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Note

Potassium Phosphate / Benzyltriethylammonium Chloride as Efficient Catalytic System for Transesterification

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Potassium phosphate (K_3PO_4) in the presence of benzyltriethylammonium chloride have been found to catalyses the transesterifications of a wide variety of aliphatic and aromatic esters with primary and secondary alcohols affording the corresponding esters in good-to-excellent yields.

INTRODUCTION

Transesterification is one of the most important organic reactions that has numerous laboratory and industrial applications.[1] The transesterification is an equilibrium process where an ester is transformed into another through interchange of the alkoxy moiety. Beside the reaction of ester with alcohols, the transformation can be achieved by reactions of an ester with carboxylic acid,[2,3] or by ester interchange reaction (coupled transesterification).[4] The methodology of transesterification reaction is a great challenge for both academic and industrial chemists. Apart from an uncatalysed transesterification,[5,6] there exsists a wide variety of methods which employ various basic catalysts such as lithium alkoxides,[7] NaOMe,[8] DBU / LiBr,[9] 4-dimethylaminopyridine (DMAP),[10,11] or K_2CO_3.[12–14]

The latter base has been reported to be effective catalyst alone,[12] in the presence of quaternary ammonium salts,[13] non-ionic surfactants,[14] or 18-crown-6.[14] Among acid catalysts, various Lewis acids and acidic salts have been found to act as efficient transesterification promoters: $Ce(SO_4)_2$,[15] $NaHSO_4$,[15] $Fe_2(SO_4)_3$,[15] $Ti(SO_4)_2$,[15] $Al(Oi\text{-}Pr)_3$,[16] $Al(Ot\text{-}Bu)_3$,[17] $Ti(OC_2H_5)_4$,[18,19] $Ti(Oi\text{-}Pr)_4$,[20] I_2,[21] Ph_2NH_2OTf,[22] BBr_3,[23] $(CH_3)_3SiI$ / I_2,[24] InI_3,[25] $(NH_4)_2Ce(NO_3)_6$,[26] and SmX_3 (X = I, OTf, Oi-Pr).[27] Furthermore, metal complexes such as $C_6H_5OCu(PPh_3)_2$[28] and heterocyclic carbenes[27,29] are also described as effective catalysts. The distannoxane complexes developed by Otera's group exhibits the most profound catalytic effect.[1,30]

Among heterogeneous catalysts, strongly basic anion-exchange resin,[31] polymer-bounded DBU,[32] molecular sieves,[33] kaolinitic clay,[34] and silica chloride,[35] were successfully used as easily-removable catalysts. Beside mentioned, the transesterification can be carried out under Mitsunobu reaction conditions,[36] or by enzymatic catalysis.[37]

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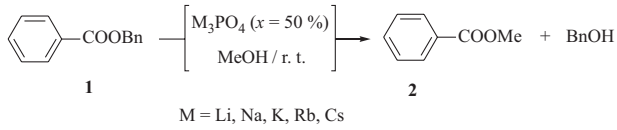
RESULTS AND DISCUSSION

Here it is reported about the profound catalytic effect of alkali metal phosphates in the presence of quaternary ammonium salts in the transesterification reactions of esters with alcohols. Transesterification of benzyl benzoate (**1**, 1 mmol) with methanol (2 ml) affording methyl benzoate (**2**) and benzyl alcohol was selected as a starting model reaction (Scheme 1). The reactions employing different alkali metal phosphates (mole fraction, $x = 50$ %) were performed in methanol as the reaction solvent (and reactant) and the products were separated by preparative chromatography.



Scheme 1.

The strong catalytic effect was observed with all alkali metal phosphates giving clean reactions and high to excellent yields (Table I).

However the activity follows the order: Li_3PO_4 < Na_3PO_4 << K_3PO_4 ≈ Rb_3PO_4 ≈ Cs_3PO_4. Apparently more ionic and basic phosphates possess higher catalytic activity than those with stronger covalent nature (Li_3PO_4). Although K_3PO_4, Rb_3PO_4 and Cs_3PO_4 were the catalysts of similar activity, K_3PO_4 was selected due to its availability and price. The optimal amount of K_3PO_4 in the same reaction was found to be 50 % (mole fraction, x), whereas smaller amounts caused significant extends of the reaction time. To enhance the solubility of K_3PO_4 in less polar alcohols, the addition of quaternary ammonium salts as phase-transfer catalysts (PTC) is essential. All additives employed ($x = 10$ %), tetra-n-butylammonium bromide (TBAB), hexadecyltrime-thylammonium bromide (cetrimonium bromide, CB), didecyldimethylammonium bromide (DDMAB), and benzyltriethylammonium chloride (BTEAC), showed a positive and similar influence on the reaction time required to achieve the high conversion.

TABLE I. The effect of alkali metal phosphates (M_3PO_4) on the model reaction (Scheme 1)

Entry	M	Time / h	Yield / %
1	Li	72	87
2	Na	20	92
3	K	0.5	92
4	Rb	0.5	93
5	Cs	0.4	96

[a] Determined by TLC.
[b] Yields of pure products isolated by chromatography.

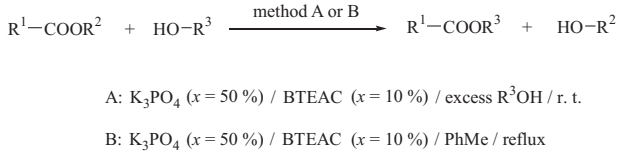
TABLE II. The effect of phase-transfer catalyst (PTC) on the K_3PO_4 ($x = 5$ %)[a] catalysed model reaction (Scheme 1)

Entry	PTC (x / %)	Time / h[b]	Yield / %[c]
1	–	6.5	90
2	TBAB (10)	4.5	95
3	CB (10)	4.0	96
4	DDMAB (10)	4.5	97
5	BTEAC (1)	6.5	92
6	BTEAC (5)	5.5	93
7	BTEAC (10)	4.0	96

[a] x, mole fraction.
[b] Determined by TLC.
[c] Yields of pure products isolated by chromatography.

However, the last one, regarding its smallest molecular weight, was selected as the most suitable (Table II).

Thus developed method based on K_3PO_4 ($x = 50$ %) / BTEAC ($x = 10$ %) was studied on the several model reactions of various esters and alcohols (Scheme 2). The reactions with alcohols of lower molecular weight were conducted in an excess of the corresponding alcohols acting as reaction solvent and reactant in the same time (method A). The reactions with alcohols of higher molecular weight, *e.g.* stearyl alcohol, were performed in refluxing toluene in the presence of only a slight excess (mole ratio 1 : 1.2) of the respective alcohol (method B). In all examples the clean conversions were observed and the expected esters were isolated by preparative chromatography in good to excellent yields (Table III).

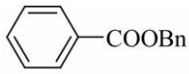
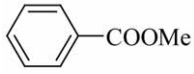
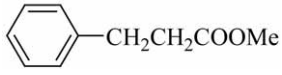
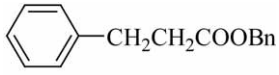
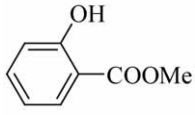
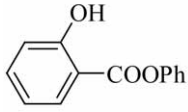
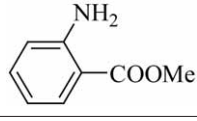


Scheme 2.

Concerning the equilibrium nature of the transesterification reaction, a good-to-high conversions in the method A were obtained due to relatively high mole ratio (*e.g.* 1 : (45–50)) of low molecular weight alcohol (R^3OH) *versus* starting ester. In contrast, the reaction conditions employed in the method B (boiling point of toluene) includes removing of lower molecular weight alcohols (R^2OH, from the parent ester) by evaporation.

Both aromatic and aliphatic esters smoothly react with lower as well as higher primary and secondary alcohols to give the corresponding esters in fair yields. Phenolic esters also react readily, whereas tertiary alcohols do not react even after prolonged reaction times. Alkali metal phosphates are apparently more reactive catalysts than the respective carbonates. For instance, K_3PO_4 *versus* K_2CO_3

TABLE III. (K_3PO_4 (x = 50 %) / BTEAC (x = 10 %))-catalysed transesterifications (Scheme 2)

Entry	R^1COOR^2	R^3	Method [a]	Time / h [b]	Yield / % [c]
1		Me	A	0.5	92
2		Et	A	1.5	84
3		n-C_5H_{11}	A[d]	1	85 (89)[e]
4		n-$C_{18}H_{37}$	B	44 (45)[e]	83 (89)[e]
5		i-Pr	A	2.5 (2.5)[e]	79 (86)[e]
6		i-Pr	A[d],[f]	7.5	89
7		*t*-Bu	A[d]	24 (24)[e]	0 (0)[e]
8		Ph	B	24 (24)[e]	0 (0)[e]
9		CH_2=$CHCH_2$	A[d]	1	83
10		CH_2=$CHCH_2$	A[d],[f]	3	85
11		Et	A	3	91
12		n-C_5H_{11}	A[d]	1	84
13		n-$C_{18}H_{37}$	B	30 (30)[e]	94 (97)[e]
14		i-Pr	A[d]	2.5 (2.5)[e]	86 (94)[e]
15		Bn	A	24	96
16		Et	A	3	96
17		n-C_5H_{11}	A	2.5	82
18		n-$C_{18}H_{37}$	B	48	69
19		i-Pr	A[d]	4 (4)[e]	90 (91)[e]
20		CH_2=$CHCH_2$	A	3	92
21		Bn	A[d]	24	79
22		Et	A	6	87
23		Et	A	4	94
24		i-Pr	A[d]	8	91
25		Me	A	0.3	88
26		i-Pr	A[d]	7 (7)[e]	92 (98)[e]

[a] All reactions using method A were performed at room temperature unless otherwise noted.
[b] Until the dissappearance of starting ester by TLC.
[c] Yields of purified products isolated by chromatography.
[d] Reactions were conducted at reflux temperature of the corresponding R^3OH.
[e] Reactions were performed using Cs_3PO_4 (x = 50 %).
[f] Using K_2CO_3 (x = 50 %) / BTEAC (x = 10 %).

under the same reaction conditions provided faster reactions with retained high yields and clean conversions. Alternatively in the cases of sluggish reactions, K_3PO_4 might be substituted with much more expensive Cs_3PO_4 to achieve slightly higher yields within shorther reaction times. According to our knowledge there is no report about the use of alkali metal phosphates as a transesterification catalysts. In contrast to several reported methods based on highly reactive basic,[7,8] or acidic[15,22–27] catalysts, potassium phosphate and benzyltriethylammonium chloride combination exhibits the ideal properties concerning the catalytic efficiency, mild basic properties, and low price.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer, and ^{1}H NMR and ^{13}C NMR spectra on a Bruker 600 for $CDCl_3$ solutions. TLC analyses were performed on Merck's (Darmstadt, Germany) DC-alufolien with Kieselgel 60F_{254}. Melting points (m.p.) and boiling points (b.p.) were determined by using a Büchi B-540 instrument. HPLC analyses were performed with a Thermo Separation Products (San Jose, USA) instrument equipped with vacuum degasser SCM 1000, quaternary gradient pump P4000, autosampler AS3000, scanning UV/Vis detector UV3000HR, and ChromQuest 251 software. Column: Watters SymmetryShield RP18 (150 × 4.6 mm; 3.5 μm); Mobile phase K_2HPO_4 (10 mmol dm^{-3}, pH = 7.5) / MeCN 40 : 60, at 254 nm. Alkali metal phosphates were purchased from Aldrich. Starting model esters were either purchased from Aldrich, or prepared by known methods.[38–40]

The general procedures for the (K_3PO_4 / BTEAC)-catalysed transesterifications:

Method A. To a solution of an ester (R^1COOR^2, 10 mmol) in the corresponding alcohol (R^3OH, 20 ml), anhydrous K_3PO_4 (1.06 g, 5 mmol, x = 50 %) and BTEAC (0.23 g, 1 mmol, x = 10 %) were added. The reaction mixture was stirred at room temperature or at the reflux temperature for the time indicated in Table III. The reaction mixture was diluted with dichloromethane (20 ml) and washed with water (40 ml). The layers were separated and the aqueous layer was extracted with dichloromethane (3 × 10 ml). The combined organic phases were dried (Na_2SO_4), filtered, and evaporated to dryness.

Method B. The same as in method A except the reactions were performed in toluene (10 ml) in the presence (mole ratio 1 : 1.2) of R^3OH (12 mmol) (Table III).

The crude products were purified by preparative chromatography.

All prepared esters are known compounds: methyl benzoate,[41] ethyl benzoate,[41] 2-propyl benzoate,[42] allyl benzoate,[43] benzyl benzoate,[41] ethyl 3-phenylpropionate,[41] 2-propyl 3-phenylpropionate,[44] allyl 3-phenylpropionate,[45] benzyl 3-phenylpropionate,[46] methyl salicylate.[41] For the products lacking characterisation data in the present literature, m.p. or b.p., spectroscopic (IR, NMR), and analytical data (TLC, HPLC) are given as supporting informations.

CONCLUSION

K_3PO_4 (x = 50 %) / BTEAC (x = 10 %) system efficiently catalyses the transesterification of a wide variety of aromatic and aliphatic esters with primary and secondary alcohols under mild reaction conditions providing a versatile, high-yielding and cost-effective approach to the ester synthesis.

Supplementary Materials. – Supporting informations to the paper are enclosed to the electronic version of the article. These data can be found on the website of *Croatica Chemica Acta* (http://public.carnet.hr/ccacaa).

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SAŽETAK

Kalijev fosfat / benziltrietilamonijev klorid kao učinkoviti katalitički sustav za transesterifikaciju

Ivica Cepanec, Andreja Živković, Anamarija Bartolinčić, Hrvoje Mikuldaš, Mladen Litvić i Sonja Merkaš

Pronađeno je da kalijev fosfat (molni udjel, $x = 50$ %) u prisustvu benziltrietilamonijeva klorida ($x = 10$ %) katalizira reakcije transesterifikacije niza alifatskih i aromatskih estera s primarnim i sekundarnim alkoholima uz nastanak odgovarajućih estera s dobrim do izvrsnim iskorištenjima.

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SUPPLEMENT

SUPPORTING INFORMATIONS

Entry 3. – n-Pentyl benzoate; 1.63 g (85 %), yellow oil, b.p. 247.8–249.1 °C; R_F = 0.69 (CH_2Cl_2); IR (film) $\nu_{max.}$/cm^{-1}: 3091, 3065, 3035, 2958, 2933, 2872, 2862, 1721 (C=O, ester), 1603, 1585, 1492; ^{1}H NMR (DMSO-d$_6$) δ/ppm: 8.05–8.04 (m, 2H), 7.56–7.53 (m, 1H), 7.45–7.42 (m, 2H), 4.32 (t, 2H, J = 6.7 Hz, CH_2), 1.79–1.75 (m, 2H, CH_2), 1.44–1.37 (m, 4H, 2xCH_2), 0.94–0.89 (m, 3H, CH_3); ^{13}C NMR (DMSO-d$_6$) δ/ppm: 166.53 (COO), 132.61, 130.45, 129.39, 128.16, 64.97 (CH_2), 28.31 (CH_2), 28.07 (CH_2), 22.22 (CH_2), 13.81 (CH_3); HPLC analysis: t_R = 12.19 min.

Entry 4. – n-Octadecyl benzoate; 3.11 g (83 %), colourless waxy crystals, m.p. 45.3–45.5 °C, R_F = 0.38 (CH_2Cl_2); IR (KBr) $\nu_{max.}$/cm^{-1}: 3091, 3062, 2920, 2850, 1717 (C=O, ester), 1604, 1585; ^{1}H NMR ($CDCl_3$) δ/ppm: 8.09–8.05 (m, 2H), 7.57–7.54 (m, 1H), 7.47–7.42 (m, 2H), 4.34 (t, 2H, J = 6.7 Hz, CH_2), 1.81–1.76 (m, 2H, CH_2), 1.28 (s, 30H, CH_2), 0.90 (t, 3H, CH_3, J = 6.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ/ppm: 166.54 (COO), 132.63, 130.41, 129.40, 128.16, 65.00 (CH_2), 31.81 (CH_2), 29.58 (CH_2), 29.47 (CH_2), 29.42 (CH_2), 29.25 (CH_2), 29.17 (CH_2), 28.60 (CH_2), 22.57 (CH_2), 13.99 (CH_3).

Entry 5. – 2-Propyl benzoate; 1.30 g (79 %), yellow oil, b.p. 244.5–245.2 °C; R_F = 0.54 (CH_2Cl_2 : n-hexane = 2:1); IR (film) $\nu_{max.}$/cm^{-1}: 3065, 3034, 2981, 2939, 2876, 1717 (C=O, ester), 1679, 1604, 1585, 1492; ^{1}H NMR ($CDCl_3$) δ/ppm: 8.06–8.03 (m, 2H), 7.56–7.39 (m, 3H), 5.30–5.21 (m, 1H, CH), 1.36 (d, 6H, J = 6.3 Hz, 2xCH_3); ^{13}C NMR ($CDCl_3$) δ/ppm: 165.91 (COO), 132.50, 130.73, 129.31, 128.07, 68.13 (CH), 21.76 (CH_3); HPLC analysis: t_R = 6.07 min.

Entry 9. – Allyl benzoate; 1.35 g (83 %), yellow oil, b.p. 230.6–232.1 °C; R_F = 0.69 (CH_2Cl_2); IR (film) $\nu_{max.}$/cm^{-1}: 3072, 3034, 2944, 2883, 1722 (C=O, ester), 1602, 1452, 1271; ^{1}H NMR ($CDCl_3$) δ/ppm: 8.07–8.05 (m, 2H), 7.53–7.51 (m, 1H), 7.42–7.39 (m, 2H), 6.05–5.99 (m, 1H, CH), 5.40 (dd, 1H, J_1 = 1.4 Hz, J_2 = 1.4 Hz, CH_2), 5.26 (dd, 1H, J_1 = 1.1 Hz, J_2 = 1.1 Hz, CH_2), 4.81 (d, 2H, J = 5.7 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ/ppm: 165.84, 132.65, 132.02, 129.94, 129.34, 128.06, 117.83, 65.18; HPLC analysis: t_R = 5.22 min.

Entry 16. – Ethyl 3-phenylpropionate; 1.71 g (96 %), colourless liquid, b.p. 198.3–199.5 °C; R_F = 0.49 (CH_2Cl_2); IR (film) $\nu_{max.}$/cm^{-1}: 3087, 3064, 3029, 2982, 2935, 1734 (C=O, ester), 1604, 1497; ^{1}H NMR ($CDCl_3$) δ/ppm: 7.30–7.20 (m, 5H), 4.13 (q, 2H, J = 7.1 Hz, CH_2Me), 2.94 (t, 2H, J = 7.8 Hz, CH_2), 2.62 (t, 2H, J = 7.8 Hz, CH_2), 1.24 (t, 3H, J = 7.1 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ/ppm: 172.81 (COO), 140.50, 128.37, 128.19, 126.12, 60.29 (CH_2Me), 35.86 (CH_2), 30.90 (CH_2), 14.10 (CH_3); HPLC analysis: t_R = 5.13 min.

Entry 17. – n-Pentyl 3-phenylpropionate; 1.81 g (82 %), yellow oil, b.p. 246.2–247.8 °C; R_F = 0.59 (CH_2Cl_2 : *n*-hexane = 2:1); IR (film) $\nu_{max.}$/cm^{-1}: 3029, 2958, 2933,

2872, 1736 (C=O, ester), 1605, 1497; ^{1}H NMR ($CDCl_3$) δ/ppm: 7.34–7.20 (m, 5H), 4.09 (t, 2H, J = 6.7 Hz, CH_2), 3.05–2.96 (m, 2H, CH_2), 2.68–2.63 (m, 2H, CH_2), 1.74–1.58 (m, 2H, CH_2), 1.47–1.26 (m, 4H, 2xCH_2), 0.98–0.91 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ/ppm: 172.81 (COO), 140.34, 128.30, 128.24, 128.06, 125.99, 72.99 (CH_2), 64.41 (CH_2), 35.71 (CH_2), 30.78 (CH_2), 28.08 (CH_2), 22.09 (CH_2), 13.73 (CH_3).

Entry 18. – n-Octadecyl 3-phenylpropionate; 2.78 g (69 %), colourless waxy crystals, m.p. 41–42 °C; R_F = 0.58 (CH_2Cl_2 : n-hexane = 2:1); IR (film) $\nu_{max.}$/cm^{-1}: 3029, 2952, 2919, 2849, 1728 (C=O, ester), 1604, 1498, 1452, 1464, 1422, 1397, 1368, 1295, 1182; ^{1}H NMR ($CDCl_3$) δ/ppm: 7.30–7.24 (m, 2H), 7.21–7.19 (m, 3H), 4.05 (t, 2H, J = 6.7 Hz, CH_2), 2.97–2.92 (m, 2H, CH_2), 2.65–2.59 (m, 2H, CH_2), 1.62–1.56 (m, 2H, CH_2CO_2), 1.26 (s, 30H), 0.90–0.86 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ/ppm: 172.85 (COO), 140.44, 128.33, 128.14, 126.08, 64.51, 35.80, 31.81, 30.88, 29.58, 29.55, 29.46, 29.40, 29.25, 29.13, 28.49, 25.77, 22.57, 14.00.

Entry 19. – 2-Propyl 3-phenylpropionate; 1.73 g (90 %), colourless oil, b.p. 252.3–252.7 °C; R_F = 0.60 (CH_2Cl_2 : n-hexane = 2:1). IR (film) $\nu_{max.}$/cm^{-1}: 3064, 3029, 2981, 2936, 2877, 1730 (C=O, ester), 1605, 1497; ^{1}H NMR ($CDCl_3$) δ/ppm: 7.31–7.16 (m, 5H), 5.03–4.93 (m, 1H, CH), 2.93 (t, 2H, J = 7.5 Hz, CH_2), 2.62–2.56 (m, 2H, CH_2), 1.22–1.18 (m, 6H, 2xCH_3); ^{13}C NMR ($CDCl_3$) δ/ppm: 172.27 (COO), 140.43, 128.25, 128.15, 126.02, 67.50 (CH), 36.07 (CH_2), 30.87 (CH_2), 21.63 (CH_3); HPLC analysis: t_R = 6.57 min.

Entry 20. – Allyl 3-phenylpropionate; 1.75 g (92 %), colourless liquid, b.p. 257.1–258.2 °C; R_F = 0.64 (CH_2Cl_2 : n-hexane = 2:1); IR (film) $\nu_{max.}$/cm^{-1}: 3029, 2931, 1738 (C=O, ester), 1650, 1605, 1497; ^{1}H NMR ($CDCl_3$) δ/ppm: 7.30–7.20 (m, 5H), 5.93–5.86 (m, 1H, CH), 5.30 (d, 1H, J = 1.4 Hz, CH_2), 5.27 (d, 1H, J = 1.4 Hz, CH_2), 4.58 (d, 2H, J = 5.7 Hz, CH_2), 2.97 (t, 2H, J = 7.7 Hz, CH_2), 2.68–2.65 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ/ppm: 172.41 (COO), 140.38, 132.10, 128.40, 128.20, 126.17, 118.09, 65.03 (CH_2), 35.76 (CH_2), 30.85 (CH_2); HPLC analysis: t_R = 5.77 min.

Entry 21. – Benzyl 3-phenylpropionate; 1.90 g (79 %), colourless oil, b.p. 258.5–259.6 °C; R_F = 0.57 (CH_2Cl_2 : n-hexane = 2:1); IR (film) $\nu_{max.}$/cm^{-1}: 3088, 3064, 3031, 2936, 1737 (C=O, ester), 1096, 1586, 1497; ^{1}H NMR ($CDCl_3$) δ/ppm: 7.38–7.17 (m, 10H), 5.11 (s, 2H, CH_2Ph), 2.97 (t, 2H, J = 8.0 Hz, CH_2), 2.69 (t, 2H, J = 8.0 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ/ppm: 172.61 (COO), 140.28, 135.78, 128.42, 128.38, 128.18, 128.09, 126.15, 66.17 (CH_2Ph), 35.78 (CH_2), 30.82 (CH_2).

Entry 24. – 2-Propyl salicylate; 1.64 g (91 %), colourless oil, b.p. 232.3–234.8 °C; R_F = 0.44 (CH_2Cl_2 : n-hexane = 1:1); IR (film) $\nu_{max.}$/cm^{-1}: 3152, 2984, 2939, 1672 (C=O, ester), 1614, 1586, 1486; ^{1}H NMR ($CDCl_3$) δ/ppm: 10.94 (s, 1H, OH), 7.85–7.82 (m, 1H), 7.46–7.40 (m, 1H), 6.98–6.95 (m, 1H), 6.89–6.84 (m, 1H), 5.35–5.24 (m, 1H, CH), 1.39 (d, 6H, J = 6.3 Hz, 2xCH_3); ^{13}C NMR ($CDCl_3$) δ/ppm: 169.60, 161.52, 135.30, 129.74, 118.83, 117.33, 112.77, 69.03 (CH), 21.68 (CH_3); HPLC analysis: t_R = 7.56 min.

Entry 26. – 2-Propyl anthranylate; 1.65 g (92 %), colourless oil, b.p. 270.5–272.4 °C; R_F = 0.48 (CH_2Cl_2); IR (film) $\nu_{max.}$/cm^{-1}: 3481, 3372, 2981, 2937, 1688 (C=O, ester), 1616, 1588, 1563, 1488, 1456, 1436; ^{1}H NMR ($CDCl_3$) δ/ppm: 7.88–7.83 (m, 1H), 7.26–7.20 (m, 1H), 6.64–6.59 (m, 2H), 5.71 (s, 2H, NH_2), 5.27–5.16 (m, 1H, $CHMe_2$), 1.34 (d, 6H, J = 6.3 Hz, 2xCH_3); ^{13}C NMR ($CDCl_3$) δ/ppm: 167.47, 150.25, 133.63, 130.99, 116.42, 115.90, 111.18, 67.35, 21.77; HPLC analysis: t_R = 5.38 min.