pressure of 2.85 mm under a 10-cm Vigreux column, and the volatile product collected at dry ice–acetone bath temperature. The resulting volatile product consisted of 1.300 g of a colorless liquid which contained a suspended white solid. Crystallization of the crude product from ether afforded 0.116 g (15%)of acetamide as white needles, mp 81.5–82.5°. The filtrate was concentrated and the residual colorless oil subjected to short-path distillation (2.75 mm and 65° bath) to give 0.467 g (25%) of oxazoline **4b** as a colorless liquid.

Oxazoline **4b**, obtained from a large-scale preparative experiment, bp 52.0–56.0° (1.75–2.10 mm) [lit.[13] 75.5–76.5° (13 mm)], was homogeneous by gas chromatography on a 6 ft × 0.094 in. column packed with 8% Carbowax 1540 on 60–80 mesh calcined diatomite support. It was further characterized by conversion to its picrate, mp 165–169°.

Anal. Calcd for $C_{14}H_{16}N_4O_8$: C, 45.66; H, 4.38; N, 15.21. Found: C, 45.36; H, 4.18; N, 14.98.

The crude volatile product from a comparable experiment was found to contain 60% of cyclohexene (**2b**) by quantitative gas chromatography on a 15 ft × 0.25 in. column packed with 10% silicone (Fluro) QF-1 on 60–80 Chromosorb using *n*-octane as an internal standard.

Reaction of *trans*-*N*-Acetyl-2-aminocyclohexylmercuric Chloride (3b) with Potassium *tert*-Butoxide. A mixture of 5.001 g (13.3 mmol) of *trans*-*N*-acetyl-2-aminocyclohexylmercuric chloride (**3b**) and 1.490 g (13.3 mmol) of potassium *tert*-butoxide in 15 ml of diglyme (distilled from CaH_2) was heated at relfux in a nitrogen atmosphere for 3.5 hr. After cooling, the resulting brown solution was found to contain less than a 1% yield of *cis*-2-methyl-4,5-tetramethylene-2-oxazoline (**4b**) by quantitative gas chromatography on a 6 ft × 0.094 in. column packed with 8% Carbowax 1540 on 60–80, acid washed, silane treated, calcined diatomite support using 0.437 g of *o*-xylene as an internal standard.

Reaction of *trans*-*N*-Acetyl-2-aminocyclohexylmercuric Chloride (3b) with Sodium Carbonate. A mixture of 2.500 g (6.64 mmol) of *trans*-*N*-acetyl-2-aminocyclohexylmercuric chloride (**3b**) and 0.800 g (7.55 mmol) of anhydrous sodium carbonate in 50 ml of benzene was heated with shaking in a high-pressure steel reaction vessel at 250° for 2 hr. After cooling, the mixture was filtered and the filtrate concentrated to yield 0.213 g of dark brown oil. The infrared spectrum of this material indicated that little or no 2-oxazoline **4b** was present.

Registry No.—**2a**, 142-29-0; **2b**, 110-83-8; **2c**, 628-92-2; **3a**, 56943-31-8; **3b**, 31718-62-4; **3c**, 56943-32-9; **3d**, 19907-98-3; **4a**, 56943-33-0; **4b**, 23236-44-4; **4b** picrate, 56943-34-1; **4c**, 56943-35-2; **5a**, 14850-23-8; **5b**, 111-66-0; **6a**, 56943-36-3; **6b**, 56943-37-4; **7a**, 56943-38-5; **7b**, 56994-88-8; mercuric nitrate, 10045-94-0; NaCl, 7647-14-5; potassium *tert*-butoxide, 865-47-4; sodium carbonate, 497-19-8.

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Ring Expansion Reaction of 1,2-Dihydroquinolines to 1-Benzazepines

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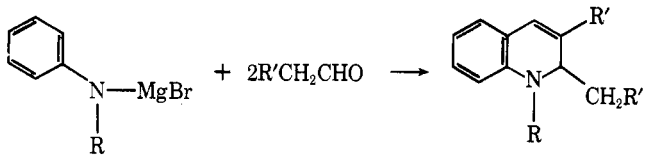
When 1-methyl-2,3-dialkyl-1,2-dihydroquinolines (**1a–c**) were treated with ethyl azidoformate, 1-methyl-2-ethoxycarbonylimino-3,4-dialkyl-2,3-dihydro-1*H*-1-benzazepines (**2a–c**) were produced in 30–80% yields. These benzazepines (**2a–c**) were obtained in 91–99% yields under a similar reaction condition from 1-methyl-2-alkylidene-3-alkyl-1,2-dihydroquinolines (**16a–c**) prepared from the corresponding 1,2,3-trialkylquinolinium chlorides (**18a–c**).

Attempts to expand smaller rings into a heterocyclic ring of 1-benzazepines have been achieved by many investigators; e.g., by the reaction of indoles with dimethyl acetylenedicarboxylate[1] or ethyl cyanoacetate,[2] by the Beckman[3] or Schmidt[4] rearrangement of tetralones, and by the treatment of 1,2-dihydroquinoline with dibromocarbene followed by the treatment of 1,2-dihydroquinoline with dibromocarbene followed by dehydrobromination.[5] The utility of azides in the azepine formation is well known.[6] This paper describes a new ring expansion reaction by ethyl azidoformate from 1-methyl-2,3-dialkyl-1,2-dihydroquinolines (**1**) to 1-methyl-2-ethoxycarbonylimino-3,4-dialkyl-2,3-dihydro-1*H*-1-benzazepines (**2**) via 1-methyl-2-alkylidene-3-alkyl-1,2-dihydroquinolines (**16**).

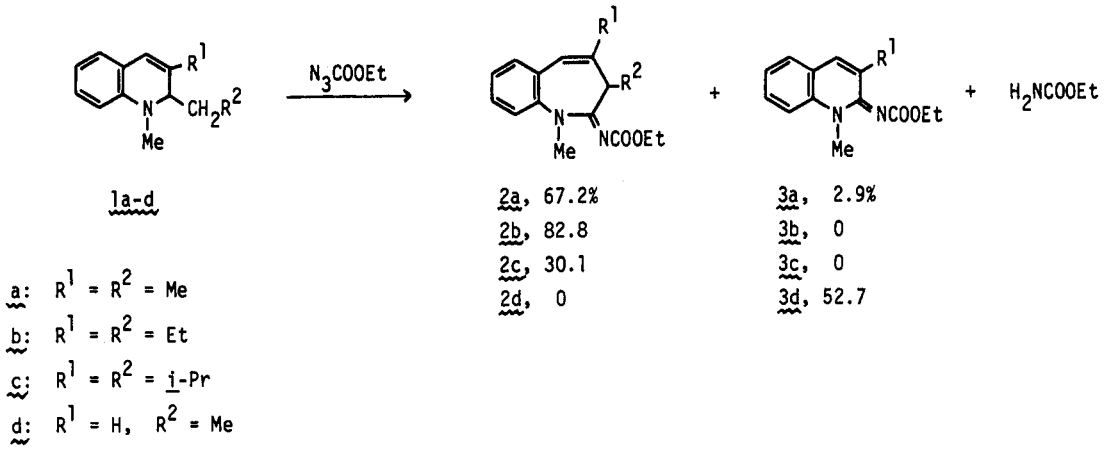
In a recent publication[7] we have reported that *N*-alkylanilinomagnesium bromides reacted with aliphatic aldehydes to give 1,2,3-trialkyl-1,2-dihydroquinolines in good yields. When the reaction of 1,3-dimethyl-2-ethyl-1,2-di-

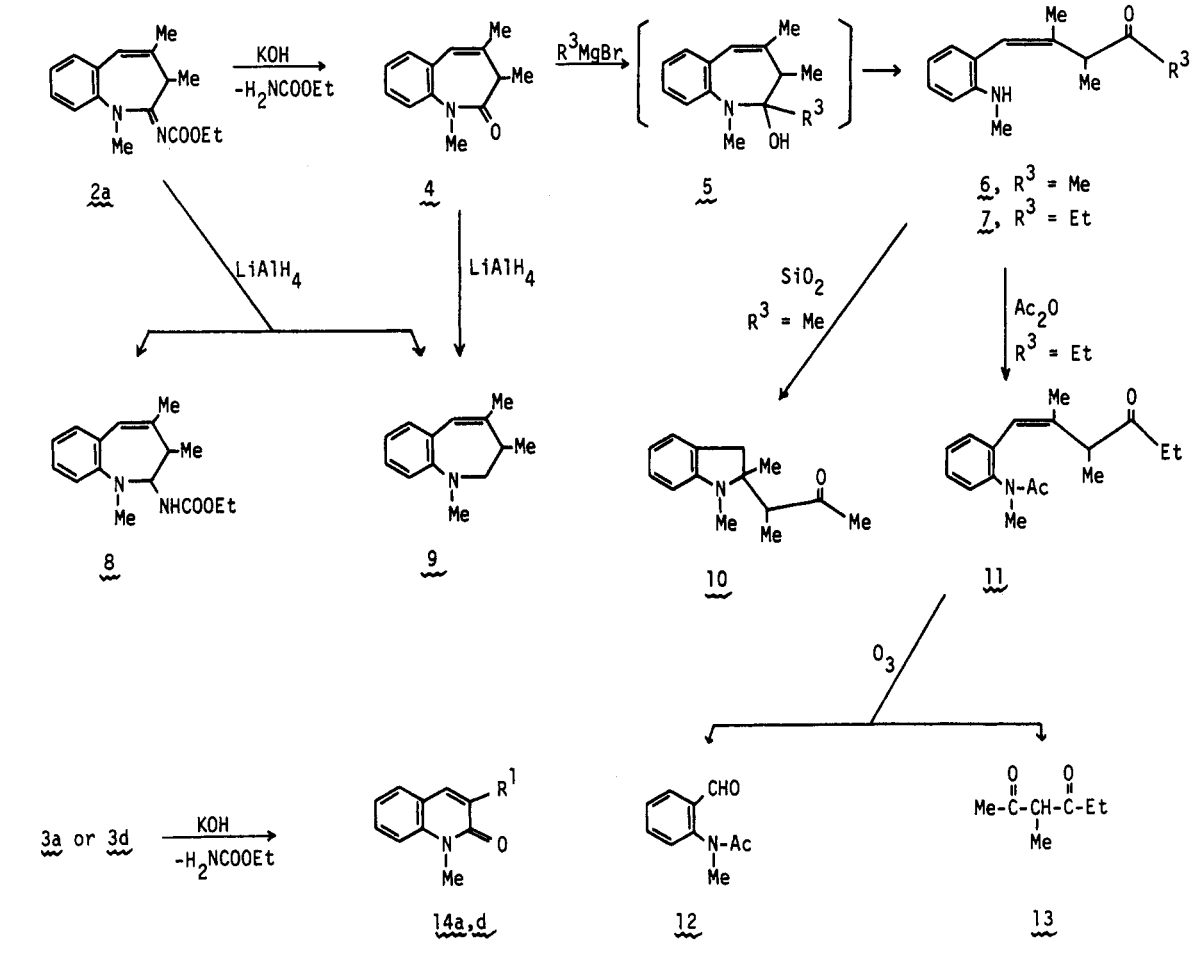


hydroquinoline (**1a**) with an excess of ethyl azidoformate was carried out in boiling ligroin, three products were produced: a yellow oil (**2a**, 67.2%), urethane (82.8%), and small amounts of crystals (**3a**, 2.9%). The NMR and ir spectra of the main product, $C_{16}H_{20}N_2O_2$ (**2a**), exhibited the presence of an ethoxycarbonylimino group, and a $>CHCH_3$ group instead of the C-2 ethyl group of the starting dihydroquinoline (**1a**). Alkali hydrolysis of **2a** produced high yields of urethane and a yellow oil (**4**) which showed lactam absorption at 1654 cm^{-1}. This carbonyl group was reduced to methylene by lithium aluminum hydride in a quantitative yield. The Grignard reaction product (**6** or **7**) of **4** with methyl- or ethylmagnesium bromide showed absorptions of a secondary amine (3410 cm^{-1}) and an acetyl or propionyl group (1705 cm^{-1}). The presence of these groups indicates that the alkylation reaction of **4** proceeded with the cleavage of the carbon–nitrogen bond.

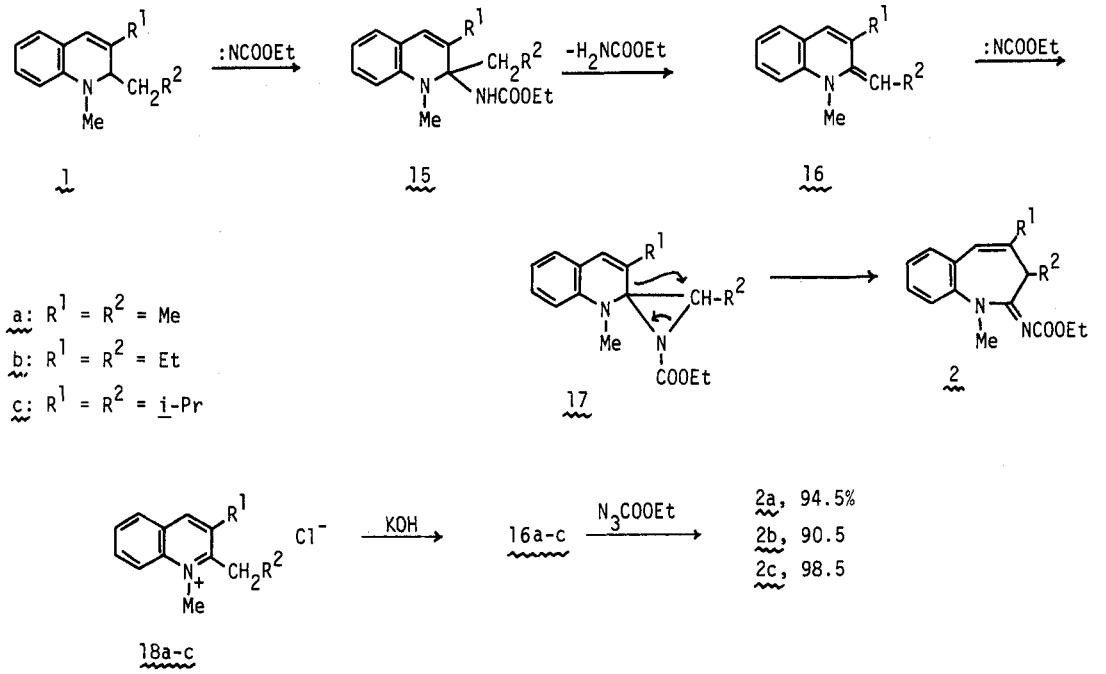
Selective oxidation of the acetylated compound (**11**) of **7** was achieved by treatment with ozone to give aldehyde **12** (47.5%) and β-diketone **13** (26.0%). The aldehyde **12** was

Scheme I





Scheme II



identified as 2-(*N*-acetyl-*N*-methylamino)benzaldehyde, and the β-diketone (**13**) was identical with 3-methyl-2,4-hexadione,[8] by spectroscopic comparisons with authentic samples prepared by independent routes, respectively. These experimental results support that **2a** is 1,3,4-trimethyl-2-ethoxycarbonylimino-2,3-dihydro-1*H*-1-benzazepine and **4** is 1,3,4-trimethyl-2-oxo-2,3-dihydro-1*H*-1-benzazepine.

Lithium aluminum hydride reduction of **2a** gave a mixture of 1,3,4-trimethyl-2-ethoxycarbonylamino-2,3-dihydro-1*H*-1-benzazepine (**8**) and 1,3,4-trimethyl-2,3-dihydro-1*H*-1-benzazepine (**9**) which was also obtained from **4**. Silica gel column chromatography caused cyclization of **6** into 1,2-dimethyl-2-(1-methyl-2-oxopropyl)indoline (**10**).

The NMR and ir spectra of the minor product, $C_{14}H_{16}N_2O_2$ (**3a**), exhibited the presence of an ethoxycarbonylimino group. Alkali hydrolysis of **3a** formed 1,3-dimethyl-2-quinolone (**14a**)[7] and urethane in quantitative yields. Thus the structure of **3a** was determined as 1,3-dimethyl-2-ethoxycarbonylimino-1,2-dihydroquinoline.

A similar treatment of 1-methyl-2-propyl-3-ethyl-1,2-dihydroquinoline (**1b**) or 1-methyl-2-isobutyl-3-isopropyl-1,2-dihydroquinoline (**1c**) with ethyl azidoformate gave 1-methyl-2-ethoxycarbonylimino-3,4-diethyl-2,3-dihydro-1*H*-1-benzazepine (**2b**, 82.8%) or 1-methyl-2-ethoxycarbonylimino-3,4-diisopropyl-2,3-dihydro-1*H*-1-benzazepine (**2c**, 30.1%), respectively. From 1-methyl-2-ethyl-1,2-dihydroquinoline (**1d**) having no substituent on the C-3 carbon, however, the expected benzazepine derivative was not isolated, but 1-methyl-2-ethoxycarbonylimino-1,2-dihydroquinoline (**3d**, 52.7%) was obtained as a main product.

It is difficult to decide now whether the reaction proceeds by way of a nitrene intermediate or by an azide mechanism. If an excess of ethyl azidoformate used supplies carbethoxynitrene required during the reaction, the ring expansion reaction of dihydroquinoline may proceed in the following stages. (Of course, the same products could be formed by the azide mechanisms not involving the nitrene intermediate.[6b]) At first, carbethoxynitrene is inserted into a carbon–hydrogen bond at the C-2 position of **1** to give 1-methyl-2-ethoxycarbonylamino-2,3-dialkyl-1,2-dihydroquinoline (**15**), which is converted into 1-methyl-2-alkylidene-3-alkyl-1,2-dihydroquinoline (**16**) accompanied by the elimination of urethane. At the second stage, **16** reacts with nitrene again to give an aziridine ring (**17**). Then the benzazepine ring (**2**) is formed by the rearrangement of the aziridine.

Previously we reported[7] that unstable 1,3-dimethyl-2-ethylidene-1,2-dihydroquinoline (**16a**) was easily produced by the alkali treatment of 1,3-dimethyl-2-ethylquinolinium chloride (**18a**) in a quantitative yield. If 2-alkylidene-1,2-dihydroquinolines (**16**) are isolated from the corresponding 1-methyl-2,3-dialkylquinolinium chlorides (**18**), and allowed to react with ethyl azidoformate, the benzazepine formation will proceed more smoothly.

2-Alkylidene-1,2-dihydroquinolines (**16a**, **16b**, and **16c**) were liberated by the alkali treatment of aqueous solutions of the corresponding quinolinium chlorides (**18a**, **18b**, and **18c**) in a nitrogen atmosphere. Subsequently, they were extracted with ligroin and heated with ethyl azidoformate to give 90–99% yields of **2a**, **2b**, and **2c**, respectively.

The reasons for the information of **3** and how the ethyl group is eliminated are still unclear. Further experiments are now in progress.

Experimental Section

Proton NMR spectra were recorded using a JNM-MH-100 (Jeol) spectrometer with tetramethylsilane as an internal standard. Infrared spectra were taken on a IR-A-2 (Jasco) spectrometer. Mass spectra were recorded using a RMU-6M (Hitachi) spectrometer. All melting points were measured on a Yanagimoto micro melting point apparatus, and are uncorrected.

1,3,4-Trimethyl-2-ethoxycarbonylimino-2,3-dihydro-1*H*-1-benzazepine (2a). Ethyl azidoformate (15.0 g, 0.13 mol) was added dropwise to a boiling solution of 1,3-dimethyl-2-ethyl-1,2-dihydroquinoline (**1a**, 8.427 g, 0.045 mol) in 20 ml of ligroin (bp 110–120°). The mixture was refluxed for 1 hr under a nitrogen atmosphere. Fractional distillation of the reaction mixture was repeated to give the following fractions.

Fraction a: bp 30–35° (0.1 mm), 3.298 g (82.8%) of urethane.

Fraction b: bp 130–132° (0.03 mm), 8.218 g (67.2%) of **2a**; ir (neat) 1680, 1614 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (d, 3, J = 7.5 Hz, C-3 CH_3), 1.42 (t, 3, J = 7.5 Hz, ethoxy CH_3), 2.12 (s, 3, C-4 CH_3), 3.55 (s, 3, NCH_3), 4.25 (q, 1, J = 7.5 Hz, C-3 H), 4.35 (q, 2, J = 7.5 Hz, OCH_2), 6.48 (s, 1, C-5 H), and 7.00–7.43 (m, 4, aromatic H); mass spectrum m/e 272 (M^+, 77), 227 (42), 199 (44), 172 (32), 145 (100), and 129 (38).

Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.45; H, 7.53; N, 10.18.

Fraction c: bp 140–145° (0.03 mm), mp 52–53°, 0.320 g (2.9%) of 1,3-dimethyl-2-ethoxycarbonylimino-1,2-dihydroquinoline (**3a**); ir (KBr) 1685, 1642 cm^{-1}; NMR ($CDCl_3$) δ 1.34 (t, 3, J = 7.0 Hz, ethoxy CH_3), 2.28 (s, 3, C-3 CH_3), 3.73 (s, 3, NCH_3), 4.18 (q, 2, J = 7.0 Hz, OCH_2), and 7.02–7.48 (m, 5, C-4 H and aromatic H).

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.80; H, 6.58; N, 11.49.

1-Methyl-2-ethoxycarbonylimino-3,4-diethyl-2,3-dihydro-1*H*-1-benzazepine (2b). In a similar manner as above for **2a**, the treatment of 1-methyl-2-propyl-3-ethyl-1,2-dihydroquinoline (**1b**, 9.702 g, 0.045 mol) with ethyl azidoformate (30 g, 0.26 mol) gave 11.111 g (82.8%) of **2b**: bp 140–145° (0.1 mm); ir (neat) 1685, 1610 cm^{-1}; NMR ($CDCl_3$) δ 0.76 (t, 3, J = 7.0 Hz, C-3 ethyl CH_3), 1.12 (t, 3, J = 7.2 Hz, C-4 ethyl CH_3), 1.20 (m, 2, C-3 ethyl CH_2), 1.23 (t, 3, J = 7.0 Hz, ethoxy CH_3), 2.35 (q, 2, J = 7.2 Hz, C-4 ethyl CH_2), 3.44 (s, 3, NCH_3), 3.66 (t, 1, J = 7.5 Hz, C-3 H), 4.19 (q, 2, J = 7.0 Hz, OCH_2), 6.32 (s, 1, C-5 H), and 6.90–7.22 (m, 4, aromatic H).

Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 71.83; H, 8.08; N, 9.42.

1-Methyl-2-ethoxycarbonylimino-3,4-diisopropyl-2,3-dihydro-1*H*-1-benzazepine (2c). In a similar manner as above for **2a**, the treatment of 1-methyl-2-isobutyl-3-isopropyl-1,2-dihydroquinoline (**1c**, 4.0 g, 16.4 mmol) with ethyl azidoformate (10.0 g, 86.9 mmol) gave 1.626 g (30.1%) of **2c**: bp 145–148° (0.05 mm); ir (neat) 1680, 1610 cm^{-1}; NMR ($CDCl_3$) δ 0.72 and 0.84 (d, 3 × 2, J = 6.5 Hz, C-3 isopropyl CH_3), 1.28 (d, 6, J = 7.0 Hz, C-4 isopropyl CH_3), 1.34 (t, 3, J = 7.5 Hz, ethoxy CH_3), 2.46 (m, 1, C-4 isopropyl CH), 3.48 (s, 3, NCH_3), 4.22 (q, 2, J = 7.5 Hz, OCH_2), 6.45 (s, 1, C-5 H), and 6.96–7.28 (m, 4, aromatic H).

Anal. Calcd for $C_{20}H_{28}N_2O_2$: C, 73.13; H, 8.59; N, 8.53. Found: C, 73.05; H, 8.67; N, 8.33.

1-Methyl-2-ethoxycarbonylimino-1,2-dihydroquinoline (3d). In a similar manner as above for **2a**, the treatment of 1-methyl-2-ethyl-1,2-dihydroquinoline (**1d**, 7.852 g, 45 mmol) with ethyl azidoformate (15.0 g, 130 mmol) gave 5.035 g (52.7%) of **3d**: mp 118–119°; ir (KBr) 1660, 1620 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (t, 3, J = 7.5 Hz, ethoxy CH_3), 3.86 (s, 3, NCH_3), 4.22 (q, 2, J = 7.5 Hz, OCH_2), 7.56 (d, 1, J = 6.5 Hz, C-3 H), 7.76 (d, 1, J = 6.5 Hz, C-4 H), and 7.10–7.58 (m, 4, aromatic H).

Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.80; H, 6.14; N, 12.06.

1,3,4-Trimethyl-2-oxo-2,3-dihydro-1*H*-1-benzazepine (4). A solution of **2a** (0.870 g, 3.2 mmol) and potassium hydroxide (0.1 g) in 50% ethanol (20 ml) was refluxed for 5 hr. After removal of the ethanol, the aqueous solution was extracted with chloroform. The extract was washed with water, dried, and concentrated. Distillation of the residue gave 178 mg (62.3%) of urethane and 640 mg (99.7%) of **4**: bp 103–105° (0.025 mm); ir (neat) 1654 cm^{-1}; NMR ($CDCl_3$) δ 1.39 (d, 3, J = 7.0 Hz, C-3 CH_3), 2.06 (s, 3, C-4 CH_3), 2.80 (q, 1, J = 7.0 Hz, C-3 H), 3.51 (s, 3, NCH_3), 6.60 (s, 1, C-5 H), and 7.08–7.50 (m, 4, aromatic H); mass spectrum m/e 201 (M^+, 78), 185 (56), 158 (64), and 145 (100).

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.43; H, 7.50; N, 6.73.

1,3,4-Trimethyl-2,3-dihydro-1*H*-1-benzazepine (9). A mixture of **4** (757 mg, 3.77 mmol) and $LiAlH_4$ (71.5 mg, 1.89 mmol) in dry ether (20 ml) was stirred for 1 hr at −10 to −5°. After the addition of 10 ml of saturated aqueous NH_4Cl the ether layer was separated, dried, and concentrated. Distillation of the residue gave 695 mg (97.7%) of **9**: bp 83–85° (0.03 mm); NMR ($CDCl_3$) δ 1.27 (d, 3, J = 7.5 Hz, C-3 CH_3), 2.02 (s, 3, C-4 CH_3), 2.54 (m, 1, C-3 H), 3.10 (s, 3, NCH_3), 3.20 (d, 2, J = 3.5 Hz, C-2 H), 6.30 (s, 1, C-5 H), and 6.68–7.31 (m, 4, aromatic H); mass spectrum m/e 187 (M^+, 100), 172 (32), 158 (32), 145 (46), 132 (94), and 117 (41).

Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.19; N, 7.48. Found: C, 83.13; H, 9.08; N, 7.51.

Lithium Aluminum Hydride Reduction of 2a. A solution of $LiAlH_4$ (180 mg, 4.74 mmol) in 10 ml of dry ether was added to a solution of **2a** (5.390 g, 19.82 mmol) in dry ether (40 ml). The mixture was stirred at −10 to −5° for 1 hr. After the addition of saturated aqueous NH_4Cl the ether layer was separated, dried, and concentrated. The residue was chromatographed on a silica gel column. The first fraction of benzene gave 2.316 g (62.5%) of **9**. The second fraction of benzene gave 1.450 g (26.7%) of 1,3,4-trimethyl-2-ethoxycarbonylamino-2,3-dihydro-1*H*-1-benzazepine (**8**): bp 98–102° (0.02 mm); ir (neat) 3420, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (d, 3, J = 6.5 Hz, C-3 CH_3), 1.27 (t, 3, J = 7.0 Hz, ethoxy CH_3), 2.08 (s, 3, C-4 CH_3), 3.37 (s, 3, NCH_3), 3.62 (q, 2, J = 7.0 Hz, OCH_2), 4.14 (m, 1, C-3 H), 5.25 (s, 1, NH), 6.41 (s, 1, C-5 H), and 6.70–7.34 (m, 4, aromatic H).

Anal. Calcd for $C_{16}H_{22}N_2O_2$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.13; H, 8.07; N, 10.01.

***N*-Methyl-2-(2,3-dimethyl-4-oxo-1-pentenyl)aniline (6).** A solution of methylmagnesium bromide (40 mmol) in 20 ml of ether was added to a solution of **4** (7.990 g, 39.8 mmol) in dry ether (20 ml). The mixture was refluxed for 1 hr. After the addition of 10 ml of saturated aqueous NH_4Cl, the ether layer was separated, dried, and concentrated. Distillation of the residue gave 6.818 g (79.8%) of **6**: bp 72–76° (0.03 mm); ir (neat) 3410, 1707 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (d, 3, J = 6.5 Hz, >CHC**H**$_3$), 1.70 (s, 3, =—CH_3), 1.91 (s, 3, $COCH_3$), 2.74 (s, 3, NCH_3), 3.48 (q, 1, J = 6.5 Hz, >CH–), 3.70 (s, 1, NH), 6.02 (s, 1, vinyl H), and 6.28–7.08 (m, 4, aromatic H).

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.17; H, 8.82; N, 6.38.

***N*-Methyl-2-(2,3-dimethyl-4-oxo-1-hexenyl)aniline (7).** In a similar manner as above for **6**, the treatment of **4** (893 mg, 4.44 mmol) with ethylmagnesium bromide (5.0 mmol) in ether (20 ml) gave 566 mg (44.6%) of **7**: bp 75–78° (0.03 mm); ir (neat) 3410, 1705 cm^{-1}; NMR ($CDCl_3$) δ 0.93 (t, 3, J = 7.0 Hz, propionyl CH_3), 1.14 (d, 3, J = 6.5 Hz, >CHC**H**$_3$), 1.75 (s, 3, =—CH_3), 2.32 (q, 2, J = 7.0 Hz, $COCH_2$), 2.82 (s, 3, NCH_3), 3.59 (q, 1, J = 6.5 Hz, >CH–), 3.80 (s, 1, NH), 6.16 (s, 1, vinyl H), and 6.40–7.30 (m, 4, aromatic H).

Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.91; H, 9.14; N, 6.03.

1,2-Dimethyl-2-(1-methyl-2-oxopropyl)indoline (10). A solution of **6** (1.010 g, 4.65 mmol) in benzene or n-hexane was passed through a silica gel column. Distillation of the eluate gave 667 mg (50.9%) of **10**: bp 89–92° (0.03 mm); ir (neat) 1701 cm^{-1}; NMR ($CDCl_3$) δ 1.06 (d, 3, J = 7.0 Hz, >CHC**H**$_3$), 1.14 (s, 3, C-2 CH_3), 2.05 (s, 3, $COCH_3$), 2.54 and 3.40 (AB quartet, 2, J = 16.0 Hz, C-3 H), 2.61 (s, 3, NCH_3), 3.05 (q, 1, J = 7.0 Hz, >CH–), and 6.18–7.06 (m, 4, aromatic H).

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.32; H, 8.80; N, 6.43.

***N*-Methyl-*N*-acetyl-2-(2,3-dimethyl-4-oxo-1-hexenyl)aniline (11).** A suspension of **7** (566 mg, 2.45 mmol), acetic anhydride (2 ml), and sodium acetate (50 mg) in 10 ml of dry benzene was refluxed for 5 hr. After the addition of 10 ml of water, the mixture was made slightly alkaline with sodium bicarbonate, and was extracted with benzene. Distillation of the extract gave 501 mg (74.8%) of **11**: bp 90–93° (0.03 mm); ir (neat) 1708, 1664 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (t, 3, J = 7.0 Hz, propionyl CH_3), 1.26 (d, 3, J = 7.0 Hz, >CHC**H**$_3$), 1.77 (s, 3, =—CH_3), 1.81 (s, 3, $COCH_3$), 2.38 (q, 2, J = 7.0 Hz, $COCH_2$), 3.17 (s, 3, NCH_3), 3.82 (q, 1, J = 7.0 Hz, >CH–), 6.28 (s, 1, vinyl H), and 7.12–7.48 (m, 4, aromatic H).

Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.57; H, 8.49; N, 5.11.

Ozone Oxidation of 11. An excess of ozone (3% ozone in oxygen, flow rate 45 ml/min) was bubbled through a solution of **11** (871 mg, 3.77 mmol) in 30 ml of chloroform at −10 to 0° for 15 min. After stirring with 10 ml of 4% sodium bisulfite, the chloroform solution was separated, dried, and concentrated. Distillation of the residue gave 107 mg (26.0%) of 3-methyl-2,4-hexadione (**13**), bp 79–81° (21 mm) (lit.[8] bp 181–183°), and 270 mg (47.5%) of 2-(*N*-acetyl-*N*-methylamino)benzaldehyde (**12**): bp 75–79° (0.1 mm); ir (neat) 1688, 1663 cm^{-1}; NMR ($CDCl_3$) δ 1.81 (s, 3, $COCH_3$), 3.31 (s, 3, NCH_3), 7.32–8.06 (m, 4, aromatic H), and 10.18 (s, 1, CHO).

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.73; H, 6.27; N, 7.90.

2-(*N*-Acetyl-*N*-methylamino)benzaldehyde (12). To a solution of 2-(*N*-methylamino)benzaldehyde[9] (220 mg, 1.63 mmol) in 5 ml of dry benzene was added acetyl chloride (160 mg, 2.04 mmol) and 2 drops of dry pyridine. The mixture was stirred for 10 min at 80°; then it was hydrolyzed with water. Distillation of the benzene extract gave 223 mg (77.3%) of **12**, bp 75–79° (0.1 mm).

Hydrolysis of 3a or 3d. A solution of **3a** (244 mg, 1.0 mmol) or **3d** (173 mg, 1.0 mmol) and potassium hydroxide (0.1 g) in 50% ethanol (10 ml) was refluxed for 1 hr. After removal of the ethanol, the aqueous solution was extracted with chloroform. The extract was washed with water and dried. Distillation of the extract gave 230 mg (100%) of 1,3-dimethyl-2-quinolone (**14a**), bp 105–109° (0.07 mm), mp 64–65° (lit.[7] mp 64–65°), or 153 mg (99.8%) of 1-methyl-2-quinolone (**14d**), bp 89–93° (0.05 mm), mp 73–74° (lit.[10] mp 74°).

Synthesis of 2 from 1-Methyl-2-alkylidene-3-alkyl-1,2-

dihydroquinolines (16a, 16b, and 16c). To a solution of 1,3-dimethyl-2-ethyl- (**18a**, 1.422 g, 6.44 mmol), 1-methyl-2-propyl-3-ethyl- (**18b**, 1.607 g, 6.44 mmol), or 1-methyl-2-isobutyl-3-isopropylquinolinium chloride (**18c**, 1.787 g, 6.44 mmol) in 10 ml of water was added 10 ml of 20% potassium hydroxide at 0–5°. Alkylidenequinoline (**16a, 16b,** or **16c**) was liberated immediately as a yellow oil, which was extracted with 40 ml of ligroin (bp 110–120°). To the boiling ligroin solution was added dropwise 1.496 g (13.0 mmol) of ethyl azidoformate. The mixture was refluxed for 1 hr. All procedures were carried out under a nitrogen atmosphere. Distillation of the reaction mixture gave 1.655 g (94.5%) of **2a**, 1.748 g (90.5%) of **2b**, or 2.083 g (98.5%) of **2c**, respectively.

Registry No.—**1a**, 51904-95-1; **1b**, 57091-58-4; **1c**, 57091-59-5; **1d**, 16021-59-3; **2a**, 57091-60-8; **2b**, 57091-61-9; **2c**, 57091-62-0; **3a**, 57091-63-1; **3d**, 57091-64-2; **4**, 57091-65-3; **6**, 57091-66-4; **7**, 57091-67-5; **8**, 57139-17-0; **9**, 57091-68-6; **10**, 57091-69-7; **11**, 57091-70-0; **12**, 57091-71-1; **16a**, 57091-72-2; **16b**, 57091-73-3; **16c**, 57091-74-4; **18a**, 55539-76-9; **18b**, 55539-77-0; **18c**, 55539-78-1; ethyl azidoformate, 817-87-8; methyl bromide, 74-83-9; ethyl bromide, 75-00-3; 2-(*N*-methylamino)benzaldehyde, 7755-70-6.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Saturated Heterocycles. IV. *trans*-Decahydroquinolines

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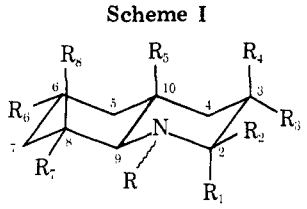
^{13}C NMR spectra of a number of methyl-substituted *trans*-decahydroquinolines and perhydrobenzo[*h*]quinolines are reported. Assignment of signals was accomplished by a combination of off-resonance decoupling, parametrization of substituent effects, and comparison with the spectra of a number of specifically deuterated analogues. Spectra of the *N*-methyl, *N*-ethyl, and *N*-isopropyl derivatives and of the hydrochlorides and trifluoroacetates of a number of the amines are tabulated. Parameters for methyl substitution, replacement of CH_2 by NH, and protonation have been calculated.

Stereochemical problems are increasingly being investigated by ^{13}C magnetic resonance techniques,[1] the chemical shifts constituting a very sensitive probe for conformational properties. Since the numerous signals of substances with high molecular weight can be assigned only with difficulty, an approach involving the recording of spectra of smaller model compounds which constitute subunits of the large molecules, combined with the tabulating of substituent effects, has been successfully applied[1] in a number of systems.

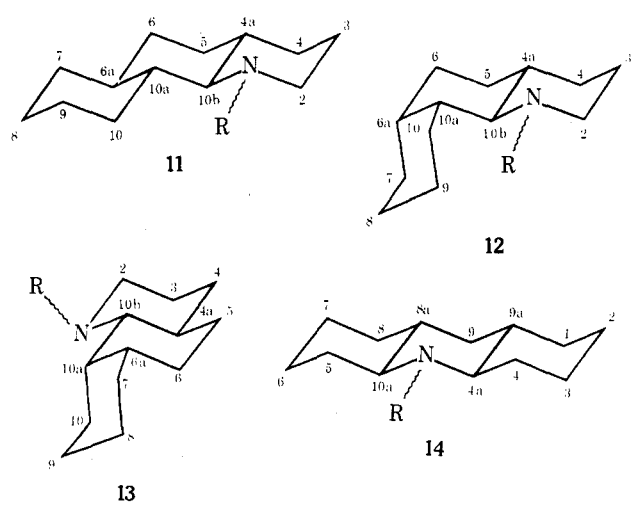
The *trans*-decahydroquinoline framework forms part of a considerable number of natural products. In order to acquire information on the conformational equilibrium of the NCH_3 group (axial–equatorial) in *N*-methylpiperidine and in *N*-methyl-*trans*-decahydroquinoline (**1**),[2] a series of methyl-substituted *trans*-decahydroquinolines[3] (Scheme I, **2–10**, R = H) and perhydrobenzo[*h*]quinolines (Scheme II, **11–13**, R = H), and their *N*-methyl, *N*-ethyl, and *N*-isopropyl derivatives [Schemes I, II, R = CH_3, CH_2CH_3 and $CH(CH_3)_2$] were synthesized[4–6] and their proton[6] and ^{13}C NMR spectra recorded. The conclusions concerning the NCH_3 equilibrium have been reported elsewhere;[2] here the complete ^{13}C NMR data of the compounds are presented and analyzed in terms of substituent parameters.

Scheme I



1. R_1–R_8 = H
2. R_1 = CH_3; R_2–R_8 = H
3. R_2 = CH_3; R_1, R_3–R_8 = H
4. R_4 = CH_3; R_1, R_2, R_4–R_8 = H
5. R_5 = CH_3; R_1–R_4, R_7–R_8 = H
6. R_5 = CH_3; R_1–R_4, R_6–R_8 = H
7. R_6 = CH_3; R_1–R_5, R_7, R_8 = H
8. R_7 = CH_3; R_1–R_6, R_8 = H
9. R_8 = CH_3; R_1–R_7 = H
10. R_5, R_7 = CH_3; R_1–R_4, R_6, R_8 = H

Scheme II



11 **12** **13** **14**

Configuration and Assignment of Signals. The ^{13}C