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Aromatics from pyrones: *para*-substituted alkyl benzoates from alkenes, coumalic acid and methyl coumalate

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The Diels–Alder reaction of coumalic acid and methyl coumalate with unactivated alkenes provides only *para*-substituted adducts in good yield.

1. Introduction

The development of new, cost-competitive processes that utilize renewable resources as feedstocks is important for a sustainable economy. The introduction of such processes not only avoids the use of petroleum, but also has the potential to provide substantial energy savings and reduce greenhouse gas emissions. Although biobased syntheses of certain commercially significant compounds, such as 1,3-propanediol, have been reported,¹ there are comparatively few reported biobased approaches² to aromatic chemicals such as terephthalic acid. As part of a collaborative effort to produce biorenewable chemicals using enzyme catalysis followed by chemical catalysis,³ we describe herein an environmentally benign synthesis of alkyl benzoates, useful intermediates for synthetic surfactants and for oxidation to terephthalic acid. The dimerization of malic acid, a natural product, with sulfuric acid produces coumalic acid.⁵

The Diels–Alder reaction of pyrones with activated alkynes (A = electron-withdrawing group) has good literature precedent.^{4,5} As shown in Scheme 1, the reaction with methyl coumalate (1) involves a cycloaddition to produce bicyclo[2.2.2]octadiene intermediate 2, which loses carbon dioxide to directly form the substituted benzene. Delaney *et al.* have utilized this reaction to produce aromatic systems.⁶ The reaction of activated alkenes with methyl coumalate produces a bicyclic lactone, 3, that cannot transform directly into an aromatic ring by loss of carbon dioxide. One way to construct aromatic rings *via* this intermediate is to dehydrogenate adduct 3 under conditions that lead to the loss of carbon dioxide.⁷

2. Results and discussion

We studied the reaction of methyl coumalate and coumalic acid with unactivated terminal alkenes. To the best of our knowledge, such terminal alkenes have not previously been reported to react



Scheme 1 Diels-Alder reactions with activated alkenes.



Scheme 2 Possible products of a Diels–Alder reaction.

with coumalic acid. Matsushita and co-workers have reported the reactions of substituted styrenes with pyrones.⁷ In order to generate the requisite bicyclo[2.2.2]octadiene intermediate, we conducted the Diels–Alder reaction in the presence of catalytic amounts of 10% Pd/C. Because we are employing unactivated alkenes in the Diels–Alder reaction, both **4** and **5** could be produced as shown in Scheme 2.

As the results in Table 1 indicate, only the *para*-substituted adducts, **4**, were produced, as evidenced by ¹H NMR spectroscopy. In Table 1, entry 4, the structure of **4d** was confirmed by comparison with an authentic sample.⁸ Aromatic ethers and aliphatic ethers are compatible with the reaction conditions.

The Diels-Alder reactions were also examined using coumalic acid. Although it was less soluble than methyl coumalate at

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Table 1 The reaction of methyl coumalate with alkenes

Entry	Substrate	Yield (%)	R group	Product
1	1-Nonene	52	-(CH ₂) ₆ CH ₃	4a
2	1-Decene	70	$-(CH_2)_7CH_3$	4b
3	1-Undecene	63	$-(CH_2)_8CH_3$	4c
4	Allyl benzene	83	-CH ₂ Ph	4d
5	Allyl phenyl ether	61	-CH ₂ OPh	4 e
6	Allyl heptyl ether	51	$-CH_2O(CH_2)_6CH_3$	4f

 Table 2
 The reaction of coumalic acid with alkenes

Entry	Substrate	Yield (%)	R group	Product
1	1-Heptene	85	-(CH ₂) ₆ CH ₃	8a
2	1-Decene	72	$-(CH_2)_7CH_3$	8b
3	1-Undecene	69	$-(CH_2)_8CH_3$	8c
4	Allyl benzene	79	-CH ₂ Ph	8d
5	Allyl phenyl ether	65	-CH ₂ OPh	8e
6	Allyl heptyl ether	66	$-CH_2O(CH_2)_6CH_3$	8f

ambient temperature, the reaction became homogeneous at around 140 $^{\circ}\mathrm{C}.$ The results are shown in Table 2.

The rationale for the remarkable regioselectivity is unclear. The result may simply be due to non-bonded steric interactions favoring the formation of adduct 6. However, we cannot rule out the production of both 6 and 7 in equilibrium with the starting materials, followed by the selective oxidation by Pd/C of 6.

3. Experimental

All starting materials were commercially available unless otherwise noted. Methyl coumalate was prepared *via* the methylation of coumalic acid.⁹ Allyl heptyl ether was prepared from 1heptanol and allyl bromide.¹⁰

Typical reaction procedure: Methyl coumalate (200 mg), olefin (5 equiv.) and 50 mg 10% Pd/C were dissolved in 7 mL mesitylene. The reaction was heated in a sealable tube in an oil bath at 200 °C for 12–16 h. The reaction vessel was then cooled to rt, the catalyst removed by filtering through a pad of Celite® and washed with ether. The filtrate was then concentrated and purified by silica gel chromatography (10:1 hexanes/ethyl acetate).

Methyl 4-heptylbenzoate (4a). ¹H NMR (300 MHz, CDCl₃): δ 7.95 (d, J = 7 Hz, 2H), 7.23 (d, J = 7 Hz, 2H), 3.90 (s, 3H), 2.65 (m, 2H), 1.59–1.26 (m), 0.88; ¹³C NMR (400 MHz, CDCl₃): δ 167.4, 144.3, 129.9, 128.9, 127.3, 52.3, 32.1, 30.0, 29.2, 26.4, 22.9, 14.3; HRMS (FAB) m/z exact mass calc. for C₁₅H₂₂O₂ 235.1693 (MH⁺), found 235.1699.

Methyl 4-octylbenzoate (4b). ¹H NMR (300 MHz, CDCl₃): δ 7.94 (d, J = 7 Hz, 2H), 7.24 (d, J = 7 Hz, 2H), 3.90 (s, 3H), 2.63 (m, 2H), 1.59–1.26 (m), 0.88; ¹³C NMR (400 MHz, CDCl₃): δ; 167.4, 148.7, 129.8, 128.6, 127.4, 52.1, 36.2, 32.1, 31.4, 29.8, 29.7, 29.5, 22.9, 14.3; HRMS (FAB) m/z exact mass calc. for C₁₆H₂₄O₂ 249.1849 (MH⁺), found 249.1815.

Methyl 4-nonylbenzoate (4c). ¹H NMR (300 MHz, CDCl₃): δ 7.96 (d, J = 7 Hz, 2H), 7.24 (d, J = 7 Hz, 2H), 3.90 (s, 3H), 2.64 (m, 2H), 1.59–1.26 (m), 0.88; ¹³C NMR (400 MHz, CDCl₃): δ 167.5, 148.7, 129.8, 128.6, 127.4, 52.1, 36.3, 32.1, 31.4, 29.8, 29.7, 29.6, 29.5, 23.5, 14.4; HRMS (FAB) m/z exact mass calc. for $C_{17}H_{26}O_2$ (MH⁺) 263.2006, found 263.2005.

Methyl 4-benzylbenzoate (4d). Spectral data matches that in the literature.⁸

Mehyl 4-(phenoxymethyl)benzoate (4e). ¹H NMR (300 MHz, CDCl₃): δ 8.05 (d, J = 7 Hz, 2H), 7.51 (d, J = 7 Hz, 2H), 7.31–6.91 (m, 5H), 5.13 (s, 2H), 3.92 (s, 3H); ¹³C NMR (400 MHz, CDCl₃): δ 167.1, 158.6, 142.5, 129.1, 128.9, 127.2, 121.4, 115.0, 69.5, 52.4; HRMS (FAB) m/z exact mass calc. for C₁₅H₁₄O₃ 243.1016 (MH⁺), found 243.1009.

Methyl 4-(heptyloxymethyl)benzoate (4f). ¹H NMR (300 MHz, CDCl₃): δ 8.03 (d, J = 7 Hz, 2H), 7.39 (d, J = 7 Hz, 2H), 4.55 (s, 2H), 3.75 (m, 2H), 1.53–1.28 (m), 0.88; ¹³C NMR (400 MHz, CDCl₃): δ 167.2, 144.3, 130.3, 128.9, 127.8, 72.0, 70.7, 52.3, 32.1, 29.9, 29.4, 26.4, 22.9, 14.3; HRMS (FAB) m/zexact mass calc. for C₁₆H₂₄O₃ 265.1798 (MH⁺), found 265.1804.

4-Pentylbenzoic acid (8a). ¹H NMR (400 MHz, CDCl₃): δ 12.06–11.6 (br, 1 H), 8.05 (d, J = 7 Hz, 2H), 7.29 (d, J = 7 Hz, 2H) 2.70 (t, J = 7 Hz, 2H), 1.73–1.53 (m, 2H) 1.53–1.22 (m, 4H), 0.93 (t, J = 7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.8, 149.8, 130.5, 128.8, 127.1, 36.3, 31.7, 31.1, 22.8, 14.3; HRMS (QTOF) m/z exact mass calc. for C₁₂H₁₆O₂ 192.115, found 191.1078 (M– H)⁻.

4-Octylbenzoic acid (8b). ¹H NMR (300 MHz, CDCl₃): δ 12.54–12.12 (br, 1 H), 8.02 (d, J = 7 Hz, 2H), 7.27 (d, J = 7 Hz, 2H), 2.67 (t, J = 7 Hz, 2H), 1.70–1.51 (m, 2H), 1.37–1.17 (m, 10H), 0.88 (t, J = 7 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 178.7, 149.8, 130.5, 128.8, 115.6, 36.4, 32.1, 31.4, 29.9, 29.7, 29.5, 22.9, 14.4; HRMS (QTOF) m/z exact mass calc. for C₁₅H₂₂O₂ 234.162, found 233.1547 (M–H)⁻.

4-Nonylbenzoic acid (8c). ¹H NMR (300 MHz, CDCl₃): δ 12.42–11.99 (br, 1 H), 8.03 (d, J = 7 Hz, 2H), 7.27 (d, J = 7 Hz, 2H), 2.67 (t, J = 7 Hz, 2H), 1.70–1.55 (m, 2H), 1.40–1.20 (m, 12H), 0.89 (t, J = 7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.8, 149.8, 130.5, 128.8, 127.1, 36.4, 32.2, 31.4, 29.9, 29.7, 29.6, 29.5, 22.9, 14.4; HRMS (QTOF) *m/z* exact mass calc. for C₁₆H₂₄O₂ 248.1776, found 247.1704 (M–H)⁻.

4-Benzylbenzoic acid (8d). ¹H NMR (300 MHz, CDCl₃): δ 12.3–11.2 (br, 1H), 8.05 (d, J = 7 Hz, 2H), 7.40–7.21 (m, 7H), 4.06 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 172.5, 147.8, 140.2, 129.2, 129.1, 128.8, 128.3, 127.5, 126.7, 42.3; HRMS (QTOF) m/z exact mass calc. for C₁₄H₁₂O₂ 212.0837, found 211.0765 (M–H)⁻.

4-(Phenoxymethyl)benzoic acid (8e). ¹H NMR (300 MHz, CDCl₃): δ 9.94 (br, 1H), 7.36–7.25 (m, 6H), 7.12–6.80 (m, 6H), 5.16 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 172.0, 152.6, 141.0, 130.5, 130.0, 129.7, 127.6, 121.1, 115.6, 69.3; HRMS (QTOF) *m/z* exact mass calc. for C₁₄H₁₂O₃ 228.0789, found 227.0714 (M–H)⁻.

4-(Heptyloxy)methyl)benzoic acid (8f). ¹H NMR (300 MHz, CDCl₃): δ 9.93 (br, 1H), 8.05 (d, *J* = 7 Hz, 2H), 7.43 (d, *J* = 7 Hz, 2H), 4.56 (s, 2H), 3.63 (d, *J* = 7 Hz, 2H), 1,64–1.15 (m, 10 H), 0.87 (t, *J* = 7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 171.9, 145.1, 128.8, 128.0, 127.5, 71.5, 71.1, 32.1, 29.9, 29.4, 26.5, 22.9, 14.3;

HRMS (QTOF) m/z exact mass calc. for C₁₅H₂₂O₃ 250.1569, found 250.1576.

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