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Synthesis, Photooxygenation, and Diels–Alder Reactions of 1-Methyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene and 1,4a-Dimethyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene

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The model dienes 1,4a-dimethyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (**1b**) and 1-methyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (**1a**) were synthesized. The intermediate, 2-bromo-*trans*-4,10-dimethyl-*trans*-3-decalone (**5b**), was prepared by bromination of the corresponding decalone, whereas 2-bromo-4-methyl-*trans*-3-decalone (**5a**) was made by a method involving the bromination of the kinetically produced 1-methyl-2-trimethylsilyl enol ether 1,4,4a,5,6,7,8,8a-*trans*-octahydronaphthalene (**4**). Dehydrobromination, followed by reduction, and then alumina dehydration, yielded the dienes **1a** and **1b**. Dye-sensitized photooxygenation of **1a** yielded as the major product the peroxide adduct. Dye-sensitized photooxygenation of **1b** gave products derived exclusively from an "ene" allylic hydrogen abstraction and shift of double bond. Reaction of the dienophile 4-phenyl-1,2,4-triazoline-2,5-dione with **1a** yielded exclusively the Diels–Alder adduct, while reaction with **1b** afforded a mixture of Diels–Alder adduct and product derived from allylic hydrogen abstraction and shift of double bond.

The study of the steric effects of axial, angular methyl groups on ring A of sesquiterpenes and related compounds led us to synthesize model compounds **1a** and **1b**. The route chosen for the synthesis was designed to serve as a model for the reexamination of 3-keto steroid bromination. The position of bromination of these steroids is determined by the stereochemistry of the A–B ring junction, and by the presence of α substituents.[1] Earlier attempts by Gunstone[2] and Yanagita[3] to brominate **3b** yielded a mixture of nonisolable products, and it was concluded, on the basis of their dehydrobromination, that the chief product was the 4-bromo derivative. Corey's bromination of tetrahydrosantonin[4] gave the 2-bromide.

Decalones **3a** and **3b** are obtained, respectively, from the reduction of octalones **2a**[5] and **2b**[6] (Scheme I). Bromination of **3b** at 0° yields exclusively 2α-bromo-*trans*-3-decalone **5b** as a white solid. The assignment of the bromine to the 2α position, on the basis of its NMR, is consistent with published results ($J_{ax,ax}$ = 13, $J_{ax,eq}$ = 6 Hz, similar to coupling constants for 2α-bromocholestanone).[7] Attempts at direct bromination of decalone **3a** gave poor yields (less than 6%) of the 2-bromo analog. The 4-bromide is the major product, indicating the important steric effects of the angular methyl group. Bromination of **3a** to yield the 2-bromide is obtained in good yield from the silyl enol ether **4**.[8] Dehydrobromination with lithium carbonate in dimethylformamide, followed by reduction of the resulting unsaturated ketone with aluminum isopropoxide, gives the respective epimeric alcohols **7a** and **7b**. Dehydration of **7b** yields only one diene, **1b**; dehydration of **7a** gives two products, separable by vapor gas chromatography. The major product (85%) is the desired diene **1a** (Scheme I). Structure proof of **1a** was accomplished by conversion of its photooxygenation products to known derivatives.

Photooxygenation.[9] The photooxygenation of dienes **1a** and **1b** yields differing results.

With diene **1b**, the crude product obtained is identified as the mixture of hydroperoxides **9** and **10**. The lack of peroxide formation, which would have resulted from the Diels–Alder type, [4 + 2] addition, is based upon the following observations: first, the NMR of the crude product shows the angular methyl group shifted downfield to δ 1.05, as the geometry of the molecule forces it into the deshielding region of the π system of the cross-conjugated double bonds in compound **9**; second, the NMR does not reveal any peaks in the region where the "expected" peroxide should occur [cf. NMR of ascaridole (Varian, spectrum 276)]; and finally, the conversion of the crude product to a known derivative. In **9** and **10** it is assumed that, because of steric hindrance, oxygen has approached from below the plane of the molecule, justifying the stereochemistry as shown. The results of photooxygenation of **1b**, and proof of structure, are shown in Scheme II.

Attempts at product separation by column chromatography failed, perhaps owing to the thermal instability of the hydroperoxides and to their ease of dehydration and/or rearrangement. The hydroperoxide mixture is oxidized with the Sarett[10,11] reagent to yield ketones **11** and **12**, which are easily separable by vapor phase chromatography. The major product **11** (85–90%) is identical with an authentic sample prepared by an alternative method.[12] Thus, the photooxygenation of **1b** proceeds exclusively by the "ene" path, abstracting a hydrogen with a shift of a double bond.

Photooxygenation of **1a** yields a mixture of products separable by silica gel column chromatography. Scheme III shows the various products formed, and proof of their structure.

On the reasonable assumption that **13** and **16** are derived from peroxide **14**, it can be seen that photooxygenation of **1a** yields at least 80% of the [4 + 2] adduct. Since there is no steric restriction to the approach of oxygen from either side, a mixture of two diastereomeric peroxides is obtained. Mild reduction of **14** yields the diastereomeric dialcohols **17**; oxidation with the Sarett reagent affords the keto alcohol **16**, which is also obtained from the rearrangement of **14** on basic alumina. Final proof is confirmed by aromatizing the keto alcohol to the naphthol derivative **18**. This also indicates that the starting diene is **1a**, rather than **8**, its iso-

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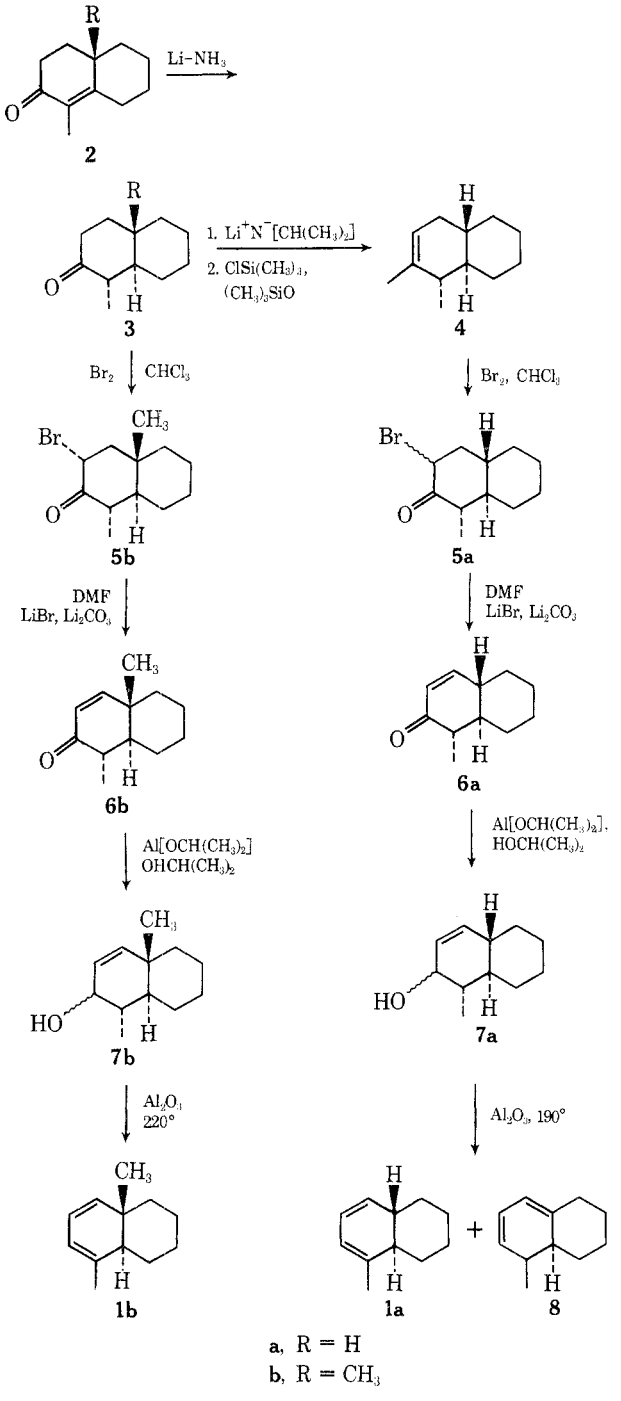
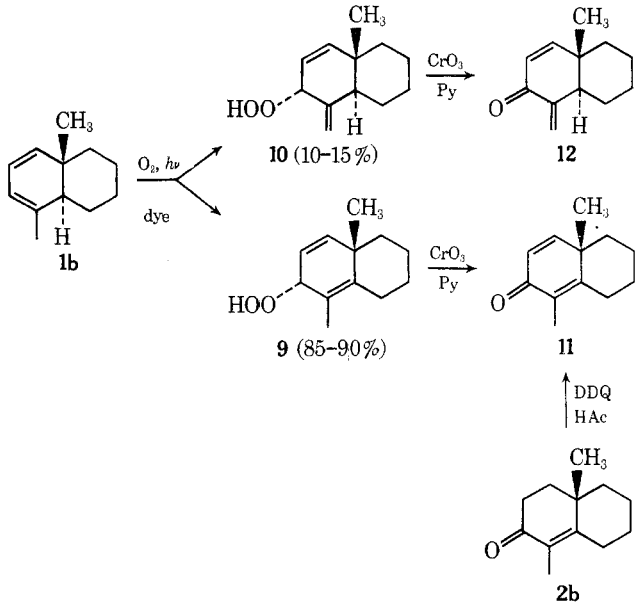
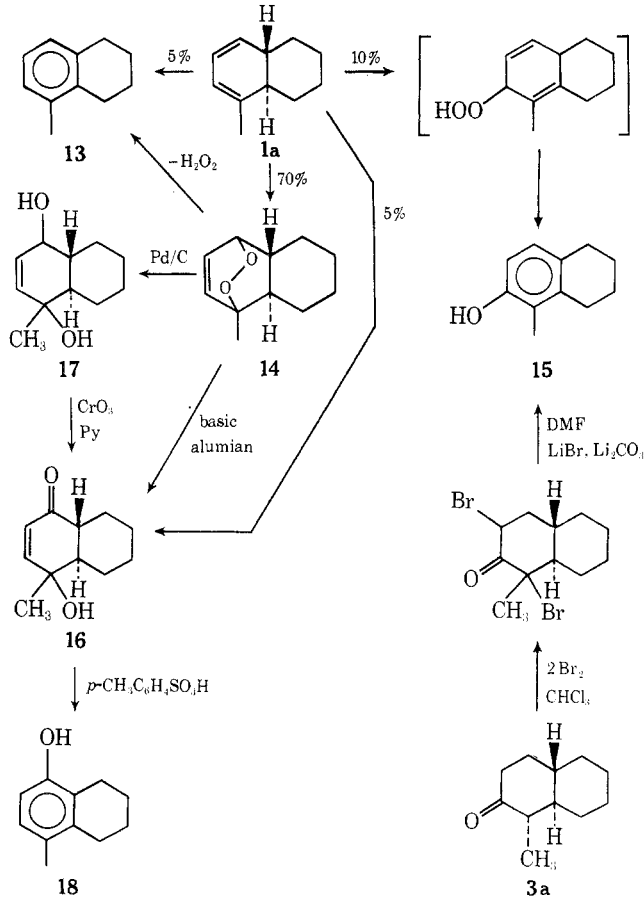
Scheme I



Scheme II
Photooxygenation of 1,4a-Dimethyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (1b)



Scheme III
Photooxygenation of 1-Methyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (1a). Proof of Structures

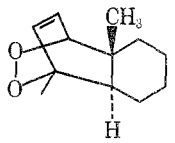


mer. The melting point of **18** and that of its acetate agree with published melting points.[13] The isomeric tetrahydronaphthol **15**, which is obtained in low yield, can be considered as being derived from an allylic "ene" reaction, followed by dehydration; its structure is established by synthesizing a sample by a different route, and comparing spectra, melting points, and mixture melting points. Final proof of the identities of the two tetrahydronaphthols **15** and **18** is obtained by comparing their NMR spectra before and after the addition of the shift reagent Pr(fod)$_3$-d_{27}. Before adding the reagent, the two NMR spectra are almost identical; upon the addition of the reagent to **15** the ortho proton shifts upfield 20 Hz; the methyl group shifts 19 Hz upfield. Addition of the same quantity of the shift reagent to **18** causes a shift of the σ proton about 20 Hz upfield, while the methyl group shifts only 1 Hz upfield.

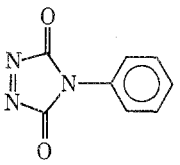
Further elution of the silica gel column with ether yields about 10% of a mixture, which was not characterized further.

The divergence in the course of reaction between dienes **1a** and **1b** can be attributed to the effect of the angular

methyl group. 1a reacts by the "normal" cycloaddition, yielding a peroxide as the major product, with the minor product resulting from a concerted "ene" abstraction of a hydrogen with a shift of a double bond. Diene **1b** has a methyl group at the 4a position, which sterically prevents approach of oxygen from above the plane, thus hindering the formation of a C–O bond. Approach from below the plane of the molecule would yield a bicyclic compound with a strong 1,3-diaxial interaction between the angular methyl group and an ethylenic bridge.

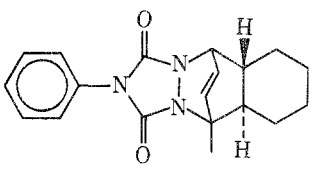


Diels–Alder Reactions. Since dienes **1a** and **1b** show different modes of reaction toward singlet oxygen, which is considered a weak dienophile, it becomes interesting to compare their reactions with a more potent dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione (**19**).



19

Reaction of **1a** and **19** proceeds smoothly and rapidly, as expected, and the crimson-red color of **19** disappears instantly. The only product isolated is the Diels–Alder adduct **20.** The assignment of the structure is based upon the



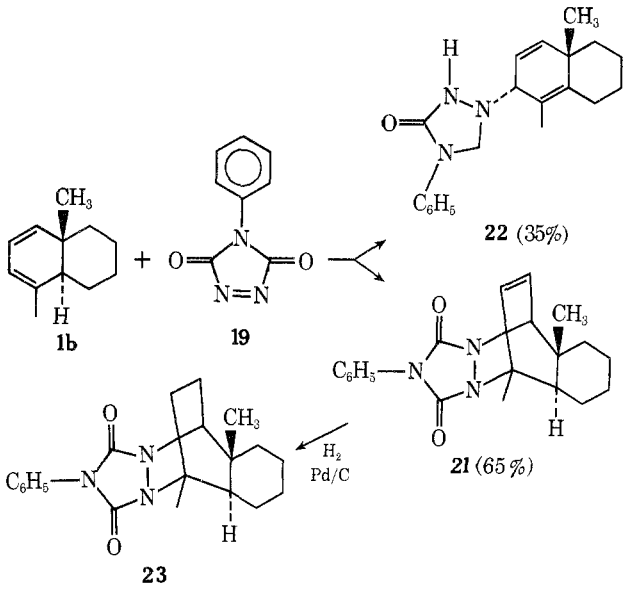
20

following: no N–H stretch in the ir spectrum; the disappearance of the 262-nm uv peak of the diene; the appearance of two olefinic protons in the NMR spectrum, δ 6.1–6.7 (six peaks), similar to those of the photooxygenation product **14**; the NMR shows also two kinds of methyl groups, at δ 1.90 and 1.85, consistent with the diastereomeric nature of the product; finally, the mass spectrum shows a molecular ion peak at *m/e* 323, exhibiting a loss of 82 at *m/e* 241, which arises from a retro-Diels–Alder reaction involving the loss of cyclohexene.

The reaction of diene **1b** with **19** also proceeds rapidly at 0°; two products are isolated by column chromatography, as shown in Scheme IV. The first product (65%) is identified as the Diels–Alder adduct **21**, based upon the following: lack of N–H stretch in the ir, two olefinic protons in the NMR at δ 5.65 and 6.15, the disappearance of the diene uv absorption at 264 nm, and a molecular ion peak M^+ at *m/e* 337. Upon hydrogenation of **21**, 1 mol of hydrogen is taken up, and the mass spectrum has molecular ion peak M^+ at *m/e* 339, with a loss of 97, corresponding to a loss of a hydrogen atom and methylcyclohexene.

The second fraction (35%) is identified as the cross-conjugated diene **22**; ir shows an N–H stretch at 3100 cm^{-1}; also, NMR shows two vinylic hydrogens at δ 5.65, and a shifted angular methyl group to δ 1.02; its molecular ion peak M^+ is at *m/e* 337, and the uv absorption of diene **1b** at 264 nm has disappeared. In **22** and **21**, it is assumed that attack is from the less hindered side, below the plane of the molecule.

Scheme IV
Diels–Alder Reactions of 1b



It is interesting to note here that **20** is such a potent dienophile that it gives a Diels–Alder adduct, even at the expense of a 1,3-diaxial interaction in **1b.** Conversely, **1b** is one of the few cis-conjugated dienes that gives a product, **22,** that is not a result of a [4 + 2] addition.

The exact mode of attack leading to product **22,** namely, the abstraction of a hydrogen with a shift of a double bond, is not yet known fully, but it is assumed here that the reaction proceeds by an "ene" concerted fashion, rather than by a radical process. This is analogous to the reaction of singlet oxygen, and of diethyl azodicarboxylate. An attempt was made to carry out a reaction of **1b** with maleic anhydride. Although not as potent as **19,** this dienophile is very reactive, more so than dimethyl acetylenedicarboxylate.[14] It reacts at room temperature with cyclohexadiene,[15] yielding the Diels–Alder adduct exclusively. However, when maleic anhydride was refluxed in benzene with **1b** up to 48 hr, the starting compounds were recovered unchanged.

Experimental Section

All melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer 137 spectrophotometer. The ultraviolet spectra were measured on a Cary 14 spectrophotometer. The NMR spectra were obtained with a Varian A-60 spectrometer; tetramethylsilane was used as an internal standard for all compounds. Mass spectra were obtained on A. E. I. MS-902 mass spectrometer.

VPC analyses were performed on a Varian Model 90-P instrument employing helium as the carrier gas. Retention times are reported in minutes from the air peak and are designated as t_R, helium flow 60 ml/min except where indicated. Column A refers to a 10 ft × 0.25 in. o.d. column of 20% Carbowax on Chromosorb W. Column B refers to a 10 ft × 0.25 in. o.d. column of 10% SE-30 on Chromosorb W. Thin layer chromatograms (TLC) were made with EM reagents silica gel GF-254 (Type 60) and developed with ether in benzene. For column chromatograms, Fisher silica gel (28–200 mesh) or Fisher alumina (80–200 mesh) was used.

Isolation involved dissolving in the indicated solvent, washing with brine, drying with magnesium sulfate, and evaporation of solvent on a rotary concentrator. Elemental analysis were performed by the Baron Consulting Co., Orange, Conn. *trans*-1,4a-Dimethyloctahydro-*trans*-2-naphthalenone (**3b**) and methyloctahydro-*trans*-2-naphthalenone (**3a**) were prepared by reduction of the corresponding octalones **2b**[6] and **2a**[5] with lithium in ammonia.[16]

***trans*-1,4a-Dimethyl-3α-bromooctahydro-*trans*-2-naphthalenone (5b).** A solution of decalone **3b** (54.0 g, 0.30 mol) in 1500 ml of chloroform at 0° was treated, all at once, with a solution of 2.00 *M* bromine in chloroform (155 ml, 0.31 mol). After an in-

duction period of 45 min, the red color disappeared. Stirring was continued at 0° for an additional 45 min. Addition of water, followed by washing with saturated sodium bicarbonate, then brine, separation of layers, and evaporation of the chloroform yielded a yellow oil, to which hexane (200 ml) was added and the solution was stored overnight under refrigeration. The resulting solid (45.1 g, 52%) was filtered and recrystallized from pentane–ether. It was identified as the 3α-bromo derivative: mp 70–71°; *m/e* molecular peak at 258.0583 (calcd, 258.0616); ir ($CHCl_3$) ν 1720 cm^{-1}; NMR ($CHCl_3$) δ 1.0 (d, 3 H, J = 6 Hz, CH_3-1), 4.80 (1 H, four lines, CHBr, $J_{3a,4a}$ = 13, $J_{3a,4e}$ = 6 Hz). Dehydrohalogenation of 1.0 g of the mother liquor showed (GLC) a mixture of starting decalone **3b**, Δ^1-octalone (**6b**), and Δ^4-octalone (**2b**) in approximately equal quantities.

Anal. Calcd for $C_{12}H_{19}OBr$: C, 55.61; H, 7.39. Found: C, 55.95; H, 7.58.

***trans*-1,4a-Dimethyl-4a,5,6,7,8,8a-hexahydro-*trans*-2(1*H*)-naphthalenone (6b).** The procedures of Holysz[17] and Corey[4] were followed. To a stirred suspension of dry lithium bromide (30.0 g) and lithium carbonate (50.0 g) in 300 ml of dimethylformamide (purified by distilling from benzene) at 125° (oil bath temperature) under nitrogen was added 24.0 g (0.15 mol) of bromo ketone **5b**. Stirring was continued for 3 hr. The reaction mixture was then cooled and filtered, and the solid was washed with hexane; to the combined filtrate and washings, brine was added, then it was extracted with hexane. Isolation by vacuum distillation (108–110°, 5 mm) gave a colorless oil in 80% yield (21.6 g): ir (film) ν 1680 (C=O), with inflection at 1610 cm^{-1} (C=C). NMR exhibits the AB pattern as two doublets, J = 9.5 Hz [centered at (CCl_4) δ 5.72 and 6.65]; also, δ 1.08 (s, 3 H, CH_3-4a), 0.94 (d, J = 6 Hz, CH_3-1). This compound was judged pure (over 98%) by GLC (column A, 160°; t_R 14.5 min).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.68; H, 9.95.

1-Methyl-4a,5,6,7,8,8a-hexahydro-*trans*-2(1*H*)-naphthalenone (6a). To 55.6 ml of a 1.8 *M* ether solution of methyllithium (100 mmol) (Alfa Inorganics, Inc.) at 0°, under nitrogen, was added, dropwise with stirring, 10.10 g (100 mmol) of diisopropylamine[18] (purified by distilling from calcium hydride) in 50 ml of dry ether, containing 20 mg of bipyridyl as indicator. To this deep-red solution of lithium diisopropylamide was added, dropwise over a period of 15 min, 16.3 g (99.8 mmol) of decalone **3a**, until the color turned faint pink. The solution was stirred for an additional 2 min; to this cold (0°) lithium enolate solution was added rapidly a quenching solution of chlorotrimethylsilane [prepared from 30 ml of freshly distilled chlorotrimethylsilane (Aldrich Chemicals) added to 10 ml of anhydrous triethylamine and 50 ml of dry ether, and filtered through a sintered glass funnel]. Within 1 min after addition, a white precipitate (LiCl) began to separate. The mixture was allowed to warm to room temperature, refluxed for 1 hr, and stirred for an additional 2 hr at room temperature. It was then partitioned between pentane and cold $NaHCO_3$. The organic layer was dried, concentrated, and distilled through a short Vigreux column to give a colorless liquid, which on GLC (column A, 160°, t_R 6.5 and 12.0 min) showed a mixture of 85–90% trimethylsilyl enol ether **4** and 10–15% starting decalone **3a**. 1-Methyl-2-trimethylsilyl enol ether 1,4,4a,5,6,7,8,8a-*trans*-octahydronaphthalene (**4**) was isolated by passing the mixture through a column of neutral alumina, eluting with pentane, and fractionally distilling (98–100°, 2 mm).

The pure (less than 2% of isomer) trimethylsilyl enol ether exhibited a mass spectrum *m/e* molecular peak at 238.1755 (calcd, 238.1752) with fragment peaks at 223 (-CH_3·), 75 [HO^+=Si-(CH_3)$_2$], and 73 [$Si^+(CH_3)_3$]; ir (film ν 1675 (sh, C=C), 750 cm^{-1} (br); NMR (CCl_4) δ 0.0 [s, 9 H, $Si(CH_3)_3$], 0.88 (d, J = 6 Hz, CH_3-1), and 4.65 (m, 1 H, CH-3).

To 19.0 g (0.080 mol) of enol ether **4** in 200 ml of chloroform containing 6.5 g (0.080 mol) of sodium acetate at −20° was added 40 ml of a 2.00 *M* Br_2–$CHCl_3$ solution (0.080 mol) in one portion. The red bromine color disappeared instantly. The mixture was stirred for 5 min, then poured into a cold saturated sodium bicarbonate solution and isolated as a light yellow oil. It was characterized as a mixture of 4:1 3β-bromide (NMR δ 4.42, m) to 3α-bromide (δ 4.78, four lines). The solution was directly dehydrobrominated in dry dimethylformamide, as above. Isolation yielded 10.5 g (80% from the decalone) of 1-methyl-4a,5,6,7,8,8a-hexahydro-*trans*-2(1*H*)-naphthalenone (**6a**): ir (film) ν 1680 (C=O), with inflection at 1610 cm^{-1} (C=C); NMR (CCl_4) δ 1.04 (d, J = 6 Hz, 3 H, CH_3-1), 5.80 (d, J = 9 Hz, 1 H, exhibiting long-range coupling, J = 2 Hz, CH-3), 6.64 (two multiplets, J = 9 Hz, 1 H, CH-4). This compound was judged over 95% pure by GLC (column A, 160°; t_R 14.0 min).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.39; H, 9.79. Found: C, 80.44; H, 9.82.

***trans*-1,4a-Dimethyl-2-hydroxy-1,2,4a,5,6,7,8,8a-*trans*-octahydronaphthalene (7b).** To a freshly distilled (40.0 g) portion of aluminum isopropoxide and 500 ml of dry isopropyl alcohol was added 17.8 g of the octalone **6b** in a 1-l. flask fitted with a long Vigreux column.[19] The mixture was allowed to boil gently, the solvent being allowed to escape slowly from the reaction mixture. After 12 hr, the distillate was tested with a solution of 2,4-dinitrophenylhydrazine, the test indicating that no more acetone was being formed. After cooling, the solution was concentrated to ca. a 50-ml volume, and cold 10% hydrochloric acid was added. The resulting acidic solution was extracted with ether and neutralized with bicarbonate. Isolation gave a pale yellow viscous oil, which was distilled at 103–105° (0.5 mm) to give 15.2 g (85%) of the alcohol **7b**, which solidified on standing: ir ($CHCl_3$) ν 3550 cm^{-1} (s, COH). NMR ($CDCl_3$) exhibited the isomeric nature of the product, δ 5.40 and 5.60 (two singlets, vinyl protons), 3.62 and 3.24 (2 m, 1 H, CHOH).

1-Methyl-2-hydroxy-1,2,4a,5,6,7,8,8a-*trans*-octahydronaphthalene (7a). This was prepared as above. Thus 5.0 g of 1-methyl-4a,5,6,7,8,8a-hexahydro-*trans*-2(1*H*)-naphthalenone (**6a**) yielded 4.30 g (85%) of the alcohol **7a** in an isomeric mixture (bp 95–97°, 92 mm): ir ($CHCl_3$) ν 3550 cm^{-1} (strong, COH); NMR ($CDCl_3$) δ 5.50 and 5.65 (two singlets, vinyl protons), 3.70 and 3.78 (2 m, 1 H, CHOH). Upon taking up in pentane, one of the two isomers crystallized, mp 86–87°.

1,4a-Dimethyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (1b). A finely ground mixture of 500 mg of the dimethyl alcohol **7b** and 1.5 g of alumina (Woelm, grade I, neutral) which had been previously treated with 2% (v/w) of pyridine,[20] in a 10 ml flask under nitrogen, was introduced into a preheated oil bath (220°) for 5.5 min. The oil bath was then removed, and the flask immediately cooled in a beaker of cold water. The combined products obtained from four runs were extracted with ether, and the solvent removed on a steam bath. Chromatography on alumina with pentane as eluent yielded the diene as a colorless liquid. (Further elution of the column with benzene gave starting alcohol.) The diene **1b** was distilled (130–132°, 65 mm) giving 920 mg (52%), *m/e* 162.1394 (calcd, 162,1404), judged over 98% pure by GLC (column B, 125°, t_R 12.0 min) at a flow rate of 30 ml helium: uv λ_{max} (95% ethanol) 264 nm (ε 5000); ir (film) ν 1650 (w), 1590 (w), 840 (m), 720 cm^{-1} (s); NMR (CCl_4) δ 0.82 (s, 3 H, CH_3-4a), 5.65 (m, 3 H).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.60; H, 11.25.

1-Methyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (1a). A finely ground mixture of 300 mg of the related 1-methyl alcohol **7a** and 1.2 g of the pyridine-treated alumina in a 10-ml flask under nitrogen was introduced in a preheated oil bath (190°) for 4.0 min. The combined products obtained from six runs were extracted with ether, and the ether evaporated on a steam bath. It was then passed through an alumina column, eluted with pentane, to yield 480 mg (28%) of a colorless liquid. (Further elution of the column with benzene gave starting alcohol.) GLC showed a mixture of two dienes which were separated (column B, 125°, flow rate 30 ml/min He, at 9.5 and 12.0 min). The first product (15%) was identified as the isomeric 1-methyl-1,5,6,7,8,8a-hexahydronaphthalene, **8**: uv λ_{max} (95% EtOH) 267 nm (ε 4800); ir (film) ν 1650 (w), 1690 (w), 700 cm^{-1} (s); NMR (CCl_4) δ 1.05 (d, J = 6 Hz, 3 H, CH_3-1) and 5.6 (m, 3 H). The second product (85%) was identified as the desired trans diene **1a**, which exhibited uv λ_{max} (95% EtOH) 262 nm (ε 4900); ir (film) ν 1650 (w), 1580 (w), 760 (m), 700 cm^{-1} (s); NMR (CCl_4) δ 1.80 (s, 3 H, CH_3-1) and 5.65 (m, 3 H).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.30; H, 10.72.

Photooxygenation of 1-Methyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (1a). A solution of 450 mg (3.05 mmol) of the diene and 30 mg of sensitizer (methylene blue or eosin Y) in 300 ml of 95% ethanol was irradiated with a 300-W light bulb, while a finely dispersed (through a bubbler) stream of oxygen was bubbled through the reaction mixture. A cold water finger was used to keep the temperature of the reaction vessel below 25°. The reaction was complete in 50 min when methylene blue was used as sensitizer, while the use of eosin Y required 12 hr. The solvent was then removed on a rotovap, keeping the temperature below 30°. The resulting product (510 mg) was chromatographed on 20 g of silica gel, using 25% hexane in benzene as eluent, to give five separate components. The first compound to be eluted (25 mg, 5%) was a liquid, identified as 1-methyl-5,6,7,8-tetrahydronaphthalene (**13**):

ir (film) ν 1610, 1440, 760, 720 cm^{-1} (identical with spectrum in Sadtler, prism 8214); NMR (CCl_4) δ 2.15 (s, 3 H, CH_3-1) and 6.88 (s, 3 H, aromatic protons).

The next component (310 mg, 70%) was a pale yellow oil, identified as the diastereomeric mixture of peroxides **14**, *m/e* molecular peak at 180.1152 (calcd, 180.1142) with abundance at 146 − (O_2 + H_2); ir (film) ν 1440, 1360, 1060, 890, 755, 705 cm^{-1}; NMR ($CDCl_3$) δ 1.28 and 1.30 (2 s, 1.2 H and 1.8 H, CH_3-1), 4.28 and 4.30 (2 m, 1 H), 6.0–6.9 (six lines, 2 H).

The third component to be eluted (45 mg, 10%) solidified upon evaporation of eluent. It was recrystallized from petroleum ether, and identified as 1-methyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene (**15**), mp 113–114°, identical with sample prepared from dibromination–dehydrobromination of parent decalone **3a** (undepressed mixture melting point).

The fourth component (25 mg, 5%) was identified as the keto alcohol **16**, identical (spectra, TLC) with ketol obtained from further treatments of the peroxide (see below), crystallized from hexane, mp 58–60°.

Further elution with ether produced 40 mg (10%) of a mixture of at least two products (TLC), which from their retention time and spectra (ir) might contain a hydroperoxide and were not investigated any further.

Structure Proof of Peroxide 14. A. Rearrangement of Peroxide 14 to the Hydroxy Ketone 16. Peroxide **14** (50 mg) was well mixed with 1.5 g of alumina (Woelm, basic, activity I)[21] in a test tube, saturated with ether, and stored at room temperature for 24 hr. The mixture was then transferred to a porous thimble of a Soxhlet extractor, and continuously extracted with ether for 24 hr. Solvent evaporation gave 40 mg (80%) of the hydroxy ketone, identical with **16** (see below).

B. Reduction of Peroxide 14 to the Dialcohol 1,4-Dihydroxy-1-methyl-1,4,4a,5,6,7,8,8a-octahydronaphthalene (17). A solution of 200 mg (1.11 mmol) of peroxide **14** in 10 ml of absolute ethanol was stirred for 8 hr with 2.0 g of 10% palladium on charcoal[10] at room temperature. The mixture was then filtered, and the filtrate concentrated. Crystallization of the residue from ether–pentane afforded 125 mg (63%) of the dialcohol **17**: mp 131–133°; *m/e* M^+ at 182.1320 (calcd, 182.1306), showing abundant fragments at 164 (− H_2O), 146 (− $2H_2O$); ir (KBr) ν 3250, 1440 (inflection 1450), 1060, 1040, 1000, 910, 875, 780, 760, 700 cm^{-1}; NMR (acetone-d_6) δ 1.02 and 1.14 (equatorial and axial CH_3), 3.60 and 3.70 (2 m, 1 H), 5.65 and 5.72 (two kinds of vinyl protons, 2 H).

Chromatography of the mother liquor yielded a mixture of starting peroxide and 1-methyl-5,6,7,8-tetrahydronaphthalene (**13**).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.54; H, 9.96. Found: C, 72.13; H, 9.67.

C. Oxidation of Dialcohol 17 to the Hydroxy Ketone 16. A solution of 100 mg of dialcohol **17** in 3 ml of pyridine was added to the Sarett reagent[11] (prepared from 80 mg of chromium trioxide added to 5 ml of pyridine). After 7 hr of stirring at room temperature, the solution was diluted with ether, and the chromium trioxide–pyridine complex was filtered and washed with ether. The combined organic layers were washed with brine, dried, and concentrated, the last traces of pyridine removed on a vacuum pump, to leave an oil which solidified on standing (90 mg, 90%). The keto alcohol was crystallized from hexane, mp 58–60°, and proved to be identical (similar spectra, and similar aromatic product) with previous keto alcohol: ir (KBr) ν 3400 (s), 1650 (s) (inflection at 1620), 810 (m), 785 (m), 760 cm^{-1} (m); NMR ($CDCl_3$) δ 1.30 and 1.38 (two kinds of CH_3), 5.75 (1 H, d, J = 10 Hz) (two kinds), and 6.62 (1 H, d, J = 10 Hz) (two kinds).

D. Aromatization of Hydroxy Ketone 16. To 75 mg (0.42 mmol) of ketol **16** in 10 ml of benzene was added 30 mg of *p*-toluenesulfonic acid monohydrate,[22] and the mixture was refluxed for 2 hr. After cooling, the solution was poured into a column of 4 g of acid-washed alumina. Elution with benzene gave 40 mg (53%) of 1-hydroxy-4-methyl-5,6,7,8-tetrahydronaphthalene (**18**), recrystallized from petroleum ether: mp 87–88° (reported[13] mp 87.5–88.5°); acetate, mp 81–82° (reported[13] mp 82°); ir (KBr) ν 3300 (s), 1580 (m), 800 (s), 730 cm^{-1} (m); NMR ($CDCl_3$) δ 1.75 (unresolved, 4 H), 2.12 (s, 3 H, CH_3-4), 2.60 (broad, 4 H), 6.47 (1 H, d, J = 7 Hz, ortho proton), and 6.80 (1 H, d, J = 7, meta proton).

Addition of the shift reagent Pr(fod)$_3$-d_{27} caused the σ hydrogen to shift upfield 20 Hz, while the methyl group shifts upfield 1 Hz. The amount of reagent added is equal to about 20% by weight of tetralone.

Synthesis of 1-Methyl-5,6,7,8-tetrahydro-2-naphthol (15). To 166 mg (1 mmol) of decalone **3a** in 10 ml of $CHCl_3$ was added 2.01 ml (2.01 mmol) of a solution of 2.00 *M* bromine in chloroform. The crude bromide was collected as a light brown oil, and dehydrobrominated as before to yield an oil which solidified on standing. Recrystallization from petroleum ether yielded 1-methyltetrahydro-2-naphthol: mp 112–113° (reported[24] mp 113–114°); ir (KBr) ν 3300 (s), 1580 (s), 1580 (m), 800 (s), 725 cm^{-1} (m); NMR ($CDCl_3$) δ 1.76 (broad, 4 H), 2.10 (s, 3 H, CH_3-1), 2.67 (broad, 4 H), 6150 (1 H, d, J = 8 Hz), and 6.80 (1h, d, J = 8 Hz). This phenol was identical with compound **15**, undepressed mixture melting point.

Addition of the shift reagent Pr(fod)$_3$-d_{27}, about 15% by weight of tetralone, caused the σ hydrogen to shift 12 Hz upfield, while the methyl singlet shifts 11 Hz upfield. Further addition to up to 20% by weight caused the σ hydrogen to shift 20 Hz upfield, while the methyl singlet shifts 19 Hz upfield.

Photooxygenation of 1,4a-Dimethyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (1b). Diene **1b** (500 mg, 3.1 mmol) in 300 ml of 95% ethanol was photooxygenated as above, using 25 mg of methylene blue as sensitizer, for 1 hr, the disappearance of the 264-nm peak on uv being noted (the same result is obtained if the reaction is run for 12 hr, sensitized with eosin Y). NMR of the crude product did not show any formation of a peroxide (no peaks between δ 6 and 7), but rather it showed a singlet at δ 5.75, suggesting hydroperoxide formation with shift of double bond. Also, the C-4a methyl group has shifted to δ 1.05. Attempts at column chromatographic separation yielded no peroxide, but a mixture of hydroperoxide and dehydration products (conjugated ketone) (ir, NMR).

The crude hydroperoxide (530 mg) has *m/e* molecular peak at 193.1222 (calcd, 193.1228), with abundant fragments at 175 (− H_2O).

Structure Proof of Hydroperoxides 9 and 10. Hydroperoxide mixture (300 mg) in 5 ml of pyridine was added to the Sarett reagent[23] (made from 250 mg of chromium trioxide to 10 ml of pyridine). The solution was stirred at room temperature for 10 hr. Ether was then added, and the solid chromium trioxide–pyridine complex was filtered and washed with ether. The combined etheral layers were washed with brine and dried. Isolation of the light brown residue by distillation (110–112°, 1 mm) gave a colorless oil (250 mg), shown to be (GLC, column B) a mixture of two major components in a 90:10 ratio, totaling 98% of the total products (two other minor peaks, about 2% total, also appeared). Separation of the two major peaks (column B, 110°, t_R 12.0 and 16.0 min) yielded as the first product (10%) a colorless oil, identified as 1-*exo*-methylene-4a-methyl-4a,5,6,7,8,8a-hexahydro-*trans*-2(4a*H*)-naphthalenone (**12**): ir (film) ν 1660, 1610, 840, 750 cm^{-1}; NMR (CCl_4) δ 0.95 (s, 3 H, CH_3-4a), 5.08 and 5.88 (2 H), 5.90 and 6.70 (2 H, 2 d, J = 10 Hz); uv λ_{max} (95% EtOH) 240 nm (ϵ 9600).

The second compound, also a colorless oil (90%), was identified as the cross-conjugated ketone 1,4a-dimethyl-5,6,7,8-tetrahydro-2(4a*H*)-naphthalenone (**11**): uv λ_{max} (95% ethanol) 238 nm (ϵ 11000); *m/e* molecular peak at 176.1201 (calcd, 176.1201); ir (film) ν 1110, 1620, 1610 cm^{-1}; NMR (CCl_4) δ 1.25 (s, 3 H, CH_3-4a), 1.95 (s, 3 H, CH_3-1), 6.20 and 6.78 (two doublets, J = 10 Hz, CH-3 and CH-4).

This ketone was identical (GLC coinjection, spectra) with an authentic sample prepared from published procedures.[24]

Diels–Alder Reactions. 4-Phenyl-1,2,4-triazoline-3,5-dione[25] with Diene 1b. To 162 mg (1.0 mmol) of diene **1b** in 10 ml of acetone, at 0° with stirring, was added dropwise a solution of 175 mg (1.0 mmol) of the dienophile in 3 ml of acetone; the red color of the dienophile disappeared instantly. At the end of the addition, the solution (faint pink) was stirred for an additional 5 min at 0°, and the solvent was removed under vacuum. Uv shows the disappearance of the diene peak at 264 nm; TLC (85:15 ether–benzene with a drop of triethylamine) showed two spots, R_f 0.71 and 0.58. Chromatography on a column of alumina and elution with ether gave as the first fraction (165 mg, 65%) the Diels–Alder adduct **21**, recrystallized from methanol: mp 142–144° dec; ir (KBr) ν 1750 and 1700 (C=O, strong), 1580 (w), 1390 (s), 775 (s), 740, 730, 690 cm^{-1}; NMR (Me_2SO-d_6, 50°) δ 1.04 (s, 3 H), 1.75 (s, 3 H), 4.40 (d, 1 H, J = 6 Hz), 5.65 (four lines, 1 H), 6.15 (d, 1 H, J = 8 Hz), 7.4 (s, 5 H); mass spectrum M^+ 337.1788 (calcd, 337.1790).

Anal. Calcd for $C_{20}H_{23}N_3O_2$: C, 71.24; H, 6.82; N, 12.46. Found: C, 70.98; H, 6.91; N, 12.33.

The second fraction (90 mg, 35%) was recrystallized from 95% ethanol: mp 184–185°; ir (KBr) ν 3100 (N–H stretch), 1750 and 1700 (C=O), 1490, 1410, 760, 750, 710, and 690 cm^{-1}; NMR (Me_2SO-d_6, 50°) δ 1.10 (s, 3 H), 1.70 (s, 3 H), 5.0 (m, 1 H), 5.65 (four lines, 2 H), 7.40 (s, 5 H); mass spectrum M^+ 337.1788 (calcd, 337.1790). It was identified as 1,4a-dimethyl-2-(4-phenylurazole)-2,4a,5,6,7,8-hexahydronaphthalene (**22**).

Anal. Calcd for $C_{20}H_{23}N_3O_2$: C, 71.24; H, 6.87; N, 12.46. Found: C, 71.33; H, 6.86; N, 12.60.

Hydrogenation of **21** in 95% ethanol with 5% Pd/charcoal as catalyst yielded, after evaporation of solvent, a solid, mp 164–166°, whose mass spectrum has molecular ion peak *m/e* 339.1946 (calcd for **23**, 339.1946) with abundant fragments at 242.

Infrared shows no peak from 3600 to 3100 cm^{-1} (no N–H stretch), and NMR shows no peak from δ 4.5 to 7.5 (no vinylic protons).

4-Phenyl-1,2,4-triazoline-3,5-dione with Diene 1a. To 74 mg (0.50 mmol) of diene **1a** in 5 ml of acetone, at 0°, was added dropwise a solution of 88 mg (0.5 mmol) of the dienophile in 2 ml of acetone. The red color disappeared instantly. The diene peak at 262 nm disappeared on the uv, and TLC (85:15 ether–benzene, with a drop of triethylamine) showed only one spot, R_f 72. Evaporation of solvent and recrystallization from ether–pentane yielded one product in quantitative yield, mp 143–145°, identified as the Diels–Alder adduct, **20**: ir (KBr) ν 1750 (s), 1700 (s), 1440 (m), 1390 (s), 765 (s), 750 (m), 725 (m), and 690 cm^{-1} (m); NMR (acetone-d_6) δ 1.90 and 1.85 (2 s, 3 H, CH_3-1, two kinds), 4.55 and 4.62 (2 m, 1 H), 6.1–6.8 (six lines, 2 H), 7.40 (s, 5 H); mass spectrum M^+ 323.1633 (calcd, 323.1636) exhibiting retro-Diels–Alder reaction at *m/e* 241 (− cyclohexene).

Anal. Calcd for $C_{19}H_{21}N_3O_2$: C, 70.62; H, 6.55; N, 13.00. Found: C, 70.30; H, 6.51; N, 12.72.

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Registry No.—**1a**, 54306-51-3; **1b**, 54306-52-4; **3a**, 21102-88-5; **3b**, 22738-31-4; **4**, 56770-99-1; **5b**, 56763-83-8; **6a**, 56771-00-7; **6b**, 56763-86-1; **7a** isomer A, 56771-01-8; **7a** isomer B, 56771-02-9; **7b** isomer A, 56771-03-0; **7b** isomer B, 56771-04-1; **8**, 56771-05-2; **11**, 707-11-9; **12**, 56771-06-3; **13**, 2809-64-5; **14** isomer A, 56771-07-4; **14** isomer B, 56816-07-0; **15**, 56771-15-4; **16** isomer A, 56771-08-5; **16** isomer B, 56771-09-6; **17**, 56771-10-9; **18**, 4242-05-1; **19**, 4233-33-4; **20**, 56771-11-0; **21**, 56771-12-1; **22**, 56771-13-2; **23**, 56771-14-3.

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A Synthesis and X-Ray Structure Determination of the Photoproducts of *A*-Homocholestan-3-one

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The stereochemistry assigned to the major (**3**) and minor (**2**) photoproducts of *A*-homocholest-4a(5)-en-3-one has been reinvestigated. The synthesis of 5β-ethyl-*A*-norcholestan-3-one is described; the compound is shown to be identical with the dihydro derivative of the major photoproduct. The synthesis of 5β-methyl-*A*-norcholestan-3-one is also described. The minor photoproduct, $C_{28}H_{46}O$, 5α-vinyl *A*-norcholestan-3-one, crystallizes in space group $P2_1$ with cell dimensions a = 10.429 (1), b = 7.369 (1), c = 15.605 (2) Å, β = 94.28 (2)°, and Z = 2. The structure was solved via the calculation of structure invariants and has been refined to a conventional R factor of 0.036. The relation of the absolute stereochemistry and the sign of the CD curves of the major and minor photoproducts and their dihydro derivatives are discussed.

The photochemistry of *A*-homocholest-4a(5)-en-3-one (**1**) and its photoproducts **2** and **3** have proven to be a rich source of mechanistic photochemical information.[2] The specificities of the observed oxadi-π-methane rearrangements and photoisomerizations of the β,γ-unsaturated ketones are summarized in Scheme I and are important in understanding the stereochemical consequences of these photoisomerizations. An essential aspect of these mechanistic evaluations centers on the stereochemical assignment of the major (**3**) and minor (**2**) photoproducts from the direct irradiation of **1**. A previous study of this system by Fisher and Zeeh[3] in 1969 led them to a set of structural assignments based on interpretations of the NMR and CD spectra of the photoproducts. In order to determine the stereochemistry of these compounds unequivocally, parallel studies of the synthesis of **5a** and an X-ray crystallographic structure determination of the minor photoproduct (**2**) were undertaken.