

Direct, Rapid and Convenient Synthesis of Esters and Thioesters Using PPh₃/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 PPh₃/N-clorobenzotriazol em CH₂Cl₂ a temperatura ambiente.

We have developed an efficient method for esterification and thioesterification of various carboxylic acids with different alcohols and thiols using PPh₃/N-chlorobenzotriazole mixed reagent in CH₂Cl₂ at room temperature.

Keywords: PPh₃, N-chlorobenzotriazole (NCBT), esters, thioesters

Introduction

Esterification is the fundamental and routinely used functional group transformation in organic chemistry¹ 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 [$\text{Cl}(\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4)_2\text{SnOSn}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2\text{Cl}$]₂ graphite bisulfate,⁷ functionalized acidic ionic liquids,^{8,9} TiO(acac)₂¹⁰ 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 PPh₃ 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) PPh₃ 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 Thermo Nicolet

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spectrometer. The nuclear magnetic resonance (NMR) spectra were provided on Bruker Ultrashield Avance III 400 MHz instruments in CDCl₃. 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 PPh₃/5,5'-dimethyl-3,3'-azoisoxazole, PPh₃/4,4'-azopyridine, Ph₂PCl/I₂/imidazole and PPh₃/[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 PPh₃/trichloroisocyanuric acid (TCCA)

To a cold solution of PPh₃ (0.327 g, 1.25 mmol) in CH₂Cl₂ (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 PPh₃/N-bromosuccinimide (NBS)

To a cold solution of PPh₃ (0.327 g, 1.25 mmol) in CH₂Cl₂ (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 PPh₃/N-chlorosuccinimide (NCS)

To a cold solution of PPh₃ (0.327 g, 1.25 mmol) in CH₂Cl₂ (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 PPh₃/NCBT

To a cold solution of PPh₃ (0.327 g, 1.25 mmol) in CH₂Cl₂ (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) ν_{\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; ¹H NMR (400 MHz, CDCl₃, 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, PhCH₂).

Benzyl 4-methylbenzoate (Table 3, entry 2)

Solid; m.p. 45–46 °C (Lit. 45–46 °C);¹⁶ IR (KBr) ν_{\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⁺–PhCH₂O, 100%), 91 (PhCH₂, 90%).

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

Solid; m.p. 65–66 °C (Lit. 66–67 °C);¹⁷ IR (KBr) ν_{\max} /cm⁻¹ 3423, 3063, 3033, 3009, 2951, 2918, 1717 (C=O), 1608, 1498, 1555, 1308, 1211 (C–O), 1115, 1010, 766, 754, 697; ¹H NMR (400 MHz, CDCl₃, 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, PhCH₂), 2.39 (s, 6H, 2CH₃).

Benzyl 4-methoxybenzoate (Table 3, entry 4)

m.p. 24-26 °C (Lit. 25-27 °C);¹⁸ IR (neat) $\nu_{\max}/\text{cm}^{-1}$ 3415, 3068, 2962, 2937, 2839, 1712(C=O), 1606, 1581, 1511, 1456, 1376, 1316, 1270, 1256 (C–O), 1167, 1099, 1029, 769, 696; ¹H NMR (400 MHz, CDCl₃, 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, PhCH₂), 3.89 (s, 3H, OCH₃).

Benzyl 2-chlorobenzoate (Table 3, entry 5)

m.p. 18-20 °C; IR (neat) $\nu_{\max}/\text{cm}^{-1}$ 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) $\nu_{\max}/\text{cm}^{-1}$ 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) $\nu_{\max}/\text{cm}^{-1}$ 3415, 3072, 3039, 2974, 2892, 1715 (C=O), 1588, 1455, 1396, 1269 (C–O), 1169, 1089, 1008, 759, 698; ¹H NMR (400 MHz, CDCl₃, 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, PhCH₂); MS (EI) *m/z* 291 (M⁺, 5%), 182 (M⁺-PhCH₂O, 87%), 91 (PhCH₂, 87%).

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

Solid; m.p. 57-58 °C (Lit. 58-60 °C);¹⁶ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3092, 3072, 3039, 2953, 2892, 1724 (C=O), 1585, 1564, 1458, 1379, 1273 (C–O), 1236, 1106, 1032, 757, 696; ¹H NMR (400 MHz, CDCl₃, 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, PhCH₂); MS (EI) *m/z* 284 (M+4, 5%), 282 (M+2, 26%), 280 (M⁺, 32%), 245 (M⁺-Cl, 38%), 173 (M⁺-PhCH₂O, 100%), 145 (M⁺-PhCl₂, 35%), 91 (PhCH₂, 100%).

Benzyl 4-nitrobenzoate (Table 3, entry 9)

Solid; m.p. 82-83 °C (Lit. 82-83 °C);¹⁶ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3112, 3051, 1712 (C=O), 1604, 1522, 1347, 1277 (C–O), 1121, 1104, 744, 715.695; ¹H NMR (400 MHz, CDCl₃, 25 °C, ppm) δ 8.32-8.25 (m, 4H, ArH), 8.50-8.40 (m, 5H, ArH), 5.44 (s, 2H, PhCH₂); MS (EI) *m/z* 257 (M⁺, 10%), 150 (M⁺-PhCH₂O, 100%), 91 (M⁺-PhCH₂, 100%).

Benzyl 3-nitrobenzoate (Table 3, entry 10)

Solid; m.p. 48-49 °C (Lit. 48-49 °C);²⁰ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3436, 3084, 3039, 2962, 2872, 1727 (C=O), 1613, 1531, 1350, 1293, 1258 (C–O), 1130, 1070, 717, 697;

¹H NMR (400 MHz, CDCl₃, 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, PhCH₂).

Benzyl cinnamate (Table 3, entry 11)

Solid; m.p. 31-32 °C (Lit. 32-33 °C);²¹ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3064, 3027, 2966, 2896, 1711 (C=O), 1636, 1310, 1162 (C–O), 980, 767, 697; MS (EI) *m/z* 238 (M⁺, 10%), 130 (M⁺-PhCH₂O, 100%), 103 (PhCH₂O, 90%), 91 (PhCH₂, 90%).

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

Solid; m.p. 122-124 °C; IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3064, 3027, 2953, 1708 (Lit. 1709, C=O),²² 1637, 1488, 1309, 1166 (C–O), 988, 820, 695; ¹H NMR (400 MHz, CDCl₃, 25 °C, ppm) δ 7.70 (d, 1H, *J* 16 Hz, PhCH=CH-), 7.49-7.29 (m, 9H, ArH), 6.49 (d, 1H, *J* 16 Hz, PhCH=CH-), 5.29 (s, 2H, PhCH₂); MS (EI) *m/z* 274 (M+2, 10%), 272 (M⁺, 35%), 164 (M⁺-PhCH₂O), 91 (M⁺-PhCH₂, 100%).

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

Solid; m.p. 148-149 °C (Lit. 147-149 °C);²² IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3072, 2925, 1711 (C=O), 1641, 1526, 1351, 1176 (C–O), 1008, 730; MS (EI) *m/z* 282 (M⁺, 10%), 175 (M⁺-PhCH₂O, 81%), 103 (PhCH₂O, 80%), 91 (PhCH₂, 100%).

Benzyl 2-phenylacetate (Table 3, entry 14)

Solid; m.p. 51-52 °C (Lit. 52 °C);²³ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3084, 3060, 3031, 2953, 1737 (C=O), 1496, 1454, 1380, 1260 (C–O), 1145, 749, 695; ¹H NMR (400 MHz, CDCl₃, 25 °C, ppm) δ 7.41-7.29 (m, 10H, ArH), 5.17 (s, 2H, PhCH₂-O), 3.71 (s, 2H, PhCH₂-CO).

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

m.p. 34-35 °C (Lit. 35 °C);²⁴ IR (neat) $\nu_{\max}/\text{cm}^{-1}$ 3084, 3063, 3030, 2953, 1736 (C=O), 1600, 1496, 1453, 1184, 1144 (C–O), 1004, 975, 744, 696; MS (EI) *m/z* 193 (M⁺-PhCH₂O, 30%), 166 ((Ph)₂CH, 100%), 91 (PhCH₂, 80%).

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

Solid; m.p. 142-144 °C (Lit. 141-144 °C);²⁵ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 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⁺-PhCH₂, 20%), 149 (M⁺-PhCH₂O, 80%), 91 (PhCH₂, 80%).

Benzyl stearate (Table 3, entry 17)

Solid; m.p. 44-45 °C (Lit. 44-45 °C);²⁶ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 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) $\nu_{\max}/\text{cm}^{-1}$ 3111, 3035, 1716 (C=O), 1522, 1407, 1261 (C–O), 1187, 1100, 747; ¹H NMR (400 MHz, CDCl₃, 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, PhCH₂).

Phenethyl 4-nitrobenzoate (Table 3, entry 19)

Solid; m.p. 60-61 °C (Lit. 59-61 °C);²⁸ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3068, 1710 (C=O), 1597, 1486, 1450, 1379, 1362, 1287 (C–O), 1051, 940, 750, 695; MS (EI) m/z 164 (M⁺-PhCH₂CH₂, 17%), 149 (4-NO₂PhCO, 80%), 104 (PhCH₂CH₂, 100%), 91 (PhCH₂, 80%).

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

Solid; m.p. 46-47 °C (Lit. 47-48 °C);²⁹ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 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-NO₂PhCO, 60%), 118 (PhCH₂CH₂CH₂, 100%), 91 (PhCH₂, 90%).

Butyl 4-nitrobenzoate (Table 3, entry 21)

m.p. 33-34 °C (Lit. 34-35 °C);³⁰ IR (neat) $\nu_{\max}/\text{cm}^{-1}$ 3117, 3080, 3060, 2963, 2938, 2868, 1717 (C=O), 1606, 1526, 1352, 1278 (C–O), 1103, 872, 846, 786, 714; ¹H NMR (400 MHz, CDCl₃, 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, OCH₂CH₂), 1.83-1.76 (m, 2H, OCH₂CH₂), 1.55-1.46 (m, 2H, CH₂CH₃), 1.01 (t, 3H, *J* 7.2 Hz, OCH₂CH₃).

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

Solid; m.p. 44-45 °C (Lit. 44 °C);³¹ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3113, 3039, 2978, 2933, 1723 (C=O), 1607, 1528, 1454, 1351, 1271 (C–O), 1102, 1060, 1014, 873, 841, 719; ¹H NMR (400 MHz, CDCl₃, 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, OCH(Ph)CH₃), 1.74 (d, 3H, *J* 6.4 Hz, OCHCH₃).

Benzhydryl 4-nitrobenzoate (Table 3, entry 23)

Solid; m.p. 131-132 °C (Lit. 132 °C);³² IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3109, 3051, 2859, 1721 (C=O), 1609, 1525, 1446, 1345, 1280 (C–O), 1261, 1116, 1103, 967, 763, 719, 699; ¹H NMR (400 MHz, CDCl₃, 25 °C, ppm) δ 8.33 (s, 4H, ArH), 8.47-8.35 (m, 10H, ArH), 7.17 (s, 1H, Ph₂CH); MS (EI) m/z 333 (M⁺, 10%), 182 (M⁺-2Ph, 88%), 165 (M⁺-NO₂PhCO₂, 100%), 151 (M⁺-Ph₂CHO, 72%).

Cyclohexyl 4-nitrobenzoate (Table 3, entry 24)

Solid; m.p. 50-51 °C (Lit. 51-52 °C);³³ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 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-NO₂PhCO, 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) $\nu_{\max}/\text{cm}^{-1}$ 3113, 1741 (C=O), 1609, 1520, 1484, 1348, 1269 (C–O), 1183, 1079, 1017, 847; ¹H NMR (400 MHz, CDCl₃, 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) $\nu_{\max}/\text{cm}^{-1}$ 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) $\nu_{\max}/\text{cm}^{-1}$ 3015, 2982, 2847, 1727 (C=O), 1610, 1515, 1489, 1267 (C–O), 1204, 1167, 1072, 1021, 842, 761; ¹H NMR (400 MHz, CDCl₃, 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, OCH₃).

Phenyl stearate (Table 3, entry 29)

Solid; m.p. 48-49 °C (Lit. 49-50 °C);³⁷ IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 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) $\nu_{\max}/\text{cm}^{-1}$ 2929, 2853, 1659 (O=C–S), 1606, 1448, 1292, 1149, 1034, 697, 861, 786, 703; ¹H NMR (400 MHz, CDCl₃, 25 °C, ppm) δ 7.58 (s, 2H, ArH), 7.20 (s, 1H, ArH), 3.73 (t, 1H, *J* 4 Hz, SCH–), 2.37 (s, 6H, 2CH₃), 2.05-1.27 (m, 10H, CH₂ cyclohexyl ring).

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

m.p. 24-26 °C (Lit. 25-27 °C);³⁸ IR (neat) $\nu_{\max}/\text{cm}^{-1}$ 3011, 2955, 2926, 2854, 1655 (O=C–S), 1602, 1578, 1508, 1462, 1315, 1259, 1213, 1167, 1031, 913; ¹H NMR (400 MHz, CDCl₃, 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–CH₂), 1.71-1.60 (m, 2H, CH₂), 1.43 (q, 2H, *J* 6.8 Hz, R–CH₂CH₃), 1.32-1.29 (m, 8H, 4CH₂), 0.89 (t, 3H, *J* 6.8 Hz, R–CH₂CH₃).

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) $\nu_{\max}/\text{cm}^{-1}$ 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)

solid; m.p. 27-29 °C (Lit. 28-30 °C);³⁹ IR (neat) $\nu_{\max}/\text{cm}^{-1}$ 3105, 2953, 2927, 2855, 1666 ($\text{O}=\text{C}-\text{S}$), 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) $\nu_{\max}/\text{cm}^{-1}$ 3113, 1643 ($\text{O}=\text{C}-\text{S}$), 1601 1521, 1349, 1318, 1203, 1193, 930, 850, 711, 691; ¹H 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) $\nu_{\max}/\text{cm}^{-1}$ 3109, 2942, 2928, 2851, 1655 ($\text{O}=\text{C}-\text{S}$), 1604, 1523, 1349, 1318, 1195, 1174, 1109, 922, 885, 848, 690; ¹H NMR (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) $\nu_{\max}/\text{cm}^{-1}$ 3333, 3088, 3064, 3027, 2917, 2843, 1680 ($\text{O}=\text{C}-\text{S}$), 1494, 1453, 1011, 994, 741, 698; MS (EI) m/z 317 (M^+ , 5%), 196 (M^+ - PhCH_2S , 10%), 166 ($(\text{Ph})_2\text{CH}$, 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) $\nu_{\max}/\text{cm}^{-1}$ 3047, 2917, 2847, 1668 ($\text{O}=\text{C}-\text{S}$), 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) $\nu_{\max}/\text{cm}^{-1}$ 3084, 3059, 3027, 2917, 2843, 1674 ($\text{O}=\text{C}-\text{S}$), 1482, 1451, 981, 741, 698; MS (EI) m/z 316 (M^+ , 3%), 193 (M^+ -4-MePhS, 60%), 166 ($(\text{Ph})_2\text{CH}$, 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 $\text{PPh}_3/5,5'$ -dimethyl-3,3'-azoisoxazole,⁵ $\text{PPh}_3/4,4'$ -azopyridine,⁶ $\text{Ph}_2\text{PCI}/\text{I}_2$ /imidazole¹³ 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 to the data from Table 1, PPh_3 /NCBT system is the best choice for direct esterification of benzoic acid (Scheme 1).

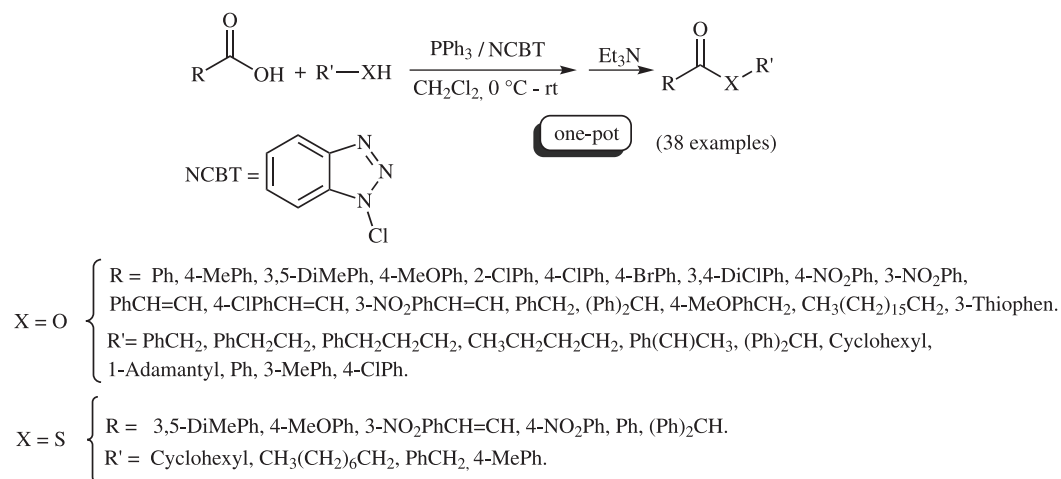
To achieve high reaction efficiency, the reaction of benzoic acid with benzyl alcohol was chosen as model reaction to investigate the applicability of PPh_3 /NCBT system in direct esterification and thioesterification reactions of carboxylic acids. The effects of different molar ratios of PPh_3 /NCBT/ $\text{RCO}_2\text{H}/\text{ROH}$ 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) | $\text{CH}_2\text{Cl}_2/\text{r.t.}^b$ | 2.5 | 85 |
| 2 | PPh_3 / <i>N</i> -bromosuccinimide (NBS) | $\text{CH}_2\text{Cl}_2/\text{r.t.}^b$ | 4.5 | 40 |
| 3 | PPh_3 / <i>N</i> -chlorosuccinimide (NCS) | $\text{CH}_2\text{Cl}_2/\text{r.t.}^b$ | 3 | 80 |
| 4 ⁵ | $\text{PPh}_3/5,5'$ -dimethyl-3,3'-azoisoxazole | $\text{CH}_3\text{CN}/\text{reflux}$ | 6.5 | 89 |
| 5 ⁶ | $\text{PPh}_3/4,4'$ -azopyridine | $\text{CH}_3\text{CN}/\text{reflux}$ | 3 | 86 |
| 6 ¹³ | Ph_2PCI , I_2 , imidazole | $\text{CH}_3\text{CN}/\text{reflux}$ | 4 | 91 |
| 7 ^{14c} | PPh_3 /[bis(acetoxy)iodo]benzene/diethylazodicarboxylate (DEAD) | THF/ r.t.^b | 16 | 76 |
| 8 | PPh_3 / <i>N</i> -chlorobenzotriazole (NCBT) | $\text{CH}_2\text{Cl}_2/\text{r.t.}^b$ | 40 min | 95 |

^aThe experimental details are shown in experimental section; ^br.t.: room temperature; ^cthe 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 PPh₃/NCBT and benzyl alcohol in CH₃CN 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 PPh₃/NCBT/RCO₂H/ROH in CH₃CN gave 100% conversion of benzoic acid to benzyl benzoate in 40 min, esterification reaction was examined in CH₂Cl₂ at the same conditions. Surprisingly, there is no difference between the rate of esterification reaction in CH₃CN and CH₂Cl₂ (Table 2, compare entries 5 and 7). At the same conditions performing the reaction in other solvents such as THF, CHCl₃, 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 PPh₃/NCBT/RCO₂H/ROH in CH₃CN and CH₂Cl₂. Because of economic consideration CH₂Cl₂ was chosen for further experiments. To investigate the chemical activities of PPh₃ and NCBT in the esterification reaction, the model reaction was carried out in the absence of PPh₃ and NCBT respectively. As summarized in Table 2, no desired product was detected in the absence of PPh₃ and NCBT (Table 2, entries 14-15).

To explore the generality and scope of the esterification and thioesterification reaction by using PPh₃/NCBT mixed reagent, the optimized reaction conditions 1.25/1.25/1/2.5 molar ratio of PPh₃/NCBT/RCO₂H/ROH or RSH in CH₂Cl₂ 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 PPh₃/NCBT system in high isolated yields.

Table 2. Conversion of benzoic acid to benzyl benzoate with PPh₃/NCBT/benzyl alcohol system under different reaction conditions

| entry | Solvent | Molar Ratio PPh ₃ /NCBT/ RCO ₂ H/ROH | time / min | Isolated yield / % |
|-------|---------------------------------|--|------------|-----------------------|
| 1 | CH ₃ CN | 1/1/1/1 | 5 h | 80 |
| 2 | CH ₃ CN | 1/1/1/1.5 | 3 h | 85 |
| 3 | CH ₃ CN | 1/1/1/2 | 2 h | 90 |
| 4 | CH ₃ CN | 1/1/1/2.5 | 2 h | 92 |
| 5 | CH ₃ CN | 1.25/1.25/1/2.5 | 40 | 95 |
| 6 | CH ₃ CN | 1.25/1.25/1/3.125 | 40 | 95 |
| 7 | CH ₂ Cl 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 ₂ Cl ₂ | 0/1.25/1/2.5 | 90 | 0 |
| 15 | CH ₂ Cl 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 cinnamic 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 $\text{PPh}_3/5,5'$ -dimethyl-3,3'-azoisoxazole,⁵ $\text{PPh}_3/4,4'$ -azopyridine,⁶ $\text{Ph}_2\text{PCl}/\text{I}_2/\text{imidazole}$ ¹³ and $\text{PPh}_3/[\text{bis}(\text{acetoxy})\text{i}odo]\text{benzene}/\text{diethylazodicarboxylate}$ (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 $\text{PPh}_3/\text{NCBT}/\text{alcohol}$ (or phenol or thiol) system

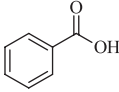
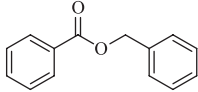
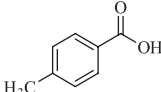
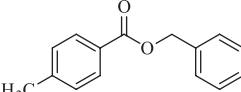
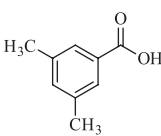
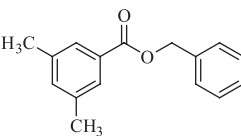
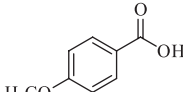
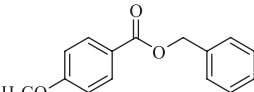
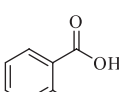
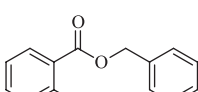
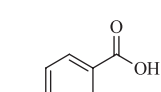
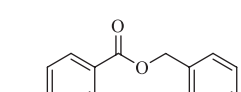
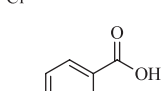
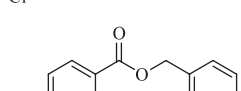
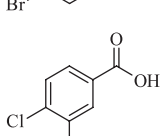
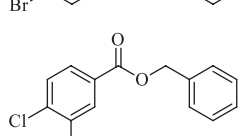
| entry | Carboxylic acid | Alcohol/phenol/ thiol | Product ^a | time / min | Yield / % |
|-------|---|-----------------------|--|------------|-----------|
| 1 |  | benzyl alcohol |  | 40 | 95 |
| 2 |  | benzyl alcohol |  | 55 | 90 |
| 3 |  | benzyl alcohol |  | 60 | 95 |
| 4 |  | benzyl alcohol |  | 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

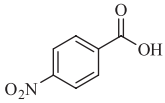
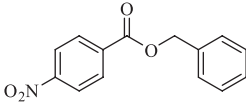
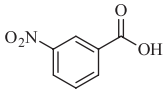
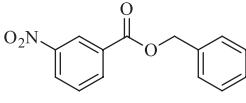
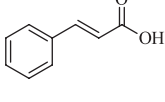
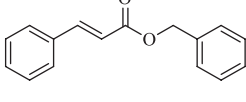
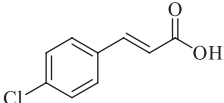
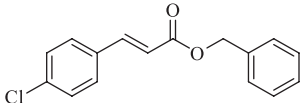
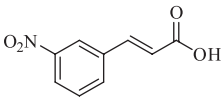
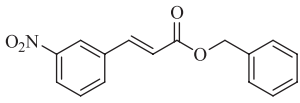
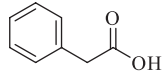
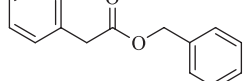
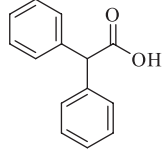
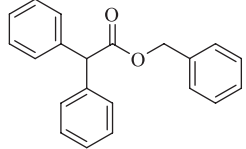
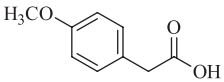
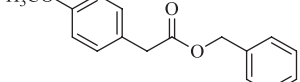
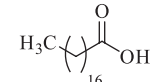
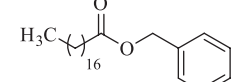
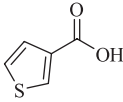
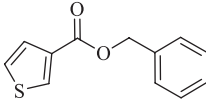
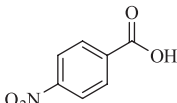
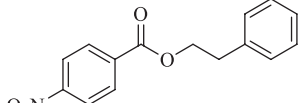
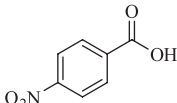
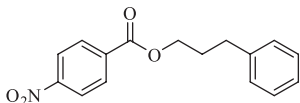
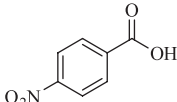
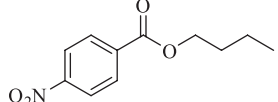
| entry | Carboxylic acid | Alcohol/phenol/ thiol | Product ^a | time / min | Yield / % |
|-------|---|-----------------------|--|------------|-----------|
| 9 |  | benzyl alcohol |  | 20 | 98 |
| 10 |  | benzyl alcohol |  | 20 | 90 |
| 11 |  | benzyl alcohol |  | 120 | 88 |
| 12 |  | benzyl alcohol |  | 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

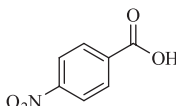
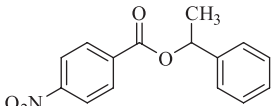
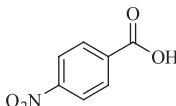
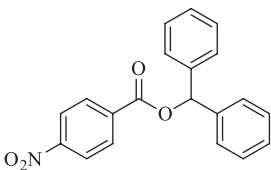
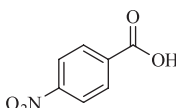
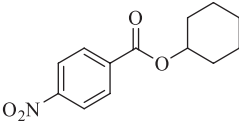
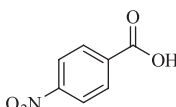
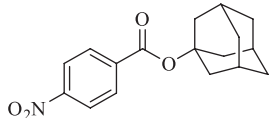
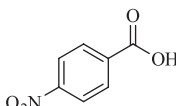
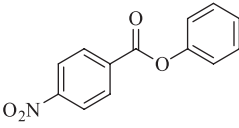
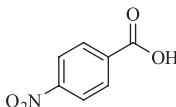
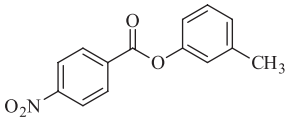
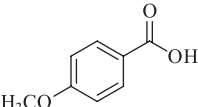
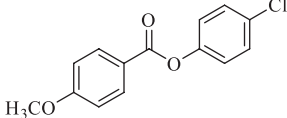
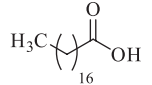
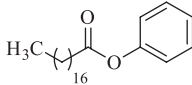
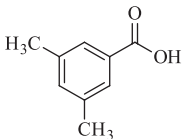
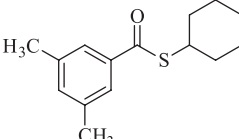
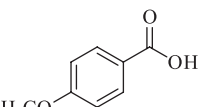
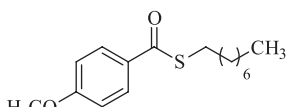
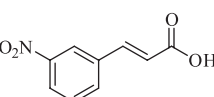
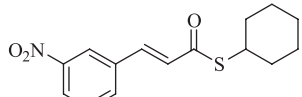
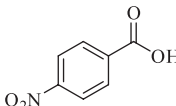
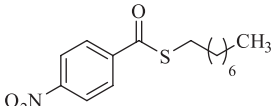
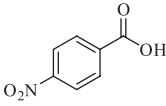
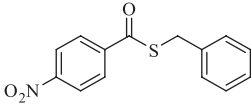
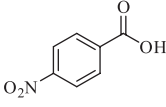
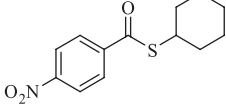
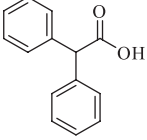
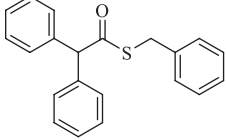
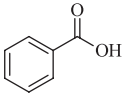
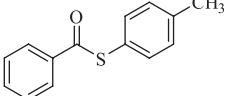
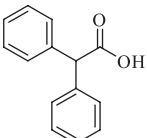
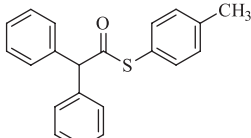
| entry | Carboxylic acid | Alcohol/phenol/ thiol | Product ^a | time / min | Yield / % |
|-------|---|------------------------|--|------------|-----------|
| 22 |  | 1-phenyl ethanol |  | 130 | 85 |
| 23 |  | benzhydrol |  | 180 | 70 |
| 24 |  | cyclohexanol |  | 100 | 92 |
| 25 |  | 1-adamantanol |  | 24 h | trace |
| 26 |  | phenol |  | 90 | 90 |
| 27 |  | <i>m</i> -cresol |  | 95 | 90 |
| 28 |  | <i>p</i> -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 |  | <i>p</i> -methyl thiophenol |  | 90 | 85 |
| 38 |  | <i>p</i> -methyl thiophenol |  | 200 | 80 |

^aAll 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 PPh₃ 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 (PPh₃ 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) PPh₃ 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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