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Some Decomposition and Rearrangement Products of Decahydronaphthalene Hydroperoxide

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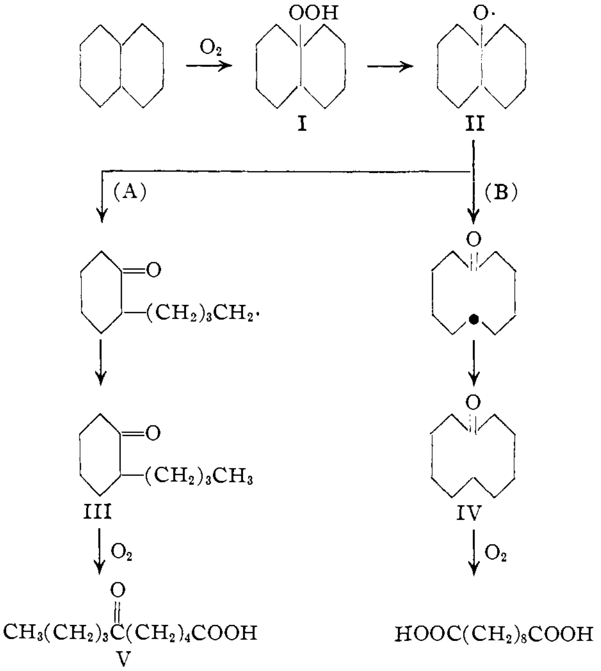
The principal acidic product of the reaction of decahydronaphthalene with oxygen, under conditions favoring decomposition of the intermediate decahydronaphthalene hydroperoxide by a free radical mechanism, was 6-oxodecanoic acid. Adipic and sebacic acids also were isolated. The keto acid was also obtained in the thermal decomposition of decahydronaphthalene hydroperoxide. A postulated intermediate, 2-*n*-butylcyclohexanone, resulted from the reduction of decahydronaphthalene hydroperoxide with ferrous sulfate. From 6-oxodecanoic acid were prepared 6-hydroxy- and 6-aminodecanoic acids and the corresponding lactone and lactam. Decahydronaphthalene hydroperoxide can be rearranged directly to 6-hydroxycyclodecanone by sulfuric acid in aqueous *t*-butyl alcohol.

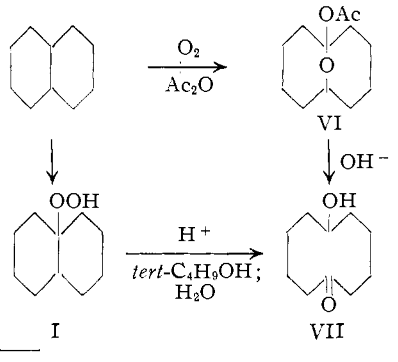
Previous investigations of the reactions of oxygen[1] and ozone[2] with decahydronaphthalene in the liquid phase have given products containing mixtures of acids which were not characterized. Oxidation of decahydronaphthalene in the vapor phase[3] also resulted in acidic degradation products, all having six or less carbon atoms. The acids resulting from the liquid phase oxidation have now been identified, affording evidence for the mechanism of decomposition of decahydronaphthalene hydroperoxide (I).



The intermediate free radical II can rearrange by either route A, yielding after abstraction of a hydrogen atom from another molecule of decahydronaphthalene, 2-*n*-butylcyclohexanone (III), which undergoes further oxidation to an oxodecanoic acid; or by route B to cyclodecanone (IV) whose oxidation product is sebacic acid. The oxidation was carried out at 120–130° in the presence of cobalt 2-ethylhexanoate, which facilitates decomposition of the hydroperoxide by a free radical mechanism. Route A was found to be greatly favored since 6-oxodecanoic acid (V) was the principal acidic product and only small amounts of sebacic acid were isolated. Adipic and butyric acids, products of further oxidation of V, were also present in the reaction mixture. The neutral portion of the oxidation product contained *trans*-4a-hydroxydecahydronaphthalene, a common oxidation product of decahydronaphthalene,[2b] and a mixture of ketones, mostly octahydro-2(1H)- and -1(2H)naphthalenones.

6-Oxodecanoic acid (V, 21% yield) and *trans*-4a-hydroxydecahydronaphthalene were also products of thermal decomposition of the hydroperoxide I in boiling isopropylbenzene. The postulated intermediate, 2-*n*-butylcyclohexanone, was prepared from *trans*-4a-hydroperoxydecahydronaphthalene in 80% yield by reduction with ferrous sulfate. No cyclodecanone was isolated in this experiment. Thus, the rearrangement of the free radical II proceeds predominantly by scission of the 1–8a bond.

Decomposition of *trans*-4a-hydroperoxydecahydronaphthalene (I) by an ionic mechanism has been shown by Criegee[4] to give products arising from scission of the 4a–8a bond. Thus, the acetate and benzoate of I rearrange on warming to esters of 11-oxabicyclo[4.4.1]undecan-1-ol (VI) which can be hydrolyzed to 6-hydroxycyclodecanone (VII). We have found that 11-oxabicyclo[4.4.1]undec-1-yl acetate can be obtained in one step from decahydronaphthalene by free radical-initiated oxidation at 115–120° in the presence of acetic anhydride. The decomposition of the intermediate hydroperoxide also proceeds to a small de-



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gree by a free radical mechanism in this reaction as evidenced by the formation of 6-oxodecanoic acid in 0.4% conversion. We have also found that acid-catalyzed rearrangement of *trans*-4a-hydroperoxydecahydronaphthalene to 6-hydroxycyclodecanone can be carried out in one step in 25% yield in *t*-butyl alcohol. Criegee[5] has reported that traces of unidentified ketones were formed along with 1,2,3,4,5,6,7,8-octahydronaphthalene from the hydroperoxide in boiling acid solution.

The structure of 6-oxodecanoic acid, unknown at the time of this work, was proved by synthesis of methyl 6-oxodecanoate from *n*-butylcadmium and δ-carbomethoxyvaleryl chloride and subsequent hydrolysis to the acid. The acid V was reduced by the Clemmensen method to decanoic acid. The acid V has been reported to be formed in 4% yield in the oxidation of 1-butylcyclohexanol with chromic acid.[6]

Hydrogenation of 6-oxodecanoic acid over Raney nickel at 125° resulted in ε-butylcaprolactone which upon hydrolysis yielded 6-hydroxydecanoic acid. The new hydroxy acid could be oxidized back to 6-oxodecanoic acid, showing that no shifting of the hydroxyl took place in the lactonization or hydrolysis steps. The oxime of the keto acid V was hydrogenated at 75° to 6-aminodecanoic acid, which at 225–255° was converted to ε-butylcaprolactam and a polyamide.

Experimental

The decahydronaphthalene used was commercial "Decalin" solvent, consisting of a mixture of *cis* and *trans* isomers.

Cobalt Salt-catalyzed Oxidation of Decahydronaphthalene.—A stream of oxygen was bubbled by means of a sintered glass gas inlet tube through 1810 g. of decahydronaphthalene containing 1 ml. of cobaltous 2-ethylhexanoate at 120–127° for eight hours. The reaction was sufficiently exothermic so that little external heating was required. The product was separated from a small water layer and dried over magnesium sulfate. The unchanged decahydronaphthalene (1170 g.) was removed by distillation under reduced pressure. Distillation of the residue gave: A, crude 4a-hydroxydecahydronaphthalene, 150 g. (26%), b.p. 66–76° (1.5 mm.); B, mixture of ketones, 129 g. (22%), b.p. 76–91° (5 mm.); and C, residue, 360 g.

Fraction A partly crystallized to *trans*-4a-hydroxydecahydronaphthalene (m.p. 50–51°) which was also shown to be the principal component of the uncrystallized portion by conversion to its chromate ester, m.p. 88°; reported[7] 86.8°. Fractionation of fraction B gave as principal cut (b.p. 79.5–80.5° at 4 mm.) *trans*-octahydro-2(1H)naphthalenone; semicarbazone, m.p. 222–230° dec.; reported[8] 228–230°. The residue (C) from distillation of the crude oxidation product was taken up in ether and extracted twice with 5% sodium hydroxide. The aqueous layer was acidified and extracted with ether. The dried extract (100 g.) was distilled to give: a forerun (mostly butyric acid); (1) crude 6-oxodecanoic acid, b.p. 150–163° (2.5 mm.), 50.6 g. (7%); and (2) b.p. 165–180° (3–5 mm.), 20.4 g. From fraction 2 was crystallized some sebacic acid, identified further as its amide. Fraction 1 when chilled crystallized to give 6-oxodecanoic acid, m.p. 44° after two recrystallizations from petroleum ether; reported m.p.[6] 46°.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.69; H, 9.74; neut. equiv., 186. Found: C, 64.73, 64.57; H, 9.87, 9.83 neut. equiv., 186, 186.

Semicarbazone: m.p. 158–158.5° (from ethanol–water); reported m.p.[6] 164°.

Anal. Calcd. for $C_{11}H_{21}O_3N_3$: C, 54.30; H, 8.70; N, 17.28. Found: C, 54.46, 54.49; H, 8.65, 8.85; N, 17.80, 17.65.

In a similar experiment, 2500 g. of decahydronaphthalene and 1 ml. of cobaltous 2-ethylhexanoate were treated with oxygen for 26 hours at 120–130°. The product was washed with water and extracted with 500 ml. of 10% sodium hydroxide. The alkaline layer was acidified with hydrochloric acid and extracted with ether. The extract (119 g.) yielded 4.8 g. of solid 6-oxodecanoic acid by crystallization and another 28.1 g. by distillation at 130–157° (2 mm.). A higher-boiling fraction (17.8 g.), b.p. 157–168° at 2 mm., partially crystallized to adipic acid, which did not depress the melting point of an authentic sample.

The neutral portion of the oxidation product gave, as in the previously described experiment, *trans*-4a-hydroxydecahydronaphthalene (18.2 g.) and ketone (142 g.) fractions. The latter (b.p. 87–93° at 3.5 mm.) gave a semicarbazone, m.p. 222–230° and a 2,4-dinitrophenylhydrazone, m.p. 221–222°. *trans*-Octahydro-1(2H)naphthalenone-2,4-dinitrophenylhydrazone is reported[8] to melt at 222–222.5°.

The crude products of the oxidation mixture can also be separated by steam distillation. The decahydronaphthalene, *trans*-4a-hydroxydecahydronaphthalene and ketones are volatile with steam; 6-oxodecanoic acid is not.

Oxidation of Decahydronaphthalene in the Presence of Acetic Anhydride.—Oxygen was passed into a solution of azodicyclohexanecarbonitrile (5 g.) and acetic anhydride (620 g.) in decahydronaphthalene (1840 g.) at 115–120° for eight hours. The exothermic nature of the reaction maintained the temperature with little external heating. The solution was washed with water four times, then twice with 250-ml. portions of 5% sodium hydroxide, then again with water. The alkaline extracts yielded 9 g. (2% on the basis of recovered decahydronaphthalene) of 6-oxodecanoic acid. The organic layer was dried over magnesium sulfate and distilled to give 1340 g. of unchanged decahydronaphthalene and hydroxydecahydronaphthalene and ketone fraction (274 g.), b.p. 97–131° at 10 mm. The residue gave crystalline 11-oxabicyclo[4.4.1]undec-1-yl acetate (74 g., 15%) and an oil (140 g.). The ester melted at 104° after recrystallization from ethyl alcohol–water; reported[4] 104.5°. The hydroxydecahydronaphthalene and ketone fractions (1055 g.) from four such runs were fractionated through a 24" glass helix-packed column in order to characterize the ketones more fully. After removal of *trans*-4a-hydroxydecahydronaphthalene (200 g.) at 95–103° (13.5 mm.), ketone A (240 g., principal cut, b.p. 100–101° (9 mm.), $n^{25}D$ 1.4842), ketone B (140 g., b.p. 114–115° (13.5 mm.), $n^{25}D$ 1.4812) and ketone C (117 g., b.p. 87–92° (3 mm.), $n^{25}D$ 1.4768) were collected. Ketone A gave an oxime, m.p. 167°, a 2,4-dinitrophenylhydrazone, m.p. 227–229°, and a semicarbazone, m.p. 212–214°; ketone B gave a semicarbazone, m.p. 171–173°; ketone C was not further investigated. The semicarbazones from ketones A and B each had the composition of a semicarbazone of an octahydronaphthalenone.

Anal. Calcd. for $C_{11}H_{19}ON_3$: C, 63.23; H, 9.15; N, 20.08. Found (A): C, 63.18, 63.28; H, 9.51, 9.75; N, 20.19, 20.12. Found (B): C, 63.83, 63.42, 63.03, 63.13; H, 8.92, 9.17, 9.11, 9.22; N, 20.13, 20.01.

The melting points of the semicarbazones indicate that the ketones are *trans*- and *cis*-octahydro-2(1H)naphthalenone. The reported values[8] are 228–230° and 182–185°, respectively. The semicarbazones of *trans*- and *cis*-octahydro-1(2H)naphthalenone melt at 270° and 230–234°.[8]

6-Oxodecanoic Acid (V) from Decahydronaphthalene Hydroperoxide.—A solution of *trans*-4a-hydroperoxydecahydronaphthalene[9] (40 g.) in isopropylbenzene (360 g.) was heated in a nitrogen atmosphere for four hours by means of an oil-bath at 152–155°. After removal by distillation of the solvent and *trans*-4a-hydroxydecahydronaphthalene (22.2 g., 62%), the 6-oxodecanoic acid, identical with that from direct oxidation of decahydronaphthalene, was distilled at 122–150° (0.9 mm.), 9.1 g. (21%). The lower-boiling fractions of the product were shown to contain some acetophenone, identified as its 2,4-dinitrophenylhydrazone.

Structure Proof of 6-Oxodecanoic Acid. A. Synthesis.—Di-*n*-butylcadmium was prepared[10] by addition of 33 g. of

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(7) K. I. Ivanov and V. K. Savinova, *Compt. rend. acad. sci. U.R.S.S.*, **48**, 31 (1945) [*C. A.*, **40**, 4706 (1946)].

(8) D. Biquard, *Bull. soc. chim.*, **8**, 725 (1941).

(9) R. Criegee, *Ber.*, **77**, 22 (1944).

(10) (a) J. Cason and F. S. Prout, This Journal, **66**, 46 (1944); (b) J. Cason, *ibid.*, **68**, 2080 (1946).

anhydrous cadmium chloride to a Grignard solution prepared from 60 g. of *n*-butyl bromide, 8 g. of magnesium and 200 ml. of ether. After replacement of the ether with benzene, a solution of δ-carbomethoxyvaleryl chloride (prepared by warming 26 g. of methyl hydrogen adipate and 25 g. of thionyl chloride at 50–70° for three hours with subsequent removal of the excess thionyl chloride by distillation) in 50 ml. of benzene was added over a 15-minute period to the di-*n*-butylcadmium solution. Stirring was continued for another hour; ice-cold dilute hydrochloric acid was added and the combined benzene layer and extracts of the water layer dried over potassium carbonate. After evaporation of the solvent, the residue was distilled to give as principal fraction 13.9 g. of methyl 6-oxodecanoate boiling at 97–103° (3.5 mm.), $n^{25}\text{D}$ 1.4376.[11] A solution of 13.0 g. of the distillate in 10 ml. of ethyl alcohol was refluxed with 50 ml. of 10% potassium hydroxide for three hours; 0.1 g. of nonsaponifiable material was removed from the solution, which was acidified with hydrochloric acid and extracted with ether. The evaporated extract was crystallized from chloroform–petroleum ether to give 9.4 g. of 6-oxodecanoic acid, m.p. 45–46°; a mixed melting point with the acid from oxidation of decahydronaphthalene showed no depression. The acid gave a semicarbazone, which did not depress the melting point of the semicarbazone from the acid obtained in the oxidation.

B. **Clemmensen Reduction.**—Ten grams of mossy zinc was stirred for five minutes with 1 g. of mercuric chloride dissolved in 10 ml. of water and 0.5 ml. of concd. hydrochloric acid. The amalgamated zinc was added to a mixture of 10 ml. of concd. hydrochloric acid, 5 ml. of water and 0.9 g. of 6-oxodecanoic acid. The reaction mixture was refluxed for three hours; an additional 5 ml. of concd. hydrochloric acid was added and refluxing continued for five hours. Upon cooling, the oily upper layer solidified, m.p. 28.5–29.5°. A mixed melting point with an authentic sample of decanoic acid was not depressed. The *p*-bromophenacyl ester melted, after purification, at 64–65°, and the melting point was not depressed when mixed with the corresponding derivative of authentic decanoic acid.

2-*n*-Butylcyclohexanone from Decahydronaphthalene Hydroperoxide.—To a stirred solution of ferrous sulfate heptahydrate (140 g., 0.5 mole) and concd. sulfuric acid (20 ml.) in water (300 ml.) and ethyl alcohol (100 ml.) was added *trans*-4a-hydroperoxydecahydronaphthalene (17 g., 0.1 mole). After 30 minutes, all the solid had disappeared and an oil had separated, 12.3 g. (80%), b.p. 90–92° (13 mm.), $n^{25}\text{D}$ 1.4620; semicarbazone, m.p. 138.5–139.5°; 2,4-dinitrophenylhydrazone, m.p. 109–110°. The latter derivative had the composition of the 2,4-dinitrophenylhydrazone of 2-*n*-butylcyclohexanone.

Anal. Calcd. for $C_{16}H_{22}O_4N_4$: C, 57.50; H, 6.64; N, 16.79. Found: C, 56.93, 57.34, 57.31; H, 6.55, 6.66, 6.65; N, 16.78, 16.64.

The properties reported in the literature for 2-*n*-butylcyclohexanone and its derivatives are conflicting: b.p. 86° (22 mm.), $n^{29}\text{D}$ 1.4504[12]; b.p. 90–91° (10 mm.), $n^{14}\text{D}$ 1.4603[13]; b.p. 97–100° (17 mm.)[14]; semicarbazone, m.p. 143–144°,[13] 150°[14]; 2,4-dinitrophenylhydrazone, m.p. 113–114°.[12]

ϵ-Butylcaprolactone.—A solution of 6-oxodecanoic acid (30 g.) in ethyl alcohol (140 ml.) was hydrogenated over Raney nickel at 2000 lb./sq. in. for three hours at 125°. The resulting oil was distilled to give 13.4 g. (49%) of ϵ-butylcaprolactone, b.p. 120–127° (5 mm.), $n^{25}\text{D}$ 1.4556. Fractionation gave a pure sample, b.p. 117° (3 mm.), $n^{25}\text{D}$ 1.4564; infrared spectrum, lactone carbonyl absorption at 5.75 μ.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.56; H, 10.66. Found: C, 70.29, 69.61, 69.96; H, 10.79, 10.62, 10.88.

6-Hydroxydecanoic Acid.—ϵ-Butylcaprolactone (13 g.) was saponified with potassium hydroxide (6 g.) in boiling water (250 ml.). Four hours were required for disappearance of the non-aqueous phase. The solution was acidified and extracted with ether. The extract yielded 11 g. (77%) of 6-hydroxydecanoic acid, m.p. 30–33°. After several recrystallizations from chloroform–petroleum ether, the acid melted at 36°.

Anal. Calcd. for $C_{10}H_{20}O_3$: C, 63.77; H, 10.70. Found: C, 63.69, 63.38; H, 10.70, 10.64.

To a 200-mg. sample of the hydroxy acid was added a solution of 80 mg. of potassium dichromate in 15 ml. of concd. sulfuric acid and 50 ml. of water. After 15 minutes, the solution was poured into cold water. An ether extract yielded 160 mg. (81%) of 6-oxodecanoic acid. Neither the acid nor its semicarbazone depressed the melting points of authentic samples, prepared as described above.

6-Aminodecanoic Acid.—6-Hydroxyiminodecanoic acid, an oil, was prepared from 6-oxodecanoic acid and hydroxylamine hydrochloride in a boiling pyridine–ethyl alcohol mixture and in aqueous sodium hydroxide. Each method gave a 95% yield. A solution of the hydroxyimino acid (8.6 g.) in methanol (35 ml.) was hydrogenated over Raney nickel at 75° and 2000 lb./sq. in. The product (8.0 g., 100%) melted at 180–185°. Pure 6-aminodecanoic acid was obtained by recrystallization from ethyl alcohol–ether and melted at 196–197° dec.

Anal. Calcd. for $C_{10}H_{21}O_2N$: C, 64.12; H, 11.30; N, 7.48. Found: C, 64.16, 63.90; H, 11.26, 11.32; N, 7.48, 7.47.

ϵ-Butylcaprolactam.—A small sample of 6-aminodecanoic acid and one drop of water were heated in a sealed, evacuated tube for three hours at 225° and then for two hours at 255° under vacuum after unsealing. The ϵ-butylcaprolactam, which sublimed to the top of the tube, was purified by resublimation, m.p. 70°.

Anal. Calcd. for $C_{10}H_{19}ON$: C, 70.93; H, 11.31; N, 8.27. Found: C, 71.09; H, 11.43; N, 8.21, 8.29.

The other product of the dehydration of 6-aminodecanoic acid was a glassy polymer, m.p. 105°, from which a brittle filament could be melt-drawn.

6-Hydroxycyclodecanone (VII) by Rearrangement of *trans*-4a-Hydroperoxydecahydronaphthalene.—A solution of 20.0 g. of *trans*-4a-hydroxyperoxydecahydronaphthalene, 5.5 ml. of concd. sulfuric acid and 3 ml. of water in 250 ml. of *t*-butyl alcohol was heated at reflux temperature for seven hours. After neutralization with sodium bicarbonate, the solution was dried over potassium carbonate and distilled. The distillate (b.p. 70–120° at 3–4 mm.) crystallized partially when triturated with cold petroleum ether to give 5.0 g. (25%) of 6-hydroxycyclodecanone, m.p. 63–68°. After recrystallization from chloroform–petroleum ether, the product did not depress the melting point of an authentic sample.

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[11] T. Moroe, *J. Pharm. Soc. Japan*, **70**, 416 (1950) [*C. A.*, **45**, 2396 (1951)] gives b.p. 119–120° (3 mm.) for ethyl 6-oxodecanoate. The method of preparation is not reported in the abstract.

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[13] G. Vavon and A. Guedon, *Bull. soc. chim.*, **47**, 901 (1930).

[14] M. Tiffeneau, B. Tchoubar and M. Saiaslambert, *ibid.*, **14**, 445 (1947).