An Efficient and Practical Total Synthesis of (±)-α-Cuparenone

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Abstract: A one-pot cyclopentannulation approach as the key step for the total synthesis of (±)-α-cuparenone is described.

Key words: alkylation, annulation, reduction, hydroboration–oxidation

α-Cuparenone (**1**), β-cuparenone (**2**), and cuparene (**3**) (Figure 1) are bicyclic sesquiterpenes belonging to the cuparene family. Compounds **1** and **2** were isolated from *Thuja orientalis* (Mayurpankhi) by Sukhdev and co-workers in 1964[1] and cuparene (**2**) was isolated by Erdtman and co-workers in 1958.[2] These compounds pose a synthetic challenge to synthetic organic chemists, because of the presence of two contiguous quaternary centers in a cyclopentane ring, which has been constructed in a variety of ways.[3]

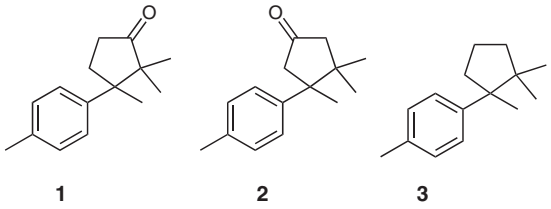

Figure 1

Many studies towards the synthesis of α-cuparenone (**1**)[4] and β-cuparenone (**2**),[5] either in racemic or optically active form, have been reported. The reported syntheses involve either construction of the quaternary center starting from a framework that contains the aromatic ring, or addition of the *p*-tolyl moiety to a cyclopentane ring derivative.[6] Other methods build up the aromatic ring starting from a cyclopentane ring.[7] Other ways have also been used for the synthesis, for example cyclopentannulation of an open-chain intermediate that has one of the quaternary centers.[5]

Most of the reported synthesis have drawbacks such as lengthy routes, expensive starting materials, tedious reaction conditions, or low overall yield. To overcome these problems, it is still necessary to develop a simple and efficient synthesis of α-cuparenone (**1**).

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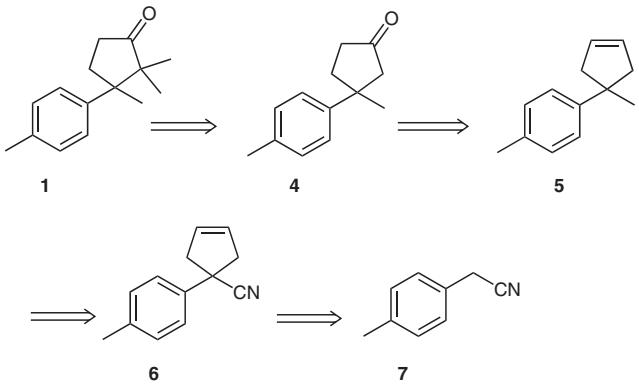
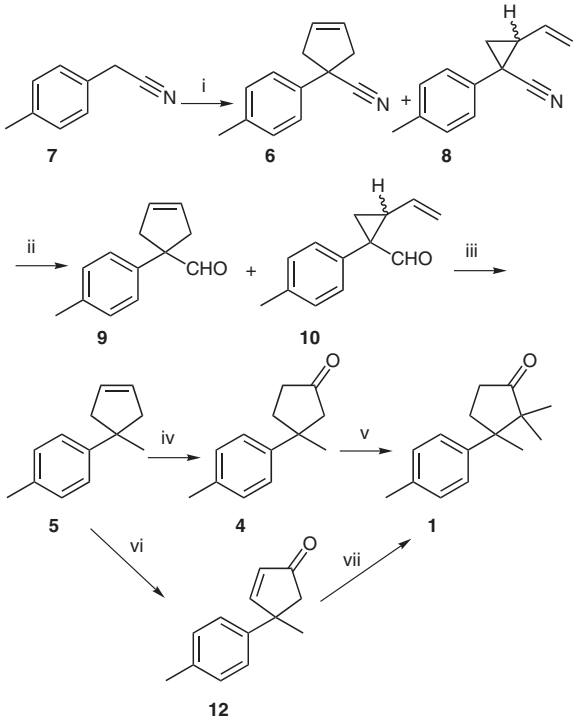
As a part of our ongoing interest towards the synthesis of naturally occurring cyclopentane rings,[8] we undertook the synthesis of α-cuparenone (**1**). We have recently accomplished a short synthesis of α-cuparenone (**1**) employing an acetophenone *gem*-diallylation strategy in which the carbon-bearing aryl group served as an electrophile. Herein we wish to report a complimentary strategy leading to a very simple and short synthesis of α-cuparenone (**1**), in which the carbon-bearing aryl group acts as a nucleophile, and which involves simple dialkylation to construct a cyclopentene ring as the key step. As is obvious from the retrosynthesis (Scheme 1), our strategy was to prepare key intermediate **5** by dialkylation and reduction of 4-methylbenzyl cyanide (**7**).



Scheme 1

The synthetic sequence as depicted in Scheme 2 shows the synthesis starting at the dialkylation of commercially available 4-methylbenzyl cyanide (**7**) by use of sodium hydride and *cis*-1,4-dichlorobut-2-ene in tetrahydrofuran to furnish cyclopentene derivative **6** along with side product **8** in a 2:1 ratio as an inseparable mixture. We went ahead with this mixture, in the hope that it would separate at the hydroboration–oxidation step. Thus, the mixture of **6** and **8** was subjected to reduction with diisobutylaluminum hydride to furnish aldehydes **9** and **10**, which were further reduced under Huang-Minlon[9] reaction conditions without further purification to furnish the required olefin intermediate **5** containing one of the quaternary centers (Scheme 2). Formation of a single product after Huang-Minlon reduction was initially surprising, but we thought that the cyclopropane product may have undergone a vinyl–cyclopropane rearrangement.[10]

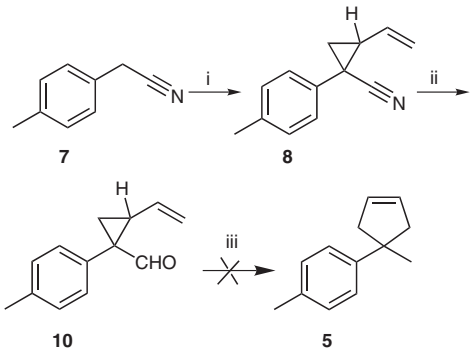
To study the fate of the vinyl–cyclopropane rearrangement, we prepared compound **8** (Scheme 3) in pure form



Scheme 2 *Reagents and conditions*: (i) NaH, *cis*-1,4-dichlorobut-2-ene, THF, r.t., 8 h, 80%; (ii) DIBAL-H, CH_2Cl_2, –78 °C, 1 h; (iii) $H_2NNH_2{\cdot}H_2O$, NaOH, diethylene glycol, 180 °C, 8 h, 60%; (iv) $BH_3{\cdot}SMe_2$, THF, H_2O_2, 3 N NaOH, IBX, DMSO, 12 h, 85%; (v) LiHMDS, MeI, DME, HMPA, 3 h, 70%; (vi) PDC, DMF, 100 °C, 8 h; (vii) ref. 8e.

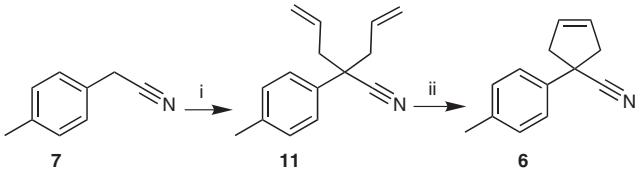
by alkylation of benzyl cyanide **7** with *trans*-1,4-dibromobut-2-ene in the presence of sodium hydride in tetrahydrofuran in 85% yield. With pure compound **8** in hand, we continued its investigation. Reduction of compound **8** with diisobutylaluminum hydride in dichloromethane at –78 °C furnished aldehyde **10** (Scheme 3), which was further subjected to Huang-Minlon[9] conditions. Unfortunately, the required olefin intermediate **5** was not observed, even after two to three trials (Scheme 3).

It was therefore concluded that when a mixture of compounds **9** and **10** was subjected to Huang-Minlon conditions, compound **10** decomposed as a result of the strain



Scheme 3 *Reagents and conditions*: (i) NaH, *trans*-1,4-dibromobut-2-ene, THF, r.t., 8 h, 85%; (ii) DIBAL-H, CH_2Cl_2, –78 °C, 1 h; (iii) $H_2NNH_2{\cdot}H_2O$, NaOH, diethylene glycol, 180 °C.

of the cyclopropane ring, and that only aldehyde **9** was converted into olefin intermediate **5** in 60% isolated yield (Scheme 2). Since direct formation of the cyclopentene functionality led to the mixture of isomers, an alternative approach was attempted to overcome this problem. Accordingly, **7** was dialkylated by use of allyl bromide and sodium hydride in tetrahydrofuran (Scheme 4); subsequent ring-closing metathesis of diallyl **11** in the presence of the Grubbs first-generation catalyst afforded the required compound **6** (Scheme 4).



Scheme 4 *Reagents and conditions*: (i) NaH, AllBr, THF, r.t., 86%; (ii) Grubbs first-generation catalyst, CH_2Cl_2, 3 h, 92%.

Olefin **5** was subjected to a sequence of hydroboration[11] and oxidation[12] by use of the borane–dimethyl sulfide complex, hydrogen peroxide/sodium hydroxide, and 2-iodoxybenzoic acid (IBX); this gave cyclopentanone **4** in almost 85% yield (Scheme 2). Finally, ketone **4** on selective dialkylation in the presence of freshly prepared lithium hexamethyldisilazide and methyl iodide[13] furnished α-cuparenone (**1**) (Scheme 2).[14]

Alternatively, **5** was readily converted into α-cuparenone (**1**) via enone **12**, furnished by allylic oxidation of **5** with pyridinium dichromate in *N*,*N*-dimethylformamide at 100 °C (Scheme 2). Enone **12**, on bis-methylation with sodium hydride and methyl iodide, followed by the reduction of the double bond by palladium on carbon, afforded α-cuparenone (**1**) (Scheme 2).[8e]

In conclusion, a very efficient and practical synthesis of α-cuparenone (**1**) has been accomplished, in which all the reaction sequences are easy to perform, are essentially mild, and proceed in excellent yields. One of the shortest and most efficient syntheses of α-cuparenone (**1**) has been achieved in five steps in 28% overall yield.

All solvents were freshly distilled before use. IR spectra were recorded on a Perkin-Elmer 68B or a Perkin-Elmer 1615 FT infrared spectrophotometer. ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded on a Bruker AC-200 spectrometer. The carbon resonances were assigned by use of DEPT experiments. Mass spectra were recorded at an ionization energy of 70 eV on a Finnigan MAT-1020 spectrometer and on an API Q STARPULSAR spectrometer using electrospray ionization. Microanalytical data were obtained on a Carlo-Erba CHNS-O EA 1108 elemental analyzer. Progress of the reactions was monitored by TLC on Merck silica gel 60 F_{254} precoated plates, and compounds were visualized by fluorescence quenching, by use of I_2, or by charring after treatment with a *p*-anisaldehyde–AcOH–H_2SO_4 mixture in EtOH. Column chromatography was performed on flash silica gel (230–400 mesh size).

1-*p*-Tolylcyclopent-3-ene-1-carbonitrile (6)

By Method A (Scheme 2): 4-Methylbenzyl cyanide (**7**; 5 g, 38 mmol) in anhyd THF (10 mL) was added to a 60% soln of NaH

[3.053 g, 76 mmol; washed with anhyd PE (2–3 ×)] in anhyd THF (15 mL) at 0 °C, and the mixture was stirred for 30 min. Dropwise addition of *cis*-1,4-dichlorobut-2-ene (4.17 g, 38 mmol) in anhyd THF (10 mL) over 20 min followed, and the mixture was stirred at r.t. for 8 h. On completion of the reaction, the mixture was quenched by the addition of sat. aq NH_4Cl (15 mL), extracted with EtOAc (3 × 40 mL), and washed with brine (2 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, EtOAc–PE, 3:97); this afforded a mixture of compounds **6** and **8** (2:1) as a yellow oil.

Yield: 5.52 g (80%).

By Method B (Scheme 4): The Grubbs first-generation catalyst (194 mg, 10 mol%) was added to a degassed homogeneous soln of **11** (synthesis described further below; 500 mg, 2.36 mmol) in anhyd CH_2Cl_2 (50 mL) under argon. The mixture was stirred at r.t. for 4 h. On completion of the reaction, the solvent was removed under vacuum and the residue was purified by flash column chromatography (silica gel, EtOAc–PE, 2:98); this gave **6** as a thick, colorless oil**.**

Yield: 390 mg (92%).

IR (neat): 817, 1514, 1640, 2238, 3029 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 2.98 (d, *J* = 15.0 Hz, 2 H), 3.33 (d, *J* = 15.0 Hz, 2 H), 5.86 (s, 2 H), 7.22 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.8, 44.5, 48.1, 124.6, 125.4, 128.3, 129.4, 134.2, 138.3.

1-*p*-Tolyl-2-vinylcyclopropane-1-carbonitrile (8)

4-Methylbenzyl cyanide (**7**; 5 g, 38 mmol) in anhyd THF (25 mL) was added to a 60% soln of NaH [3.6 g, 76 mmol; washed with anhyd PE (2–3 ×)] in anhyd THF (10 mL) at 0 °C, and the mixture was stirred for 30 min. Then *trans*-1,4-dibromobut-2-ene (8.16 g, 38 mmol) in anhyd THF (10 mL) was added dropwise over 20 min, and the mixture was stirred at r.t. for 8 h. On completion of the reaction, the mixture was quenched by the addition of sat. aq NH_4Cl (15 mL), extracted with EtOAc (3 × 40 mL), and washed with brine (2 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, EtOAc–PE, 3:97); this afforded compound **8** as a yellow oil.

Yield: 5.8 g (85%).

IR (neat): 817, 1216, 1514, 1640, 2237, 3019 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.69–1.83 (m, 2 H), 2.09–2.21 (m, 1 H), 2.39 (s, 3 H), 5.35–5.41 (m, 2 H), 5.71–5.88 (m, 1 H), 7.09–7.25, (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.9, 21.4, 22.9, 33.5, 118.4, 120.1, 125.4, 129.5, 132.6, 134.3, 137.3.

MS (EI, 70 eV): *m*/*z* = 207.07 [M^+ + Na].

Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 84.99; H, 7.05; N, 7.32.

1-Methyl-4-(1-methylcyclopent-3-enyl)benzene (5)

A mixture of **6** and **8** (4 g, 21 mmol) was taken up in anhyd CH_2Cl_2 under argon, and the temperature was lowered to –78 °C. A 2 M soln of DIBAL-H in toluene (20 mL, 43.5 mmol) was added dropwise, and the mixture was stirred at the same temperature until completion of the reaction. It was then quenched at –78 °C by the dropwise addition of 2 N HCl and subsequently warmed to r.t. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure; this afforded aldehyde **9** and **10** as an inseparable mixture, which was used without further purification.

To a stirred soln of the crude mixture of aldehyde **9** and **10** (4.1 g, 22 mmol) in diethylene glycol (20 mL) was added hydrazine monohydrate (3.85 mL, 88 mmol) and NaOH (3.52 g, 88 mmol). The mixture was heated to reflux for 8 h, and after completion of the reaction it was diluted with H_2O (10 mL) and extracted with EtOAc (3 × 25 mL). The combined organic layers were then washed with H_2O (3 × 20 mL) and brine (1 × 15 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, EtOAc–PE, 2:98); this afforded **5**.

Yield: 2.2 g (60%).

IR (neat): 816, 1215, 1650, 2926, 3020 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.38 (s, 3 H), 2.30 (s, 3 H), 2.45 (d, *J* = 14.2 Hz, 2 H), 2.73, (d, *J* = 14.2 Hz, 2 H), 5.71 (s, 2 H), 7.11 (d, *J* = 8.34 Hz, 2 H), 7.20 (d, *J* = 8.34 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.8, 31.3, 45.7, 47.7, 125.8, 128.8, 129.3, 134.6, 148.6.

MS (EI, 70 eV): *m*/*z* = 173.27 [M^+ + 1].

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.75; H, 9.48

3-Methyl-3-*p*-tolylcyclopentanone (4)

$BH_3{\cdot}SMe_2$ (0.331 mL, 3.4 mmol) was added to a soln of olefin **5** (300 mg, 1.7 mmol) in anhyd THF at 0 °C. The mixture was allowed to warm to r.t. and stirred for 4 h. It was then cooled to 0 °C, and treated with aq NaOH (2.8 mL, 8.7 mmol) and 30% H_2O_2 (0.98 mL, 8.7 mmol). The mixture was allowed to warm to r.t. After 3 h, the volatile materials were removed under reduced pressure and the residue was dissolved in EtOAc (15 mL) and washed with H_2O (3 × 10 mL) and brine (1 × 10 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure; this afforded an alcohol, which was used without further purification.

To a stirred soln of this alcohol in anhyd DMSO (10 mL) was added IBX (732 mg, 2.6 mmol), and the mixture was stirred at r.t. for 4 h. After completion of the reaction, the mixture was diluted with H_2O (15 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were then washed with H_2O (3 × 10 mL) and brine (1 × 15 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, EtOAc–PE, 5:95); this afforded **4**.

Yield: 0.276 g (85%); white solid; mp 58–59 °C.

IR ($CHCl_3$): 815, 1246, 1246, 1614, 1720, 3019 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.39 (s, 3 H), 2.21–2.29 (m, 2 H), 2.35 (s, 3 H), 2.25–2.37 (m, 2 H), 2.46 (d, *J* = 17.7 Hz, 1 H), 2.65 (d, *J* = 17.7 Hz, 1 H), 7.22–7.32 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.9, 29.5, 35.9, 36.7, 43.5, 52.8, 96.2, 125.5, 129.2, 135.7, 145.4.

MS (EI, 70 eV): *m*/*z* = 189.27 [M^+ + 1].

2,2,3-Trimethyl-3-*p*-tolylcyclopentanone (1)

LiHMDS (371 mg, 2.2 mmol) and HMPA (cat.) were added to a stirred soln of **4** (200 mg, 1.0 mmol) in anhyd DME, and the mixture was stirred for a few min before MeI (0.325 mL, 5.0 mmol) in anhyd DME was added dropwise. The mixture was stirred for 3 h, quenched with sat. aq NH_4Cl, and extracted with EtOAc (3 × 50 mL). The extracts were washed with brine (1 × 20 mL) and the combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, EtOAc–PE, 3:97).

Yield: 152 mg (70%); colorless oil.

IR (neat): 815, 1460, 1510, 1735, 2960 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.6 (s, 3 H), 1.20 (s, 3 H), 1.30 (s, 3 H), 1.90 (m, 1 H), 2.30 (s, 3 H), 2.50 (m, 2 H), 2.60 (m, 1 H), 7.20–7.30 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.4, 20.8, 22.1, 25.9, 29.7, 33.8, 48.3, 53.2, 126.4, 128.9, 135.8, 141.9, 222.7.

MS (EI, 70 eV): *m*/*z* (%) = 216 (75) [M^+].

2-Allyl-2-*p*-tolylpent-4-enenitrile (11)

4-Methylbenzyl cyanide (**7**; 1.0 g, 7.6 mmol) in anhyd THF (10 mL) was added to a soln of 60% NaH [0.68 g, 16.7 mmol; washed with anhyd PE (2–3 ×)] in anhyd THF (15 mL) at 0 °C. The mixture was stirred for 30 min and then AllBr (1.49 mL, 16 mmol) in anhyd THF (5 mL) was added dropwise over 5 min and the mixture was stirred at r.t. for a further 8 h. On completion of the reaction, the mixture was quenched by the addition of sat. aq NH_4Cl soln (10 mL), extracted with EtOAc (3 × 20 mL), and washed with brine (1 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, EtOAc–PE, 3:97).

Yield: 1.3 g (86%); yellowish oil.

IR (neat): 815, 1642, 1514, 2237, 2982 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 2.71 (m, 2 H), 5.18 (m, 4 H), 5.69 (m, 2 H), 7.2 (d, *J* = 16 Hz, 2 H), 7.3 (d, *J* = 16 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.9, 44.12, 47.2, 119.9, 121.5, 126.1, 129.4, 131.7, 134.6, 137.4.

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