

in common the ability to undergo photoisomerizations. They also possess in common the fact that a specific turning over of two atoms appears to be the major rearrangement result. In benzenoid systems *o*-xylene gives, in addition to elimination products, *m*- and *p*-xylene in 11:1 ratio during the first 30 min of photolysis.¹⁷ Furthermore, mesitylene forms 1,2,4-trimethylbenzene exclusively upon photolysis,¹⁸ and *o*-di-*t*-butylbenzene is reported to give mostly *m*-di-*t*-butylbenzene in the first 6 hr of reaction.¹⁵ In other systems, specific inversion of two carbons could have occurred but cannot, by the nature of the labeling, be distinguished.¹⁶ Obviously the benzenoid systems have not been completely elucidated, and the mechanism of rearrangement may vary from system to system. In *t*-butyl systems relief of strain has been cited as a driving force for rearrangement¹⁵ but this obviously is not a

prerequisite. Of the various valence bond isomers considered for benzenoid photochemical rearrangements, it is perhaps surprising that ring opening to form a dicyclopropenyl, an analog of Ullman's azirine or thioaldehyde **20**, has not been considered. A dicyclopropenyl can theoretically lead to the observed rearrangement products in benzenoid systems and as a description of the excited species leading to rearrangement could be considered. In this regard the formation of a benzene derivative by thermal rearrangement of a dicyclopropenyl is of considerable interest.⁴⁹

Further work both on the mechanism of the rearrangement as well as the scope and application to other systems is currently under way and will be the subject of future reports.

(49) R. Breslow, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 243-245.

Transannular and Interannular Effects in 1,8-(1',8')-Naphthalynaphthalene and Related Compounds¹

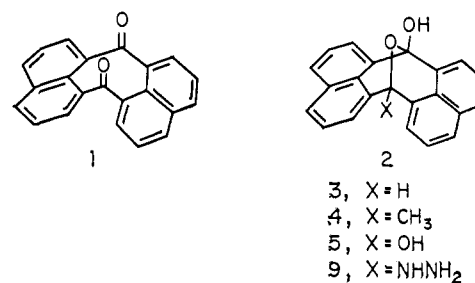
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Abstract: Reactions at the nonaromatic carbon atoms of 1,8-(1',8')-naphthalynaphthalene and related compounds lead either to oxygen bridging (as **2**) or formation of a transannular carbon-carbon bond (as **10**). Spectral evidence indicates considerable electronic interaction between the two formally insulated naphthalene chromophores.

In 1,8-(1',8')-naphthalynaphthalene^{2,3} (**1**) and related compounds of the same carbon skeleton, there is available a single, rather rigid conformation free of distorted bond angles. We wish to discuss here two general consequences of this arrangement which are reflected in the chemical and physical properties of these molecules. The first of these is a marked tendency for transannular reactions to occur, leading either to direct carbon-carbon bonding between the two nonaromatic carbon atoms or, alternatively, to formation of an oxygen bridge between these centers. The well-investigated *peri* interactions of simple naphthalenes⁴ provide ample precedent for such reactions; the results described below demonstrate that they are highly favored, and indeed appear to be unavoidable, in the rigid array of **1**. A second property we find to be general in these molecules is electronic interaction between the two classically insulated naphthalene systems as evidenced by their abnormal spectral properties.

We consider first reactions of **1** leading to transannular oxygen bridging. Treatment of the diketone with a variety of nucleophiles leads to formation of hemiketals of the general structure **2**. In no case have



we observed normal reaction of the second carbonyl group, and the ketol-hemiketal equilibrium appears to lie far to the side of the bridged product. Infrared spectra of all these substances show strong hydroxyl absorption and are transparent in the carbonyl region. Thus, sodium borohydride reduction of **1** furnishes **3** as the only isolable product, and reaction of the diketone with excess methyl lithium gives only the corresponding methyl hemiketal **4**. Similarly, acid-catalyzed hydration of **1** leads in high yield to the stable hydrate **5**, a compound which sublimes unchanged at 190° *in vacuo* and is not dehydrated by prolonged treatment with *p*-toluenesulfonic acid and refluxing benzene in a water separator. Exposure of the dione to typical Clemmensen reduction conditions yields only the hydrate **5**, as does attempted reduction with hydriodic acid and red phosphorus in acetic acid at 145° over 2 days. Failure to isolate reduction products from these reac-

(1) A portion of this work has appeared in preliminary form: W. C. Agosta, *Tetrahedron Letters*, 3635 (1966).

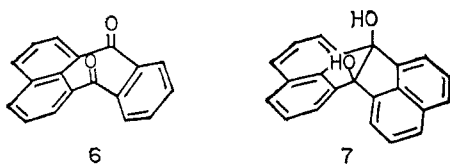
(2) R. L. Letsinger and J. A. Gilpin, *J. Org. Chem.*, **29**, 243 (1964).

(3) The systematic name for this compound is 7H,14H-cycloocta-[1,2,3-*de*:5,6,7-*d'e'*]dinaphthalene-7,14-dione.

(4) A timely review of this topic has appeared: V. Balasubramanian, *Chem. Rev.*, **66**, 567 (1966).

tions demonstrates a remarkable stability of the ketone hydrate relative to the diketone. Resistance to reduction by hydriodic acid implies that the bridgehead carbonium ion resulting from loss of hydroxyl anion must be extremely poor, since one would otherwise expect formation of bridgehead iodide and subsequently its reduction products.

This strong interaction of the carbonyl groups of **1** may be contrasted with the case of 7,12-dihydropleiadene-7,12-dione (**6**) and its derivatives, in which reactions at one or both carbonyls can take place without transannular involvement and bridging occurs only exceptionally.⁵ This difference is presumably ascribable to two factors. The greater rigidity of the naphthalynaphthalene system leads to decreased entropy loss on bridging, and models of the hydroxy ketones corresponding to hemiketals **2** show that the hydroxyl group is thrust into the π cloud of the transannular carbon-oxygen double bond, an unfavorable interaction relieved by hemiketal formation. On the other hand, molecular models of **6** indicate that here the carbonyl groups are farther apart and that the molecule is considerably more flexible.⁶



A second type of transannular reaction of diketone **1** involves carbon-carbon bond formation and is exemplified by photoreduction. Irradiation of a dilute solution of the compound in isopropyl alcohol gives the pinacol⁷ **7** in a novel intramolecular example of a photolytic benzpinacol reaction.⁸ A rather more striking reaction occurs on treatment of **1** with hydrazine and potassium hydroxide in refluxing ethylene glycol. With exclusion of air under these typical Wolff-Kishner conditions the known² deep purple hydrocarbon acenaphth[1,2-*a*]acenaphthylene (**8**) is formed in good yield (76%). The course of this transformation is discussed below.

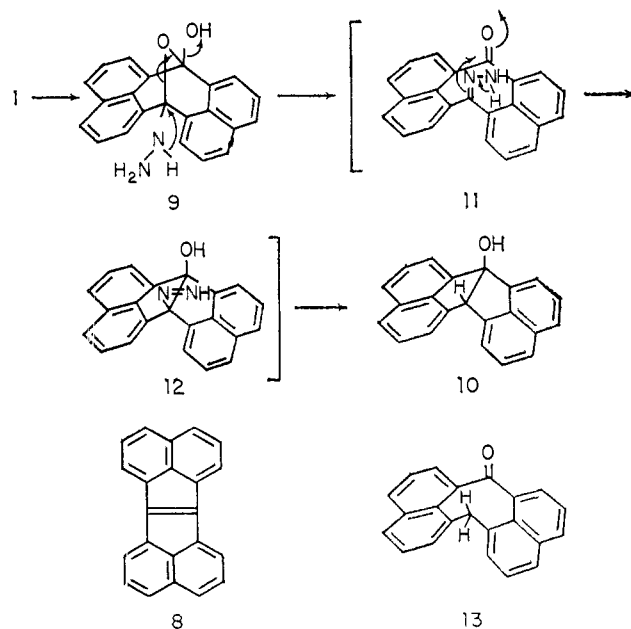
Hydrazine adds to **1** just as other nucleophiles to give **9**, a stable adduct isolable in high yield in separate preparative experiments. While **9** is unaffected by heat alone to at least 260°, it is smoothly converted by potassium hydroxide in hot ethylene glycol to the alcohol **10**, a second intermediate in the sequence leading to **8**. If the original conditions used on diketone **1** are modified so that the temperature does not exceed 150°, alcohol **10** may be isolated (81%) and no olefin is formed. The final step, dehydration of **10** to the olefin **8**, is a thermal reaction; the alcohol easily loses water in refluxing ethylene glycol with or without added base to give **8** in high yield.

(5) (a) A. Rieche, H. Sauthoff, and O. Müller, *Ber.*, **65**, 1371 (1932); (b) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965); (c) M. E. C. Biffin, L. Crombie, and J. A. Elvidge, *J. Chem. Soc.*, 7500 (1965); (d) P. T. Lansbury, J. F. Bieron, and M. Klein, *J. Am. Chem. Soc.*, **88**, 1477 (1966).

(6) 7,12-Dihydropleiadene-7,12-dione undergoes rapid molecular inversion at room temperature (*cf.* ref 5d); the inversion barrier in 1,8-(1',8')-naphthalynaphthalene is not yet known (*cf.* ref 1).

(7) As noted below this pinacol is the synthetic precursor of **1**, to which it is oxidized by lead tetraacetate (*cf.* ref 2).

(8) G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900); A. Schönberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947).



The transformation from **9** to **10** is, of course, the most interesting part of this sequence. We believe that the most plausible pathway for this change is *via* the ketomono-hydrazone **11**, which can arise by cleavage of the oxygen bridge and loss of water from **9**.⁹ Of possible routes from **11** to **10** we favor a prototropic shift with concomitant bridging to **12**, which should rapidly lose nitrogen to give alcohol **10**. This process has the advantage of avoiding transannular crowding, and it also provides a possible explanation for the observation that sodium acetate is just as effective a catalyst for the reaction as potassium hydroxide. An ordinary Wolff-Kishner reaction with such mild base would be unusual, but a prototropic shift placing charge on the transannular oxygen (rather than on carbon) might require only milder conditions. The formation of **10** suggests in any event that this alcohol may be regarded as the "homoenol"¹⁰ of the unknown ketone **13**. If this is correct, equilibrium seems strongly to favor the alcohol, for we have been unable to produce or trap **13** starting with **10**.

The structure of alcohol **10** is evident from the following considerations. The compound loses water not only thermally, but also at room temperature on treatment with phosphorus oxychloride in pyridine solution, to give olefin **8**. It is also independently available by hydroboration of **8**¹¹ in the presence of excess sodium borohydride and boron trifluoride etherate, followed by oxidation with basic hydrogen peroxide.¹² We found this hydroboration best carried out using a large excess of diborane; even then the reaction is quite slow, as judged by the rate of fading of the intense purple color of the olefin. Furthermore, the organoboron intermediate reverts fairly readily to starting material. In an attempt to effect protonolysis

(9) An alternative pathway involving initial loss of diimide from **9** to give hemiketal **3** as an intermediate is not only unprecedented but ruled out by the complete stability of **3** to the reaction conditions.

(10) (a) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **88**, 1905 (1966), and previous papers in this series; (b) P. Carter, R. Howe, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 914 (1965); R. Howe and S. Winstein, *ibid.*, **87**, 915 (1965); (c) T. Fukunaga, *ibid.*, **87**, 916 (1965).

(11) The central double bond of hydrocarbon **8** displays olefinic rather than aromatic properties (*cf.* ref 2).

(12) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

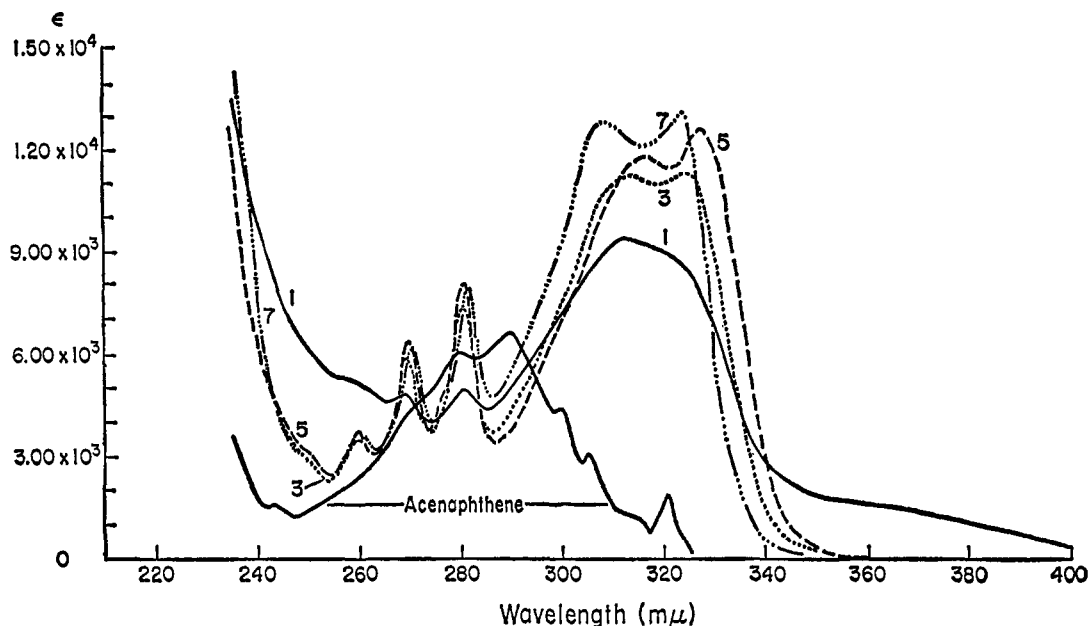


Figure 1. Ultraviolet spectra in 95% ethanol of unbridged (1), oxygen-bridged (3, 5), and carbon-carbon bonded (7) systems. The spectrum of acenaphthene is shown for comparison. All compounds show an additional maximum above 210 $m\mu$ ($\log \epsilon \sim 5$).

of the colorless boron adduct, it was heated with propionic acid in diethylene glycol dimethyl ether, conditions commonly employed for this transformation.¹³ Instead of the anticipated **14**, starting olefin **8** was the major product of this reaction. While slow thermal liberation of alkene from simple organoboranes occurs under conditions allowing the continuous removal of the hydrocarbon formed,¹⁴ the easily reversed addition encountered here with **8** is rather unusual.

If the reaction of **1** with hydrazine and base is carried out in the presence of air, the yield of **8** is diminished somewhat, and up to 10% of a colorless second hydrocarbon is obtained. This is identical with the product of hydrogenation of **8** in benzene over palladium on carbon, and must therefore be **14**. Exposure of pure **8** to the Wolff-Kishner conditions in air also gives this reduction product in about the same amount, a result indicating that **14** need not arise *via* an independent mechanism from the dione **1**. The reduction of reactive double bonds by hydrazine and oxygen by way of intermediate formation of diimide is well documented.¹⁵

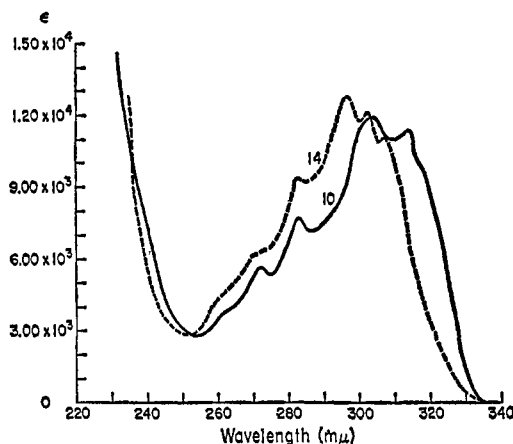


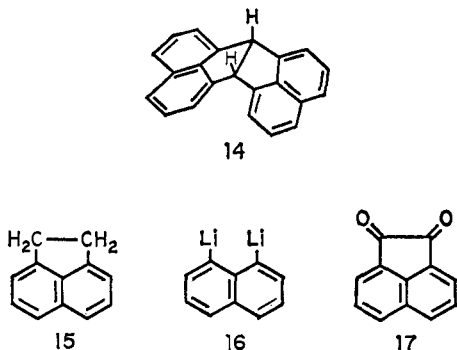
Figure 2. Ultraviolet spectra in 95% ethanol showing effect of substitution (*cf.* spectrum of **7**).

The ultraviolet spectrum (Figure 1) of 1,8-(1',8')-naphthalynaphthalene (**1**) is of some interest in connection with evidence of transannular reactivity. Below 350 $m\mu$, the spectrum of **1** is similar to those of other compounds described here, consistent with severely reduced carbonyl-ring interaction.¹⁶ Beyond 350 $m\mu$, however, diketone **1** displays unique absorption which may be attributable to transannular interaction of the carbonyl groups.

The curves recorded in Figures 1 and 2 illustrate the second general characteristic of these systems which we wish to report. While the classical ultraviolet chromophore of these compounds (other than **1**) is that of a 1,8-dialkynaphthalene, they all possess spectra divergent from this simple model. Comparison with the typical absorption for this chromophore shown by acenaphthene¹⁷ (**15**) reveals unexpected, high intensity

(16) The severely reduced carbonyl-ring interaction in **1** was first pointed out by Letsinger (*cf.* ref 2).

(17) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Spectrum No. 212.



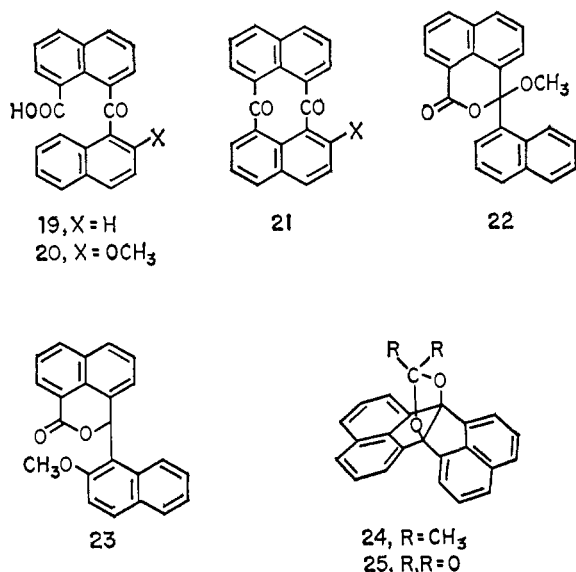
(13) H. C. Brown and K. Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959).

(14) (a) L. Rosenblum, *ibid.*, **77**, 5016 (1955); (b) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1137 (1957); (c) R. Köster, *Ann.*, **618**, 31 (1958).

(15) (a) E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Letters*, 347 (1961); (b) S. Hünig, H.-R. Müller, and W. Thier, *ibid.*, 353 (1961), and earlier references cited therein.

absorption between 300 and 340 μ . Minor spectral effects due to *peri* interactions are well known in naphthalenes,⁴ but this explanation does not seem available here. The changes observed are too great and are also relatively insensitive to the presence or absence of transannular bridging. The phenomenon is particularly noteworthy in the spectrum of **14** (Figure 2), a compound free of heteroatoms and for which acenaphthene should be a quite appropriate classical model. Further, in the series hydrocarbon **14**, monool **10**, diol **7**, the position of this absorption is directly influenced by substitution at the two nonaromatic carbon atoms (297 μ in **14**, 304 μ in **10**, 309 μ in **7**). We believe that these data indicate appreciable electronic interaction between the two naphthalene rings. Such interactions of formally insulated chromophores have been observed previously in a number of chemically distinct systems, but physical interpretation of these observations has proved difficult, even for the simple case of two ethylenic bonds.¹⁸ We refrain, therefore, from proposing specific models or structures to explain these spectral results.¹⁹

We have used in these experiments 1,8-(1',8')-naphthalynaphthalene (**1**) prepared *via* the sequence reported by Letsinger, involving condensation of 1,8-dilithionaphthalene (**16**) with acenaphthenequinone (**17**) to give diol **7**, followed by oxidative cleavage with lead tetraacetate.² In a search for an alternative route permitting more convenient, although considerably less elegant, preparation of the diketone we attempted to repeat reactions described some 30 years ago by Knapp.²⁰ These involved straightforward Friedel-Crafts closure of readily available 8-(1'-naphthoyl)-1-



(18) (a) For example, abnormal ultraviolet spectra are reported for triptycene [P. D. Bartlett and E. S. Lewis, *J. Am. Chem. Soc.*, **72**, 1005 (1950)], lower members of the para[*m,n*]cyclophane series [D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954)], and norbornadiene [C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, *ibid.*, **82**, 5450 (1960)]. (b) The problem posed by the electronic spectrum of norbornadiene is discussed by M. B. Robin and N. A. Kuebler, *J. Chem. Phys.*, **44**, 2664 (1966).

(19) The electron spin resonance spectrum of the triplet produced on irradiation of **14** in a rigid matrix is under examination by Dr. E. Wasserman (Bell Telephone Laboratories). Preliminary results appear compatible with rapid energy transfer from one naphthalene system to the other (E. Wasserman, private communication.)

(20) W. Knapp, *Monatsh. Chem.*, **67**, 332 (1936).

naphthoic acid (**19**)²¹ and its 2'-methoxy derivative (**20**)²⁰ to the corresponding diones **21**. In our hands these efforts failed, both under the original conditions (treatment with phosphoric anhydride in hot toluene) and with a variety of other procedures. In any case, it is doubtful that the reported products actually were diketones **21**. Both compounds were readily soluble in aqueous sodium hydroxide and gave highly colored solutions in concentrated sulfuric acid;²⁰ yet we find diketone **1** prepared using 1,8-dilithionaphthalene quite insoluble in aqueous base, while Letsinger has noted² that it gives a colorless solution in concentrated sulfuric acid.

In connection with these efforts we prepared the previously undescribed methyl esters of acids **19** and **20** using diazomethane, as well as the pseudoester **22** which is formed along with the normal ester on Fischer esterification of **19**. Attempted hydrogenolysis of the ketone carbonyl of **20** fails under even fairly severe conditions (3 atm of hydrogen at 65° in acetic acid over palladium on carbon), and the only pure product isolated is the corresponding lactone **23**. Examination of molecular models shows that adsorption of the ketone carbonyl on the catalyst surface must be quite difficult.

Diol **7** reacts readily with acetone in the presence of perchloric acid to give a high melting (mp >355°) acetonide **24**. On heating **7** with diethyl carbonate and base, transesterification occurs to furnish the cyclic carbonate **25** which is completely hydrolyzed during attempted chromatography over neutral alumina.

Experimental Section

7,14-Endoxy-7H,14H-cycloocta[1,2,3-de:5,6,7-d'e']dinaphthalen-7-ol (3). A solution of 50 mg of dione in 10 ml of dimethylformamide was added dropwise to a stirred solution of 50 mg of sodium borohydride in 10 ml of isopropyl alcohol at room temperature; the resulting mixture was stirred 19 hr. Excess borohydride was destroyed with acetic acid, and ~100 ml of brine was added. The resulting solid was filtered and washed with water to remove sodium chloride. The remaining material was crystallized from benzene to give 31 mg (62%) of small prisms, mp 300–304°. This melting point was unchanged on recrystallization; infrared: 3340 (s, broad), 1200 (s), 780 (s), and 772 (s) cm^{-1} (KBr); ultraviolet: λ_{max} 214 μ (log ϵ 4.98), 260 (3.54), 269 (3.77), 281 (3.87), 314 (4.05), and 324 (4.05) (EtOH).

Anal. Calcd for C₂₂H₁₄O₂: C, 85.16; H, 4.55. Found: C, 85.00; H, 4.60.

7,14-Endoxy-7-methyl-7H,14H-cycloocta[1,2,3-de:5,6,7-d'e']dinaphthalen-14-ol (4). A suspension of 50 mg of **1** in 5.0 ml of freshly distilled tetrahydrofuran and 5.0 ml of ether was treated dropwise with ~2 equiv (0.18 ml of 1.88 *M* solution) of methyl-lithium in 2.5 ml of ether. As the methyl-lithium was added the solution became homogeneous. The solution was stirred 1 hr and then treated with water and the product extracted into ether and benzene. The crude product from this extraction (45 mg) was crystallized from ethyl acetate containing cyclohexane to give 28 mg (53%) of granules, mp 287–300°. Three recrystallizations from the same solvent pair gave an analytical sample, mp 301–302°; infrared: 3370 (m, broad), 1210 (m), 830 (m), and 774 (s) cm^{-1} (KBr); ultraviolet: λ_{max} 213 μ (log ϵ 5.03), 259 (3.59), 269 (3.80), 281 (3.90), 315 (4.04), and 327 (4.06) (EtOH); nmr: δ 2.42 (singlet, 3.0 H), 4.06 (broad singlet, 0.95 H), and 7.5 (multiplet, 12 H) (CDCl₂).

Anal. Calcd for C₂₂H₁₆O₂: C, 85.16; H, 4.97. Found: C, 84.93; H, 5.03.

7,14-Endoxy-7H,14H-cycloocta[1,2,3-de:5,6,7-d'e']dinaphthalene-7,14-diol (5). A solution of 30 mg of **1** in 1.80 ml of acetic acid containing 0.57 ml of concentrated hydrochloric acid was heated at reflux for 90 min and cooled and the product precipitated by addition of water. This product was recrystallized once from

(21) R. Weiss and P. Fastmann, *ibid.*, **47**, 727 (1926).

aqueous acetic acid to give 30 mg of colorless crystals (94%). A sample was sublimed [190° (0.06 mm)] for analysis; mp $321\text{--}323^\circ$; infrared: 3501 (s), 3365 (ms, broad), 790 (s), and 775 (s) cm^{-1} (KBr); ultraviolet: λ_{max} 212 $\text{m}\mu$ ($\log \epsilon$ 5.02), 260 (3.57), 270 (3.80), 281 (3.90), 316 (4.07), and 327 (4.10) (EtOH).

Anal. Calcd for $\text{C}_{22}\text{H}_{14}\text{O}_3$: C, 80.96; H, 4.33. Found: C, 80.95; H, 4.27.

The same product was obtained (52%) on treatment of 19.7 mg of **1** with approximately 300 mg of zinc amalgam in 0.50 ml of acetic acid containing 0.50 ml of concentrated hydrochloric acid at reflux for 19 hr. No other crystalline product could be recovered.

The same product was obtained (55%) on treatment of 20 mg of **1** in 0.30 ml of acetic acid with 0.05 ml of concentrated hydriodic acid, ~ 30 mg of red phosphorus, and ~ 12 mg of iodine for 45 hr at 145° . A second 0.05-ml portion of hydriodic acid was added after 20 hr. No other crystalline product could be recovered.

Attempted Dehydration of Hydrate 5. A mixture of 5 mg of hydrate, 1 mg of *p*-toluenesulfonic acid, and 10 ml of benzene was heated at reflux using a water separator for 20 hr. The mixture was then taken directly to dryness *in vacuo* and the residue dissolved in acetone and ether. This solution was washed three times with water and dried. Removal of solvent left 5 mg of off-white crystalline solid. The infrared spectrum of this material showed no carbonyl absorption and appeared to be only that of impure starting material. Recrystallization from acetic acid gave hydrate **5**; the infrared spectrum was identical with that of authentic material.

cis-6b,12b-Dihydroxy-6b,12b-dihydroacenaphth[1,2-a]acenaphthylene (7) from 1. A solution of 10 mg of **1** in 460 ml of redistilled reagent-grade isopropyl alcohol was irradiated for 1 hr under nitrogen with a Hanovia Type L mercury lamp in a quartz immersion well using a Pyrex filter. Removal of solvent left crystalline material which from its infrared spectrum was chiefly diol **7**. This was purified by chromatography over 5:2 silicic acid-Celite using benzene containing 5% ether as eluent. The resulting 5.5 mg of material was recrystallized from acetone to give material identical in infrared spectrum (KBr) with authentic **7**; mp and mmp $316\text{--}318^\circ$.

Acenaphth[1,2-a]acenaphthylene (8) from 1. A mixture of 168 mg of **1**, 5.0 ml of ethylene glycol, 2.5 ml of 10% aqueous potassium hydroxide, and 1.0 ml of 97% hydrazine was heated in an oil bath at 120° for about 20 min and the water allowed to distil out. After water was removed the solution was flushed with nitrogen; the temperature was raised to 180° and the mixture refluxed under nitrogen for 1 hr and 40 min. The mixture was cooled and diluted with water and the purple product extracted into benzene. The organic solution was washed with dilute hydrochloric acid and then water and dried. The crude product resulting from removal of solvent was recrystallized from cyclohexane to give 115 mg (76%) of dark purple crystals, mp $284\text{--}286^\circ$ (lit.² mp $285\text{--}286.5^\circ$); infrared: 1474 (m), 1451 (ms), 1444 (s), 1420 (m), 1199 (m), 820 (s), and 765 (s) cm^{-1} (KBr) [lit.² infrared: 1471 (m), 1447 (s), 1418 (m), 1202 (m), 822 (s), 766 (s)]; ultraviolet: λ_{max} 209 $\text{m}\mu$ ($\log \epsilon$ 4.86), 225.5 (4.71), 232.5 (4.61), 243 (4.35), 292 (4.09), 337 (4.02), 342 (4.03), 387 (4.16), and 405.5 (4.16) (EtOH) [lit.² ultraviolet: λ_{max} 224.5 $\text{m}\mu$ ($\log \epsilon$ 4.72), 232 (4.61), 244.5 (4.36), 291 (4.09), 385 (4.19), and 404 (4.17) (EtOH)].

If the reaction were run in air the yield of olefin **8** dropped to 55–60%, and 6–10% of hydrocarbon **14** could be obtained after chromatography over Woelm neutral alumina (II). Exposure of the olefin to the same reaction conditions in air yielded the dihydro compound in similar amount.

7,14-Endoxy-7-hydrazino-7H,14H-cycloocta[1,2,3-de:5,6,7-d'e']-dinaphthalen-14-ol (9). A suspension of 20 mg of **1** in 1.0 ml of ethylene glycol containing 0.2 ml of 97% hydrazine was heated at 120° for 1 hr, during which time the dione slowly dissolved to give a clear pale yellow solution. Upon cooling, this solution deposited cream needles. The mixture was diluted with water, and the needles were filtered off, washed, and dried, yielding 20 mg (90%). Two recrystallizations from ethanol gave an analytical sample; melting point behavior: partial melting near 260° , followed by recrystallization and slight darkening, $260\text{--}340^\circ$; did not remelt up to 345° ; infrared: 3450 (m, very broad), 1222 (m), and 790 (s) cm^{-1} (KBr).

Anal. Calcd for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.72; H, 4.80; N, 8.14.

cis-6b-Hydroxy-6b,12b-dihydroacenaphth[1,2-a]acenaphthylene (10) from 1. In an experiment similar to the preparation of **8** from **1**, but employing 20.3 mg of **1**, 0.5 ml of 10% aqueous potassium hydroxide, 0.2 ml of 97% hydrazine, and 1.0 ml of ethylene glycol, the reaction temperature was held at 120° for about 15 min and then raised to 150° for 20 min. By the end of this period a purple color was just beginning to develop. The mixture was cooled

and worked up as before. From the benzene solution was recovered a colorless crystalline product which, after one recrystallization, amounted to 15.7 mg (81%). Another recrystallization gave material, mp $207\text{--}210^\circ$, mixture melting point with alcohol from hydroboration below, $208\text{--}210^\circ$; the infrared spectrum was identical with that of analytically pure **10** prepared by hydroboration of **8**.

The potassium hydroxide solution used in the above experiment could be replaced by 74 mg of sodium acetate in 0.5 ml of water with essentially no change in the results.

Treatment of the hydrazine adduct **9** under these conditions using potassium hydroxide furnished **10** in similar yield.

Treatment of 20 mg of **3** under the above conditions using potassium hydroxide led to recovery of starting material only (infrared spectrum in KBr).

cis-6b-Hydroxy-6b,12b-dihydroacenaphth[1,2-a]acenaphthylene (10) by Hydroboration of 8. A magnetically stirred mixture of 30 mg of **8** and 342 mg of sodium borohydride in 8 ml of diglyme (distilled from lithium aluminum hydride) was cooled to 0° and treated dropwise with a solution of 1.56 ml of boron trifluoride etherate (distilled) in 6 ml of diglyme. The resulting homogeneous solution was allowed to warm to room temperature overnight. It faded during this period to colorless. Several tiny pieces of ice were added cautiously to destroy excess diborane; the mixture was cooled to 0° , and 1.0 ml of 10 *M* sodium hydroxide was added dropwise followed by 2 ml of 30% aqueous hydrogen peroxide. The mixture was warmed to room temperature over 2 hr and was then worked up with ether and water. The organic layer furnished 26 mg of crystals, mp $196\text{--}208^\circ$. These were recrystallized with some difficulty from benzene-cyclohexane and then cyclohexane to give matted needles, mp $209\text{--}211^\circ$; infrared: 3420 (m, broad), 1190 (m), 795 (s), and 775 (s) cm^{-1} (KBr); ultraviolet: λ_{max} 216 $\text{m}\mu$ ($\log \epsilon$ 5.14), 262 (sh) (3.58), 272 (3.75), 283 (3.89), 304 (4.08), and 314 (4.06) (EtOH).²² Occasionally stout prisms were obtained; these showed the same melting point and infrared spectrum in KBr.

Anal. Calcd for $\text{C}_{22}\text{H}_{14}\text{O}$: C, 89.77; H, 4.79; mol wt, 294. Found: C, 89.75; H, 4.84; mol wt, 294 (mass spectrum).

If, after destruction of diborane, the reaction mixture was heated to reflux with 0.6 ml of propionic acid, it quickly turned from colorless to purple. After 45-min heating 20 mg (67%) of **8** could be recovered by extraction with benzene; mp $283\text{--}287^\circ$; the infrared spectrum was identical with that of starting material.

Acenaphth[1,2-a]acenaphthylene (8) from Alcohol 10. A. Phosphorus Oxychloride in Pyridine. Solutions of 10 mg of alcohol **10** and 0.03 ml of phosphorus oxychloride, each in 0.5 ml of pyridine at 0° , were mixed. The resulting solution stood at room temperature for 30 min during which time a purple color developed. It was then diluted with benzene and washed with dilute hydrochloric acid and then water. After drying and removal of solvent there remained purple crystals. Two recrystallizations from cyclohexane gave 4.4 mg (47%) of olefin, mp $282\text{--}284^\circ$; infrared spectrum identical with that of authentic material.

B. Thermal Dehydration. A suspension of 4.9 mg of **10** in 0.5 ml of ethylene glycol was immersed in an oil bath at 125° and the temperature raised over 20 min to 180° . A purple color was visible after brief heating. The mixture was held at 180° for 2 hr, cooled, diluted with water, and extracted with benzene. Removal of solvent furnished 4.5 mg of purple crystals; the infrared spectrum was virtually identical with that of authentic material.

cis-6b,12b-Dihydroacenaphth[1,2-a]acenaphthylene (14). A solution of 20 mg of **8** in 10 ml of benzene containing ~ 5 mg of 5% palladium on carbon was stirred at room temperature under 1 atm of hydrogen. The solution quickly faded from dark purple to colorless. Removal of catalyst and solvent left colorless crystals which separated from ethanolic solution as long silky needles. Several recrystallizations gave an analytical sample, mp $216\text{--}219^\circ$; infrared: 1594 (m), 830 (m), 805 (m), and 774 (s) cm^{-1} (KBr); ultraviolet: λ_{max} 218 $\text{m}\mu$ ($\log \epsilon$ 5.17), 272 (sh) (3.79), 283 (3.97), 297 (4.11), 302.5 (4.08), and 307.5 (4.04) (EtOH);²² nmr: δ 5.68 (singlet, 1.9 H) and 7.5 (multiplet, 12 H) (CCl_4).

Anal. Calcd for $\text{C}_{22}\text{H}_{14}$: C, 94.93; H, 5.07; mol wt, 278.1095. Found: C, 94.57; H, 5.11; mol wt, 278.1100 (mass spectrum).

Methyl 8-(1'-Naphthoyl)-1-naphthoate. A solution of 200 mg of keto acid **19** in 20 ml of methanol was heated to reflux and treated dropwise with 0.9 ml of acetyl chloride, and heating continued for

(22) Identical maxima and virtually unchanged intensities are found in cyclohexane solution.

14 hr. The crude product remaining on removal of solvent was crystallized with difficulty from methanol. Several recrystallizations from the same solvent gave an analytical sample, mp 140–143°; infrared: 1724 (s), 1651 (m), 1276 (s), 1110 (m), and 774 (ms) cm^{-1} (KBr).

Anal. Calcd for $\text{C}_{23}\text{H}_{16}\text{O}_3$: C, 81.15; H, 4.74. Found: C, 80.98; H, 4.59.

The same compound could be obtained more readily (96%) by diazomethane esterification of the keto acid.

Methyl Pseudo-8-(1'-naphthoyl)-1-naphthoate. A solution of 200 mg of keto acid **19** in 20 ml of methanol was warmed to achieve homogeneous solution, treated with 0.9 ml of acetyl chloride, and then left at room temperature overnight. The crystalline material which had separated was twice recrystallized from methanol to give an analytical sample, mp 204.5–206°; infrared: 1715 (s) and 1290 (ms) cm^{-1} (KBr).

Anal. Calcd for $\text{C}_{23}\text{H}_{16}\text{O}_3$: C, 81.15; H, 4.74. Found: C, 81.10; H, 4.73.

Methyl 8-(2'-Methoxy-1'-naphthoyl)-1-naphthoate. A solution of 200 mg of methoxy keto acid **20** in 15 ml of methanol was esterified with excess diazomethane in ether. After several recrystallizations the product ester showed mp 161°; infrared: 1721 (s), 1651 (m), and 1275 (ms) cm^{-1} (KBr).

Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{O}_4$: C, 77.82; H, 4.90. Found: C, 77.57; H, 4.86.

3-(2'-Methoxy-1'-naphthyl)naphthalide (23). A solution of 500 mg of methoxy keto acid **20** in 25 ml of acetic acid containing 100 mg of 5% palladium on carbon was shaken under 3 atm of hydrogen for 18 hr at 65°. The yellow glass resulting from removal of solvent and catalyst crystallized readily from ethanol to give 140 mg of product, mp 177–179° (29%). Further crystallization gave an analytical sample, mp 180–181°; infrared: 1721 (s) cm^{-1} (CH_2Cl_2).

Anal. Calcd for $\text{C}_{23}\text{H}_{16}\text{O}_3$: C, 81.15; H, 4.74. Found: C, 80.95; H, 4.98.

Acetonide 24. A solution of 200 mg of **7** in 200 ml of acetone containing 4 ml of 70% perchloric acid was left at room temperature 18 hr. To the resulting clear, dark brown solution was added excess solid sodium bicarbonate and then water and ether. The organic layer was separated, washed, and dried. Removal of solvent left colorless crystals contaminated with yellow oil which was washed away with cyclohexane, yield 180 mg (80%). One recrystallization from benzene gave an analytical sample which did not melt below 355°; infrared: 1092 (s), 1025 (s), 792 (s), and 779 (s) cm^{-1} (KBr); nmr: δ 1.22 (singlet) and 7.2–8.0 (multiplet) (CDCl_3).

Anal. Calcd for $\text{C}_{25}\text{H}_{18}\text{O}_2$: C, 85.69; H, 5.18. Found: C, 85.97; H, 5.39.

Carbonate Ester 25. A mixture of 32 mg of **7** and 14 mg of potassium *t*-butoxide in 16 ml of diethyl carbonate (distilled) was heated at reflux under nitrogen for 66 hr. The cooled solution was diluted with ether, washed with water, and dried. Removal of solvent left off-white crystals which were recrystallized from benzene, yield 32 mg (92%). One further recrystallization gave an analytical sample, mp 314–315°; infrared: 1810 (s), 1795 (s), 1050 (ms), and 780 (s) cm^{-1} (KBr).

Anal. Calcd for $\text{C}_{23}\text{H}_{12}\text{O}_3$: C, 82.13; H, 3.60. Found: C, 81.78; H, 3.64.

Attempted chromatography over Woelm neutral alumina (II) resulted in complete hydrolysis; only a small amount of diol could be recovered by elution with methanol.

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The Piperidino Dechlorination of Chloroquinolines. Solvent Effects on the Reaction Kinetics¹

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Abstract: The kinetics of the reaction of 2- and 4-chloroquinolines with piperidine have been investigated in five different solvents. With both isomeric substrates, the reactivity order is qualitatively predicted by the dielectric constant in the case of aprotic solvents (toluene, ethyl acetate, DMSO). The so-called α -aza effect of 2-chloroquinoline is also observed with such solvents and is believed to originate from electrostatic effects. The reactivity of a chloroquinoline is exalted by H-bonding interaction with a hydroxylic solvent (methanol) especially for the γ -chloro isomer. Base catalysis is practically absent at low piperidine concentrations in toluene solution. However, it can be detected as a small kinetic factor in neat piperidine; this effect is larger for the α than for the γ isomer. Use of *N-d*-piperidine in toluene solution results in a small *inverse* isotope effect for the γ -chloro isomer and practically no effect for the α -chloro isomer. The present investigation includes a preliminary study on the scope of autocatalytic phenomena with respect to structure of the substrate and to solvent, and on a reliable evaluation of the "uncatalytic" rate constants under several conditions involving the 4 isomer.

Nucleophilic substitution involving six-membered-ring N-heteroaromatic substrates is characterized by the basicity of the aza group. Special features of the reaction include acid catalysis (or autocatalysis), bifunctional catalysis, and specific interactions with the reagent and/or the solvent.^{2,3}

(1) Nucleophilic Heteroaromatic Substitution. XXV. Work carried out under a CNR (Rome) research contract at the Universities of Rome (G. I. and G. S.) and Trieste (G. M.) on the basis of a conjoint program. Presented in part by G. I. at the Gordon Conference on the Chemistry of Heterocyclic Compounds (New Hampton, N. H., July 4–8, 1966). For part XXIV, see M. Calligaris, P. Linda, and G. Marino, *Tetrahedron*, 23, 813 (1967).

Specific interactions involving the aza derivative as the proton acceptor may consist of salt formation or of hydrogen-bond formation and also depend on the proton donor ability of the species present in the medium. The most familiar nucleophiles possibly concerned with such interactions are the primary or secondary amines and the thiols as having an ionizable hydrogen atom bound to the nucleophilic atom; the most familiar solvents are the alcohols because of their hydroxylic character.

- (2) G. Illuminati, *Advan. Heterocyclic Chem.*, 3, 285 (1964).
(3) R. G. Shepherd and J. L. Fedrick, *ibid.*, 4, 145 (1965).