phase was removed, washed several times with water, dried, and fractionally distilled.

10-Ketoundecanoic Acid.—Run 2 described before and in Table I was duplicated except that 27.5 g. (0.15 mole) of 10-undecenoic acid was added over a 2-hr. period in place of dodecene-1. The product was finally poured into excess, cold, dilute hydrochloric acid and the precipitated solid was isolated, dried, and taken up in benzene. After filtration and removal of the benzene the product was extracted with cold pentane to leave 18.0 grams of 10-ketoundecanoic acid, m.p. 52°, while the pentane contained 7.5 g. of cruder product. The keto acid was recrystallized from ethyl acetate, m.p. 57–59° (lit.[10] m.p. 58–60°).

Anal. Calcd. for $C_{11}H_{20}O_3$: neut. equiv., 280. Found: neut. equiv., 282.

2-Dodecanone Using *p*-Benzoquinone.—Palladium chloride (0.020 mole), *p*-benzoquinone (0.10 mole), 1-dodecene 0.10 mole), and 50 ml. of DMF were placed in a 250-ml. round-bottomed flask fitted with a stirrer, condenser, thermometer, and dropping funnel, and 1 ml. of water was added from the dropping funnel. The solution temperature rose to 70°. After 0.25 hr. an additional 1 ml. of water was added, and heat was applied to maintain a 70° temperature. A third milliliter of water was introduced at 0.75 hr. and a milliliter at 2.5 hr. The mixture was cooled and flooded with water after a total reaction time of 3 hr. and the product was extracted with pentane. The pentane solution was washed several times with water and then dried. Removal of the solvent left 17 g. of an oil which was analyzed by v.p.c. and found to contain 13.5 g. of 2-dodecanone (77%). Only trace amounts of other C_{12} ketone isomers were detected.

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[10] J. Casey and F. S. Prout, *J. Am. Chem. Soc.*, **66**, 48 (1944).

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peri-Substituted Naphthalene Compounds. VI.[1,2] Acenaphth[1,2-*a*]acenaphthylene

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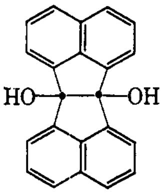
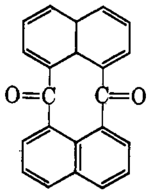
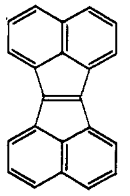
With the availability of 1,8-dilithionaphthalene,[1] a variety of *peri*-substituted naphthalene compounds have become accessible. The present paper reports the preparation of *cis*-6b,12b-dihydroxy-6b,12b-dihydroacenaphth[1,2-*a*]acenaphthylene (I) and conversion of this diol to diketone II and to hydrocarbon III.



I



II



III

Diol I was obtained in 14% yield on hydrolyzing the products from reaction of equimolar quantities of 1,8-dilithionaphthalene and acenaphthenequinone. It is a colorless, crystalline solid melting at 319–321°. The assigned structure is supported by the infrared spectrum (bands attributable to hydrogen bonded O–H at 3.00 and 3.12 μ), the mass spectrum (molecular ion at *m/e* 310), a Zerewitinoff determination (two active hydrogen atoms per molecule), and the elemental analysis. Of the two possible stereoisomeric forms, only that with *cis* fusion of the five-membered rings seems a plausible structure in view of the method of formation and the high degree of strain that would exist in the *trans* isomer. It was indeed found that diol I was produced by oxidation of acenaphth[1,2-*a*]acenaphthylene (III) with osmium tetroxide, a reagent well established to add *cis* to carbon–carbon double bonds. Furthermore, a sharp melting, crystalline ester was obtained from the reaction of I with benzeneboronic acid.

Oxidation of diol I with lead tetraacetate afforded 1,8-naphthalylnaphthalene (II) in 81% yield. A molecular model of this substance indicates that the carbonyl groups would not lie in the plane of either naphthalene ring. In agreement with the expectation that the geometry would lead to inhibition of resonance involving these groups, it was found that the carbonyl stretching frequency for II was 25 cm.$^{-1}$ greater than that for 1,8-dibenzoylnaphthalene and the extinction coefficient for the maximum occurring at 280 mμ was only 1120, as compared to 9680 for 1,8-dibenzoylnaphthalene. Also of interest is the fact that II dissolved in concentrated sulfuric acid to give a colorless solution, whereas naphthalene compounds which possess oxygen functions at the α-position in general give highly colored sulfuric acid solutions.[4] The ion formed from II seems best formulated as one in which hybridization of the carbonium ion is largely sp^3 and conjugation with the aromatic rings is minimal as a consequence of the molecular geometry.

On addition of I to hydrogen fluoride a green solution was obtained. Hydrolysis and chromatography of the resulting dark precipitate afforded in 29% yield a deep purple, sublimable hydrocarbon, $C_{22}H_{12}$. The same compound was obtained in 7% yield when a solution of diol I in sulfuric acid was hydrolyzed. The mass spectrum (molecular ion of mass 276) was consistent with an aromatic hydrocarbon structure, and the infrared spectrum was unusually simple, consisting of three strong bands (6.91, 12.16, and 13.06 μ), three medium intensity bands (6.80, 7.05, and 8.32 μ), and a few very weak bands. Evidence that no rearrangement of the carbon skeleton had occurred was provided by the fact that the purple hydrocarbon was reconverted to diol I by treatment with osmium tetroxide and hydrolysis of the resulting ester. These facts identify the hydrocarbon as acenaphth[1,2-*a*]acenaphthylene (III).

Formation of III from I involves elimination of *cis*-hydroxyl groups. A few other cases of production of olefinic substances from glycols under conditions for the pinacol rearrangement have been reported. For example, Bachmann and Chu[5] obtained 1,2-diarylacenaphthylenes as well as the expected pinacolones on treating 1,2-bis-*p*-chlorophenyl-1,2-acenaphthenediol and the corresponding fluorophenyl analog with iodine in acetic acid. In addition, Gomberg and Bachmann[6] reported that $\Delta^{9,9'}$-bixanthene was formed when 9,9′-bixanthydrol was warmed in an acetic acid–sulfuric acid solution. This result was questioned by Bergmann and Schuchardt,[7] who failed to obtain the bixanthene

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[1] Paper V, R. L. Letsinger, J. A. Gilpin, and W. J. Vullo, *J. Org. Chem.*, **27**, 672 (1962).

[2] This work was supported in part by the National Science Foundation.

[3] Dow Chemical Co. Fellow, 1961–1962.

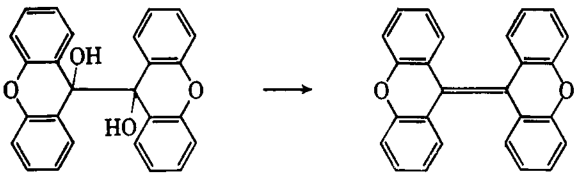
[4] A solution of 1,8-dibenzoylnaphthalene in sulfuric acid is red (λ_{max} 523 mμ).

[5] W. E. Bachmann and E. J. Chu, *J. Am. Chem. Soc.*, **58**, 1118 (1936).

[6] M. Gomberg and W. E. Bachmann, *ibid.*, **49**, 236 (1927).

[7] E. Bergmann and W. Schuchardt, *Ann.*, **487**, 240 (1931).

under these conditions; however, in confirmation of the observation of Gomberg and Bachmann, we obtained a low yield of $\Delta^{9,9'}$-bixanthene from the reaction of 9,9'-bixanthydrol with sulfuric acid. Bachmann and Chu explained the appearance of 1,2-diarylacenaphthylenes in their reactions by assuming that small amounts of hydrogen iodide present in the mixture of iodine and acetic acid converted the diols to diiodides which then lost iodine. This explanation is not applicable for the elimination reactions leading to compound III and to $\Delta^{9,9'}$-bixanthene. It seems likely in these cases that the reactions involve loss of a positive oxygen fragment situated β to a carbonium ion.



Acenaphth[1,2-*a*]acenaphthylene yielded (95%) a colorless dibromide, probably the *cis*-6b,12b isomer, when treated with an equivalent amount of bromine in chloroform solution. The ease of the addition reaction indicates the low degree of "aromatic" character of the bond at the 6b,12b-position. On being heated to 210° the dibromide lost bromine, regenerating the purple hydrocarbon. Dehalogenation also was effected by warming the dibromide with aqueous sodium hydroxide.

Experimental

The carbon–hydrogen analyses were performed by Miss Hilda Beck and by the Micro-Tech Laboratories in Skokie, Illinois. Infrared spectra were obtained with a Baird double beam recording spectrophotometer with the samples in potassium bromide. The ultraviolet spectra were taken with a Beckman DK-2 spectrophotometer.

***cis*-6b,12b-Dihydroxy-6b,12b-dihydroacenaphth[1,2-*a*]acenaphthylene.**—To an ether solution of 1,8-dilithionaphthalene,[1] prepared from 4.0 g. of 1,8-dibromonaphthalene, was added in small portions 2.7 g. of acenaphthenequinone. After the red mixture had refluxed for 6 hr. it was hydrolyzed with saturated ammonium chloride solution. On concentrating the organic layer to a small volume and diluting with hexane, a yellow solid (3.5 g., m.p. 130–210°) precipitated. The crude diol (0.62 g., 14%, m.p. 290–300°) was obtained as an almost colorless residue by extracting the solid with several portions of warm carbon tetrachloride. For purification, the diol was chromatographed on silica gel, using benzene–ethyl ether mixtures as eluent, and the fractions melting above 300° were combined and recrystallized from acetone. Compound I thus prepared melted at 319–321°; $\lambda_{\max}^{\mathrm{EtOH}}$ 224 mμ (log ε 4.78), 270 (3.67), 281 (3.79), 306 (4.07), 323 (4.08). The major bands in the infrared spectrum were found at 3.12, 9.10, 12.03, and 12.80 μ. There were no absorption bands in the carbonyl region.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.1; H, 4.55; active hydrogen, 2. Found: C, 84.3; H, 4.47; active hydrogen,[8] 2.03 g. atom per 310-g. sample (*i.e.*, per mole).

When the mixture from reaction of 1,8-dilithionaphthalene with acenaphthenequinone was carbonated on Dry Ice prior to hydrolysis, the yield of diol I was the same and only trace quantities of acidic products were isolated.

1,8-Naphthalylnaphthalene.—A mixture of 0.1012 g. (0.327 mmole) of diol I and 0.1483 g. (0.335 mmole) of lead tetraacetate in 10 ml. of dry benzene was allowed to react at room temperature for 2 hr. and then warmed on a steam bath for several minutes. The solution was washed with dilute hydrochloric acid, dilute sodium hydroxide, and water, respectively. Evaporation of the solvent afforded 0.0818 g. (81%) of ketone II, melting above 300°. After three recrystallizations from acetone–benzene the ketone melted at 333–334°; $\lambda_{\max}^{\mathrm{EtOH}}$ 220 mμ (log ε 3.86), 280 (plateau, 3.05); $\lambda_{\max}^{\mathrm{concd}\ H_2SO_4}$ 220 mμ (log ε 4.07), 340 (3.78); major bands in infrared, 5.92, 7.77, 9.52, 11.90, and 12.82 μ.

Anal. Calcd. for $C_{22}H_{12}O_2$: C, 85.7; H, 3.92. Found: C, 85.7; H, 3.91.

Benzeneboronate Ester of *cis*-6b,12b-Dihydroxy-6b,12b-dihydroacenaphth[1,2-*a*]acenaphthylene.—On warming a benzene solution containing 0.1009 g. (0.325 mmole) of diol I and 0.0402 g. (0.330 mmole) of benzeneboronic acid, filtering the solution to remove small amounts of suspended matter, and concentrating the solution, crystals of the benzeneboronate ester of diol I were obtained, 0.0941 g. (73%), m.p. 326–333°. After three recrystallizations from benzene the compound melted at 347–348°. The sample burned with a strong green flame, indicative of boron, and the strongest band in the infrared spectrum occurred at 7.46 μ, characteristic of a boron–oxygen compound.

Anal. Calcd. for $C_{28}H_{17}O_2B$: C, 84.9; H, 4.33. Found: C, 85.0; H, 4.75.

As further evidence for the ester structure, a 23.9-mg. sample was stirred in an aqueous dioxane solution containing mannitol to hydrolyze it. On extraction with ether and evaporation of the ether, 8 mg. of diol I was recovered. As obtained in this way it was somewhat impure, m.p. 270–295°; however, the infrared spectrum was almost identical with that of the purified material and the sample did not give a green flame on burning. Titration of the aqueous layer required 4.6 × 10^{-5} mole of sodium hydroxide, 76% of the theoretical value for the boron in the sample.

Acenaphth[1,2-*a*]acenaphthylene.—A mixture of diol I (0.700 g.) and 15 ml. of anhydrous hydrogen fluoride in a copper vessel was allowed to stand 45 min. at 0° and then poured onto ice. On extracting with benzene, washing the benzene solution with water, drying, and evaporation, a dark solid was obtained. This material was then taken up in chloroform and chromatographed on alumina, using hexane–benzene mixtures as the eluent, to give 0.1983 g. (29%) of acenaphth[1,2-*a*]acenaphthylene, m.p. 284–285°, as purple crystals. The analytical sample, m.p. 285–286.5°, was obtained by recrystallization from a benzene–hexane mixture; $\lambda_{\max}^{\mathrm{EtOH}}$ 224.5 mμ (log ε 4.72), 232 (4.61), 244.5 (4.36), 291 (4.09), 385 (4.19), 404 (4.17).

Anal. Calcd. for $C_{22}H_{12}$: C, 95.6; H, 4.38. Found: C, 94.3; H, 4.56.

Diol I was not changed by heating in refluxing acetic acid for 7 hr. or in phosphoric acid at 100° for 16 hr.

Hydroxylation of Acenaphth[1,2-*a*]acenaphthylene.—A solution containing 0.046 g. (0.18 mmole) of osmium tetroxide and 0.050 g. (0.18 mmole) of acenaphth[1,2-*a*]acenaphthylene in 15 ml. of ether was allowed to stand for 6 days, during which the purple color of the solution disappeared. Ether was then removed, water (4 ml.), ethanol (1.3 ml.), and sodium sulfite (0.6 g.) were added, and the mixture was refluxed for 4 hr. Extraction with ether and evaporation of the ether afforded 0.0326 g. (58%) of diol I, m.p. 295–300°. After two recrystallizations from an acetone–ether mixture the product melted at 313–318°. The product was identified by its infrared spectrum and a mixture melting point with the diol obtained from the reaction of 1,8-dilithionaphthalene.

6b,12b-Dibromo-6b,12b-dihydroacenaphth[1,2-*a*]acenaphthylene.—To a red solution of acenaphth[1,2-*a*]acenaphthylene (0.0452 g., 0.163 mmole) in chloroform was added dropwise an 0.85-ml. aliquot (0.16 mmole) of a 1.0% (by volume) solution of bromine in chloroform. Upon completion of the addition the solution was a pale yellow. The solution was shaken successively with a dilute sodium bisulfite solution and with water. On evaporation of the solvent 0.0677 g. (95%) of the dibromide derivative was obtained. On the melting point block a sample turned purple at 210–220° and melted at 248–255°. The analytical sample was recrystallized three times from benzene. Its behavior on heating was the same as that of the material isolated directly from the reaction mixture.

Anal. Calcd. for $C_{22}H_{12}Br_2$: C, 60.58; H, 2.8. Found: C, 60.51; H, 3.0.

The substance produced by heating the dibromide above 220° was acenaphth[1,2-*a*]acenaphthylene. This hydrocarbon (m.p. 255–257°, identified by the infrared spectrum) was likewise obtained (76% yield) when the dibromide was heated with excess aqueous, ethanolic sodium hydroxide on a steam bath.

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(8) Method described in I. Gattermann and T. Wieland, "Die Praxis des organischen Chemikers," Walter De Gruyter and Co., Berlin, 1959, pp. 79–81.