fell to 8 psi, the vessel was repressurized to 16 psi from the hydrogen cylinder. After 11 such repressurizations, $H_2$ uptake ceased (~5 h). The reaction vessel was connected in series to a copper trap containing ~300 g of NaF pellets, a calibrated glass trap cooled in liquid $N_2$, and a vacuum pump. The contents of the reaction vessel were slowly (~2 h) pumped through the trap system. When the reaction vessel had pumped dry, the vacuum was disconnected and the glass trap was warmed to room temperature. It contained 6.5 mL of colorless liquid. GLC analysis (6 ft × 1/8 in. 10% UCW-982 column, oven temperature = 25 °C, He carrier gas at 40 mL/min) showed two components in a 71:29 ratio. They were identified by comparison of their GLC retention time and mass spectroscopic cracking pattern (GC/MS) as 2-methylpentane and 3-methylpentane, respectively.

**Hydrogenation of Quinoline.** Following the preocedure employed for 4-methyl-2-pentanane, 3.0 g (0.023 mol) of quinoline was reduced over 0.3 g of $PtO_2$ for 1.5 h at 8–16 psi hydrogen pressure. After removing the HF by aspirator, the residue was dissolved in 50 mL of $H_2O$, made alkaline by the addition of 20% aqueous KOH, and extracted with three 100-mL portions of ether. The combined ether extracts were dried ($MgSO_4$) and concentrated on a rotary evaporator. Bulb-to-bulb distillation of the residue (0.1 mm) gave 2.7 g of oil. GLC analysis (10 ft × 1/4 in. 10% SE-30 column at 200 °C) showed three well-resolved peaks: A (retention time = 6 min, 75%), B (retention time = 9 min, 17%), C (retention time = 13 min, 8%). Peaks B and C were identified as quinoline and 1,2,3,4-tetrahydroquinoline, respectively, by co-injection with authentic samples. Peak A was collected by preparative GLC and identified as 5,6,7,8-tetrahydroquinoline: mass spectrum *m/e* 133.0895, calcd for $C_9H_{11}N$ 133.0891; NMR δ 8.32 (d, 1 H), 6.8–7.3 (m, 2 H), 1.1–1.6, and 2.0–2.5 (m, 8 H).

**Registry No.**—Dodecanoic acid, 143-07-7; dodecyl ether, 4542-57-8; 5,6,7,8-tetrahydroquinoline, 10500-57-9.

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# Difunctional Derivatives of *syn*-Dimethanoperhydro-*s*-hydrindacene


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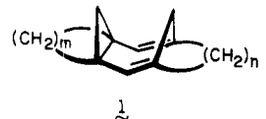
Prompted by a desire to prepare a bisannulated homotropilidene whose localized *cis*-divinylcyclopropane structure might be sufficiently destabilized to force adoption of neutral homoaromatic character, a study of the reducibility of difunctional *syn*-dimethanoperhydro-*s*-hydrindacenes was undertaken. Thus, 4-acetyl-*s*-hydrindacene was converted to the quinone **5** by two different series of reactions. The first consisted of a sequence involving Baeyer–Villiger oxidation, hydride reduction, and Fremy salt oxidation of the resulting phenol. The second involved Beckmann rearrangement, hydrolysis, and dichromate oxidation of the aniline. The quinone adds 2 mol of diazomethane exclusively from the same surface but in opposite senses to give bispyrazoline **8**, photolysis of which provides the desired bishomoquinone **10**. The structure and stereochemistry of **8** and **10** follow unequivocally from their subsequent conversion to **11**, **12**, and **13** and the $^{13}C$ NMR spectra of the entire series of compounds. All attempts to force these difunctional derivatives to undergo either reductive 1,4-elimination or cleavage have proven uniformly unsuccessful.


Each of our groups has had an interest in molecules capable of rapid degenerate valence isomerization and, in particular, in the question of possible removal of the barrier to Cope rearrangement to arrive at a neutral homoaromatic ground state species. These interests overlapped in work on the attempted synthesis of doubly annulated 3,4-homotropilidenes of general formula **1** and, more specifically, the hydrocarbon

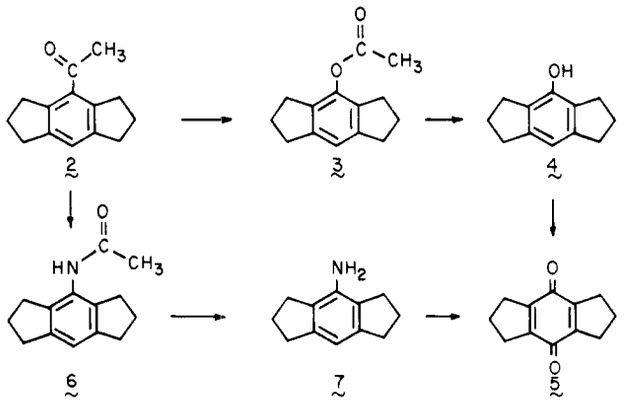



**1**

with $m = n = 3$. This paper describes the results of those experiments which have provided access to several disubstituted *syn*-dimethanoperhydro-*s*-hydrindacene precursors to **1** and outlines the difficulties encountered in our attempts to subsequently introduce the divinylcyclopropane part structure.

4-Acetyl-*s*-hydrindacene (**2**) has previously been synthesized in connection with Arnold and Rondestvedt's study of Mills–Nixon effects.[2] Although Baeyer–Villiger oxidation of **2** proved to be typically sluggish, prolonged refluxing with *m*-chloroperbenzoic acid in dichloromethane afforded acetate **3** in 84% yield based upon recovered ketone. More vigorous conditions appeared to cause competing decomposition of the ester formed. Treatment of the derived phenol (**4**) with Fremy's salt[4] led in 87% yield to the bright yellow *p*-quinone **5**, access to which could also be gained by sequential Beckmann rearrangement of **2**-oxime, hydrolysis of **6**, and sodium dichromate oxidation of aniline **7**.

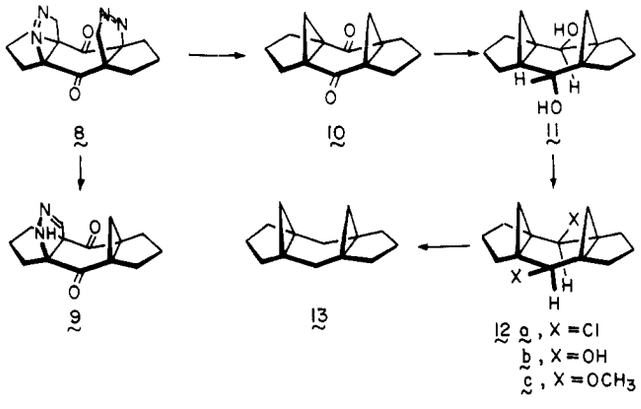
As in the case of duroquinone,[5] **5** enters into dipolar cycloaddition with diazomethane to form a single bispyrazoline in >80% isolated yield. Analysis of the symmetry required by



the $^{13}C$ NMR spectrum of this adduct (seven lines) as well as those of its further transformation products (to be discussed subsequently) established unequivocally that addition had occurred in opposite directions to the same face of the quinone as in **8**.

When treated with small amounts of perchloric acid in acetic acid at room temperature, **8** was converted to a viscous oil from which a crystalline substance could be isolated by column chromatography in 47% yield. The elemental analysis denoted that one molecule of nitrogen had been liberated. The $^1H$ NMR spectrum clearly revealed the presence of an >NH proton at $\delta$ 5.6 and an olefinic proton at 6.3. The infrared spectrum showed bands at 3240 and 1635 $cm^{-1}$. These data identify the product as **9** where it seems reasonable that the residual heterocyclic ring experienced prototropic shift during cyclopropane formation.

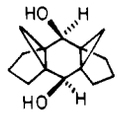
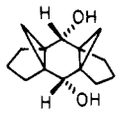
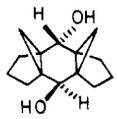
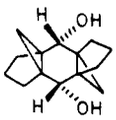
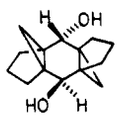
When irradiated in acetone solution with a 450-W Hanovia lamp through Pyrex, **8** was transformed in high yield to **10**.



This diketone exhibits an AB pattern ($J$ = 3.5 Hz) for the cyclopropyl hydrogens and a relatively narrow multiplet for the overlapping signals of the methylene protons attached to the five-membered rings. In this system, $\delta_{AB}$ amounts to 1.08 ppm due chiefly to the carbonyl anisotropy, well in the range observed with other bishomoquinones.[5-7] The symmetry of **10** follows also from the $^{13}C$ NMR spectrum (5 lines), although the composite data remain inadequate for the purpose of relative configurational assignment to the two cyclopropane rings.

Lithium aluminum hydride reduction of **10** in tetrahydrofuran permitted ultimate establishment of the stereochemistry in this series. The major component (mp 183–185 °C) of the mixture of isomeric diols formed under these conditions was isolated by repeated recrystallization from chloroform or by preparative thin layer chromatography and exhibits *eight* peaks in its $^{13}C$ NMR spectrum. From among all configurational possibilities for diols of this general formula (Table I), it can be seen that this spectrum conforms uniquely to the trans diol having $C_s$ symmetry, given by structure **11**. This finding requires cis orientation of the cyclopropane rings in **11** ($C_{2v}$ rather than $C_i$ symmetry in **10**) and also reduces the possible structural assignments to **8** to the one depicted ($C_2$ rather than $C_i$ symmetry). The $^{13}C$ NMR of this heterocycle had already limited the possibilities to the structure shown and the one in which addition had occurred in opposite senses on opposite faces.

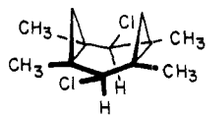
Table I. Symmetry Considerations for the Various Possible Dimethanodihydro-*s*-hydrindacene Diols

| Isomer | Point group | Anticipated number of $^{13}C$ peaks |
|---|---|---|
|  | $C_{2v}$ | 5 |
|  | $C_{2v}$ | 5 |
|  | $C_s$ | 8 |
|  | $C_s$ | 9 |
|  | $C_i$ | 7 |

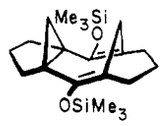
With sodium borohydride, **10** was converted to a different mixture of diols in which one of the cis isomers of $C_{2v}$ symmetry (mp 210–212 °C) predominated. The substance is believed to be **12b** for steric reasons and because the chemical shifts of its two different cyclopropyl protons are similar to those in **12a** and **12c** (see Experimental Section). Treatment of either set of diols with dry hydrogen chloride in benzene–chloroform solution at 0 °C led to formation of a single dichloride in essentially quantitative yield. As anticipated,[8,9] rapid conversion of the biscyclopropylcarbinol moieties to their respective cations was accompanied by stereospecific capture of chloride ion from the direction syn to the three-membered rings. In accord with this analysis, the $^1H$ NMR spectrum of **12a** consists inter alia of a singlet of area 2 at $\delta$ 4.52 for the >C*H*Cl protons and an AB quartet ($J$ = 7 Hz) with $\delta_A$ = 0.63 and $\delta_B$ = 1.04 for the methylene hydrogens bonded to the cyclopropane rings. Since the $^{13}C$ NMR spectrum shows but *five* lines, the dichloride must possess $C_{2v}$ symmetry (see Table I). To be quite sure that no structural bond reorganization had occurred, **12a** was reduced with sodium borohydride in aqueous diglyme at room temperature, advantage being taken of the high solvolytic reactivity of this substance and the known ability of $NaBH_4$ to capture transient carbocations by hydride transfer.[10] The resultant mixture was dominated by the previously characterized[8] cis hydrocarbon **13** (90%). Although the minor constituent remains unidentified, it is decidedly not *anti*-dimethanoperhydro-*s*-hydrindacene.[8] Upon dissolution in methanol containing sodium carbonate, **12a** was converted to ether **12c** without difficulty.

The difunctional derivatives **10–12** were viewed as suitable precursors to the desired bisannulated homotropilidene. This hypothesis required, of course, that 1,4 reductive elimination or cleavage be possible under conditions where the hydro-

carbon product would suffer no further reaction. In the case of **12a**, support for this condition was garnered from the earlier finding that **14** undergoes essentially quantitative conversion



**14**



**15**

to 1,3,5,7-tetramethylhomotropilidene.[9] However, **12a** was unreactive to these conditions (lithium amalgam, ether, 25 °C), the dichloride being totally recovered after 24 h. Since the amalgam in refluxing dioxane (2 h) proved adequate to destroy **12a** without giving rise to a volatile product, this reaction was reexamined at 45 °C (18 h), but the consequences of this moderate temperature were similarly disastrous. What organic product had been generated had evidently polymerized and precipitated with the lithium chloride.

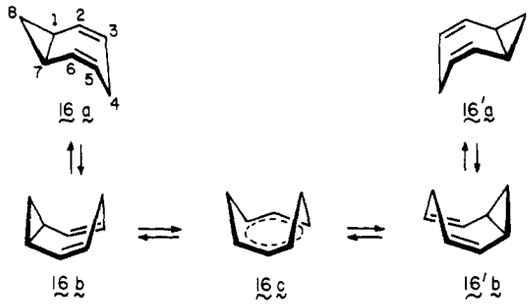
At this point, recourse was made to sodium–potassium alloy (1:5) because of the known greater potential of this couple. Upon admixture with **12a** in tetrahydrofuran-$d_8$ solution at −45 °C there was observed the rather rapid disappearance of the $\delta$ 4.74 singlet and cyclopropane AB quartet which characterize the dichloride, and appearance of a $\delta$ 5.00 singlet. Attempts to isolate a product from such reactions yielded only polymer. At longer reaction times (still at −45 °C), there was obtained in low yield a dihydro olefin (*m/e* 188) whose structure has remained elusive. Ether **12c** was inert to this reagent.

This development suggested the possibility that the desired hydrocarbon might be more easily reduced than its dichloride precursor. The reduction of **12a** under polarographic conditions was therefore briefly investigated. In anhydrous tetrahydrofuran 0.1 M in tetra-*n*-butylammonium perchlorate, **12a** did not undergo reduction until −3.46 V (vs. Ag/0.1 M $AgClO_4$ in THF), just prior to solvent breakdown (−3.69 V). Cyclic voltammetry revealed the process to be irreversible as expected. In anhydrous hexamethylphosphoramide solution, reduction occurred at −2.82 V again just on the fringe of solvent breakdown (−3.10 eV). For comparison purposes, the same technique applied to (1-chloroethyl)cyclopropane led to reduction at −2.03 V in HMPA,[11] thereby providing some indication of the striking difficulty of electron transfer to **12a**. By analysis of the polarographic wave heights, it could be established that the reduction of **12a** involves somewhat more than one electron per molecule (1.2–2 $\epsilon$). However, we cannot be certain of the species that is being further reduced.

When a solution of **12a** in tetrahydrofuran-$d_8$ cooled to −45 °C was treated with *tert*-butyllithium and allowed to warm slowly, solvent dedeuteration was observed prior to consumption of dichloride. Addition of sodium iodide to a solution of **12a** in dry acetone[12] at room temperature caused gradual decomposition without providing evidence for a transient product. These findings, as well as our inability to reduce **10** directly[13] to the bistrimethylsiloxy diene **15**, led us to seek a method wherein the diene would be immediately trapped as a metal complex upon generation. As an extension of Collman's interesting work,[14] **12a** was treated directly with disodium tetracarbonylferrate in tetrahydrofuran and benzene solution at various temperatures. However, it again did not prove possible to deter the onset of dark coloration and decomposition at temperatures above 25 °C (where no reaction occurred).

## Discussion

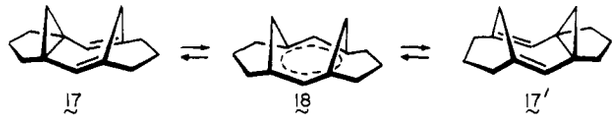
The study of symmetrical molecules capable of completely reversible Cope rearrangement has played a central role in the development of our understanding of fluxional behavior. Discovery by Doering and Roth in 1963[15] of the rapid degenerate valence isomerism in bicyclo[5.1.0]octa-2,5-diene (3,4-homotropilidene, **16**) set the stage for the subsequent elaboration of more highly bridged divinylcyclopropane systems such as bullvalene, barbaralane, semibullvalene, and many of their derivatives. That the measured barrier to Cope rearrangement in **16** ($E_a$ = 12.6–13.0 kcal/mol, $\Delta H^{\ddagger}$ = 11.8–12.3 kcal/mol)[16,17] is somewhat higher than those of its congeners ($\Delta H^{\ddagger}$ = 4.8–13.3 kcal/mol)[18] is due to the greater thermodynamic preference for transoid conformers **16a** and



**16a** **16'a** **16b** **16c** **16'b**

**16'a** (by ca. 4 kcal/mol),[9] and the electronic requirement that isomerization occur via cisoid transition state **16c**. Consequently, the experimentally determined activation parameters necessarily encompass the free energy difference between **16a** and **16b** (**16'a** and **16'b**) as well as the energy demands for 6-electron reorganization. Although 2,6-disubstitution of **16** does cause a decrease in rearrangement rate, perhaps because of steric destabilization of the cisoid conformation,[19] the influence of methyl groups at the 1,3,5, and 7 positions appears to be minimal.[9,17,20]

One structural modification which serves to constrain the homotropilidene ring system to a cisoid conformation is given in generalized form by **1**. Among the many possible members of this series, **17** was considered particularly interesting because of its unique combination of ring strain and strongly canted orbitals. Although the extent to which the trimethylene bridges would destabilize **17** and **17'** relative to **18** was not



**17** **18** **17'**

known, the possibility of altering the relative stabilities of the localized and delocalized forms of this homotropilidene sufficiently to make **18** the ground state was intriguing. One consequence of the removal of the barrier to Cope rearrangement would be evolution of **18** as a neutral homoaromatic ground state species.

The effect of bracketing the 1 and 6 positions of cycloheptatriene with a trimethylene bridge, studied by Vogel,[21] is to shift the equilibrium heavily in favor of the norcaradiene form. In contrast, Paquette has shown that comparable bridging across $C_2$ and $C_8$ of semibullvalene does not lead to development of a gross equilibrium imbalance in favor of one valence isomer.[22] Rather, this highly fluxional nucleus uniquely accommodates the additional ring in a manner which generates approximately equal amounts of the two tautomers at room temperature. No bishomobenzene character is observed, but unsymmetrical substitution is not expected to be conducive to reduction of the Cope transition state energy to a negative value. The most obvious characteristic of **17** is the inherently symmetrical arrangement of the two trimethylene bridges, the resulting effect of which on valence isomerization has not heretofore been examined. The possibility that such a structural modification might merge the two valleys of tautomerism into a single valley of resonance was of especial interest.

The predescribed experimental observations clearly reveal

that dichloride **12a** does not share with its lower homologue **14** the same propensity for 1,4 reductive elimination. The difficulties accompanying introduction of the divinylcyclopropane part structure could be the result of substantially increased ground state strain in the bisannulated homotropilidene,[23] an unusual electronic structure for this hydrocarbon which renders the molecule particularly susceptible to further rapid reaction, a combination of these factors, or yet other considerations. A final resolution of these questions must await an alternate viable synthesis of **17** (**18**), or at least some further appreciation of the effect of bisannulation upon the energetics of [3,3]sigmatropic rearrangements, particularly in degenerate Cope systems.

## Experimental Section

Proton magnetic resonance spectra were recorded with Varian A-60A and HA-100 instruments, while carbon magnetic resonance spectra were obtained with a Bruker 90 spectrometer. Apparent splittings are given in all cases. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrometer, whereas mass spectra were obtained with an AEI-MS9 instrument at an ionizing potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

**4-Acetyl-*s*-hydrindacene (2).** Freshly distilled acetic anhydride (37.7 g, 0.37 mol) was added during 45 min to a vigorously stirred slurry of *s*-hydrindacene (28.57 g, 0.176 mol)[24] and anhydrous aluminum chloride (114.3 g, 0.857 mol) in 600 mL of 1,1,2,2-tetrachloroethane cooled to −35 °C. After 2 h the mixture was poured onto 1200 g of ice and 480 mL of concentrated hydrochloric acid. The organic phase was separated and the aqueous phase extracted with ether. The combined organic layers were washed with saturated sodium bicarbonate solution and brine prior to drying and solvent evaporation. Recrystallization of the residue from methanol afforded 34.8 g (97%) of **2** as colorless crystals, mp 75–78 °C (lit.[11] mp 80–81 °C).

**4-Acetoxy-*s*-hydrindacene (3).** A solution of *m*-chloroperbenzoic acid (35 g, 0.20 mol) in dichloromethane (450 mL, freshly distilled from $CaCl_2$) was added during 1 h to a solution of **2** (12 g, 0.06 mol) in 200 mL of the same solvent cooled to −35 °C. The mixture was allowed to warm slowly to room temperature overnight and then refluxed for 64 h. After cooling, the excess peracid was removed by washing with cold 10% sodium hydroxide solution (2 × 100 mL), water, and brine. Drying and evaporation left an oil which was chromatographed on activity I silica gel (elution with benzene). There was obtained 8.69 g (67.1%) of **3** and 2.4 g (20%) of recovered **2**. Recrystallization of **3** from ethanol and ether–pentane afforded colorless crystals: mp 75–76 °C; $\nu_{max}$ 1760 $cm^{-1}$; $\delta_{Me_4Si}$ ($CDCl_3$) 7.05 (s, 1), 3.06–2.73 (m, 8), 2.45 (s, 3), and 2.40–2.06 (m, 4).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.57; H, 7.45.

**4-Hydroxy-*s*-hydrindacene (4).** To a stirred suspension of lithium aluminum hydride (7.0 g, 0.184 mol) in anhydrous ether (150 mL) was added dropwise a solution of **3** (6.96 g, 0.032 mol) in 30 mL of ether. The mixture was heated at reflux for 6 h, cooled in ice, and treated slowly with 20% hydrochloric acid until clear. The organic phase was washed with water and brine, dried, and evaporated. The residue was sublimed (100 °C, 0.05 mm), taken up in hot 10% sodium hydroxide solution, filtered, neutralized with concentrated hydrochloric acid, and cooled to precipitate the phenol. Recrystallization from ethanol gave 4.71 g (84.5%) of **4**: mp 166–166.5 °C; $\delta_{Me_4Si}$ ($CDCl_3$) 6.76 (s, 1), 4.42 (br s, 1), 3.04–2.70 (m, 8), and 2.28–1.94 (m, 4).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.57; H, 8.00.

**4-Acetamido-*s*-hydrindacene (6).** A 4-g sample of **2** was treated with 10 g of hydroxylamine in 80 mL of 7% aqueous sodium hydroxide solution. The mixture was heated with stirring and enough ethanol was added to keep the compound in solution. After being heated at the reflux temperature for 2 h and cooled, the reaction mixture was diluted with water and filtered. There was isolated 3.7 g (92%) of oxime, mp 165–167 °C (lit.[25] mp 162–163 °C).

The oxime (4 g) was dissolved in a mixture of glacial acetic acid and acetic anhydride (60 mL, 1:1). While cooled in ice water, the solution was saturated with dry hydrogen chloride, left overnight (20 h) at room temperature, and diluted with water. The resulting precipitate was separated by filtration, washed with water, and recrystallized from ethanol–benzene. There was obtained 3.8 g (95%) of **6**, mp 249–250 °C (lit.[25] mp 248–250 °C).

**4-Amino-*s*-hydrindacene (7).** A suspension of **6** (450 mg) in 25% sulfuric acid (40 mL) was treated with sufficient ethanol (ca. 30 mL) to give an almost clear solution. This mixture was heated at reflux for 24 h, treated if necessary with charcoal, filtered while hot, cooled,[26] and neutralized with 20% sodium hydroxide solution. The precipitated amine (285 mg, 80%) was filtered and recrystallized from methanol, mp 85–86 °C.

Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73. Found: C, 83.14; H, 8.57.

**4,8-Hydrindacenequinone (5). A. Fremy's Salt Oxidation of Phenol 4.** A mixture of **4** (730 mg, 4.2 mmol), ether (60 mL), water (100 mL), disodium hydrogen phosphate (3.7 g), and sodium hydroxide (1.8 g) was combined at 0 °C and 2.25 g of moist nitroso disodium sulfonate[27] was added. The flask was tightly stoppered and shaken for 5 h at room temperature. Second and third 2.25-g portions of oxidant were introduced after 5 and 16 h of elapsed time, and after 19 h the mixture was separated, washed with water and brine, dried, and evaporated without heat. Elution of the residue through Florisil with toluene returned 80 mg of **4** and furnished 610 mg (86.9% based on recovered **4**) of quinone **5**. Sublimation gave bright yellow crystals: mp 148–150 °C; $\nu_{max}^{KBr}$ 1649 $cm^{-1}$; $\delta_{Me_4Si}$ ($(CD_3)_2CO$) 2.69 (t, $J$ = 3.7 Hz, 8) and 2.00 (quintet, $J$ = 3.7 Hz, 4).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.14; H, 6.53.

**B. Dichromate Oxidation of Aniline 7.** A solution of **7** (1.6 g, 9.2 mmol) in 400 mL of 25% sulfuric acid (heating necessary) was cooled while adding ether (100 mL) and a saturated aqueous solution of sodium dichromate (0.9 g) during 15 min. After 6–7 h at room temperature, the ether layer was separated and replaced with 100 mL of fresh solvent. After the addition of an equal amount of oxidant, the mixture was stirred overnight. The ether layer was again separated, a third portion of oxidant was added, and the mixture was immediately extracted with ether (300 mL). The combined ether layers were washed with sodium bicarbonate solution, dried, and evaporated. The dark yellow residue was treated with pentane, filtered through neutral alumina (activity 2.5), and freed of solvent. There was isolated 0.90 g of **5**, mp 148–150 °C.

**Diazomethane Addition to 5.** Freshly sublimed quinone (1.36 g, 7.23 mmol) was dissolved in ether (50 mL), cooled to −78 °C, treated with 45 mL of 0.49 M ethereal diazomethane, and maintained for 5 days in a sealed vessel at −3 °C. The remaining solvent was pipetted away from the crystals which had deposited and these were recrystallized from chloroform–ether to give 1.63 g (81.7%) of **8** as a fine white powder, mp 153–154 °C dec; $\nu_{max}^{KBr}$ 1715 and 1553 $cm^{-1}$; $\delta_{Me_4Si}$ ($CD_3CN$) 4.91 and 4.65 (ABq, $J_{AB}$ = 20 Hz, 4) and 2.27–1.72 (m, 12); $^{13}C$ NMR ($CD_3CN$) 200.68, 115.46, 91.72, 60.35, 37.90, 35.26, and 21.39 ppm.

Anal. Calcd for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.58. Found: C, 61.65; H, 6.03; N, 20.73.

**Acid Catalyzed Decomposition of Bispyrazoline 8.** A solution of **8** (340 mg, 1.25 mmol) in 40 mL of glacial acetic acid was treated at room temperature with 10 drops of 70% perchloric acid. Nitrogen evolution commenced immediately. The clear yellow solution was kept at room temperature for 2 h, neutralized with sodium carbonate, and extracted with ether. The concentrated extract was chromatographed on neutral alumina (activity 2.5), elution with pentane–ether (10:1) affording 140 mg (47%) of **9** as a crystalline solid, mp 222 °C dec; $\nu_{max}^{KBr}$ 3240 and 1635 $cm^{-1}$; the $^1H$ NMR spectrum clearly revealed the N-*H* proton at $\delta$ 5.6 and the olefinic proton at 6.3.

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.73; H, 6.60. Found: C, 68.75; H, 6.54.

**Photochemical Decomposition of 8. Bishomoquinone 10.** A solution of bispyrazoline **8** (56 mg, 0.206 mmol) in dry distilled acetone (400 mL) was irradiated through Pyrex with a 450-W Hanovia lamp for 8 h. The concentrated residue was chromatographed on alumina (activity 2.5; elution with ether–hexane (1:1)) to give 42 mg (94.2%) of **10**: mp 149–150 °C; $\nu_{max}^{KBr}$ 1678 and 1662 $cm^{-1}$; $\delta_{Me_4Si}$ ($CDCl_3$) 2.31 and 1.23 (ABq, $J_{AB}$ = 3.5 Hz, 4) and 2.12–1.93 (m, 12); $^{13}C$ NMR ($CDCl_3$) 203.88, 46.88, 28.50, 23.83, and 19.48 ppm.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.63; H, 7.83.

**Lithium Aluminum Hydride Reduction of 10.** A solution of **10** (50 mg, 0.23 mmol) in anhydrous tetrahydrofuran (3 mL) was added to lithium aluminum hydride in 5 mL of the same solvent under nitrogen. The mixture was heated at reflux for 100 min, cooled, and treated with 0.4 mL of water and 0.4 mL of 15% sodium hydroxide solution, and filtered. Solvent removal afforded a residue which was recrystallized from chloroform–pentane (2:1) to give 49 mg (96.4%) of diol mixture. Repeated recrystallization from chloroform (or preparative TLC isolation) afforded pure trans diol **11**: mp 183–185 °C; $\nu_{max}^{KBr}$ 3360 and 3320 $cm^{-1}$; $\delta_{Me_4Si}$ ($CDCl_3$) 4.33 (m, 2), 2.22–2.01 (m,

4), 1.82–1.13 (m, 10), 0.58 (d, $J$ = 6.2 Hz, 2), and 0.33 (d, $J$ = 6.2 Hz, 2); $^{13}$C NMR ($CDCl_3$) 73.67, 66.09, 37.63, 35.53, 34.53, 29.14, 20.58, and 13.65 ppm.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 75.86; H, 9.09.

**Conversion of 11 to *cis*-Dichloride 12a.** A 101 mg (0.46 mmol) sample of diol **11** was dissolved with heating in 150 mL of benzene and 10 mL of chloroform under nitrogen. A mixture of nitrogen and dry hydrogen chloride was bubbled through this solution at 0 °C for 2 h. Evaporation of solvent and sublimation of the residue at 68–70 °C and $5 \times 10^{-3}$ Torr afforded 117 mg (99.2%) of **12a** as a white solid: mp 123–125 °C dec; $\delta_{Me_4Si}$ ($CCl_4$) 4.52 (s, 2), 2.28–2.04 (m, 4), 1.74–1.42 (m, 8), 1.04 (d, $J$ = 7 Hz, 2), and 0.63 (d, $J$ = 7 Hz, 2); $^{13}$C NMR ($CDCl_3$) 69.01, 44.24, 35.39, 20.61, and 17.48 ppm.

Anal. Calcd for $C_{14}H_{18}Cl_2$: C, 65.38; H, 7.05. Found: C, 65.28; H, 6.99.

***syn*-Dimethanoperhydro-*s*-hydrindacene (13).** A solution of **12a** (62 mg, 0.33 mmol) in 1 mL of dry diglyme was introduced into a vigorously stirred solution of sodium borohydride (750 mg, 19.7 mmol) in 65% aqueous diglyme (5 mL) during 15 min at room temperature. Stirring was continued for another 30 min prior to pouring into water (20 mL) and extraction with pentane (5 × 20 mL). The combined organic phases were washed with water (3 × 5 mL), dried, and carefully evaporated. Analysis of the product by VPC (2 m 6.5% Se-30, 90 °C) revealed the presence of two components in a 9:1 ratio. The main component was isolated by preparative VPC (25 mg, 60%) and shown to be the cis hydrocarbon **13** by spectral comparison. The minor constituent was not identified, although it was established that it is not the trans hydrocarbon.

**Solvolysis of 12a in Methanol.** A solution of **12a** (84 mg, 0.33 mmol) in methanol (5 mL) was treated with a small amount of sodium carbonate and stirred at room temperature under a dry argon atmosphere for 3 h. The mixture was filtered and evaporated. Molecular distillation of the residue (75 °C, 0.005 mm) gave 36 mg (44.3%) of **12c**: $\delta_{Me_4Si}$ (THF-$d_8$) 3.82 (s, 2), 3.35 (s, 6), 2.39–0.72 (m, 12), 0.54 (d, $J$ = 6 Hz, 2), and 0.37 (d, $J$ = 6 Hz, 2); *m/e* 248.1781 (calcd 248.1776).

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 76.69; H, 9.70.

**Sodium Borohydride Reduction of 10.** A solution of **10** (806 mg, 3.73 mmol) and sodium borohydride (5 g) in 300 mL of 2-propanol was heated at reflux for 18 h, evaporated, and partitioned between water and dichloromethane. The organic phase was dried and evaporated to leave a residue which was recrystallized twice from chloroform. There was obtained 350 mg (42.7%) of cis diol **12b**: mp 210–212 °C; $\nu_{max}^{KBr}$ 3380 cm$^{-1}$; $\delta_{Me_4Si}$ ($CDCl_3$) 3.19 (s, 2), 2.07–0.96 (br m, 14), 0.92 (d, $J$ = 5.7, Hz, 2), and 0.27 (d, $J$ = 5.7 Hz, 2).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 75.86; H, 9.09.

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