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Electro-organic Reactions. Part 46. Diels-Alder Trapping of *o*-Quinodimethane Generated by Redox-Mediated Cathodic Reduction of α,α'-Dibromo-*o*-xylene in the Presence of Hindered Dienophiles[1]

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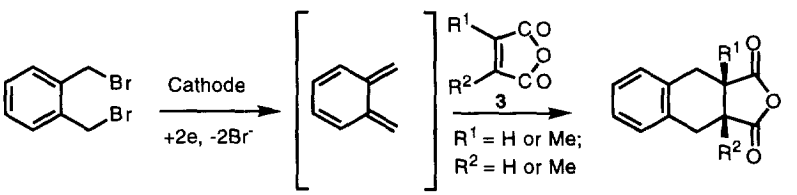
Abstract: Hindered, electron-deficient alkenes **5-11** have been prepared, including analogues of maleic anhydride, *N*-phenylmaleimide and benzoquinone. Cyclic voltammetry showed that most of these compounds can undergo reduction to form relatively persistent radical-anions, which can mediate the reductive cleavage of α,α'-dibromo-*o*-xylene. Preparative electrolytic reduction of α,α'-dibromo-*o*-xylene was performed in the presence of the alkenes **5-11**; in several cases the Diels-Alder adducts of the alkenes and *o*-quinodimethane could be isolated, with particularly high yields of cycloadducts being obtained from the dienophiles **5a**, **5b** and **6a**.

Introduction

Recently we described how electrochemical reduction of α,α'-dibromo-*o*-xylene (**1**),[2] in the presence of maleic anhydride and its derivatives **3**, gave products **4** from the Diels-Alder trapping of the intermediate *o*-quinodimethane (**2**) (Scheme 1). We noted that the reduction potentials of the anhydrides used were less negative than that of the dibromide **1** and presented evidence for a mechanism in which the anhydride acted as an electron-transfer mediator for the irreversible reduction of the dibromide. Cyclic voltammetric (c.v.) studies at rapid sweep speeds (up to 500 V s^{-1}) have shown that maleic anhydride and dimethylmaleic anhydride can both undergo reversible reduction. At the lower sweep speed of 1 V s^{-1}, however, maleic anhydride showed an irreversible c.v., whereas reduction of dimethylmaleic anhydride was still quasi-reversible. This suggested that the presence of alkyl substituents on the anhydride increases the lifetime of the corresponding radical-anion in solution and might enhance the ability to act as an electron transfer mediator. We therefore decided to prepare some hindered dienophiles, to study their electrochemical properties and to examine their effectiveness in trapping electrochemically generated *o*-quinodimethane.



1 **2** **4**

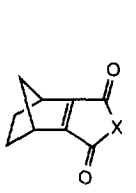
Scheme 1. Diels-Alder reactions of electrochemically generated *o*-quinodimethane with maleic anhydride and its derivatives.

RESULTS AND DISCUSSION

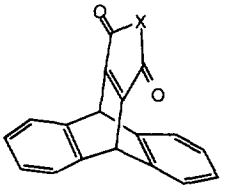
(i) Preparation of the Dienophiles

The anhydride **5a** was prepared from cyclopentadiene by a known procedure.[3] Treatment of **5a** with aniline, followed by acetic anhydride, gave the imide **5b** in 85% yield. The anhydride **6a** was prepared from anthracene[4] and then was converted into the imide **6b** (92 % yield). The quinones **6c**, **6d** and **7** were prepared by oxidation of the Diels-Alder adducts of anthracene with *p*-benzoquinone,[5] 1,4-naphthoquinone[6] and **6c** respectively.[7] The ester **8** was made by direct cycloaddition of diethyl acetylenedicarboxylate to anthracene.[8]

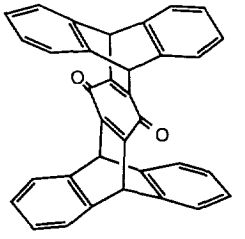
Bromination of 2-methyl-2-propylcyclopentane-1,3-dione with *N*-bromosuccinimide in carbon tetrachloride according to the procedure of Gualtieri and co-workers[9] gave a mixture of the cyclopentenedione **9a** and the related bromo compound (±)-**9b**.[10] These two main products were separated by flash chromatography and the bromide (±)-**9b** was then used in a Diels-Alder reaction with anthracene ($AlCl_3$, CH_2Cl_2, reflux) to give, after crystallisation, the diastereoisomerically pure cycloadduct (±)-**10a** in 70% yield. The nmr spectrum of (±)-**10a** contains a peak at δ 0.08 (3 H, s), implying that the methyl substituent on the five-membered ring is close to the shielding region of one of the aromatic rings. The stereoselective formation of cycloadduct **10a** in preference to **10b** minimises steric repulsions and is explicable on either thermodynamic or kinetic grounds; a force-field calculation indicated that **10a** lies 1.9 kcal mol^{-1} lower in enthalpy than the isomer **10b**. Dehydrobromination of **10a** (Et_3N, $CHCl_3$, 20 °C, 20 min) gave the hindered enedione **11** in 81% yield.



5a X = O
5b X = NPh



6a X = O
6b X = NPh
6c X = CH=CH
6d X = *o*-C_6H_4



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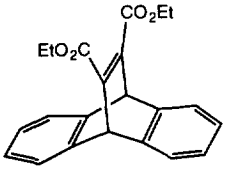

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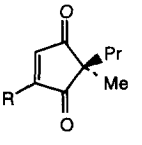
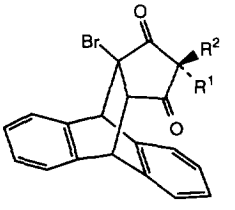
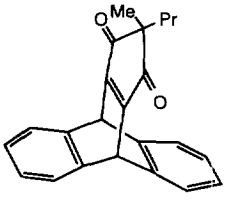


9a R = H
(±)-**9b** R = Br



(±)-**10a** R^1 = Me; R^2 = Pr
(±)-**10b** R^1 = Pr; R^2 = Me



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(ii) Cyclic Voltammetry (c.v.)

Cyclic voltammetric data for the reduction of the various dienophiles are given in Table 1. We have previously shown by c.v. that the reduction of dimethylmaleic anhydride becomes irreversible upon addition of α,α'-dibromo-*o*-xylene (**1**), thus showing that this anhydride can act as an electron-transfer mediator for reduction of the less easily reduced dibromide. The cyclic voltammograms of the dienophiles **5a**, **5b**, **6d** and **11** showed a similar loss of reversibility upon addition of the dibromide **1**.

Table 1. Dienophile reduction potentials (E^o)[a] and reaction with electrogenerated *o*-quinodimethane. The peak potential for irreversible reduction of the dibromide **1** is included for comparison.

Dienophile	$-E^o$/V *vs.* SCE	Diels-Alder adduct (% yield)
(**1**	1.38[b]	—)
5a	1.01	**12a** (78)
5b	1.04	**12c** (98)
6a	0.86[b]	**13a** (83)
6b	2.00	**13b** (48)
6c	0.37	note c
6d	0.54	**13d** (43) note d
7	0.84	note e
8	1.61	note e
9a	1.09[b]	**14a** (16%); **14b** (6%)
11	1.15	note e

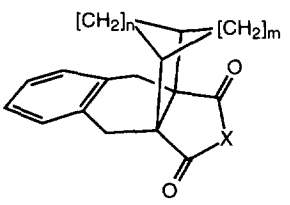
a. Measured by cyclic voltammetry at 1 - 500 V s^{-1}, Hg bead cathode, DMF-Bu_4NPF_6 (0.1 M); b. irreversible reduction, therefore the peak potential (E_p) measured; c. no Diels-Alder adduct could be isolated and the quinone underwent reduction to the corresponding hydroquinone; d. crystallises as a 1:1 complex with anthracene, which presumably arises by partial cycloreversion; e. no Diels-Alder adduct could be isolated and the majority of the dienophile was recovered.

(iii) Preparative Scale Reductions

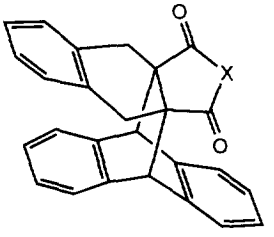
Controlled potential electrolyses were carried out using a divided cell, at an Hg pool cathode, with DMF-Et_4NBr (0.1 M) electrolyte. Potentials were referred to an Ag/AgBr electrode, so are not directly comparable to the E^o values in Table 1. Effectively electrolysis was performed at just past the first reduction peak potential.

Bartlett *et al.* found the norbornenedicarboxylic anhydride **5a** to be a somewhat unreactive dienophile, which failed to react with cyclopentadiene, either alone or in the presence of $AlCl_3$; however, by using a silica gel catalyst they did obtain a 3:2 mixture of *anti-* and *syn-* Diels-Alder adducts, both of which arose by attack on the *exo* face of the norbornenedicarboxylic anhydride.[3] When we electrolysed α,α'-dibromo-*o*-xylene, in the presence of **5a**, we were able to isolate a stereoisomerically pure cycloadduct in 78% yield. A ^1H NOESY NMR spectrum was obtained on this product, but because of overlapping resonances it was not possible to distinguish with certainty between the alternative structures **12a** and **12b**. However, given that the cycloaddition is almost certainly irreversible and that addition to norbornene derivatives usually occurs faster on the *exo* rather than the *endo* face,[12] it is likely that the product is **12a**. The *N*-phenylimide **5b** also reacted with electrochemically generated *o*-quinodimethane to give a high yield of a single stereoisomer, for which the structure **12c** is proposed.

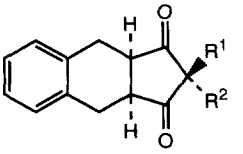
We also performed the ultrasound-promoted reduction of α,α'-dibromo-*o*-xylene by zinc dust, in the presence of the anhydride **5a**, by analogy with the general procedure of Han and Boudjouk.[13] This gave an almost quantitative yield of the Diels-Alder adduct **12a** as a single stereoisomer. Thus the anhydride **5a**, which was identified as a good trap for *o*-quinodimethane through the mechanistic insight provided by our electrochemical studies, also reacts efficiently with conventionally generated *o*-quinodimethane. Although the use of zinc metal appears to be a simple and high yielding alternative to electrochemistry for the laboratory scale preparation of compound **12**, we believe that the electrochemical approach may have advantages for large scale work because it does not require the use of ultrasound and it avoids the production of harmful zinc residues. The mercury cathode could probably be replaced by a less toxic, solid metal electrode.



12a X = O; n =1; m = 2
12b X = O; n = 2; m = 1
12c X = NPh; n = 1; m = 2
12d X = NPh; n = 2; m = 1



13a X = O
13b X = NPh
13c X = CH=CH
13d X = *o*-C_6H_4



14a R^1 = Me; R^2 = Pr
14b R^1 = Pr; R^2 = Me

9,10-Dihydro-9,10-ethenoanthracene-11,12-dicarboxylic anhydride (**6a**) has been previously reported to undergo a Diels-Alder reaction with cyclopentadiene in the absence of catalyst.[14] The reaction of

anhydride **6a** with *o*-quinodimethane is stereochemically unambiguous and by using the electrochemical conditions we were able to prepare the adduct **13a** in 83% yield. The corresponding imide **13b** was obtained from **6b** in only 48% yield; in this case the dienophile **6b** has such a negative reduction potential that it cannot act as a mediator for electron transfer to the dibromide **1**.

The attempted trapping of electrochemically generated *o*-quinodimethane by the ester **8** failed to give any Diels-Alder adduct and most of the ester **8** could be recovered unchanged. Ester **8** has too negative a reduction potential to act as a mediator and is also an inherently poorer dienophile than the anhydrides and imides.

The quinone **6c** is the most easily reduced of the potential dienophiles in Table 1 and was found to undergo reduction to the hydroquinone upon preparative electrolysis in the presence of the dibromide **1**. The somewhat less easily reducible quinone **6d** gave Diels-Alder addduct **13d** in 43% yield; anthracene was a by-product of this reaction, which suggests that partial cycloreversion of **6d** had occurred. No Diels-Alder adduct could be obtained from the extremely hindered quinone **7**.

The cyclopentenedione derivative **9a** underwent cylcoaddition of *o*-quinodimethane to give low yields of two diastereoisomeric adducts **14a** and **14b**, which could be distinguished by comparing the chemical shifts of the alkyl substituents in their ^{1}H NMR spectra. Thus the 2-Me substituents of **14a** and **14b** occurred at δ 0.38 and 1.10 respectively, implying that in the former compound the methyl group is close to the shielding region of the aromatic ring. It is known that 2,2-dialkylcyclopent-4-ene-1,3-dione derivatives are relatively poor dienophiles because of the unfavourable steric effects of the alkyl substituents.[15] The even more hindered dienophile **11** failed to yield any cycloadducts with *o*-quinodimethane.

CONCLUSIONS

These results are consistent with our previously proposed mechanism for electrochemical production of *o*-quinodimethane, in which electron-deficient alkenes can function as electron-transfer mediators. The highest yields of Diels-Alder adducts were obtained for those dienophiles which could undergo reversible one-electron reduction with E^o values up to *ca* 0.5 V less negative than the peak potential for the reduction of α,α'-dibromo-*o*-xylene (**1**). Bulky substituents on the dienophile tend to prolong the lifetime of the corresponding radical-anion and are often well tolerated in Diels-Alder reactions of *o*-quinodimethane, but extremely hindered 'dienophiles' are not able to undergo cycloaddition.

EXPERIMENTAL SECTION

Materials and General Procedures

These have been described in reference 2. Relatively fast sweep cyclic voltammetry employed an Hg-coated Pt electrode (0.7 mm diameter) and a modular apparatus consisting of a waveform generator (Hi-Tek PPR1), a potentiostat with IR compensation (Hi-Tek DT2101) and a Nicolet 310 storage oscilloscope exiting to an X-Y recorder (Philips PM 8271). The force-field calculations were performed using PCMODEL V5.0 (Serena Software, Bloomington, Indiana, USA).

Preparation of the Dienophiles

Imide ***5b***. Anhydride **5a** (0.20 g, 1.22 mmol), aniline (0.113 g, 1.22 mmol) and ether (4 ml) were refluxed together for 10 min. The cream-coloured solid which separated on cooling was filtered off and recrystallised from toluene to give the white intermediate amido-acid (266 mg, 85%), m.p. 186-187 °C; ν_{max}/cm^{-1} (KBr) 3314, 1697 and 1534. A portion of this intermediate (176 mg, 0.68 mmol) was heated with Ac_2O (2 ml) and anhydrous NaOAc until the amido-acid dissolved. The mixture was cooled and the yellow crystals which separated were washed with Et_2O to give **5b** (145 mg, 85% from **5a**), m.p. 136-137 °C; ν_{max}/cm^{-1} (KBr) 1772 and 1709; δ_H (250 MHz, $CDCl_3$) 1.26-1.33 (2 H, m), 1.60 (1 H, dt, *J* 9 and 1.4 Hz), 1.96 (1 H, d of quintets, *J* 9 and 2 Hz), 3.46-3.49 (2 H, m) and 7.26-7.47 (5 H, m); δ_C (63 MHz, $CDCl_3$) 25.2, 40.2, 51.4, 126.4, 127.4, 129.0, 132.3, 155.8 and 165.4. (MS found *m/z*: 239.0946 $C_{15}H_{13}NO_2$ requires 239.0947).

Imide ***6b***. Anhydride **6a** (0.200 g, 0.73 mmol) was treated with aniline (0.73 mmol) as in the preceding experiment to give the corresponding amido-acid (0.246 mg, 92%), m.p. 280 °C; cyclization of a portion (0.200 g) of this intermediate as above gave **6b** (0.190 g, 92% from **6a**) as white crystals, m.p. 320-322 °C ν_{max}/cm^{-1} (KBr) 1770 and 1717; δ_H (250 MHz, DMSO-d_6) 5.82 (2 H, s), 7.03-7.10 (4 H, m), 7.28-7.45 (5 H, m) and 7.54-7.60 (4 H, m). (MS found *m/z*: 239.0947. $C_{15}H_{13}NO_2$ requires 239.0946).

Bromodiketone (±)-**10a**. 5-Bromo-2-methyl-2-propylcyclopent-4-ene-1,3-diene [(±)-**9b**][9] (0.200 g, 0.87 mmol) and anthracene (0.150 g, 0.87 mmol) were refluxed for 3h in dichloromethane in the presence of $AlCl_3$ (0.115 g, 0.87 mmol). The cooled reaction mixture was washed with water, dried ($MgSO_4$) and evaporated to leave a solid residue which was recrystallised from light petroleum to give the *bromodiketone* (±)-**10a** (0.250 g 70 %) as pale yellow crystals, m.p. 147-149 °C; ν_{max}/cm^{-1} (KBr) 1720; δ_H (250 MHz, $CDCl_3$) 0.08 (3 H, s), 0.82 (3 H, t), 1.06-1.65 (4 H, m), 3.43 (1 H, d, *J* 4 Hz), 4.78 (1 H, d, *J* 4 Hz), 4.90 (1 H, s), 7.06-7.53 (8 H, m). (MS found *m/z*: 408.0725 $C_{23}H_{21}BrO_2$ requires 408.0725).

Diketone **11**. The bromodiketone (±)-**10a** (0.171 g, 0.42 mmol) was dissolved in $CHCl_3$ (5 ml) and treated with Et_3N (116 µl, 0.83 mmol) at room temperature. After 20 min the reaction mixture was diluted with $CHCl_3$ (20 ml) and washed with 2 M HCl (2 x 10 ml), then with water (2 x 10 ml). The organic extract was dried ($MgSO_4$) and concentrated to leave a yellow solid. Recrystallisation from CH_2Cl_2-light petroleum gave the *diketone* **11** (0.111g, 81%) as yellow crystals, m.p. 183-184 °C; ν_{max}/cm^{-1} (KBr) 1688; δ_H (250 MHz, $CDCl_3$) 0.62 (3 H, t, *J* 7 Hz), 0.70-0.85 (2 H, m), 1.05 (3 H, s), 1.52-1.56 (4 H, m), 5.56 (2 H, s), 6.99-7.07 (4 H, m), 7.37-7.45 (4 H, m). (MS found *m/z*: 328.1463 $C_{23}H_{20}O_2$ requires 328.1463).

Preparative Scale Reductions

Adduct ***12a***. α,α'-Dibromo-*o*-xylene (**1**) (0.50 g, 1.9 mmol) and the anhydride **5a** (0.311 g, 1.9 mmol) were co-electrolysed at 20 °C in a 1 M solution of Et_4NBr in DMF (100 ml), using a reduction potential equal to the peak potential of the anhydride as observed by c.v. (-0.70 V *v* Ag/AgBr). After 4 F mol^{-1} with respect to **1** had been passed the mixture was poured into water (200 ml) and extracted with ether (3 x 80 ml). The combined ether extracts were dried and evaporated to leave a brown residue. Recrystallisation

from toluene gave *adduct* ***12a*** as white crystals (0.40 g, 78 %), m.p. 180-181 °C; ν_{max}/cm^{-1} (KBr) 1843 and 1778; δ_H (250 MHz, $CDCl_3$) 1.44-1.55 (2 H, m), 1.69 (1 H, dt, *J* 11 and 1.4 Hz), 1.73-1.82 (2 H, m), 2.18 (1 H, d of quintets, *J* 11 and 2 Hz), 2.60-2.63 (2 H, m), 2.67 (2 H, d, *J* 15 Hz), 3.26 (2 H, d, *J* 15 Hz) and 7.08-7.25 (4 H, m). (MS found *m/z*: 268.1099. $C_{17}H_{16}O_3$ requires 268.1099).

Adduct ***12c***. α,α'-Dibromo-*o*-xylene (**1**) (0.40 g, 1.52 mmol) and the imide **5b** (0.36 g, 1.52 mmol) were co-electrolysed at a reduction potential of -0.73 V *v* Ag/AgBr. After 2 F mol^{-1} with respect to **1** had been passed the mixture was worked up as in the preceding experiment and recrystallised from ether to give the *adduct* ***12c*** as white crystals (0.512 g, 98 %), m.p. 233-234 °C; ν_{max}/cm^{-1} (KBr) 1772 and 1705; δ_H (250 MHz, $CDCl_3$) 1.53-1.60 (2 H, m), 1.67 (1 H, dt, *J* 11 and 1.4 Hz), 1.71-1.78 (2 H, m), 2.27 (1 H, d of quintets, *J* 11 and 2 Hz), 2.65-2.67 (2 H, m), 2.73 (2 H, d, *J* 14 Hz), 3.32 (2 H, d, *J* 14 Hz) 6.68-6.72 (2 H, m) and 7.10-7.32 (7 H, m). (MS found *m/z*: 343.1576. $C_{23}H_{21}NO_2$ requires 343.1572).

Adduct ***13a***. α,α'-Dibromo-*o*-xylene (**1**) (0.50 g, 1.9 mmol) and the anhydride **6a** (0.36 g, 1.52 mmol) were co-electrolysed at a reduction potential of -0.45 V *v* Ag/AgBr. After 4 F mol^{-1} with respect to **1** had been passed the mixture was worked up as in the previous experiments and the product was triturated with ether to give the *adduct* ***13a*** as a white solid (0.595 g, 83 %), m.p. 255-256 °C; ν_{max}/cm^{-1} (KBr) 1840 and 1779; δ_H (250 MHz, $CDCl_3$) 2.34 (2 H, d, *J* 14 Hz), 3.25 (2 H, d, *J* 14 Hz), 4.53 (2 H, s) and 7.02-7.48 (12 H, m). (MS found *m/z*: 378.1256 $C_{26}H_{18}O_3$ requires 378.1256).

Adduct ***13b***. α,α'-Dibromo-*o*-xylene (**1**) (0.50 g, 1.9 mmol) and the imide **6b** (0.66 g, 1.9 mmol) were co-electrolysed at a reduction potential of -0.93 V *v* Ag/AgBr. After 2 F mol^{-1} with respect to **1** had been passed the mixture was worked up as in the previous experiments and the product was triturated with ether to give the *adduct* ***13b*** as a white solid (0.410 g, 48 %), m.p. 288-289 °C; ν_{max}/cm^{-1} (KBr) 1774 and 1715; δ_H (250 MHz, $CDCl_3$) 2.38 (2 H, d, *J* 14 Hz), 3.30 (2 H, d, *J* 14 Hz), 4.59 (2 H, s), 5.98-6.02 (2 H, m) and 7.03-7.49 (15 H, m) (MS found *m/z*: 453.1729. $C_{32}H_{23}NO_2$ requires 453.1729).

Adduct ***13d***. α,α'-Dibromo-*o*-xylene (**1**) (0.40 g, 1.50 mmol) and the quinone **6d** (0.50 g, 1.50 mmol) were co-electrolysed at a reduction potential of -0.90 V *v* Ag/AgBr. After 2 F mol^{-1} with respect to **1** had been passed the mixture was worked up as in the previous experiments and the product was crystallised from CH_2Cl_2-Et_2O to give the *1:1 complex of the adduct* ***13d*** *with anthracene* as white crystals (0.284 g, 43 %), m.p. 194-195 °C; ν_{max}/cm^{-1} (KBr) 1655; δ_H (250 MHz, $CDCl_3$) 2.35 (2 H, d, *J* 14 Hz), 3.42 (2 H, d, *J* 14 Hz), 4.77 (2 H, s), 6.78-6.87 (6 H, m), 7.06-7.12 (2 H, m), 7.20-7.36 (4 H, m), 7.44-7.52 (6 H, m), 7.59-7.66 (2 H, m), 7.79-8.05 (4 H, m) and 8.44 (2 H, s). [MS found *m/z*: 178.0782 $C_{14}H_{10}$ (anthracene) requires 178.0782].

Adducts **14a** and **14b**. α ,α'-Dibromo-*o*-xylene (**1**) (0.250 g, 0.95 mmol) and 2-methyl-2-propylcyclopent-4-ene-1,3-dione (**9a**) (0.144 g, 0.95 mmol) were co-electrolysed at a reduction potential of -0.72 V *v* Ag/AgBr. After 4 F mol^{-1} with respect to **1** had been pased the mixture was worked up as usual to

give a yellow oil. Flash chromatography with light petroleum-dichloromethane (4:1) as eluant gave **14a** (0.040 g, 16 %) and **14b** (0.015 g, 6%).

14a Had m.p. 75 °C; ν_{max}/cm^{-1} (KBr) 1714; δ_H (250 MHz, $CDCl_3$) 0.38 (3 H, s), 0.82 (3 H, t, *J* 7 Hz), 1.09-1.24 (2 H, m), 1.48-1.56 (2 H, m), 2.81-2.90 (2 H, m), 3.09-3.17 (2 H, m), 3.30-3.34 (2 H, m), 7.07-7.15 (4 H, m). (MS found *m/z*: 256.1463 $C_{17}H_{20}O_2$ requires 256.1463).

14b Had m.p. 111 °C; ν_{max}/cm^{-1} (KBr) 1718; δ_H (250 MHz, $CDCl_3$) 0.15-0.30 (2 H, m), 0.52 (3 H, t, *J* 7 Hz), 1.10 (3 H, s), 1.22-1.29 (2 H, m), 2.83-2.92 (2 H, m), 3.12-3.19 (2 H, m), 3.37-3.42 (2 H, m), 7.11 (4 H, s). (MS found *m/z*: 256.1463 $C_{17}H_{20}O_2$ requires 256.1463).

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