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Studies Related to the Conversion of 9,10-Anthraquinones to Anthracenes

Thomas R. Criswell and Bruce H. Klanderman*

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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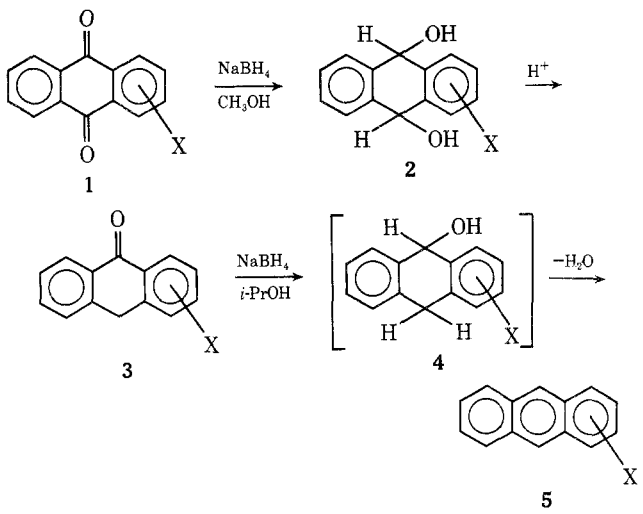
A facile method for the conversion of certain 9,10-anthraquinones to anthracenes *via* successive heterogeneous alcoholic sodium borohydride reductions and dehydrations has been developed. Several halo- and methyl-substituted anthracenes have been prepared by this procedure and the intermediate 9,10-dihydroxy-9,10-dihydroanthracenes and anthrones have been isolated and characterized. Ir and nmr spectroscopy have been employed for determination of the isomer distribution of 9,10-dihydroxy-9,10-dihydroanthracenes and unsymmetrically substituted anthrones.

The reduction of an appropriately substituted anthraquinone provides a potential route to many anthracene derivatives which are otherwise difficult to obtain. We wish to report that sodium borohydride in a lower alcohol is an effective reagent for this purpose. The intermediates formed during this reduction have been identified and their conformational and keto–enol relationships studied.

Sodium borohydride reduction of anthraquinones in diglyme under widely different reaction conditions has been reported. In one instance,[1] the difficult-to-purify products contained boron, whereas anthrahydroquinone was the product reported in the second case.[2] Later investigators[3,4] claimed 35–50% yields of anthracenes for the reduction of the corresponding anthraquinones in refluxing sodium borohydride–diglyme solutions. Evidence was also given for the formation of some anthracene derivatives (50–70%) when the reduction was run in the presence of boron trifluoride or aluminum chloride. Under these conditions, anthraquinone gave a mixture of anthracene and 9,10-dihydroanthracene. More recently,[5,6] sodium borohydride in methanol has been used to obtain 9,10-dihydroxy-9,10-dihydroanthracenes from the corresponding anthraquinones. Reductions wherein lithium aluminum hydride has been used have given conflicting results.[7,8]

We have found that a three-step procedure involving two reduction–dehydration sequences using sodium borohydride in methanol or 2-propanol converts many anthraquinones (**1**) to anthracenes (**5**) in a straightforward fashion, *via* the successive formation of 9,10-dihydroxy-9,10-dihydro intermediates, anthrones, and 9-hydroxy-9,10-dihydro intermediates. The steps are schematically represented wherein X represents one or more substituents on either or both end rings.



Procedures described in the Experimental Section have been generalized and represent a skeletal framework from which one can adapt procedures for specific anthraquinones. Table I lists the pertinent data for a number of anthraquinones. An additional specific procedure for the synthesis of 1,4-dimethoxyanthracene (**5j**) is included, because the literature preparation[9] for **5j** is not readily reproducible in our hands. Compound **5j** has been shown to be a useful diagnostic tool for detecting the presence of benzyne intermediates,[10] and satisfactory yields are not obtained by the general stepwise procedure discussed above.

The yield of 9,10-dihydroxy-9,10-dihydroanthracene (**2a**) was lower than the yields for **2** from substituted anthra-

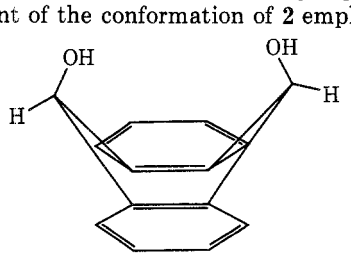
Table I
Sodium Borohydride Reduction of Anthraquinones. Yields and Melting Points of Isolable Compounds

Anthraquinone (1)	9,10-Dihydroxy-9,10-dihydroanthracene (2) Yield, %	Mp, °C[a]	Anthrone (3) Yield, %	Mp, °C	Anthracene (5) Yield, %	Mp, °C
H (**a**)	65	158–165[b]	93	158–170[c]	78	213–215[d]
2-Methyl (**b**)	95	165–176[e]	54	116–124[f]	24	206–207[g]
1,4-Dimethyl (**c**)	87	195–215[h]	n.r.			
2,7-Dimethyl (**d**)	88	195–197[e]	83	185–194[i]	94	233–235[j]
1-Chloro (**e**)	n.r.					
2-Chloro (**f**)	84	178–184[e]	97	184–189[k]	30	219–220[l]
1,5-Dichloro (**g**)	90	215–220[m]	82	175–178[n]	67	178–181[o]
1,8-Dichloro (**h**)	88	180–189[p]	98	223–233[q]	47	151–160[r]
1,2,3,4,6,7-Hexachloro[s] (**i**)	84	230–235[e]	n.r.			
1,4-Dimethoxy (**j**)	95	141–143[t]	52	127–170[e]	62	134–136[u]

[a] There is frequent disparity of melting points for **2** between the literature and the reported values in Table I, as well as between published reports. This may be due to the presence of varying proportions of cis–trans mixtures. See footnotes *g* and *i*. [b] Lit. mp 195°: C. Dufraisse and J. Houpillart, *C. R. Acad. Sci.*, **205**, 740 (1937). [c] Lit. mp 163–170°: W. R. Orndorff and C. L. Bliss, *Amer. Chem. J.*, **18**, 453 (1896). [d] Lit. mp 218°: E. Clar, "Polycyclic Hydrocarbons," Vol. 1, Academic Press, New York, N. Y., 1964, p 290. [e] Satisfactory microanalytical data were obtained for this new compound. [f] Lit. mp 100°: H. Limpricht, *Justus Liebigs Ann. Chem.*, **314**, 237 (1900). [g] Lit. mp 203°: E. Bornstein, *Ber.*, **15**, 1820 (1882). [h] Lit. mp 241–242°: Y. Lepage, *Bull. Soc. Chim. Fr.*, 1759 (1961). [i] Lit. mp 171°: F. Mayer and H. Gunther, *Ber.*, **63**, 1455 (1930). [j] Lit. mp 240°: V. L. Kravtsov, *Ukr. Khim. Zh.*, **29**, 957 (1963). [k] Lit. mp 156°: E. B. Barnett and M. A. Matthews, *J. Chem. Soc.*, **123**, 2549 (1923). [l] Lit. mp 215°: H. Schilling, *Ber.*, **46**, 1066 (1913). [m] Cis isomer lit. mp 205–209°; trans isomer lit. mp 220–224° (ref 12). See also ref 11. [n] Lit. mp 178–180°: A. Eckert and R. Pollak, *Monatsh. Chem.*, **38**, 11 (1917). [o] Lit. mp 185°: footnote *l*. [p] Trans isomer lit. mp 160° yellow, 176° dec; cis isomer lit. mp 215° dec (ref 5). [q] 1,8-Dichloro-9-anthrone lit. mp 167°: footnote *k*. 4,5-Dichloro-9-anthrone lit. mp 198°: E. B. Barnett, J. W. Cook, and M. A. Matthews, *Recl. Trav. Chim. Pays-Bas*, **45**, 68 (1926). [r] Lit. mp 156°: footnote *l*. [s] Preparation similar to that of N. S. Dokunikhin, Z. Z. Moiseeva, and V. A. Mayatnikova, *Zh. Org. Khim.*, **2**, 516, (1966). [t] Lit. mp 192° (ref 9). Value corrected to 152–153°: Y. Lepage, *Ann. Chim. (Paris)*, **4**, 1137 (1959). Compound **2j** was obtained *via* the stepwise reduction procedure outlined in the Experimental Section. A specific preferred preparative scheme for compounds **3j** and **5j** is also contained in the Experimental Section and the data for these compounds are included in Table I. [u] Lit. mp 137° (ref 9).

quinones but notably higher than that from $LiAlH_4$ reduction.[8] The synthetic advantage of sodium borohydride over $LiAlH_4$ is further indicated by the 1,5-dichloroanthraquinone reduction sequence. A 59% yield of **2g** was obtained[11] by $LiAlH_4$ reduction (20 days) of **1g**, while the sodium borohydride method gave **2g** in 90% yield in 24 hr. The Meerwein–Ponndorf reduction of **1** to **2** occurs with poorer yields[12] than those realized *via* sodium borohydride reduction. Also, the identity of the Meerwein–Ponndorf reduction product varied with the aluminum alkoxide used with a given anthraquinone. However, the Meerwein–Ponndorf reduction of **1e** to **2e** was successful, whereas **2e** could not be prepared *via* the sodium borohydride method despite several attempts. Compounds **2c** and **2i** could not be dehydrated to **3**, possibly for steric reasons. Thus the sodium borohydride reduction of anthraquinones described above may be the method of choice for the synthesis of some substituted anthracenes, but other reduction methods such as the zinc and ammonium hydroxide reduction may be preferable for other substituted anthracenes.[13,14] The nature and position of substituents seem to have a large effect upon the relative merits of a given method.

We have studied the isomeric distribution and the axial–equatorial conformation of the hydroxyl groups of **2**, as well as the position of the keto–enol equilibria of **3**. Compound **2** can be considered a dibenzo-1,4-cyclohexadiene and as such exists in the boat conformation with quasi-axial and equatorial hydroxyl groups.[5,15,16] The first treatment of the conformation of **2** employed infrared



2

analysis of C–O stretching frequencies to assign hydroxyl-group orientation.[5] Absorption at 1030–1060 cm^{-1} was assigned to equatorial hydroxyl groups and absorption at 960–1000 cm^{-1} to axial hydroxyl groups.[5] Initially, we attempted to correlate the C–O stretching frequencies as was done previously,[5] but our conclusions were inconsistent. A more recent report[14] mentions the use of the O–H stretching region of infrared spectra for stereochemical analysis. Intramolecular hydrogen bonding indicative of cis isomers was evidenced by lower frequency broad absorption, compared to higher frequency, less broad absorption for nonhydrogen-bonded hydroxyl groups of trans isomers. We then used the O–H stretching frequencies for primary stereochemical assignments, reinterpreted the C–O stretching frequency assignments, and refined the assignments by use of the nmr data as described in the following.

The O–H stretching region of the infrared spectra, obtained from KBr pressings, was used to determine the presence of hydrogen bonding[16] which in turn indicated the presence of diaxial hydroxyl cis isomer, the only isomer in which hydrogen bonding (intramolecular) could occur between the hydroxyl groups. Absence of hydrogen bonding indicated trans isomer because of the impossibility for intramolecular hydrogen bonding. Intramolecular hydrogen bonding would also be impossible for a diequatorial hydroxyl cis isomer; however, ring conversion would give the equally or more stable diaxial hydroxyl cis isomer, especially for those compounds containing peri substituents. The nmr spectra were then used in a more quantitative fashion to indicate the distribution of isomers in solution. A degree of uncertainty is inherent in the interpretation of the nmr spectra in the sense that assignment of the 9,10-proton absorptions to specific isomers is not readily possible, but the larger absorption in each case was given the same assignment as that obtained from the infrared spectra. A detailed discussion of the spectra follows, along with additional comments on the spectral correlations and assignments.

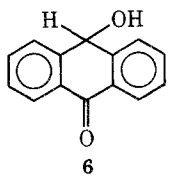
Table II
Nmr[a] and Ir[b] Data for 2

Compd	Aromatic protons	9,10 Protons	9,10 Hydroxyl protons	9,10 Protons after D_2O addition[c]	Major isomer, %	Infrared absorption[d]	Assignment for major isomer[d]
2a[e]	2.40–2.91 (m, 8)	4.80 (s, 2)	4.47 (broad s, 2)	4.47 (s, 0.18) 4.73 (s, 1.82)	91	3220 (s, broad) 1030 (s)	Cis
2b	2.31–2.96 (m, 7)	4.42 (s, 0.55) 4.69 (s, 1.45)	3.82 (broad s, 2)	4.42 (s, 0.55) 4.69 (s, 1.45)	73	3250 (s, broad) 1030 (s)	Cis
2c	2.36–2.95 (m, 6)	4.35 (broad s, 2)[f]	4.67 (broad s, 2)[g]	4.33 (s, 2)	100	3330 (s, broad) 1040 (m) 990 (s)	Trans
2d	2.47–2.98 (m, 6)	4.47 (s, 0.36) 4.73 (s, 1.64)	3.91 (broad s, 2)	4.47 (s, 0.36) 4.71 (s, 1.64)	82	3220 (s, broad) 1030 (s) 1000 (w)	Cis
2f	2.42–2.87 (m, 7)	4.51 (s, 0.25) 4.76 (s, 1.75)	3.71 (broad s, 2)	4.51 (s, 0.25) 4.76 (s, 1.75)	88	3260 (s, broad) 1035 (s) 990 (w)	Cis
2g	2.33–2.65 (m, 6)	4.18 (quartet, 4)		4.38 (s, 2)	100	3310 (s, broad) 985 (s)	Trans
2h	2.33–2.71 (m, 6)	3.55 (d, 1) 4.15 (d, 1)	3.45 (d, 1) 4.30 (d, 1)	3.55 (s, 1)[h] 4.15 (s, 1)	100	3430 (s, broad) 965 (s)	Trans
2i	2.22 (d, 2)	4.23 (s, 1.25) 4.31 (s, 0.75)	5.70 (s, 0.75) 5.71 (s, 1.25)	4.19 (s, 1.25) 4.28 (s, 0.75)	63	3420 (s, broad) 990 (s)	Trans
2j	2.36–2.76 (m, 6)	4.23 (t, 2)	4.84 (t, 2)	4.19 (s, 1.50) 4.27 (s, 0.50)	75	3380 (s, broad) 985 (s)	Trans

[a] Chemical shift in τ units *vs.* TMS, DMSO-d_6 solvent (25° unless otherwise specified) with TMS or hexamethyldisiloxane (HMDSO) used as internal reference. [b] Infrared absorption in cm^{-1}. [c] Addition of D_2O caused elimination of 9,10-hydroxyl proton resonance accompanied by appearance of a DOH resonance in the range τ 6.2–7.0 and did not alter aromatic proton chemical shift. [d] All OH absorption indicates some hydrogen bonding, because the infrared spectra were obtained in the solid state. The differences observed and assignments made relate, therefore, to relative amounts and types (intramolecular *vs.* intermolecular) of hydrogen bonding. [e] Nmr spectra obtained at 110°. [f] Coalesced triplet character. [g] Coalesced doublet character. [h] The 9- and 10-proton absorptions for this compound are nonidentical because of the peri Cl location; therefore, the two absorptions do not represent two isomers. The nmr of 1,8-dichloroanthracene shows the 9 and 10 protons at τ 0.99 and 1.36, respectively.

The infrared spectra for **2a, 2b, 2d,** and **2f** showed broad O–H stretch absorption centering below 3300 cm^{-1} (see Figure 1 and Table II), indicative of cis isomers. Trans isomers were assigned to **2c, 2g, 2h, 2i,** and **2j** based on somewhat less broad absorption centering above 3300 cm^{-1}. Obviously, smaller amounts of the other isomer in each case could not be ruled out for these compounds in the solid state based on the infrared spectra. The spectrum for **2g** shows a significant shoulder absorption below 3300 cm^{-1} and may indicate intramolecular hydrogen bonding of the equatorial hydroxyl with the peri chlorine, especially since one hydroxyl of the trans isomer must be equatorial. For **2h,** the equatorial hydroxyl need not be near the peri chlorines, and no hydrogen bonding is indicated. Because of the inconsistencies with the literature concerning the assignment of C–O absorptions as noted above, the appropriate regions of the infrared spectra were examined. Interestingly, with one exception (**2c**), a direct correlation, different from that postulated previously,[5] existed between the cis and trans assignments and the position of absorption in the 1000 cm^{-1} region. The compounds given cis assignments (**2a, 2b, 2d,** and **2f**) showed strong absorption between 1020 and 1050 cm^{-1} and little or no absorption between 960 and 1000 cm^{-1}, whereas the compounds given trans assignments (**2c, 2g, 2h, 2i,** and **2j**) gave strong absorption between 960 and 1000 cm^{-1}, and **2c** showed additional significant absorption between 1020 and 1050 cm^{-1}. In light of the rather good correlation, the absorption in the 1000-cm^{-1} region may indicate the "depth" of the boat conformation as reflected in the C–C–O absorption. Thus, for cis isomers the boat form would be "deeper" with the ends drawn somewhat closer due to hydrogen bonding.

Table II gives the nmr data for compounds **2.** The relative shapes and areas of the 9,10-proton absorption and 9,10-hydroxyl proton absorption coupled with the changes observed with the addition of deuterium oxide were useful in obtaining a more quantitative estimate of the relative amounts of cis and trans isomers. Usually, the spectra of the samples treated with deuterium oxide were simpler to evaluate because of the elimination of 9,10-hydroxyl proton absorption. Compounds **2a, 2b, 2d,** and **2f** were composed of 73–91% cis isomer. The parent compound (**2a**) with no substituents had 91% cis isomer, compared with 72–88% for the β-substituted compounds (**2b, 2d,** and **2f**). These observations are in good accord with the complementary observations of Cristol and coworkers,[16] who reported cis diol as the major product for sodium borohydride reduction of some anthraquinones with no peri substituents. A similar correlation was observed for the dihydroxydihydro compounds (**2c, 2g, 2h, 2i,** and **2j**) formed from anthraquinones with peri substituents; trans isomers were obtained as 63–100% of the product. The intermediacy of oxanthrones (**6**) or the corresponding boron esters, as



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suggested by Cristol,[16] and the subsequent stereochemical control by peri substituents nicely explain the stereochemistry of the major product. Note that for the 1,8-dichloro compound, the high stereoselectivity can be obtained only if the carbonyl group peri to the chlorines is reduced first. These arguments assume that isomerizations (*via* a dihydroanthrenyl cation) have not occurred appreciably during work-up conditions.

Anthrones (**3**) are known to exist in solution as keto-enol equilibrium mixtures. The nmr results in Table III show the keto–enol ratios obtained in deuterated dimethyl sulfoxide and chloroform at the indicated temperatures.

Table III
Nmr[a] Data for 3

Compd	Temp, °C	Solvent	Aromatic proton resonance[b]	Methylene proton resonance[c]	Keto:enol ratio
3a	110	DMSO-d_6	1.62–2.77 (m, 9.2)	5.75 (s, 0.8)	40:60
	25	$CDCl_3$	2.42–3.58 (m, 8.4)	6.55 (s, 1.6)[d]	80:20
3b	25	DMSO-d_6	1.55–3.19 (m, 8.5)	5.16 (s, 0.5)	25:75
	25	$CDCl_3$	1.73–3.42 (m, 8.6)	5.42 (s, 0.4)	20:80
3d	25	DMSO-d_6	1.76–3.36 (m, 7.4)	5.36 (s, 0.6)	30:70
	25	$CDCl_3$	1.77–3.39 (m, 7.4)	5.42 (s, 0.6)	30:70
3f	25	DMSO-d_6	1.51–4.27 (m, 8.6)	5.09 (s, 0.4)	20:80
	25	$CDCl_3$	1.67–3.29 (m, 8.5)	5.31 (s, 0.5)	25:75
3g	25	DMSO-d_6	1.24–2.80 (m, 7.5)	4.89 (s, 0.5)	25:75
	25	$CDCl_3$	1.25–2.83 (m, 7.6)	5.86 (s, 0.4)	20:80
3h	110	DMSO-d_6	1.52–2.95 (m, 7.5)[e]	5.91 (s, 0.30)	15:85
	55	$CDCl_3$	1.82–3.02 (m, 7.0)[f]	5.98 (s, 1.0)	50:50
3j	25	DMSO-d_6	2.40–3.29 (m, 7.0)	4.89 (s, 1.0)	50:50
	25	$CDCl_3$	2.18–3.30 (m, 6.9)	4.86 (s, 1.1)	55:45

[a] Expressed in τ units. [b] Addition of D_2O did not in general change aromatic proton resonances. [c] Addition of D_2O caused elimination of methylene proton (in equilibrium with the enol form) resonance accompanied by the appearance of a resonance due to DOH in the range τ 5.71–7.05. [d] Addition of D_2O caused diminution of the intensity of the methylene proton resonance accompanied by the appearance of a resonance due to DOH. [e] In the aromatic region, a multiplet centered at τ 1.60 (1.0 peri H) was assigned to the 10-OH isomer, a multiplet centered at τ 1.96 (0.5 peri H) was assigned to the 10-keto isomer, and a broad singlet at τ 1.52 (0.5 H) was assigned to the 9 H of the 10-OH isomer. Addition of D_2O caused elimination of the latter peak. [f] In the aromatic region, a multiplet centered at τ 1.92 (1.0 peri H) was assigned to the 10-keto isomer.

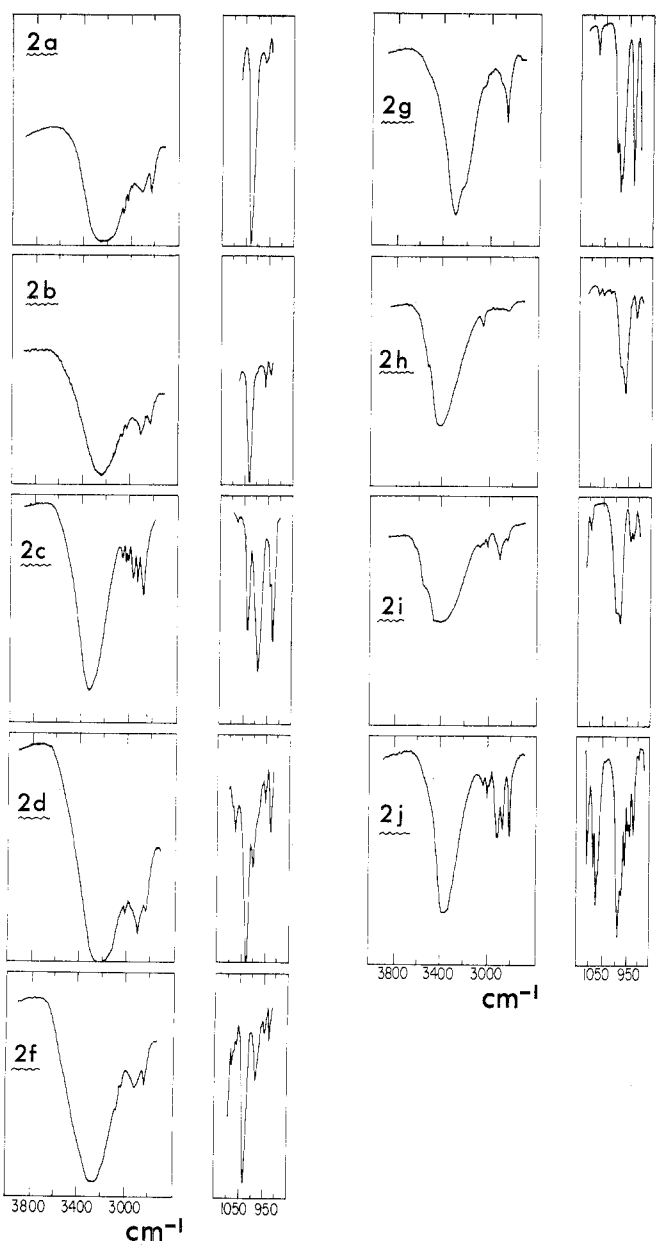
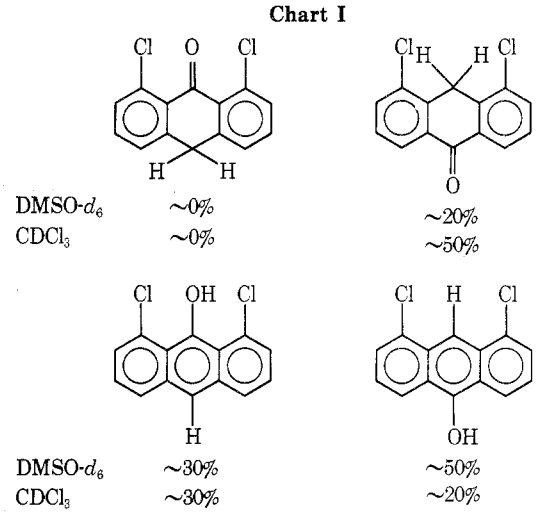


Figure 1. Pertinent regions of infrared spectra for **2**.

Compounds for which the spectra could be obtained at the same temperature in both solvents exhibit keto–enol equilibria ratios that are approximately the same in both solvents for a given compound. However, temperature seems to affect the equilibrium position markedly (**3a** and **3h**). One compound, **3h**, is particularly interesting because two different keto and two different enol forms can arise from the dehydration of **2h**. Chart I indicates the approximate amount of each isomer present in each solvent, based on assignments made with the nmr data in Table III and the footnotes. (The spectra are somewhat ambiguous and the assignments are the most reasonable consistent with certain requirements, for example, the same ratio of structural isomers for each solvent.) Note that one keto form and both enol forms exist in significant amounts for each solvent. The favorable effect of hydrogen bonding for the 9-hydroxyl form is thus demonstrated by the absence of the 9-keto form. Peri substitution has some effect on the mode of dehydration for **2h** to **3h** as is evidenced by the ~1:2 ratio of 9- and 10-substituted anthrones (**3h**).

Chart I



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Experimental Section

Nmr spectra were determined with a Bruker scientific HX-90 spectrometer in DMSO-d_6 or $CDCl_3$ with TMS or HMDS (hexamethyldisiloxane) as internal reference, and all values are nor-

malized with respect to TMS. Infrared spectra were determined with a Beckman IR-12 spectrophotometer; KBr pressings (solid state) were used because most of the materials were not soluble in good solvents for infrared studies.

Generalized Procedure for Anthraquinone Reductions. 1. 9,10-Dihydroxy-9,10-dihydroanthracenes. An anthraquinone (0.08–0.10 mol) was placed in methanol (400–500 ml) and the resulting suspension was stirred while cooling to 0–5° with an ice bath. Solid sodium borohydride (13–15 g, 0.35–0.40 mol) was added in small portions to the suspension at such a rate as to prevent a temperature rise (30–60 min). During continuous stirring at 0–5° (2–4 hr), the reaction mixture assumed an orange color and became nearly homogeneous, and often a white material precipitated. The reaction mixture was poured into an ice-water mixture and stirred. The white precipitate which formed was collected, thoroughly washed with water, and air dried, yield of product 80–90%.

2. Conversion of 9,10-Dihydroxy-9,10-dihydroanthracenes to Anthrones. A suspension of 4 g of 9,10-dihydroxy-9,10-dihydroanthracene in hot 5 *N* HCl (125 ml) was stirred for 3–6 hr. The white, suspended material gradually assumed a yellow color. The anthrone was collected by filtration, thoroughly washed with water, and dried. Recrystallization or trituration afforded material of greater purity, yield of anthrone 80–95%.

3. Conversion of Anthrones to Anthracenes. An anthrone (0.08–0.10 mol) was suspended in 2-propanol (400–500 ml). After addition of sodium borohydride (0.40–0.90 mol), the reaction mixture was refluxed with stirring for 24–36 hr. The reddish-brown reaction mixture was poured with stirring into ice water which had been purged with nitrogen. In most instances, precipitation of the desired anthracene occurred. Addition of dilute acid was necessary in some instances in order to decompose unreacted sodium borohydride and to induce precipitation. The yellow solid was collected, washed thoroughly with water, and air dried. The dehydration of **4** is spontaneous under the reaction conditions, yield of crude anthracene 49–80%. Appropriate recrystallization was necessary for purification (ethanol or dichloromethane–methanol).

1,4-Dimethoxyanthraquinone (1j). Quinizarin (100 g, 0.42 mol), methyl *p*-toluenesulfonate (220 g, 1.18 mol), and sodium carbonate (70 g, 0.66 mol) were combined in *o*-dichlorobenzene (1.6 l.) and gently refluxed for 20 hr. The reaction mixture was allowed to cool to 95–100°, at which time water (100 ml) was added dropwise (5–10 min). The mixture was steam distilled to remove the solvent, and the precipitate which formed was collected by filtration and recrystallized from ethanol, yield 87.1 g (78%), mp 171–173° (lit.[17] mp 171°).

1,4-Dimethoxyanthracene. To a mixture of 50 g of 1,4-dimethoxyanthraquinone in 750 ml of diglyme at 5° was added sodium borohydride (30 g) in portions (15 min), and the mixture was stirred at 5–15° for 1.75 hr (total) before it was added to approximately 2.5 l. of ice water. An ether layer was added, and 200 ml of acetic acid was then added carefully. The reaction mixture (approximately 4 l.) was heated on a steam bath for 4 hr. Much bubbling occurred as the mixture was heated (at about 50°), and an orange precipitate began to form. The mixture was cooled overnight, and the orange precipitate was filtered off, washed, and dried to give 24.5 g (52%), mp 127–170°, of 1,4-dimethoxyanthrone.

To a mixture of 24.4 g of the anthrone in 375 ml of diglyme at 5–10° was added sodium borohydride (15 g). The mixture was stirred at 5–15° for 2 hr before it was added to approximately 2.0 l. of ice water. An ether layer was added, and 125 ml of acetic acid was then added carefully. Then 50 ml of concentrated hydrochloric acid was added, and the mixture was stirred at room temperature for 2 hr. The yellow precipitate was removed by filtration and washed with water to give 20.7 g, mp 127–132°.

Recrystallization and purification were effected by dissolving the crude product in 100 ml of methylene chloride and adding 400 ml of methanol dropwise. This mixture was cooled and a yellow product was obtained (14 g, 62%), mp 134–136°.

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Rearrangements of Azidoquinones. XII. Thermal Conversion of 2-Azido-3-vinyl-1,4-quinones to Indolequinones[1]

Paul Germeraad and Harold W. Moore*[2]

Department of Chemistry, University of California, Irvine, California 92664

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2-Azido-3-vinyl-1,4-quinones (**1**) thermally undergo a facile ring closure to indolequinones (**2**). The synthetic utility of this reaction is illustrated in the synthesis of 1,2,5,10-tetrahydro-3*H*-pyrrolo[1,2-*a*]benzo[*f*]indole-5,10-dione (**12**), the naphthoquinone analog of the mitosene ring system. The mechanism of the thermal ring closure is also discussed and, based upon kinetic data, a concerted process is suggested.

Azidoquinones are uniquely versatile synthetic reagents which are easily prepared and relatively stable under normal laboratory conditions. They are penultamate precursors to a large variety of other compounds, *e.g.*, α-cyanoalkylidene-$\Delta^{\alpha,\beta}$-butenolides,[3] 2-cyano-4-cyclopentene-1,3-diones,[4] azepine-2,5-diones,[5] diacyl cyanides,[6] 3-cyano-2-aza-1,4-quinones,[7] aminoquinones,[8] cyanoketenes,[9] 4-acetoxy-1,2-quinone-2-(*N*-acetyl)imines,[10] *trans,trans*-1,4-