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Article

Direct, Rapid and Convenient Synthesis of Esters and Thioesters Using PPh_3/*N*-Chlorobenzotriazole System

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Desenvolvemos um método eficiente de esterificação e tioesterificação de uma série de ácidos carboxílicos com diferentes álcoois e tióis usando o reagente misto PPh_3/*N*-clorobenzotriazol em CH_2Cl_2 a temperatura ambiente.

We have developed an efficient method for esterification and thioesterification of various carboxylic acids with different alcohols and thiols using PPh_3/*N*-chlorobenzotriazole mixed reagent in CH_2Cl_2 at room temperature.

Keywords: PPh_3, *N*-chlorobenzotriazole (NCBT), esters, thioesters

Introduction

Esterification is the fundamental and routinely used functional group transformation in organic chemistry[1] and it is extensively employed for the protection and further manipulation of the carboxylic acid functional group as well as the synthesis of natural products. Traditionally, the simple condensation between a carboxylic acid and an alcohol is the most straightforward way to esterification. The difficulty stems primarily from the equilibration of the condensation reaction. The commonest approach to bias the equilibrium in favor of the product side is either by using the reactants in excess and/or continuously removing of the water formed during the reaction. The former treatment is not desirable in terms of "atom economy"[2] since the excess reactant remains to be separated from the reaction mixture. On the other hand, azeotropy is most frequently invoked, but a variety of dehydration methods have been put forth, although 100% conversion and, hence, 100% yield are, in general, not easy to achieve. Another problem emerges from the base or acid catalysts which are inevitably employed in this reaction. Under such conditions, the tolerance of a wide spectrum of functional groups that is often required in modern synthetic chemistry is not easy to achieve. Activation of the carboxylic acid or alcohol components with a stoichiometric amount of promoter such as carbodiimides,[3] diethylazodicarboxylate,[4] 5,5´-dimethyl-3,3'-azoisoxazole,[5] azopyridines,[6] $[\{Cl(C_6F_{13}C_2H_4)_2SnOSn(C_2H_4C_6F_{13})_2Cl\}_2]$ graphite bisulfate,[7] functionalized acidic ionic liquids,[8,9] $TiO(acac)_2$,[10] is another possible but uneconomical choice. These reactions historically faced purification challenges and often haunt the chemist in the isolation of the desired product. Development a new, simple, efficient, and highly profitable esterification method under mild reaction conditions and without tedious and difficult purification steps, is highly desirable and challenging.

The *N*-halo reagents in combination with PPh_3 have found widespread use in synthetic organic chemistry.[11] In the present study, esterification and thioesterification of carboxylic acids were investigated by using *N*-chlorobenzotriazole (NCBT, as an *N*-halo reagent) PPh_3 system. The reaction proceeds under mild, essentially neutral conditions and has been well documented for a variety of substrates.

Experimental

General

The products were purified by column chromatography. The purity determinations of the products were accomplished by thin layer chromatography (TLC) on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The Fourier transform infrared (FTIR) spectra were recorded on an Avatar 370 FT-IR Therma Nicolet

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spectrometer. The nuclear magnetic resonance (NMR) spectra were provided on Bruker Ultrashield Avance III 400 MHz instruments in $CDCl_3$. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV, in *m/z* (rel%). NCBT was prepared and purified by the method described in the literature.[12] Preparation of benzyl benzoate by using PPh_3/5,5'-dimethyl-3,3'-azoisoxazole, PPh_3/4,4'-azopyridine, Ph_2PCl/I_2/imidazole and PPh_3/[bis(acetoxy) iodo]benzene/diethylazodicarboxylate (DEAD) mixed reagents was performed according the methods reported previously.[5,6,13,14]

Preparation of benzyl benzoate by using PPh_3/trichloroisocyanuric acid (TCCA)

To a cold solution of PPh_3 (0.327 g, 1.25 mmol) in CH_2Cl_2 (3 mL), TCCA (0.0974 g, 0.42 mmol) was added with continuous stirring. Benzoic acid (0.122 g, 1 mmol) was then added and stirring was continued for 15 min. Benzyl alcohol (0.270 g, 2.5 mmol) was added and the temperature was raised up to room temperature. The white suspension was neutralized by triethylamine (0.175 mL). Stirring was continued for 2.5 h at room temperature. The progress of the reaction was followed by TLC. Upon completion of the reaction, the concentrated residue was passed through a short silica-gel column using *n*-hexane–ethyl acetate (8:1) as eluent. Benzyl benzoate was obtained with 85% yield after removing the solvent under reduced pressure.

Preparation of benzyl benzoate by using PPh_3/N-bromosuccinimide (NBS)

To a cold solution of PPh_3 (0.327 g, 1.25 mmol) in CH_2Cl_2 (3 mL), NBS (0.223 g, 1.25 mmol) was added with continuous stirring. Benzoic acid (0.122 g, 1 mmol) was then added and stirring was continued for 15 min. Benzyl alcohol (0.270 g, 2.5 mmol) was added and the temperature was raised up to room temperature. The red suspension was neutralized by triethylamine (0.175 mL). Stirring was continued for 4.5 h at room temperature. The progress of the reaction was followed by TLC. Upon completion of the reaction, the concentrated residue was passed through a short silica-gel column using *n*-hexane–ethyl acetate (8:1) as eluent. Benzyl benzoate was obtained with 40% yield after removing the solvent under reduced pressure.

Preparation of benzyl benzoate by using PPh_3/N-chlorosuccinimide (NCS)

To a cold solution of PPh_3 (0.327 g, 1.25 mmol) in CH_2Cl_2 (3 mL), NCS (0.166 g, 1.25 mmol) was added with continuous stirring. Benzoic acid (0.122 g, 1 mmol) was then added and stirring was continued for 15 min. Benzyl alcohol (0.270 g, 2.5 mmol) was added and the temperature was raised up to room temperature. The pale yellow solution was neutralized by triethylamine (0.175 mL). Stirring was continued for 3 h at room temperature. The progress of the reaction was followed by TLC. Upon completion of the reaction, the concentrated residue was passed through a short silica-gel column using *n*-hexane–ethyl acetate (8:1) as eluent. Benzyl benzoate was obtained with 80% yield after removing the solvent under reduced pressure.

Preparation of benzyl benzoate by using PPh_3/NCBT

To a cold solution of PPh_3 (0.327 g, 1.25 mmol) in CH_2Cl_2 (3 mL), freshly prepared NCBT (0.194 g, 1.25 mmol) was added with continuous stirring. Benzoic acid (0.122 g, 1 mmol) was then added and stirring was continued for 15 min. Benzyl alcohol (0.270 g, 2.5 mmol) was added and the temperature was raised up to room temperature. The pale yellow solution was neutralized by triethylamine (0.175 mL). Stirring was continued for 40 min at room temperature. The progress of the reaction was followed by TLC. Upon completion of the reaction, the concentrated residue was passed through a short silica-gel column using *n*-hexane–ethyl acetate (8:1) as eluent. Benzyl benzoate was obtained with 95% yield after removing the solvent under reduced pressure.

Benzyl benzoate (Table 3, entry 1)

m.p. 20-21°C (Lit. 19-21 °C);[15] IR (neat) υ_{max}/cm^{-1} 3423, 3088, 3064, 3033, 2949, 2892, 1716 (C=O), 1601, 1585, 1451, 1376, 1314, 1270 (C–O), 1175, 1109, 1069, 710, 697; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.14-8.11 (m, 2H, ArH), 7.62-7.58 (m, 1H, ArH), 7.51-7.41 (m, 7H, ArH), 5.41 (s, 2H, Ph$\underline{CH_2}$).

Benzyl 4-methylbenzoate (Table 3, entry 2)

Solid; m.p. 45-46 °C (Lit. 45-46 °C);[16] IR (KBr) υ_{max}/cm^{-1} 3391, 3088, 3031, 2962, 2896, 1706 (C=O), 1609, 1454, 1370, 1267 (C–O), 1175, 1100, 751, 700; MS (EI) *m/z* 226 (M^+, 10%), 118 (M^+–$PhCH_2O$, 100%), 91 ($PhCH_2$, 90%).

Benzyl 3,5-dimethylbenzoate (Table 3, entry 3)

Solid; m.p. 65-66 °C (Lit. 66-67 °C);[17] IR (KBr) υ_{max}/cm^{-1} 3423, 3063, 3033, 3009, 2951, 2918, 1717 (C=O), 1608, 1498, 1555, 1308, 1211 (C–O), 1115, 1010, 766, 754, 697; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 7.73 (s, 2H, ArH), 7.50-7.48 (d, 2H, *J* 6.8 Hz, ArH) 7.45-7.36 (m, 3H, ArH), 7.22 (s, 1H, ArH), 5.39 (s, 2H, Ph$\underline{CH_2}$), 2.39 (s. 6H, $2CH_3$).

Benzyl 4-methoxybenzoate (Table 3, entry 4)

m.p. 24-26 °C (Lit. 25-27 °C);[18] IR (neat) υ_{max}/cm^{-1} 3415, 3068, 2962, 2937, 2839, 1712(C=O), 1606, 1581, 1511, 1456, 1376, 1316, 1270, 1256 (C–O), 1167, 1099, 1029, 769, 696; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.91 (td, 2H, *J* 9.2, 2.4 Hz, ArH), 7.49-7.46 (m, 2H, ArH), 7.44-7.29 (m, 3H, ArH), 6.97-6.93 (m, 2H, ArH), 5.37 (s, 2H, Ph$\underline{CH_2}$), 3.89 (s, 3H, O$\underline{CH_3}$).

Benzyl 2-chlorobenzoate (Table 3, entry 5)

m.p. 18-20 °C; IR (neat) υ_{max}/cm^{-1} 3064, 3027, 2925, 2847, 1722 (Lit. 1729, C=O),[19] 1589, 1484, 1451, 1378, 1290 (C–O), 1131, 1046, 936, 751, 740.

Benzyl 4-chlorobenzoate (Table 3, entry 6)

m.p. 25-26 °C (Lit. 25-26 °C);[16] IR (neat) υ_{max}/cm^{-1} 3431, 3064, 3035, 2949, 1721 (C=O), 1594, 1487, 1400, 1270 (C–O), 1114, 1092, 1014, 758, 696.

Benzyl 4-bromobenzoate (Table 3, entry 7)

Solid; m.p. 51-52 °C (Lit. 52-53 °C);[16] IR (KBr) υ_{max}/cm^{-1} 3415, 3072, 3039, 2974, 2892, 1715 (C=O), 1588, 1455, 1396, 1269 (C–O), 1169, 1089, 1008, 759, 698; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 7.97 (d, 2H, *J* 8.4 Hz, ArH), 7.61 (d, 2H, *J* 8.4 Hz, ArH), 7.49-7.38 (m, 5H, ArH), 5.40 (s, 2H, Ph$\underline{CH_2}$); MS (EI) *m/z* 291 (M$^+$, 5%), 182 (M$^+$–$PhCH_2O$, 87%), 91 ($PhCH_2$, 87%).

Benzyl 3,4-dichlorobenzoate (Table 3, entry 8)

Solid; m.p. 57-58 °C (Lit. 58-60 °C);[16] IR (KBr) υ_{max}/cm^{-1} 3092, 3072, 3039, 2953, 2892, 1724 (C=O), 1585, 1564, 1458, 1379, 1273 (C–O), 1236, 1106, 1032, 757, 696; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.16 (d, 1H, *J* 2 Hz, ArH), 7.91 (dd, 1H, *J* 8.4, 2 Hz, ArH), 7.53 (d, 1H, *J* 8.4 Hz, ArH), 7.48-7.39 (m, 5H, ArH), 5.39 (s, 2H, Ph$\underline{CH_2}$); MS (EI) *m/z* 284 (M+4, 5%), 282 (M+2, 26%), 280 (M$^+$, 32%), 245 (M$^+$–Cl, 38%), 173 (M$^+$–$PhCH_2O$, 100%) 145 (M$^+$–$PhCl_2$, 35%), 91($PhCH_2$, 100%).

Benzyl 4-nitrobenzoate (Table 3, entry 9)

Solid; m.p. 82-83 °C (Lit. 82-83°C);[16] IR (KBr) υ_{max}/cm^{-1} 3112, 3051, 1712 (C=O), 1604, 1522, 1347, 1277 (C–O), 1121, 1104, 744, 715.695; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.32-8.25 (m, 4H, ArH), 8.50-8.40 (m, 5H, ArH), 5.44 (s, 2H, Ph$\underline{CH_2}$); MS (EI) *m/z* 257 (M$^+$, 10%), 150 (M$^+$–$PhCH_2O$, 100%), 91 (M$^+$–$PhCH_2$, 100%).

Benzyl 3-nitrobenzoate (Table 3, entry 10)

Solid; m.p. 48-49 °C (Lit. 48-49 °C);[20] IR (KBr) υ_{max}/cm^{-1} 3436, 3084, 3039, 2962, 2872, 1727 (C=O), 1613, 1531, 1350, 1293, 1258 (C–O), 1130, 1070, 717, 697; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.91 (s, 1H, ArH), 8.45-8.41 (m, 2H, ArH), 7.68 (t, 1H, *J* 8 Hz, ArH), 7.51-7.29 (m, 5H, ArH), 5.45 (s. 2H, Ph$\underline{CH_2}$).

Benzyl cinnamate (Table 3, entry 11)

Solid; m.p. 31-32 °C (Lit. 32-33 °C);[21] IR (KBr) υ_{max}/cm^{-1} 3064, 3027, 2966, 2896, 1711 (C=O), 1636, 1310, 1162 (C–O), 980, 767, 697; MS (EI) *m/z* 238 (M$^+$, 10%), 130 (M$^+$–$PhCH_2O$, 100%), 103 ($PhCH_2O$, 90%), 91 ($PhCH_2$, 90%).

(*E*)-Benzyl 3-(4-chlorophenyl)acrylate (Table 3, entry 12)

Solid; m.p. 122-124 °C; IR (KBr) υ_{max}/cm^{-1} 3064, 3027, 2953, 1708 (Lit. 1709, C=O),[22] 1637, 1488, 1309, 1166 (C–O), 988, 820, 695; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 7.70 (d, 1H, *J* 16 Hz, Ph$\underline{CH}$=CH–), 7.49-7.29 (m, 9H, ArH), 6.49 (d, 1H, *J* 16 Hz, PhCH=$\underline{CH}$–), 5.29 (s, 2H, Ph$\underline{CH_2}$); MS (EI) *m/z* 274 (M+2, 10%) 272 (M$^+$, 35%), 164 (M$^+$–$PhCH_2O$), 91 (M$^+$–$PhCH_2$, 100%).

(*E*)-Benzyl 3-(3-nitrophenyl)acrylate (Table 3, entry 13)

Solid; m.p. 148-149 °C (Lit. 147-149 °C);[22] IR (KBr) υ_{max}/cm^{-1} 3072, 2925, 1711 (C=O), 1641, 1526, 1351, 1176 (C–O), 1008, 730; MS (EI) *m/z* 282 (M$^+$, 10%), 175 (M$^+$–$PhCH_2O$, 81%), 103 ($PhCH_2O$, 80%) 91 ($PhCH_2$, 100%).

Benzyl 2-phenylacetate (Table 3, entry 14)

Solid; m.p. 51-52 °C (Lit. 52 °C);[23] IR (KBr) υ_{max}/cm^{-1} 3084, 3060, 3031, 2953, 1737 (C=O), 1496, 1454, 1380, 1260 (C–O), 1145, 749, 695; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 7.41-7.29 (m, 10H, ArH), 5.17 (s, 2H, Ph$\underline{CH_2}$–O), 3.71 (s, 2H, Ph$\underline{CH_2}$–CO).

Benzyl 2,2-diphenylacetate (Table 3, entry 15)

m.p. 34-35 °C (Lit. 35 °C);[24] IR (neat) υ_{max}/cm^{-1} 3084, 3063, 3030, 2953, 1736 (C=O), 1600, 1496, 1453, 1184, 1144 (C–O), 1004, 975, 744, 696; MS (EI) *m/z* 193 (M$^+$–$PhCH_2O$, 30%), 166 ($(Ph)_2CH$, 100%), 91 ($PhCH_2$, 80%).

Benzyl 2-(4-methoxyphenyl)acetate (Table 3, entry 16)

Solid; m.p. 142-144 °C (Lit. 141-144 °C);[25] IR (KBr) υ_{max}/cm^{-1} 3063, 3035, 2957, 2839, 1713 (C=O), 1606, 1511, 1455, 1315, 1257 (C–O), 1167, 1100, 1028, 768, 750, 796; MS (EI) *m/z* 256 (M$^+$, 5%), 164 (M$^+$–$PhCH_2$, 20%), 149 (M$^+$–$PhCH_2O$, 80%), 91 ($PhCH_2$, 80%).

Benzyl stearate (Table 3, entry 17)

Solid; m.p. 44-45°C (Lit. 44-45 °C);[26] IR (KBr) υ_{max}/cm^{-1} 3092, 2955, 2917, 2849, 1743 (C=O), 1471, 1393, 1286 (C–O), 961.

Benzyl thiophene-3-carboxylate (Table 3, entry 18)

Solid; m.p. 139-141°C (Lit. 140-142 °C);[27] IR (KBr) υ_{max}/cm^{-1} 3111, 3035, 1716 (C=O), 1522, 1407, 1261 (C–O), 1187, 1100, 747; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.18-8.17 (m, 1H, ArH), 7.60-7.58 (m, 1H, ArH), 7.48-7.33 (m, 6H ArH), 5.36 (s, 2H, Ph$\underline{CH_2}$).

Phenethyl 4-nitrobenzoate (Table 3, entry 19)

Solid; m.p. 60-61 °C (Lit. 59-61 °C);[28] IR (KBr) υ_{max}/cm^{-1} 3068, 1710 (C=O), 1597, 1486, 1450, 1379, 1362, 1287 (C–O), 1051, 940, 750, 695; MS (EI) *m/z* 164 (M^+–$PhCH_2CH_2$, 17%), 149 (4-NO_2PhCO, 80%), 104 ($PhCH_2CH_2$, 100%), 91 ($PhCH_2$, 80%).

3-Phenylpropyl 4-nitrobenzoate (Table 3, entry 20):

Solid; m.p. 46-47 °C (Lit. 47-48 °C);[29] IR (KBr) υ_{max}/cm^{-1} 3120, 2958, 1716 (C=O), 1602, 1523, 1352, 1286 (C–O), 1103, 870, 746, 717, 700; MS (EI) *m/z* 284 (M^+, 5%), 149 (4-NO_2PhCO, 60%), 118 ($PhCH_2CH_2CH_2$, 100%), 91 ($PhCH_2$, 90%).

Butyl 4-nitrobenzoate (Table 3, entry 21)

m.p. 33-34 °C (Lit. 34-35 °C);[30] IR (neat) υ_{max}/cm^{-1} 3117, 3080, 3060, 2963, 2938, 2868, 1717 (C=O), 1606, 1526, 1352, 1278 (C–O), 1103, 872, 846, 786, 714; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.30 (d, 2H, *J* 8.8 Hz, ArH), 8.22 (d, 2H, *J* 8.8 Hz, ArH), 4.39 (t, 2H, *J* 6.8 Hz, O$\underline{CH_2}CH_2$), 1.83-1.76 (m, 2H, $OCH_2\underline{CH_2}$), 1.55-1.46 (m, 2H, $\underline{CH_2}CH_3$), 1.01 (t, 3H, *J* 7.2 Hz, $OCH_2\underline{CH_3}$).

1-Phenylethyl 4-nitrobenzoate (Table 3, entry 22)

Solid; m.p. 44-45 °C (Lit. 44 °C);[31] IR (KBr) υ_{max}/cm^{-1} 3113, 3039, 2978, 2933, 1723 (C=O), 1607, 1528, 1454, 1351, 1271 (C–O), 1102, 1060, 1014, 873, 841, 719; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.32-8.29 (m, 2H, ArH), 8.27-8.24 (m, 2H, ArH), 7.49-7.34 (m, 5H, ArH), 6.18 (q, 1H, *J* 6.4 Hz, O$\underline{CH}$(Ph)CH_3), 1.74 (d, 3H, *J* 6.4 Hz, OCH$\underline{CH_3}$).

Benzhydryl 4-nitrobenzoate (Table 3, entry 23)

Solid; m.p. 131-132 °C (Lit. 132 °C);[32] IR (KBr) υ_{max}/cm^{-1} 3109, 3051, 2859, 1721 (C=O), 1609, 1525, 1446, 1345, 1280 (C–O), 1261, 1116, 1103, 967, 763, 719, 699; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.33 (s, 4H, ArH), 8.47-8.35 (m, 10H, ArH), 7.17 (s, 1H, $Ph_2\underline{CH}$); MS (EI) *m/z* 333 (M^+, 10%), 182 (M^+–2Ph, 88%) 165 (M^+–NO_2PhCO_2, 100%) 151 (M^+–Ph_2CHO, 72%).

Cyclohexyl 4-nitrobenzoate (Table 3, entry 24)

Solid; m.p. 50-51 °C (Lit. 51-52 °C);[33] IR (KBr) υ_{max}/cm^{-1} 2117, 2938, 2860, 1720 (C=O), 1609, 1528, 1454, 1348, 1319, 1278 (C–O), 1115, 1013, 835, 719; MS (EI) *m/z* 168 (M^+–cyclohexyl, 45%), 149 (4-NO_2PhCO, 60%), 104 (PhCO, 100%), 82 (cyclohexyl, 90%).

Phenyl 4-nitrobenzoate (Table 3, entry 26)

Solid; m.p. 130-132 °C (Lit. 129-132 °C);[34] IR (KBr) υ_{max}/cm^{-1} 3113, 1741 (C=O), 1609, 1520, 1484, 1348, 1269 (C–O), 1183, 1079, 1017, 847; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.41 (dd, 2H, *J* 6.4, 2.8 Hz, ArH), 8.38 (dd, 2H, *J* 6.4, 2.8 Hz, ArH), 7.50-7.46 (m, 2H ArH), 7.36-7.33 (m, 1H, ArH), 7.28-7.24 (m, 2H, ArH).

m-Tolyl 4-nitrobenzoate (Table 3, entry 27)

Solid; m.p. 86-87 °C (Lit. 87 °C);[35] IR (KBr) υ_{max}/cm^{-1} 3109, 3080, 2985, 2921, 2850, 1736 (C=O), 1607, 1529, 1487, 1352, 1273 (C–O), 1236, 715; MS (EI) *m/z* 257 (M^+, 5%), 149 (M^+–(*m*-MePhO)), 103 (*m*-MePhO, 62%).

4-Chlorophenyl 4-methoxybenzoate (Table 3, entry 28)

Solid; m.p. 97-99 °C (Lit. 97-99 °C);[36] IR (KBr) υ_{max}/cm^{-1} 3015, 2982, 2847, 1727 (C=O), 1610, 1515, 1489, 1267 (C–O), 1204, 1167, 1072, 1021, 842, 761; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.16 (dd, 2H, *J* 6.8, 2 Hz, ArH), 7.41 (dd, 2H, *J* 6.8, 2 Hz, ArH), 7.17 (dd, 2H, *J* 6.8, 2 Hz, ArH), 1.48 (dd, 2H, *J* 7.2, 2 Hz, ArH), 3.92 (s, 3H, O$\underline{CH_3}$).

Phenyl stearate (Table 3, entry 29)

Solid; m.p. 48-49 °C (Lit. 49-50 °C);[37] IR (KBr) υ_{max}/cm^{-1} 2954, 2917, 2849, 1743 (C=O), 1741, 1393 (C–O), 961, 754.

S-Cyclohexyl 3,5-dimethylbenzothioate (Table 3, entry 30)

Solid; m.p. 57-58 °C (Lit. 56-58 °C);[38] IR (KBr) υ_{max}/cm^{-1} 2929, 2853, 1659 (O=C–S), 1606, 1448, 1292, 1149, 1034, 697, 861, 786, 703; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 7.58 (s, 2H, ArH), 7.20 (s, 1H, ArH), 3.73 (t, 1H, *J* 4 Hz, S$\underline{CH}$–), 2.37 (s, 6H, $2CH_3$), 2.05-1.27 (m, 10H, $\underline{CH_2}$ cyclohexyl ring).

S-Octyl 4-methoxybenzothioate (Table 3, entry 31)

m.p. 24-26 °C (Lit. 25-27 °C);[38] IR (neat) υ_{max}/cm^{-1} 3011, 2955, 2926, 2854, 1655 (O=C–S), 1602, 1578, 1508, 1462, 1315, 1259, 1213, 1167, 1031, 913; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 7.97 (d, 2H, *J* 8.8 Hz, ArH), 6.93 (d, 2H, *J* 8.8 Hz, ArH), 3.06 (t, 2H, *J* 7.6 Hz, S–$\underline{CH_2}$), 1.71-1.60 (m, 2H, CH_2), 1.43 (q, 2H, *J* 6.8 Hz, R–$\underline{CH_2}CH_3$), 1.32-1.29 (m, 8H, $4CH_2$), 0.89 (t, 3H, *J* 6.8 Hz, R–$CH_2\underline{CH_3}$).

(*E*)-*S*-Cyclohexyl 3-(3-nitrophenyl)prop-2-enethioate (Table 3, entry 32)

Solid; m.p. 141-143 °C (Lit. 142-145 °C);[39] IR (KBr) υ_{max}/cm^{-1} 2930, 2852, 1681 (O=C–S), 1530, 1448, 1350,

1050, 997, 736, 702; MS (EI) *m/z* 291 (M^+, 5%), 175 (M^+–cyclohexyl–S, 100%), 115 (cyclohexyl–S, 80%), 82 (cyclohexyl, 100%).

S-Octyl 4-nitrobenzothioate (Table 3, entry 33)

m.p. 27-29 °C (Lit. 28-30 °C);[39] IR (neat) υ_{max}/cm^{-1} 3105, 2953, 2927, 2855, 1666 (O=C–S), 1605, 1528, 1349, 1202, 923, 848.

S-Benzyl 4-nitrobenzothioate (Table 3, entry 34)

Solid; m.p. 85-86 °C (Lit. 85.4-86.5 °C);[40] IR (KBr) υ_{max}/cm^{-1} 3113, 1643 (O=C–S), 1601 1521, 1349, 1318, 1203, 1193, 930, 850, 711, 691; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.32 (dd, 2H, *J* 7.2, 2 Hz, ArH), 8.14 (dd, 2H, *J* 7.2, 2 Hz, ArH), 7.42-7.28 (m, 5H, ArH), 4.39 (s, 2H, PhCH_2).

S-Cyclohexyl 4-nitrobenzothioate (Table 3, entry 35)

Solid; m.p. 139-140 °C; IR (KBr) υ_{max}/cm^{-1} 3109, 2942, 2928, 2851, 1655 (O=C–S), 1604, 1523, 1349, 1318, 1195, 1174, 1109, 922, 885, 848, 690; ^{1}H NMR [6] (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.32-8.29 (m, 2H, ArH), 8.13-8.10 (m, 2H, ArH), 3.82-3.76 (m, 1H, SCH–), 2.06-1.48 (m, 10H, CH_2 cyclohexyl ring).

S-Benzyl 2,2-diphenylethanethioate (Table 3, entry 36)

Solid; m.p. 61-63 °C (Lit. 62-64 °C);[41] IR (KBr) υ_{max}/cm^{-1} 3333, 3088, 3064, 3027, 2917, 2843, 1680 (O=C–S), 1494, 1453, 1011, 994, 741, 698; MS (EI) *m/z* 317 (M^+, 5%), 196 (M^+–$PhCH_2S$, 10%), 166 ($(Ph)_2CH$, 100%), 91 ($PhCH_2$, 90%).

S-*p*-Tolyl benzothioate (Table 3, entry 37)

Solid; m.p. 75-77 °C (Lit. 76.5-77 °C);[42] IR (KBr) υ_{max}/cm^{-1} 3047, 2917, 2847, 1668 (O=C–S), 1482, 1450, 1274, 1203, 1169, 897, 808, 773, 689; MS (EI) *m/z* 228 (M^+, 10%), 122 (M^+–*p*-MePhS, 80%), 105 (PhCO, 100%), 91 ($PhCH_2$, 90%).

S-*p*-Tolyl 2,2-diphenylethanethioate (Table 3, entry 38)

Solid; m.p. 96-98 °C (Lit. 98 °C);[43] IR (KBr) υ_{max}/cm^{-1} 3084, 3059, 3027, 2917, 2843, 1674 (O=C–S), 1482, 1451, 981, 741, 698; MS (EI) *m/z* 316 (M^+, 3%), 193 (M^+–4-MePhS, 60%), 166 ($(Ph)_2CH$, 100%), 90 ($PhCH_2$, 80%).

Results and Discussion

In continuation of our study to extend the scope of *N*-halo reagents in conjunction with PPh_3,[11,44] we investigated the applicability of PPh_3/trichloroisocyanuric acid (TCCA), PPh_3/*N*-bromosuccinimide (NBS), PPh_3/*N*-chlorosuccinimide (NCS) and PPh_3/(NCBT) systems in direct esterification reaction of benzoic acid with benzyl alcohol (Table 1, entries 1-3 and 8). Recently, direct esterification reaction was also reported by using PPh_3 and an electron deficient reagent such as PPh_3/5,5'-dimethyl-3,3'-azoisoxazole,[5] PPh_3/4,4'-azopyridine,[6] Ph_2PCl/I_2/imidazole[13] and PPh_3/[bis(acetoxy)iodo]benzene/diethylazodicarboxylate (DEAD)[14] (Table 1, entries 4-7). As is apparent from Table 1, PPh_3/(NCBT) mixed reagent is the most efficient mixed-reagent system, for conversion of benzoic acid to benzyl benzoate. Replacement of NCBT by every above-mentioned mixed reagent systems produces benzyl benzoate in longer reaction time.

According the data from Table 1, PPh_3/NCBT system is the best choice for direct esterification of benzoic acid (Scheme 1).

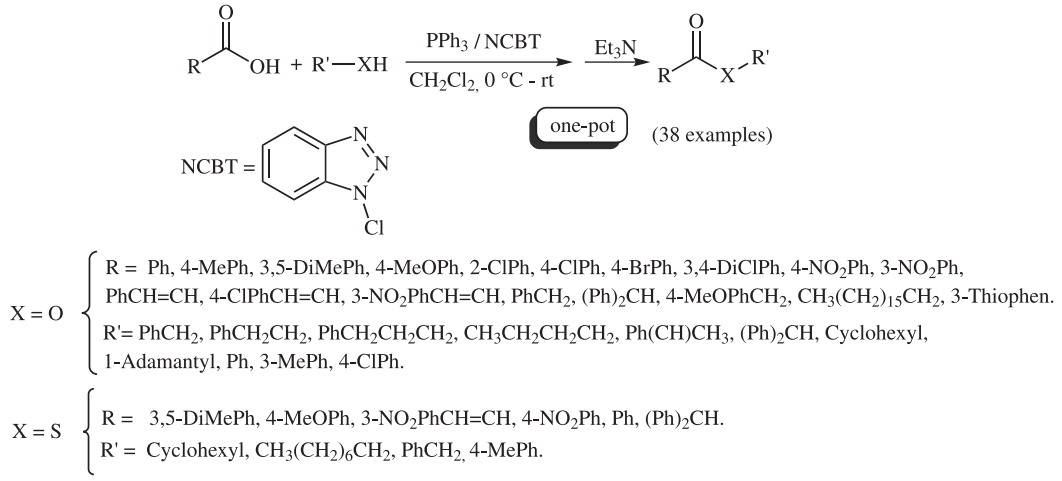
To achieve high reaction efficiency, the reaction of benzoic acid with benzyl alcohol was chosen as model reaction to investigate the applicability of PPh_3/NCBT system in direct esterification and thioesterification reactions of carboxylic acids. The effects of different molar ratios of PPh_3/NCBT/RCO_2H/ROH in various solvents were examined on the model reaction.

Treating a solution of PPh_3 (1 equiv.) and NCBT (1 equiv.) in CH_3CN at room temperature with different

Table 1. Esterification of benzoic acid with benzyl alcohol by using different mixed reagent system[a]

entry	Mixed reagents	Reaction condition	time / h	Isolated yield / %
1	PPh_3/trichloroisocyanuric acid (TCCA)	CH_2Cl_2/r.t.[b]	2.5	85
2	PPh_3/*N*-bromosuccinimide (NBS)	CH_2Cl_2/r.t.[b]	4.5	40
3	PPh_3/*N*-chlorosuccinimide (NCS)	CH_2Cl_2/r.t.[b]	3	80
4[5]	PPh_3/5,5'-dimethyl-3,3'-azoisoxazole	CH_3CN/reflux	6.5	89
5[6]	PPh_3/4,4'-azopyridine	CH_3CN/reflux	3	86
6[13]	Ph_2PCl, I_2, imidazole	CH_3CN/reflux	4	91
7[14,c]	PPh_3/[bis(acetoxy)iodo]benzene/diethylazodicarboxylate (DEAD)	THF/r.t.[b]	16	76
8	PPh_3/*N*-chlorobenzotriazole (NCBT)	CH_2Cl_2/r.t.[b]	40 min	95

[a]The experimental details are shown in experimental section; [b]r.t.: room temperature; [c]the result corresponds to the esterification reaction of *p*-nitrobenzoic acid with benzyl alcohol.



Scheme 1.

molar ratios of benzoic acid and benzyl alcohol afforded benzyl benzoate in high yield over 2-5 h (Table 2, entries 1-4). Increasing the molar ratios of PPh_3/NCBT and benzyl alcohol in CH_3CN gave 100% conversion of benzoic acid to benzyl benzoate in 40 min (Table 2, entries 5-6). As the applying 1.25/1.25/1/2.5 molar ratios of PPh_3/NCBT/ RCO_2H/ROH in CH_3CN gave 100% conversion of benzoic acid to benzyl benzoate in 40 min, esterification reaction was examined in CH_2Cl_2 at the same conditions. Surprisingly, there is no difference between the rate of esterification reaction in CH_3CN and CH_2Cl_2 (Table 2, compare entries 5 and 7). At the same conditions performing the reaction in other solvents such as THF, $CHCl_3$, 1,4-dioxane, acetone, toluene and hexane produced the desired product with lower yield and in longer reaction time (Table 2, entries 8-13). The best result was obtained by applying 1.25/1.25/1/2.5 molar ratios of PPh_3/NCBT/ RCO_2H/ROH in CH_3CN and CH_2Cl_2. Because of economic consideration CH_2Cl_2 was chosen for further experiments. To investigate the chemical activities of PPh_3 and NCBT in the esterification reaction, the model reaction was carried out in the absence of PPh_3 and NCBT respectively. As summarized in Table 2, no desired product was detected in the absence of PPh_3 and NCBT (Table 2, entries 14-15).

To explore the generality and scope of the esterification and thioesterification reaction by using PPh_3/NCBT mixed reagent, the optimized reaction conditions 1.25/1.25/1/2.5 molar ratio of PPh_3/NCBT/RCO_2H/ROH or RSH in CH_2Cl_2 were used for the synthesis of a series of esters and thioesters (Table 3). According to the results obtained (Table 3) esters and thioesters were prepared from the reaction of aromatic and aliphatic carboxylic acids with primary and secondary aliphatic and benzylic alcohols, phenols and aliphatic and aromatic thiols by using PPh_3/NCBT system in high isolated yields.

Table 2. Conversion of benzoic acid to benzyl benzoate with PPh_3/NCBT/ benzyl alcohol system under different reaction conditions

entry	Solvent	Molar Ratio PPh_3/NCBT/ RCO_2H/ROH	time / min	Isolated yield / %
1	CH_3CN	1/1/1/1	5 h	80
2	CH_3CN	1/1/1/1.5	3 h	85
3	CH_3CN	1/1/1/2	2 h	90
4	CH_3CN	1/1/1/2.5	2 h	92
5	CH_3CN	1.25/1.25/1/2.5	40	95
6	CH_3CN	1.25/1.25/1/3.125	40	95
7	CH_2Cl_2	1.25/1.25/1/2.5	40	95
8	THF	1.25/1.25/1/2.5	100	80
9	$CHCl_3$	1.25/1.25/1/2.5	80	90
10	1,4-dioxane	1.25/1.25/1/2.5	90	65
11	acetone	1.25/1.25/1/2.5	70	75
12	toluene	1.25/1.25/1/2.5	60	72
13	hexane	1.25/1.25/1/2.5	90	55
14	CH_2Cl_2	0/1.25/1/2.5	90	0
15	CH_2Cl_2	1.25/0/1/2.5	90	0

The aromatic carboxylic acids with electron-withdrawing substituents were rapidly reacted with benzyl alcohol and converted into their corresponding esters in a very short reaction time (20-35 min) with 100% conversion (Table 3, entries 6-10). In spite of inductive effect of chlorine which caused *o*-chlorobenzoic acid (pK_a = 2.89) stronger acid than *p*-chlorobenzoic acid (pK_a = 4.03), *o*-chlorobenzoic acid was converted to the corresponding ester in longer reaction time than *p*-chlorobenzoic acid (*e.g.*, compare entry 5 with 6). Difference in reactivity between *o*-chlorobenzoic acid and *p*-chlorobenzoic acid can be rationalized by the steric effect of chlorine in

ortho position of aromatic ring. The reaction of aromatic carboxylic acids bearing electron-donating substituents, with benzyl alcohol was completed in longer reaction time (55-70 min) than the above-mentioned acids (*e.g.*, compare entries 2-4 with 6-10). By now, we can conclude that the electron deficiency in carbonyl group plays an important role in the reaction rate of esterification. This effect has been observed in the esterification reaction of cinnanic acid and substituted cinnamic acids (*e.g.*, compare entries 11 with 12-13). PPh_3/NCBT system converted aliphatic carboxylic acids to the corresponding esters in a more longer reaction time (Table 3, entries 14-17). In comparison, primary aliphatic alcohols have low reactivity than primary benzylic ones towards *p*-nitro benzoic acid (Table 3, entries 19-21). Also, secondary alcohols have little reactivity than primary alcohols in the presence of PPh_3/NCBT system (Table 3, entries 22-24). As is to be expected, tertiary alcohols because of steric hindrance were resistant to react with carboxylic acids by using the above-mentioned mixed reagent (Table 3, entry 25). As far as we know, none of the reported methods on esterification reaction by using PPh_3/5,5'-dimethyl-3,3'-azoisoxazole,[5] PPh_3/4,4'-azopyridine,[6] Ph_2PCl/I_2/imidazole[13] and PPh_3/[bis(acetoxy)iodo]benzene/diethylazodicarboxylate (DEAD)[14] have shown any reactivity from tertiary alcohols towards benzoic acids. In order to gain more insight into the general applicability of this method, we also studied the possibility of applying PPh_3/NCBT system to the reaction of carboxylic acids with phenols. On the basis of the results obtained from Table 3, aromatic and aliphatic carboxylic acids react smoothly with phenols, and the corresponding esters are produced with high yields (Table 3, entries 26-29). This mixed reagent system also converts aliphatic and aromatic carboxylic acids to the corresponding thioesters with primary and secondary aliphatic and aromatic thiols (Table 3, entries 30-38).

Table 3. Conversion of different carboxylic acids to different esters and thioesters by using PPh_3/NCBT/alcohol (or phenol or thiol) system

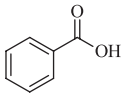
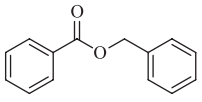
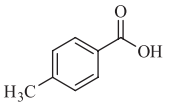
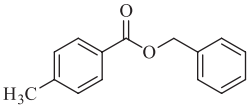
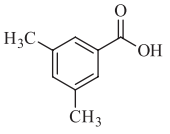
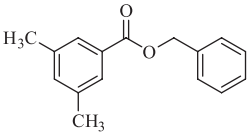
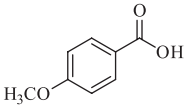
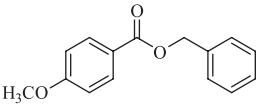
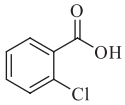
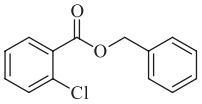
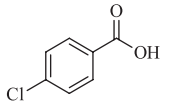
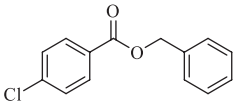
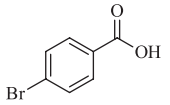
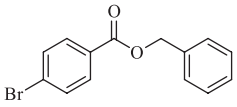
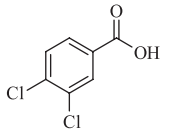
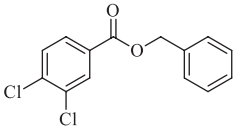
entry	Carboxylic acid	Alcohol/phenol/ thiol	Product[a]	time / min	Yield / %
1		benzyl alcohol		40	95
2		benzyl alcohol		55	90
3		benzyl alcohol		60	95
4		benzyl alcohol		70	89
5		benzyl alcohol		60	80
6		benzyl alcohol		35	85
7		benzyl alcohol		35	85
8		benzyl alcohol		25	90

Table 3. continuation

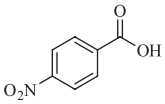
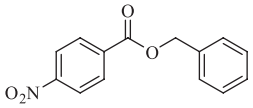
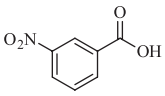
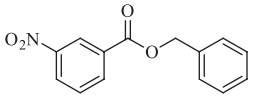
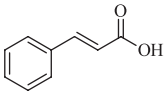
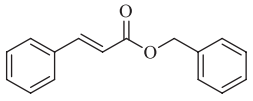
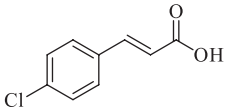
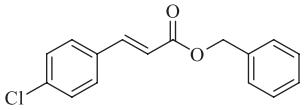
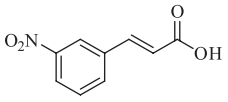
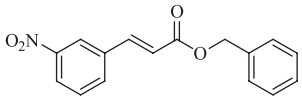
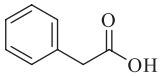
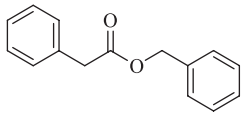
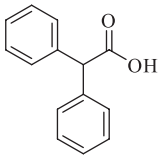
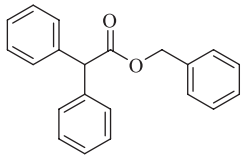
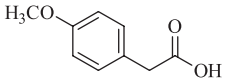
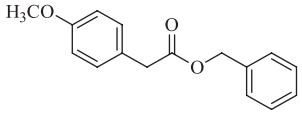
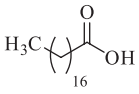
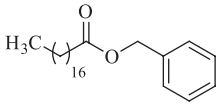
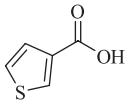
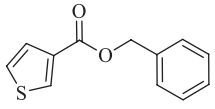
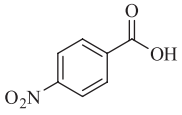
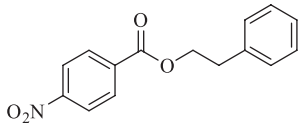
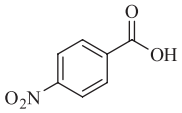
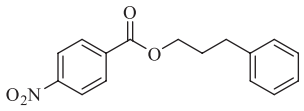
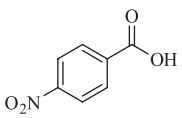
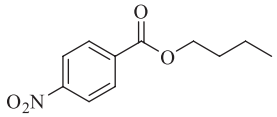
entry	Carboxylic acid	Alcohol/phenol/ thiol	Product[a]	time / min	Yield / %
9		benzyl alcohol		20	98
10		benzyl alcohol		20	90
11		benzyl alcohol		120	88
12		benzyl alcohol		100	85
13		benzyl alcohol		80	92
14		benzyl alcohol		100	85
15		benzyl alcohol		110	80
16		benzyl alcohol		130	85
17		benzyl alcohol		120	90
18		benzyl alcohol		180	87
19		2-phenyl ethanol		50	90
20		3-phenyl-1-propanol		90	90
21		1-butanol		110	85

Table 3. continuation

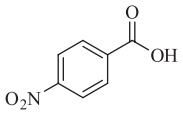
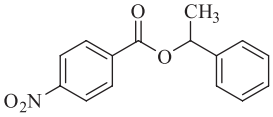
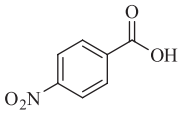
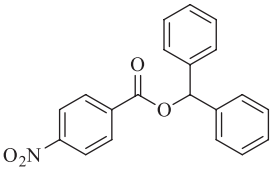
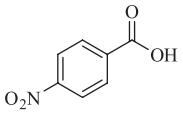
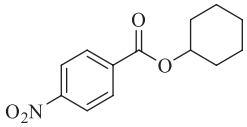
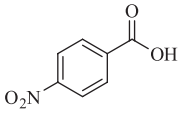
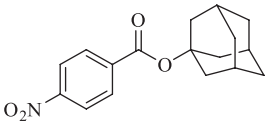
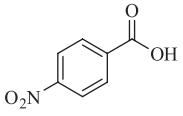
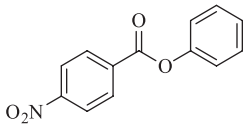
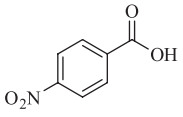
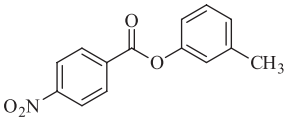
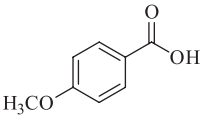
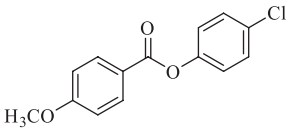
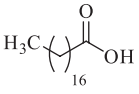
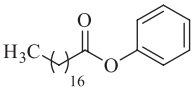
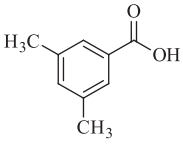
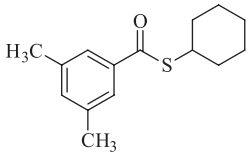
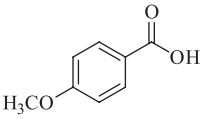
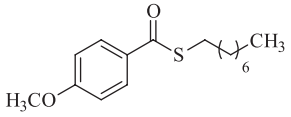
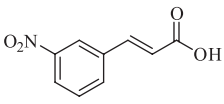
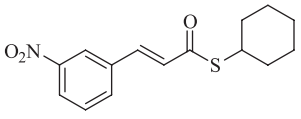
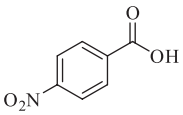
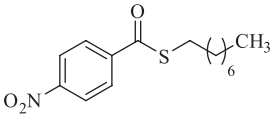
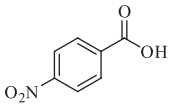
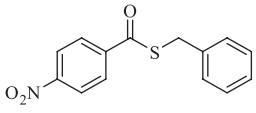
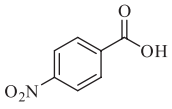
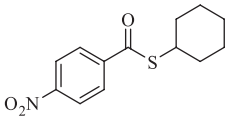
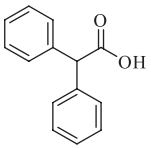
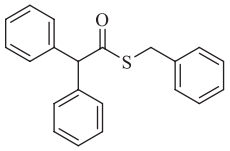
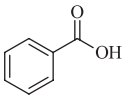
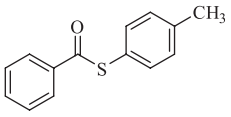
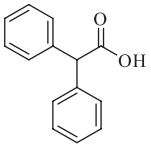
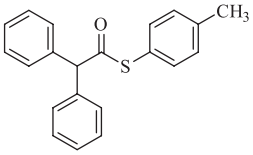
entry	Carboxylic acid	Alcohol/phenol/ thiol	Product[a]	time / min	Yield / %
22		1-phenyl ethanol		130	85
23		benzhydrol		180	70
24		cyclohexanol		100	92
25		1-adamantanol		24 h	trace
26		phenol		90	90
27		*m*-cresol		95	90
28		*p*-chlorophenol		100	95
29		phenol		150	87
30		cyclohexanthiol		90	85
31		1-octanthiol		120	90
32		cyclohexanthiol		120	90
33		1-octanthiol		120	80

Table 3. continuation

entry	Carboxylic acid	Alcohol/phenol/ thiol	Product[a]	time / min	Yield / %
34		benzyl mercaptan		40	95
35		cyclohexanthiol		65	92
36		benzyl mercaptan		120	80
37		*p*-methyl thiophenol		90	85
38		*p*-methyl thiophenol		200	80

[a]All the products were identified by comparing their spectral data with those of an authentic sample.

In our experiments, the completion of the reaction was confirmed by the disappearance of the carboxylic acids on TLC followed by the disappearance of acidic OH stretching frequency at 3400-2400 cm^{-1} in FTIR spectra. Also, absorption bands at 1743-1706 and 1393-1144 cm^{-1} due to carbonyl and C–O group of esters in FTIR spectra confirmed the ester formation. Formation of thioesters was also confirmed by appearance of an absorption bands at 1681-1643 cm^{-1} due to carbonyl group (O=C–S) of thioesters. All of the products were known compounds and characterized by the IR and comparison of their melting points with known compounds. The structure of selected products was further confirmed by ^1H NMR spectroscopy and mass spectrometry.

Conclusion

In this study, we introduced the application of NCBT (as an *N*-halo reagent) in conjunction with PPh_3 for esterification and thioesterification reactions. In comparison with the previously reported methods, the present protocol offers several advantages: (*i*) the reaction proceeds smoothly with a wide range of carboxylic acids (aromatic and aliphatic) and alcohols /or phenols and thiols. (*ii*) the reagents (PPh_3 and NCBT) offers easy handling and simple work-up; (*iii*) this method has satisfactory yields of a variety of esters and thioesters; (*iv*) in contrast to the previously reported systems, which proceeded by dehydration reaction between carboxylic acids and alcohols, in the present method, esters are produced in a short reaction time. (*v*) PPh_3 and NCBT system could be considered as an attractive and useful contribution to the present organic synthesis for direct esterification and thioesterification of different carboxylic acids.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgement

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References

1. Sutherland, I. O. In *Comprehensive Organic Chemistry*; Barton, D. H. R.; Ollis, W. D., eds.; Pergamon: Oxford, 1979, Vol. 2, p. 868.
2. Trost, B. M.; *Science* **1991**, *254*, 1471; Sheldon, R. A.; *Chem. Ind. (London)* **1997,** 12.

3. Buzas, A.; Egnell, C.; Freon, P.; *C. R. Acad. Sci.* **1962**, *255*, 945; Neises, B. Steglich, W.; *Angew. Chem., Int. Ed.* **1978**, *17*, 522; Hassner, A.; Alexanian, V.; *Tetrahedron Lett.* **1978**, *19,* 4475; Zhang, M.; Vedantham, P.; Flynn, D. L.; Hanson, P. R.; *J. Org. Chem.* **2004**, *69*, 8340.
4. Mitsunobu, O.; *Synthesis* **1981**, *1*. 1.
5. Iranpoor, N.; Firouzabadi, H; Khalili, D.; *Org. Biomol. Chem.* **2010**, *8*, 4436.
6. Iranpoor, N.; Firouzabadi, H; Khalili, D.; Motevalli. S.; *J. Org. Chem.* **2008**, *73*, 4882.
7. Xiang, J.; Orita, A.; Otera, J.; *Angew. Chem., Int. Ed.* **2002**, *41*, 4117.
8. Kore, R.; Srivastava, R.; *Catal. Commun.* **2011**, *12*, 1420.
9. Cai, Y. Q.; Yu, G. Q.; Liu, C. D.; Xu, Y. Y.; Wang, W.; *Chin. Chem. Lett.* **2012**, *23*, 1.
10. Chen, C. T.; Munot, Y. S.; *J. Org. Chem.* **2005**, *70*, 8625.
11. Hiegel, G. A.; Nguyen, J.; Zhou, Y.; *Synthetic Commun.* **2004**, *34*, 2507; Khazaei, A.; Mallakpour, S.; Zolfigol, M. A.; Ghorbani-Vagheie, R.; Kolvari, E.; *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 1715.
12. Hughes, T. V.; Hammond, S. D.; Cava, M. P.; *J. Org. Chem.* **1998**, *63*, 401.
13. Nowrouzi, N.; Mehranpour, A. M.; Ameri Rad, J.; *Tetrahedron* **2010**, *66*, 9596.
14. But, T. Y. S.; Toy, P. H.; J. Am. Chem. Soc. **2006**, *128*, 9636.
15. Rosenberg, M. G.; Brinker, U. H.; *J. Org. Chem*. **2003**, *68*, 4819.
16. Li, Y.; Deng, W. P.; Du, W.; *Tetrahedron* **2012**, *68*, 3611.
17. Yoshimasa, M.; Nobuhiro, K.; Toshikazu. T.; *Chem. Lett.* **2007**, *36*, 102.
18. Eliel, E. L.; Anderson, R. P.; *J. Am. Chem. Soc*. **1952**, *74*, 547.
19. Jaszay, Z. M.; Petnehazy, I.; Toeke, L.; *Synth. Commun*. **1998**, *28*, 2761.
20. Niyogy, Y.; *J. Indian Chem. Soc.* **1930**, *7*, 577.
21. Lu, X.; Long, T, E.; *J. Org. Chem.* **2010**, *75*, 249.
22. Zhang, B.; Feng, P.; Cui, Y.; Jiao, N.; *Chem. Commun.* **2012**, *48*, 7280.
23. Thalluri, K.; Nadimpally, K. C.; Chakravarty, M. P.; Paul, A.; Mandal, B.; *Adv. Synth. Catal.* **2013**, *355*, 448.
24. Froeyen, P.; *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *91*, 145.
25. Bhawal, B. M.; Khanapure, S. P.; Biehl, E. R.; *Synthesis* **1991**, *2*, 112.
26. Pereira, W.; Close, V. A.; Patton, W.; Halpern, B.; *J. Org. Chem.* **1969**, *34*, 2032.
27. Mackay, D.; *Can. J. Chem.* **1966**, *44*, 2881.
28. Tian, J.; Gao, W. C.; Zhou, D. M.; Zhang, C.; *Org. Lett.* **2012**, *14*, 3020.
29. Koga, K.; Seki, H.; Yamada, S.; *Chem. Pharm. Bull.* **1967**, *15*, 1948.
30. Satoshi, I.; Takeshi, H.; Hirokazu, U.; *Adv. Synth. Catal.* **2012**, *354*, 3480.
31. Strazzolini, P.; Giumanini, A.G.; Verardo, G.; *Tetrahedron* **1994**, *50*, 217.
32. Perusquia-Hernandez, C.; Lara-Issasi, G. R.; Frontana-Uribe, B. A.; Cuevas-Yanez, E.; *Tetrahedron Lett.* **2013**, *54*, 3302.
33. Ohshima, T.; Iwasaki, T.; Maegawa, Y.; Yoshiyama, A.; Mashima, K.; *J. Am. Chem. Soc.* **2008**, *130*, 2944.
34. Arde, P.; Ramanjaneyulu, B. T.; Reddy, V.; Saxena, A.; Anand, R. V.; *Org. Biomol. Chem.* **2012**, *10*, 848.
35. Baddeley, G.; *J. Chem. Soc*. **1944**, 330.
36. Arisawa, M.; Igarashi, Y.; Kobayashi, H.; Yamada, T.; Bando, K.; Ichikawa, T.; Yamaguchi, M.; *Tetrahedron* **2011**, *67*, 7846.
37. Hosseini-Sarvari, M.; Sodagar, E.; *C. R. Chim.* **2013**, *16*, 229.
38. Burhardt, M. N.; Taaning, R. H.; Skrydstrup, T.; *Org. Lett*. **2013**, *15*, 948.
39. Takido, T.; Toriyama, M.; Itabashi, K.; *Synthesis* **1988**, *5*, 404.
40. Henao Castañeda, I. C.; Pereanez, J. A.; Jios, J. L.; *J. Mol. Struct.* **2012**, *1028*, 7.
41. Romero; R.; *Bol. Inst. Quim. Univ. Mexico*, **1952**, *4*, 3.
42. Arisawa, M.; Kuwajima, M.; Toriyama, F.; Li, G.; Yamaguchi, M.; *Org. Lett.* **2012**, *14*, 3804.
43. Petrova, R. G.; Churkina, T. D.; Kandor, I. I.; Dostovalova, V. I.; Freidlina, R. Kh.; *B. Acad. Sci USSR. CH+.***1985**, *34*, 2331; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, *11*, 2519.
44. Akhlaghinia, B.; Rouhi-Saadabad, H.; *Can. J. Chem.* **2013**, *9*, 181; Kiani, A.; Akhlaghinia, B.; Rouhi-Saadabad, H.; Bakavoli, M.; *J. Sulfur Chem*. **2013**, DOI 10.1080/17415993.2013.801476; Iranpoor, N.; Firouzabadi, H.; Akhlaghinia, B.; Nowrouzi, N.; *J. Org. Chem*. **2004**, *69*, 2562; Iranpoor, N.; Firouzabadi, H.; Azadi, R.; Akhlaghinia, B.; *J. Sulfur Chem*. **2005**, *26*,133; Akhlaghinia, B.; *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 1783; Akhlaghinia, B.; *Phosphorus, Sulfur Silicon Relat. Elem.* **2005**, *180*, 1601; Akhlaghinia, B.; Samiei, S.; *Phosphorus, Sulfur Silicon Relat. Elem*. **2009**, *184*, 2525; Iranpoor, N.; Firouzabadi, H.; Akhlaghinia, B.; Azadi, R.; *Synthesis* **2004**, *1*, 92; Akhlaghinia, B.; Pourali, A. R.; *Synthesis* **2004**, *11*, 1747; Akhlaghinia, B.; *Synthesis* **2005**, *12*, 1955; Iranpoor, N.; Firouzabadi, H.; Akhlaghinia, B.; Nowrouzi, N.; *Tetrahedron Lett.* **2004**, *45*, 3291.

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