

SYNTHESIS OF 2-METHYLHEPTADECANE AND 14-METHYLPENTADECAN-3-ONE

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2-Methylheptadecane (*I*) is the sex pheromone of the family *Arctiidae* (tiger moth) and was isolated by Roelof and Carde¹ and assigned structure *I* on the basis of spectral data. Haque et al.² isolated a granular white solid (m.p. 80 °C) from the ether extract of dried and powdered plant of *Parthenium hysterophorous* L. (*Compositae*) and proposed its structure, 14-methylpentadecan-3-one (*II*) on the basis of spectroscopic data. Literature records³⁻⁵ a few synthesis of *I* and *II*. We report herein a short and facile synthesis of these compounds. The sequence of reactions employed in their synthesis is outlined in Scheme 1.

Coupling reaction⁶ of isopropylmagnesium bromide with 11-bromo-1-undecene at -10 °C using catalytic amount of lithium tetrachlorocuprate in anhydrous tetrahydrofuran afforded olefin *III*. Treatment of *III* with acetoxyborohydride⁷, prepared in situ from sodium borohydride and mercuric acetate in tetrahydrofuran, followed by oxidation with alkaline hydrogen peroxide resulted in the formation of alcohol *IV* in quantitative yield. Alcohol *IV* was converted into corresponding bromide *V* in reaction with phosphorus tribromide in ether. Coupling of bromide *V* with 1-butylmagnesium bromide in dry tetrahydrofuran in the presence⁶ of catalytic amount of dilithium tetrachlorocuprate at -10 °C yielded hydrocarbon *I*.

Pyridinium chlorochromate⁸ oxidation of alcohol *IV*, in dry dichloromethane afforded aldehyde *VI* which on treatment with ethylmagnesium bromide in dry ether followed by pyridinium chlorochromate oxidation in dichloromethane gave ketone *II* in good yield (cf. ref.³).

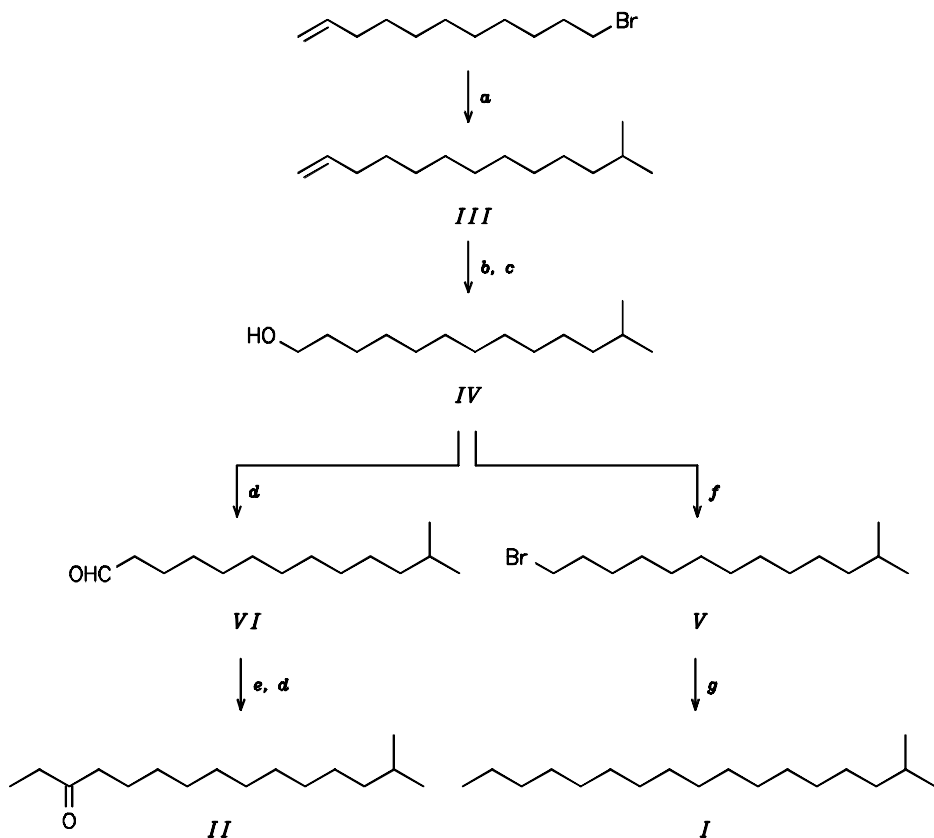
EXPERIMENTAL

All the glassware used for the experiment was thoroughly dried in an oven and cooled under the stream of nitrogen. Purity of the samples was checked by TLC using silica gel impregnated with 13% calcium sulfate. Silica gel (Acme, 60 – 80 mesh) was used for column chromatography. IR spectra were recorded in Perkin-Elmer 377 spectrophotometer (wavenumber in cm⁻¹) and ¹H NMR spectra (in CCl₄ or CDCl₃) on a Varian EM-390 instrument using tetramethylsilane as an internal standard.

Chemical shifts are given in ppm (δ -scale), J in Hz. Unless otherwise stated, all the organic extracts were dried over anhydrous sodium sulfate.

12-Methyltridec-1-ene (*III*)

To the Grignard reagent (prepared from magnesium turnings (0.24 g, 10 mmol) and 2-bromopropane (1.23 g, 10 mmol) in dry tetrahydrofuran (15 ml) under nitrogen) added 11-bromo-1-undecene (2.33 g, 10 mmol) in dry tetrahydrofuran (5 ml) at $-10\text{ }^{\circ}\text{C}$ and stirred for 30 min. To this a catalytic amount of 0.1 M dilithium tetrachlorocuprate in tetrahydrofuran (1.5 ml) was added, stirred for 4 h



a, $(\text{CH}_3)_2\text{CHMgBr}$, $\text{Li}_2\text{CuCl}_4/\text{THF}$; **b**, NaBH_4 , $\text{Hg}(\text{OAc})_2$; **c**, H_2O_2 , NaOH ; **d**, PCC , CH_2Cl_2 ;
e, $\text{C}_2\text{H}_5\text{MgBr}/\text{THF}$; **f**, PBr_3 , pyridine/ether; **g**, $\text{CH}_3(\text{CH}_2)_3\text{MgBr}$, $\text{Li}_2\text{CuCl}_4/\text{THF}$

SCHEME 1

and then left overnight. The resulting solution was decomposed with a saturated aqueous solution of ammonium chloride (20 ml) and extracted with ether (4×25 ml), the combined ethereal extract was washed with brine (2×10 ml) and dried. Evaporation of the solvent under reduced pressure followed by chromatographic purification over silica gel employing light petroleum ether as eluent furnished pure olefin *III*; yield 0.82 g (42%). IR spectrum (neat): 2 940, 2 845, 1 640, 1 420, 1 340, 1 250, 1 200, 1 070, 910, 790. ^1H NMR spectrum: 5.6 – 6.0 m, 1 H ($-\text{CH}=\text{CH}_2$); 4.9 – 5.2 m, 2 H ($-\text{CH}=\text{CH}_2$); 2.0 m, 2 H (allylic methylene); 1.27 bs, 17 H ($8 \times -\text{CH}_2-$, $-\text{CH}<$); 0.85 d, 6 H ($2 \times \text{CH}_3$, $J = 6$). For $\text{C}_{14}\text{H}_{28}$ (196.4) calculated: 85.6% C, 14.4% H; found: 85.5% C, 14.5% H.

12-Methyltridecan-1-ol (*IV*)

A dry 100 ml flask equipped with magnetic stirring bar, septum inlet and reflux condenser was flushed with nitrogen. The flask was charged under nitrogen with sodium borohydride (0.76 g, 20 mmol) followed by the addition of tetrahydrofuran (40 ml) via syringe. The flask is immersed in an ice-bath, and mercuric acetate (3.18 g, 10 mmol) was added slowly under a blanket of nitrogen. The contents were allowed to stir for 1 h at 0 °C. The reaction mixture was brought to room temperature and the olefin *III* (3.9 g, 20 mmol) was added dropwise. The contents were further stirred for 16 h at room temperature for complete hydroboration.

The organoborane solution prepared as above was cooled to 0 °C and 3 M aqueous sodium hydroxide (8 ml) was added slowly to the reaction mixture. Hydrogen peroxide (8 ml, 30% aqueous solution) was introduced dropwise to the stirred reaction mixture. The temperature was then raised slowly, and the reaction mixture was heated at 70 °C for 1 h, during which the mercury coagulated. The contents were brought to room temperature, decanted to separate mercury, and saturated with sodium chloride. Isolation of the product was accomplished by a separatory funnel, and the aqueous layer was extracted with ethyl ether (3×20 ml). The combined tetrahydrofuranethyl ether extract was washed with water (2×10 ml) and brine (1×10 ml). The organic layer was concentrated under reduced pressure and purified by column chromatography to yield 3.6 g (85%) of alcohol *IV*. IR spectrum (neat): 3 380, 2 940, 2 860, 1 470, 1 330, 1 090, 800, 770. ^1H NMR spectrum: 3.7 t, 2 H ($-\text{CH}_2\text{OH}$, $J = 6$); 1.27 bs, 21 H ($10 \times -\text{CH}_2-$, $-\text{CH}<$); 0.8 d, 6 H ($2 \times \text{CH}_3$, $J = 6$). For $\text{C}_{14}\text{H}_{30}\text{O}$ (214.4) calculated: 78.4% C, 14.1% H; found: 78.5% C, 14.2% H.

12-Methyl-1-bromotridecane (*V*)

Phosphorus tribromide (1.2 g, 4.4 mmol) was added dropwise to an ice-cold and well stirred solution of compound *IV* (1.98 g, 9.2 mmol) and pyridine (0.1 ml) in anhydrous ether (50 ml). After keeping it overnight, the resulting solution was refluxed for 4 h. It was cooled, decomposed with cold aqueous 10% sodium hydrogen carbonate solution (20 ml), extracted with ether (4×10 ml) and dried. Evaporation of the solvent under reduced pressure afforded bromide *V*; yield 2.4 g (93%). IR spectrum (neat): 3 060, 2 940, 1 470, 1 455, 1 270, 1 050, 920, 805. ^1H NMR spectrum: 3.5 t, 2 H ($-\text{CH}_2\text{Br}$, $J = 6$); 1.8, 2 H ($-\text{CH}_2\text{CH}_2\text{Br}$); 1.2 bs, 18 H ($9 \times -\text{CH}_2-$); 0.8 d, 6 H ($2 \times \text{CH}_3$, $J = 6$). For $\text{C}_{14}\text{H}_{29}\text{Br}$ (277.3) calculated: 60.6% C, 10.5% H; found: 60.7% C, 10.4% H.

2-Methylheptadecane (*I*)

To the Grignard reagent (prepared from magnesium turnings (0.29 g, 12 mmol) and 1-bromobutane (1.64 g, 12 mmol) in dry tetrahydrofuran (15 ml) under nitrogen bromide *V* (3.32 g, 12 mmol) in dry tetrahydrofuran (5 ml) was added at -10 °C and stirred for 30 min. To this a catalytic amount of 0.1 M dilithium tetrachlorocuprate in tetrahydrofuran (2 ml) was added, stirred for 4 h and then left overnight. The resulting solution was decomposed with a saturated aqueous solution of ammonium

chloride (20 ml) and extracted with ether (4×25 ml), the combined ethereal extract was washed with brine (2×10 ml) and dried. Evaporation of the solvent under reduced pressure followed by chromatographic purification over silica gel using light petroleum ether furnished pure compound *I*; yield 1.22 g (40%). IR spectrum (neat): 2 850, 2 780, 1 450, 1 250, 1 090, 1 015, 900, 815, 720. ^1H NMR spectrum: 1.2 bs, 30 H ($15 \times -\text{CH}_2-$); 0.85 m, 9 H ($3 \times \text{CH}_3$).

12-Methyltridecan-1-al (*VI*)

To pyridinium chlorochromate (3.6 g, 16.7 mmol) in methylene chloride (40 ml) alcohol *IV* (2.68 g, 12.5 mmol) in dichloromethane (15 ml) was added under stirring. In a short time a black mass separated and the stirring continued further for 2 h. Hexane (50 ml) was added, the mixture was allowed to settle and then passed through a short pad of silica gel. Removal of the solvent under reduced pressure afforded aldehyde *VI*; yield 2.4 g (84%). IR spectrum (neat): 2 950, 2 890, 2 705, 1 730, 1 470, 1 360, 1 180, 910, 740. ^1H NMR spectrum: 9.87 bs, 1 H ($-\text{CHO}$); 2.2 m, 2 H ($-\text{CH}_2-\text{CH}=\text{O}$); 1.25 bs, 19 H ($9 \times -\text{CH}_2-$, $-\text{CH}<$); 0.85 d, 6 H ($2 \times \text{CH}_3$, $J = 6$). For $\text{C}_{14}\text{H}_{28}\text{O}$ (212.4) calculated: 79.2% C, 13.3% H; found: 79.0% C, 13.4% H.

14-Methylpentadecan-3-one (*II*)

Aldehyde *VI* (2.12 g, 10 mmol) on reaction with ethylmagnesium bromide (1.33 g, 10 mmol) in dry tetrahydrofuran (40 ml) followed by pyridinium chlorochromate oxidation of the obtained alcohol in dichloromethane afforded the desired ketone *II* after chromatographic purification. IR spectrum (CCl_4): 2 850, 1 715, 1 440, 1 340, 1 100, 740. ^1H NMR spectrum: 2.2 m, 4 H ($-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2$); 1.25 bs, 19 H ($9 \times -\text{CH}_2-$, $-\text{CH}<$); 0.83 m, 9 H ($3 \times \text{CH}_3$). For $\text{C}_{16}\text{H}_{32}\text{O}$ (240.4) calculated: 79.9% C, 13.4% H; found: 80.2% C, 13.2% H.

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