the National Science Foundation (GP-7817) and the National Institutes of Health (GM-13585) is acknowledged with thanks.

A Study of the Enolization of the *syn* and *anti* Photodimers of 1,4-Naphthoquinone

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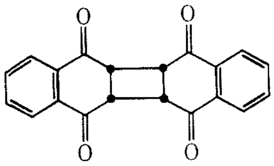
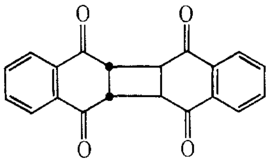
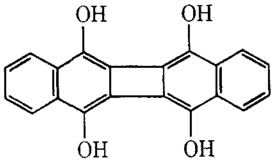
The isolation of the *syn* (I) and *anti* (II) photodimers of 1,4-naphthoquinone was reported recently.[1] In the presence of alkali both I and II led to tetraol (III).[1,2]


I

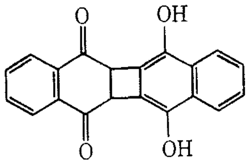

II

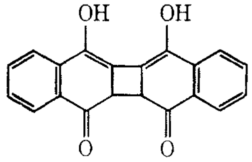

III

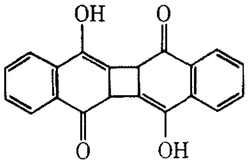
If III is treated with concentrated sulfuric acid, complete ketonization occurs, leading quantitatively to II. Similar treatment of I also produces II. The question as to whether the latter reaction proceeds *via* tetraol III or *via* a partially ketonized derivative thereof urged us to investigate the enolization aptitude of I and II in mild and strong acidic media.

When II was refluxed in acetic acid a yellowish color gradually developed. Concentration of the filtrate, which contained no trace of the monomeric 1,4-naphthoquinone, led to the isolation of orange-red crystals. Molecular weight determination by mass spectrometry[3] (mass 316) and elemental analysis ($C_{20}H_{12}O_4$) indicated that this compound was isomeric with II. The infrared spectrum exhibits a medium peak at 1605 cm^{-1} and a strong peak at 1589 cm^{-1} which may be assigned to two differently environed benzene nuclei, *i.e.*, a naphthalene and a *ortho*-substituted benzene moiety, respectively. A typical olefinic band of medium intensity was observed at 1640 cm^{-1}. A sharp carbonylic absorption appears at 1668 cm^{-1}. A broad absorption band between 3650 and 3100 cm^{-1}, with maximum intensity at 3410 cm^{-1}, indicates the presence of hydroxyl groups. The ultraviolet spectrum of this isomeric compound is very similar to that of II, and the *syn* dimer (I).

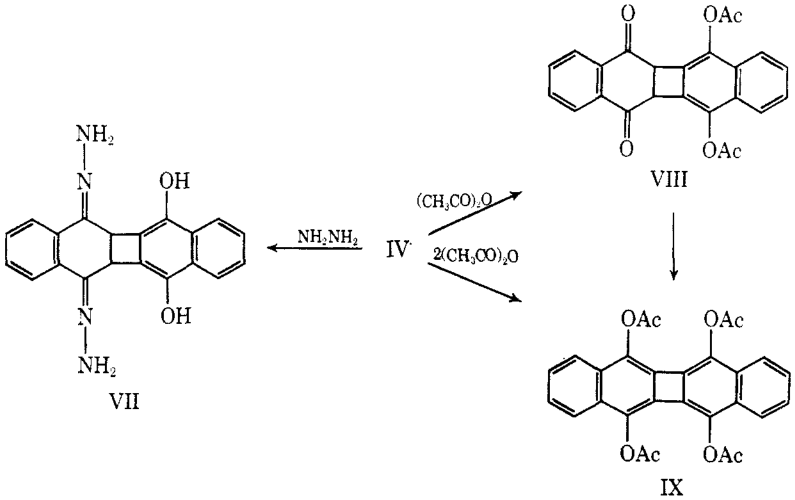
On the basis of the spectroscopic data and chemical properties, the three most likely structures for the isomeric orange-red compound are IV, V, and VI. Structures V and VI, however, are unlikely on account of strain, since the sp^3 hybridized carbon atoms in the C_4 ring would prevent the adjacent sp^2 hybridized carbon atoms from attaining planar configuration, required for significant π bonding. This argument is in fact analogous to Bredt's rule.[4] One also has to consider the driving force for the observed enolization of II, which would doubtlessly be aromatization, thus favoring structure IV.


IV


V


VI

The presence of two carbonyl groups in IV was proved by treatment with excess hydrazine, whereby a dihydrazone (VII) was obtained. When IV was refluxed in dioxane containing 2 mol of acetic anhydride the cor-



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[1] J. Dekker, P. Janse van Vuuren, and D. P. Venter, *J. Org. Chem.*, **33**, 464 (1968).

[2] J. M. Bruce, *J. Chem. Soc.*, 2782 (1962).

[3] J. Dekker and D. P. Venter, *J. Amer. Chem. Soc.*, **90**, 1225 (1968).

[4] J. Bredt, *Ann. Acad. Sci. Fennicae*, **29A** [2] 000 (1927); *Chem. Abstr.*, **22**, 1152 (1928); D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 398.

responding diacetate (VIII) was obtained. The infrared spectrum of VIII exhibited typical acetate (1768 cm^{-1}), carbonylic (1688 cm^{-1}), and olefinic (1642 cm^{-1}) absorptions. The tetraacetate (IX)[1,2] was obtained by refluxing IV or VIII in acetic anhydride containing sodium acetate.

The enolization of II in strongly acidic medium (dioxane containing concentrated hydrochloric acid) led to a mixture of II and a yellow diol (IVa). The relative amounts of II and IVa depended on the acid strength and reaction time. No complete isomerization of II to IVa could be established by variation of these two factors, indicating that an equilibrium had apparently set in. Under the conditions employed the equilibrium ratio was 3:1 in favor of IVa. The structure of IVa was supported by spectroscopic data and chemical conversion to VII, VIII, and IX. Both elemental analysis ($C_{20}H_{14}O_5$) and mass spectrum (mass 316) were consistent with a hydrate of the orange-red diol (IV), *i.e.*, $C_{20}H_{12}O_4H_2O$.

The hydrated diol (IVa) was converted quantitatively into the anhydrous diol (IV) by refluxing in anhydrous benzene or by heating at 160° for 24 hr. The reverse was accomplished by recrystallization of IV from aqueous ethanol. The infrared spectrum of IVa resembles that of IV with only slight differences in the positions and intensities of the corresponding bands. The associated hydroxyl absorption displayed an upward shift to 3440 cm^{-1}. The most interesting feature of the spectrum of IVa is the splitting of the olefinic absorption into two bands (1639 and 1633 cm^{-1}). The band at 1633 cm^{-1} can only be rationalized by assuming intermolecular hydrogen bonding between a molecule water (water of crystallization) and the olefinic bonds adjacent to the C_4 ring. The π electrons in olefins can act as proton acceptors in inter- and intramolecular hydrogen bonding,[5] resulting in a shift to lower frequency, as was observed.

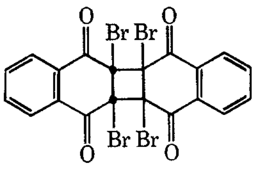
The diol (IV)[6] appeared to be stable in neutral solution and was recovered unchanged after reflux in dioxane. When the solution contained hydrochloric acid, however, a mixture of II and IV was obtained in the same ratio (1:3) as when II was treated similarly, indicating that the following equilibrium should exist in acidic medium: $\text{II} \rightleftarrows \text{IV}$.

Owing to its thermal instability, the *syn* dimer (I) isomerized rapidly and completely in dioxane containing hydrochloric acid, leading to a mixture of II and IV (ratio 1:3). This was to be expected, since ketonization of the initially formed IV should preferably lead to the less strained *anti* dimer (II).

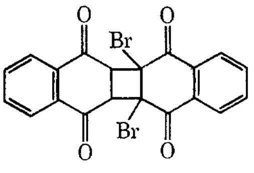
The tetraol (III) behaves like a highly unsaturated compound, decomposing easily in solution. In ethanol III displayed a blue fluorescence, which faded slowly upon standing at room temperature, finally disappearing within 4 hr.[7] Consequent evaporation of the solvent afforded the diol (IV) as sole product. Treatment of III with ethanolic hydrochloric acid produced a mixture of II and IV (ratio 1:3). If, however, a solution of III in cold concentrated sulfuric acid was added to excess water, II was obtained as the sole product.[1] Similar treatment of IV with sulfuric acid led to the same result.[8]

1,4-Diketo-1,2,3,4-tetrahydronaphthalene and its 2-methyl derivative enolize rapidly and completely in acidic media and there is no sign of an equilibrium.[9] In contrast, there is no rapid enolization of the *anti* dimer (II), and a definite equilibrium is established between II and IV. This equilibrium, and the spontaneous ketonization of III to IV in neutral media, may be related to the electron distribution in the region of the central C_4 ring. The data presented obey the generalization formulated by Streitwieser and coworkers,[10] "aryl positions adjacent to a fused strained ring have enhanced acidity and reduced reactivity toward electrophilic substitution," *i.e.*, the atomic orbitals used to construct the fused C_4 ring have higher p character. Hence the 5–5a, 5b–6, 11–11a, and 11b–12 bonds in III should accordingly have higher s character. Further, in order to minimize cyclobutadienoid configuration, these bonds are forced to attain maximum s character, accounting for its spontaneous ketonization to IV in neutral media. The 5–5a and 11b–12 bonds in IV also exhibit high s character, although to a lesser extent.

The typical olefinic nature of these bonds was illustrated amply by (i) the olefinic absorption in the infrared spectra of III (1655 cm^{-1}) and IV (1640 cm^{-1}) and (ii) the facile bromination of III and IV to X and XI, respectively.[11]



X



XI

The influence of the five-membered ring on the different reactivities of the 4 and 5 positions in indan to electrophilic substitution—originally discovered by Mills and Nixon[12]—has been investigated by various authors.[13] Our results, as well as those published by Streitwieser and coworkers,[10] and Cava and coworkers,[14] have established that a four-membered ring, condensed to a naphthalene moiety in the b position, results in a higher bond order of the aryl bonds adjacent to the strained four ring.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 221 spectrophotometer. Mass spectra were obtained on a M.S. 9 mass

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[5] L. Joris, P. von R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, **90**, 327 (1968), and references cited therein. A. W. Baker and A. T. Shulgin, *ibid.*, **81**, 4524 (1959); G. Eglinton, J. Martin, and W. Parker, *J. Chem. Soc.*, 1243 (1965); I. D. Campbell, G. Eglinton, and R. A. Raphael, *ibid.*, *B*, 338 (1968).

[6] Henceforward IV denotes both IV and IVa, unless explicitly stated otherwise.

[7] The conversion of I into IV proceeds markedly slower in dioxane, owing to its lower polarity.

[8] In some cases a mixture of II and III was obtained.

[9] R. H. Thomson, *J. Chem. Soc.*, 1737 (1950).

[10] A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, **90**, 1357 (1968).

[11] The chemistry of X and XI will be dealt with in a future publication.

[12] W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

[13] W. C. Lothrop, *J. Amer. Chem. Soc.*, **62**, 132 (1940); J. Vaughan and G. J. Wright, *J. Org. Chem.*, **33**, 2580 (1968); H. C. Longuett-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **42**, 756 (1946); F. P. K. de Jong and J. P. Wibaut, *Rec. Trav. Chim. Pays-Bas*, **83** (5), 437 (1964); P. M. Nair and G. Gopakumar, *Tetrahedron Lett.*, 709 (1964); J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, 1665 (1965); H. Meier, Eu. Mueller, and H. Shur, *ibid.*, **23**, 3713 (1967); H. Meier, J. Heiss, H. Suhr, and Eu. Mueller, *ibid.*, **24**, 2307 (1968).

[14] M. P. Cava, B. Hwang, and J. P. van Meter, *J. Amer. Chem. Soc.*, **85**, 4032 (1963).

spectrometer. In the case of VII and VIII no mass spectra were obtained. Melting points were determined on a Gallenkamp (design no. 889339) apparatus and are uncorrected.

A. 6,11-Diketo-5,12-dihydroxy-5b,6,11,11a-tetrahydrodibenzo[*b*,*h*]biphenylene (IV). 1. From II in Dioxane Containing Hydrochloric Acid.—A mixture of finely powdered II (1 g), dioxane (100 ml), and concentrated HCl (5 ml) was refluxed for 3 hr. The reaction product was precipitated with excess water, filtered, washed with water, and dried at 100°. The enolized product (0.56 g) was separated from unchanged II (0.185 g) by three successive extractions of the dried precipitate with 75-ml portions of boiling ethanol which were cooled to 20° and filtered. (II is practically insoluble in cold ethanol). The separate filtrates were rapidly concentrated until crystals began separating from the hot solution. After cooling, the crystalline product was filtered off.

a. The Anhydrous Diol (IV).—A boiling solution of the crude diol in anhydrous benzene was concentrated rapidly, whereupon IV separated as orange-red needles: mp 235° (blackening commencing at 220°); mass of molecular ion, *m/e* 316; $\nu_{\max}^{\mathrm{KBr}}$ 3410, 1668, 1640, 1589, 1274, 1248, 735 cm^{-1}; $\lambda_{\max}$ (in ethanol) 231 mμ (E 33,700).

Anal. Calcd for $C_{20}H_{12}O_4$: C, 75.95; H, 3.16. Found: C, 75.90; H, 3.20.

b. The Hydrated Diol (IVa).—A concentrated solution of the crude diol in ethanol (20 ml) was treated with water (4 ml). Upon cooling IVa separated as yellow needles: mp 235° (change in color to organge-red at 130–135°, blackening commencing at 220°); mass of molecular ion, *m/e* 316; $\nu_{\max}^{\mathrm{KBr}}$ 3440, 1672, 1639, 1633, 1590, 1275, 1242, 733 cm^{-1}.

Anal. Calcd for $C_{20}H_{12}O_4 \cdot H_2O$: C, 71.86; H, 4.19. Found: C, 71.81; H, 4.12.

2. From II in Acetic Acid.—A solution of II (0.5 g) in acetic acid (200 ml) was refluxed for 24 hr. The yellowish solution was concentrated to a small volume (25 ml) and left for 2 hr at 20°. Unchanged II was filtered off. The filtrate was concentrated to a smaller volume (5 ml), whereupon IV (0.015 g) separated as orange-red crystals.

3. From III in Dioxane Containing Hydrochloric Acid.—A mixture of III (0.1 g), dioxane (10 ml), and concentrated HCl (0.5 ml) was refluxed for 5 hr. The reaction mixture was treated as in procedure A1, yielding II (0.02 g) and IV (0.06 g), respectively.

B. 6,11-Diketo-5,12-dihydroxy-5b,6,11,11a-tetrahydrodibenzo[*b*,*h*]-biphenylenedihydrazone (VII).—A boiling solution of IV (0.2 g) in ethanol (40 ml) was treated with 80% hydrazine hydrate (1 ml). The yellow solution darkened rapidly and pale yellow needles of the dihydrazone (VII) separated. Compound VII (0.09 gm) was filtered from the hot reaction mixture and washed with cold ethanol: mp 231° (with violent decomposition); $\nu_{\max}^{\mathrm{KBr}}$ 3340, 1602, 1328, 765, 723 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}O_2N_4$: C, 69.76; H, 4.65; N, 16.28. Found: C, 69.72; H, 4.60; N, 16.20.

C. 5,12-Diacetoxy-6,11-diketo-5b,6,11,11a-tetrahydrodibenzo[*b*,*h*]-biphenylene (VIII).—A boiling solution of IV (0.1 g) in dioxane (2 ml) was treated with acetic anhydride (0.065 g) and anhydrous sodium acetate (0.05 g), and the mixture refluxed for 3 min. Dilution with excess water led to the precipitation of VIII (0.064 g). Recrystallization from ethanol afforded colorless needles: mp 192–194°; $\nu_{\max}^{\mathrm{KBr}}$ 1768, 1688, 1356, 1281, 1194,1177 cm^{-1}.

Anal. Calcd for $C_{24}H_{16}O_6$: C, 71.99; H, 4.03. Found: C, 71.94; H, 3.97.

D. 5,6,11,12-Tetraacetoxydibenzo[*b*,*h*]biphenylene (IX).—A mixture of IV (0.02 g), acetic anhydride (5 ml), and anhydrous sodium acetate (0.5 g) was refluxed for 2 hr and cooled. The crystalline product was filtered off, and washed successively with acetic acid and water. Recrystallization of the crude IX (0.027 g) from acetic anhydride yielded yellow needles: mp 358–360° (lit.[2] mp 358–360°); the product was identified by ir spectroscopy.

E. Acetylation of VIII.—A mixture of VIII (0.02 g), acetic anhydride (5 ml), and anhydrous sodium acetate (0.5 g) was treated as in procedure D. Recrystallization of the crude product (0.025 g) produced yellow needles, identical with IX.

F. Ketonization of IV (or IVa). 1. In Concentrated Sulfuric Acid.—Compound IV (0.025 g) was dissolved in cold concentrated H_2SO_4 (2 ml), and the solution poured into ice cold water (20 ml). The greyish precipitate was washed with water and recrystallized from acetic acid, yielding colorless plates of II (0.019 g), mp 246–248° (lit.[1] mp 246–248°), identified by ir spectroscopy.

2. In Dioxane Containing Hydrochloric Acid.—A solution of IV (0.05 g) in dioxane (10 ml) was treated with concentrated HCl (1 ml). The mixture was refluxed for 5 hr, cooled, and treated with excess water. The precipitate was treated as in procedure A1, whereby II (0.007 g) and IVa (0.025 g) were obtained.

G. Ketonization of III. 1. In Dioxane Containing Hydrochloric Acid.—A solution of III (0.05 g) in dioxane (20 ml) was treated with concentrated HCl (1 ml). The reaction mixture was treated as in procedure F2, whereby II (0.01 g) and IV (0.026 g) were obtained.

2. In Ethanol.—A solution of III (0.025 g) in ethanol (30 ml) was refluxed until the blue fluorescence disappeared (5 hr). Concentration of the solution yielded crystalline IV (0.021 g). In dilute ethanolic solution (0.002 g/25 ml) complete conversion of III into IV at room temperature (20°) was established within 4 hr. In a similarly concentrated solution of III in dioxane ketonization was completed within 12 hr.

H. 5a,5b,11a,11b-Tetrabromo-5,6,11,12-tetraketo-5,5a,5b,-6,11,11a,11b,12-octahydrodibenzo[*b*,*h*]biphenylene (X).—Bromine (0.1165 g, 0.00073 mol) was added to a stirred suspension of III (0.05 g, 0.00015 mol) in benzene (12 ml). The mixture was stirred at room temperature for 1.5 hr. The crystalline product (X) (0.04 g) was filtered off and washed with ether: mp 255–258° dec; $\nu_{\max}^{\mathrm{KBr}}$ 1692, 1591, 1250, 1005 cm^{-1}.

Anal. Calcd for $C_{20}H_8O_4Br_4$: C, 38.01; H, 1.28; Br, 50.59. Found: C, 38.00; H, 1.28; Br, 50.94.

I. 5a,11b-Dibromo-5,6,11,12-tetraketo-5,5a,5b,6,11,11a,-11b,12-octahydrodibenzo[*b*,*h*]biphenylene (XI).—Bromine (0.21 g, 0.0013 mol) was added to a solution of IV (0.2 g, 0.00063 mol) in boiling ethanol (20 ml). The colorless crystals of XI (0.2 g) which quickly separated were filtered off, washed with cold ethanol, and recrystallized from ethanol: mp 165–170° dec; $\nu_{\max}^{\mathrm{KBr}}$ 1704, 1686, 1591, 1254, 717 cm^{-1}; mass of molecular ion, *m/e* 472.

Anal. Calcd for $C_{20}H_{10}O_4Br_2$: C, 50.66; H, 2.13. Found: C, 50.63; H, 2.11.

Registry No.—I, 14734-20-4; II, 14734-19-1; IV, 19817-49-3; VII, 19817-50-6; VIII, 19817-51-7; X, 19817-52-8; XI, 19817-53-9.

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Hydrazine Derivatives. II. Side Reactions in the Preparation of 1,1′-Azobisformamides[1]

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During the preparation of a series of 1,1′-azobis(N-substituted formamides)[2] from dialkyl azodiformates and amines, 1,6-dialkylbiureas were frequently isolated as by-products. It is the purpose of this note to discuss the competitive and consecutive reactions occurring when dialkyl azodiformates (**1**) and amines react and to consider the sources of various by-products.

The first two reactions (1 and 2) are a facile lab-

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(1) Part I: C. M. Kraebel, S. M. Davis, and M. J. Landon, *Spectrochim. Acta*, **23A**, 2451 (1967).

(2) C. M. Kraebel and S. M. Davis, *J. Chem. Eng. Data*, **14**, 133 (1969).