Asian Journal of Chemistry; Vol. 33, No. 11 (2021), 2671-2674

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23358

N-Aroylbenzotriazoles as Efficient Reagents for *o*-Aroylation in Absence of Organic Solvent

BARAMEE PHUNGPIS[1,*] and VIWAT HAHNVAJANAWONG[2]

[1]Faculty of Natural Resources, Rajamangala University of Technology Isan Sakonnakhon Campus, Sakonnakhon 47160, Thailand
[2]Department of Chemistry and Centre of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

*Corresponding author: E-mail: barameephungpis@yahoo.com

Received: 6 June 2021; *Accepted*: 3 August 2021; *Published online*: 20 October 2021; AJC-20548

N-Aroylbenzotriazoles have been shown to be efficient reagents for esterification in the absence of organic solvent. Grinding of *N*-aroylbenzoytiazoles with twofold excess of alcohols for a couple of hours at room temperature gave corresponding esters in high percentage of yields.

Keywords: *N*-Aroylbenzotriazoles, Aroylation reagent, Grinding, Esterification.

INTRODUCTION

A wide range of synthetic methods have been developed for formation of ester from treatment of carboxylic acids or their derivatives with alcohols. Protic acids, *e.g.*, HCl, H_2SO_4, H_3PO_4 and Lewis acids such as $Zn(ClO_4)_2{\cdot}6H_2O$, $InCl_3$, $SnCl_2$, $Fe_2(SO_4)_3$, $FeCl_3$, $NiCl_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ and I_2 have been employed as catalysts for the esterification of carboxylic acids with alcohols [1-10]. Coupling between carboxylic acids and alcohols by the use of special coupling agents provides another synthetic method for synthesizing good percentage of yields of esters. Some commonly used special coupling agents are dicyclohexylcarbodiimide/dimethylaminopyridine (DCC/DMAP),1-methyl-2-halopyridinium iodide in the presence of tri-*n*-butylamine, dimethylsulfamoyl chloride combined with tri-methylamine and triphenylphosphine dihalide in the presence of DMAP [11-14].

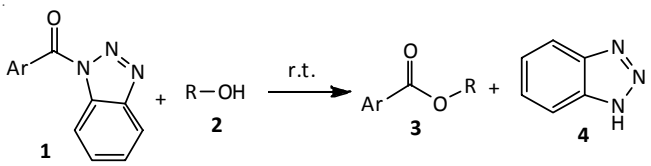
Acylation of alcohols by treatment with activated carboxylic acid derivatives, *i.e.*, acyl chlorides or anhydrides in the presence of base such as triethylamine and pyridine also leads to the formation of esters [15]. Benzoylation of alcohols with benzoyl chloride in the presence of *N*,*N*,*N*,*N*-tetramethylethylenediamine (TMEDA) at –78 ºC, for instance, proceeds rapidly to give excellent yields of corresponding benzoate esters [16]. Acetylation of alcohols with acetic anhydride catalyzed by $Cu(OTf)_2$ gives high yields of acylated products under mild conditions [17].

Apart from acyl halide and anhydride, benzoylimidazole, in the presence of pyridinium salt, has been shown to be active acylation reagent for esterification. Reaction between a range of alcohols and benzoylimidazole produces the corresponding ester products in high yields at room temperature [18]. *N*-Formyl benzotriazole and *N*-(trifluoroacetyl)benzotriazole have also been demonstrated to be effective *o*-formylating and *o*-trifluoroacetylating agents, respectively. *N*-Formylbenzotriazole formulates alcohols to give excellent yields of corresponding formates in ether at room temperature. Trifluoroacetylation of alcohols, on the other hand, has to performed in refluxing THF to afford trifluoroacetate esters in satisfactory yields [19,20].

Recently, we have reported successful cross-coupling between *N*-aroylbenzotriazoles and aromatic aldehydes catalyzed by *N*-heterocyclic carbene generated from ionic liquid [Bmim]Br [21] is also reported. In continuation of our interest using *N*-aroylbenzotriazoles as acylation agent, herein, the aroylation of alcohols (**2**) using *N*-aroylbenzotriazoles (**1**) as aroylation reagents (**Scheme-I**) is reported. Benzotriazole (**4**) byproduct can be readily recovered and reuses as substrate for preparation of *N*-aroylbenzotriazoles (**1**) [22]. Moreover, no byproducts is generated from this aroylation.

EXPERIMENTAL

Chemicals and solvents were commercially obtained and used without further purification. IR spectra were recorded



1 2 3 4

Scheme-I: Aroylation of alcohols (**2**) to afford ester products (**3**)

on a FTIR Perkin-Elmer instrument. ^{1}H and ^{13}C NMR spectra were recorded by a VARIAN MERCURY plus spectrometer (400 MHz). $CDCl_3$ was used as solvent and internal standard.

General procedure for aroylation of alcohols 2a-i by grinding with *N*-aroylbenzotriazoles (1a-d): A mixture of *N*-aroylbenzotriazole **1** (1.0 mmol) and the corresponding alcohol **2** (2.0 mmol) was ground together in a mortar using pestle for the time described in Tables 1 and 2. Completion of the reaction was monitored by TLC in hexane:dichloromethane (1:1) solvent systems. The resulting mixture was purified by preparative thin layer chromatography (silica gel, elution with 50% dichloromethane/hexane) to provide desired ester **3** and benzotriazole (**4**).

Benzyl benzoate (3a): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 3068, 3034, 2952, 2890, 1721, 1603, 1585, 1452, 1377, 1272 and 712; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (2H, d, *J* = 7.2 Hz, 2-*H* and 6-*H*), 7.56 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.44 (4H, m, Ar-*H*), 7.38 (2H, t, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.36 (1H, t, *J* = 7.6 Hz, 4-*H*′) and 5.37 (2H, s, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 66.8, 128.1, 128.2, 128.4, 128.6, 129.7, 130.2, 133.0, 136.2 and 166.4.

TABLE-1
EFFECT ON MOLAR RATIO OF *N*-BENZOYLBENZOLETRIAZOLE (**1a**) TO BENZYL ALCOHOL (**2a**) ON THE ACYLATION REACTION

Entry	Molar ratio **1a:2a**	Time (h)	Yield of **3a** (%)	Yield of **4** (%)
1	1:1	2	47	46
2	1:2	2	91	91
3	1:3	2	91	92

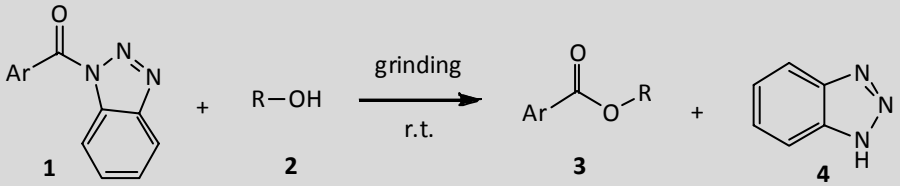
Benzyl 4-chlorobenzoate (3b): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 3036, 2953, 2929, 1722, 1645, 1595, 1488, 1456, 1270 and 759; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.38 (7H, m, Ar-*H*) and 5.35 (1H, s, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 67.1, 128.3, 128.4, 128.6, 128.7, 129.0, 131.2, 135.8, 139.5 and 165.5.

Benzyl 4-methylbenzoate (3c): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3089, 3051, 2986, 2958, 1719, 1616, 1455 and 1272; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.45 (2H, d, *J* = 7.6 Hz, 2′-*H* and 6′-*H*), 7.45 (2H, d, *J* = 7.2 Hz, 3′-*H* and 5′-*H*), 7.36 (1H, t, *J* = 7.2 Hz, 4′-*H*), 7.23 (2H, d, *J* = 8.0 Hz, 3-*H* and 5-*H*), 5.35 (2H, s, CH_2) and 2.40 (3H, s, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 66.6, 127.4, 128.1, 128.2, 128.6, 129.1, 129.7, 136.2, 143.8 and 166.6.

Benzyl 4-methoxybenzoate (3d): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3087, 3052, 2986, 2958, 1718, 1613, 1455 and 1275; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.45 (2H, d, *J* = 7.6 Hz, 2′-*H* and 6′-*H*), 7.45 (2H, d, *J* = 7.2 Hz, 3′-*H* and 5′-*H*), 7.36 (1H, t, *J* = 7.2 Hz, 4-*H*), 7.24 (2H, d, *J* = 8.0 Hz, 3-*H* and 5-*H*), 5.35 (2H, s, CH_2) and 2.41 (3H, s, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 66.5, 113.4, 122.5, 128.3, 128.6, 129.1, 129.7, 136.2, 143.6 and 166.1.

4-Chlorobenzyl benzoate (3e): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3061, 2950, 2924, 2853, 1720, 1605, 1493, 1452, 1269 and 1088; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06

TABLE-2
OPTIMIZED CONDITIONS DATA OF AROYLATION IN ABSENCE OF ORGANIC SOLVENT



1 2 3 4

Entry	Ar	R	Time (h)	Yield of **3** (%)	Yield of **4** (%)
1	4-ClC_6H_4 (**1b**)	C_6H_5 (**2a**)	2.0	92 (**3b**)	92
2	4-MeC_6H_4 (**1c**)	C_6H_5 (**2a**)	2.5	89 (**3c**)	88
3	4-$MeOC_6H_4$ **1d**)	C_6H_5 (**2a**)	2.5	89 (**3d**)	87
4	C_6H_5 (**1a**)	4-ClC_6H_4 (**2b**)	2.0	92 (**3e**)	91
5	4-ClC_6H_4 (**1b**)	4-ClC_6H_4 (**2b**)	2.0	95 (**3f**)	90
6	4-MeC_6H_4 (**1c**)	4-ClC_6H_4 (**2b**)	2.5	91 (**3g**)	90
7	4-$MeOC_6H_4$ **1d**)	4-ClC_6H_4 (**2b**)	2.5	90 (**3h**)	86
8	C_6H_5 (**1a**)	4-MeC_6H_4 (**2c**)	2.0	90 (**3i**)	88
9	4-ClC_6H_4 (**1b**)	4-MeC_6H_4 (**2c**)	2.0	93 (**3j**)	89
10	4-MeC_6H_4 (**1c**)	4-MeC_6H_4 (**2c**)	2.5	89 (**3k**)	88
11	4-$MeOC_6H_4$ (**1d**)	4-MeC_6H_4 (**2c**)	2.5	89 (**3l**)	88
12	C_6H_5 (**1a**)	$CH_3CH_2CH_2$ (**2d**)	3.0	76 (**3m**)	73
13	C_6H_5 (**1a**)	$(CH_3)_2CH$ (**2e**)	3.5	73 (**3n**)	71
14	C_6H_5 (**1a**)	$CH_3(CH_2)_2CH_2$ (**2f**)	3.0	78 (**3o**)	76
15	C_6H_5 (**1a**)	$(CH_3)_2CHCH_2$ (**2g**)	3.5	74 (**3p**)	72
16	C_6H_5 (**1a**)	$CH_3CH_2CHCH_3$ (**2h**)	3.5	72 (**3q**)	70
17	C_6H_5 (**1a**)	$(CH_3)_3C$ (**2i**)	3.5	70 (**3r**)	68

(2H, d, *J* = 7.2 Hz, 2-*H* and 6-*H*), 7.56 (1H, t, *J* = 7.2 Hz, 4-*H*), 7.45 (2H, t, *J* = 7.6 Hz, 3-*H* and 5-*H*), 7.40 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.36 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*) and 5.34 (2H, s, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.9, 128.5, 128.8, 129.5, 129.7, 129.9, 133.1, 134.0, 134.5 and 166.4.

4-Chlorobenzyl 4-chlorobenzoate (3f): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 2953, 2922, 2879, 2855, 1716, 1632, 1488, 1273 and 1119; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.53 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 7.42 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 7.33 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*) and 5.31 (2H, s, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): ν 66.1, 122.5, 128.4, 128.8, 129.9, 131.1, 131.8, 134.9, 139.7 and 165.6.

4-Chlorobenzyl 4-methylbenzoate (3g): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3036, 2949, 2856, 1716, 1615, 1493, 1270 and 1170; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.38 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.36 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.25 (2H, d, *J* = 8.0 Hz, 3-*H* and 5-*H*), 5.31 (2H, s, CH_2) and 2.40 (3H, s, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): ν 21.6, 65.8, 127.3, 128.3, 128.4, 129.1, 129.5, 129.7, 134.1, 134.8 and 166.5.

4-Chlorobenzyl 4-methoxybenzoate (3h): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3050, 2948, 2853, 1721, 1608, 1512, 1373, 1284 and 1130; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.39 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 7.36 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 6.92 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 5.30 (2H, s, CH_2) and 3.87 (3H, s, Ar-OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 66.5, 113.6, 122.3, 122.5, 128.7, 129.5, 130.8, 131.7, 134.9 and 163.6.

4-Methylbenzyl benzoate (3i): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3053, 1720, 1676, 1518, 1450 and 1270; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (2H, d, *J* = 7.2 Hz, 2-*H* and 6-*H*), 7.56 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.44 (2H, t, *J* = 7.6 Hz, 3-*H* and 5-*H*), 7.35 (2H, d, *J* = 7.6 Hz, 2′-*H* and 6′-*H*), 7.20 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 5.34 (2H, s, CH_2) and 2.37 (3H, s, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 66.8, 128.3, 129.3, 129.6, 129.7, 130.4, 133.0, 133.1, 138.2 and 166.5.

4-Methylbenzyl 4-chlorobenzoate (3j): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 2953, 2920, 2855, 1721, 1630, 1597, 1462 and 1278; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.41 (2H, d, *J* = 7.6 Hz, 3-*H* and 5-*H*), 7.33 (2H, t, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.21 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 5.31 (2H, s, CH_2) and 2.38 (3H, s, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 66.9, 128.5, 128.8, 129.3, 129.8, 131.1, 132.8, 138.3, 139.4 and 165.7.

4-Methylbenzyl 4-methylbenzoate (3k): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 2959, 2857, 1721, 1615, 1518, 1457, 1272 and 1100; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.35 (2H, d, *J* = 7.6 Hz, 3-*H* and 5-*H*), 7.23 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.19 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 5.31 (2H, s, CH_2), 2.41 (3H, s, Ar-CH_3) and 2.37 (3H, s, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 21.7, 66.5, 127.4, 128.3, 129.1, 129.2, 129.7, 133.2, 138.0, 143.6 and 166.7.

4-Methylbenzyl 4-methoxybenzoate (3l): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3019, 2925, 2862, 1718, 1619, 1512, 1454, 1268 and 1101; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.34 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.20 (2H, d, *J* = 7.6 Hz, 3′-*H* and 5′-*H*), 6.92 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 5.30 (2H, s, CH_2), 3.87 (3H, s, Ar-OCH_3) and 2.38 (3H, s, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 55.4, 66.4, 113.6, 122.8, 128.2, 129.2, 131.7, 133.4, 137.9, 163.4 and 166.3.

***n*-Propyl benzoate (3m):** Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 2957, 2863, 1721, 1595, 1453, 1373, 1270 and 889; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.60 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.45 (2H, t, *J* = 8.0 Hz, 3-*H* and 5-*H*), 4.18 (2H, t, *J* = 7.2 Hz, OCH_2CH$_2$CH$_3$), 1.71-1.80 (2H, m, OCH$_2$CH_2CH$_3$) and 0.91 (3H, t, *J* = 7.2 Hz, OCH$_2$CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 69.0, 128.8, 128.9, 129.8, 132.6 and 166.2.

***iso*-Propyl benzoate (3n):** Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 2957, 2857, 1709, 1601, 1488, 1369, 1280 and 808; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.60 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.45 (2H, t, *J* = 8.4 Hz, 3-*H* and 5-*H*), 4.74-4.81 (1H, m, OC*H*(CH$_3$)$_2$) and 1.45 (6H, d, *J* = 7.2 Hz, OCH(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6, 24.0, 66.5, 128.8, 128.9, 129.8, 130.2 and 166.2.

***n*-Butyl benzoate (3o):** Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 2924, 2853, 1723, 1596, 1487, 1374, 1269 and 759; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.59 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.45 (2H, t, *J* = 8.4 Hz, 3-*H* and 5-*H*), 4.32 (2H, t, *J* = 7.2 Hz, OCH_2CH$_2$CH$_2$CH$_3$), 1.70 (2H, quint, *J* = 7.2 Hz, OCH$_2$CH_2CH$_2$CH$_3$), 1.36-1.42 (2H, m, OCH$_2$CH$_2$CH_2CH$_3$) and 0.88 (3H, t, *J* = 7.2 Hz, OCH$_2$CH$_2$CH$_2$-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 19.3, 30.6, 65.4, 128.8, 128.9, 129.8, 130.2 and 166.6.

***iso*-Butyl benzoate (3p):** Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 2956, 2827, 1711, 1609, 1511, 1461, 1374, 1253 and 846; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.60 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.45 (2H, t, *J* = 8.4 Hz, 3-*H* and 5-*H*), 4.38 (2H, d, *J* = 7.2 Hz, OCH_2CH(CH$_3$)$_2$), 1.77-1.84 (H, m, OCH$_2$C*H*(CH$_3$)$_2$) and 0.92 (6H, d, *J* = 6.8 Hz, OCH$_2$CH(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 27.9, 71.7, 128.8, 128.9, 129.8, 130.2 and 166.2.

***sec*-Butyl benzoate (3q):** Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 2930, 2843, 1710, 1607, 1512, 1456, 1375, 1267 and 823; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.60 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.45 (2H, t, *J* = 8.4 Hz, 3-*H* and 5-*H*), 4.81-4.90 (1H, m, OC*H*(CH$_3$)CH$_2$CH$_3$), 1.67 (2H, quint, *J* = 7.2 Hz, OCH(CH$_3$)CH_2CH$_3$), 1.42 (3H, d, *J* = 6.8 Hz, OCH(CH_3)CH$_2$CH$_3$) and 0.94 (3H, d, *J* = 7.2 Hz, OCH(CH$_3$)CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.3, 19.5, 29.0, 72.8, 128.8, 128.9, 129.8, 130.2 and 166.1.

***tert*-Butyl benzoate (3r):** Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 2924, 2860, 1720, 1596, 1456, 1374, 1269 and 756; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.60 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.45 (2H, t, *J* = 8.4 Hz, 3-*H* and 5-*H*) and 1.41 (9H, s, OC(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.0, 81.1, 128.8, 128.9, 129.8, 132.3 and 165.8.

Benzotriazole (4): White solid; mp 95-97 ºC (lit. 95-97 ºC) [23]; IR (KBr, ν_{max}, cm^{-1}): 3254, 3080, 2959, 2794, 2711, 1623, 1595, 1511, 1458, 1210, 1006, 752 and 741; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, 1H, *J* = 6.2 Hz, 4-*H* of Ar-*H*),

7.93 (d, 1H, *J* = 6.2 Hz, 7-*H* of Ar-*H*) and 7.41-7.54 (m, 2H, 5-*H* and 6-*H* of Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.9, 126.2 and 138.7.

RESULTS AND DISCUSSION

In the first place, an acylated reagent, *i.e. N*-aroylbenzotriazles (**1a-d**) was synthesized by reported procedure [22,23]. Then, *N*-benzoylbenzotriazole (**1a**; Ar = C_6H_5) was used as a model reagent for optimizing the reaction conditions by carrying out the reaction with benzyl alcohol (**2a**; R = $C_6H_5CH_2$) at room temperature with molar ratios of 1:1, 1:2 and 1:3. After 2 h, the employment of twofold and threefold excess of benzyl alcohol (**2a**) similarly gave 91% yield of ester benzyl benzoate (**3a**). Benzotriazole (**4**) by-product was also obtained in 91 and 92% yields, respectively (Table-1, entries 2, 3).

Since the yield maximum of 91% was obtained from molar ratio 1:2 of *N*-benzoylbenzotriazole (**1a**) to benzyl alcohol (**2a**), this treatment was selected as the optimized condition for acylation reaction (Table-1, entry 2). Several benzylic esters **3b-l** could be obtained in high yields by grinding mixture of corresponding *N*-aroylbenzotriazoles (**1a-d**) and benzylic alcohols **2a-d** under the optimized conditions (Table-2). Electron-donating substituents on the aromatic ring of *N*-aroylbenzotriazoles (**1c-d**) slightly decreased the yields of ester products and slightly increased reaction times (Table-2; entries 2, 3, 6, 7, 10 and 11).

Aroylation of other 1º, 2º and 3º alcohols **2d-i** by grinding with *N*-benzoylbenzotriazole (**1a**) under the optimized conditions also readily provided corresponding propyl esters **3d-e** as well as butyl esters **3f-i** in good yields (Table-2). Steric hindrance from the alkyl groups of alcohols (**2e**, **g-i**) slightly reduced the yield of obtained esters as well as slightly increased reaction times (Table-2, entries, 13, 15-17). In addition to satisfactory yields of ester products, an abundance of benzotriazole (**4**) was obtained as byproduct.

Conclusion

Grinding of *N*-aroylbenzotriazoles with alcohols with a pestle and mortar under the optimized conditions gave high yields of corresponding esters and benzotriazoles within a few hours. Electron-donating substituents on aromatic ring of *N*-aroylbenzotriazoles and also steric hindrance from alkyl groups of alcohols caused slight reduction of the yields and slight increasing of the reaction times.

ACKNOWLEDGEMENTS

Financial support from the Thailand Science Research and Innovation and Faculty of Natural Resources, Rajamangala University of Technology Isan Sakonnakhon Campus are gratefully acknowledged.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. A. Rodríguez, M. Nomen, B.W. Spur and J.J. Godfroid, *Tetrahedron Lett.*, **39**, 8563 (1998); https://doi.org/10.1016/S0040-4039(98)01958-3
2. S. Feng, *IOP Conf. Ser.: Earth Environ. Sci.*, **440**, 022019 (2020); https://doi.org/10.1088/1755-1315/440/2/022019
3. G. Bartoli, J. Boeglin, M. Bosco, M. Locatelli, M. Massaccesi, P. Melchiorre and L. Sambri, *Adv. Synth. Catal.*, **347**, 33 (2005); https://doi.org/10.1002/adsc.200404171
4. T. Mineno and H. Kansui, *Chem. Pharm. Bull. (Tokyo)*, **54**, 918 (2006); https://doi.org/10.1248/cpb.54.918
5. C.S. Cho, D.T. Kim, H.-J. Choi, T.-J. Kim and S.C. Shim, *Bull. Korean Chem. Soc.*, **23**, 539 (2002); https://doi.org/10.5012/bkcs.2002.23.4.539
6. G.-S. Zhang, *Synth. Commun.*, **28**, 1159 (1998); https://doi.org/10.1080/00397919808005956
7. G.V.M. Sharma, A.K. Mahalingam, M. Nagarajan, A. Ilangovan and P. Radhakrishna, *Synlett*, 1200 (1999); https://doi.org/10.1055/s-1999-2806
8. R.N. Ram and I. Charles, *Tetrahedron*, **53**, 7335 (1997); https://doi.org/10.1016/S0040-4020(97)00416-X
9. N. Iranpoor, H. Firouzabadi and M.A. Zolfigol, *Synth. Commun.*, **28**, 1923 (1998); https://doi.org/10.1080/00397919808007166
10. K. Ramalinga, P. Vijayalakshmi and T.N.B. Kaimal, *Tetrahedron Lett.*, **43**, 879 (2002); https://doi.org/10.1016/S0040-4039(01)02235-3
11. B. Neises and W. Steglich, *Angew. Chem. Int. Ed. Engl.*, **17**, 522 (1978); https://doi.org/10.1002/anie.197805221
12. K. Saigo, M. Usui, K. Kikuchi, E. Shimada and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **50**, 1863 (1977); https://doi.org/10.1246/bcsj.50.1863
13. K. Wakasugi, A. Nakamura, A. Iida, Y. Nishii, N. Nakatani, S. Fukushima and Y. Tanabe, *Tetrahedron*, **59**, 5337 (2003); https://doi.org/10.1016/S0040-4020(03)00734-8
14. A.R. Sardarian, M. Zandi and S. Motevally, *Acta Chim. Slov.*, **56**, 729 (2009).
15. G. Höfle, W. Steglich and H. Vorbrüggen, *Angew. Chem. Int. Ed. Engl.*, **17**, 569 (1978); https://doi.org/10.1002/anie.197805691
16. T. Sano, K. Ohashi and T. Oriyama, *Synthesis*, 1141 (1999); https://doi.org/10.1055/s-1999-3521
17. K.L. Chandra, P. Saravanan, R.K. Singh and V.K. Singh, *Tetrahedron*, **58**, 1369 (2002); https://doi.org/10.1016/S0040-4020(01)01229-7
18. S.T. Heller, T. Fu and R. Sarpong, *Org. Lett.*, **14**, 1970 (2012); https://doi.org/10.1021/ol300339q
19. A.R. Katritzky, H.-X. Chang and B. Yang, *Synthesis*, 503 (1995); https://doi.org/10.1055/s-1995-3959
20. A.R. Katritzky, B. Yang and D. Semenzin, *J. Org. Chem.*, **62**, 726 (1997); https://doi.org/10.1021/jo961537r
21. B. Phungpis and V. Hahnvajanawong, *Asian J. Chem.*, **33**, 651 (2021); https://doi.org/10.14233/ajchem.2021.23113
22. B. Phungpis, V. Hahnvajanawong and P. Theramongkol, *Der Pharma Chem.*, **8**, 167 (2016).
23. B.S. Furniss, A.J. Hannaford, P.W.G. Smith and A.R. Tatchell, Vogel's Textbook of practical Organic Chemistry, Longman Group: U.K., Ed.: 5, p. 163 (1989).