Acylation–Cycloalkylation. Reaction of Phenylacetyl Chloride with Cyclohexene

Joseph T. Valko and Joseph Wolinsky*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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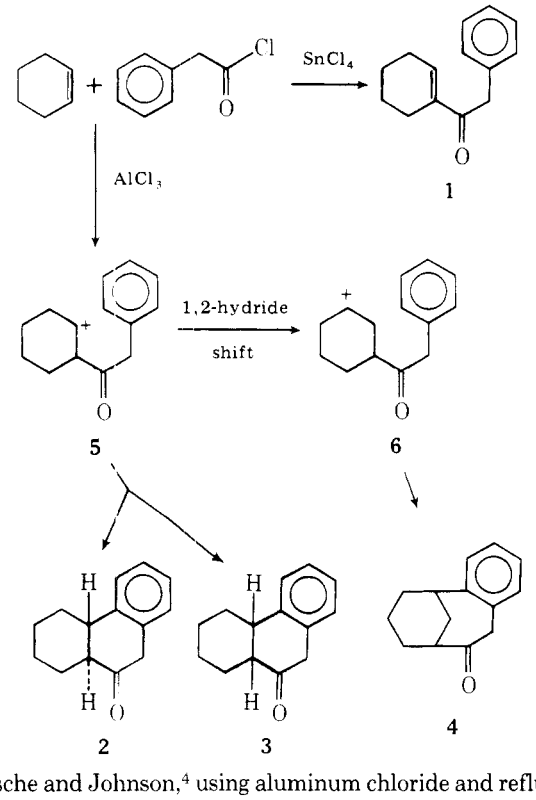
The aluminum chloride complex of phenylacetyl chloride undergoes an acylation–cycloalkylation reaction with cyclohexene to afford *cis*-hexahydro-9-phenanthrone (**3**) along with chloro and unsaturated ketones which are products of acylation. 4,5-Benzobicyclo[4.3.1]decan-2-one (**4**) is formed when the acid chloride is not precomplexed with aluminum chloride. If care is not taken in the workup and handling of reaction products, isomerization of *cis*-**3** to *trans*-hexahydro-9-phenanthrone (**2**) occurs. The stereochemistry of ketones **2** and **3** was established by conversion to the known *cis*-1,2,3,4,4a,10a-hexahydrophenanthrene (**17**) and *trans*-1,2,3,4,4a,10a-hexahydrophenanthrene (**21**), respectively. The reaction of the aluminum chloride complex of phenylacetyl chloride with 1-methylcyclohexene at 0 °C is stereoselective, affording *cis*- and *trans*-methylhydrophenanthrones **30** and **31** in a ratio of 4.4:1. When conducted in refluxing methylene chloride, the reaction is far less selective, affording ketones **30** and **31** in a ratio of 68:32.

In pursuing our studies of an acylation–alkylation approach to the synthesis of cyclic ketones,[1] we have conducted an investigation of the reaction of phenylacetyl chloride with cyclohexene. Cook[2] and Bergs[3] reported that the stannic chloride catalyzed condensation of these reactants gave (phenylacetyl)cyclohexene (**1**) and no tricyclic products.



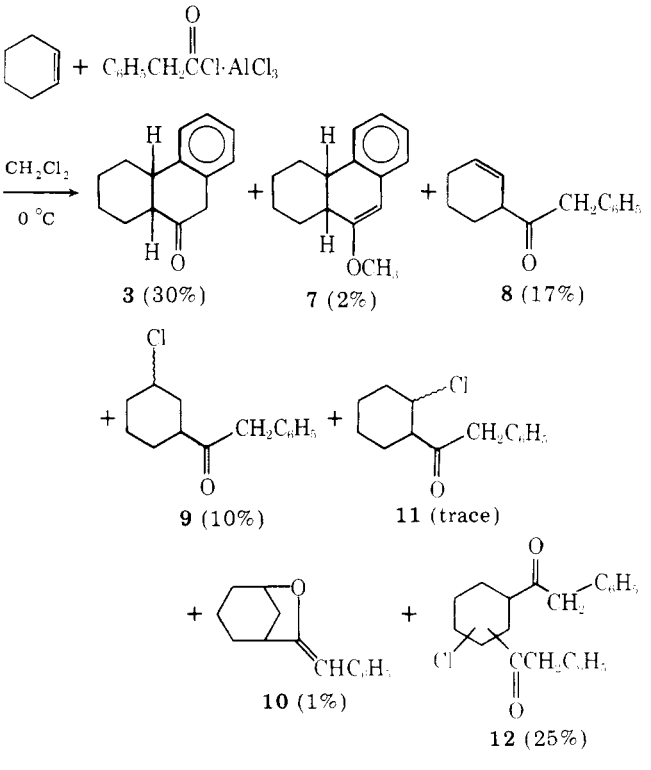
Gutsche and Johnson,[4] using aluminum chloride and refluxing carbon disulfide, obtained a low yield of a mixture of tricyclic ketones from which a crystalline hydrophenanthrone, which we have now shown to be the trans isomer **2**, was isolated by way of the formation of its insoluble semicarbazone derivative. Syntheses of a mixture of *cis*- and *trans*-hydrophenanthrones **3** and **2** have been described by Parham,[5] and more recently a photochemical conversion of **1** to **2** and **3** has been reported by Tada.[6] Herein we report that a carefully worked up phenylacetyl chloride–cyclohexene reaction offers a stereospecific route to the less thermodynamically stable *cis*-hydrophenanthrone **3** in fair yield.

Our work began with a confirmation of the results described by Cook[2] and by Gutsche and Johnson.[4] The Gutsche and Johnson procedure was easily reproduced and pure *trans*-ketone **2** was isolated via its semicarbazone derivative. When the crude ketone mixture was subjected to column chromatography, pure samples of three ketones, in almost equal proportion, were isolated: *cis*-hydrophenanthrone **3**, *trans*-hydrophenanthrone **2**, and 4,5-benzobicyclo[4.3.1]decan-2-one (**4**). The bicyclo ketone **4** presumably arises by cyclization of carbonium ion **6**. The structure of **4** was suggested by the appearance of a distinct AB quartet for two benzylic hydrogens and seven nonequivalent aliphatic carbon atoms in its ^{13}C NMR spectrum.[7]

When the reaction of cyclohexene was conducted at 0 °C with a methylene chloride solution of the aluminum chloride complex of phenylacetyl chloride, followed *by workup with an alcohol* (generally methanol) *and careful washing*, there was isolated by column chromatography the array of products shown in Scheme I.

The noncyclized products[8] apparently arise by loss of a proton from, or acquisition of chloride ion by, the intermediate carbocations **5** and **6**. Methyl enol ether **7** is an artifact of the

Scheme I



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workup procedure using methanol. Enol ether **10** may be formed directly from carbocation **6** or from 3-chloro ketone **9**. Diketone **12**, which has not been completely characterized, must arise from the reaction of the acid chloride–aluminum chloride complex with unsaturated ketone **8**.

When the reaction of cyclohexene with phenylacetyl chloride in methylene chloride at 0 °C or at reflux was conducted without preforming the aluminum chloride complex, *cis*-ketone **3** (25%) was accompanied by bicyclodecanone **4** (15%) and reduced amounts (~7%) of noncyclized products **1**, **8**, **9**, and **11**. The γ-chloro ketone **9** is converted to bicyclodecanone **4** by the action of aluminum chloride, suggesting that the failure to observe **4** in the reaction of cyclohexene with the aluminum chloride complex of phenylacetyl chloride is due to the absence of excess aluminum chloride.

Slow addition of aluminum chloride[9] to a refluxing methylene chloride solution of phenylacetyl chloride and cyclohexene followed by careful workup led to the formation of *cis*-hydrophenanthrone **3** (14%) accompanied by ketone **1** (12%), bicyclodecanone **4** (4%), and chloro ketone **9** (3%).

By modifying the Gutsche and Johnson procedure to the extent of adding ethanol to the crude reaction mixture after hydrolysis on ice, there was obtained a reaction mixture essentially identical with that obtained in refluxing methylene chloride, that is, a mixture comprised largely of *cis*-ketone **3** and bicyclodecanone **4** essentially free of the *trans*-ketone **2**.

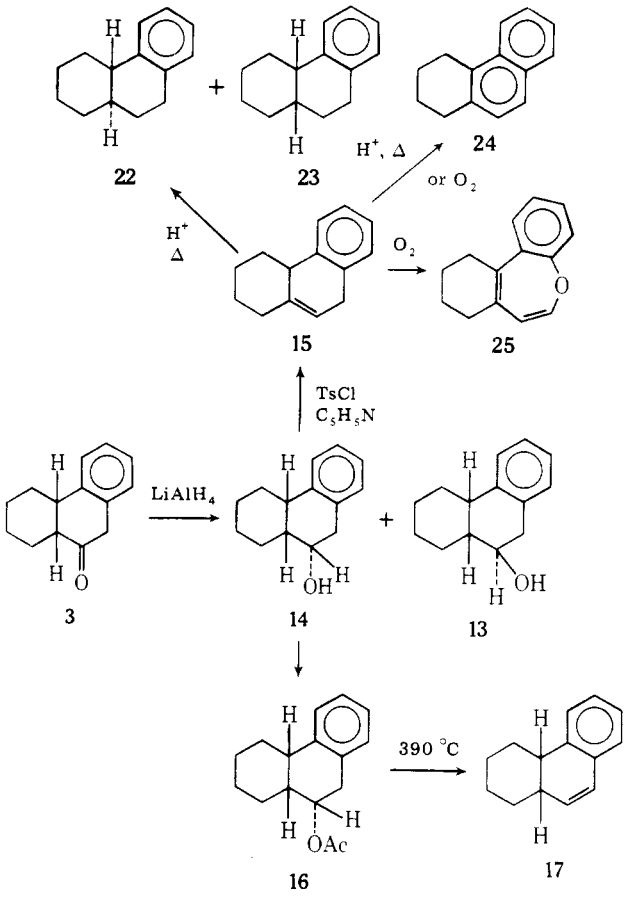
In all of the carefully worked up and nondistilled reactions we have conducted, the crude product appears to be free of detectable amounts of *trans*-ketone **2**. A thorough search for **2** among the products obtained employing the preformed acid chloride–aluminum chloride complex was made by examining the infrared spectra of chromatography fractions where the *trans*-ketone **2** normally emerges. The infrared spectra of ketones **2** and **3** show differences in the 12.9–13.39 μm region. The combined chromatography fractions where ketone **2** normally emerges were also reduced with lithium aluminum hydride and chromatographed, and fractions where the major reduction product, alcohol **19**, emerges were analyzed by NMR (in particular, the 3.4–3.9 ppm region). Neither procedure, both of which have proven reliable in our work with ketones **2** and **3**, indicated the presence of detectable amounts of *trans*-**2**.

The stereospecific formation of the less thermodynamically stable cis ketone led us to survey the stability of **3** under a variety of conditions. It was found that the aluminum chloride complex of **3** in methylene chloride (deep emerald green) can be formed and hydrolyzed without isomerization to *trans*-ketone **2**. The *trans*-ketone **2** and bicyclodecanone **4** were similarly unaffected by treatment with aluminum chloride in methylene chloride. Dry hydrogen chloride can be passed for 30 min through a refluxing methylene chloride solution of the aluminum chloride complex of *cis*-ketone **3** without noticeable isomerization. Isomerization of *cis*-**3** also did not occur when hydrogen chloride was passed briefly, 15 min, through its refluxing solution in methylene chloride; however, partial isomerization to *trans*-**2** was noted when ether was used as a solvent.

In contrast to the stability of *cis*-**3** under the conditions of the Friedel–Crafts reaction is the ease with which it converts to the *trans*-ketone **2** under other circumstances. Samples of *cis*-**3** containing byproducts capable of releasing hydrogen chloride cause its gradual isomerization to *trans*-**2** even at 0 °C. In our early work this was traced to the presence of a small amount of phenylacetyl chloride in the crude product which apparently survives thorough washing with water. As a consequence, we turned to using alcohols in the workup to insure the complete destruction of the acid chloride. On several occasions we have observed the isomerization of *cis*-**3** to *trans*-**2** during, or shortly after, distillation and attribute this to the thermal release of hydrogen chloride from ketones **9**, **11**, or **12**.

The *cis*-ketone **3** is stable in acetic acid. Hydrogen chloride, hydrogen bromide, or sulfuric acid in acetic acid converts *cis*-**3** into an equilibrium mixture of 61% *trans*-**2** and 39% *cis*-**3** within a period of less than 30 min. With 1 M sulfuric acid in methanol, *cis*-ketone **3** is largely converted to methyl enol ether **7**, accompanied by some isomerization. Equilibration of *cis*-**3** with 1 M potassium hydroxide in methanol under nitrogen also takes place in less than 30 min. In view of these observations, we do not understand the claim by Tada and co-workers[6] that *cis*-**3** and *trans*-**2** are stable to acid and base.

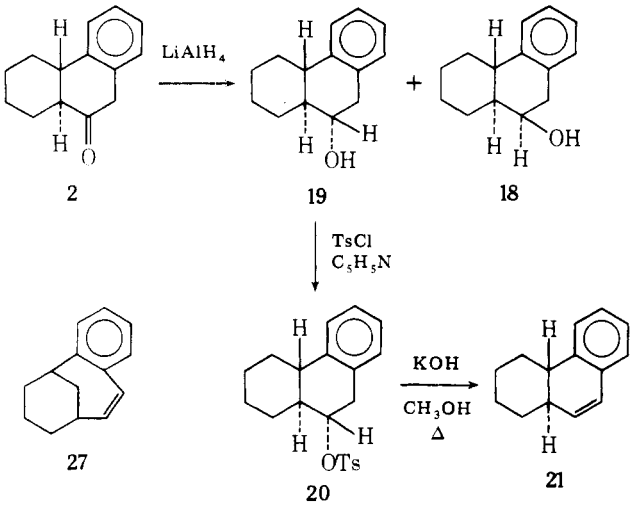
We turn now to the stereochemistry of ketones **2** and **3**. Wolf–Kishner reduction of the semicarbazone derivatives of **2** and **3** proved unexceptable as a means of establishing the configuration of the ketones since equilibration occurred and both compounds afforded essentially the same mixture of 58% *trans-as*-octahydrophenanthrene (**22**) and 42% *cis-as*-octahydrophenanthrene (**23**).[10] Lithium aluminum hydride reduction of *cis*-ketone **3** gave alcohols **13** and **14** in a ratio of 4:96. Treatment of alcohol **14** with tosyl chloride in pyridine at ambient temperature for 4 days gave only the nonconjugated olefin **15**. Olefin **15** readily disproportionated on refluxing with *p*-toluenesulfonic acid in carbon tetrachloride to afford equal proportions of tetrahydrophenanthrene **24** and *as*-octahydrophenanthrenes **22** and **23** (19:81 ratio).[13] Bubbling air through a methylene chloride solution of olefin **15** for several days ultimately produced a mixture of **24** and what is tentatively assigned as benzoxepin **25**[14] in an isolated ratio of 93:7, respectively.



Since trans elimination of alcohol **14** led only to **15** we turned to a procedure involving a cis elimination. Acetylation of alcohol **14** afforded acetate **16** which on pyrolysis at 390 °C yielded the known *cis*-1,2,3,4,4a,10a-hexahydrophenanthrene

(17)[5] and thus established a cis ring juncture in ketone **3**.

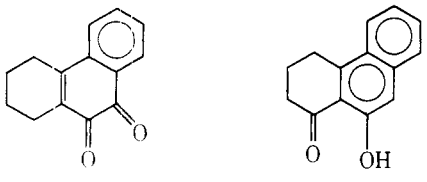
Lithium aluminum hydride reduction of *trans*-ketone **2** gave a mixture of alcohols **18** and **19** in a ratio of 17:83. Tosylation of alcohol **19** gave the stable tosylate **20** which, when heated with potassium hydroxide in methanol, afforded the known *trans*-1,2,3,4,4a,10a-hexahydrophenanthrene (**21**),[15] thereby demonstrating a trans ring juncture in ketone **2**.



2 19 18 27 20 21

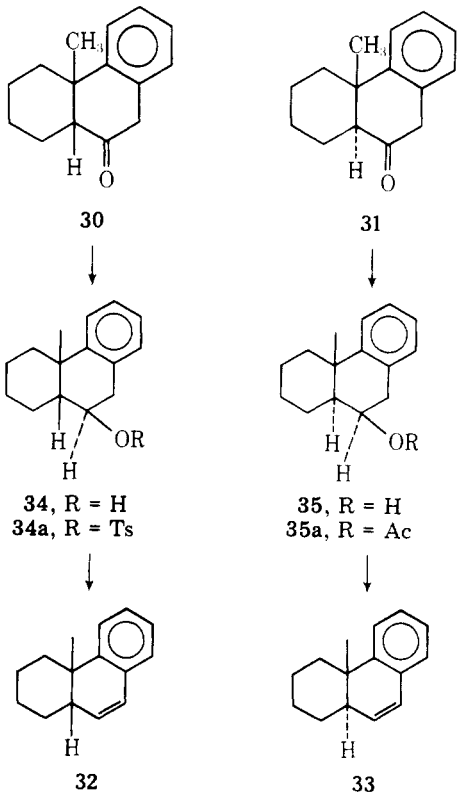
The olefin **27** was prepared from bicyclodecanone **4** in a related manner.

The sensitivity of ketones **2** and **3** to oxygen has already been noted.[4] We have found that air oxidation of either *cis*-**3** or *trans*-**2** adsorbed on silica gel or in alkaline methanol affords the bright red-orange tetrahydrophenanthraquinone **28**.[16] Quinone **28** has also been found to result on brief ozonation (~60 s for 400 mg) of 1,2,3,4-tetrahydro-10-phenanthrenol in ethyl acetate at −78 °C. If an ether solution of *cis*-**3** is exposed to air, a moss green compound **29**[17] can be isolated from the crystals which are slowly deposited.



28 29

When the phenylacetyl chloride–aluminum chloride complex was reacted with 1-methylcyclohexene at 0 °C, the reaction was found to be only stereoselective, producing *cis*-ketone **30** in 22% yield and *trans*-ketone **31**[18] in 5% yield. The stereochemistry of these ketones was established by their conversion to olefins **32** and **33**, respectively.[19] The reaction was also conducted by simultaneous addition of the acid chloride–aluminum chloride complex and 1-methylcyclohexene to refluxing methylene chloride and by addition of a mixture of the acid chloride and olefin to aluminum chloride in refluxing methylene chloride. Under these latter conditions, the reaction became progressively less selective (ratios of **30**/**31** of 68:32 and 55:45, respectively), but the combined yields of tricyclic ketones increased from 27 to 37 to 48%, respectively.



30 31 32 33

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137-B. Proton NMR spectra were determined with Varian Associates A-60 and Perkin-Elmer Model R-32 spectrometers. The ^{13}C NMR spectra were obtained on a Varian Associates CFT-20 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as an internal standard. Ultraviolet spectra were recorded on a Cary 15 spectrophotometer. Mass spectra were provided by the Purdue University Mass Spectral Service employing Hitachi-RMU-6A or CEC-21-110 spectrometers. Gas chromatographic analyses were obtained with a Perkin-Elmer 226 capillary gas chromatograph. Microanalyses were performed by Dr. C. S. Yeh and C. M. Lam.

Reaction of Phenylacetyl Chloride–Aluminum Chloride Complex with Cyclohexene. To a stirred slurry of 8.0 g (60 mmol) of $AlCl_3$ in 350 mL of CH_2Cl_2 at 0 °C was added dropwise over 15 min a solution of 8.0 g (50 mmol) of phenylacetyl chloride in 25 mL of CH_2Cl_2. After being stirred for an additional 15 min, the mixture was filtered with suction through Celite. Nitrogen gas was bubbled through the stirred yellow solution at 0 °C while 5.0 g (60 mmol) of freshly distilled cyclohexene in 25 mL of CH_2Cl_2 was added dropwise over a period of 60 min. After an additional 60 min, 40 mL of MeOH was added to the deep red solution dropwise (slowly at first) over 20 min. The resulting clear pink solution was poured over ice in a separatory funnel, and 100 mL of 4% HCl was added. The CH_2Cl_2 layer was extracted three times with ice-cold 4% HCl, saturated $NaHCO_3$ solution, and water until clear yellow. The CH_2Cl_2 layer was dried, 0.5 mL of pyridine was added, and the solvent was removed under reduced pressure to afford 12.0 g of yellow oil.

Column chromatography was performed using 100 g of Sargent-Welch 60–200 mesh silica gel packed under pentane in a 250 mL buret. A total of 4 g of the crude oil in 5 mL of CCl_4 was applied to the column, which was eluted sequentially under 5 psi of nitrogen pressure with 150 mL of pentane, 900 mL of 2% ether in pentane, 500 mL of 5% ether, 300 mL of 10% ether, 200 mL of 50% ether, 300 mL of 100% ether, and 300 mL of pentane while collecting 30-mL fractions.

***cis*-4b,6,7,8,8a,10-Hexahydro-9(5*H*)-phenanthrone (3).** Ketone **3** emerged between 1150 and 1600 mL on chromatography as described above and was tightly bracketed by ketones **8** and **9**. About 1.2 g of material that was approximately 54% ketone **3** was obtained from 4.0 g of the crude oil. The cis ketone is almost always encountered as an oil, has a faint characteristic odor (**2** is odorless), and quickly yellows in air. The purest sample of **3** crystallized on standing in a refrigerator and showed mp 33–34 °C (sealed tube); IR (neat) 3.40 5.85, 13.31 μm; NMR (CCl_4) 7.3–6.95 (m, 4), 3.47 (s, 2), 3.3–2.8 (brd m, 1), 2.8–1.1 (m, 9) ppm; mass spectrum, *m/e* (rel. intensity) 200 (90), 145 (100), 129 (31).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.18; H, 7.72.

The orange 2,4-DNP derivative of *cis*-ketone **3** was recrystallized from EtOAc and EtOH and displayed mp 180–181 °C.

Anal. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.14; H, 5.29. Found: C, 63.30; H, 5.51.

The semicarbazone of *cis*-ketone **3** was recrystallized from MeOH and showed mp 201–202 °C dec.

Anal. Calcd for $C_{15}H_{19}N_3O$: C, 70.01; H, 7.44. Found: C, 70.29; H, 7.36.

***cis*-9-Methoxy-4b,5,6,7,8,8a-hexahydrophenanthrene (7).** Enol ether **7** is a liquid and emerged from chromatography between 250 and 325 mL, bracketed by telomeric alkyl chlorides and enol ether **10**. *cis*-Enol ether **7**: IR (neat) 3.44, 6.09, 6.72, 6.90, 7.21, 7.94, 8.38, 8.56, 12.30, 13.35 μm; NMR (CCl_4) 7.2–6.7 (m, 4), 5.38 (brd s, 1), 3.63 (s, 3), 3.2–1.8 (m, 2), 1.8–1.2 (m, 8) ppm; mass spectrum, *m/e* (rel. intensity) 214 (100), 199 (9), 185 (18), 172 (18), 171 (36), 141 (22), 115 (18).

6-Benzylidene-7-oxabicyclo[3.2.1]octane (10). The crude reaction mixture as described earlier was first distilled[20] to give 7.2 g of oil, bp 110–115 °C (0.35 mm), which was then chromatographed as described above. The crystalline residues of the fractions collected between 325 and 600 mL were recrystallized twice from MeOH to obtain 53 mg (4.4%) of **10** per gram of distillate. Compound **10** readily converts to a yellowish viscous oil on exposure to air. An analytical sample of **10** showed mp 80–83 °C (sealed tube); IR (KBr) 3.40, 5.99, 6.28, 8.86, 10.45, 10.98, 14.40 μm; NMR (CCl_4) 7.55–6.9 (m, 5), 5.06 (s, 1), 4.84 (m, 1), 2.78 (m, 1), 2.3–1.2 (m, 8) ppm; mass spectrum, *m/e* (rel. intensity) 200 (95), 122 (87), 118 (87), 105 (100), 84 (50), 82 (47), 77 (64), 67 (65), 54 (54).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.19; H, 8.23.

Ozonolysis of **10** in CH_2Cl_2 at −78 °C followed by reductive workup with Zn and HOAc yielded, on chromatography, benzaldehyde, isolated as its 2,4-DNP derivative, mp 237.5–238.5 °C (lit.[21] 237 °C), and other carbonyl-containing products which were not fully characterized.

2-Chloro-1-(phenylacetyl)cyclohexane (11). Column fractions collected between 800 and 1000 mL were recrystallized from methanol to yield colorless plates: mp 39–41 °C; IR (melt) 3.42, 5.82, 6.68, 6.88, 13.13, 13.62, 14.14 μm; NMR (CCl_4) 7.19 (s, 5), 4.2–3.8 (m, 1), 3.69 (s, 2), 2.5–3.0 (m, 1), 2.5–1.0 (m, 8) ppm; mass spectrum, *m/e* (rel. intensity) 236 (13), 145 (38), 91 (43), 81 (100).

3-Chloro-1-(phenylacetyl)cyclohexane (9). Column fractions collected between 1650 and 1900 mL were combined and recrystallized twice from MeOH to give plates: mp 69–71.5 °C; IR (CCl_4) 3.39, 5.82, 6.90, 8.95, 10.10, 13.15, 14.30 μm; NMR ($CDCl_3$) 7.23 (s, 5), 4.33 (brd m, 1), 3.72 (s, 2), 2.7–1.4 (m, 10) ppm; mass spectrum, *m/e* (rel. intensity) 236 (19), 147 (34), 145 (100), 117 (44), 91 (98), 82 (26), 81 (86), 65 (34), 41 (43), 39 (36).

3-(Phenylacetyl)cyclohexene (8). This ketone was isolated as an oil from chromatography fractions collected between 800 and 1150 mL: IR (neat) 5.82, 6.70, 7.55, 10.16, 13.22, 14.2 μm; NMR ($CDCl_3$) 7.25 (s, 5), 5.79 (m, 2), 3.76 (s, 2), 3.19 (brd m, 1), 2.2–1.4 (m, 6) ppm.

The semicarbazone of ketone **8** was purified by trituration with MeOH and showed mp 237–238.5 °C.

***trans*-4b,6,7,8,8a,10-Hexahydro-9(5*H*)-phenanthrone (2).** The crude mixture from the reaction of phenylacetyl chloride with cyclohexene as described above was dissolved in 15 mL of glacial HOAc, and 1 mL of 48% HBr was added. After being stirred at ambient temperature for 60 min, the solution was poured into 50 mL of water and extracted with 50 mL of CH_2Cl_2. The CH_2Cl_2 layer was washed with water and saturated $NaHCO_3$ solution and dried. Solvent removal under reduced pressure followed by distillation of the residue yielded 7.2 g of light yellow oil, bp 93–111 °C (0.2 mm). Chromatography as described above for *cis*-ketone **3** afforded crystalline material in fractions collected between 1300 and 1600 mL. Recrystallization from MeOH yielded 626 mg (5.3%) of ketone **2**: mp 65–66 °C (lit.[4] 66–66.5 °C); IR (KBr) 3.38, 3.48, 5.84, 6.94, 12.93, 13.11, 13.78 μm; NMR (CCl_4) 7.36–7.1 (m, 4), 3.46 (s, 2), 2.85–1.0 (brd m, 10) ppm; mass spectrum, *m/e* (rel. intensity) 200 (100), 145 (83), 139 (59), 115 (41).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.81; H, 7.92.

The semicarbazone of ketone **2** was prepared and recrystallized with difficulty from MeOH, mp 221.5–222.5 °C dec (lit.[4] 221–222 °C).

The 2,4-DNP derivative of ketone **2** was recrystallized from EtOAc to yield orange needles and yellow fluff crystals, mp 197–198 °C (lit.[4] 195.5–198 °C).

When 85 mg of *trans*-ketone **2** was kept for 30 min in 3 mL of methanol containing 1 drop of concentrated H_2SO_4, an oil was obtained after pouring the solution into water and extracting with CH_2Cl_2. Thin-layer chromatography with 10% ether in pentane gave 32 mg (35%) of the methyl enol ether of *trans*-ketone **2**, R_f 0.6, as a low-melting solid: IR (melt) 6.12, 7.73, 7.96, 8.38, 8.52, 9.63, 12.39, 13.37, 13.71 μm; NMR (CCl_4) 7.15–6.75 (m, 4), 5.42 (brd s, 1), 3.66 (s, 3), 2.65–1.0 (m, 10) ppm; mass spectrum, *m/e* (rel. intensity) 214 (24), 158 (33), 141 (50), 129 (38), 128 (67), 127 (25), 115 (100), 63 (24), 41 (31), 39 (34). There was also recovered 38 mg of *trans*-ketone **2** which was partially isomerized to *cis*-ketone **3**.

Wolf-Kishner Reduction of *trans*-Ketone 3. A mixture of 1.51 g of KOH and 390 mg (1.57 mmol) of the semicarbazone derivative of *trans*-ketone **3** in 10 mL of trimethylene glycol was heated under nitrogen at 195 °C for 7 h and was then poured into 20 mL of water, 5 mL of 5% hydrochloric acid, and 15 mL of CH_2Cl_2. The organic layer was washed with water and dried, and the solvent was removed to afford 244 mg of light brown oil. Thin-layer chromatography, eluting twice with pentane and extracting the first band, yielded 183 mg of a colorless oil which proved to be a mixture of *cis*-**23** and *trans*-**22** by capillary gas chromatography.

Essentially the same mixture of **22** and **23** was obtained when the semicarbazone of *cis*-ketone **2** was subjected to the conditions described above.

4,5-Benzobicyclo[4.3.1]decan-2-one (4). A solution of 10.0 g (65 mmol) of phenylacetyl chloride and 6.0 g (74 mmol) of freshly distilled cyclohexene in 200 mL of CH_2Cl_2 was added dropwise over 60 min to a refluxing slurry of 9.5 g (70 mmol) of $AlCl_3$ in 100 mL of CH_2Cl_2. After an additional 60 min the brown-black solution was poured over ice in a separatory funnel, and after shaking 30 mL of EtOH was added followed by 100 mL of 4% HCl. The CH_2Cl_2 layer was extracted with 4% HCl, saturated $NaHCO_3$ solution, and water until clear yellow. The solution was dried, 0.5 mL of pyridine was added, and the solvent was removed under reduced pressure to yield 17 g of yellow oil. Distillation of this residue afforded 5.5 g of oil, bp 116–127 °C (0.86 mm), which was chromatographed as described earlier. Fractions collected between 1550 and 1950 mL were combined and recrystallized from MeOH to yield 731 mg (8%) of ketone **4**. An analytical sample was prepared by sublimation in vacuo: mp 74–74.5 °C; IR (KBr) 3.39, 5.87, 13.08, 13.49 μm; NMR (CCl_4) 7.25–6.95 (m, 4), 4.52 (d, 1, J = 13 Hz), 3.31 (d superimposed on brd m, 2, J = 13 Hz), 3.0–1.0 (complex m, 9) ppm; ^{13}C NMR ($CDCl_3$) 211.77 (s), 141.71 (s), 131.53 (d, 2), 131.12 (s), 127.13 (d), 126.45 (t), 50.72 (t), 45.71 (d), 38.82 (d), 35.96 (t), 28.87 (t), 28.14 (d), 18.73 (t) ppm; mass spectrum, *m/e* (rel. intensity) 200 (100), 144 (31), 129 (58), 116 (29), 115 (49), 91 (33).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.92; H, 8.05.

The semicarbazone of ketone **4** was recrystallized from EtOH and exhibited mp 199.5–201 °C dec.[22]

Anal. Calcd for $C_{15}H_{19}N_3O$: C, 70.01; H, 7.44. Found: C, 70.29; H, 7.68.

The 2,4-DNP derivative of ketone **4** was recrystallized from EtOAc and gave two isomers: orange, mp 168.5–173.5 °C, and yellow, mp 210–213 °C. The elemental analysis was performed on the latter isomer.

Anal. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.14; H, 5.29. Found: C, 63.14; H, 5.69.

Lithium Aluminum Hydride Reduction of *cis*-Ketone 3. Chromatographic fractions described earlier (2.4 g) that were rich in *cis*-ketone **3** were slowly added to 280 mg (7.2 mmol) of $LiAlH_4$ in 20 mL of ether. After 30 min, water was added, the slurry was filtered, and the filtrate was dried. Solvent removal under a nitrogen stream yielded 2.2 g of solid, which was applied to a silica gel column in 7 mL of CCl_4 and eluted sequentially under 5 psi of nitrogen pressure with 200 mL of 5% ether, 1400 mL of 10% ether, 800 mL of 25% ether, 300 mL of 50% ether, 300 mL of 100% ether, and 300 mL of pentane.

Fractions collected between 2000 and 2750 mL were combined and recrystallized several times (hexane–ether) to provide 630 mg of *trans,cis*-alcohol **14** as crystalline mats, mp 120.5–122 °C. An analytical sample displayed mp 121–122 °C; IR (KBr) 3.0, 9.48, 9.57, 9.73, 13.05, 13.68 μm; NMR ($CDCl_3$) 7.5–7.0 (m, 4), 4.12 (d of d of d, 1, $J_{8a,9}$ = 2.8 Hz), 2.95 (m, 3), 2.7–1.0 (m, 10) ppm; mass spectrum, *m/e* (rel. intensity) 202 (100), 184 (89), 145 (51), 143 (51), 142 (45) 141 (59), 129 (39), 128 (34), 115 (35).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.97; H, 8.81.

cis,cis-Alcohol **13** can be isolated from the mother liquor from the recrystallization of **14** by repeated thin-layer chromatography (50% ether in pentane), followed by three recrystallizations from hexane. Alcohols **14** and **13** were isolated in a ratio of 96:4, respectively. An analytical sample of **13** displayed mp 82–84.8 °C; IR (KBr) 3.0, 9.65, 9.99, 13.03, 13.48 μm; NMR ($CDCl_3$) 7.25–7.0 (m, 4), 4.18 (d of d of d, 1, $J_{8a,9} \geq 8.3$ Hz), 3.3–2.5 (d of d of d superimposed on m, 3), 2.3–1.1 (m, 10) ppm; mass spectrum, *m/e* (rel. intensity) 202 (56), 185 (52), 184 (100), 156 (39), 145 (40), 142 (78), 141 (86), 129 (52), 128 (51), 115 (52), 105 (42), 91 (46).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.89; H, 8.90.

Dehydration of *trans,cis*-Alcohol 14 with *p*-Toluenesulfonyl Chloride. To 423 mg (2.0 mmol) of *p*-toluenesulfonyl chloride in 3 mL of pyridine was added in one portion 178 mg (0.9 mmol) of alcohol **14** in 2 mL of CH_2Cl_2. The solution was stirred at ambient temperature for 4 days and was then poured into 20 mL of water and 10 mL of CH_2Cl_2. The organic layer was thoroughly extracted with 1% HCl and dried, and the solvent was removed by warming in a stream of nitrogen to leave 160 mg of crude 1,2,3,4,4a,9-hexahydrophenanthrene (**15**) as a slightly yellowish oil: NMR ($CDCl_3$) 7.3–6.9 (m, 4), 5.48 (brd s, 1), 3.5–3.2 (m, 2), 3.2–2.8 (m, 1), 2.5–1.0 (m, 8) (a trace of tosylate was evident) ppm.

Reaction of Hexahydrophenanthrene 15 with Air. Dry air was bubbled through a solution of 160 mg of **15** in 5 mL of CH_2Cl_2 for 7–10 days, the solvent being replenished as needed. The yellowish oil that remained on evaporation was applied to a preparative thin-layer plate and eluted three times with pentane. Extraction of the band with R_f 0.2 gave 101 mg of 1,2,3,4-tetrahydrophenanthrene (**24**): IR (neat) 3.3, 3.41, 12.02, 12.49, 13.04, 13.54 μm; λ_{max} (EtOH) (log ε) 231 (4.96), 283 (3.76), 316 (2.75), 324 (2.75) nm; NMR ($CDCl_3$) 8.1–7.0 (complex m, 6), 3.3–2.7 (m, 4), 2.1–1.7 (m, 4) ppm; mass spectrum, *m/e* (rel. intensity) 182 (100), 165 (28), 154 (87), 153 (43), 152 (33), 141 (34), 69 (32).

Extraction of the band with R_f 0.08 afforded 8.5 mg of a yellowish oil which was tentatively assigned as benzoxepin **25**: IR (neat) 3.29, 3.41, 6.0, 6.09, 8.16, 9.02, 9.2, 9.81, 12.77, 13.24 μm; λ_{max} (EtOH) (log ε) 242 (4.33), 269 (3.41), 341 (2.64), 375 (2.54), 396 (2.45) nm; NMR ($CDCl_3$) 7.3–6.9 (m, 4), 6.41 (d, 1, J = 5.9 Hz), 5.87 (d, 1, J = 5.9 Hz), 2.5–2.2 (m, 4), 1.8–1.5 (m, 4) ppm; ^{13}C NMR ($CDCl_3$) 156.71 (s, 1, J_{H-C} = 170 Hz), 148.81 (d, 1), 140.22 (s, 1), 134.76 (s, 1), 128.51 (d, 1), 126.65 (d, 1), 126.23 (d, 1), 126.11 (d, 1), 119.08 (s, 1), 117.96 (d, 1), 29.82 (t, 1), 28.75 (t, 1), 23.08 (t, 2) ppm; mass spectrum, *m/e* (rel intensity) 198 (100), 170 (33), 169 (24), 157 (62), 142 (40), 141 (64), 129 (24), 128 (46), 115 (37).

Acetate 16. A solution of 256 mg (1.3 mmol) of alcohol **14** in 15 mL of freshly distilled acetic anhydride was stirred at ambient temperature for 5 days and was then poured into 100 mL of water and stirred for 3 h. This mixture was extracted with CH_2Cl_2. The CH_2Cl_2 solution was extracted with $NaHCO_3$ solution and dried, and the solvent was removed to yield 292 mg of yellow oil. Thin-layer purification with 20% ether in pentane yielded 245 mg (80%) of viscous oil. Recrystallization from MeOH yielded crystals: mp 74–75.5 °C; IR (neat) 3.4, 5.72, 8.1, 9.75, 12.98, 13.5 μm; NMR ($CDCl_3$) 7.18 (m, 4), 5.19 (brd m, 1), 3.0 (m, 2), 2.7–2.0 (m, 2), 2.07 (s, 3), 2.0–1.0 (m, 8) ppm; mass spectrum, *m/e* (rel intensity) 184 (77), 142 (52), 141 (100), 128 (41), 43 (81).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.48; H, 8.41.

***cis*-1,2,3,4,4a,10a-Hexahydrophenanthrene (17).** Into a "loop-the-loop" Pyrex tube (8 mm o.d.) filled with glass helices and immersed in a Wood's metal bath at 392 °C was admitted 126 mg (0.52 mmol) of acetate **16** in a nitrogen stream. The exiting vapors were condensed in a dry ice cooled tube. Thin-layer purification of the pyrolysate with pentane yielded 26 mg (27%) of *cis*-**17**: IR (neat) 3.30, 3.41, 3.50, 6.71, 6.9, 12.65, 13.45, 14.48 μm; NMR ($CDCl_3$) 7.1 (m, 4), 6.45 (d of d, 1, $J_{9,10}$ = 9.7 Hz, $J_{9,10a} \leq$ 2.0 Hz), 5.76 (d of d, 1, $J_{9,10}$ = 9.7 Hz, $J_{10,10a} \leq$ 2.0 Hz), 2.70 (m, 2), 2.1–1.1 (m, 8) ppm; mass spectrum, *m/e* (rel. intensity) 184 (56), 142 (53), 141 (100), 128 (43), 115 (26), 84 (23).

A superior procedure for preparing *cis*-**17** involved pyrolysis of the (*S*)-methyl xanthate of alcohol **14**. A mixture of 556 mg of pentane-washed 50% sodium hydride (oil dispersion) suspended in 10 mL of hexane and 144 mg (0.7 mmol) of alcohol **14** in 10 mL of benzene was refluxed for 1 h and cooled, and 2 mL of carbon disulfide was added. After heating for 7 h, 1 mL of methyl iodide was added. After refluxing for 2 h, water and methylene chloride were added. The organic layer was washed with water, dried, and evaporated to leave 400 mg of an orange oil. Thin-layer chromatography using pentane gave 25 mg of dimethyl trithiocarbonate and 167 mg (80%) of xanthate: IR (neat) 8.2, 9.45, 10.45, 13.00, 13.53 μm; NMR ($CDCl_3$) 7.4–7.0 (m, 4), 5.99 (m, 1), 3.18 (m, 3), 2.55 (s, 3), 2.35 (m, 2), 2.0–1.1 (m, 7) ppm; mass spectrum, *m/e* (rel. intensity) 185 (34), 184 (100), 143 (25), 142 (23), 141 (41), 129 (30), 128 (26), 117 (57), 84 (21).

Heating 84 mg of the xanthate to 195 °C in a sublimation apparatus under aspirator pressure gave a liquid condensate which when purified by thin-layer chromatography, eluting twice with pentane, afforded 21 mg (40%) of *cis*-**17**.

Lithium Aluminum Hydride Reduction of *trans*-Ketone 2. To 250 mg (6.4 mmol) of lithium aluminum hydride in 35 mL of ether was slowly added 1.2 g (6.0 mmol) of ketone **2**. After 30 min, water was added, the slurry was filtered and rinsed, and the filtrate was dried. Solvent removal yielded 1.1 g of crystalline clumps. The solid was recrystallized from hexane–ether to give 791 mg (65%) of *trans,trans*-alcohol **19**: mp 90.0–90.5 °C; IR (KBr) 3.0, 3.45, 6.97, 9.6, 9.91, 12.92, 13.49 μm; NMR ($CDCl_3$) 7.4–7.0 (m, 4), 3.71 (d of d of d, 1, $J_{8a,9}$ = 7.5 Hz), 2.94 (d of d of d, 2), 2.55–2.1 (m, 3), 2.05–1.8 (m, 3), 1.6–0.9 (m, 5) ppm; mass spectrum, *m/e* (rel. intensity) 202 (71), 184 (100), 142 (45), 141 (54), 129 (32), 128 (33), 115 (42), 105 (31), 91 (33).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.16; H, 9.05.

Thin-layer chromatography of the mother liquors from the recrystallization of **19** using 50% ether in pentane yielded 166 mg (14%) of the higher R_f *cis,trans*-alcohol **18**: mp 102–102.5 °C; IR (KBr) 3.0, 3.43, 9.25, 12.98, 13.79 μm; NMR ($CDCl_3$) 7.4–7.0 (m, 4), 3.94 (m, 1, $J_{8a,9}$ = 2.3 Hz), 2.98 (d of d of d, 2), 2.52 (m, 2), 2.1–1.1 (m, 9) ppm; mass spectrum, *m/e* (rel. intensity) 202 (12), 184 (100), 156 (27), 142 (47), 141 (65), 129 (23), 128 (29), 115 (32).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.91; H, 8.72.

Tosylate 20. To a mixture of 15 mL of pyridine and 1.2 g (6.3 mmol) of *p*-toluenesulfonyl chloride was added 489 mg (2.4 mmol) of alcohol **19** in 10 mL of CH_2Cl_2, and the mixture was stirred at ambient temperature for 8 days. The mixture was poured into 30 mL of water and 15 mL of CH_2Cl_2. The CH_2Cl_2 was extracted thoroughly with 1% HCl and dried, and the solvent was removed to yield 684 mg of solid. Recrystallization from methylene chloride–methanol afforded 613 mg (71%) of colorless crystals: mp 107–108 °C; IR (KBr) 3.43, 6.26, 6.7, 6.9, 7.4, 8.48, 9.14, 10.87, 11.41, 11.82, 12.28, 12.9, 13.43 μm; NMR ($CDCl_3$) 7.82 (d, 2), 7.5–6.8 (m, 6), 4.6 (m, 1, $J_{8a,9}$ = 8.9 Hz), 3.08 (m, 2), 2.45 (s, 3), 2.6–0.9 (m, 10) ppm; mass spectrum, *m/e* (rel. intensity) 186 (43), 182 (85), 172 (100), 154 (30), 107 (35), 91 (74), 65 (32).

Anal. Calcd for $C_{21}H_{24}O_3S$: C, 70.76; H, 6.79. Found: C, 70.67; H, 6.97.

***trans*-1,2,3,4,4a,10a-Hexahydrophenanthrene (21).** To a refluxing solution of 1.1 g (19.6 mmol) of KOH in 8 mL of MeOH was added 147 mg (0.43 mmol) of tosylate **20** in 3 mL of CH_2Cl_2 dropwise over 10 min. After being heated for 4.5 h, the solution was cooled, 15 mL of CH_2Cl_2 was added, and the mixture was poured into 20 mL of water. The CH_2Cl_2 was extracted with water and dried. Solvent removal yielded 76 mg (96%) of olefin **21** (a colorless oil that solidified in the refrigerator): IR (neat) 3.32, 3.42, 12.75, 13.51, 14.51 μm; NMR ($CDCl_3$) 7.15 (m, 4), 6.43 (d of d, 1, $J_{9,10}$ = 9.5 Hz, $J_{9,10a}$ = 2.4 Hz), 5.78 (d of d, 1, $J_{9,10}$ = 9.5 Hz, $J_{10,10a} \leq$ 1Hz), 2.4–1.4 (m, 10) ppm; mass spectrum, *m/e* (rel. intensity) 184 (64), 142 (52), 141 (100), 128 (30), 115 (21).

Lithium Aluminum Hydride Reduction of Bicyclodecanone 4. To 86 mg (23 mmol) of $LiAlH_4$ in ether was added 419 mg (2.0 mmol) of ketone **4** in ether. After 30 min, water was added, the precipitate was filtered out, and the filtrate was dried. Solvent removal under a nitrogen stream gave 418 mg of very viscous oil. The oil was applied to a silica gel column and eluted sequentially under 5 psi of nitrogen pressure with 200 mL of 5% ether, 900 mL of 10% ether, 700 mL of 25% ether, 300 mL of 50% ether, 300 mL of 100% ether, and 300 mL of pentane. The fractions that were collected between 1600 and 1900 mL were recrystallized twice from hexane to yield 93 mg (23%) of one epimer of 4,5-benzobicyclo[4.3.1]decan-2-ol (**26**): mp 85.5–88 °C; IR (KBr) 3.07, 3.45, 6.97, 9.61, 9.82, 13.21, 13.51 μm; NMR ($CDCl_3$) 7.02 (s, 4), 4.1–3.7 (m, 1), 3.7–2.6 (m, 5), 2.6–1.0 (m, 8) ppm; mass spectrum, *m/e* (rel. intensity) 202 (100), 184 (36), 141 (32), 131 (34), 129 (54), 128 (43), 117 (32), 116 (26), 115 (50), 105 (38), 92 (27), 91 (46).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.87; H, 9.17.

Column fractions that were collected between 2000 and 2200 mL yielded the other epimer of 4,5-benzobicyclo[4.3.1]decan-2-ol (**26**) as a viscous oil: NMR ($CDCl_3$) 7.2–7.0 (m, 4), 3.92 (m, 1), 3.5–2.7 (m, 3), 2.6–1.1 (m, 9), 2.28 (s, 1, OH) ppm.

4,5-Benzobicyclo[4.3.1]dec-2-ene (27). A solution of 211 mg (1.0 mmol) of the epimeric mixture of alcohol **26** and 82 mg of *p*-toluenesulfonic acid in 10 mL of benzene was refluxed for 4 h and then extracted with $NaHCO_3$ solution. The benzene layer was dried, and the solvent was removed under a nitrogen stream to give 149 mg of oil. Thin-layer chromatography using pentane and extraction of the band with R_f 0.5 yielded 17.5 mg (10%) of olefin **27** as an oil: IR (neat) 3.43, 6.71, 6.91, 12.67, 13.27 μm; NMR ($CDCl_3$) 7.2–7.0 (brd s, 4), 6.39 (d, 1, J = 11.8 Hz), 5.81 (d of d, 1, J = 11.8 and 7.3 Hz), 3.22 (m, 1), 2.71 (m, 1), 2.2–1.0 (m, 8) ppm; mass spectrum, *m/e* (rel. intensity) 184 (60), 169 (25), 155 (24), 143 (46), 142 (51), 141 (100), 130 (35), 129 (98), 128 (76), 127 (21), 115 (78), 91 (25), 77 (25), 69 (22), 63 (29), 51 (34).

1,2,3,4-Tetrahydro-9,10-phenanthraquinone (28). A solution

of 117 mg of ketone **3** in 3 mL of methanol containing 3 drops of 0.8 M KOH was stirred for 20 min while exposed to air. The solution was poured into 10 mL of water with 5 mL of CH_2Cl_2, and 2 mL of 4% HCl was added. The CH_2Cl_2 layer was washed with saturated $NaHCO_3$ and salt water and dried. Solvent removal yielded 101 mg of red-brown oil. About 2 mL of ether was added, and 10.4 mg of red-orange needles was collected, mp 139–140.5 °C (lit.[16] red-orange needles, dec > 120 °C). The mother liquor contained 92 mg of oil which can be recycled. An analytical sample of quinone **28** was recrystallized from acetone: mp 139.5–140.5 °C; IR (KBr) 3.41, 5.90, 6.03, 6.22, 7.29, 7.77, 7.97, 12.99 μm; λ_{max} (EtOH) (log ε) 260 (4.35), 344 (3.19), 425 (3.02) nm; NMR ($CDCl_3$) 7.98 (d, 1, J = 8 Hz), 7.73–7.25 (m, 3), 2.8–2.3 (m, 4), 2.0–1.5 (m, 4) ppm; mass spectrum, *m/e* (rel. intensity) 212 (12), 185 (16), 184 (100), 183 (21), 166 (15), 156 (26), 155 (18), 128 (34), 115 (18).

Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.36; H, 5.68.

The quinoxaline derivative of quinone **28** recrystallized as lemon yellow granules from ethanol–chloroform, mp 196.4–197.6 °C.

1-Keto-1,2,3,4-tetrahydro-10-phenanthrenol (29). A total of 1.45 g of chromatography fractions rich in ketone **3** was dissolved in 20 mL of ether and allowed to stand in contact with air overnight. The darkened oil which remained was redissolved in 5 mL of ether, and the vial was stoppered and kept at ambient temperature. The orange solution turned red in a few days and after a week began to deposit yellow-brown crystals. The crystals were removed and rinsed with ether, and the filtrate was returned to the vial, allowed to evaporate to about 5 mL, and restoppered. In about 4 days a second crop was collected. This process was repeated over a period of 3 weeks, by which time 387 mg of crude crystals had been collected. A 257-mg portion of the solid was applied as a $CHCl_3$ solution to two thin-layer plates and eluted twice with ether–pentane–chloroform (2:6:2). The foremost yellow band was extracted with acetone to yield 55 mg of brownish-green crystalline lumps. This solid was recrystallized twice from acetone to yield 18 mg of clear, forest green plates. An analytical sample showed mp 156.5–158 °C (violet melt); IR (KBr) 2.94, 3.42, 6.10, 6.17, 6.27, 6.31, 6.42, 7.33, 7.8, 8.31, 9.80, 13.23, 14.18 μm; λ_{max} (EtOH) (log ε) 233 (4.40), 255 (3.91), 264 (3.83), 291 (4.00), 363 (4.12) nm; NMR ($CDCl_3$) 8.23 (d, 1, J = 8 Hz), 7.94 (d, 1, J = 8 Hz), 7.7–7.2 (m, 3), 6.92 (brd s, 1, OH), 2.84 (t, 2), 2.57 (m, 2), 1.88 (quint, 2) ppm; mass spectrum, *m/e* (rel. intensity) 212 (100), 197 (37), 183 (33), 165 (26).

Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.43; H, 5.82.

Reaction of Phenylacetyl Chloride with 1-Methylcyclohexene. The slow addition of 1-methylcyclohexene (7.59 g) to the aluminum chloride complex of phenylacetyl chloride (9.99 g) was followed by the workup procedure described for the reaction with cyclohexene to give 15.31 g of yellow oil which was distilled to yield 2.35, bp 40–118 °C (0.8 mm), and 5.44 g, bp 121–135 °C (0.8 mm). A 2.5-g sample of the latter fraction was applied to a silica gel column and eluted sequentially with 150 mL of pentane, 900 mL of 2% ether, 500 mL of 5% ether, 300 mL of 10% ether, 200 mL of 50% ether, 300 mL of ether, and 300 mL of pentane. Column fractions eluting between 1350 and 1550 mL appeared to be primarily *trans*-ketone **31**, displaying an NMR methyl signal at 1.0 ppm. Relatively pure *cis*-ketone **30** emerged from the column between 1550 and 1900 mL: IR (neat) 5.81, 6.70, 8.08, 9.65, 9.87, 13.14, 13.62 μm; NMR ($CDCl_3$) 7.25 (m, 4), 3.62 (s, 2), 2.34 (m, 2), 1.8–1.2 (m, 7), 1.12 (s, 3) ppm.

***(cis*-4b,8a)-4b-Methyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-9-ol (34).** Chromatography fractions (1.0 g) containing *cis*-ketone **30** were reduced with 224 mg of lithium aluminum hydride in ether as described earlier to give 966 mg of viscous oil. This oil was applied to a silica gel column and eluted sequentially under 5 psi of nitrogen pressure with 200 mL of 5% ether, 900 mL of 10% ether, 600 mL of 25% ether, 300 mL of 50% ether, 300 mL of 100% ether, and 300 mL of pentane. Fractions collected between 1650 and 1850 mL were combined and recrystallized from hexane to yield 177 mg of alcohol **34**: mp 106.0–107.5 °C; IR (KBr) 3.05, 9.53, 9.70, 13.26, 13.72 μm; NMR ($CDCl_3$) 7.4–6.9 (m, 4), 4.16 (d of d of d, 1, $J_{8a,9}$ = 9.0 Hz), 3.12 (d of d, 1, J = 5.9 and 15.1 Hz), 2.75 (d of d, 1, J = 10 and 15.1 Hz), 1.95 (s, 1, OH), 2.2–1.5 (m, 9), 1.42 (s, 3) ppm.

***cis*-4a-Methyl-1,2,3,4,4a,10a-hexahydrophenanthrene (32).** To 445 mg (2.3 mmol) of *p*-toluenesulfonyl chloride in 7 mL of pyridine was added 101 mg (0.47 mmol) of alcohol **34** in 7 mL of CH_2Cl_2, and the resulting solution was stirred at ambient temperature for 9 days. The reaction mixture was then poured into 20 mL of water and 15 mL of CH_2Cl_2, and the resulting organic layer was extracted eight times with 1% HCl, dried, and evaporated under a nitrogen stream to yield 161 mg of an oil. Thin-layer chromatographic purification of this oil by two elutions with pentane followed by extraction of the foremost band yielded 95 mg (57%) of tosylate **34a** as an oil: IR (neat) 7.35, 8.41, 8.51, 9.13, 10.80, 11.30, 11.96, 12.31, 13.20, 13.69, 14.29 μm; NMR ($CDCl_3$) 7.82 (d, 2, J = 8.0 Hz), 7.4–6.9 (m, 6), 4.99 (d of d of d, 1, $J_{8a,9}$ = 8.9 Hz), 3.23 (d of d, 1, J = 6.2 and 16.0 Hz), 2.94 (d of d, 1, J = 8.9 and 16.0 Hz), 2.40 (s, 3), 2.0–1.0 (m, 7), 1.35 (s, 3) ppm.

To a solution of 803 mg (14 mmol) of potassium hydroxide in 5 mL of MeOH at reflux was added dropwise over 3 min 95 mg (0.26 mmol) of tosylate **34a** in 3 mL of CH_2Cl_2. After being refluxed for 4.5 h, the reaction mixture was poured into 20 mL of water and 10 mL of CH_2Cl_2. The resulting organic layer was extracted twice with water, dried, and evaporated under a nitrogen stream to give 64 mg of oil. Thin-layer chromatographic purification of this residue using two elutions with pentane and extraction of the foremost band yielded 46 mg (88%) of olefin **32** as an oil: IR (neat) 3.42, 6.73, 6.91, 12.71, 13.22 μm; NMR ($CDCl_3$) 7.4–6.9 (m, 4), 6.35 (d, 1, J = 9.5 Hz), 5.90 (d of d, 1, J = 9.5 and 5.6 Hz), 2.4–0.9 (m, 9), 1.10 (s, 3) ppm; mass spectrum, *m/e* (rel. intensity) 198 (15), 183 (23), 155 (32), 142 (35), 141 (100), 128 (30), 115 (53), 63 (22), 51 (26).

***trans*-4a-Methyl-1,2,3,4,4a,10a-hexahydrophenanthrene (33).** Chromatography fractions containing *trans*-ketone **31** (1.0 g) from the reaction of phenylacetyl chloride with 1-methylcyclohexene in refluxing methylene chloride were reduced with 225 mg of lithium aluminum hydride in the usual manner to obtain 946 mg of viscous yellow oil. This oil was applied to a silica gel column and eluted sequentially with 200 mL of 5% ether, 700 mL of 10% ether, 600 mL of 25% ether, 300 mL of 50% ether, 300 mL of 100% ether, and 300 mL of pentane. The fractions collected between 1250 and 1550 mL were combined to give 342 mg of alcohol **35** as an oil: IR (neat) 2.98, 9.70, 13.20, 13.89 μm; NMR ($CDCl_3$) 7.4–7.0 (m, 4), 4.13 (d of d of d, 1, $J_{8a,9}$ = 2.4 Hz), 3.31 (d of d, 1, J = 6.1 and 18 Hz), 2.90 (d of d, 1, J = 2.9 and 18 Hz), 2.3–1.2 (m, 10), 1.29 (s, 3) ppm.

Alcohol **35** was dissolved in 15 mL of acetic anhydride, 2–3 drops of pyridine were added, and the solution was stirred at ambient temperature for 10 days. The solution was poured into 50 mL of water and stirred overnight. The mixture was extracted with methylene chloride, the resulting organic layer was washed with water and dried, and the solvent was removed under a nitrogen stream to give 273 mg of oil. Purification of this oil by thin-layer chromatography using two elutions with 20% ether in pentane yielded 152 mg (37%) of oil, which crystallized from methanol to give acetate **35a**: mp 81–82 °C; IR (neat) 3.43, 5.75, 8.02, 9.65, 13.16, 13.96 μm; NMR ($CDCl_3$) 7.4–7.0 (m, 4), 5.22 (m, 1), 3.31 (d of d, 1, J = 6.3 and 18 Hz), 2.89 (d of d, 1, J = 2.9 and 18 Hz), 1.96 (s, 3), 2.3–1.0 (m, 9), 1.25 (s, 3) ppm.

Pyrolysis of 66 mg of acetate **35a** at 360 °C in a slow stream of nitrogen was followed by thin-layer chromatography eluting four times with pentane to yield 25 mg (49%) of olefin **33**: IR (neat) 3.42, 6.76, 6.92, 12.81, 13.26 μm; NMR ($CDCl_3$) 7.4–7.0 (m, 4), 6.41 (d of d, 1, $J \simeq$ 3.1 and 9.3 Hz), 5.60 (d of d, 1, $J \simeq$ 2.3 and 9.3 Hz), 2.5–1.0 (m, 9), 0.98 (s, 3) ppm; mass spectrum, *m/e* (rel. intensity) 198 (63), 183 (80), 155 (58), 142 (32), 141 (100), 129 (40), 128 (53), 115 (60), 39 (36).

Registry No.—**2**, 19634-96-9; **2** semicarbazone, 69401-70-3; **2** 2,4-DNP, 69401-71-4; **2** methyl enol ether, 69402-72-5; **3**, 19634-95-8; **3** 2,4-DNP, 69401-73-6; **3** semicarbazone, 69401-74-7; **4**, 69401-75-8; **4** semicarbazone, 69401-76-9; **4** 2,4-DNP, 69401-77-0; **7**, 69401-78-1; **8**, 69401-79-2; **8** semicarbazone, 69401-80-5; **9**, 69401-68-9; **10**, 69401-69-0; **12**, 69402-02-4; **13**, 69401-81-6; **14**, 69401-82-7; **14** (*S*)-methyl xanthate, 69401-83-8; **15**, 62690-91-9; **16**, 69401-84-9; **17**, 16804-86-7; **18**, 69401-85-0; **19**, 69401-86-1; **20**, 69401-87-2; **21**, 16804-85-6; **22**, 20480-67-5; **23**, 20480-66-4; **24**, 1013-08-7; **25**, 69401-88-3; **26** isomer 1, 69401-89-4; **26** isomer 2, 69429-03-4; **27**, 69401-90-7; **28**, 69401-91-8; **28** quinoxaline deriv., 69401-92-9; **29**, 69401-93-0; **30**, 69401-94-1; **31**, 69401-95-2; **32**, 69401-96-3; **33**, 69401-97-4; **34**, 69401-98-5; **34a**, 69401-99-6; **35**, 69402-00-2; **35a**, 69402-01-3; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; phenylacetyl chloride, 103-80-0; aluminum chloride, 7446-70-0.

References and Notes

(1) J. Wolinsky, R. Lau, J. J. Hamsher, and C. M. Cimarusti, *Synth. Commun.*, **2**, 327 (1972).
(2) J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 1098 (1933).
(3) H. Bergs, *Chem. Ber.*, **67**, 238 (1934).
(4) C. D. Gutsche and W. S. Johnson, *J. Am. Chem. Soc.*, **68**, 2239 (1946).
(5) W. E. Parham and L. J. Czuba, *J. Am. Chem. Soc.*, **90**, 4030 (1968). The authors would like to express their gratitude to the late Professor Parham for having provided NMR spectra of the mixture of ketones **2** and **3**.
(6) M. Tada, H. Saiki, K. Miura, and H. Shinozaki, *Bull. Chem. Soc. Jpn.*, **49**, 1666 (1976).
(7) The spectral data eliminate the symmetric 4,5-benzobicyclo[4.2.2]-decan-2-one which might have formed by another 1,2-hydride shift in ion **6**, followed by cycloalkylation.
(8) A convenient method for removing ketones **1** and **8** and enol ethers **7** and

10 from the crude reaction mixture involved exposure to ozone at −78 °C (~20 min for 10 g) followed by reductive workup with zinc and acetic acid.
(9) H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *J. Am. Chem. Soc.*, **82**, 1452 (1960).
(10) The ratio of hydrocarbons **22** and **23** was determined by capillary gas chromatography. These compounds were not separated by thin-layer chromatography. Chromic acid oxidation[11] and infrared spectroscopy[12] did not prove to be reliable methods for analyzing mixtures of **22** and **23**.
(11) J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936); J. W. Cook, C. L. Hewett and A. M. Robinson, *ibid.*, 168 (1939); J. W. Cook, N. A. McGinnis, and S. Mitchell, *ibid.*, 286 (1944); R. A. Barnes and A. D. Olin, *J. Am. Chem. Soc.*, **78**, 3830 (1956); M. Tada and H. Shinozaki, *Chem. Lett.*, 1111 (1972).
(12) L. A. Paquette, M. J. Kukla, and J. C. Stowell, *J. Am. Chem. Soc.*, **94**, 4920 (1972); H. Christol, A. Gaven, Y. Pietrasanta, and J. L. Vernet, *Bull. Soc. Chim. Fr.*, 4510 (1971).
(13) R. C. Harvey and M. Halonen, *Can. J. Chem.*, **45**, 2630 (1967).
(14) See A. M. Jeffrey and D. M. Jerina, *J. Am. Chem. Soc.*, **94**, 4048 (1972), for the formation of a benzoxepin by air oxidation of dihydronaphthalene. Oxepin **25** also results from the action of air on *cis*-**17**, but is not formed from *trans*-**21**.
(15) W. L. Nelson and D. D. Miller, *J. Med. Chem.*, **13**, 807 (1970). The authors would like to express their gratitude to Professor Nelson for kindly providing copies of the NMR and IR spectra of this olefin.
(16) G. N. Walker, *J. Am. Chem. Soc.*, **79**, 3508 (1957); J. v. Braun and O. Bayer, *Chem. Ber.*, **58**, 2682 (1925).
(17) The isomer of **29** with the carbonyl at the C-4 position has been reported as a colorless solid: G. Haberland, G. Kleinert, and H-J. Siegert, *Chem. Ber.*, **71**, 2623 (1938).
(18) The proportions of ketones **30** and **31** were determined by a combination of thin-layer chromatography and NMR spectroscopy.
(19) See M. Fetizon, G. Moreau, and B. Waegell, *Bull. Soc. Chim. Fr.*, 1229 (1967).
(20) Distillation raises the yield of **10** from ~1.1 to 4.4%.
(21) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", Wiley, New York, p 320.
(22) This semicarbazone derivative may be identical with the unidentified semicarbazone described by Parham and co-workers.[23]
(23) W. E. Parham, E. L. Wheeler, and R. M. Dodson, *J. Am. Chem. Soc.*, **77**, 1166 (1955).

Chiral Spiranes. Optical Activity and Nuclear Magnetic Resonance Spectroscopy as a Proof for Stable Twist Conformations

Wolter ten Hoeve and Hans Wynberg*

Department of Organic Chemistry, The University, Nijenborgh, 9747 AG Groningen, The Netherlands

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The double Michael reaction between 1,3-indandione or 1,3-cyclohexanedione and 1,5-disubstituted pentadien-3-ones gives *cis*- and/or *trans*-spiranes **1–6** depending on the reaction conditions. Use of (−)-quinine as a catalyst gives optically active *trans*-spiranes. The cyclohexanone ring in the *trans*-spiranes was assigned a stable twist conformation as deduced from the symmetry of the ^1H NMR and ^{13}C NMR spectra. The twist conformation was confirmed by an X-ray structure determination. Using the ^{13}C NMR method via diastereoisomer formation with (*S*)-(+)-butane-2,3-dithiol, the enantiomeric purity of *trans*-**4** was found to be 30 ± 5%. Optically pure *trans*-**4**, obtained via crystallization, had $\Delta\epsilon_{max}$ +4.1. Chiroptical properties of *trans*-**3**, *trans*-**4**, and *trans*-**6** were recorded.

Among cyclohexane derivatives stable twist conformations are seldom encountered. This may be due to the fact that in cyclohexane itself the twist conformation has an energy which lies about 5 kcal/mol above the energy of the chair conformation, while the energy of the boat conformation is some 6 kcal/mol higher than the energy of the chair conformation.[1] Thus, the existence of stable twist conformations is ignored in several cases,[2,3a,4] although in the case of cyclohexanone the energy of the twist conformation is only 2.7 kcal/mol higher than the energy of the chair conformation.[1] It has been shown by X-ray analysis that 1,4-cyclohexanedione is a twisted molecule[5] and in some *tert*-butylcyclohexane derivatives a twist conformation is most favorable.[6]

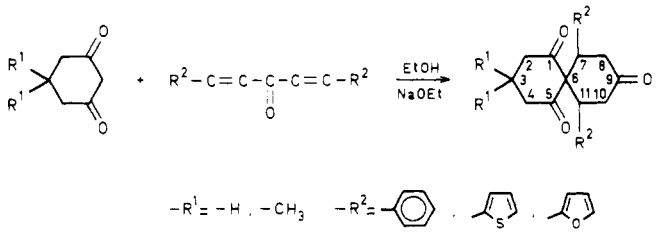
Most cyclohexane derivatives having a stable twist conformation are chiral molecules. For example, cyclohexane (if this molecule existed as a compound with a stable twist conformation),[7] 1,4-cyclohexanedione (if this molecule did not have two interconvertible twist conformations), and twistane are all chiral molecules having D_2 symmetry (see Figure 1).

When we turn to 1,3-disubstituted cyclohexanes, which are chiral in chair or boat form (i.e., the trans isomer), we note that these compounds lack all elements of symmetry but that a C_2 axis is present when the twist conformation is obtained.

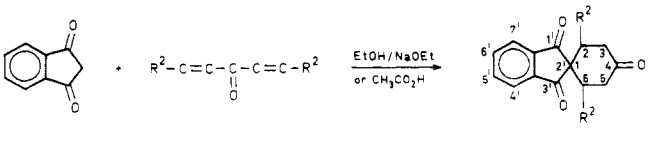
Having these facts in hand we turned our attention to several spiranes synthesized in our laboratory some ten years ago by a double Michael reaction between cyclic 1,3-diketones and 1,5-disubstituted pentadien-3-ones[2] (Scheme I).

The cyclohexanone ring in these spiranes was assigned a chair conformation with both R^2 groups being equatorial. As has been pointed out a cyclohexanone ring has only a small energy difference between twist and chair conformation, and because in these spiranes the cyclohexanone moiety is completely rigid (by the presence of the 1,3-cyclohexanedione moiety and the bulky R^2 groups, which do not allow interconversion of axial and equatorial substituents) it should be possible to obtain such spiranes with a stable (and chiral) twist conformation of the cyclohexanone moiety. The possibility of obtaining e,e and e,a isomers of this spiroketone type was demonstrated conclusively by the fact that the double Michael reaction between 1,3-indandione and dibenzalacetone gave rise to two different spiroketones depending on the reaction conditions (sodium ethoxide/ethanol or acetic acid, respectively)[3a] (Scheme II). The two isomers were assigned an e,e (cis) and an a,e (trans) configuration for the two respective phenyl groups with the cyclohexanone moiety having a chair

Scheme I



Scheme II



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