tions containing varying concentrations of methanol and 1,3-cyclohexadiene. Relative quantum yields for formation for products II, III, and IV were determined by glpc. Stern–Volmer plots (eq 1) were

$$\Phi_0/\Phi = 1 + k_q\tau[Q] \qquad (1)$$

linear. k_q and τ represent quenching rate constant and triplet lifetime, respectively. Values for $k_q\tau$ and τ are given in Table I, in which k_q is assumed to be 1.1×10^{10} sec^{-1}.[8]

TABLE I

QUENCHING OF THE REACTION OF 1-PHENYLCYCLOHEXENE WITH METHANOL BY 1,3-CYCLOHEXADIENE IN ACETONITRILE

[Methanol], 10^{-2} M	$k_q\tau$, M^{-1}	τ, 10^{-8} sec
8.3	655	5.95
12.5	484	4.40
16.7	394	3.58
20.8	329	2.99

Rate constants for unimolecular triplet decay (k_D) and the sum of bimolecular rate constants for hydrogen atom and proton abstraction ($k_2 + k_5$) were obtained from the plot of $1/\tau$ *vs.* [methanol] according to eq 2

$$1/\tau = k_D + (k_2 + k_5)[\text{methanol}] \qquad (2)$$

and were found to be 0.60×10^7 and 1.31×10^8 M^{-1} sec^{-1}, respectively. From the product ratios, $k_2 = 1.07 \times 10^8$ M^{-1} sec^{-1} and $k_5 = 0.23 \times 10^8$ M^{-1} sec^{-1}. These values are subject to the assumptions previously stated.

Experimental Section

Materials.—1-Phenylcyclohexene, phenylcyclohexane, and 3-methoxyacetophenone were purchased from the Aldrich Chemical Co. Cyclohexadiene was obtained from Matheson Coleman and Bell. 1-Hydroxymethyl-1-phenylcyclohexane was prepared according to the method of Wilt and Roberts.[9] 1-Methoxy-1-phenylcyclohexane was prepared as follows: A solution of 1-phenylcyclohexanol (8.6 g, 0.05 mol) and concentrated sulfuric acid (3 drops) in 50 ml of methanol was stirred at room temperature for 15 hr. The solution was then poured into a separatory funnel containing 150 ml of ether and 100 ml of a saturated sodium chloride solution. The ether layer was separated, washed with a 5% sodium bicarbonate solution, and dried over anhydrous sodium sulfate. Removal of the ether yielded a liquid which upon distillation gave 1-methoxy-1-phenylcyclohexane (7.5 g, 82%), bp 91–92° (0.6 mm). *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.15; H, 9.67.

Photolysis of 1-Phenylcyclohexene.—A degassed solution of 3 g of 1-phenylcyclohexene in 100 ml of methanol in a quartz vessel was irradiated for 96 hr in a Rayonet photochemical reactor containing lamps having peak emission at 3500 Å. Four major products were isolated by column chromatography (Al_2O_3): phenylcyclohexane (13%), 1-methoxy-1-phenylcyclohexane (26%), 1-hydroxymethyl-1-phenylcyclohexane (7%), and the dimer of 1-phenylcyclohexene (46%). The first three products were identified by comparison of ir spectra with those of authentic samples. The fourth product exhibited a mass spectral parent peak of 316 corresponding to a dimer of 1-phenylcyclohexene. It had the following spectral properties: ir (thin film) 3020, 2900, 1450, 920, 735, 700 cm^{-1}; nmr (60 MH_2, CCl_4) τ 8.5 (m, 16 H), 7.15 (m, 2 H), 2.75 (m, 10 H).

Kinetic Study.—All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450-W). Samples in 12-mm Pyrex vessels were placed in holders approximately 6 cm from the immersion well. The light was filtered by a 1-mm Corex jacket fitted over the light source. Samples in 12-mm Pyrex test tubes were degassed to 10^{-3} mm in three freeze–thaw sequences. After the last thawing, an atmosphere of helium was placed over the solutions. The solutions were irradiated to about 15% completion at a constant temperature of 25.7°. Excess solvent was removed under reduced pressure. The extent of reaction was measured by glpc, 3% SE-30 column, using 1-dodecane as an internal reference. Both the loss of 1-phenylcyclohexene and the production of products was measured, the first method being easier to monitor.

In a typical run, 1 ml of 0.05 M 1-phenylcyclohexene in acetonitrile was added to each of the reaction vessels. To each vessel was also added 1 ml of a 0.5 M methanol in acetonitrile solution and a variable amount of a 0.3 M 1,3-cyclohexadiene in acetonitrile solution. Reaction vessels were then brought to equal volume by the addition of the appropriate amount of acetonitrile.

Attempted Sensitization of the Reaction of 1-Phenylcyclohexene in Methanol.—A solution of 1-phenylcyclohexene (0.80 g, 0.005 mol) in methanol (50 ml) was divided into two portions. To one portion was added 3-methoxy acetophenone (1.5 g, 0.01 mol). Both solutions were degassed, placed under a helium atmosphere, and irradiated at 3500 Å. After 96 hr, the sensitized solution had reacted to about 30% completion while the unsensitized solution had failed to react.

Registry No.—I, 771-98-2; I dimer, 32239-45-5; III, 32249-58-4; methanol, 67-56-1.

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[8] P. J. Wagner and I. Kochvar, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

[9] J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3434 (1962).

The Clemmensen Reduction of 2-Acetonaphthone

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Received May 24, 1971

The Clemmensen reduction of ketones has been reviewed[2] and mechanisms[2b,c,3] accounting for major products have been proposed. We have used the Clemmensen reaction to reduce the carbonyl group of 2-acetonaphthone (**1**) and have observed the hydrocarbon products **3**, **4**, and **5**, formation of which requires reduction of the naphthalene nucleus (Scheme I). The maximum combined yield (16%) of these hydrocarbons was realized when boiling toluene and mossy zinc amalgam were used (Table I). Other combinations of reagents studied and the yields of the resulting volatile hydrocarbons as well as nonsteam-volatile products are reported in Table I.

The conventional Clemmensen reduction[2a] (procedures D and E) of **1** gave low yields (30–40%) of **2** and mainly condensation products which include **7**, **8**, and **9**. In addition, since distillation of the condensation products resulted in some pot residue, polymerization products may be present.

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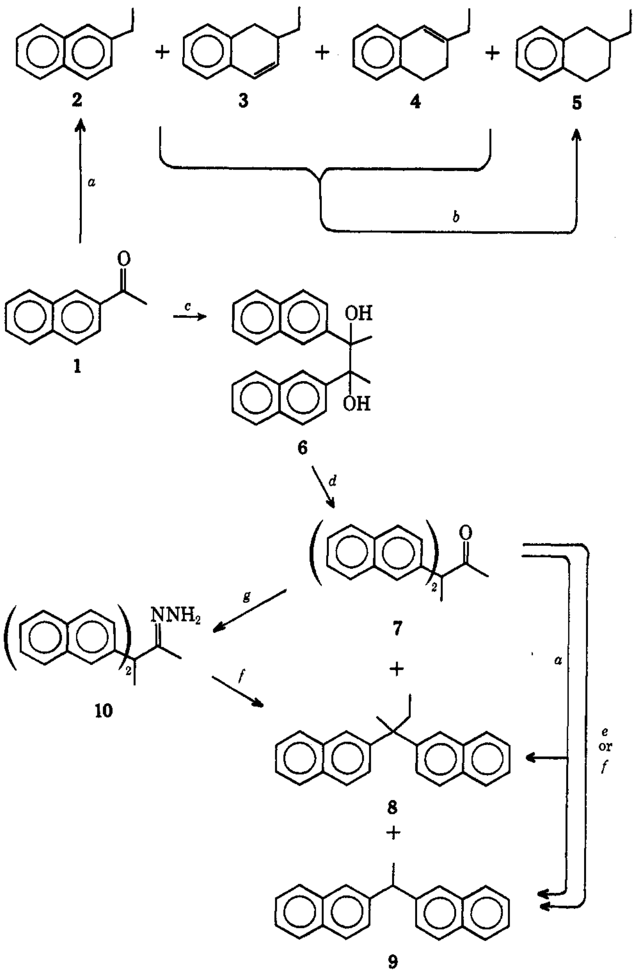
[1] (a) National Science Foundation, Science Faculty Fellowship, 1970–1972, Grant 60052; (b) Undergraduate Research Assistant, 1970.

[2] (a) E. L. Martin, *Org. React.*, **1**, 155 (1942); (b) D. Stascheweski, *Angew. Chem.*, **71**, 726 (1959); (c) J. G. St. C. Buchanan and P. D. Woodgate, *Quart. Rev., Chem. Soc.*, **23**, 522 (1969).

[3] (a) J. H. Brewster, *J. Amer. Chem. Soc.*, **76**, 6361, 6364, 6368 (1954); (b) T. Nakabayashi, *ibid.*, **82**, 3900, 3906, 3909 (1960); (c) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, 1965, p 58.

SCHEME I



[a] Zn(Hg), HCl, toluene—procedure A. [b] Pd/C, H_2. [c] Zn(Hg), HCl, toluene—procedure C. [d] H^+, Δ. [e] NH_2NH_2, OH^-, DEG, Δ. [f] OH^-, DEG, Δ. [g] $NH_2NH_2 \cdot 2HCl$.

TABLE I

CLEMMENSEN REDUCTION OF 2-ACETONAPHTHONE

Procedure	Yield[a] of steam-volatile hydrocarbon products, %				Yield[b] of nonsteam-volatile products, %		
	2	**3**	**4**	**5**	**7**	**8**	**9**
A	61	14	1	1	2	2	1
B	54	<1	<1	<1	21	15	7
C	42[c]	0	0	0	3[d]	34	12
D	40	<1	<1	<1	12	31	12
E	30	<1	<1	<1	17	15	6

[a] Yields based on combined weight of steam-distilled products and their glc[7a] peak ratios. [b] Yields based on weight of distilled products and their glc[7b] peak ratios. [c] A trace of **12** and 1% of **13** were observed through glc.[7a] [d] In addition, 5% of the diol from the pinacol condensation of **1** was isolated from the nonsteam-volatile fraction.

Despite the numerous reports[4a,b] of the Clemmensen reduction of **1**, the formation of **3**, **4**, and **5** has gone unreported. Perhaps this is a result of the frequent use of picric acid in the purification[4b,c] of **2**. However, it should be noted that loss of a methoxy group and hydrogenation of the aromatic nucleus was observed in the Clemmensen reduction of β-(1,5-dimethoxy-4-naphthoyl)propionic acid.[4d]

These results should be considered in selecting a reduction procedure for aromatic ketones, since unwanted side products may be obtained in the Clemmensen reduction. It must be assumed that other examples of this behavior have gone unnoticed.

Our combined instrumental data (glc, ir, nmr, mass, and uv spectra) appeared to exclude those isomers of **3**, **4**, and **5** that could arise by reduction[5] of the aromatic ring *not adjacent* to the carbonyl group. To establish this point rigorously, the hydrocarbon mixture containing **3**, **4**, and **5** was hydrogenated until only **5** remained (Scheme I) and the glc of the latter was compared with that of its isomer, 6-ethyl-1,2,3,4-tetrahydronaphthalene (**11**), prepared by independent Friedel–Crafts synthesis from tetralin.[6] Since the glc[7a] retention times are different, **11** must be absent, and its absence shows that it is not produced by the Clemmensen reduction of **1**; hence isomers of **3** and **4** must also be absent. The stability of **2** to Clemmensen reduction is evidence against its being a precursor to **3**, **4**, or **5**.[8]

Since alcohols and olefins have been shown to be intermediates in reduction at benzylic or allylic positions,[3a,9] we prepared 1-(2-naphthyl)ethanol (**12**) and 2-vinylnaphthalene (**13**) and subjected them to Clemmensen reduction (procedure A). The alcohol **12** was reduced to **2**:**3**:**4**:**5**:**13** (300:13:1:2:69), whereas **13** yielded **2**:**3**:**4**:**5**:**13** (103:5:1:2:85).

As shown in Table I, in the absence of toluene[2a] (procedures D and E) or stirring (procedures B, C, D, and E), the formation of dimeric products is favored. At room temperature in toluene with stirring (procedure C), the pinacol **6** could be isolated. Under conditions of procedure A, the pinacol **6** was readily converted to the expected products **7** and **8** and the unexpected cleavage product **9** in the ratio 45:1:1 as determined by glc analysis.[7b] It is of interest that application of procedure A to **6** yields a lower ratio of **8**:**9** (1:1) than its application to **7**, which gives the **8**:**9** ratio as 15:1.

These findings caused us to use the Wolff–Kishner reduction for the preparation[10a] of **2** in 82–91% yield. However, conventional Wolff–Kishner conditions were unsuited to the reduction of **7** to **8** since base-promoted cleavage[10b] to **9** is a strongly competing side reaction. This side reaction may be minimized by treatment of **7** with hydrazine dihydrochloride and then alkali.[11]

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(4) (a) E. Clemmensen, *Ber.*, **46**, 1837 (1913); (b) see J. E. Faraday and A. S. Freeborn, "Encyclopedia of Hydrocarbon Compounds," Chemical Publishing Co., New York, N. Y., 1964, pp 84–88, for six references; (c) for a convenient procedure for the separation, purification, and cleavage of the picrates of **1** and **15**, see A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1966, p 767; (d) L. F. Fieser and E. B Hershberg, *J. Amer. Chem. Soc.*, **58**, 2382 (1936).

(5) Our data do not exclude exchange of protons in the aromatic ring of **3**, **4**, or **5**.

(6) C. M. Staveley and J. C. Smith, *J. Inst. Petrol., London*, **42**, 55 (1956).

(7) (a) A 0.25 in. (o.d.) × 12 ft copper column containing 80–100 mesh, acid-washed Chromosorb W coated with 25% Carbowax 20M was used in a Beckman GC-2A instrument operating at 220°. (b) A 0.125 in. (o.d.) × 8 ft stainless steel column containing 80–100 mesh, acid-washed, DMCS-treated Chromosorb W coated with 5% of UC W-98 silicone rubber was used in a Hewlett-Packard 5750 instrument operating at 280°. (c) Glc preparative separations were made with an F & M Model 700 chromatograph using a 0.375 in. (o.d.) × 10 ft column containing 80–100 mesh, acid-washed Chromosorb W coated with 25% Carbowax 20M and heated at 150°.

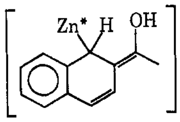
(8) 2-Ethylnaphthalene was recovered unchanged after exposure to the reduction conditions of procedure A for 4 days.

(9) M. Poutsma and E. Wolthus, *J. Org. Chem.*, **24**, 875 (1959).

(10) (a) E. J. Eisenbraun and H. Hall, *Chem. Ind. (London)*, 1535 (1970); (b) B. C. L. Weedon in "Techniques of Organic Chemistry," Vol. XI, Part II, A. Weissberger, Ed., Interscience, New York, N. Y., 1963, p 664.

(11) W. Nagata and H. Itazaki, *Chem. Ind. (London)*, 1194 (1964).

An extension of the mechanisms proposed by Brewster[3a] for the reduction of saturated and α,β-unsaturated ketones accounts for the above mentioned products. The selectivity of reduction in the substituted ring of **1** suggests attachment of zinc as shown in structure **14**.



14

* Zn denotes electron-rich metal surface

Acid-catalyzed isomerization and disproportionation of a mixture of **2**, **3**, **4**, and **5** show that **3** is most affected by the conditions of procedure A[12] and hence is a likely intermediate.

We established by glc analysis[7a] that the ethyl group does not migrate in the Clemmensen reduction (procedure A) of **1** or 1-acetonaphthone (**15**).[13] However, in addition to 1-ethylnaphthalene, three partially reduced hydrocarbons were observed in a combined yield of 5% in the reduction of **15** (procedure A) as compared to 16% total yield of **3**, **4**, and **5** from **1**. The glc retention times[7a] of these unidentified hydrocarbons were similar to those of **3**, **4**, and **5**.

Experimental Section[14]

Zinc Amalgams.—Zinc amalgams were prepared as follows. The desired weight of zinc [Fisher, certified reagent, mossy, or Baker and Adamson, technical (90%) dust] was placed in a flask and covered with an equal weight of distilled water. A volume of 37% hydrochloric acid equal to 5% of that of the water was added with vigorous swirling. After 1 min, the calculated amount of mercuric chloride (Fisher, certified reagent) to give a 3.5% amalgam was added and the resulting mixture was then shaken vigorously for 15 min. The amalgam was washed twice with distilled water and used at once.

General Procedures.—The Clemmensen reductions were carried out using one of the following procedures.

Procedure A.—To 220 g of mossy zinc amalgam was added 85 g (0.50 mol) of 2-acetonaphthone in 250 ml of toluene, 133 ml of distilled water, and 311 ml of concentrated hydrochloric acid. The reaction mixture was refluxed vigorously for 96 hr or until no ketone was present as determined by glc analysis.[7b] Concentrated hydrochloric acid (50 ml) was added about every 8 hr during the reaction period.

Procedure B.—To 22 g of zinc dust amalgam was added 8.5 g (0.05 mol) of 2-acetonapthone in 25 ml of toluene, 13 ml of distilled water, and 31 ml of concentrated hydrochloric acid. The refluxing reaction mixture was vigorously stirred with a mechanical stirrer (Teflon paddle) until no ketone was present.[7b] Concentrated hydrochloric acid (6 ml) was added every 2 hr during the reaction period.

Procedure C.—Same as B, excepting that a Vibro stirrer, Model No. E-1, was used to stir the reaction mixture and the reaction was carried out at 15–25°.

Procedure D.—Same as B, excepting that toluene was not used.

Procedure E.—Same as D, excepting that mossy zinc was used to prepare the amalgam.

At the end of the heating period for any of the above procedures, the reaction mixture was cooled and decanted from the amalgam residue. The residue was washed thoroughly with ether, and the washings were combined with the reaction mixture and extracted with ether. The extracts were combined, washed with water and saturated sodium bicarbonate solution, dried (Na_2SO_4), and concentrated to give a yellow, viscous residue. This residue was steam distilled to separate the more volatile products. The steam distillate was extracted with ether, dried (Na_2SO_4), concentrated, and analyzed by glc.[7a] The residue from the steam distillation was extracted with ether, dried (Na_2SO_4), concentrated, distilled at *ca.* 160° (0.2 mm), and analyzed by glc.[7b] Separation of components was achieved by preparative glc[7c] and by column chromatography on neutral alumina. Final purification was realized by distillation and crystallization. Products were identified by spectral and elemental analysis. Data on products follow.

1,2-Dihydro-2-ethylnaphthalene (**3**).—Bp 232–234°;[15] ir (neat) 3.30, 3.40, 3.48, 3.53, 6.72, 6.88, 7.01, 7.24, 7.77, 8.37, 8.94, 9.64, 11.05, and 11.58 μ; mass spectrum (70 eV) *m/e* (rel intensity) 158 (16), 130 (11), 129 (100), 128 (33) 127 (12), and 27 (7); nmr (CCl_4) δ 8.16–7.77 (m, 4, ArH), 7.44–7.27 (2d, 1, vinylic adjacent to ring), 6.94–6.75 (2d, 1, vinylic), 2.97–2.08 (m, 3, $-CH_2-$benzylic and –CH–allylic), 1.72–1.21 (m, 2, $-CH_2-$nonbenzylic), 0.94 (t, 3, $-CH_3$); uv max (95% EtOH) 212 nm (log ε 4.60), 217.5 (4.63), 224 (4.47) and 261 (4.23).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.26; H, 8.94.

3,4-Dihydro-2-ethylnaphthalene (**4**).[16]—Mass spectrum (70 eV) *m/e* (rel intensity) 158 (41), 143 (29), 129 (100), 128 (43), 127 (13), and 115 (19); nmr (CCl_4) δ 6.98–6.81 (m, 4, ArH), 6.06 (broad s, 1, vinylic), 2.92–2.02 (m, 6, $-CH_2-$benzylic and $-CH_2-$allylic), 1.09 (t, 3, $-CH_3$).

1,2,3,4-Tetrahydro-2-ethylnaphthalene (**5**).—Mass spectrum (70 eV) *m/e* (rel intensity) 160 (54), 131 (63), 115 (23), 105 (20), 104 (100) and 91 (33); nmr (CCl_4) δ 7.02–6.82 (m, 4, ArH), 3.03–2.13 (broad m, 4, $-CH_2-$benzylic), 1.83–0.81 (broad m, 8, $-CH_2-$nonbenzylic, –CH and $-CH_3$); boiling point, ir, and uv agree with reported values.[6]

3,3-Di(2-naphthyl)-2-butanone (**7**).—Mp 144–145°;[17a] ir ($CHCl_3$) 5.86, 6.12, 6.25, 7.37, 7.83, 8.83, 10.37, and 10.51 μ; mass spectrum (70 eV) *m/e* (rel intensity) 324 (1), 282 (25), 281 (100), 266 (21), 265 (29), and 153 (13); nmr (CCl_4) δ 7.89–7.03 (m, 14, ArH), 2.13 (s, 3, $-COCH_3$), 2.00 (s, 3, $-CCH_3$);[17b] uv max (95% EtOH) 219 nm (log ε 5.01), 222 (5.06), 268 (4.10), and 276 (4.10).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; N, 6.21. Found: C, 88.66; H, 6.37.

2,2-Di(2-naphthyl)butane (**8**).—Mp 90–92°; ir (Nujol) 6.15, 6.27, 7.72, 7.87, 8.38, 8.87, 10.56, 11.69 and 12.22 μ; mass spectrum (70 eV) *m/e* (rel intensity) 310 (21), 282 (24), 281 (100), 266 (16), 265 (22), and 153 (15); nmr (CCl_4) δ 7.82–6.82 (m, 14, ArH), 2.28 (quartet, 2, $-C\mathbf{H_2}CH_3$), 1.69 (s, 3, $-C\mathbf{H_3}$), 0.73 (t, 3, $-CH_2\mathbf{CH_3}$); uv max (95% EtOH) 217 nm (log ε 4.99), 231 (5.05), 235 (5.08), 266.5 (4.11), and 275.5 (4.10).

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.73; H, 7.24.

1,1-Di(2-naphthyl)ethane (**9**).—Mp 95–96° (lit.[18] 95°); ir (Nujol) 6.13, 6.24, 8.86, 10.37, 10.51, 11.13, 11.58, and 12.10 μ; mass spectrum (70 eV) *m/e* (rel intensity) 282 (51), 268 (23), 267 (100), 266 (15), 265 (31), 252 (15); nmr (CCl_4) δ 7.92–7.11 (m, 14, ArH), 4.35 (quartet, 1, Ar_2CH), 1.76 (d, 3, $ArCH\mathbf{CH_3}$); uv max (95% EtOH) 217 nm (log ε 5.00), 231.5 (5.08), 267 (4.08), and 276 (4.07).

Catalytic Hydrogenation of a Mixture of 3, 4, and 5.—To 100 mg of 10% Pd/C was added a solution of 1 g of a mixture of **3**,

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(12) Exposure of a mixture of **2**, **3**, **4**, and **5** (6.0:4.6:1.7:1) under the conditions of procedure A for 3 days resulted in the new ratio 5.8:3.4:1.7:1.

(13) MMe. Elphimoff-Felkin and P. Sarda, *Tetrahedron Lett.*, 3045 (1969).

(14) Nmr spectra were obtained with a Varian HR-100 or A-60 spectrometer. Peak positions are reported in terms of parts per million downfield from internal TMS standard in CCl_4 or $CDCl_3$ solvent. Mass spectra were obtained with a CEC Model 21-103C mass spectrometer. Ir and uv spectra were obtained on Beckman IR-5A and Cary 14 spectrophotometers, respectively. Melting points were taken with a Thomas–Hoover capillary melting point apparatus and are corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The petroleum ether, bp 60–68°, was distilled before use.

(15) For Emich's method, see A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 86.

(16) The boiling point, ir, and uv agree with those reported by H. Christol, R. Jacquier, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 248 (1958).

(17) (a) M. P. Balfe, J. Kenyon, and C. E. Searle, *J. Chem. Soc.*, 380 (1951). These authors report the formation of a compound, mp 144–145°, by the treatment of 1,2-dimethyl-1,2-di(2-naphthyl)-1,2-ethanediol, mp 184°, with acetic anhydride for 1.5 hr at reflux. They reported that the compound was probably a mixture of the two possible rearrangement products. However, our data indicate that **7** is formed exclusively when procedure C is used. (b) The distinction between the $-COCH_3$ and $-CH_2\mathbf{CH_3}$ was made by nmr analysis of **7** which had been subjected to acid-catalyzed enolization in D_2O.

(18) R. Quelet, C. Borgel, and R. Durand, *C. R. Acad. Sci.*, **240**, 1900 (1955).

4, and 5 (28:2:1)[7a] in 150 ml of ethanol. This stirred mixture was hydrogenated at 25° and 1 atm for 5 hr. After filtration through Dicalite and evaporation of the solvent, glc[7a] analysis indicated the presence of only **5**.

Wolff–Kishner Reduction of 7 to a Mixture of 8 and 9.—The apparatus and procedure used has been described[10a] except that the product was isolated by ether extraction. From 16.2 g (0.05 mol) of **7** was isolated 14.5 g of crude crystalline reaction products. These products were taken up in petroleum ether[14] and subjected to column chromatography using acidic and basic alumina with petroleum ether[14] as the eluent. Concentration of the eluate gave white crystals (12.9 g) which were shown by glc[7b] to be a mixture of **8**:**9** (3:7).

Base-Catalyzed Cleavage of 7.—The reaction vessel was a 25-ml, one-necked, flat-bottomed, stainless steel flask equipped with a Dean–Stark trap. A ball joint on the trap fitted with a Teflon O-ring provided a seal with the flask. The top of the trap directly above the reaction flask was threaded and fitted with a screw cap containing a glass tube which constituted a helium inlet. The tube was sealed to the screw with silicone rubber. The glass joint above the stopcock of the trap was fitted with a straight-bore glass condenser which acted as the helium outlet. A 0.25-g (0.77 mmol) sample of **7**, 0.3 g of KOH pellets, 0.3 g of NaOH pellets, and 10 ml of diethylene glycol were added to the flask and the assembled system was purged for several minutes with a fast stream of helium. The flow was lessened to maintain a slight positive pressure and the flask was lowered into a preheated (250°) Wood's metal bath. After 3 hr of heating, the reaction mixture was allowed to cool under a helium atmosphere. The resulting brown reaction mixture was extracted with ether. The ethereal extracts were combined, washed with water, dried (Na_2SO_4), and concentrated, giving a dark brown oil. The oil was taken up in petroleum ether[14] and subjected to column chromatography using a silica gel, neutral alumina column, and petroleum ether as the eluent. Concentration of the eluate gave a faint yellow oil which crystallized on trituration with petroleum ether.[14] Recrystallization from 95% ethanol gave 150 mg (70%) of **9** as white crystals: mp 95–96° (lit.[18] mp 95°).

Clemmensen Reduction of 7.—Two grams (6.2 mmol) of **7** was reduced using the conditions of procedure A. After 4 days, less than 10% of **7** had reacted to give **8**:**9** (15:1) as determined by glc analyses.[7b] However, addition of powdered zinc amalgam resulted in 95% reduction in an additional 24 hr to give 1.1 g (54% combined yield) of a mixture of **8**:**9** (15:1).[7b]

Wolff–Kishner Reduction of 7 to 8.—By use of procedure A,[11] 0.65 g (2 mmol) of **7** gave 0.55 g (88%) of **8**.

Isolation and Reduction of 6.—Steam distillation of the products from the reduction of 25 g (0.15 mol) of **1**, using procedure C, gave 12 g of nonvolatile residue. This residue was triturated with hot petroleum ether[14] and the liquid was decanted leaving crude **6**. Recrystallization from 1:1 chloroform–ethanol gave 1.1 g (4.5%) of white, crystalline **6**: mp 182–184° (lit.[17a,19] mp 184°); ir ($CHCl_3$) 2.80, 6.25, and 8.88 μ; mass spectrum (70 eV) *m/e* (rel intensity) 281 (9), 172 (25), 171 (31), 155 (10) 127 (13), and 43 (100); nmr ($CDCl_3$) δ 7.96–7.13 (m, 14, ArH), 2.30 (s, 2, –OH), 1.65 (s, 6, $-CH_3$); nmr (CD_3COCD_3) δ 8.03–7.23 (m, 14, ArH), 2.04 (broad s, 2, –OH), 1.63 (s, 6, $-CH_3$); uv max (95% EtOH) 219 nm (log ϵ 5.42), 232 (5.43), 269 (4.09), and 277 (4.01).

Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47. Found: C, 83.94; H, 6.36.

The reduction of 0.24 g (0.7 mmol) of **6** using procedure A gave **7**:**8**:**9** (5:1:1) as shown by glc analysis.[7b]

Reduction of 1-Acetonaphthone (15).—The reduction of 8.5 g (0.05 mol) of **15** using procedure A gave 1-ethylnaphthalene in 82% yield as shown by glc analysis.[7a] Three other volatile hydrocarbons were also observed by glc analysis (combined yield 5%); they had retention times like those of **3**, **4**, and **5**. The nonvolatile fraction showed three major components in a ratio of 1:1.25:1.50, which were similar in retention times to **7**, **8**, and **9**.

6-Ethyl-1,2,3,4-tetrahydronaphthalene (**11**).—This compound was prepared as outlined previously[6] except that nitroethane was used as solvent: mass spectrum (70 eV) *m/e* (rel intensity) 160 (41), 145 (35), 132 (27), 131 (100), 117 (21), and 115 (20); nmr (CCl_4) δ 6.91–6.59 (m, 3, ArH), 2.99–2.27 (broad m, 6, $ArCH_2-$), 2.01–1.52 (broad m, 4, $-CH_2$-nonbenzylic), 1.17 (t, 3, $-CH_3$). The boiling point, ir, and uv agreed with reported values.[6]

1-(2-Naphthyl)ethanol (**12**).—A 75.6-g (0.44 mol) sample of **1** was reduced with diisobutylaluminum hydride[20] to give 69.6 g (95%) of crude **12** which, when recrystallized twice from petroleum ether,[14] gave 67.1 g (88%) of pure **12**, mp 70–72° (lit.[21] mp 71–72°).

2-Vinylnaphthalene (**13**).—A sample of **13** was prepared from **12** in 41% yield as described.[22] Conversion of the crude product to picrate and its recrystallization from methanol gave yellow needles, mp 90–92° (lit.[22] mp 91–92°). Chromatographic regeneration gave 2.5 g (35%) of **13**, mp 64–66° (lit.[21,22] mp 65–66°). Glc analysis indicated the purity of **13** to be 98%.[7a]

Registry No.—**1**, 93-08-3; **3**, 31861-77-5; **4**, 31861-78-6; **5**, 32367-54-7; **6**, 32298-43-4; **7**, 32298-44-5; **8**, 32298-45-6; **9**, 32298-46-7.

Acknowledgments.—We are grateful to the National Science Foundation and the American Petroleum Institute for partial support. We thank Dr. O. C. Dermer for reading the manuscript.

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Cholesterol 26-Hydroperoxide[1]

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Received June 1, 1971

Recent investigations have shown that the autoxidation of cholesterol proceeds *via* hydroperoxide formation at the tertiary 20α and 25 positions as well as the secondary 24 position of the side chain.[2] The present communication reports the isolation of another cholesterol hydroperoxide identified as 3β-hydroxy-5-cholestene 26-hydroperoxide (I). Upon sodium borohydride reduction of the hydroperoxide I, a single diol was obtained which was identified as 5-cholestene-3β,26-diol (II) by comparison of its chromatographic and physical properties with those of an authentic sample. Further proof of the structure of compound I was obtained from its infrared absorption at 3610 and 3540 cm^{-1}, characteristic of the OH stretching of the hydroxyl and hydroperoxyl groups, respectively; from its proton magnetic resonance spectra which shows the C_{27}-methyl protons as a three-proton doublet at δ 0.94 and the C_{26}-methyl protons as a two-proton multiplet at δ 3.92, deshielded 2.05 ppm by the 26-hydroperoxyl group; and from its high-resolution mass spectral analysis. The four major thermal decomposition products of the compound I were identified by their chromatographic and spectral properties as 5-cholestene-3β,26-diol (II), 3β-hydroxy-5-cholesten-26-al (III),

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[1] (a) Supported by the Medical Research Council of Canada (Grant MA-4051) and the Conseil de la Recherche Médicale du Québec. (b) Presented at the 14th Annual Meeting of the Canadian Federation of Biological Societies, Toronto, June 1971, Abstract 367.

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