Synthesis of 8- and 10-Methyl-substituted 8,9,10,11-Tetrahydro-7*H*-cycloocta[*de*]naphthalenes and Their 9-Oxo Derivatives

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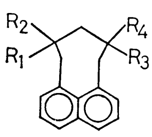
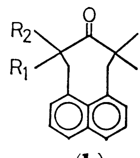
A novel and convenient method for the synthesis of the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene ring system is described. Reaction of diethyl acetonedicarboxylate and 1,8-bis(bromomethyl)naphthalene gave the eight-membered pericyclized compound, diethyl 9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,10-dicarboxylate, which was then converted, through several steps, into various kinds of 8- and 10-methyl-substituted 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes and their 9-oxo derivatives, as well as the unsubstituted compounds, 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene and 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one. The hydrocarbon, 8,8,10,10-tetramethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]-naphthalene was prepared from 8,8,10,10-tetrakis(tosyloxymethyl)-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene.

Despite considerable current interest in the chemistry of peri-substituted naphthalenes,1) few studies have been made on the eight-membered pericyclized naphthalene derivatives, 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes (**1**). The only compound of this ring system so far known is the unsubstituted hydrocarbon **1a**, which was synthesized by Nelsen and Gillespie in five steps from acenaphthylene.2) Recently, as a part of studies on the chemistry of pericyclic naphthalene derivatives, a report was given on the syntheses of some derivatives of **1a** starting from 1,8-naphthalenedicarboxylic anhydride.3) A novel and convenient method was worked out for the synthesis of the tetrahydrocycloocta[*de*]naphthalene ring **1**, which can be applied to the syntheses of various substituted compounds of this ring system besides **1a**. This paper deals with the syntheses of several 8- and 10-methyl-substituted 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes (**2a**—**7a**) as well as some 9-oxo derivatives (**1b**—**7b**) which do not seem to have been reported.

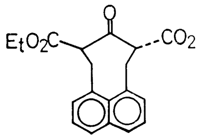


(**a**)



(**b**)

1; $R_1=R_2=R_3=R_4=H$
2; $R_1=CH_3$, $R_2=R_3=R_4=H$
3; $R_1=R_3=CH_3$, $R_2=R_4=H$
4; $R_1=R_4=CH_3$, $R_2=R_3=H$
5; $R_1=R_2=CH_3$, $R_3=R_4=H$
6; $R_1=R_2=R_3=CH_3$, $R_4=H$
7; $R_1=R_2=R_3=R_4=CH_3$



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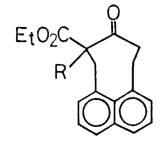

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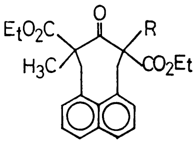

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a; R=H, **b**; $R=CH_3$

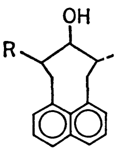
For the formation of the tetrahydrocycloocta[*de*]-naphthalene skeleton **1**, diethyl acetonedicarboxylate (**8**) was allowed to react with 1,8-bis(bromomethyl)-naphthalene (**9**) prepared from 1,8-naphthalenedicarboxylic anhydride.3) By the reaction between equimolar amounts of **8** and **9** in refluxing ethanol, using sodium ethoxide as a condensing agent, diethyl 9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,10-dicarboxylate (**10**) with the desired peri-eight-membered ring was obtained. Compound **10**, when treated with sodium ethoxide in ethanol, underwent deethoxycarbonylation to yield ethyl 9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8-carboxylate (**11a**). Alkaline hydrolysis of the *β*-keto esters **10** and **11a** was accompanied by decarboxylation to afford 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one (**1b**). The Clemmensen reduction of ketone **1b** gave the parent hydrocarbon **1a** identical with that previously reported.2)

Methylation of the *β*-keto ester **10** gave a mixture from which diethyl 8-methyl-9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,10-dicarboxylate (**12a**) and diethyl 8,10-dimethyl-9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,10-dicarboxylate (**12b**) were isolated by fractional crystallization in 60 and 22% yields, respectively. Repeated methylation of **10** with excess of the reagents afforded only **12b**. By alkaline hydrolysis and concurrent decarboxylation the monomethyl keto diester **12a** was converted almost in a quantitative yield into 8-methyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one (**2b**), which afforded the corresponding hydrocarbon **2a** on Clemmensen reduction.

On the other hand, alkaline treatment of dimethyl keto diester **12b** in boiling dioxane yielded a mixture of geometrical isomers, which was separated by recrystallization to give *cis*-8,10-dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one (**3b**) and its *trans* isomer **4b** in 64 and 23% yields, respectively. **4b** was also prepared more efficiently from keto diester **10** having a *trans* structure by the following reaction. **10** was reduced by lithium aluminum hydride to give triol **13a**, which was converted by treatment with methanesulfonyl chloride in pyridine into dimesylate **13b**. Treatment of **13b** with excess lithium aluminum hydride in boiling ether afforded *c*-8,*t*-10-dimethyl-

8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-*r*-9-ol (**13c**), which, on Jones oxidation, gave the desired *trans*-8,10-dimethyl ketone **4b** in a 40% overall yield from **10**.

Monomethyl keto diester **12a** was then converted into 8,8,10-trimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta-[*de*]naphthalen-9-ol (**14c**) through the same steps as in the preparation of **13c** from the keto diester **10**. Reduction of **12a** with lithium aluminum hydride gave a triol **14a**, which, on treatment with 2 mol of methanesulfonyl chloride in pyridine, was converted into **14b**. Subsequent hydrogenolysis of **14b** with lithium aluminum hydride afforded a 59% overall yield of the trimethyl alcohol **14c**. Similarly, 8,8,-10,10-tetramethyl-8,9,10,11-tetrahydro-7*H*-cycloocta-[*de*]naphthalen-9-ol (**15c**) was derived from the dimethyl keto diester **12b** in a 78% yield by the successive reduction, mesylation and hydrogenolysis (**12b**→**15a**→**15b**→**15c**). On the other hand, methylation of the keto monoester **11a** gave ethyl 8-methyl-9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8-carboxylate (**11b**), which was then converted, on reactions similar to the above through a diol **16a** and a monomesylate **16b**, into 8,8-dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-ol (**16c**) in only 12% overall yield from **11a**. Each of the methyl alcohols **14c**, **15c**, and **16c** was oxidized by Jones reagent to give the corresponding α-methyl ketones, **6b**, **7b**, and **5b**, respectively.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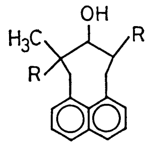
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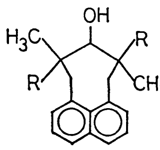
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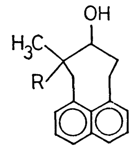
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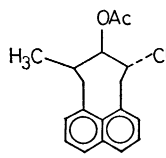
a; R = CH_2OH, **b**; R = CH_2OMs, **c**; R = CH_3

cis-8,10-Dimethyl ketone **3b** underwent Clemmensen reduction to give only the corresponding hydrocarbon **3a**, while the *trans*-dimethyl ketone **4b** gave, on Clemmensen reduction, a mixture of three compounds, which was isolated by chromatography on alumina to yield the desired *trans*-8,10-dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**4a**) (48% yield) along with the *trans*-dimethyl alcohol **13c** (8%) and its acetate **17** (26%), the acetoxyl group being derived from the solvent (acetic acid). The carbonyl groups of the *gem*-dimethyl ketone **5b** and the trimethyl ketone **6b** were smoothly reduced by Wolff-Kishner reactions to afford the corresponding hydrocarbons, 8,8-dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**5a**) and 8,8,10-trimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**6a**), respectively.

An attempt to transform **6b** into **6a** by Clemmensen reduction resulted in the formation only of intractable substances with a small amount of **6b**. On the other hand, Clemmensen reduction of the tetramethyl ketone **7b** produced only the tetramethyl alcohol **15c** instead of the hydrocarbon **7a**, while by the Wolff-Kishner procedure **7b** was recovered unchanged with a small amount of alcohol **15c**. Hydrogenolysis of the mesylate ester of the tetramethyl alcohol **15c** (**18**) using the same conditions as in the transformation of **13b** into **13c** caused only *O*-mesyl bond cleavage to regenerate **15c**. The great difficulty in effecting these reactions might be caused by steric hindrances,[4,5] expected to greatly increase in highly methylated compounds such as **6** and **7**, as compared to those in the lower homologs (**1**—**5**).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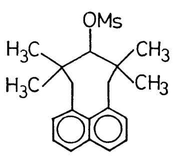
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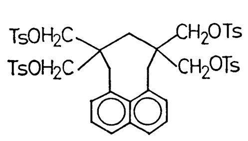
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8,8,10,10-Tetrakis(tosyloxymethyl)-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**19**), which is expected as another precursor of compound **7a**, was prepared according to the method previously reported.[3] Treatment of the tosylate **19** with lithium aluminum hydride in ether led to hydrogenolysis of the tosyloxy groups to yield, with an unidentified compound, the desired hydrocarbon, 8,8,10,10-tetramethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**7a**).

Experimental

All the melting points were uncorrected. The IR spectra were determined on a JASCO IR-G spectrometer calibrated with polystyrene. The proton NMR spectra were determined on a Varian HA-100D spectrometer (at 100 MHz) using chloroform-*d*, acetone-d_6 and pyridine-d_5 as solvents, and tetramethylsilane as an internal standard; the spectra of compounds **4a**, **4b**, and **10**, which changed markedly around or below room temperature, were measured under cooling, while other samples were measured at room temperature. Mass spectra were determined on a CEC 21-110B instrument.

*Diethyl 9-Oxo-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalene-8,10-dicarboxylate (**10**).* 1,8-Bis(bromomethyl)naphthalene (**9**) was prepared from 1,8-naphthalenedicarboxylic anhydride.[3]

To a stirred and cooled (at 0 °C) solution of sodium ethoxide in ethanol (prepared from 11.6 g of sodium and 1.14 l of absolute ethanol) was added quickly a solution of diethyl acetonedicarboxylate (**8**) (52 g) in dry dimethyl sulfoxide (0.14 l, distilled on calcium hydride) and absolute ethanol (0.14 l). After 8 min stirring a solution of the dibromide **9** (80 g) in dry dimethyl sulfoxide (0.86 l) was added over a period of 3 min and the mixture was stirred under reflux for 30 min. The reaction mixture was then poured into cracked ice and water (*ca.* 5 l) and the resulting cloudy solution was left at room temperature for 3 days. The precipitated solid was collected and crystallized from ethanol, giving the desired peri-eight-membered ring compound **10** as colorless fine needles (28 g, 31%); mp 146—147 °C; MS : *m/e* 354.146 (M^+ ($^{12}C_{21}{}^{1}H_{22}{}^{16}O_5$) = 354.147); IR (Nujol): ν_{max} 1707 (ketone C=O), 1742 cm^{-1} (ester C=O); NMR ($CDCl_3$): δ 1.26 and 1.33 (each 3H, t, J = 7.1 Hz, CH_3).

Found: C, 70.83; H, 6.15%. Calcd for $C_{21}H_{22}O_5$: C, 71.17 : H, 6.26%.

The crude keto diester **10** (20 g) was refluxed with a solution of sodium hydroxide (12 g) in ethanol (400 ml) and water (600 ml) for 30 h. After treatment with hydrochloric acid, the precipitated solid was collected and recrystallized from methanol to give *8,9,10,11-tetrahydro-7*H*-cycolocta*[de]*naph-*

*thalen-9-one (**1b**)* (10.8 g, 92%) as colorless needles; mp 195—196 °C; MS : *m/e* 210.103 (M$^+$ ($^{12}\mathrm{C}_{15}{}^{1}\mathrm{H}_{14}{}^{16}\mathrm{O}_{1}$)=210.103); IR (Nujol): $\nu_{\max}$ 1695 cm^{-1} (C=O); NMR (CDCl$_3$): δ 2.80 (4H, t, J=7.1 Hz, 8,10-H), 3.77 (4H, t, J=7.1 Hz, 7,11-H).
Found: C, 85.80; H, 6.56% Calcd for $\mathrm{C_{15}H_{14}O}$: C, 85.86; H, 6.71%.

*Ethyl 9-Oxo-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalene-8-carboxylate (**11a**).* 2.5 g of the keto diester **10** was treated with a solution of sodium ethoxide in ethanol (prepared by dissolving 7.0 g of sodium in 500 ml of absolute ethanol) and the mixture was stirred vigorously for 3 days. The reaction mixture was then acidified, diluted with water (*ca.* 2 l) and left at room temperature for 16 days. The crystals formed were removed by filtration and recrystallized from ethaonl to give the keto monoester **11a** (1.48 g, 75%) as colorless needles; mp 128—129 °C; MS : *m/e* 282.126 (M$^+$ ($^{12}\mathrm{C}_{18}{}^{1}\mathrm{H}_{18}{}^{16}\mathrm{O}_{3}$)=282.126); IR (Nujol): $\nu_{\max}$ 1705 (ketone C=O), 1744 cm^{-1} (ester C=O); NMR (CDCl$_3$): δ 1.32 (3H, t, J=7.0 Hz, CH$_3$), 4.28 (2H, q, J=7.0 Hz, $\mathrm{C\underline{H}_2CH_3}$).
Found: C, 76.27; H, 6.33%. Calcd for $\mathrm{C_{18}H_{18}O_3}$: C, 76.57; H, 6.43%.

*Diethyl 8-Methyl-9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*-naphthalene-8,10-dicarboxylate (**12a**).* A solution of the crude keto diester **10** (18.5 g) in dry dimethyl sulfoxide (50 ml) was added to a solution of sodium ethoxide prepared by dissolving 1.44 g of sodium in 300 ml of absolute ethanol. To this mixture was added a solution of methyl iodide (6 ml) in absolute ethanol (40 ml) over a period of 5 min and the mixture was stirred overnight at room temperature. The reaction mixture was poured into water and the resulting solid was collected. Recrystallization of this solid from ethanol (500 ml) gave 11.2 g (60%) of the monomethyl compound **12a** as colorless needles; mp 129—130 °C; IR (Nujol): $\nu_{\max}$ 1715 (ketone C=O), 1733, and 1738 cm^{-1} (ester C=O); NMR (CDCl$_3$): δ 1.01 (3H, s, CH$_3$), 1.20 and 1.28 (each 3H, t, J=6.7 and 7.1 Hz, respectively, CH$_3$).
Found: C, 71.80; H, 6.36%. Calcd for $\mathrm{C_{22}H_{24}O_5}$: C, 71.72; H, 6.57%.

The mother liquor from the above was concentrated to yield 4.4 g (22%) of *diethyl 8,10-dimethyl-9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalene-8,10-dicaroboxylate (**12b**).* The compound was prepared more efficiently (80%) by repeating the methylation procedure described above and obtained as colorless prisms by recrystallization from ethanol; mp 162—163.5 °C; IR (Nujol): $\nu_{\max}$ 1709 (ketone C=O), 1734 cm^{-1} (ester C=O); NMR (CDCl$_3$): δ 0.95 and 1.76 (each 3H, s, CH$_3$), 1.22 and 1.31 (each 3H, t, J=6.8 and 7.1 Hz, respectively, CH$_3$).
Found: C, 72.50; H, 6.80%. Calcd for $\mathrm{C_{23}H_{26}O_5}$: C, 72.23; H, 6.85%.

*Ethyl 8-Methyl-9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*-naphthalene-8-carboxylate (**11b**).* To a stirred solution of sodium ethoxide in ethanol (prepared by dissolving 0.18 g of sodium into 25 ml of absolute ethanol) was added a solution of the keto monoester **11a** (0.26 g) in dry dimethyl sulfoxide (10 ml) and the mixture was stirred for 2 h at room temperature. A solution of methyl iodide (2 ml) in absolute ethanol (10 ml) was then added and the mixture was stirred for 20 h at room temperature. The reaction mixture was concentrated, mixed with saturated salt solution and extracted with ethyl acetate. The extracts were washed with saturated salt solution and dried over sodium sulfate, the solvnet then being evaporated. The residue was chromatographed on alumina with hexane as eluant to give the monomethyl keto ester **11b** (0.26 g, 94%). This was recrystallized from ethanol for analysis (needles); mp 106—106.5 °C: IR (Nujol): $\nu_{\max}$ 1705 (ketone C=O), 1728 and 1721 cm^{-1} (ester C=O); NMR (CDCl$_3$): δ 1.26 (3H, s, CH$_3$), 1.30 (3H, t, J=7.0 Hz, CH$_3$), 4.28 (2H, q, J=7.0 Hz, $\mathrm{OC\underline{H}_2CH_3}$).
Found: C, 76.87; H, 6.50%. Calcd for $\mathrm{C_{18}H_{18}O_3}$: C, 76.57; H, 8.43%.

*8-Methyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-one (**2b**).* Methyl keto diester **12a** (1.53 g) was refluxed with a solution of potassium carbonate (1.5 g) in dioxane (35 ml) and water (25 ml) for 3 days. The reaction mixture was treated with hydrochloric acid and the precipitated solid was collected. The solid was recrystallized from ethanol to give 0.93 g (99%) of the monomethyl ketone **2b** as colorless needles; mp 158—159 °C; IR (Nujol): $\nu_{\max}$ 1694 cm^{-1} (C=O); NMR (CDCl$_3$): δ 1.20 (3H, d, J=6.8 Hz, CH$_3$).
Found: C, 85.79; H, 7.23%. Calcd for $\mathrm{C_{16}H_{16}O}$: C, 85.68; H, 7.19%.

cis-*8,10-Dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-one (**3b**).* Dimethyl keto diester **12b** (9.83 g) was refluxed with a solution of sodium hydroxide (6 g) in dioxane (0.5 l) and water (0.5 l) for 3 days. After treatment with hydrochloric acid the precipitated solid was collected and recrystallized from ethanol, giving 4.0 g (64%) of the *cis*-dimethyl ketone **3b** as colorless needles; mp 230—231 °C; IR (Nujol): $\nu_{\max}$ 1694 cm^{-1} (C=O); NMR (CDCl$_3$): δ 0.97 (6H, d, J=6.8 Hz, CH$_3$).
Found: C, 85.70; H, 7.91%. Calcd for $\mathrm{C_{17}H_{18}O}$: C, 85.67; H, 7.61%. On concentration of the above mother liquor, 1.43 g (23%) of the *trans* isomer **4b** was obtained. The compound was prepared more efficiently from the keto diester **10** as follows.

trans-*8,10-Dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-one (**4b**).* Keto diester **10** (11 g) was stirred under reflux with lithium aluminum hydride (6 g) in dry ether (0.5 l) and dry benzene (0.1 l) for 12 days. The reaction mixture was treated with hydrochloric acid and the precipitated solid was collected and dried *in vacuo* to give 6.32 g (75%) of *8,10-bis(hydroxymethyl)-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**13a**)*; mp 165—166 °C; IR (Nujol): $\nu_{\max}$ 3250 and 3420 (sh) cm^{-1} (OH); NMR (pyridine-d_5): δ 5.82 and 6.20 (br, OH).

To a stirred solution of triol **13a** (2.6 g) in pyridine (15 ml) was added dropwise a solution of methanesulfonyl chloride (1.5 ml) in pyridine (6 ml) over a period of 1 min. The mixture was stirred for 40 h at room temperature. The reaction mixture was then poured into ice water and the resulting solid was collected. Recrystallization of this solid from ethanol yielded 2.75 g (68%) of c-*8*,t-*10-bis(mesyloxymethyl)-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen*-r-*9-ol (**13b**)* as a colorless microcrystalline solid; mp 167.5—169 °C; IR (Nujol): $\nu_{\max}$ 3540 (OH), 1171 and 1350 cm^{-1} (mesyl ester); NMR (pyridine-d_5–CDCl$_3$ (2 : 1)): δ 6.14 (br, OH), 3.02 and 3.14 (each 3H, s, mesyl group).

To a stirred and boiled suspension of lithium aluminum hydride (*ca.* 6 g) in dry ether (0.3 l) was added a solution of the dimesylate **13b** (6.5 g) in dry benzene (0.1 l) over a period of 5 min. The mixture, after further addition of dry ether (0.1 l), was stirred under reflux for 14 days. The reaction mixture was then poured into ice-hydrochloric acid (*ca.* 4 l) and the mixture was allowed to stand at room temperature for 30 days. The precipitated solid was collected and chromatographed on alumina with benzene as eluant, yielding 2.65 g (73%) of c-*8*,t-*10-dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen*-r-*9-ol (**13c**).* The compound was further pruified by recrystallization from benzene-petroleum ether; mp 135—135.5 °C; IR (Nujol): $\nu_{\max}$ 3440 and 3570 cm^{-1} (OH); NMR (CDCl$_3$) : δ 0.85 (3H, d, J=7.0 Hz, CH$_3$), 1.18 (3H, d, J=6.9 Hz, CH$_3$)

and 1.26 (s, OH).
Found: C, 84.80; H, 8.50%. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39%.

To a stirred and cooled (at 0 °C) solution of the dimethyl alcohol **13c** (0.747 g) in acetone (75 ml) was added dropwise the Jones reagent (prepared from 13.4 g of chromic anhydride in 25 ml of water and 12 ml of concentrated sulfuric acid) over a period of 5 min. The resulting mixture was stirred at 0 °C for 30 min. After addition of 2-propanol, the insoluble substance was removed by filtration and washed with acetone. The filtrate and washings were combined, concentrated, mixed with water and left to stand overnight. The solid precipitated was collected and chromatographed on alumina (deactivated on exposure to air) with benzene as eluant to give the *trans*-dimethyl ketone **4b** (0.59 g, 80%).

Ketone **4b** was recrystallized from aqueous ethanol to give colorless needles; mp 126—127 °C; IR (Nujol) : ν_{max} 1692 cm^{-1} (C=O); NMR ($CDCl_3$) : δ 0.94 and 1.45 (each 3H, d, J=6.5 Hz, CH_3).
Found: C, 85.60; H, 7.71%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

Using the same sequence of reactions as in the preparation of **4b** from **10**, compounds **6b**, **7b**, and **5b** were prepared from the corresponding keto esters **12a**, **12b**, and **11b**, through the steps, (**12a**→**14a**→**14b**→**14c**→**6b**), (**12b**→**15a**→**15b**→**15c**→**7b**), and (**11b**→**16a**→**16b**→**16c**→**5b**), respectively.

*8-Methyl-8,10-bis(hydroxymethyl)-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**14a**)* (Yield, 87%); mp 168—169 °C; IR (Nujol): ν_{max} 3220 and 1030 cm^{-1} (OH); NMR (pyridine-d_5): δ 1.58 (s, CH_3), 5.6 (br, OH). *8-Methyl-8,10-bis(mesyloxymethyl)-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**14b**)* (Yield, 71%); mp 103—104 °C; IR (Nujol): ν_{max} 3560 (OH), 1344 and 1175 cm^{-1} (mesyl ester); NMR ($CDCl_3$): δ 1.22 and 1.21 (each s, CH_3), 2.77, 3.02, 2.98 and 3.06 (each s, mesyl group), the complex methyl signals indicate that **14b** is a mixture of isomers. *8,8,10-Trimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**14c**)* (Yield, 95%); mp 114.5—116 °C; IR (Nujol): ν_{max} 3335 cm^{-1} (OH); NMR ($CDCl_3$): δ 0.75, 1.05, 1.18, 1.21, and 1.27 (each s, CH_3), the unexpectedly complicated methyl proton signals of **14c** suggest that **14c** is a mixture of isomers; Found: C, 85.20; H, 8.69%. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72%. *8,8,10-Trimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-one (**6b**)* (Yield, 85%); colorless needles (from benzene–petroleum ether); mp 124.5—125 °C; IR (Nujol): ν_{max} 1696 cm^{-1} (C=O); NMR ($CDCl_3$): δ 0.99 (3H, d, J=6.8 Hz, CH_3), 0.92 and 1.43 (each 3H, s, CH_3). Found: C, 85.89; H, 8.09%. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99%.

*8,10-Dimethyl-8,10-bis(hydroxymethyl)-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**15a**)* (Yield, 93%); mp 171—172 °C; IR (Nujol): ν_{max} 3275 and 1030 cm^{-1} (OH); NMR (pyridine-d_5): δ 1.42 and 1.72 (each 3H, s, CH_3), 5.78 (br, OH). *8,10-Dimethyl-8,10-bis(mesyloxymethyl)-*8,9,10,11*-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**15b**)* (Yield, 92%); mp 155—156 °C; IR (Nujol): ν_{max} 3570 (OH), 1376 and 1174 cm^{-1} (mesyl ester); NMR (acetone-d_6): δ 1.12 and 1.34 (each s, CH_3), 3.01 and 3.15 (each s, mesyl group) and 4.08 (br, OH). *8,8,10,10-Tetramethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**15c**)* (Yield, 90%); mp 177—178 °C; IR (Nujol): ν_{max} 3460 and 3600 cm^{-1} (OH); NMR ($CDCl_3$): δ 0.90 and 1.21 (each 6H, s, CH_3) and 1.41 (s, OH); Found: C, 85.30; H, 9.23%. Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.01%. *8,8,10,10-Tetramethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-one (**7b**)* (Yield, 82%); colorless needles (from benzene–petroleum ether); mp 133—133.5 °C; IR (Nujol): ν_{max} 1683 cm^{-1}(C=O); NMR ($CDCl_3$): δ 0.92 and 1.48 (each 6H, s, CH_3); Found: C, 85.86; H, 8.27%. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33%.

*8-Methyl-8-hydroxymethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**16a**)* (Yield, 60%); mp 138—139 °C; IR (Nujol): ν_{max} 3330 cm^{-1}(OH); NMR ($CDCl_3$–pyridine-d_5 (2:1)): δ 1.34 (s, CH_3), 5.20 and 5.74 (each br, OH). Treatment of **16a** with 1 mol of methanesulfonyl chloride in pyridine under the same conditions as in the preparation of **13b** from **13a** afforded *8-methyl-8-mesyloxymethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**16b**)*; IR (neat): ν_{max} 3530 (OH), 1340 and 1170 cm^{-1} (mesyl ester). *8,8-Dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-ol (**16c**)* (Yield, *ca.* 20% from **16a**); mp 114.5—115.5 °C; IR (Nujol): ν_{max} 3300 cm^{-1}(OH); NMR ($CDCl_3$): δ 0.92 and 1.09 (each 3H, s, CH_3), 1.24 (s, OH); Found: C, 84.70; H, 8.45%. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39%. *8,8-Dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalen-9-one (**5b**)* (Yield, 66%); mp 110—111 °C; IR (Nujol): ν_{max} 1695 cm^{-1} (C=O); NMR ($CDCl_3$): δ 0.93 and 1.42 (each 3H, s, CH_3); Found: C, 85.78; H, 7.80%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

*8,9,10,11-Tetrahydro-7*H*-cycloocta*[de]*naphthalene (**1a**), 8-Methyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalene (**2a**),* cis-*8,10-Dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalene (**3a**) and* trans-*8,10-Dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalene (**4a**).* The compounds were prepared by Clemmensen reductions of the corresponding 9-ketones, **1b**, **2b**, **3b**, and **4b**, respectively, by the following procedure.

The ketone (1.0 g) in benzene (30 ml) was stirred under reflux for 30 h with amalgamated zinc (34 g), concentrated hydrochloric acid (100 ml) and acetic acid (150 ml). The mixture was cooled and extracted with ether repeatedly. The ether extracts were worked up as usual to leave a brown oil, which was purified by chromatography on alumina with hexane as eluant. The products were obtained as colorless needles by recrystallization from aqueous alcohol.

Compound **1a** (Yield, 92%); mp 57.5—58 °C (lit, mp 55—56 °C[2]); MS: *m/e* 196.126 ($M^+(^{12}C_{15}{}^1H_{16})$=196.125) (Found: C, 91.71; H, 8.26%); the compound showed spectral features similar to those reported by Nelsen and Gillespie.[2]

Compound **2a** (Yield, 74%); mp 40—41 °C; NMR ($CDCl_3$): δ 1.02 (CH_3); Found: C, 91.50; H, 8.60%. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63%.

Compound **3a** (Yield, 63%); mp 116—117 °C; NMR ($CDCl_3$): δ 0.84 (6H, d, J=6.8 Hz, CH_3); Found: C, 90.80; H, 8.90%. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99%.

Compound **4a** (Yield, 48%); mp 65—66 °C; NMR ($CDCl_3$): δ 0.80 (3H, d, J=6.7 Hz, CH_3) and 1.22 (3H, d, J=7.0 Hz, CH_3); Found: C, 91.30; H, 9.03%. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99%. After **4a** had been obtained, further elution with benzene afforded the acetate ester of the *trans*-dimethyl alcohol **13c** (**17**) (Yield, 26%); mp 141.5—142 °C, whose IR spectrum (Nujol) showed absorptions at 1734 and 1241 cm^{-1} characteristic of the acetate ester group, and whose NMR spectrum [($CDCl_3$): δ 0.77 and 1.18 (each 3H, d, J=7.0 Hz, CH_3) and 1.85 (3H, s, acetyl CH_3)] was in line with the structure. Further elution with ethyl acetate gave the *trans*-dimethyl alcohol **13c** (Yield, 8%), whose melting point and spectral data were identical with those of the authentic sample prepared from **13b**.

*8,8-Dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalene (**5a**).* *gem*-Dimethyl ketone **5b** (0.22 g), potassium hydroxide (0.4 g), hydrazine hydrate (0.5 ml) and diethylene glycol (7 ml) were combined and refluxed at 130—140 °C for 1.5 h. The condenser was then removed and the reddish solution heated until the temperature reached 200 °C. After 15 h reflux at this temperature, the cooled reaction mixture was diluted with water, acidified and extracted with ethyl acetate. The organic extracts were washed with saturated brine solution, dried over sodium sulfate and finally concentrated to give a light brown solid. Chromatography on alumina using hexane as eluant yielded 0.18 g (86%) of the 8,8-dimethyltetrahydrocycloocta[*de*]naphthalene **5a**; mp 69—70 °C; NMR ($CDCl_3$): δ 0.80 and 1.16 (each 3H, s, CH_3). Found: C, 91.25; H, 8.80%. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99%.

*8,8,10-Trimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalene (**6a**).* Trimethyl ketone **6b** (0.3 g) was subjected to Wolff-Kishner reduction using the same procedure as in the preparation of **5a**. The crude product was chromatographed on alumina with hexane as an eluant to give 0.2 g (70%) of the hydrocarbon **6a**; mp 89—90 °C; NMR ($CDCl_3$): δ 0.80 (3H, d, J=6.8 Hz, CH_3), 0.81 and 1.16 (each 3H, s, CH_3). Found: C, 90.56; H, 9.46%. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30%.

*8,8,10,10-Tetramethyl-8,9,10,11-tetrahydro-7*H*-cycloocta*[de]*naphthalene (**7a**).* 8,8,10,10-Tetrakis(tosyloxymethyl)-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**19**) was prepared from tetraethyl 1,1,3,3-propanetetracarboxylate and 1,8-bis(bromomethyl)naphthalene (**9**).[3]

To a stirred and boiled slurry of excess lithium aluminum hydride in dry ether (0.3 l) was added a solution of the tosylate **19** (2.0 g) in dry ether (0.1 l) over a period of 5 min. The mixture, after further addition of dry ether (0.1 l), was stirred under reflux for 3 days and cooled. The reaction mixture was poured onto ice-hydrochloric acid and the mixture was extracted with ether. The ethereal extracts were combined, washed with saturated brine solution and dried over sodium sulfate. After removal of the solvent the residue was taken up in a small amount of hexane–benzene and chromatographed on alumina. Elution with hexane gave 0.24 g (44%) of the desired tetramethyltetrahydrocycloocta[*de*]naphthalene **7a**. Further elution with benzene yielded an unidentified compound (0.14 g), which, after recrystallization from hexane, melted at 160—161 °C. Hydrocarbon **7a** was recrystallized from aqueous ethanol to give colorless needles; mp 112—113 °C; NMR ($CDCl_3$): δ 0.74 and 1.29 (each 6H, s, CH_3). Found: C, 90.68; H, 9.34%. Calcd for $C_{19}H_{24}$: C, 90.41; H, 9.59%.

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