e	15	88	87	84	80	219-220
4f	20	86	83	80	76	140-142

TABLE 5 : Yield (%) using Amberlyst A 26 (hydroxide form), as support.

Compd. No.	Time (min)	Solvent			
		Acetone	Acetonitrile	DCM	Ethanol
3a	50	81	79	74	72
3b	45	80	78	75	71
4a	15	79	76	72	70
4b	20	81	74	71	69
4c	20	78	75	73	72
4d	15	80	77	75	71
4e	15	76	73	70	67
4f	20	78	75	74	71

TABLE 6 : Yield (%) using Indion 820 (chloride form), as support.

Compd. No.	Time (min)	Solvent			
		Acetone	Acetonitrile	DCM	Ethanol
3a	45	88	85	84	80
3b	50	86	83	81	78
4a	15	87	85	82	81
4b	20	84	81	79	75
4c	20	88	83	80	76
4d	15	85	82	78	74
4e	15	86	84	82	77
4f	20	88	85	81	78

(n) 2-(6-bromochroman-2-yl)-1-tosyl-1H-benzimidazole (4f)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.41 (s, 3H, -CH_3), 2.52 (m, 2H, 3'-CH_2), 3.01 (m, 2H 4' -CH_2), 5.96 (dd, 1H, 2'-H), 6.55-6.58 (d, 1H, 8'-Ar-H), 7.17-7.20 (d, 1H, Ar- H) 7.26-7.42 (m, 4H, Ar-H), 7.75-7.77 (m, 1H, Ar-H), 7.93-7.96 (d, 2H, Ar-H), 8.03-8.06 (d, 1H, 7-Ar-H)

RESULTS AND DISCUSSION

In the present investigation, for 2-(4-bromophenyl)-1H-benzimidazole anion Amberlyst A 26 (hydroxide form) was found to be a better support, followed by Indion 820 (chloride form) and Amberlite IRA 400 (chloride form), on the basis of yield of products. The superiority of solvent was found to be dependent totally on support such that acetonitrile, acetone and dichloromethane were better solvent for Amberlite IRA 400 (chloride form), Amberlyst A 26 (hydroxide form) and Indion 820 (chloride form) respectively. Whereas for 2-(6-bromochroman-2-yl)-1H-benzimidazole, Amberlite IRA 400 (chloride form) was found to be a better support, followed by Indion 820 (chloride form) and Amberlyst A26 (hydroxide form). Among the solvents acetone was found to be the best solvent on the basis of purity and yield of products followed by other solvents as acetone> acetonitrile> dichloromethane >ethanol.

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