

## Dicarboxylic acid esters from the carbonylation of unsaturated esters under mild conditions

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### Abstract

The methoxycarbonylation of unsaturated acids or esters catalysed by Pd complexes of bis(ditertiarybutyl-phosphinomethyl)benzene (DTBPMB) produces  $\alpha,\omega$ -diesters with selectivities >95%, even if the double bond is deep in the chain or conjugated to the carbonyl group; unsymmetrical esters can also be produced with high selectivity.

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$\alpha,\omega$ -Dicarboxylic acids and their esters are important industrial chemicals used in the synthesis of polyesters and polyamides such as nylon 6.6. They also find uses as lubricants or plasticizers. They are often made by oxidation of cyclic alkanes or by carbonylation reactions, although the latter generally lead to mixtures of products with the added carboxylate group being distributed along the carbon chain [1]. Drent and coworker [2] has reported that 3-pentenitrile can be methoxycarbonylated to methyl 5-cyanopentanoate with terminal selectivities as high as 93% (98% selectivity to cyano esters) using Pd complexes of a variety of diphosphines including bis(ditertiarybutylphosphinomethyl)benzene (DTBPMB) in the presence of methane sulphonic acid (MSA) and that the same system promotes the carbonylation of methyl 3-pentenoate to dimethyl 1,6-hexanedioate (96% selectivity) in methanol

containing anisole at 60 bar and 100 °C [3]. We have recently reported that this system is also very active and selective for the methoxycarbonylation of terminal or internal alkenes to terminal esters under very mild conditions [4,5] and for the methoxycarbonylation of vinyl acetate to protected lactate esters [6,7].

We now report our studies on the use of the same catalytic system for the methoxycarbonylation of unsaturated acids and esters, in which we make  $\alpha,\omega$ -diesters with very high selectivity from a range of starting materials with terminal or internal double bonds. The results are summarised in Table 1.

Although no reaction was observed at 25 °C and 1 bar CO, the methoxycarbonylation of methyl propenoate proceeded efficiently in the presence of Pd/DTBPMB and MSA at 20 bar and 40 °C to give dimethyl 1,4-butanedioate. The branched isomer was not detected, although 20% of the substrate was lost under the reaction conditions to the Michael addition product, methyl 3-methoxypropanoate. Using methyl methacrylate as the substrate, dimethyl 2-methylbutanedioate was produced selectively with no interference from Michael addition (Fig. 1).

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Table 1  
Methoxycarbonylation of unsaturated acids and esters to diesters of  $\alpha,\omega$ -dicarboxylic acids<sup>a</sup>

Substrate	Amount of substrate/mmol <sup>a</sup>	Conversion of substrate/%	Selectivity to $\alpha,\omega$ -diester%
Methyl propenoate	22	100	77 <sup>b</sup>
Methyl 2-methylpropenoate	19	100	100
Methyl 3-pentenoate <sup>c</sup>	21	100	99
2-Pentenoic acid <sup>c,d</sup>	9.9	100	97.3
4-Pentenoic acid <sup>c,d</sup>	9.1	100	96.3
3-Hexenoic acid <sup>c</sup>	17	17.3	100
Methyl oleate <sup>f</sup>	6	100 <sup>g</sup>	>95% <sup>h</sup>
Methyl linoleate <sup>f</sup>	6	100 <sup>i</sup>	82% <sup>h</sup>
Methyl linolenate	6	100 <sup>j</sup>	83% <sup>h</sup>
Butyl propenoate <sup>e</sup>	14	100	95 <sup>k</sup>
Butyl 2-methylpropenoate <sup>c</sup>	13	100	93.4 <sup>k,l</sup>

<sup>a</sup> [Pd] = 0.008 mol dm<sup>-3</sup>, [DTBMPB] = 0.04 mol dm<sup>-3</sup>, [MSA] = 0.08 mol dm<sup>-3</sup>, substrate (2 cm<sup>3</sup>, the equivalent number of moles of substrate is shown in the table), methanol (10 cm<sup>3</sup>), P<sub>CO</sub> = 20 bar, 40 °C, 3 h.

<sup>b</sup> 23% Methyl 3-methoxypropanoate.

<sup>c</sup> 50 °C.

<sup>d</sup> 4 h.

<sup>e</sup> 1 bar, 25 °C.

<sup>f</sup> 22 h.

<sup>g</sup> 17% Isomerised monoester.

<sup>h</sup> Di-methyl nonadecendioate.

<sup>i</sup> 20% Unsaturated compounds.

<sup>j</sup> 20% Unsaturated compounds.

<sup>k</sup> Methyl butyl ester.

<sup>l</sup> Dimethyl 2-methylbutanedioate (6.6%).

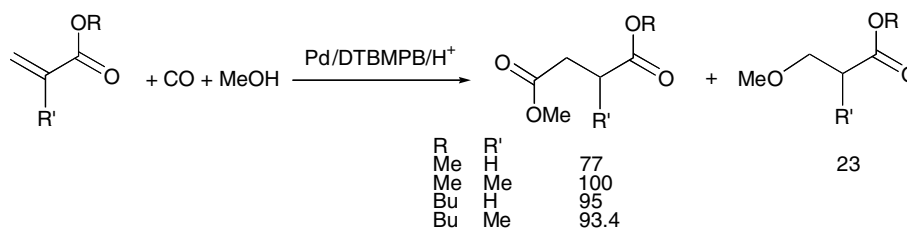


Fig. 1. The formation of butanedioic esters from propenoic acids by methoxy carbonylation.

These reactions show that a double bond conjugated to a carbonyl group can be carbonylated using this system. Methyl 3-pentenoate is transformed selectively into dimethyl 1,6-hexanedioate. More remarkable, however, is the reaction of 2-pentenoic acid to give the same product with excellent selectivity. This reaction not only shows that unsaturated acids can be used as substrates, but also that a double bond can be isomerised out of conjugation and selectively carbonylated once it reaches the end of the chain. The same product is also obtained for methyl 4-pentenoic acid, so this system can transform a mixture of pentenoate esters or acids selectively into dimethyl adipate. These reactions are summarised in Fig. 2.

We were interested in how deep the double bond could be within the chain but still allow the formation of  $\alpha,\omega$ -diesters. We found that not only does methyl 3-hexenoic acid (Fig. 2) produce dimethyl 1,7-heptanedioate, but that even methyl oleate (methyl 9-octadecenoate) is transformed into dimethyl 1,19-nonadecanedioate (identified

by GCMS and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy) with very high conversion and selectivity (Table 1, and Fig. 3). This selectivity with methyl oleate is remarkable, since previous attempts at this reaction have usually provided products in which the new ester group is introduced onto any one of the chain C atoms in an unselective manner or, in the case of palladium based catalysts, selectively onto either end of the double bond without isomerisation [8]. Selective formation of the  $\alpha,\omega$ -diacid or ester has previously been the province of metathesis (see below) or of enzyme chemistry as these products can be formed by over oxidation of long chain carboxylic acids when carrying out cytochrome p450 oxidations to  $\omega$ -hydroxycarboxylic acids [9]. There is considerable interest in these longer chain diesters, with the C<sub>18</sub> diester being prepared from the self metathesis of methyl oleate [10]. That process, however, only proceeds to equilibrium (initial yield of ca. 25%) and only ca. 50% (based on C atoms) of the methyl oleate can be converted into dimethyl 1,18-octadecanedioate, the other 50% producing the other self

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