Tetrahedron Vol. 38, No. 22, pp. 3335 to 3338, 1982
Printed in Great Britain.

0040-4020/82/223335-04$03.00/0

SYNTHESIS OF *cis*-6,6,9-TRIMETHYL-$\Delta^{3,4}$-OCTALIN-2-ONE AND *cis*-6,9-DIMETHYL-6-CARBOMETHOXY-$\Delta^{3,4}$-OCTALIN-2-ONE

POTENTIAL DE SYNTHONS FOR THE CONSTRUCTION OF PENTACYCLIC TRITERPENES

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(*Received in UK* 15 *February* 1982)

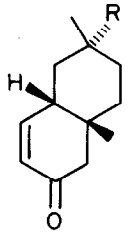
Abstract—Synthesis of the bicyclic enones (1 and 2) which are precursors for the rings DE of the pentacyclic triterpenes, β-amyrin and glycyrrhetinic acid has been reported from the readily available 6 - methoxy - 2 - naphthoic acid.

Although the basic and common problems in synthesis such as the construction of ring systems, introduction of angular Me groups and control of stereochemistry have been solved for steroids,[1] synthesis of pentacyclic triterpenes, continues to be challenging due to their greater complexity and difficult stereochemical features. Notable achievements in this area to date are the synthesis of lupeol,[2] alnusenone,[3] shionone,[4] germanicol,[5] tetrahymanol[6] and serratenediol.[7] In addition, a biogenetic synthesis, involving the cyclisation of the bicyclic poyolefinic epoxide leading to a mixture of β-amyrin, δ-amyrin and germanicol has been reported.[8]

In connection with a programme of work on the convergent synthesis of pentacyclic triterpenes, we explored the possibility of coupling of the two fragments AB and DE synthons such as **1** and **3**. Most of the synthetic investigations[9-14] involving this type of approach, the coupling of the fragments was usually accomplished either by the alkylation of the active methylene group or by the nucleophilic addition of the electron rich species on the CO carbon. These methods, however, would entail the utilisation of acid catalysed cyclisation to close the C-ring and usually suffer from poor yield. An approach involving the construction of ring C through a cycloaddition of suitably substituted synthons AB and DE appeared to be feasible and was explored. We report the synthesis of octalenones (**1** and **2**) which form the DE rings of β-amyrin and glycyrrhetinic acid. The choice of the above octalenones was supported by the consideration that they contain suitable functional groups for cycloaddition with the AB ring synthon **3**.

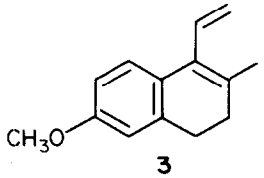
Synthesis of the octalenones (**1** and **2**) was readily accomplished from the known[15] 6 - methoxy - 2 - methyl - 1,2,3,4 - tetrahydro - 2 - naphthoic acid (**4**) which was obtained by the reductive methylation of 6 - methoxy - 2 - naphthoic acid using metal-ammonia solutions. To achieve the synthesis of octalenone (**1**), which contains *gem*-dimethyl, conversion of the carboxyl group to the Me should be effected prior to anisole ring reduction. Otherwise, it would incorporate potential difficulties to deal with the carboxyl group chemospecifically in the presence of the α,β-unsaturated ketone of the enone carboxylic acid **18**. The acid **4**, furnished the methyl ester **5** which gave the primary alcohol **6** on reduction with vitride reagent (70% benzene solution of sodium dihydrobismethoxyethoxy aluminate).

The next step involved the conversion of the alcohol **6** to the 2,2 - dimethyl - 6 - methoxy tetralin (**10**). Thus the alcohol **6** was transformed to the tosylate **7** and attempted hydrogenolysis of the latter either with LAH or metal-ammonia reagent failed. In another attempt, the alcohol **6** was converted to the bromide **8** and subjected to the reductive cleavage with lithium in ammonia[16] which furnished the desired tetralin **10** in 16% yield. However the alcohol **6** could be readily oxidised[17] to the aldehyde **9** and Wolff-Kishner reduction of the latter afforded the 2,2 - dimethyl - 6 - methoxy tetralin (**10**) in



1 R=CH_3

2 R=$COOCH_3$



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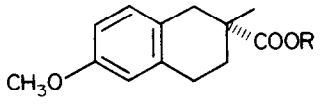
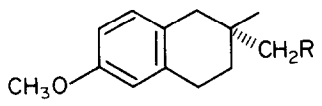


4 R=H

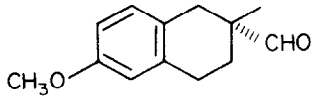
5 R=CH_3



6 R=OH

7 R=OTs

8 R=Br



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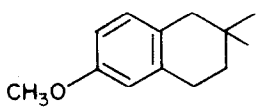
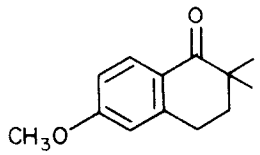
an overall yield of 50%. In an alternative method, the tetrealin **10** was prepared from 6 - methoxytetral - 1 - one. Thus methylation of 6 - methoxytetral - 1 - one with methyl iodide in the presence of potassium t-butoxide in benzene afforded 2,2-dimethyl 6 - methoxytetral - 1 - one (**11**) which was subjected to hydrogenolysis of the CO group. The presence of gem-dimethyl thwarted all our attempts of direct conversion of the CO group into the hydrocarbon **10** by the viable reduction procedures. However reduction of the ketone **11** gave the alcohol **12** which was converted into the acetate **13** and the latter was reductively cleaved[18] with lithium in liquid ammonia to the desired compound **10**.

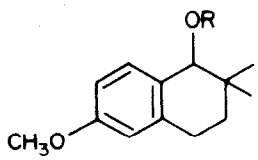
Lithium–ammonia reduction of the tetralin **10** in tetrahydrofuran and t-butanol gave the compound **14** which was hydrolysed with methanolic hydrochloric acid to the enone[19] **15**.



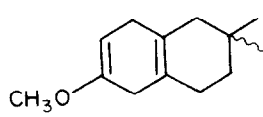
10



11



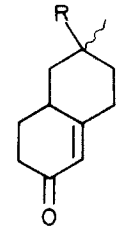
12 R = H
13 R = $COCH_3$

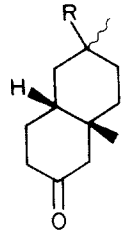


14 R = CH_3
17 R = COOH

The penultimate step in the synthesis included the introduction of an angular Me group with the desired *cis*-stereochemistry. This was accomplished by the copper catalysed conjugate addition of methylmagnesium iodide to enone **15**. Thus, treatment of the enone, **15** with methylmagnesium iodide in the presence of a catalytic amount of anhydrous cuprous chloride gave a complex mixture from which trimethyl decalone **16** was isolated in 45% yield. The configuration of the angular Me group was tentatively fixed as β on the basis of analogous observations.[20] Dehydrogenation of the decalone **16** with DDQ furnished the octalenone **1**.

The tetrahydro acid **4** was subjected to metal-ammonia reduction to obtain the hexahydro acid **17** which was hydrolysed to the enoneacid **18**. This acid (**18**) was esterified and the ester **19** was treated with methylmagnesium iodide in the presence of cuprous chloride to obtain dimethyldecalone **20**. This decalone **20**, ultimately, was converted to enoneacid methyl ester **2** using DDQ in dioxan. The cycloaddition of these enones **1** and **2** with diene **3** for constructing the pentacyclic skeleton present in the triterpenes will be reported elsewhere.[21]





15 R = CH_3 **16** R = CH_3
18 R = COOH **20** R = $COOCH_3$
19 R = $COOCH_3$

EXPERIMENTAL

All m.ps and b.ps are uncorrected. UV spectra were recorded on Unicam model Sp 700A spectrometer and IR spectra on Perkin–Elmer models 700 and 397 spectrometers. ^{1}H NMR spectra were recorded on Varian T-60 spectrometer; Chemical shifts are reported ($CDCl_3$ as solvent) with respect to Me_4Si ($\delta = 0$). All organic extracts were dried over anhyd Na_2SO_4.

Methyl - 6 - methoxy - 2 - methyl - 1,2,3,4 - tetrahydro - 2 - naphthoate (**5**). A soln of **4** (7.2 g) in dry MeOH (75 ml) and conc. H_2SO_4 (5 ml) was refluxed on water bath for 6 h. Excess of solvent was removed and the contents were poured into ice-cold water. This was extracted with ether (3 × 100 ml), the combined ethereal extract thoroughly washed with $NaHCO_3$, water and dried. Removal of solvent followed by short-path distillation afforded the ester (5.7 g), b.t. 155–160°/7 mm Hg; γ_{max} 1720, 1600 and 1500 cm^{-1}; δ 1.1 (3H, s, $-CH_3$), 1.5–3.2 (3 + 2H, m, methylene), 3.6 (3H, s, $-OCH_3$), 3.7 (3H, s, $-COOCH_3$) and 6.5–6.9 (3H, m, Ar–H). (Found: C, 72.06; H, 8.1. $C_{14}H_{18}O_3$ requires: C, 71.77; H, 7.74%.)

6 - *Methoxy - 2 - methyl - 1,2,3,4 - tetrahydronaphthyl - 2 - carbinol* (**6**). To a stirred soln of **5** (6.9 g) in dry benzene (80 ml) Vitride reagent (14 ml, 9 g) was added during 15 min, under N_2. The stirring was continued for 2 h and the mixture poured into ZN HCl (100 ml). This was extracted with benzene (2 × 100 ml) and washed with water, brine and then dried. Evaporation of the solvent followed by distillation under diminished pressure afforded **6** (5.3 g, 86%); b.t. 133–135°/2 mm Hg; γ_{max} 3400, 1600 and 1580 cm^{-1}; δ 1.0 (3H, s, $-CH_3$), 1.7 (1H, s, –OH), 1.8–3.0 (3 × 2H, m, methylene), 3.5 (2H, s, $-CH_2O-$) 3.8 (3H, s, $-OCH_3$) and 6.6–7.1 (3H, m, ArH). (Found: C, 75.19; H, 9.14. $C_{13}H_{18}O_2$ requires: C, 75.69; H, 8.80%.)

6 - *Methoxy - 2 - methyl - 1,2,3,4 - tetrahydronaphthyl - 2 - carbinyl tosylate* (**7**). The alcohol **6** (2 g) was dissolved in dry benzene (50 ml) and to this was added a soln of *p*-toluenesulfonyl chloride (1.9 g) in dry benzene (10 ml), and dry pyridine (3 ml). The soln was allowed to stand at 0° for 9 h poured into water and the mixture was made alkaline with ammonia. The ppt was filtered off, dried and crystallised from benzene-chloroform to obtain **7** (3.26 g, 90%), m.p. 141–142°; γ_{max} 1600, 1510 cm^{-1}; δ 1.0 (3H, s, $-CH_3$), 1.8–3.0 (3 × 2H, m, $-CH_2-$), 2.5 (3H, *s*, $ArCH_3$), 3.7 (3H, +2H, s, $-OCH_3$ + $-CH_2O_2S$) and 6.6–7.9 (7H, m, ArH). (Found: C, 76.53; H, 7.32. $C_{20}H_{24}O_3S$ requires: C, 76.89; H, 7.74%.)

Reduction of 6 - methoxy - 2 - methyl - 1,2,3,4 - tetrahydronaphthyl - 2 - carbinyl tosylate (**7**)

(a) *With lithium aluminium hydride.* To a slurry of LAH (0.26 g) in anhyd THF (20 ml) was added a soln of **7** (1.2 g) in dry THF (10 ml) and the resulting mixture was heated under reflux with stirring for 14 h. The cooled mixture was hydrolysed with water and the inorganic salt washed with 6N HCl. The layers were separated and the aqueous layer was extracted with ether (2 × 100 ml). The combined organic extracts were washed with 5% NaOHaq and then water. The organic layer was dried and evaporation of the solvent followed by short-path distillation afforded **6**.

(b) *With metal-ammonia reagent.* Onto a suspension of **7** (0.12 g) in dry ether (20 ml), ammonia (200 ml) was distilled. Li (0.12 g) was added in small pieces. The deep blue coloured complex was stirred for 30 min. Ammonium chloride was added to discharge the colour. Ammonia was completely evaporated and the residue was dissolved in water, extracted with ether

(2 × 100 ml) and dried. Evaporation of the solvent gave **6**.

2 - *Bromomethyl* - 6 - *methoxy* - 2 - *methyl* - 1,2,3,4 - *tetrahydronaphthalene* (**8**). A mixture of redistilled PBr_3 (4 g), dry benzene (50 ml) and dry pyridine (12 ml) was stirred for 15 min. The flask was cooled to −5° and a mixture of **6** (2 g) and dry pyridine (15 ml) was added slowly from the dropping funnel with stirring over a period of 10 min. The stirring was continued for 1 h longer and then the cooling bath was allowed to warm upto room temp. The mixture was left overnight, at room temp. The contents were poured into ice-cold water acidified with 6N HCl (20 ml) and extracted with ether (2 × 100 ml). Drying and evaporation of the solvent gave a crude material which was eluted with benzene:hexane (1:1) mixture over column silicagel to obtain **8** (2.4 g). γ_{max} 1600 and 1510 cm^{-1}; δ 1.1 (3H, s, $-CH_3$), 1.8–3.0 (3 × 2H, m, methylene), 3.4 (2H, s, $-CH_2Br$), 3.8 (3H, s, $-OCH_3$) and 6.6–7.1 (3H, m, ArH).

Reduction of the bromide (**8**). Li (0.14 g) was dropped into a mixture of **6** (1.4 g) and anhyd ammonia (*ca* 200 ml). The blue coloured soln was stirred for 45 min then ammonium chloride was added to discharge the blue colour. Ammonia was completely evaporated, the residue was dissolved in water. The aqueous layer was extracted with ether (2 × 100 ml) the combined solvent extract was washed thoroughly with water and dried. Evaporation of the solvent followed by elution with hexane over silicagel column gave **10**, (0.15 g, 15%). b.t. 115–120°/2 mm Hg: γ_{max} 1600 and 1500 cm^{-1}; δ 0.96 (6H, s, gem-dimethyl), 1.54 (2H, t, homobenzylic), 2.4 (2H, s, benzylic), 2.75 (2H, t, benzylic), 3.7 (3H, s, $-OCH_3$) and 6.4–6.8 (3H, m, ArH). (Found: C, 82.00; H, 9.80. $C_{13}H_{18}O$ requires: C, 82.06; H, 9.54%.)

2 - *Formyl* - 6 - *methoxy* - 2 - *methyl* - 1,2,3,4 - *tetrahydronaphthalene* (**9**). To a stirred suspension of pyridinium chlorochromate (5 g) in anhyd CH_2Cl_2 (30 ml) was added **4** (5.15 g) in one portion. After 2 h anhyd ether (100 ml) was added to the mixture and the supernatant liquid was decanted from the gum. The ether layer was washed with dil HCl, $NaHCO_3$aq, water and then dried. Upon removal of the solvent a dark liquid was obtained (5 g). Purification by column chromatography over silicagel (benzene:chloroform, 1:1) gave **9**, (4.28 g, 70%). γ_{max} 2850, 1710, 1600 and 1510 cm^{-1}; δ 1.1 (3H, s, $-CH_3$) 1.6–3.0 (3 × 2H, m, $-CH_2-$), 3.7 (3H, s, $-OCH_3$) 6.4–6.8 (3H, m, Ar–H) and 10.1 (1H, s, -CHO). (Found: C, 76.30; H, 7.90. $C_{13}H_{16}O_2$ requires: C, 76.44; H, 7.90%.)

2,2 - *Dimethyl* - 6 - *methoxy* - 1,2,3,4 - *tetrahydronaphthalene* (**10**) *from aldehyde* (**9**). A soln of **9** (4.10 g) in freshly distilled diethylene glycol (50 ml) and 85% hydrazine hydrate (15 ml) was heated at 120° for 3 h and then cooled to room temp. KOH (1 g) was added and the alkaline mixture was heated to 210° over 5 h, and then maintained at this temp for an additional 1 h. The cooled mixture was poured into water and extracted with ether (3 × 100 ml). The combined ethereal extract was washed and dried. Evaporation of solvent upon purification gave **10** (2.28 g, 60%).

2,2 - *Dimethyl* - 6 - *methoxytetral* - 1 - *one* (**11**). 6 - Methoxytetral - 1 - one (3.52 g) dissolved in dry benzene was added at 0° to anhyd t-BuOK prepared from K (1.76 g) and t-BuOH (20 ml). MeI (7 ml) was added dropwise during 30 min. After the addition was complete, the reaction was kept at ambient temp for 3 h. The contents were poured into water, extracted with benzene (3 × 100 ml). The combined organic extract was thoroughly washed with $Na_2S_2O_3$aq, water and then dried. Evaporation of the solvent followed by vacuum distillation afforded **11** (3.96 g, 91%). b.t. 165°/2 mm Hg; ν_{max} 1690, 1600 and 1510 cm^{-1}; δ 1.18 (6H, s, *gem* dimethyls), 1.84 (2H, t, homobenzylic), 2.86 (2H, t, benzylic), 3.80 (3H, s, $-OCH_3$), 6.5–6.8 (2H, m, ArH) and 7.92 (1H, d, ArH). (Found: C, 75.80; H, 7.70. $C_{13}H_{16}O_2$ requires: C, 76.44; H, 7.90%.)

2,2 - *Dimethyl* - 1 - *hydroxy* - 6 - *methoxy* - 1,2,3,4 - *tetrahydronaphthalene* (**12**). To a stirred soln of **11** (3.87 g) in dry benzene (50 ml), Vitride reagent (4.4 ml, 3.08 g) was added during 15 min under N_2. The stirring was continued for 2 h then the mixture was poured into 6N HCl (200 ml), extracted with benzene (2 × 50 ml), washed with water, brine and then dried. Evaporation of the solvent furnished the crude product (38 g) which on distillation gave **13** (3.32 g, 85%). b.t. 125–130°/2 mm Hg; ν_{max} 3400 and 1600 cm^{-1}; δ 0.93 (3H, s, $-CH_3$), 0.97 (3H, s, $-CH_3$), 1.42 (1H, s, -OH), 1.60–1.90 (2H, m, homobenzylic), 2.80 (2H, t, benzylic), 3.78 (3H, s, $-OCH_3$), 4.20 (1H, t, methine), 6.5–6.8 (2H, m, ArH) and 7.26 (1H, *d*, ArH). (Found: C, 75.31; H, 9.07. $C_{13}H_{18}O_2$ requires: C, 75.69; H, 8.80%.)

1 - *Acetoxy* - 2,2 - *dimethyl* - 6 - *methoxy* - 1,2,3,4 - *tetrahydronaphthalene* (**13**). The alcohol **12** (3.2 g) was acetylated with a mixture of Ac_2O (20 ml) and pyridine (5 ml) by heating it on water bath for 5 h. The contents were cooled to room temp and poured onto crushed ice and the solid was filtered off, washed with dil HCl and dried. Crystallisation from hexane-$CHCl_3$ gave **13** (3.6 g, 100%). m.p. 73°; ν_{max} 1720 and 1600 cm^{-1}; δ, 0.96 (3H, s, $-CH_3$), 1.06 (3H, s, $-CH_3$), 1.8 (2H, m, homobenzylic), 2.1 (3H, s, $-OCOCH_3$), 2.8 (2H, t, benzylic), 3.8 (3H, s, $-OCH_3$), 5.7 (1H, s, -CHOAc), 6.6–6.8 (2H, m, Ar–H) and 7.2 (1H, d, Ar–H). (Found: C, 71.97; H, 8.09. $C_{15}H_{20}O_3$ requires: C, 72.25; H, 8.12%.)

Reduction of the acetate (**13**). To anhyd ammonia (*ca* 300 ml), **14** (3.2 g) was added and stirred for 5 min. Li (0.35 g) was added in small peices during 10 min. The deep blue coloured soln was stirred for 30 min and quenched with ammonium chloride. Ammonia was evaporated and the usual work-up gave **10** (1.7 g, 70%).

2,2 - *Dimethyl* - 6 - *methoxy* - 1,2,3,4,5,8 - *hexahydronaphthalene* (**14**). A mixture of **10** (2.28 g) in dry THF (5 ml) and t-BuOH (5 ml) was added to anhydrous ammonia (*ca* 200 ml). Na (2.2 g) was added in small pieces till the deep blue colour persisted. The deep blue soln was stirred for 3 h then MeOH was added carefully to destroy excess metal. Ammonia was evaporated, the residue was dissolved in water, and extracted with hexane (2 × 100 ml). Combined solvent extract was washed and dried. Evaporation of the solvent afforded **14** which was used for further reaction without purification. ν_{max} 1680 and 1660 cm^{-1}.

6,6 - *Dimethyl* - $\Delta^{1,9}$ - *octalin* - 2 - *one* (**15**). The above **14** (2 g) in MeOH (50 ml) and 5% HClaq was refluxed for 20 min. Excess of the solvent was removed under diminished pressure, poured into water and extracted with ether (2 × 75 ml). The combined ethereal extract was washed with water, brine and dried. Removal of the solvent followed by crystallisation from hexane gave **10** (1.62 g, 90%). m.p. 76°; ν_{max} 1680 cm^{-1}; λ_{max} 242 nm (ϵ = 14,500); δ 1.03 (3H, s, $-CH_3$), 1.10 (3H, s, $-OCH_3$) and 5.8 (1H, s, olefinic). (Found: C, 80.41; H, 10.29. $C_{12}H_{18}O$ requires: C, 80.85; H, 16.18%.) (Semicarbasone, m.p. 218–220°.) (Found: C, 65.89; H, 9.486; N, 17.38. $C_{13}H_{21}N_3O$ requires: C, 66.35; H, 9.00; N, 17.86%.)

cis - 6,6,9 - *Trimethyl* - *decal* - 2 - *one* (**16**). To Mg (0.75 g) in dry ether (15 ml), MeI (2.4 ml) was added dropwise under N_2, with stirring. After 30 min abs THF was added slowly. The solvent was distilled off until the b.p. was 62° and the mixture was cooled to room temp. Anhyd cuprous chloride (200 mg) was added followed by **15** (1.4 g) in dry THF (20 ml). After 30 min the mixture was cooled to 8° and sat NH_4Claq was added. The mixture was diluted with ether and the aqueous soln was discharged. The organic phase was washed successively with aqueous $Na_2S_2O_3$aq, sat NH_4Claq, water, brine and then dried. Evaporation of the solvent accompanied by purification over column silicagel (hexane:$CHCl_3$, 1:1) gave the material (1 g) which was again purified by preparative TLC (hexane) to obtain **16** (0.87 g, 45%), m.p. 47–49°; ν_{max} 1700 cm^{-1}; δ 0.88 (3H, s, $-CH_3$); 0.892 (3H, s, $-CH_3$) and 0.912 (3H, s, $-CH_3$). (Found: C, 80.11; H, 11.19. $C_{13}H_{22}O$ requires: C, 80.35; H, 11.41%.) 2,4-DNP, m.p. 188.5°. (Found: C, 57.01; H, 6.66; N, 12.9. $C_{20}H_{26}N_4O_6$ requires: C, 57.40; H, 6.26; N, 13.39%.)

cis - 6,6,9 - *Trimethyl* - $\Delta^{3,4}$ - *octalin* - 2 - *one* (**1**). To **16** (0.38 g) in anhyd benzene (25 ml), DDQ (0.5 g) was added and refluxed for 36 h. The contents were cooled, the precipitated hydroquinone was filtered off, washed with small portions of benzene. The filtrate was washed with 2N NaOH and dried. Removal of the solvent gave the crude product which was passed through column silicagel (benzene:$CHCl_3$, 9:1) to give **1** (0.15 g, 40%). ν_{max} 1680 cm^{-1}; δ 0.89 (3H, s, α-CH_3), 0.91 (3H, s, β-CH_3) 0.94 (3H, s, $-CH_3$), 5.88 (1H, d, -olefinic) and 6.82 (1H, *dd*, -olefinic). (Found: c, 81.5; H, 10.8. $C_{13}H_{20}O$ requires: C, 81.2; H, 10.4%.)

6 - *Methoxy* - 2 - *methyl* - 1,2,3,4,5,8 - *hexahydro* - 2 - *naphthoic acid* (**17**). A soln containing **3** (4.4 g), dry THF (15 ml) and t-BuOH (15 ml) was added to distilled ammonia (*ca* 300 ml). Na (3.3 g) was added in small pieces and the deep blue coloured soln was stirred for 3 h. MeOH was added gently to decolourise the mixture. Ammonia was evaporated, the residue was dissolved in water and acidified with conc. HClaq. Extracted with ether (3 × 100 ml) and was dried. Evaporation of the solvent gave **17**. ν_{max} 1700, 1660 cm^{-1}.

6 - *Carbomethoxy* - 6 - *methyl* - $\Delta^{1,9}$ - *octalin* - 2 - *one* (**19**). The above crude **17** (3.5 g) in MeOH (100 ml) and 5% HCl (5 ml) was refluxed for 20 min. Excess MeOH was evaporated, poured into water and extracted with ether (2 × 100 ml). The usual work up gave the crude **18** which was esterified with methanolic H_2SO_4 to furnish **19** (3 g) on purification by column chromatography over silicagel ($CHCl_3$:benzene, 5:4), ν_{max} 1700 and 1680 cm^{-1}; δ 1.2 (3H, s, $-CH_3$), 3.8 (3H, *s*, $-COOCH_3$) and 5.8 (3H, s, olefinic). (Found: C, 69.94; H, 8.48. $C_{13}H_{18}O_3$ requires: C, 70.24; H, 8.16%.) 2,4-DNP, m.p. 181°. (Found: N, 13.6. $C_{19}H_{22}N_4O_6$ requires: N, 13.92%.)

cis - 6 - *Carbomethoxy* - 6,9 - *dimethyl decal* - 2 - *one* (**20**). To Mg (0.75 g) in dry ether (150 ml) MeI (2.4 ml) was added dropwise under N_2. After 30 min dry THF (45 ml) was added slowly. The solvent was distilled until the b.p. was 62°, the mixture was cooled to room temp and cuprous chloride (0.2 g) followed by **19** (1.4 g) in THF (20 ml) was added. After 30 min the mixture was cooled to 8° and sat NH_4Claq was added. The work-up followed by purification over column chromatography (benzene:$CHCl_3$, 1:1) gave **20** as gum. ν_{max} 1710 cm^{-1}; δ, 0.9 (3H, s, $-CH_3$), 1.2 (3H, s, $-CH_3$) and 3.7 (3H, s, $-COOCH_3$). (Found: C, 70.43; H, 9.23. $C_{14}H_{22}O_3$ requires: C, 70.55; H, 9.3. $C_{14}H_{22}O_3$ requires C, 70.55; H, 9.3%.) 2,4-DNP m.p. 188°. (Found: C, 57.01; H, 6.66; N, 12.9. $C_{20}H_{26}N_4O_6$ requires: C, 57.40; H, 6.26; N, 13.39%.)

cis - 6 - *Carbomethoxy* - 6,9 - *dimethyl* - $\Delta^{3,4}$ - *octalin* - 2 - *one* (**2**). To **20** (0.24 g) in anhyd benzene (25 ml), DDQ (0.5 g) was added, refluxed for 36 h. The contents were cooled, then the precipitated hydroquinone was filtered off, washed with small portions of benzene. The filtrate was washed with 2N NaOH and dried. Removal of solvent gave the crude product which was purified through column silicagel (benzene:$CHCl_3$, 7:3) to **1** (0.095 g). ν_{max} 1710 and 1680 cm^{-1}; δ 0.9 (3H, s, $-CH_3$), 1.2 (3H, s, $-CH_3$), 3.7 (3H, s, $-COOCH_3$), 5.98 (1H, d, α-olefinic) and 6.92 (1H, *dd*, β-olefinic). 2,4-DNP m.p. 180–182°. (Found: N, 13.29. $C_{20}H_{24}N_4O_6$ requires: N, 13.41%.)

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