Mono- and Bicyclic Cyclopentenes by Rearrangement of 1-Methylcyclobutylmethanols: Synthesis of (±)-Cuparene and Formal Syntheses of (±)-Laurene and (±)-Herbertene[1]

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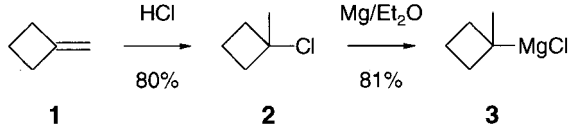
Abstract: Addition of 1-methylcyclobutylmagnesium chloride (**3**) to acyclic (**4d**, **e**) and cyclic ketones (**4a–c**) yields 1-methylcyclobutylmethanols (**5a–e**), which may be rearranged to mono- (**11–14**) and bicyclic cyclopentenes (**6–10**), respectively. Compounds **11**, **12**, and **13** are known precursors of (±)-laurene (**15**), (±)-cuparene (**16**), and (±)-herbertene (**17**), respectively. The cyclopentene **11** has been used in a two step synthesis of (±)-cuparene (**16**).

Key words: 1-methylcyclobutylmethanols, cascade rearrangements, mono- and bicyclic cyclopentenes

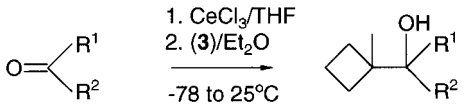
The cyclobutylmethyl to cyclopentyl rearrangement is an important method for the construction of cyclopentanes.[2] New reagents for the synthesis of suitable precursors should therefore be welcome. It was in this context that we generated the hitherto unknown 1-methylcyclobutylmagnesium chloride (**3**), studied its addition to acyclic (**4d**,**e**) and cyclic ketones (**4a–c**), and rearranged the 1-methylcyclobutylmethanols (**5a–e**) formed. In all cases, high yields of mono- (**11–14**) and bicyclic cyclopentenes (**6–10**), respectively, were obtained. Of these, **11**,[3] **12**[4] and **13**[5] are known precursors of (±)-laurene (**15**),[6] (±)-cuparene (**16**)[7] and (±)-herbertene (**17**),[8] respectively. However, as will be shown later, **11** may be used in a short synthesis of (±)-cuparene (**16**) as well.

For the generation of 1-methylcyclobutylmagnesium chloride (**3**), the readily available methylenecyclobutane (**1**)[9] was first hydrochlorinated to 1-chloro-1-methyl-cyclobutane (**2**)[10] and then reacted with magnesium in diethyl ether (Scheme 1). For the following reactions, the ketones **4a–e** were first complexed with cerium(III) chloride (2.0 equiv) in tetrahydrofuran before the addition of the Grignard reagent **3** (1.6 equiv).[11] The reactions were complete after 15 min at –78°C and 2 hours at room temperature (Scheme 2). In the absence of cerium(III) chloride the yields of the products decreased sharply.



Scheme 1

Quantitative rearrangements were observed when **5a–e** were heated with equimolar amounts of a 0.074 M solution of anhydrous *p*-toluenesulfonic acid in benzene for 3 h to 70°C (Method A). With the exception of **7**, only hydrocarbons were formed (Scheme 3). In all cases, the



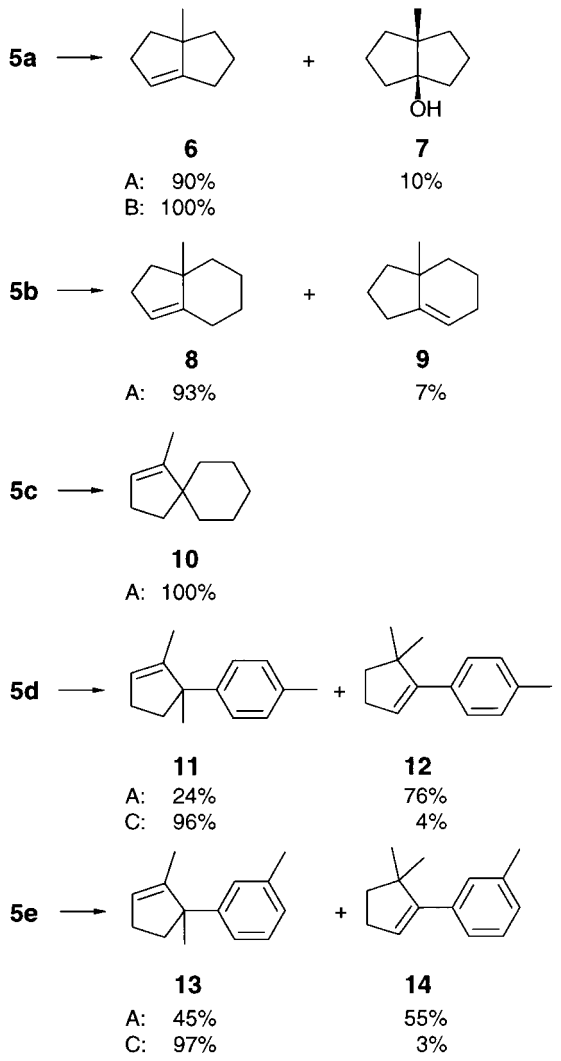
4	R^1	R^2	5	Yield (%)
a	$-(CH_2)_3-$		a	87
b	$-(CH_2)_4-$		b	53
c	$-(CH_2)_5-$		c	61
d	CH_3	p-tolyl	d	41
e	CH_3	m-tolyl	e	62

Scheme 2

product formation involved a cyclobutylmethyl to cyclopentyl rearrangement (**10**,**11**,**13**), eventually followed by a second cyclobutylmethyl to cyclopentyl rearangement (**6**,**7**), a cyclopentylmethyl to cyclohexyl rearrangement (**8**,**9**), or a 1,2-methyl shift (**12**,[12] **14**). With thionyl chloride in pyridine (Method B), the formation of **7** could be avoided, and with hydrochloric acid in methanol (Method C), the 1,2-methyl shifts leading to **12** and **14** could be suppressed.[13]

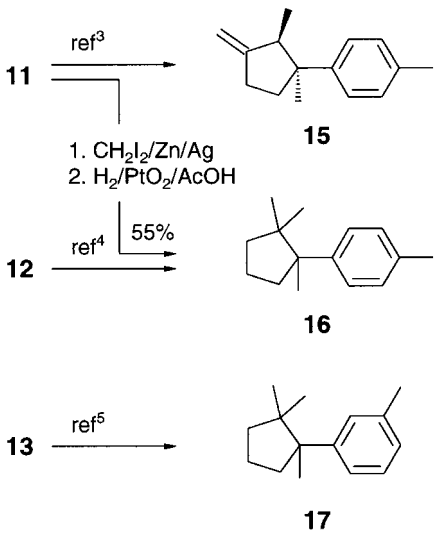
Of the products formed, **11** has formerly been used by McMurry[3] in a five step synthesis of (±)-laurene (**15**), **12** by de Mayo[4] in a four step synthesis of (±)-cuparene (**16**), and **13** by Turner[5] in a two step synthesis of (±)-herbertene (**17**). We adopted the protocol of Turner[5] and applied it to **11**. Towards this end, **11** was cyclopropanated with diiodomethane/zinc-silver,[14] and the two stereoisomeric cyclopropanes formed were hydrogenated over platinium dioxide in acetic acid. As was to be expected, both cyclopropanes collapsed to a single product, i.e. (±)-cuparene (**16**) (Scheme 4). After a single chromatography, the product was pure.

In summary, 1-methylcyclobutylmagnesium chloride (**3**) adds to acyclic and cyclic ketones with formation of 1-methylcyclobutylmethanols, which may be rearranged to mono- und bicyclic cyclopentenes of great structural diversity. The addition products to acyclic ketones yield monocyclic cyclopentenes (**11–14**), and the addition products to cyclic ketones bicyclooctenes (**6**, **7**), bicyclononenes (**8**, **9**) or spiro[4.5]decenes (**10**), depending on the ring size of the ketone used. The monocyclic cyclopentene **11** was used in a two step synthesis of (±)-cuparene (**16**). It is obvious, that with other cyclobutane-based Grignard reagents and/or other ketones than those em-



Method A: p-TsOH/benzene; Method B: $SOCl_2$/pyridine; Method C: HCl/MeOH

Scheme 3



Scheme 4

ployed here, other substitution patterns and/or frameworks should be accessible.

^1H and ^{13}C NMR spectra were measured on a Bruker AMX 300 spectrometer using $CDCl_3$ as solvent, and $CHCl_3$ (δ_H = 7.24) and $CDCl_3$ (δ_C = 77.00), respectively, as internal standards. Analytical GC was carried out on a Carlo-Erba GC 6000 Vega Series 2 instrument employing a split/splitless injector, a FID 40 detector, and hydrogen as the carrier gas, or on a Carlo-Erba GC 6000 Vega Series 2 instrument employing a thermal conducticity detector, and H_2 as the carrier gas. The latter instrument was used for preparative GC as well. Product ratios were not corrected for relative response. R_f values are quoted for Macherey & Nagel Polygram SIL G/UV_{254} plates. Colourless substances were detected with 3.5% alcoholic 12-molybdophosphoric acid (Merck) and subsequent warming. Impregnated TLC plates were prepared by dipping the plates for 10 sec into a solution of 10% (w/w) $AgNO_3$ in MeOH/H_2O (2:1, v/v) and drying for 1 h at 110°C. The silica gel impregnated with 10% (w/w) $AgNO_3$ for column chromatography was prepared by adding the theoretical amount of silica gel to a solution of $AgNO_3$ in MeCN, evaporation of the solvent on a rotary evaporator, and drying the residue for 48 h at 80°C/0.5 mbar prior to use. 1-Chloro-1-methylcyclobutane (**2**)[10] (purity 97%, GC) was prepared by hydrochlorination of methylenecyclobutane (**1**).[9] The ^{13}C NMR data were in accord with literature data.[15] Of the solvents used, Et_2O (Na), THF ($LiAlH_4$) and pyridine (KOH) were dried as indicated and distilled. The benzene used was of analytical grade. All preparations were carried out under argon. All new compounds gave satisfactory elemental analyses (**5a–e**, **6**, **10**: C ± 0.29, H ± 0.21) or correct high resolution mass spectral data (**7–9**, **14**).

1-Methylcyclobutylmagnesium Chloride (3):
Mg turnings (1.94 g, 80 mmol) and a few crystals of I_2 were covered with Et_2O (50 mL), and a small portion of the full amount of **2** (8.37 g, 80 mmol) was added under argon with stirring. The reaction was started by heating briefly until the rest of **2** was added at such a rate as to maintain a gentle reflux. After the addition was complete, the mixture was heated for 2.5 h at reflux. The solution (50 mL) was transferred to a stock vessel and two aliquots titurated in a four weeks interval. In both cases the solution was 1.28 M (81%).

1-Methylcyclobutylmethanols 5a–e; General Procedure:
Finely powdered $CeCl_3 \cdot 7H_2O$ (8.94 g, 24 mmol) was dehydrated for 6 h at 140°C/0.6 mbar. The dry material was suspended in THF (85 mL) and stirred under Ar overnight. After the appropriate ketone **4** (12 mmol) had been added, stirring was continued for 2 h until the mixture was cooled to –78°C and a 1.28 M solution of **3** in Et_2O (15.0 mL, 19.2 mmol) was added dropwise. After 15 min at –78°C and 2 h at r.t. the mixture was hydrolyzed with 2 N HCl (50 mL). The aqueous phase was extracted with Et_2O (4 × 40 mL), and the combined organic phases were washed with aq sat $NaHCO_3$ solution (60 mL), brine (60 mL) and dried ($MgSO_4$). The solvents were evaporated and the crude products were either chromatographed directly (**5a–c**), or to achieve a better separation from unchanged starting material, were treated with $NaBH_4$ (400 mg, 11 mmol) in EtOH (70 mL) for 4 h at r.t. (**5d**,**e**). In this case, the reaction mixture was diluted with H_2O (75 mL) and extracted with Et_2O (6 × 75 mL), and the combined extracts were washed with brine (2 × 50 mL), dried ($MgSO_4$) and concentrated. In all cases, a final chromatography on silica gel (0.05–0.20 mm) in pentane/Et_2O [**5a**,**c**,**d**,**e** (5:1); R_f 0.19 (**5a**), 0.36 (**5c**), 0.35 (**5d**), 0.21 (**5e**); **5b** (9:1); R_f 0.14 (**5b**)] yielded the pure products. With the exception of **5c** (mp 28–30°C), all products were colourless liquids.

1-(1-Methylcyclobutyl)cyclobutanol (**5a**):
^1H NMR: δ = 1.11 (s, 3 H, CH_3), 1.42–1.60 (m, 4 H), 1.62–1.78 (m, 1 H), 1.80–2.12 (m, 6 H), 2.21–2.30 (m, 2 H).
^{13}C NMR: δ = 12.4, 14.1 (t), 20.9 (q), 28.0, 31.2 (t), 43.0, 80.2 (s).

1-(1-Methylcyclobutyl) cyclopentanol (**5b**):
^{1}H NMR: δ = 1.16 (s, 3 H, CH_3), 1.42–1.82 (m, 13 H), 1.82–2.07 (m, 2 H).
^{13}C NMR: δ = 13.8 (t), 23.8 (q), 24.6, 29.3, 35.3 (t), 44.0, 86.7 (s).

1-(1-Methylcyclobutyl) cyclohexanol (**5c**):
^{1}H NMR: δ = 0.96–1.12 (m, 1 H), 1.15 (s, 3 H, CH_3), 1.20–1.46 (m, 7 H), 1.46–1.58 (m, 4 H), 1.58–1.72 (m, 2 H), 1.80–1.98 (m, 1 H), 2.12–2.26 (m, 2 H).
^{13}C NMR: δ = 14.2, 21.6 (t), 23.2 (q), 25.8, 27.5, 30.1 (t), 45.9, 73.7 (s).

1-(1-Methylcyclobutyl)-1-(p-tolyl)ethanol (**5d**):
^{1}H NMR: δ = 0.92 (s, 3 H, CH_3), 1.11–1.23 (m, 1 H), 1.38–1.50 (m, 1 H), 1.41 (s, 3 H, CH_3), 1.52–1.66 (m, 1 H), 1.62 (s, 1 H, OH), 1.70–1.88 (m, 1 H), 2.24 (s, 3 H, CH_3), 2.34 (ddd, *J* = 10, 10, 10 Hz, 1H), 2.49 (ddd, *J* = 10, 10, 10 Hz, 1 H), 7.02 (AA'-part of an AA'BB'-system, 2 H), 7.21 (BB'-part of an AA'BB'-system, 2 H).
^{13}C NMR: δ = 13.8 (t), 20.9, 23.4, 23.6 (q), 27.6, 28.7 (t), 46.3, 76.6 (s), 125.9, 128.2 (d), 135.9, 142.8 (s).

1-(1-Methylcyclobutyl)-1-(m-tolyl)ethanol (**5e**):
^{1}H NMR: δ = 0.92 (s, 3 H, CH_3), 1.11–1.23 (m, 1 H), 1.38–1.50 (m, 1 H), 1.41 (s, 3 H, CH_3), 1.52–1.66 (m, 1 H, OH), 1.65 (s, 1 H), 1.70–1.88 (m, 1 H), 2.26 (s, 3 H, CH_3), 2.34 (ddd, *J* = 10, 10, 10 Hz, 1 H), 2.49 (ddd, *J* = 10, 10, 10 Hz, 1 H), 6.92–7.00 (m, 1 H), 7.08–7.11 (m, 2 H), 7.12–7.15 (m, 1 H).
^{13}C NMR: δ = 13.8 (t), 21.7, 23.3, 23.7 (q), 27.6, 28.7 (t), 46.3, 76.7 (s), 123.1, 126.7, 127.1, 127.4 (d), 137.0, 145.8 (s).

Rearrangement of 5a–e to Mono- and Bicyclic Cyclopentenes 6, 8, 10–14; General and Typical Procedures:
Method A: To a solution of anhyd *p*-TsOH in benzene (0.074 M, 13.5 mL, 1.00 mmol) was added the appropriate substituted methanol **5** (1.00 mmol) and the mixture was heated to 70 °C. After 3 h, the mixture was diluted with pentane (5 mL), washed with aq sat $NaHCO_3$ solution (3 × 5 mL), dried (molecular sieves 3 Å) and concentrated. The residue was subjected to preparative GC on column A (3.5 m × 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh) or column B (3.5 m × 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh), or chromatographed on a silica gel column coated with 10% (w/w) $AgNO_3$ in pentane. **6**,**7**: column A, 120 °C, retention times (min): 3.67 (**6**), 7.46 (**7**), 7.77 (**5a**); **8**,**9**: column B, 8.5 min at 95 °C, 20 °C/min to 190 °C, retention times (min) 7.75 (**8**), 9.53 (**9**); **10**: column A, 140 °C, retention time (min): 7.09 (**10**); **11**,**12**: column A, 185 °C, retention time (min): 5.60 (**11**,**12**); **13**,**14**: chromatography on silica gel coated with 10% (w/w) $AgNO_3$ in pentane, R_f 0.09 (**13**), 0.07 (**14**). The ^{1}H NMR data of **11**,[3] **12**[4] and **13**[5] were identical with literature data. The ^{13}C NMR have not yet been reported and are given below. With the exception of **7** (mp 39–41°C), all products were colourless liquids.

3a-Methyl-1,2,3,3a,4,5-hexahydropentalene (**6**):
^{1}H NMR: δ = 1.00 (s, 3 H, CH_3), 1.25–1.37 (m, 1 H), 1.51–1.70 (m, 2 H), 1.73–1.81 (m, 1 H), 1.83–2.08 (m, 2 H), 2.09–2.19 (m, 2 H), 2.33–2.45 (m, 1 H), 2.60–2.75 (m, 1 H), 5.11 (mc, 1 H, H-6).
^{13}C NMR: δ = 22.5 (q), 22.5, 26.4, 35.8, 38.6, 40.3 (t), 55.5 (s), 116.0 (d), 158.2 (s).

6a-Methyloctahydropentalen-3a-ol (**7**):
^{1}H NMR: δ = 0.98 (s, 3 H, CH_3), 1.35 (br s, 1 H, OH), 1.42–1.73 (m, 10 H), 1.74–1.85 (m, 2 H).
^{13}C NMR: δ = 22.4 (t), 23.1 (q), 41.1, 41.8 (t), 50.2, 89.6 (s).

7a-Methyl-2,4,5,6,7,7a-hexahydro-1H-indene (**8**):
^{1}H NMR: δ = 1.00 (s, 3 H, CH_3), 1.10–1.29 (m, 2 H), 1.50–1.64 (m, 3 H), 1.67–1.81 (m, 3 H), 1.90–2.07 (m, 1 H), 2.09–2.35 (m, 3 H), 5.14 (mc, 1 H, H-3).
^{13}C NMR: δ = 22.8 (q), 22.9, 26.4, 27.8, 29.2, 41.1, 41.8 (t), 45.7 (s), 119.1 (d), 149.7 (s).

3a-Methyl-2,3,3a,4,5,6-hexahydro-1H-indene (**9**):
^{1}H NMR: δ = 0.95 (s, 3 H, CH_3), 1.10–1.29 (m, 2 H), 1.50–1.80 (m, 6 H), 1.92–2.03 (m, 2 H), 2.07–2.22 (m, 1 H), 2.32–2.48 (m, 1 H), 5.26 (mc, 1 H, H-7).
^{13}C NMR: δ = 19.1 (q), 20.5, 24.2, 25.2, 29.2, 36.3 (t), 40.2 (s), 41.5 (t), 116.4 (d), 147.9 (s).

1-Methylspiro[4.5]dec-1-ene (**10**):
^{1}H NMR: δ = 1.00–1.45 (m, 8 H), 1.50–1.70 (m, 2 H), 1.58 (mc, 3H, CH_3), 1.73 (t, J = 6.5 Hz, 2 H, H-4), 2.14 (mc, 2 H, H-3), 5.24 (mc, 1 H, H-2).
^{13}C NMR: δ = 12.4 (q), 23.4, 26.1, 29.1, 34.2 (coincidence of two lines) (t), 49.9 (s), 122.7 (d), 147.8 (s).

1-(1,2-Dimethylcyclopent-2-enyl)-4-methylbenzene (**11**):
^{13}C NMR: δ = 13.1, 20.9, 24.1 (q), 29.9, 43.3 (t), 53.3 (s), 125.1, 126.1, 128.8 (d), 134.9, 145.4, 146.7 (s).

1-(5,5-Dimethylcyclopent-1-enyl)-4-methylbenzene (**12**):
^{13}C NMR: δ = 21.1, 27.4 (q), 29.3, 42.4 (t), 46.5 (s), 126.8, 127.3, 128.6 (d), 135.0, 136.1, 151.9 (s).

1-(1,2-Dimethylcyclopent-2-enyl)-3-methylbenzene (**13**):
^{13}C NMR: δ = 13.1, 21.7, 24.0 (q), 29.9, 43.3 (t), 53.5 (s), 123.3, 125.2, 126.2, 126.9, 127.9 (d), 137.4, 146.7, 148.4 (s).

1-(5,5-Dimethylcyclopent-1-enyl)-3-methylbenzene (**14**):
^{1}H NMR: δ = 1.20 (s, 6 H, 2 CH_3), 1.85 (t, *J* = 6 Hz, 2 H, H-4'), 2.34 (s, 3 H, CH_3), 2.36 (dt, *J* = 2.5, 6 Hz, 2 H, H-3'), 5.70 (t, *J* = 2.5 Hz, 1 H, H-1´), 7.02–7.24 (m, 4 H).
^{13}C NMR: δ = 21.5, 27.4 (q), 29.4, 42.4 (t), 46.6, 124.5, 127.2, 127.3, 127.7, 128.3 (d), 137.3, 138.0, 152.1 (s).

Method B: To a solution of **5a** (140 mg, 1.00 mmol) in pyridine (3.0 mL) was added at 0 °C with stirring a solution of $SOCl_2$ (236 mg, 2.00 mmol) in the same solvent (1.0 mL). After 3 h at 0 °C, GC analysis [3.5 m × 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 100 °C, rel. retention times: 1.00 (**6**), 2.12 (**5a**)] indicated complete rearrangement to **6**. The mixture was diluted with H_2O (5 mL) and extracted with pentane (3 × 5 mL), and the combined extracts were washed with aq sat NH_4Cl (4 × 5 mL) and dried (molecular sieves 3 Å). Preparative GC yielded a sample identical (^{1}H NMR) with authentic **6**.

Method C: To a solution of the appropriate alcohol **5d,e** (836 mg, 4.20 mmol) in MeOH (10.0 mL) was added concd HCl (1.0 mL) and the mixture was heated to reflux. After 2 h, the solution was neutralized with 10% aq NaOH, diluted with H_2O (6 mL), and extracted with pentane (3 × 10 mL). The combined organic phases were washed with brine (10 mL) and dried ($MgSO_4$). The solvent was evaporated, and the remaining material (741 mg (95%) from **5d**, 726 mg (93%) from **5e**) was subjected to capillary GC [30 m–0.32 mm (i.d.) deactivated fused-silica capillary column coated with 0.25 µm DB FFAP; 10 min 100 °C, 10 °C/min to 220 °C; 0.6 bar H_2; retention times (min): 9.34 (**11**), 9.51 (**12**), 7.46 (**13**), 7.95 (**14**)] indicating a product ratio of 96:4 for **11** and **12**, and of 97:3 for **13** and **14**.

(±)-Cuparene (16):
To a stirred suspension of freshly prepared zinc-silver couple[14] (3.93 g) in anhyd Et_2O (8.0 mL) under N_2 was added a 96:4 mixture of **11** and **12** (560 mg, 3.00 mmol) followed by CH_2I_2 (8.04 g, 30.0 mmol). After the vigorous reaction had subsided, the mixture was heated for 2 h to reflux. After dilution with pentane (20 mL) the solution was decanted, the residue was washed with pentane (10 mL), and the combined organic phases were successively treated with sat aq NH_4Cl solution (30 mL), washed with H_2O (2 × 15 mL), and dried

($MgSO_4$). The solvent was evaporated and the residue chromatographed on silica gel (0.05–0.20 mm) in pentane (column 60 × 1.5 cm; R_f 0.44, 0.50) yielding 570 mg (95%) of a 70:30 mixture of two stereoisomeric cyclopropanes according to capillary GC [30 m × 0.32 mm (i.d.) deactivated fused-silica capillary column coated with 0.25 µm DB FFAP; 10 min 100 °C, 10 °C/min to 220 °C; 0.6 bar H_2; retention times (min): 12.40 (70%), 13.56 (30%)]. A fraction of this material (100 mg, 0.50 mmol) was dissolved in glacial AcOH (20 mL) and hydrogenated over PtO_2 (1.0 g) and 1.1 atm hydrogen pressure at r.t. in a shaking gear until capillary GC [retention times (min): 11.90 (**16**), 12.40, 13.56] indicated that the reaction was complete (4.5 h). After dilution with pentane (30 mL) the mixture was filtrated, and the filtrate was washed with H_2O (3 × 30 mL), satd aq $NaHCO_3$ solution (30 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed on silica gel (0.05–0.20 mm) in pentane (column 60 × 1.5 cm; R_f 0.52) yielding 55 mg (55%) of pure **16**. The ^1H and ^{13}C NMR data were in accord with literature data.[16]

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