Solid-Liquid Phase-Transfer Catalysis without Added Solvent. A Simple, Efficient, and Inexpensive Synthesis of Aromatic Carboxylic Esters by Alkylation of Potassium Carboxylates

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The preparation of carboxylic esters from the acids is commonly performed by two methods:

- classical esterification with excess alcohol under acidic and dehydrating conditions[1]; recent examples use chlorotrimethylsilane[2,3] or supported sulfuric acid catalyst[4], one-pot methods via acyl chlorides[5] or carboxylic-carbonic anhydrides[6], or methods employing polynitroaryl halides in pyridine[7,8,9].
- carboxylate salt alkylation by halides or sulfates. The anion is either prepared *in situ* (by reaction of the acid with a base) or preformed from an aqueous solution of acid and base. Then, activation of the carboxylate salt is achieved[1]: by use of polar aprotic solvents[10,11,12] or of aprotic apolar solvents under phase-transfer catalysis employing substituted ammonium or sulfonium salts[13,14,15], polymer conditions[16,17], or crown ethers[18]. This reaction has also been performed with impregnated reagents[19] or using alkyldiphenylsulfonium species as alkylating agents[20,21].

We have recently shown[22] that potassium acetate can be alkylated in nearly quantitative yield without the use of a solvent in the presence of catalytic amounts of a tetraalkylammonium salt. Performance of this alkylation is easier than alkylation under classical phase-transfer conditions.

Benzoate anion is far less reactive than acetate anion as can be seen from the results obtained from the alkylation of these anions with alkyldiphenylsulfonium salts[20] under phase-transfer conditions.

Table 1. *O*-Alkylation of Aromatic Carboxylates under Solid-Liquid Phase-Transfer Conditions without added Solvent (ammonium/R^1—COOK = 0.1 mol/mol)

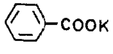
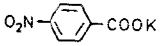
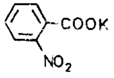
R^1—COOM	R^2—X or X—R^2—X	Ammonium[a] Catalyst	Method	Time [h]	Temperature [°C]	Yield [%]		m.p. [°C] or b.p. [°C]/torr		Conditions and Yields reported
						G.L.C.	isolated	found	reported or Molecular Formula[h]	
	C_2H_5—Br[b]	**1** or **2**	A or B	14	38	100	96	b.p. 94°/14	b.p. 87°/10[23]	R^1—COOH + R^2—$S^{\oplus}(C_6H_5)_2$ $ClO_4^{\ominus}$/CH_2Cl_2; r.t., 7 h; 100%[20]
	C_6H_5—CH_2—Br[b]	**2**	A or B	8	r.t.	98	92	b.p. 112–114°/0.1	b.p. 170–171°/1[23]	R^1—COOH + R^2—OH/2-chloro-3,5-dinitropyridine; r.t. 30 min; 86%[9] R^1—COOH + R^2—X/Amberlite/hexane; 50°C, 6 h; 73%[16] R^1—COONa + R^2—Cl + (*n*-$C_4H_9)_4N^{\oplus}J^{\ominus}$; reflux, 5 h; 100%[13] R^1—COOK + R^2—Br/H_2O/TBAB; 100°C, 6 h; 85%[26]
	n-C_8H_{17}—Br[b]	**1** or **2**	A or B	2	85	100	92	b.p. 102–103°/0.1	b.p. 305–306°/760[25]	R^1—COOK + R^2—Br, + 18-crown-6/$CHCl_3$; r.t., 22 h; 90%[18]; 85°C, 40 h; 58%[19]
	n-$C_{16}H_{33}$—Br[b]	**1** or **2**	A or B	24	50	98	90	b.p. 170°/0.2	b.p. 300–301°/9[25]	
	Br—$(CH_2)_4$—Br[c]	**1** or **2**	A or B	1	85	86	84	m.p. 78–79°	m.p. 79°[11]	R^1—COOH + R^2—X_2/KF/DMF; 120°C, 30 min; 93%[11]
	Br—$(CH_2)_{12}$—Br[c]	**1**	A or B	24	85	96	88			
	i-C_3H_7—Br[b]	**2**	A or B	24	60	92	91	b.p. 115°/11	b.p. 218°/760[23]	R^1—COOH + R^2—$S^{\oplus}(C_6H_5)_2$ $ClO_4^{\ominus}$/CH_2Cl_2; r.t., 7 h; 100%[20] R^1—COOH + Cl—CO—OR^2/$(C_2H_5)_3N$/4-di-NH_2-pyridine, CH_2Cl_2; r.t., 30 min; 96%[6] R^1—COOH + R^2—X/Amberlite/hexane; 50°C, 3 h; 60%[16]
	c-C_6H_{11}—Br[b]	**2**	A or B	24	85	21	20	b.p. 93–95°/1	b.p. 285°/760[23]	
	2-Br-*n*-C_8H_{17}[b]	**1** or **2**	A or B	24	85	79	76	b.p. 98–99°/1	b.p. 218–219°/760[25]	
	$(C_2H_5O)_2SO_2$[b]	**2**	A	24	r.t.	100	91	b.p. 181–182/760	b.p. 186°/760[23]	R^1—COOH + R^2—OH + $ClSi(CH_3)_3$; 78°C, 48 h; 81%[2] R^1—COOH + R^2—OH/2-chloro-1,3,5-trinitrobenzene; r.t., 2 h; 91%[8]
	C_6H_5—CH_2—Br[b]	**1**	A	8	r.t.	98	93	m.p. 83–84°	m.p. 84.7°[27]	R^1—COOH + R^2—OH/2-chloro-3,5-dinitropyridine; r.t., 30 min; 76%[9] R^1—COOK + R^2—Br/18-crown-6/$CHCl_3$; r.t., 22 h; 90%[18] R^1—COOH + R^2—OH/2-chloro-1-methylpyridinium chloride + 9-methyl-2-oxo-3,4-dihydro-2*H*-pyrido[1,2-*a*]pyrimidine; r.t., 4 h; 95%[38]
	n-C_8H_{17}—Br[b]	**2**	A	3	85	98	92	b.p. 175–176°/1	b.p. 170–175°/5[28]	
	n-$C_{16}H_{33}$—Br[b]	**2**	A	40	85	98	93	m.p. 55–56°	m.p. 58.4°[28]	
	$(C_2H_5O)_2$[b]	**1** or **2**	A	6	r.t.	95	93		b.p. 173°/18[23]	
	C_6H_5—CH_2—Br[b]	**2**	A	8	r.t.	98	89	m.p. 103–104°	m.p. 101–102°[29]	
	n-C_8H_{17}—Br[b]	**1** or **2**	A	3	85	98	94	b.p. 170°/1	b.p. 168–169°/1[30]	
	n-$C_{16}H_{33}$—Br[b]	**2**	A	40	85	98	91	m.p. 58–59°	$C_{23}H_{37}NO_4$ (391.5)	

Table 1. (continued)

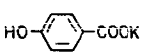
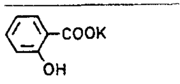
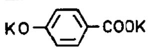
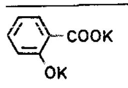
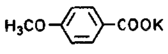
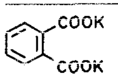
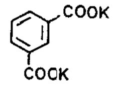
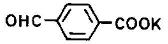
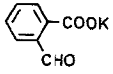
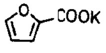
R^1—COOM	R^2—X or X—R^2—X	Ammonium[a] Catalyst	Method	Time [h]	Temperature [°C]	Yield [%]		m.p. [°C] or b.p. [°C]/torr		Conditions and Yields reported
						G.L.C.	isolated	found	reported or Molecular Formula[h]	
	$(H_3CO)_2SO_2$[d]	1 or 2	A	60	r.t.	78	68	b.p. 140–141°/11	b.p. 270–280°/760[23]	R^1—COOH + R^2—OH + $ClSi(CH_3)_3$; 65°C, 1 h; 90%[3] R^1—COOH + R^2—OH/BF_3; 65°C, 30 min; 94%[39]
	C_6H_5—CH_2—Br[d]	1 or 2	A	24	r.t.	89	83	m.p. 111–112°	m.p. 111°[31]	
	$(H_3CO)_2SO_2$[d]	1 or 2	A	24	r.t.	84	79	b.p. 46°/0.1	b.p. 226°/760[23]	R^1—COOH + R^2—OH/BF_3; 65°C, 3 h[39] R^1—COONa + R^2—$Cl/(C_2H_5)_3N/NaJ$; 75°C, 2 h; 96%[24]
	C_6H_5—CH_2—Br[d]	2	A	8	r.t.	96	91	b.p. 133–134°/1	b.p. 158°/2[31]	R^1—COONa + R^2—$Cl/(C_2H_5)_3N/NaJ$; 100°C, 2 h; 89%[24] R^1—COONa + R^2—Cl/DMSO; 105°C, 15 min; 93%[41]
	$(H_3CO)_2SO_2$[e]	1	A or B	24	r.t.	88	83	b.p. 92–93°/1	b.p. 160°/20[23]	
	$(C_2H_5O)_2SO_2$[e]	2	A or B	15	60	87	81	b.p. 100–102°/1	b.p. 148–149°/14[23]	
	C_6H_5—CH_2—Br[e]	1 or 2	A or B	24	40	85	81	m.p. 118–119°	m.p. 115°[31]	
	n-C_8H_{17}—Br[e]	1 or 2	A or B	80	85	84	81		$C_{23}H_{38}O_3$ (362.5)	
	CH_3J[e,f]	2	A	24	r.t.	86	80	b.p. 76–78°/1	b.p. 127°/11[23]	R^1—COONa + R^2—Cl/DMSO; r.t., 12 h; 78%[41]
	$(C_2H_5O)_2SO_2$[e,g]	1 or 2	A	24	r.t.	80	75	b.p. 81°/1	b.p. 180–185°/113[23]	
	C_6H_5—CH_2—Br[e]	1 or 2	A	8	r.t.	89	81	m.p. 49–50°		
	$(H_3CO)_2SO_2$[b]	1 or 2	A	24	r.t.	83	76	b.p. 142–144°/10	b.p. 160°/20[23]	
	n-C_8H_{17}—Br[b]	1 or 2	A	3	85	95	80	b.p. 133°/1	not reported[32]	R^1—COCl + R^2—OH; 34%[32]
	$(C_2H_5O)_2SO_2$[e]	1 or 2	A	24	60	82	77	b.p. 125–127°/1	b.p. 172°/12[23]	R^1—COOK + R^2—Br/DMF; 150°C, 4 h; 82%[43]
	H_2C=CH—CH_2—Br[e]	2	A	16	60	90	88	b.p. 141–142°/1	b.p. 147–150°/1[33]	R^1—COOK + R^2—Br/DMF; 100°C, 8 h; 61%[43] $(R^1$—$CO)_2O$ + R^2—$Br/K_2CO_3/NaJ/(C_2H_5)_3N$/toluene; 140°C, 4 h; 82%[44]
	C_6H_5—CH_2—Br[e]	2	A	16	60	88	85	b.p. 135–138°/0.1	b.p. 277°/15[23]	R^1—COOK + R^2—Br/DMF; 100°C, 8 h; 58%[43] R^1—COONa + R^2—Cl/DMF; 90°C, 60 h; 94%[45] R^1—COONa + R^2—Br (excess)/H_2O/1. ammonium salt, 2. azeotrop. dist., 150°C, 3 h; 91%[46]

Table 1. (continued)

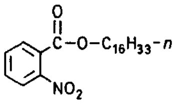
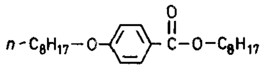
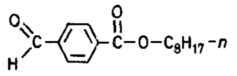
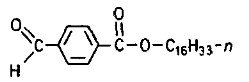
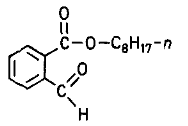
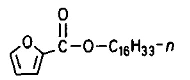
R^1—COOM	R^2—X or X—R^2—X	Ammonium[a] Catalyst	Method	Time [h]	Temperature [°C]	Yield [%]		m.p. [°C] or b.p. [°C]/torr		Conditions and Yields reported
						G.L.C.	isolated	found	reported or Molecular Formula[h]	
	n-C_8H_{17}—Br[e]	**1**	A	16	85	91	87	b.p. 141–143°/0.1	b.p. 222–229°/2.3[34]	R^1—COOK + R^2—Br/DMF; 150 °C, 8 h; 72 %[43] R^1—COOH + R^2—Cl/$(C_2H_5)_3N$; 150 °C, 5.5 h; 98 %[48] R^1—COONa + R^2—Br (excess)/H_2O/1. ammonium salt, 2. azeotrop. dist., 160 °C, 3 h; 91 %[47]
	2-Br-n-C_8H_{17}[e]	**1**	A	24	85	74	72	b.p. 138–139°/0.1	b.p. 211–213°/2[34]	
	n-C_4H_9—CH(C_2H_5)—CH_2—Br[e]	**2**	A	24	85	98	97	b.p. 140–141°/0.1	b.p. 215–219°/0.5[35]	
	$(C_2H_5O)_2SO_2$[e]	**2**	A	36	60	80	78	b.p. 134–136°/1	b.p. 170°/2.4[23]	
	n-C_8H_{17}Br[e]	**1** or **2**	A	80	85	84	77	b.p. 220°/1	b.p. 225–228°/2[34]	
	$(H_3CO)_2SO_2$[e]	**1** or **2**	A	60	60	4				
	H_2C=CH—CH_2—Br[e]	**1**	A	60	85	30	25	b.p. 170–172°/5		R^1—COOH + NaOH + $(H_3CO)_2SO_2$/H_2O + ammonium salt; 90 °C, 60 h; 94 %[42] R^1—COOH + NaOH + $(H_3CO)_2SO_2$/H_2O + ammonium salt; 90 °C, 60 h; 94 %[42] R^1—COOH + R^2—Cl/$(C_2H_5)_3N$/ethanediol; 130 °C, 1.5 h; 100 %[40]
	C_6H_5—CH_2—Br[e]	**1** or **2**	A	60	85	20	20			
	n-C_8H_{17}—Br[e]	**1** or **2**	A	80	85	17	14			
	$(C_2H_5O)_2SO_2$[b]	**1**	A	20	40	100	91		b.p. 142°/13[36]	
	n-C_8H_{17}—Br[b]	**1** or **2**	A	24	85	100	92		$C_{16}H_{22}O_3$ (262.3)	
	n-$C_{16}H_{33}$—Br[b]	**2**	A	24	85	100	85	m.p. 54°	$C_{24}H_{38}O_3$ (374.5)	
	$(C_2H_5O)_2SO_2$[b]	**2**	A	18	r.t.	94	87		b.p. 240–243°/760[37]	
	n-C_8H_{17}—Br[b]	**1** or **2**	A	24	85	98	91		$C_{16}H_{22}O_3$ (262.3)	
	$(C_2H_5O)_2SO_2$[b]	**1**	A	13	60	88	81		b.p. 128–129°/95[23]	R^1—COOH + R^2—OH + ClSi$(CH_3)_3$; 60 °C, 1 h; 85 %[3] R^1—COOH + R^2—J/Amberlite/hexane; r.t., 10 h; 92 %[17] R^1—COOH + R^2—OH/BF_3; 78 °C, 4 h; 76 %[39]
	C_6H_5—CH_2—Br[b]	**1**	A	15	r.t.	97	91	b.p. 101°/0.1	b.p. 179–181°/18[23]	
	n-C_8H_{17}—Br[b]	**1** or **2**	A	24	85	93	88	b.p. 125°/1	b.p. 126–127°/1[23]	
	n-$C_{16}H_{33}$—Br[b]	**1** or **2**	A	24	85	100	89	m.p. 41–42°	$C_{21}H_{36}O_3$ (336.5)	

[a] **1** = TBAB (tetrabutylammonium bromide), **2** = Aliquat 336.
[b] R^1—COOK/R^2—X = 1.1/1 (mol/mol).
[c] R^1—COOK/R^2—X = 2/1 (mol/mol).
[d] R^1—COOK/R^2—X = 1/1 (mol/mol).
[e] R^1—COOK/R^2—X = 1/2 (mol/mol).
[f] With the more reactive dimethyl sulfate, the temperature increases during the addition and yield is lower.
[g] Yield decreases at higher temperatures.
[h] The microanalyses were in good agreement withe the calculated values: C ±0.16; H ±0.17.

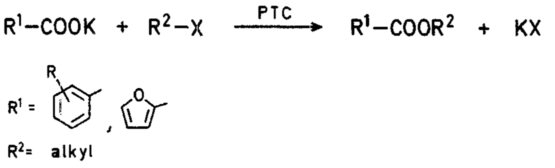
Table 2. G.L.C. Analysis of Product Esters. Conditions: SE 30, 15% 1 m/chromosorb WAW020-C25 column, carrier N_2, p = 1.2 Kg

Ester	Oven Temperature [°C]	Internal Standard	Retention time [min]	
			ester	internal standard
ethyl benzoate	120	diethyl diethylmalonate	1.6	4
benzyl benzoate	210	dibutyl phthalate	1.5	2.5
octyl benzoate	220	dibutyl phthalate	1.3	2.2
cetyl benzoate	250	diethyl dibenzylmalonate	5.8	2.4
1,2-dibenzoxyethane	280	dibutyl phthalate	0.6	1.6
1.12-dibenzoxydodecane	295	cetyl 2-nitrobenzoate	5.5	3
isopropyl benzoate	120	methyl benzoate	1.8	1
cyclohexyl benzoate	180	octyl benzoate	1.7	3
2-octyl benzoate	220	dibutyl phthalate	0.9	1.9
ethyl 4-nitrobenzoate	210	dibutyl phthalate	0.8	2.5
benzyl 4-nitrobenzoate	240	dibutyl phthalate	2	1.2
octyl 4-nitrobenzoate	240	dibutyl phthalate	1.3	1.2
cetyl 4-nitrobenzoate	280	cetyl benzoate	5.4	2.3
ethyl 2-nitrobenzoate	150	diethyl butylmalonate	2.9	1.5
benzyl 2-nitrobenzoate	240	octyl benzoate	1.8	0.8
octyl 2-nitrobenzoate	210	dibutyl phthalate	4.4	2.8
cetyl 2-nitrobenzoate	280	cetyl benzoate	5.3	2.3
methyl 4-hydroxybenzoate	155	ethyl 4-ethoxybenzoate	1.2	2.8
benzyl 4-hydroxybenzoate	270	bis[2-ethylhexyl] phthalate	0.7	2.1
methyl 2-hydroxybenzoate	155	ethyl 4-ethoxybenzoate	0.9	3.5
benzyl 2-hydroxybenzoate	230	diethyl phthalate	1.7	0.7
methyl 4-methoxybenzoate	150	diethyl diethylmalonate	1.8	1.2
octyl 4-methoxybenzoate	250	octyl benzoate	1.4	0.7
ethyl 4-ethoxybenzoate	160	diethyl diethylmalonate	2.8	1
benzyl 4-benzyloxybenzoate	295	didecyl phthalate	2.4	4.4
octyl 4-octyloxybenzoate	290	octyl benzoate	2.4	1.7
methyl 2-methoxybenzoate	140	diethyl diethylmalonate	1.8	1.4
ethyl 2-ethoxybenzoate	160	diethyl diethylmalonate	1.8	1
benzyl 2-benzyloxybenzoate	290	dioctyl terephthalate	1.4	2.3
diethyl phthalate	160	methyl 4-methoxybenzoate	2	0.9
diallyl phthalate	180	diethyl phthalate	2.4	1.4
dibenzyl phthalate	270	bis [2-ethylhexyl] phthalate	3.1	2.1
dioctyl phthalate	270	bis [2-ethylhexyl] phthalate	3.2	2.1
bis [2-ethylhexyl] phthalate)	270	dioctyl phthalate	2.1	3.2
diethyl isophthalate	180	diallyl phthalate	1.7	2.4
dioctyl isophthalate	290	bis[2-ethylhexyl] phthalate	2	1.1
dimethyl terephthalate	170	diethyl phthalate	1.3	1.8
diallyl terephthalate		dibutyl phthalate	1.4	2
dibenzyl terephthalate	290	bis[2-ethylhexyl] phthalate	2.6	1.1
dioctyl terephthalate	290	bis[2-ethylhexyl] phthalate	2.3	1.1
ethyl 4-formylbenzoate	155	ethyl 4-ethoxybenzoate	1.4	2.8
octyl 4-formylbenzoate	240	dihexyl phthalate	1.2	2.5
cetyl 4-formylbenzoate	295	cetyl benzoate	1.9	1.1
ethyl 2-formylbenzoate	155	ethyl 4-ethoxybenzoate	1.3	2.8
octyl 2-formylbenzoate	240	dihexyl phthalate	1.15	2.5
ethyl 2-furoate	120	ethyl benzoate	0.8	1.6
benzyl 2-furoate	200	dibutyl phthalate	1.2	3.6
octyl 2-furoate	220	dibutyl phthalate	0.9	2.2
cetyl 2-furoate	270	diethyl dibenzylmalonate	2.5	1.6

Table 3. ^{1}H-N.M.R. (90 MHz, Solvent/TMS$_{int}$) Data of the New Esters

Ester	Solvent	δ [ppm]
	$CDCl_3$ + DMSO-d_6	0.85 (m, CH_3); 1.3 [m, $(CH_2)_{13}$]; 1.7 (m, CO—O—CH_2—C$\underline{H}_2$); 4.27 (t, CO—O—C$\underline{H}_2$); 7.5–8 (2m, 4H_{arom})
	acetone-d_6	0.9 (m, 2CH_3); 1.35 [m, 2$(CH_2)_5$]; 1.6–2.0 (m, 2C$\underline{H}_2$—CH_2—O); 4 (t, C$\underline{H}_2$—O—Ar); 4.3 (CO—O—C$\underline{H}_2$); 6.85, 9.7 (2d, 2 × 2H_{arom})
	CCl_4	0.9 (m, 3H); 1.25 [m, $(CH_2)_5$]; 1.75 (m, CO—O—CH_2—C$\underline{H}_2$); 4.3 (t, CO—O—C$\underline{H}_2$); 7.85, 8.1 (2d, 2 × 2H_{arom}); 10 (s, CHO)
	acetone-d_6 + DMSO-d_6	0.9 (m, 3H); 1.25 [m, $(CH_2)_{13}$]; 1.75 (m, CO—O—CH_2—C$\underline{H}_2$); 4.3 (t, CO—O—C$\underline{H}_2$); 7.85, 8.1 (2d, 2 × 2H_{arom}); 9.9 (s, CHO)
	CCl_4	0.9 (m, CH_3); 1.3 [m, $(CH_2)_5$]; 1.7 (m, CO—O—CH_2—C$\underline{H}_2$); 4.3 (t, CO—O—C$\underline{H}_2$); 7.4–8.1 (2m, 4H_{arom}); 9.5 (s, CHO)
	acetone-d_6	0.9 (m, CH_3); 1.3 [m, $(CH_2)_{13}$]; 1.75 (m, CO—O—CH_2—C$\underline{H}_2$); 4.3 (t, CO—O—C$\underline{H}_2$); 6.65 (m, 1H_{arom}); 7.3 (m, 1H_{arom}); 7.8 (m, 1H_{arom})

We now report that our procedure without solvent can be extended to the case of different potassium arenecarboxylates. Among all the studied examples, the only failures are those with cyclohexyl bromide and potassium benzoate (giving mainly elimination) and with dipotassium terephthalate where ester yields < 30% are obtained with the different alkylating reagents used. We have further studied the alkylation of *o*- and *p*-hydroxybenzoic acid salts; in the studied examples, alkylation proceeded selectively at the COOK group.



$R^1-COOK + R^2-X \xrightarrow{PTC} R^1-COOR^2 + KX$

The reaction is either carried out with the separately prepared potassium carboxylate (from the acid and potassium hydroxide in water, followed by evaporation; Method A) or from the potassium carboxylate in admixture with the ammonium salt (prepared by heating a mixture of the acid, potassium hydroxide, and the ammonium salt; Method B). Whereas Method A affords better yields of the desired esters and gives reproducible results even on a larger scale (0.2 mol), Method B is easier to perform.

The method described here affords high yields of esters under mild conditions, even with poorly reactive alkyl halides, solvents or expensive reagents are not required, and work-up is simple. In Table 1, the recently published results obtained with reactive alkylating agents are given for comparison.

O-Alkylation of Potassium Carboxylates under Solid-Liquid Phase-Transfer Conditions; General Procedures:

Method A: The potassium carboxylate is prepared by dissolving the acid in the stoichiometric amount of aqueous potassium hydroxide solution. Water is then evaporated at 60°C/0.1 torr (~ 6 h). The dry potassium carboxylate is mechanically ground to a fine powder. The ammonium catalyst (0.1 equiv/COOK group), the alkylating agent (ratio salt/electrophile given in Table 1), and the powdered salt (11 mmol) are placed in a 60 ml flask. The mixture is shaken for 15 min, then left for an appropriate time and temperature; finally it is diluted twice with ether (30 ml) (warm ethyl acetate for cetyl esters) and the mixture is filtered through a short column of florisil (5 g). The crude product is analyzed by G.L.C. with an internal standard (see Table 2) and finally purified by chromatography on silica gel or by recrystallization (for slighty soluble esters).

Method B: In a 60 ml flask, a mixture of the crushed acid (11 mmol), finely ground potassium hydroxide (1 equiv/COOH group), and the ammonium salt (0.1 equiv/COOH group) is shaken at room temperature for 5 min and then heated at 140°C for 10 min. The resultant cake is ground to a powder. Then, Method A is followed for reaction with the alkylating agent and work-up.

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