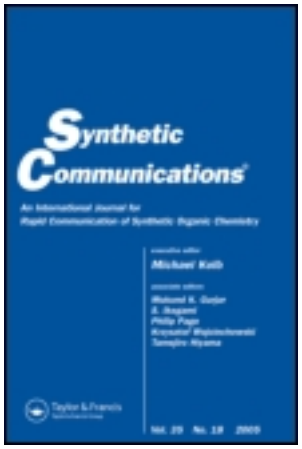

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DABCO-Promoted Efficient and Convenient Synthesis of Benzofurans

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DABCO-PROMOTED EFFICIENT AND CONVENIENT SYNTHESIS OF BENZOFURANS

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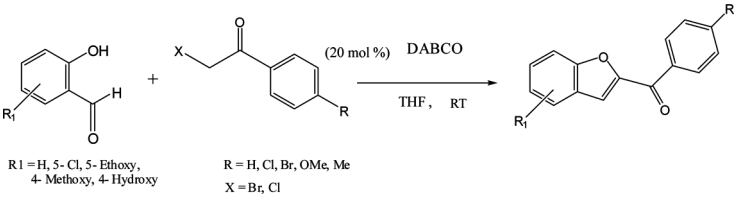
Organic Chemistry Division I, Indian Institute of Chemical Technology, Hyderabad, India

GRAPHICAL ABSTRACT



Abstract *An efficient and convenient synthesis of benzofurans has been described from phenacyl halides and* o*-hydroxy benzaldehyde in the presence of DABCO. The procedure is applicable for a variety of phenacyl halides and provide a variety of benzofurans. DABCO act as a base and as well as nucleophile.*

Keywords DABCO; phenacyl halide; salicylaldehyde

INTRODUCTION

Many biologically active natural products [1] contain a benzofuran ring as a core unit. Some of the benzofuran derivatives[2] find applications as pharmaceuticals,[3] antifungal agents,[4] antitumor agents,[5] antioxidants, and as antagonists of angoitension II.[6] In addition to this, a few benzofuran derivatives are used in cosmetic formulations[7] and act as brightening agents.[8] Because of the biological importance of benzofurans, there is continuous interest in the development of convenient and efficient synthesis of benzofurans. There are various approaches[9] for the construction of benzofuran ring from different starting materials, but these methods are not popular because starting material is not readily available and use of Pd catalyst[10] is expensive. Most commonly, the Rap–Stoermer reaction[11] has been employed for the synthesis of benzofuran, which involves the cyclization of phenacyl bromide with *o*-hydroxy benzaldehyde in the presence of a base. This strategy is widely accepted because of the easy availability of starting material, which may

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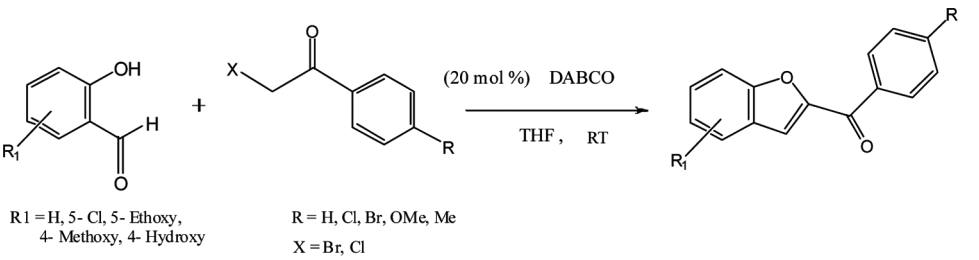
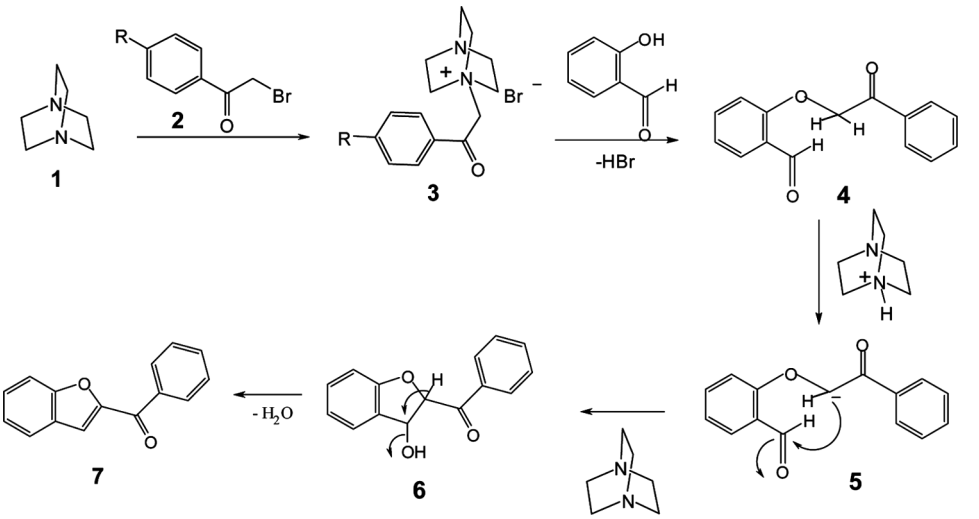


Scheme 1. DABCO-mediated efficient and convenient synthesis of benzofurans.

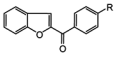
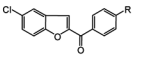
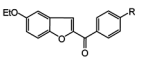
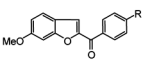
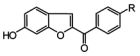
generate a large number of benzofuran derivatives. However, the reported methods have some disadvantages such as use of corrosive strong bases,[12] which are detrimental to other functionalities such as ester and nitrile. In addition to this, some of the methods require expensive palladium catalyst, high boiling solvents (dimethylformamide, DMF),[13] and longer reaction time (24–72 h).[14] In view of this, there is a need to develop efficient, convenient, and safe general method for the synthesis of benzofurans that avoids the use of harmful solvents.

1,4-Diazabicyclo[2,2,2]octane (DABCO) has been employed as a organic-hindered base for various organic reactions such as deprotection of peptides,[15] as a catalyst for the Baylis–Hillman reaction,[16] isoxazole preparation[17] *o*-alkylation of phenols,[18] and deprotection of benzylic trimethylsilyl ethers.[19] To the best of our knowledge, there is no report on the synthesis of benzofuran using organic bases. In continuation of our research in the development of nonmetallic reagents,[20] herein we report a simple, efficient, and general method for the preparation of substituted benzofurans by the reaction of salicylaldehyde with phenacyl bromide (Scheme 1).



Scheme 2. Plausible mechanism for the preparation of benzofuran.

Table 1. Synthesis of benzofuran compounds from *o*-hydroxy salicylic acid and phenacyl halides

Entry	Salicyladehyde	Phenacyl halide	Time (min.)	[a]Product	[b]Yield (ref)
					
1		R = H, X = Br	6	R = H	94 (23)
2		R = H, X = Cl	6	R = H	91 (23)
3		R = Cl, X = Br	8	R = Cl	89 (23)
4		R = Cl, X = Cl	8	R = Cl	90 (23)
5		R = Br, X = Br	8	R = Br	87 (2)
6		R = Br, X = Cl	9	R = Br	86 (2)
7		R = OMe, X = Br	5	R = OMe	95 (24)
8		R = OMe, X = Cl	4	R = OMe	95 (24)
9		R = Me, X = Br	5	R = Me	93 (25)
10		R = Me, X = Cl	6	R = Me	92 (25)
					
11		R = H, X = Br	5	R = H	96 (26)
12		R = H, X = Cl	5	R = H	95 (26)
13		R = Cl, X = Br	7	R = Cl	92 (26)
14		R = Cl, X = Cl	8	R = Cl	92 (26)
15		R = Br, X = Br	8	R = Br	91 (3)
16		R = Br, X = Cl	8	R = Br	90 (3)
17		R = OMe, X = Br	4	R = OMe	97 (26)
18		R = OMe, X = Cl	4	R = OMe	97 (26)
19		R = Me, X = Br	5	R = Me	96 (26)
20		R = Me, X = Cl	5	R = Me	95 (26)
					
21		R = H, X = Br	9	R = H	88
22		R = H, X = Cl	9	R = H	87
23		R = Cl, X = Br	11	R = Cl	86
24		R = Cl, X = Cl	12	R = Cl	86
25		R = Br, X = Br	11	R = Br	86
26		R = Br, X = Cl	12	R = Br	85
27		R = OMe, X = Br	8	R = OMe	93
28		R = OMe, X = Cl	8	R = OMe	93
29		R = Me, X = Br	9	R = Me	92
30		R = Me, X = Cl	8	R = Me	90
					
31		R = H, X = Br	12	R = H	89 (12)
32		R = H, X = Cl	12	R = H	88 (12)
33		R = Cl, X = Br	14	R = Cl	88 (25)
34		R = Cl, X = Cl	15	R = Cl	87 (25)
35		R = Br, X = Br	15	R = Br	87
36		R = Br, X = Cl	16	R = Br	88
37		R = OMe, X = Br	10	R = OMe	90 (27)
38		R = OMe, X = Cl	10	R = OMe	89 (27)
39		R = Me, X = Br	11	R = Me	89
40		R = Me, X = Cl	11	R = Me	87
					
41		R = H, X = Br	15	R = H	84 (25)
42		R = H, X = Cl	15	R = H	83 (25)
43		R = Cl, X = Br	16	R = Cl	82
44		R = Cl, X = Cl	16	R = Cl	81
45		R = Br, X = Br	17	R = Br	80
46		R = Br, X = Cl	18	R = Br	81
47		R = OMe, X = Br	12	R = OMe	88
48		R = OMe, X = Cl	12	R = OMe	89
49		R = Me, X = Br	14	R = Me	88
50		R = Me, X = Cl	15	R = Me	88

[a]All the exhibited physical and spectral (NMR, mass, IR) properties in accordance with the assigned structure.

[b]Isolated yield.

Initially we have carried out the reaction of salicylaldehyde (1 equi.) and α-bromo acetophenones (1 equi.) in the presence of 10 mol% of DABCO at room temperature and the expected product benzofuran was isolated in 60% yield (15 min). To improve the yield, the reaction was performed with increased DABCO (15, 20 mol%). It was noted that 20 mol% DABCO was optimal. Decrease in (10 mol%) or increase (25 mol%) did not improve the yield. Next, the reaction was studied in different solvents such as benzene, toluene, dichloromethane, tetrahydrofuran THF and acetonitrile. THF was the solvent of choice in terms of reaction time and yield. We presume that initially phenacyl bromide (**2**) reacts with DABCO (**1**) and forms the quaternary salt 3.[21] Later, it reacts with salicylaldehyde. Subsequent cyclization dehydration gives the expected product (**7**). DABCO act as a base as well as nucleophile[22] (Scheme 2).

Next we investigated various substituted salicylaldihyde and phenacyl bromide in the optimized condition. It was observed that salicylaldehyde with electron-withdrawing substituents (entries 1–20) reacted effectively with phenacyl bromide and led to good yields of benzofuran, whereas the reaction of benzaldehyde bearing electron-donating substituents (entries 21–50) gave relatively poor yields. The present protocol was very efficient and applicable for a variety of phenacyl halides. The importance of the present procedure is that phenacyl chloride also reacts efficiently and results in corresponding benzofurans. This method may be applicable for the preparation of large number of benzofurans because of the easy availability of phenacyl chloride and salicyladehyde. Some of the reported methods require corrosive base, higher temperature and longer reaction time. However, the present procedure using DABCO was very efficient at room temperature and resulted in good yield. From Table 1, it can be observed that substituted phenacyl halides such as bromo and chloro also react smoothly to give benzofuran in good yield.

In conclusion, we have developed an efficient, convenientm and mild protocol for the synthesis of functionalized benzofurans using DABCO. The method is applicable for a variety of functionalized aldehyde as well as phenacyl halides. Moreover, the use of organic base, operational simplicity, and efficient reaction are distinct advantages of the protocol.

EXPERIMENTAL

All reactions were carried out without any special precautions in an atmosphere of air. Chemicals were purchased from Fluka and S. D. Fine Chemicals. thin-layer chromatography (TLC) used precoated silica-gel plates (60 F_{254}, 0.2 mm layer; E. Merk ^{1}HNMR spectra were measured on Varian 200 or Bruker 300 spectrometers in $CDCl_3$; δ in ppm, J in hertz. Mass spectra were determined on VG Autospec; in m/z.

General Procedure

A mixture of salicylaldehyde (1 equi.), phenacyl halide (1 equi.), and DABCO (20 mol% in 2 ml of tetrahydrofuran, THF) was stirred at room temperature for the stipulated time period (see Table 1). After completion of the reaction as indicated by TLC, it was diluted with water and extracted with ethyl acetate. The combined

organic layer was washed with water and dried over Na_2SO_4. Removal of solvent under reduced pressure gave crude products, which were purified through a column (hexane–EtoAc) to get the pure product. All the products were characterized by infrared (IR), mass, and NMR spectroscopy.

Characteristic Data of New Compounds

Entries (21 and 22). Solid; mp 152–154 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.56 (t, 3H, $J = 6.7$ Hz), 4.30 (q, 2H, $J = 6.7$ Hz), 7.11−7.45 (m, 4H), 7.66−7.69 (m, 5H); FABMS: m/z 267 (M^+). IR (KBR) $\nu = 3022$, 2999, 1670, 1512, 1388, 1040, 817, 715 cm^{-1}. HRMS calculated for $C_{17}H_{14}O_3$: 267.0945; gound: 267.0927. Anal. calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.29; O, 18.02. Found: C, 76.83; H, 5.38, O; 18.01.

Entries (23 and 24). Solid; mp 168−174 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.55 (t, 3H, $J = 6.7$ Hz), 4.31 (q, 2H, $J = 6.7$ Hz), 6.90 (d, 1H, $J = 7.5$ Hz), 7.20 (t, 1H, $J = 7.5$ Hz), 7.31 (d, 1H, $J = 3.0$ Hz), 7.50 (d, 2H, J = 8.3 Hz), 7.62 (s, 1H), 8.22 (d, 2H, $J = 8.3$ Hz); FABMS: m/z 301 ($M^+ + 1$), 300, 284, 279. IR (KBR) $\nu = 3020$, 2998, 1672, 1500, 1380, 1040, 807, 725 cm^{-1}. HRMS calculated for $C_{17}H_{13}ClO_3$: 300.0553, found: 300.0327. Anal. calcd. for $C_{17}H_{13}ClO_3$: C, 67.89; H, 4.36; O, 15.96. Found: C, 67.83; H, 4.38; O, 15.88.

Entries (25 and 26). Solid; mp 176-178 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.52 (t, 3H, $J = 6.7$ Hz), 4.22 (q, 2H, $J = 6.7$ Hz), 6.99 (1H, d, $J = 7.1$ Hz), 7.12 (t, 1H, $J = 7.1$ Hz), 7.32−7.70 (m, 4H), 8.1 (d, 2H, $J = 8.7$ Hz); FABMS: m/z 346, 344 (M^+). IR (KBR) $\nu = 3012$, 2989, 1679, 1380, 1044, 819, 735 cm^{-1}. HRMS calculated for $C_{17}H_{13}BrO_3$: 344.0048; found: 344.0042. Anal. calcd. for $C_{17}H_{13}BrO_3$: C, 59.15; H, 3.80; O, 13.90. Found: C, 59.13; H, 3.78; O, 13.77.

Entries (27 and 28). Solid; mp 192–194 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.56 (t, 3H, $J = 6.7$ Hz), 3.78 (s, 3H), 4.30 (q, 2H, $J = 6.7$ Hz), 7.00 (m, 3H), 7.2 (s, 1H), 7.77–8.10 (m, 4H); FABMS: m/z 319 (M^++Na). IR (KBR) $\nu = 3010$, 1677, 1520, 1368, 1060, 827, 725 cm^{-1}. HRMS calculated for $C_{18}H_{16}O_4Na$: 319.0946; found: 319.0732. Anal. calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; O, 21.60. Found: C, 72.93; H, 5.43; O, 21.55.

Entries (29 and 30). Solid; mp 186–188 °C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.55 (t, 3H, $J = 6.7$ Hz), 2.31 (s, 3H), 4.31 (q, 2H, $J = 6.7$ Hz), 6.90 (d, 1H, $J = 7.5$ Hz), 7.20 (t, 1H, $J = 7.5$ Hz), 7.11–7.75 (m, 6H); FABMS: m/z 281 ($M^+ + 1$). IR (KBR) $\nu = 3022$, 2999, 1667, 1377, 1050, 817, 733 cm^{-1}. HRMS calculated for $C_{18}H_{16}O_3$: 280.1099; found: 280.1097. Anal. calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75; O, 17.12. Found: C, 77.10; H, 5.68; O, 17.11.

Entries (35 and 36). Solid; mp 176–178 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.81 (s, 3H), 7.15 (d, 1H, $J = 3.14$ Hz), 7.28 (d, 2H, $J = 7.6$ Hz), 7.90–8.11 (m, 5H); FABMS: m/z 352 (M^++Na). IR (KBR) $\nu = 3000$, 2977, 1667, 1522, 1378, 1020, 827 cm^{-1}. HRMS calculated for $C_{16}H_{11}BrO_3Na$: 352.9789; found: 352.9777. Anal. calcd. for $C_{16}H_{11}BrO_3$: C, 58.03; H, 3.35; O, 14.49. Found: C, 58.11; H, 3.32; O, 14.41.

Entries (39 and 40). Solid; mp 155–157 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.30 (s, 3H), 3.81 (s, 3H), 7.15 (s, 1H), 7.32 (d, 2H, $J = 7.6$ Hz), 7.70 (s, 1H), 7.88–8.01 (m, 4H); FABMS: m/z 267 ($M^+ + 1$). IR (KBR) $\nu = 3022$, 1667, 1532, 1049 cm^{-1}. HRMS calculated for $C_{17}H_{14}O_3$: 266.0942; found: 266.0927. Anal. calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30; O, 18.02. Found: C, 76.60; H, 5.28; O, 18.11.

Entries (43 and 44). Solid; mp 222–224 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.11 (s, 1H), 7.27 (d, 1H, $J = 7.7$ Hz), 7.41 (d, 1H, $J = 8.1$ Hz), 7.66 (s, 1H), 8.1 (d, 2H, $J = 8.6$ Hz), 8.21 (d, 2H, $J = 8.6$ Hz); FABMS: m/z 295 (M^++Na). IR (KBR) $\nu = 3002$, 2979, 1690, 1502, 1050, 715 cm^{-1}. HRMS calculated for $C_{15}H_9ClO_3Na$: 295.01378; found: 295.01372. Anal. Calcd. for $C_{15}H_9ClO_3$: C, 66.07; H, 3.33; O, 17.60. Found: C, 66.10; H, 3.38; O, 17.61.

Entries (45 and 46). Solid; mp 212–214 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.05–7.40 (m, 3H), 7.76 (s, 1H), 7.9–8.0 (m, 4H); FABMS: m/z 318, 316 (M^+). IR (KBR) $\nu = 3012$, 2999, 1677, 1512, 1488, 1041, 715 cm^{-1}. HRMS calculated for $C_{15}H_9BrO_3$: 315.9735; found: 315.9722. Anal. calcd. for $C_{15}H_9BrO_3$: C, 56.81; H, 2.86; O, 15.13. Found: C, 56.80; H, 2.88; O, 15.11.

Entries (47 and 48). Solid; mp 201–203 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.80 (s, 3H), 6.95 (m, 2H), 7.41 (s, 1H), 7.55 (d, 1H, $J = 6.7$ Hz), 7.77 (d, 1H, $J = 7.9$ Hz), 7.97 (s, 1H), 7.99 (m, 2H); FABMS: m/z 269 ($M^+ + 1$). IR (KBR) $\nu = 3020$, 1667, 1522, 1388, 1034 cm^{-1}. HRMS calculated for $C_{16}H_{12}O_4$: 268.0735; found: 268.0732. Anal. calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51; O, 23.86. Found: C, 71.60; H, 4.48; O, 23.81.

Entries (49 and 50). Solid; mp 212–214 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.42 (s, 3H), 7.20–7.41 (m, 3H), 7.66 (s, 1H), 7.81–8.12 (m, 4H); FABMS: m/z 253 ($M^+ + 1$). IR (KBR) $\nu = 3002$, 2999, 1660, 1378, 1040, cm^{-1}. HRMS calculated for $C_{16}H_{12}O_3$: 252.0786, Found: 252.0778. Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79; O, 19.03. Found: C, 76.10; H, 4.78; O, 19.01.

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