Selective Monoesterification of the Longer Carbon Chain in a Mixture of Dicarboxylic Acids by Adsorbing and Aligning the Acids on Alumina

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Selective monoesterification of the longer carbon chain in a mixture of dicarboxylic acids, [dodecanedioic acid (C_{12}) plus glutaric acid (C_5), adipic acid (C_6), pimelic acid (C_7), suberic acid (C_8), or sebacic acid (C_{10})] was achieved by adsorbing and aligning the acids on alumina.

The use of solid adsorbents such as alumina and silica gel as a reaction medium is a recent advance in organic synthesis.[1,2] Usually it is the reagents that are supported, but there are a few examples of substrate support, for example ozonolysis of aliphatic esters,[3] terminal (ω) chlorination of octanoic acid,[4] enone photocycloaddition,[5] selective reduction of dicarbonyl compounds,[6] and monomethyl esterification of dicarboxylic acids.[7] This paper presents a new type of selective reaction.

Fatty acids, when adsorbed on air–water interfaces, occupy an area of 0.205 nm^2 per molecule; this value is independent of chain length or molecular weight.[8] The molecules are aligned with their axes perpendicular to the interface in a close-packed, rigid array. We have previously shown that the same type of aggregation of carboxylic acids occurs on alumina under certain conditions.[7] If two dicarboxylic acids are adsorbed in this manner, rapid reaction of the non-adsorbed carboxy group of say, a C_{12} chain is possible, but a shorter chain dicarboxylic acid would be expected to be much less reactive.

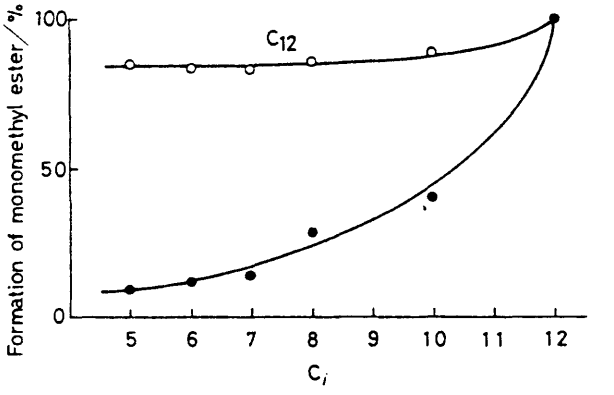

Figure 1. Monomethyl ester formation for C_{12} (○) and C_i (i = 5—8, 10) (●) adsorbed in the molar ratio 6:1 where C_i is the aliphatic dicarboxylic acid having i carbon atoms. *Ca.* 6 mol. equiv. of diazomethane was added.

The samples were prepared as follows. Alumina powder with a known adsorption capacity of 0.4 mmol/g[7] (the reference catalyst of the Catalysis Society of Japan: JRC-ALO-5)† was added to a dimethylformamide (DMF) solution containing two different carboxylic acids, dodecanedioic acid (C_{12}), plus one of glutaric acid (C_5), adipic acid (C_6), pimelic acid (C_7), suberic acid (C_8), or sebacic acid (C_{10}). The acids were present in sufficient quantity to produce 80% surface saturation (0.32 mmol/g). The mixture was allowed to stand for 8 h at 30 °C with occasional shaking. The DMF was slowly removed under reduced pressure. Diazomethane was introduced in a steam of dry nitrogen into a vigorously agitated reaction vessel containing the sample and cyclohexane.[7]

The results given in Figure 1 illustrate the selectivity of the reaction showing (i) that selective preferential monoesterification of the C_{12} acid occurs and (ii) that differences in chain length of the shorter chain acid affects the reactivity of the shorter chain. The larger the difference in the number of carbon atoms, the higher the selectivity becomes. The combination of C_{12} and C_5 acids was the most effective one for the selective monomethyl esterification. An 89% yield of the monomethyl ester of C_{12} was obtained in contrast to a 9% yield for the monomethyl ester of C_5.

† Merck's neutral aluminium oxide 90 for column chromatography (Art. 1077) was also an effective adsorbent for this selective monomethyl esterification.

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