

Selective monoesterification of dicarboxylic acids catalysed by ion-exchange resins

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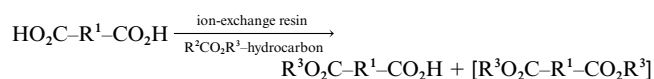
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Symmetrical dicarboxylic acids with 4–14 carbon atoms gave selectively the corresponding monoesters in high yields in the transesterification catalysed by strongly acidic ion-exchange resins in ester–hydrocarbon mixtures. It was found that the rate of the esterification of the dicarboxylic acids is much higher than that of the monocarboxylic acids formed. This result can explain the high selectivity for the monoester formation and can also be explained by the existence of an aqueous layer on the surface of the resins. This method of selective esterification is quite simple and practical.

Introduction

Methods for the selective protection of one of two identical functional groups, which exist in symmetrical positions in a molecule, are important in organic synthesis. It is also worth studying the preparation of monoesters of symmetrical diacids when the cyclic anhydrides are not readily available. Dicarboxylic acids have been reported to be selectively monoprotected in a few ways. They give monomethyl esters in the reaction with diazomethane or dimethyl sulfate in the presence of alumina or silica gel.¹ Methods to obtain monoesters *via* cyclic compounds have been developed.² Enzymatic methods to give monoesters have been thoroughly reviewed.³ Monoesterification of diacids using alkyl halides under phase-transfer catalysis⁴ and using alcohols and acid catalysts such as sulfuric acid⁵ have also been reported. Selective monoacylation of diols has been studied more extensively.⁶

We have found that symmetrical diols are selectively monoacylated in ester–alkane⁷ and monotetrahydropyranylated in dihydropyran–hydrocarbon mixtures⁸ in reactions catalysed by acidic ion-exchange resins. These studies suggest that similar selectivity appears in the reactions catalysed by wet ion-exchange resins when the following conditions are fulfilled: (1) the solubility in water decreases in the following order: starting materials > monoprotected products > diprotected products and/or the solubility in the organic solvents increases in the reverse order, and (2) the dissolving power of the solvents is appropriate. These results along with the fact that esterification is often used to protect the carboxy group⁹ prompted us to study the monoesterification of symmetrical dicarboxylic acids by transesterification¹⁰ catalysed by sulfonic acid-type ion-exchange resins (Scheme 1). A part of the results described in



Scheme 1

this paper has been published as a preliminary report.¹¹ This method of monoesterification is quite simple and practical.

Results and discussion

Conditions for monoesterification

Fig. 1 shows an example of the relation between the prod-

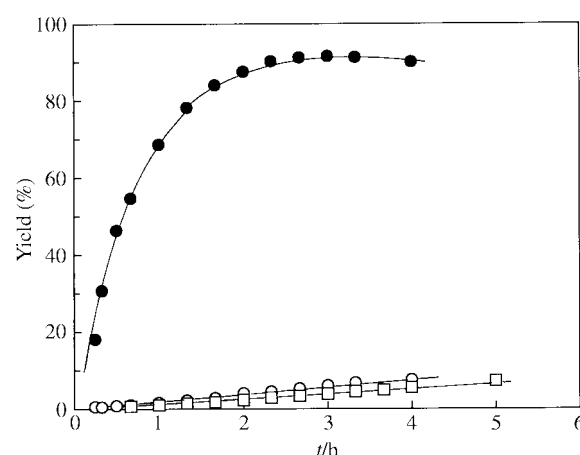





Fig. 1 Yields vs. reaction time. Hexanedioic acid or hexanedioic acid monobutyl ester (1 mmol) and Dowex 50WX2 (50–100 mesh) (1.0 g) were stirred at 70 °C in HCO_2Bu –octane (1 : 1, 10 cm^3): monoester (●) and diester (○) from the diacid; and the diester (□) from the monoester.

uct yields and the reaction period in the esterification of hexanedioic acid. The acid (1 mmol) and Dowex 50WX2 (50–100 mesh) (1.0 g) were stirred in butyl formate–octane (1 : 1, 10 cm^3) at 70 °C. The yield of the monoester reached 91% when that of the diester was 5%, and yields of the two esters did not change so much even after the yield of the monoester reached a maximum. These results show that the monoester reacts much more slowly than the dicarboxylic acid and that the rate of the formation of the diester does not increase very much even after most of the dicarboxylic acid has been consumed. That the yield of the diester does not increase rapidly even after most of the dicarboxylic acid has been consumed is uncommon in an ordinary successive reaction and enhances the value of this reaction because the timing to terminate the successive esterification is not so important.

Table 1 shows that all the symmetrical dicarboxylic acids with 5–14 carbon atoms gave the corresponding monobutyl esters in high yields in the transesterification catalysed by the strongly acidic ion-exchange resin in butyl formate–octane mixtures. By the use of propyl formate and ethyl propionate instead of butyl formate, hexanedioic acid yielded the corresponding propyl and ethyl esters (Table 1, entries 8 and 9). These results confirm the general applicability and practical utility of this method. The reaction rates were lower in the reaction of

Table 1 Selective monoesterification of HO₂C-R¹-CO₂H with R²CO₂R³ catalysed by ion-exchange resin^a

Entry	Ester				T/°C	t/min	Yield (%)	
	R ¹	R ²	R ³	%			Monoester	Diester
1	<i>cis</i> -CH=CH-	H	Bu	50	100	100	89	6
2	<i>trans</i> -CH=CH-	H	Bu	50	100	180	87	8
3	(CH ₂) ₃	H	Bu	50	70	180	95	5
4	(CH ₂) ₃	Me	Bu	50	70	440	92	5
5	(CH ₂) ₄	H	Bu	50	70	160	91	5
6 ^b	(CH ₂) ₄	H	Bu	50	70	360	89	5
7 ^c	(CH ₂) ₄	H	Bu	50	70	340	93	6
8	(CH ₂) ₄	H	Pr	50	70	160	85	6
9	(CH ₂) ₄	Et	Et	25	70	240	72	7
10	(CH ₂) ₆	H	Bu	20	100	100	92	5
11	(CH ₂) ₆	Me	Bu	20	100	240	88	5
12 ^d	(CH ₂) ₈	H	Bu	10	100	260	93	4
13 ^d		H	Bu	20	100	1020	89	5
14 ^d		H	Bu	20	100	540	88	5
15 ^{d,e}		H	Bu	35	110	102	89	6
16 ^d	(CH ₂) ₁₂	H	Bu	10	100	750	89	6
17 ^d	(CH ₂) ₁₂	H	Bu	3	100	2340	89	3
18 ^d	(CH ₂) ₁₂	Me	Bu	5	110	1500	80	4

^a Dicarboxylic acid (1.0 mmol) and Dowex 50WX2 (50–100 mesh) (1.0 g) were heated at 70 °C in an R²CO₂R³-octane mixture (10 cm³). ^b The solvent was the ester-benzene mixture. ^c The solvent was the ester-toluene mixture. ^d Amount of solvent was 20 cm³. ^e Amount of the catalyst 2.0 g.

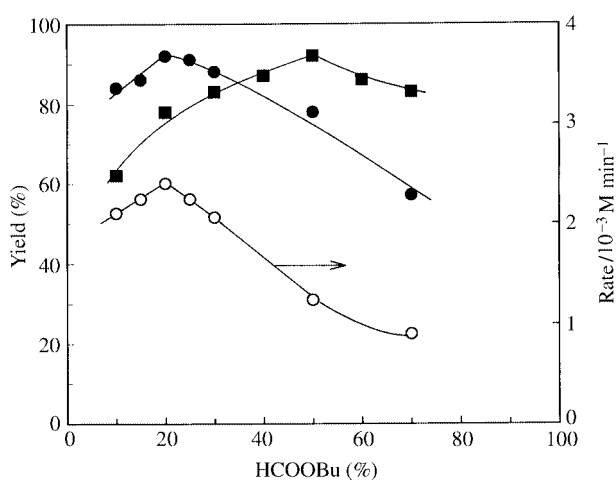


Fig. 2 Yield and rate vs. solvent composition. Octanedioic acid or hexanedioic acid (1 mmol) and Dowex 50WX2 (50–100 mesh) (1.0 g) were stirred at 70 °C in HCOOBu-octane (10 cm³): yield of the monoester at 5% yield of the diester (●) and rate of monoester formation (○) in the reaction of octanedioic acid. The yield (■) in the reaction of hexanedioic acid.

butyl acetate than in that of butyl formate (Table 1, entries 4 and 11).

Each dicarboxylic acid has a peculiar butyl formate-octane solvent ratio that gives the highest selectivity. Generally, the larger the number of carbon atoms in a dicarboxylic acid, the smaller the butyl formate:octane ratio to realize the highest selectivity. Fig. 2 shows the relation between the composition of solvents and the yields of the monoester at the yield of 5% of the diesters in the reaction of octanedioic acid and hexanedioic acid. The yields of the monoesters increased and then decreased as the ratio of butyl formate rose in the solvent. The percentages of butyl formate in the solvent at which the maximum yields were attained were 20% and 50%. This result may be explained partly by the inference that octanedioic acid is more

soluble in the solvents than hexanedioic acid and that butyl formate dissolves the dicarboxylic acids and the monoesters more than octane does. The rate of monoesterification of octanedioic acid varied in a similar way to the yields of the monoester at a 5% yield of the diester. As will be described later, it is presumed that the higher the percentage of butyl formate in the mixed solvent, the lower the amount of the dicarboxylic acids in the aqueous layer on the resin. The decrease in the amount of dicarboxylic acids in the aqueous layer is inferred to reduce the rate of monoester formation. This inference may explain at least partly why the selectivity for monoester formation was low when the percentage of butyl formate in the solvent was very high.

The reaction in benzene and toluene was slower than that in octane (Table 1, entries 6 and 7). This result may be elucidated by the inference that the higher dissolving power of the aromatic solvents reduces the concentration of the diacids in the aqueous layer.

In the reaction of the diacids having not more than six carbon atoms, the amount of the solvent (butyl formate-octane) hardly influenced the selectivity for monoester formation. On the other hand, in the reaction of diacids having more than eight carbon atoms, an increase in the amount of solvent raised the selectivity.

The amount of catalyst is very important. To realize high selectivity in the esterification of dicarboxylic acids we need to use more than about ten times as much ion-exchange resin as we used in the selective acylation⁴ and tetrahydropyranlation⁵ of diols (Table 2).

To examine the performance of the catalysts, hexanedioic acid and an ion-exchange resin were stirred at 70 °C in a mixture of butyl formate and octane (1 : 1) (Table 3). Almost all the sulfonic-type ion-exchange resins of wet types showed nearly the same monoester selectivity as Dowex 50W. Dowex 50WX2 (50–100 mesh) lost 75% of its weight by being dried over P₂O₅. The dried resin showed lower selectivity than the original resin. The amounts of the wet and the dried catalysts were chosen so that similar initial rates were obtained. The selectivity of

Table 2 Amount of catalyst and selectivity^a

Amount of catalyst/g	Yield (%) ^b	Yield (%) ^c	
		Monoester	Diester
0.2	16	53	44
0.4	44	61	15
1.0	85	89	9
1.6	85	87	6
2.0	83	85	6
3.0	79	80	7

^a Hexanedioic acid (1.0 mmol) and Dowex 50WX2 (50–100 mesh) were heated at 100 °C in HCO₂Bu–octane (1:1, 10 cm³). ^b Yield of mono-butyl ester at 5% yield of the diester. ^c Yields when amount of the monoester reached a maximum.

Table 3 Selectivity and catalytic activity of ion-exchange resins^a

Resin	Yield (%) ^b	Rate ^c /10 ⁻³ M min ⁻¹
Dowex 50WX2 (50–100 mesh) ^d	91	1.5
Dowex 50WX2 (50–100 mesh) ^{d,e}	32	0.6
Dowex 50WX2 (200–400 mesh) ^d	90	0.7
Dowex 50WX8 (200–400 mesh) ^f	90	1.6
Dowex 50WX4 (200–400 mesh) ^g	88	1.1
Dowex 50WX8 (50–100 mesh) ^f	88	1.3
Amberlite IR-120 (plus)	85	0.8
Amberlite IR-118 (H)	83	1.0
Amberlyst 15 (wet)	74	0.3
Amberlyst 15 ^h	33	1.6
Amberlyst XN-1010 ^h	17	0.5
Nafion NR-50 ^h	13	0.4

^a Hexanedioic acid (1 mmol) and a resin (1.0 g) were heated at 70 °C in HCO₂Bu–octane (1:1, 10 cm³). ^b Yield of the monoester at 5% yield of the diester. ^c Initial rate of monoester formation. ^d 2% cross-linking. ^e Dried resin (0.2 g) was used. ^f 8% Cross-linking. ^g 4% Cross-linking. ^h For non-aqueous application.

Nafion, Amberlyst 15, Amberlyst XN-1010 which are for non-aqueous application and inferred to contain little water, was low. This result also shows that a certain amount of water in the resins is essential for the high selectivity. The carboxylic acid-type resin (Amberlite IRC-50) was inactive. Dowex 50WX2 (50–100 mesh) was used in all the esterification described hereafter because it dispersed most easily in the solutions.

Rationalization of the selectivity

Fig. 1 also shows the yield of the diester in the reaction of hexanedioic acid monobutyl ester (starting material). Conditions of this reaction were the same as those of the esterification of the diacid noted in Fig. 1. The yields of the diester in the reaction of the monoester (starting material) were much lower than the yields of the monoester in the reaction of the diacid. This outcome shows that the diacid reacted much more rapidly than the monoester to realize the selective formation of the monoester from the diacid.

We presume that the selectivity arises from the factors enumerated below. (1) An acidic water layer is formed on the surface of the resins, because the sulfonic acid-type ion-exchange resins usually contain 50–80% water.¹² (2) A partition equilibrium between the aqueous layer and the aprotic ester–hydrocarbon layer is setup, and the ratios of the dicarboxylic acids in the water layer are much higher than those of the formed monoesters. (3) The diacids react in preference to the monoesters in the aqueous layer and/or at the interface between the aqueous and the nonaqueous liquid layer. (4) The monoesters move from the aqueous layer into the organic layer, which does not contain catalytic protons, and remain there without reacting further.

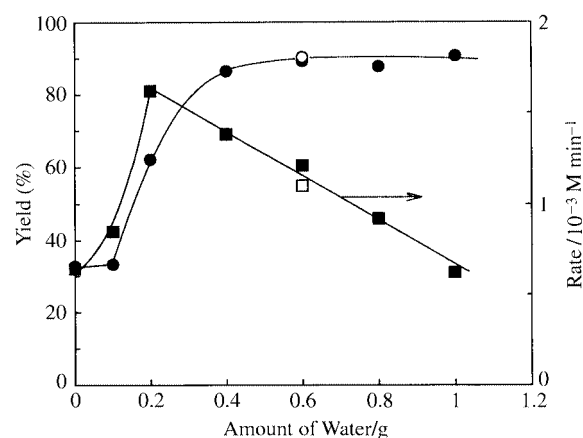


Fig. 3 Yield and rate vs. amount of water. Hexanedioic acid (1 mmol) and dried Dowex 50WX2 (50–100 mesh) (0.2 g) and water were stirred at 70 °C in HCO₂Bu–octane (1:1, 10 cm³): yield of the monoester at 5% yield of the diester (●) and rate of monoester formation (■). The yield (○) and the rate (□) in the reaction catalysed by the original wet resin (1.0 g) are also shown.

When the catalyst dried over P₂O₅ was used, the selectivity, the rate of the formation of the monoester and the maximum yield of the monoester were low (Table 2 and Fig. 3). When increasing amounts of water were added to the reaction system using the dried catalyst, the rate of monoester formation rose, exhibited maximum values, and then declined (Fig. 3). The yield of the monoester at the 5% yield of the diester rose at first and then became nearly constant. It was also found that the amount of the water contained in the original Dowex 50W was suitable for the high selectivity and reactivity. These results support at least in part the proposed mechanism noted before.

Hexanedioic acid and hexanedioic acid monobutyl ester were stirred in a vessel containing water and butyl formate–octane mixture in the absence of catalysts. The monoester hardly existed in the water layer, while the diacid did mostly. The higher the percentage of butyl formate in the organic layer, the lower the amount of the diacid in the water layer. On the basis of the model experiment it is inferred that the concentration of butyl formate in the water layer of the catalysts increases and the concentration of diacids decreases when the ratio of butyl formate in the solvent rises. This inference seems to explain at least in part the result that the selectivity and the reaction rate first increased and then decreased as the percentage of butyl formate in the solvent was elevated (Fig. 2), for the transesterification is supposed to occur in the water layer of the catalysts and/or the interface between the water layer and the organic layer.

Experimental

Reagents and solvents were purchased and used without purification. GLC analyses were performed on an instrument with an autoinjector. The column was a 30 m × 0.25 mm i.d. fused silica capillary column coated with NEUTRABOND-5.

An example of monoesterification of symmetrical dicarboxylic acids for analytical purposes

A mixture of hexanedioic acid (0.146 g, 1 mmol), Dowex 50WX2 (50–100 mesh) (1.0 g), pentadecane (GLC internal standard, 0.02 cm³), and butyl formate–octane (1:1 (v/v), 10 cm³) was stirred at 70 ± 1 °C. Samples of the supernatant liquid were then removed periodically and analysed by GLC.

The retention times of the monoester and the diester were identical to those of authentic samples prepared by the conventional method.

The yields of monoesters at a particular yield of diesters were derived from plots of product yield vs. time, such as that shown in Fig. 1.

An example of monoesterification of symmetrical dicarboxylic acids for preparative purposes

Hexanedioic acid (0.73 g, 5.0 mmol) and Dowex 50WX2 (50–100 mesh) (5.0 g) were stirred at 70 ± 1 °C in a mixture of butyl formate (25 cm³) and octane (25 cm³) and the mixture was monitored by GLC. After 3 h the catalyst was removed by filtration and the solution was evaporated. The residue was chromatographed with hexane–EtOAc (4:1) on a silica gel column to give hexanedioic acid monobutyl ester¹³ (0.82 g, 85%) and hexanedioic acid dibutyl ester^{14–16} (0.05 g, 3%). The monoester: $R_f = 0.29$ in hexane–EtOAc (4:1); ¹H NMR (270 MHz, CDCl₃) δ 0.93 (t, 3H), 0.91–0.96 (t, 3H), 1.31–1.45 (m, 2H), 1.56–1.74 (m, 6H), 2.30–2.42 (m, 4H), 4.05–4.10 (t, 2H). The diester: $R_f = 0.58$ in 20% EtOAc–hexane; ¹H NMR δ 0.93 (t, 6H), 1.30–1.45 (m, 4H), 1.55–1.74 (m, 8H), 2.25–2.36 (m, 4H), 4.08 (t, 4H).

Pentanedioic acid monobutyl ester.^{17,18} ¹H NMR δ 0.93 (t, 3H), 1.31–1.45 (m, 2H), 1.56–1.64 (m, 2H), 1.90–2.01 (m, 2H), 2.37–2.46 (m, 4H), 4.08 (t, 2H).

Pentanedioic acid dibutyl ester.^{19,20} ¹H NMR δ 0.93 (t, 6H), 1.31–1.45 (m, 4H), 1.58–1.66 (m, 4H), 1.89–2.00 (m, 2H), 2.37 (t, 4H), 4.08 (t, 4H).

Hexanedioic acid monopropyl ester.²¹ ¹H NMR δ 0.94 (t, 3H), 1.58–1.74 (m, 6H), 2.29–2.42 (m, 4H), 4.03 (t, 2H).

Hexanedioic acid monoethyl ester.²² ¹H NMR δ 1.26 (t, 3H), 1.62–1.76 (m, 4H), 2.29–2.42 (tt, 4H), 4.07 (t, 2H).

Octanedioic acid monobutyl ester. ¹H NMR δ 0.923 (t, 3H), 1.33–1.41 (m, 6H), 1.57–1.67 (m, 6H), 2.28–2.37 (tt, 4H), 4.07 (t, 2H); ¹³C NMR (CDCl₃) δ 13.7, 19.1, 24.5, 24.7, 28.7, 28.7, 30.7, 33.8, 34.3, 64.2, 173.9, 179.1; IR (film, cm⁻¹) 2959, 2936, 2871, 2671, 1736 (C=O), 1709 (C=O), 1464, 1416, 1244, 1179, 1136, 1092, 1021, 942, 738.

Octanedioic acid dibutyl ester.^{14,15,19,23,24} ¹H NMR δ 0.93 (t, 6H), 1.31–1.42 (m, 8H), 1.55–1.65 (m, 8H), 2.28 (t, 4H), 4.06 (t, 4H).

Decanedioic acid mono butyl ester.²⁵ ¹H NMR δ 0.93 (t, 3H), 1.31–1.45 (m, 10H), 1.56–1.65 (m, 6H), 2.23–2.37 (tt, 4H), 4.07 (t, 2H).

trans-Cyclohexane-1,2-dicarboxylic acid monobutyl ester. ¹H NMR δ 0.92 (t, 3H), 1.24–1.43 (m, 6H), 1.56–1.61 (m, 2H), 1.79–1.81 (m, 2H), 2.06–2.18 (m, 2H), 2.57–2.64 (m, 2H), 4.06–4.10 (t, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 13.6, 19.0, 25.2, 25.2, 28.8, 28.9, 30.6, 44.5, 44.6, 64.4, 175.0, 180.9.

cis-Cyclohexane-1,2-dicarboxylic acid monobutyl ester.¹⁷ ¹H NMR δ 0.92 (t, 3H), 1.34–1.49 (m, 6H), 1.56–1.63 (m, 2H), 1.77–1.80 (m, 2H), 2.00–2.05 (m, 2H), 2.84–2.85 (m, 2H), 4.07–4.11 (t, 2H); ¹³C NMR δ 13.6, 19.1, 23.6, 23.8, 26.0, 26.4, 30.5, 30.9, 42.5, 64.4, 173.6, 179.3.

trans-Cyclohexane-1,4-dicarboxylic acid monobutyl ester.²⁶ ¹H NMR δ 0.93 (t, 3H), 1.33–1.59 (m, 6H), 1.60–1.64 (m, 2H), 2.06–2.10 (m, 4H), 2.27–2.33 (m, 2H), 4.06 (t, 2H); ¹³C NMR δ 13.7, 19.1, 27.8, 27.9, 30.7, 30.9, 42.1, 42.5, 64.3, 96.1, 175.5, 180.5.

Tetradecanedioic acid monobutyl ester. ¹H NMR δ 0.93 (t, 3H), 1.16–1.45 (m, 18H), 1.55–1.78 (m, 6H), 2.26–2.38 (tt, 4H), 4.07 (t, 2H).

Tetradecanedioic acid dibutyl ester.^{14,23} ¹H NMR δ 0.93 (t, 6H), 1.26–1.45 (m, 20H), 1.55–1.63 (m, 8H), 2.26–2.31 (t, 4H), 4.04–4.09 (t, 4H).

Butyl esters of maleic acid and fumaric acid are mentioned in many reports.²⁷ A number of papers referred to dipropyl ester and diethyl ester of hexanedioic acid.^{14,15,28}

Drying of ion-exchange resin

Dowex 50WX2 (50–100 mesh) (1 g) was kept over P₂O₅ (30 g) in a desiccator. The weight of the resin decreased to 26% in 1 day and 25% in 7 days. The resin dried for 7 days was used in the transesterification.

Esterification catalysed by the dried resin and water

A mixture of hexanedioic acid (0.146 g, 1 mmol), the dried Dowex 50WX2 (50–100 mesh) (0.2 g), pentadecane (GC internal standard, 20 μ l), water, and butyl formate–octane (1:1 (v/v), 10 cm³) was stirred at 70 ± 1 °C. Samples of the supernatant organic layer were then removed periodically and analysed by GLC.

Distribution of dicarboxylic acid and monoester in aqueous layer

Hexanedioic acid (0.073 g), hexanedioic acid monobutyl ester (0.107 g), pentadecane (0.01 cm³), water (0.4 cm³), and HCO₂Bu–octane (5 cm³) were stirred for 10 min at 70 °C. The organic layer and the water layer were injected into the GLC. When the percentages of HCO₂Bu in the organic layer were 20, 40 and 60%, the percentages of the diacid in the water layer were 94, 86 and 62%. The percentages of the monoester in the water layer were less than 1% in all the conditions examined.

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