Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 4377–4381

TETRAHEDRON

Highly efficient syntheses of 3-aryl-2-cycloalken-1-ones and an evaluation of their liquid crystalline properties

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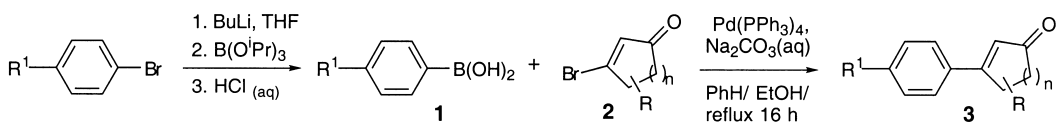
Received 3 January 2003; revised 18 March 2003; accepted 10 April 2003

Abstract—Cycloalkenones are shown to be mesogens and can be synthesised in near quantitative yields by a convergent palladium(0)-catalysed cross-coupling strategy; a 2-methyl group induces a change of phase from smectic to nematic.

In recent years transition metal-catalysed reactions have been extensively used to form carbon–carbon σ-bonds between sp^2 carbon centres.[1] Suzuki's group[2–4] reported the synthesis of biaryls by the palladium(0)-catalysed cross coupling of an arylboronic acids with aryl bromides. This method has been applied by Gray and co-workers[5] to the preparation of substituted biphenyl and terphenyl units in liquid crystalline assemblies. Suzuki and co-workers[6] have shown that a reasonably efficient cross-coupling reaction of alkylboronic esters with organic halides is catalysed by palladium(0) in the presence of thallium(I) salts. Gilchrist and Summersell[7] used a palladium(0) catalyst for the cross-coupling of a bromodiene with 3-iodo-2-cyclohexen-1-one in satisfactory yield via a bromozinc intermediate.

Our group has been interested in developing efficient syntheses of aryl cyclic enones, an assembly that has been shown to be a useful core structure for new liquid crystalline materials both in racemic[8,9] and optically pure forms.[10] However, in our hands, a conventional approach involving metalation of bromoarenes with *n*-butyllithium and subsequent addition to enol ethers of cyclic 1,3-diketones rarely gave the desired 3-aryl-2-cycloalken-1-ones in yields above 50%, and Grignard methods were even less satisfactory. Moreover, such metalations restrict the scope of functionality that could be present. We report herein an efficient solution to this problem, thereby providing a general and direct method for the preparation of 3-aryl-2-en-1-ones by the palladium(0)-catalyzed cross coupling of arylboronic acids with 3-bromo-2-en-1-ones (Scheme 1). The arylboronic acids **1** were prepared by addition of *n*-butyllithium to the requisite aryl bromide, followed by treatment with triisopropyl borate, then with dilute hydrochloric acid. The cyclic 3-bromo-2-en-1-ones **2** were prepared (>95% yield) by addition of triethylamine (1.1 equiv.) and the appropriate 1,3-diketone to a stirred suspension of triphenylphosphine dibromide[11] (1.1 equiv.) in benzene; the subsequent solution was then kept at 20°C for 2 h. Chromatography on silica gel afforded the 3-bromo-2-en-1-ones as oils that were used directly. The 3-bromo-2-en-1-ones were coupled with the arylboronic acids using tetrakis-(triphenylphosphine)palladium(0) as a catalyst (0.3 mol%) to give the corresponding 3-aryl-2-cycloalken-1-ones. The procedure provides near quantitative yields (Table 1) and is very convenient since drying of the reagents is not necessary. Moreover, it is amenable to scaling up: 15 g of **3a** was prepared in one run and without substantial diminution in yield (96%). As a comparison, one acyclic 3-bromo-2-en-1-one was submitted



Scheme 1.

Keywords: palladium(0); arylboronic acids; cycloalkenone.

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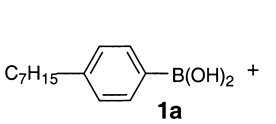
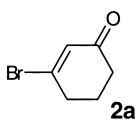
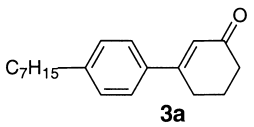
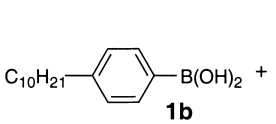
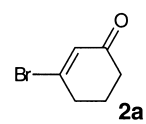
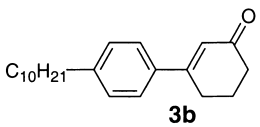
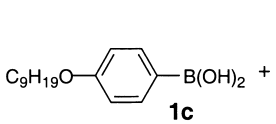
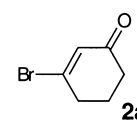
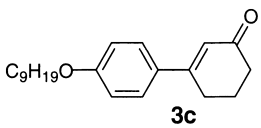
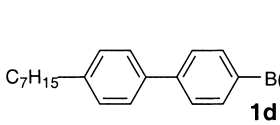
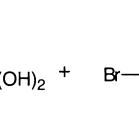
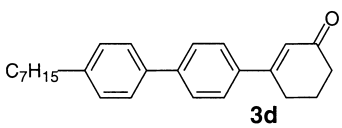
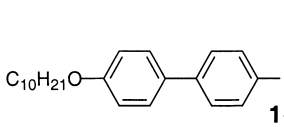
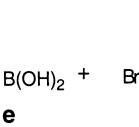
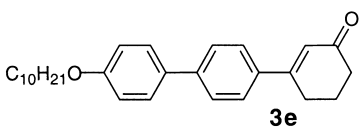
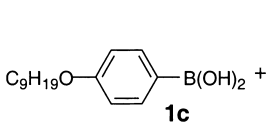
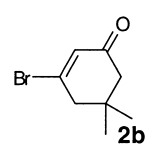
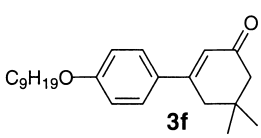
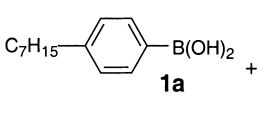
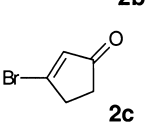
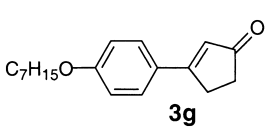
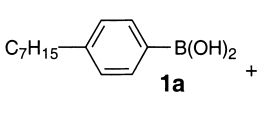
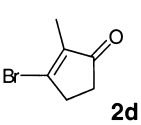
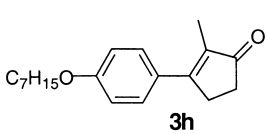
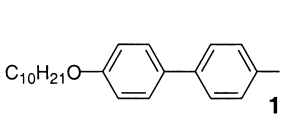
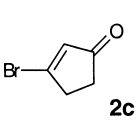
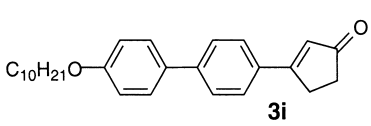
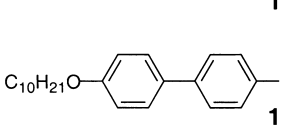
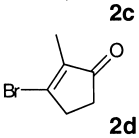
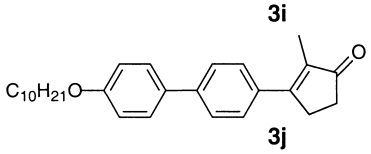
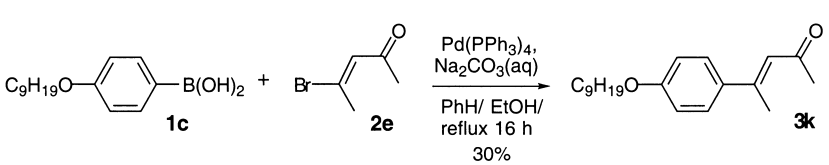
0040–4020/03/$ - see front matter
doi:10.1016/S0040-4020(03)00620-3

Table 1. Palladium(0) catalysed coupling of boronic acids with 3-bromo-2-cycloalken-1-ones

Boronic acid	Bromocycloalkenone	Aryl enone	Yield (%)
 **1a**	 **2a**	 **3a**	97
 **1b**	 **2a**	 **3b**	96
 **1c**	 **2a**	 **3c**	92
 **1d**	 **2a**	 **3d**	95
 **1e**	 **2a**	 **3e**	92
 **1c**	 **2b**	 **3f**	98
 **1a**	 **2c**	 **3g**	97
 **1a**	 **2d**	 **3h**	96
 **1e**	 **2c**	 **3i**	96
 **1e**	 **2d**	 **3j**	98

to the Suzuki coupling (Scheme 2); the corresponding arylated enone was obtained, although in poor yield.

Determination of melting points and any phase transitions for the arylated 2-cycloalken-1-ones revealed a number of interesting features. The more planar 3-aryl-2-cyclopenten-1-one **3g** (mp 67–69°C) evidently packs more tightly than the 3-aryl-2-cyclohexen-1-one **3a** (mp 24°C) with its distorted chair conformation. The presence of a 2-methyl group in the 3-aryl-2-cyclopenten-1-one **3h** (mp 44–45°C)



1c **2e** **3k**

Scheme 2.

Table 2. Transition and onset temperatures of mesogenic cycloalkenones

Enone	Transition temperature (°C)[a]	Onset temperature (°C)[b]
3d	K-86-SmA-112-I	80.8; 106.5
3e	K-97-SmB-144- SmA-169-I	85.8; 132.4; 156.9
3i	K-169-SmA-186-I	167.4; 184.7
3j	K-63-N-68-I I-65-N-SmA-44-K[c]	57.8; 63.2

[a] Transition temperatures were obtained from polarising microscopy.
[b] Onset temperatures were determined from differential scanning calorimetry on heating.
[c] The transition temperatures I-65-N-SmA-44-K were observed on cooling.

lowers the ordering of the molecules in the solid state, in comparison with that of the unsubstituted derivative **3g**. The tricyclic systems **3i** and **3j** are mesogenic: whereas both the cyclohexenone **3e** and the cyclopentenone **3i** each show smectic phases above the melting points, the methyl-substituent in 2-cyclopenten-1-one **3j** gives rise to a dramatic depression of the phase transitions by some 100°C. The ability of a methyl group to confer a nematic phase (less ordered relative to the smectic phase observed in the unsubstituted derivative) is noteworthy, and the 2-cyclopenten-1-one **3j** is one of the few cyclic enones that has been reported to exhibit nematic phase behaviour. A strong nematic phase is indicated because long alkoxy substituents typically confer smectic phase characteristics. Unlike the substituted phenyl-2-cyclohexen-1-ones **3a**,**3b**,**3c** and **3f**, which at their melting points (K) become isotropic liquids, the biphenylyl-2-cyclohexen-1-ones **3d** and **3e** are mesogenic and display smectic (Sm) phases (Table 2).

Materials for fast switching thin film transistor liquid crystal displays (TFT-LCD) require a high dielectric anisotropy ($\Delta\varepsilon$) (obtained by attaching highly polar groups in the direction of the long molecular axis), combined with a low birefringence (Δn). Although the conjugation of a polar group such as cyanide attached to an arene, a typical feature of many liquid crystal materials, gives a high $\Delta\varepsilon$ it also leads to an undesirably high optical anisotropy. In contrast, the enones described here have been investigated and shown to have high $\Delta\varepsilon$ and low Δn,[12] most probably because of lower polar conjugation compared with a substituted nitrile system. The materials described here are potential candidates for display applications.

1. Experimental

1.1. General

Transition temperatures (uncorrected) were determined on a Zeiss Universal polarising microscope equipped with a Linkam hot stage with integrated controller. All liquid crystalline compounds were also characterised using a Perkin–Elmer DSC-7 differential scanning calorimeter. ^{1}H and ^{13}C NMR spectra were run on a Bruker AM-250 instrument at 250 and 68.8 MHz, respectively. Microanalytical data were obtained on a Perkin–Elmer 2400 CHN elemental analyser. Low-resolution mass spectra were obtained on a Kratos MS-25 instrument, and high-resolution spectra were obtained on a Kratos MS-80HR instrument. Infrared spectra were recorded on a Perkin–Elmer 684 or 157G instrument. Thin-layer chromatography was performed on Merck 0.2 mm aluminium-backed silica gel 60 F_{254} plates and visualized using an alkaline $KMnO_4$ spray or by ultraviolet light. Flash column chromatography was performed using Sorbsil C60 40/60A silica gel. Petroleum ether (40–60 fraction) and ethyl acetate were distilled before use; tetrahydrofuran was distilled over sodium and benzophenone; dichloromethane was distilled over calcium hydride. Evaporation refers to the removal of solvent under reduced pressure.

The following compounds were prepared by literature procedures: 3-bromo-2-cyclohexen-1-one,[13] 3-bromo-5,5-dimethyl-2-cyclohexen-1-one,[14] 3-bromo-2-cyclopenten-1-one[15] and 3-bromo-2-methyl-2-cyclopenten-1-one,[14] 4-heptylphenylboronic acid,[5] 4-decylphenylboronic acid,[5] 4-nonyloxyphenylboronic acid,[5] 4′-heptylbiphenyl-4-ylboronic acid[5] and 4′-decyloxybiphenyl-4-ylboronic acid.[5]

1.1.1. 3-Bromo-2-cyclopenten-1-one (2c).[15] Triethylamine (0.57 g, 5.6 mmol), freshly distilled from lithium aluminium hydride, and cyclopentane-1,3-dione (0.50 g, 5.1 mmol) were added to a suspension of dibromo-triphenylphosphorane (2.34 g, 5.6 mmol) in benzene (8 mL). The mixture was stirred at 20°C for 2 h, then evaporated and the residue filtered through a short column of silica gel using diethyl ether. Evaporation of the eluant afforded (**2c**) as a colourless oil (0.76 g, 96%); IR (film) λ_{max} 1715, 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.37 (1H, m), 2.95 (2H, m), 2.50 (2H, m); ^{13}C NMR ($CDCl_3$) δ 204.8 (s), 161.2 (s), 135.7 (d) 37.2 (t), 37.0 (t).

1.1.2. 4-Bromopent-3-en-2-one (2e). Triethylamine (2.22 g, 22.0 mmol), freshly distilled from lithium aluminium hydride, and pentane-2,4-dione (2.0 g, 20.0 mmol) were added to a suspension of dibromo-triphenylphosphorane (8.40 g, 20.0 mmol) in benzene (20 mL). The mixture was stirred at 50°C for 24 h, then evaporated and the residue filtered through a short column of silica gel eluted with 1:1 diethyl ether: petroleum ether. Evaporation of the eluant afforded (**2k**) as a pale brown oil (1.56 g, 48%); IR (film) λ_{max} 1700 (C=O), 1605 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.66 (1H, m), 2.69 (3H, s, CH_3), 2.14 (3H, s, CH_3CO) which was used promptly in coupling reactions.

1.2. Preparation of arylboronic acids: general procedure

n-Butyllithium (34.8 mL, 2.5 M in hexanes, 87.0 mmol) was added dropwise to a stirred, cooled solution (−78°C) of the appropriate aryl bromide (62.2 mmol) in dry THF. The resulting solution was stirred magnetically at −78°C for 2 h. A cooled solution (−78°C) of triisopropylborate (23.3 g, 124 mmol) in dry THF was then added and the mixture was allowed to warm to 20°C over 16 h. Hydrochloric acid (1 M, 150 mL) was added and the mixture was stirred for 1 h. The mixture was extracted with diethyl ether (2×100 mL) and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was evaporated to give a white solid that was recrystallised from methanol to give the boronic acid as a white crystalline solid.

1.3. Cross-coupling of arylboronic acids with 3-bromo-2-en-1-ones: general procedure

A solution of the arylboronic acid (2.60 mmol) in ethanol (15 mL) was added to a stirred mixture of the 3-bromo-2-en-1-one (2.0 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.6 mg, 6.0 μmol) in benzene (30 mL) and aqueous sodium carbonate (2 M, 30 mL) at 20°C. The stirred mixture was heated under reflux (approx. 95°C) for 16 h. The product was extracted into diethyl ether (2×50 mL) and the combined ethereal extracts were washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography or recrystallisation to give the 3-arylated-2-cycloalken-1-one.

1.3.1. Cycloalkenone (3a). Chromatography using 1:4 ethyl acetate: light petroleum afforded **3a** as a yellow oil (0.52 g, 97%) that solidified on standing, mp 24°C; IR (nujol) λ_{max} 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39 (2H, d, J=8.0 Hz, aryl-2,6-H), 7.14 (2H, d, J=8.0 Hz, aryl-3,5H), 6.35 (1H, m, vinylic), 2.74 (2H, td, J=7.0, 1.0 Hz, C$H_2$$CH_2CH_2CO$), 2.55 (2H, t, J=8.0 Hz, CH_2aryl), 2.39 (2H, m, CH_2CH_2-CH_2CO), 2.05 (2H, m, $CH_2CH_2CH_2CO$), 1.53 (2H, quintet, J=8.0 Hz, CH_2CH_2alkyl), 1.35–1.10 (8H, m, alkyl), 0.97 (3H, t, J=8.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 200.0 (s), 159.7 (s), 145.4 (s), 135.9 (s), 128.8 (d), 126.0 (d), 124.6 (d), 37.3 (t), 35.7 (t), 31.8 (t), 31.2 (t), 29.2 (t), 29.1 (t), 28.0 (t), 22.8 (t), 22.7 (t), 14.1 (q). LRMS (EI) *m/e* 270 (M^+, 66%), 242 (49), 204 (40), 120 (43), 91 (45); HRMS calcd for $C_{19}H_{26}O$ 270.1984, found 270.1974.

1.3.2. Cycloalkenone (3b). Chromatography using 1:4 ethyl acetate: light petroleum afforded **3b** as a yellow oil (0.60 g, 96%); IR (nujol) λ_{max} 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (2H, d, J=9.0 Hz, aryl-2,6H), 7.29 (2H, d, J=9.0 Hz, aryl-3,5H), 6.34 (1H, t, J=1.5 Hz, vinylic), 2.68 (2H, td, J=7.0, 1.5 Hz, C$H_2$$CH_2CH_2CO$), 2.56 (2H, t, J=8.0 Hz, CH_2aryl), 2.48 (2H, m, $CH_2CH_2CH_2CO$), 2.06 (2H, m, $CH_2CH_2CH_2$-CO), 1.56 (2H, quintet, J=8.0 Hz, OCH_2CH_2aryl), 1.25–1.15 (14H, m, alkyl), 0.93 (3H, t, J=8.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 200.0 (s), 159.6 (s), 145.5 (s), 135.9 (s), 128.8 (d), 126.1 (d), 124.6 (d), 37.3 (t), 35.7 (t), 31.9 (t), 31.3 (t), 30.9 (t), 29.6 (t), 29.5 (t), 29.3 (t), 29.3 (t), 28.0 (t), 22.8 (t), 22.7 (t), 14.1 (q).

1.3.3. Cycloalkenone (3c). Chromatography using dichloromethane, followed by recrystallisation from light petroleum afforded **3c** (0.58 g, 92%), as prisms, mp 51–52°C; IR (nujol) λ_{max} 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44 (2H, d, J=8.0 Hz, aryl), 6.83 (2H, d, J=8.0 Hz, aryl), 6.33 (1H, t, J=1.0 Hz, vinylic), 3.93 (2H, t, J=6.0 Hz, OCH_2), 2.67 (2H, td, J=5.5, 1.0 Hz, C$H_2$$CH_2CH_2CO$), 2.38 (2H, m, $CH_2CH_2CH_2CO$), 2.17 (2H, quintet, J=6.0 Hz, CH_2CH_2-alkyl), 1.72 (2H, m, $CH_2CH_2CH_2CO$), 1.45–1.15 (12H, m, alkyl), 0.82 (3H, t, J=6.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 199.9 (s), 160.9 (s), 159.2 (s), 130.5 (s), 127.6 (d), 123.6 (d), 114.6 (d), 68.2 (t), 37.2 (t), 31.9 (t), 29.5 (t), 29.4 (t), 29.3 (t), 29.2 (t), 27.8 (t), 26.0 (t), 22.8 (t), 22.7 (t), 14.1 (q). Anal. calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62%; found: C, 80.20; H, 9.82%.

1.3.4. Cycloalkenone (3d). Recrystallisation from 1:5 ethyl acetate: light petroleum afforded **3d** (0.66 g, 95%), as prisms, mp 86°C; IR (nujol) λ_{max} 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.63 (4H, m, aryl), 7.54 (2H, d, J=7.5 Hz, aryl), 7.27 (2H, d, J=7.5 Hz, aryl), 6.49 (1H, t, J=1.0 Hz, vinylic), 2.82 (2H, td, J=7.0, 1.2 Hz, C$H_2$$CH_2CH_2CO$), 2.65 (2H, t, J=8.1 Hz, CH_2alkyl), 2.51 (2H, m, CH_2CH_2-CH_2CO), 2.18 (2H, m, $CH_2CH_2CH_2CO$), 1.75–1.59 (2H, m, alkyl), 1.41–1.24 (8H, m, alkyl), 0.82 (3H, t, J=7.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 199.9 (s), 159.7 (s), 142.9 (s), 142.8 (s), 137.3 (s), 137.1 (s), 129.0 (d), 127.1 (d), 126.9 (d), 126.6 (d), 125.0 (t), 37.3 (t), 35.7 (t), 31.8 (t), 31.5 (t), 29.3 (t), 29.2 (t), 28.0 (t), 22.8 (t), 22.7 (t), 14.1 (q). Anal. calcd for $C_{25}H_{30}O$: C, 86.66; H, 8.73%; found: C, 86.85; H, 8.48%.

1.3.5. Cycloalkenone (3e). Chromatography using dichloromethane, followed by recrystallisation from light petroleum afforded **3e** (0.74 g, 92%), as prisms, mp 97°C; IR (nujol) λ_{max} 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52 (4H, m, aryl), 7.48 (2H, d, J=7.5 Hz, aryl), 6.91 (2H, d, J=7.5 Hz, aryl), 6.42 (1H, t, J=1.0 Hz, vinylic), 3.90 (2H, t, J=6.5 Hz, OCH_2), 2.75 (2H, td, J=5.5, 1.0 Hz, C$H_2$$CH_2CH_2CO$), 2.44 (2H, m, $CH_2CH_2CH_2CO$), 2.22 (2H, m, $CH_2CH_2CH_2CO$), 1.74 (2H, quintet, J=6.5 Hz, OCH_2CH_2), 1.45–1.17 (14H, m, alkyl), 0.82 (3H, t, J=6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 199.9 (s), 159.2 (s), 142.8 (s), 142.5 (s), 136.7 (s), 132.2 (s), 128.1 (d), 126.8 (d), 126.6 (d), 124.9 (d), 118.3 (t), 114.9 (d), 68.1 (t), 37.3 (t), 31.9 (t), 29.6 (t), 29.4 (t), 29.3 (t), 29.3 (t), 28.0 (t), 26.1 (t), 22.8 (t), 22.7 (t), 14.1 (q). Anal. calcd for $C_{28}H_{36}O_2$: C, 83.12; H, 8.97%; found: C, 82.85; H, 8.77%.

1.3.6. Cycloalkenone (3f). Recrystallisation from light petroleum afforded **3f** (0.67 g, 98%), as prisms, mp 63°C; IR (nujol) λ_{max} 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.56 (2H, d, J=7.5 Hz, aryl), 6.92 (2H, d, J=7.5 Hz, aryl), 6.38 (1H, t, J=1.0 Hz, vinylic), 3.98 (2H, t, J=5.5 Hz, OCH_2), 2.61 (2H, d, J=1.0 Hz, =CCH_2), 2.30 (2H, s, CH_2CO), 1.76 (2H, quintet, J=5.5 Hz, OCH_2CH_2), 1.51–1.25 (12H, m, alkyl), 1.12 (6H, s, 2× CH_3), 0.91 (3H, t, J=5.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 200.1 (s), 160.8 (s), 157.0 (s), 130.8 (s), 127.7 (d), 122.5 (d), 114.7 (d), 68.2 (t), 50.9 (t), 42.1 (t), 33.6 (t), 31.9 (t), 29.5 (t), 29.4 (t), 29.3 (t), 29.2 (t), 28.5 (q), 25.6 (t), 22.7 (t), 14.1 (q). Anal. calcd for $C_{23}H_{34}O_2$: C, 80.65; H, 10.00%; found: C, 80.77; H, 9.77%.

1.3.7. Cycloalkenone (3g). Recrystallisation from light petroleum afforded **3g** (0.53 g, 97%), as prisms, mp 67–69°C; IR (nujol) λ_{max} 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50 (2H, d, J=9.0 Hz, aryl), 6.83 (2H, d, J=9.0 Hz, aryl), 6.35 (1H, t, J=1.0 Hz, vinylic), 3.90 (2H, t, J=6.0 Hz, OCH_2), 2.87 (2H, m, C$H_2$$CH_2CO$), 2.42 (2H, m, CH_2CH_2CO), 1.71 (2H, quintet, J=6.0 Hz, OCH_2CH_2), 1.45–1.10 (8H, m, alkyl), 0.81 (3H, t, J=6.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 209.7 (s), 174.1 (s), 161.8 (s), 128.6 (s), 126.4 (d), 125.2 (d), 114.7 (d), 68.2 (t), 35.3 (t), 31.8 (t), 29.1 (t), 29.0 (t), 28.6 (t), 25.9 (t), 22.6 (t), 14.1 (q); LRMS (EI) *m/e* 272 (M^+, 49%), 174 (100), 57 (18); HRMS calcd for $C_{18}H_{24}O_2$ 272.1769, found 272.1776.

1.3.8. Cycloalkenone (3h). Recrystallisation from light petroleum afforded **3h** (0.55 g, 96%), as prisms, mp 44–45°C; IR (nujol) λ_{max} 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (2H, d, J=9.0 Hz, aryl), 6.96 (2H, d, J=9.0 Hz, aryl), 4.00

(2H, t, J=7.0 Hz, OCH_2), 2.89 (2H, m, CH_2CH_2CO), 2.51 (2H, m, CH_2CH_2CO), 1.98 (3H, t, J=2.0 Hz, CH_3), 1.80 (2H, quintet, J=7.0 Hz, OCH_2CH_2), 1.50–1.25 (8H, m, alkyl), 0.89 (3H, t, J=7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 209.8 (s), 166.0 (s), 160.3 (s), 134.7 (s), 129.3 (d), 128.6 (s), 114.5 (d), 66.2 (t), 33.9 (t), 31.8 (t), 29.2 (t), 29.1 (t), 28.9 (t), 26.0 (t), 22.6 (t), 14.1 (q), 10.2 (q); LRMS (EI) *m/e* 286 (M^+, 94%), 188 (100), 171 (39), 110 (16); HRMS calcd for $C_{19}H_{26}O_2$ 286.1928, found 286.1933.

1.3.9. Cycloalkenone (3i). Recrystallisation from light petroleum afforded **3i** (0.75 g, 96%), as prisms, mp 169°C; IR (nujol) λ_{max} 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.66 (4H, m, aryl), 7.62 (2H, d, J=9.0 Hz, aryl), 6.96 (2H, d, J=9.0 Hz, aryl), 6.69 (1H, t, J=1.0 Hz, vinylic), 4.00 (2H, t, J=6.5 Hz, OCH_2), 3.14 (2H, m, CH_2CH_2CO), 2.69 (2H, m, CH_2CH_2CO), 1.71 (2H, quintet, J=6.5 Hz, OCH_2CH_2), 1.58–1.37 (14H, m, alkyl), 0.75 (3H, t, J=6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 209.3 (s), 173.6 (s), 159.4 (s), 143.7 (s), 132.2 (s), 132.1 (s), 128.1 (d), 127.3 (d), 127.0 (d), 126.9 (d), 115.0 (d), 68.2 (t), 35.3 (t), 31.9 (t), 29.6 (t), 29.4 (t), 29.3 (t), 29.2 (t), 28.6 (t), 26.1 (t), 22.7 (t), 14.1 (q); LRMS (EI) *m/e* 390 (M^+, 100%), 250 (60); HRMS calcd for $C_{27}H_{34}O_2$ 390.2458, found 390.2559.

1.3.10. Cycloalkenone (3j). Recrystallisation from light petroleum afforded **3j** (0.79 g, 98%), as white needles, mp 63°C; IR (nujol) λ_{max} 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.56 (4H, m, aryl), 7.48 (2H, d, J=7.5 Hz, aryl), 6.93 (2H, d, J=7.5 Hz, aryl), 3.94 (2H, t, J=7.0 Hz, OCH_2), 2.87 (2H, m, CH_2CH_2CO), 2.47 (2H, m, CH_2CH_2CO), 1.96 (3H, t, J=2.0 Hz, CH_3), 1.74 (2H, quintet, J=7.0 Hz, OCH_2CH_2), 1.45–1.12 (14H, m, alkyl), 0.83 (3H, t, J=7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 209.7 (s), 166.0 (s), 159.2 (s), 142.0 (s), 136.2 (s), 134.5 (s), 132.3 (s), 128.1 (d), 126.1 (d), 126.7 (d), 114.9 (d), 68.2 (t), 34.0 (t), 31.9 (t), 29.6 (t), 29.4 (t), 29.3 (t), 29.2 (t), 29.1 (t), 26.1 (t), 22.7 (t), 14.1 (q), 10.1 (q). Anal. calcd for $C_{28}H_{36}O_2$: C, 83.11; H, 8.97%; found: C, 83.05; H, 9.08%.

1.3.11. 3-(4-Nonyloxyphenyl)-pent-3-en-2-one (3k). Chromatography using 1:4 diethyl ether: light petroleum afforded **3k** (0.18 g, 30%), as prisms, mp 52–52.5°C; ^{1}H NMR ($CDCl_3$) δ 7.39 (2H, d, J=8.0 Hz, aryl), 6.83 (2H, d, J=8.0 Hz, aryl), 6.44 (1H, d, J=1.0 Hz, vinylic), 3.92 (2H, t, J=6.0 Hz, OCH_2), 2.47 (3H, d, J=1.0 Hz, $=CCH_3$), 2.23 (3H, s, $COCH_3$), 1.73 (2H, quintet, J=6.0 Hz, OCH_2CH_2), 1.45–1.12 (12H, m, alkyl), 0.80 (3H, t, J=6.0 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 198.8 (s), 160.2 (s), 153.4 (s), 134.2 (s), 127.8 (d), 122.7 (d), 114.4 (d), 68.1 (t), 32.3 (q), 31.9 (t), 29.5 (t), 29.4 (t), 29.3 (t), 29.2 (t), 26.0 (t), 22.7 (t), 18.0 (q), 14.1 (q). LRMS (EI) *m/e* 302 (M^+, 100%), 287 (33), 175 (87), 149 (77); HRMS calcd for $C_{20}H_{30}O_2$ 302.2238, found 302.2246.

Acknowledgements

We are grateful for financial support of this work by Hitachi Research Laboratory, Hitachi Ltd, Japan including provision of a studentship (to L. D. F.).

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