(11 500), 284 (9300), 300 (sh, 3000); mass spectrum, *m/e* (relative intensity) 217, 216 (100), 215, 213, 191, 190 (88), 189; ^{1}H NMR ($CDCl_3$) 7.12-7.77 (m, 6 H), 6.10 (s, 2 H), 4.44 (s, 2 HO), 3.84 ppm (s, 2 H). Anal. Calcd for C and H: C, 94.44; H, 5.55. Found: C, 93.9; H, 5.7.

B. Electrochemical Decarboxylation.[17] The diacid was placed in a cooled electrolysis cell equipped with a reflux condenser and a magnetic stirrer. The electrolysis was carried out on 2.5 g of **6** (11.4 mmol) in 90 mL of pyridine-water (80:20) and 1.9 mL of triethylamine during 4 h at 100 V and 0.6-0.8 A. The mixture was poured onto 400 mL of 10% HCl, worked up in the usual manner, and chromatographed on 80 g of silica gel. Elution with benzene afforded 350 mg (20%) of a product identical with that described above.

Thermal Rearrangement of 7. Preparation of Cycloocta[*def*]fluorene (1). The following thermolysis apparatus was constructed for this experiment. In an horizontal pyrolysis oven was placed a glass tube (90 cm in length and 1.5 cm in diameter) filled with glass chips (1-2 mm) and equipped with a capillary inlet, a nitrogen gas inlet, and an efficiently cooled (-78 °C) outlet. The solution of the compound to be pyrolyzed was injected with a syringe into the inlet with an adjustable motor-driven system at a fixed rate. The oven was heated to 400 °C for 45 min and flushed with nitrogen. A solution of 200 mg of **7** (0.9 mmol) in 1.2 mL of benzene was introduced into the oven at a rate of 1 mL/min. The system was washed with dichloromethane, and the mixture was filtered, evaporated, and chromatographed on 110 g of Florisil. The column was eluted with benzene-hexane (1:1). In the first fraction (50 mL) 26 mg of 4,5-methylenephenanthrene (**5**) was recovered, and in the second fraction 165 mg (84%) of cycloocta[*def*]fluorene (**1**) (red oil) was obtained: IR (neat) 3060, 3020, 2930, 1425, 1400, 1160, 820, 770, 730, 680 cm^{-1}; UV (cyclohexane) 253 nm (ϵ 29 500), 273 (sh, 21 200), 300 (4600), 246 (sh, 1360); mass spectrum, *m/e* (relative intensity) 216 (M, 100), 215, 191, 190, 189, 187; ^{1}H NMR ($CDCl_3$) 6.83-7.80 (m, 6 H), 5.90 (dd, 2 H, J_1 = 10 Hz, J_2 = 2 Hz), 3.68 ppm (s, 2 H). Anal. Calcd for $C_{17}H_{12}$: C, 94.44; H, 5.55. Found: C, 94.3; H, 5.6.

Irradiation of Cycloocta[*def*]fluorene (1). A solution of 50 mg (0.23 mmol) of **1** in 200 mL of dry purified cyclohexane was irradiated for 40 min (external, Hanovia 150-W lamp). After evaporation of the solvent, 46 mg of **7** was obtained which exhibited the same spectral properties as those mentioned above.

Preparation of Anions 13 and 14. The hydrocarbon **1** or **5** (ca. 0.1 mmol) was placed in an NMR tube and dissolved in 0.5 mL of THF-d_8. The tube was washed with a stream of argon for 10 min and cooled to -70 °C. *n*-BuLi (0.15 mL) in cyclohexane (3 M) was added, and the tube was sealed. A red color developed slowly. The temperature was then allowed to reach room temperature, and the NMR spectrum was recorded. The field/frequency of the spectrometer (Varian HA-100D) was locked to the cyclohexane band (δ 1.63). The ^{1}H NMR spectrum of cycloocta[*def*]fluorenyl anion **13** is as follows: 7.08 (d, 4 H, J = 8 Hz), 6.38 (t, 2 H, J = 8 Hz), 5.83 (s, 1 H), 5.42 (dd, 2 H, J_1 = 10 Hz, J_2 = 4 Hz), 4.96 ppm (dd, 2 H, J_1 = 10 Hz, J_2 = 4 Hz). The ^{1}H NMR spectrum of the cyclopenta[*def*]phenanthrenyl anion (**14**) is as follows: 7.73 (s, 2 H), 7.41 (m, 4 H), 7.05 (dd, 2 H, J_1 = 8 Hz, J_2 = 2 Hz), 6.06 ppm (s, 1 H).

Quenching of Anions 13 and 14. (a) With H_2O. The contents of the NMR tubes were added to 30 mL of water, extracted with CH_2Cl_2, and evaporated. A quantitative yield of the starting hydrocarbon was obtained.

(b) With D_2O. Under the same conditions, quenching with D_2O of anion **13** quantitatively afforded 11-deuteriocycloocta[*def*]fluorene (**1a**): ^{1}H NMR ($CDCl_3$) 6.83-7.75 (m, 6 H), 5.90 (dd, 2 H, J_1 = 10 Hz, J_2 = Hz), 5.68 (dd, 2 H, J_1 = 10 Hz, J_2 = 2 Hz), 3.65 ppm (s, 1 H); mass spectrum, *m/e* 218, 217, 216, 215, 192, 191, 190. Cyclopenta[*def*]phenanthrenyl anion (**14**) afforded quantitatively 9-deuteriocyclopenta[*def*]phenanthrene (**5a**): ^{1}H NMR ($CDCl_3$) 7.1-7.55 (m, 8 H), 3.86 ppm (br s, 1 H).

Quenching of Anion 14 with MeI. The anion prepared from 250 mg of **5** was quenched with MeI and afforded 240 mg of 9-methylcyclopenta[*def*]phenanthrene (**5b**): ^{1}H NMR ($CDCl_3$) 7.75-7.85 (m, 8 H), 4.40 (q, 1 H, J = 8 Hz), 16.5 ppm (d, 3 H, J = 8 Hz).

Registry No. 1, 60047-82-7; **1a**, 72867-25-5; **5**, 203-64-5; **5a**, 26037-53-6; **5b**, 30436-39-6; **6**, 60047-83-8; **7**, 60047-84-9; **13**, 60016-22-0; **14**, 23560-20-5.

Aromatization of 1,4-Dihydrobenzocycloalkenes, 1,4-Dihydronaphthocycloalkenes, and Related Systems

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A series of methyl-substituted 1,4-dihydrobenzenes has been prepared, and the rates of oxidation of these molecules by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) have been measured. Existing evidence points to the involvement of a positively charged intermediate which is formed as an ion pair in an initial rate-limiting hydride transfer to DDQ. Series of cycloalkyl-fused 1,4-dihydrobenzenes and 1,4-dihydronaphthalenes (fused 1,2 and 2,3) have been prepared and the rates of their DDQ induced aromatization have been studied. The results are explained on the basis of inductive effects associated with the size of the fused ring and exocyclic vs. endocyclic bond order preferences.

In an earlier paper we discussed the preparation and properties of bisannelated benzenes in which two small rings are fused either meta or para to one another about the benzene nucleus.[1] Differences in physical properties were observed to depend not only upon the degree of strain imposed on the aromatic nucleus but also upon the position at which this strain is introduced. A simple consideration of Kekulé resonance forms suggests a potential explanation for these differences. In the case of meta-bisannelated benzenes, the two Kekulé forms are nonequivalent, one having the double bonds endocyclic (**1b**) and the other having them exocyclic (**1a**) to the small rings. For the para-fused system (**2**) where $m = n$, both forms are equivalent.

In the case of annelated naphthalenes **3** and **4**, the situation is similar with one important difference. The

(1) (a) R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **42**, 300 (1977); (b) R. P. Thummel, *J. Am. Chem. Soc.*, **98**, 628 (1976); (c) R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **43**, 3170 (1978).

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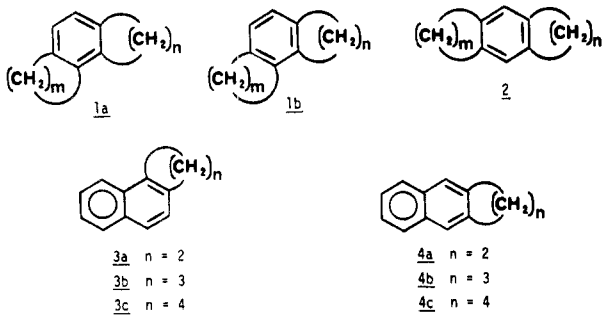


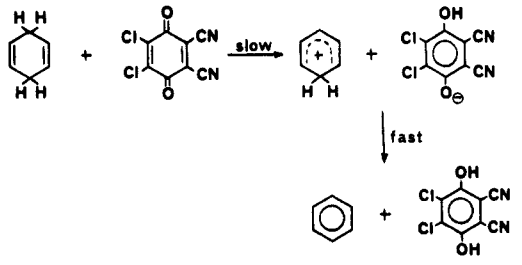
double bonds in the central rings are already localized to some extent as a result of benzo ring fusion. Thus we can picture the most important resonance contributor as being the one with a high degree of double bond character between carbons one and two and single bond character between carbons two and three.

In the course of developing a general route to the preparation of compounds such as **3** and **4**,[2] we discovered that the rate of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) induced aromatization of their 1,4-dihydro precursors could provide some interesting insight into the effect of ring strain and rehybridization on such reactions.

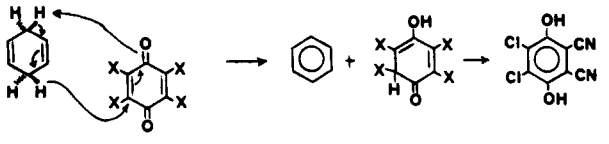
To correctly interpret the rates observed for the DDQ-induced dehydrogenation of a series of annelated 1,4-dihydrobenzenes and 1,4-dihydronaphthalenes, it became important for us to more completely understand the mechanism which was functioning in this reaction. In particular, we had to establish whether the reaction proceeded via the single-step concerted transfer of two hydrogens to the quinone molecule or by way of a stepwise transfer of first a hydride followed by a proton.

The two-step mechanism (Scheme I) was initially set forth by Braude, Jackman, Linstead, and co-workers in an extensive study of quinone-promoted dehydrogenations.[3] They proposed the rate-limiting transfer of a hydride to the quinone to give a pentadienyl cation which then rapidly lost a proton to provide the aromatic product and a hydroquinone. A reinvestigation of this reaction by Roček, Stoos, and Müller fairly conclusively ruled out the possible alternative of a homolytic pathway based on the greatly enhanced reactivity of tropylidene and triphenylcyclopropene, both of which would form a stabilized aromatic species by loss of a hydride, thus explaining the concurrent stabilization of the transition state involved in these processes.[4] These workers also compiled evidence supporting a cyclic concerted elimination in the case of 1,4-cyclohexadiene oxidations (Scheme II).[5] In particular, they cite as evidence against the rate-limiting formation of a carbonium ion intermediate the greatly enhanced rate of oxidation of 1,4-cyclohexadiene as compared with analogous 1,4-dienes which are incapable of aromatization, such as 1,4-pentadiene or 3,3-dimethyl-1,4-cyclohexadiene. They further claim that the greater reactivity of *cis*-3,6-dimethyl-1,4-cyclohexadiene as compared to the trans isomer substantiates a claim for the transfer of two cis hydrogens to the quinone molecule. A more recent variation of this mechanism set forth by Müller involves solvent participation in a concerted, termolecular reaction (Scheme III).[6] Müller's strongest argument in favor of the synchronous loss of both hydrogen atoms is based upon

Scheme I

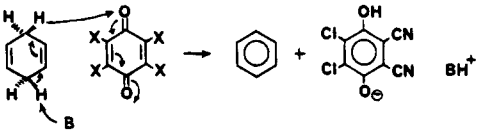


Scheme II



X = Cl or CN

Scheme III



a deuterium isotope effect of 10.0 in the oxidation of perdeuterio-1,4-cyclohexadiene. He qualifies this argument by pointing out an isotope effect of similar magnitude for the oxidation of anisyl alcohol in which only a single C–D bond is broken.[7] Without further reviewing evidence that has been adequately set forth elsewhere, let it suffice to say that none of the mechanisms proposed up to now adequately explain all experimental observations regarding this reaction. In this paper we would like to present some additional evidence in support of a two-step mechanism and suggest a compromise explanation.

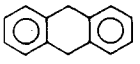
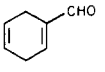
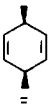
Results and Discussion

Let us begin by considering the relative rates of aromatization of 1,4-dihydrobenzene (**5**), 1,4-dihydronaphthalene (**6**), and 9,10-dihydroanthracene (**7**). If the reaction involved the concerted transfer of two hydrogens to the quinone molecule or to the quinone and a solvent molecule, one would expect the transition state for this reaction to at least in part resemble the aromatized products which result. Thus the relative energies of these transition states should reflect the resonance energy gained in the aromatization step. This gain in resonance energy is expected to be 36 kcal/mol for **5**, 25 kcal/mol for **6**, and 11.5 kcal/mol for **7**.[8] The relative rates of oxidation for these systems in a concerted process should therefore be of the order **5** > **6** > **7**. Our observations are inconsistent with this prediction, showing **6** to aromatize about three times faster than either **5** or **7**.[9]

Support for a positively charged intermediate is provided by examination of the rates of oxidation of the series **5**, **8**–**14** as summarized in Table I. These eight compounds show relative rates of dehydrogenation by DDQ which increase very consistently as the number of methyl sub-

(2) R. P. Thummel, W. E. Cravey, and W. Nutakul, *J. Org. Chem.*, **43**, 2473 (1978).
(3) E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 3123, 3133 (1960).
(4) P. Müller and J. Roček, *J. Am. Chem. Soc.*, **94**, 2716 (1972).
(5) F. Stoos and J. Roček, *J. Am. Chem. Soc.*, **94**, 2719 (1972).
(6) P. Müller, *Helv. Chim. Acta*, **56**, 1243 (1973).
(7) A large isotope effect (k_H/k_D = 6.9) is also observed for triphenylcyclopropene in which only a single C–H bond cleavage is involved.[4]
(8) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, p 241.
(9) With DDQ in benzene at 25 °C, 1,4-dihydronaphthalene is found to be 4.7 times more reactive than 9,10-dihydroanthracene: Professor Paul Müller, private communication.

Table I. Rates of Oxidation with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone in Glacial Acetic Acid at 25 °C

substrate	no.	molarity ($\times 10^{-2}$)	$10^2 k_2$, M^{-1} s^{-1}	k_{rel}
	5	7.8	5.12	0.34
	6	3.04	15.0	1.0
	7	2.99	5.2	0.34
	8	5.53	150	10
	9	1.72	900	60
	10	3.01	1500	100
	11	1.28	2600	173
	12	3.10	6140	409
	13	2.82	18900	~1200
	14	2.36	*a*	>1200
	15	3.83	0.09	0.006
	16[b]			0.49
	17[b]			0.023

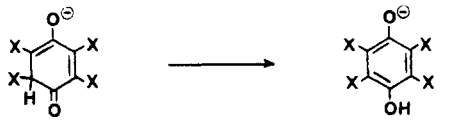
[a] Too fast to measure. [b] Reference 5.

stituents on the ring is increased from zero to four. The overall difference between the unsubstituted parent compound **5** and 1,2,4,5-tetramethyl-3,6-dihydrobenzene (**14**) is more than a factor of 3500. This evidence points strongly to the intermediacy of a positively charged species which would be inductively stabilized by additional methyl groups. Further evidence is provided by the very slow rate of oxidation of 3,6-dihydrobenzaldehyde (**15**) in which an intermediate carbonium ion would be destabilized by the electron-withdrawing aldehyde group.

Of all the evidence presented by Roček on the aromatization of 1,4-dihydro aromatics, perhaps the most worthy of note is the substantial difference in the rate of oxidation of *cis*- and *trans*-1,4-dimethyl-1,4-dihydrobenzenes (**16** and **17**). He observes that the cis isomer reacts about 20 times faster than the trans and attributes the greater reactivity of this isomer to the cis orientation of the two hydrogens which are being transferred to the quinone.[5] The preference for a cis elimination does not, however, necessitate the synchronous removal of the two hydrogens. Müller points out that the rate difference between **16** and **17** can be explained on purely stereoelectronic grounds.[6] The plain fact also remains that it is impossible for **17** to aromatize by a synchronous bimolecular pathway.

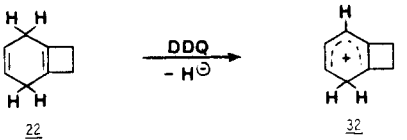
The presence of methyl groups at carbons one and four should result in additional stabilization of the resulting carbonium ion. Nevertheless the rates observed for **16** and **17** are not in good agreement with the other as a systems **9**, **10**, and **11**. Apparently the statistical availability of hydrogens is not a controlling factor, and the steric demands of the reaction are much more subtle and important than previously considered.

In presenting a compromise explanation, it is worthwhile to note that Trost has discussed a similar dichotomy of mechanism for the quinone promoted 1,2-dehydrogenations of acenaphthene.[10] In this reaction he also found good evidence for both a preferred cis elimination as well as a discrete carbonium ion intermediate. These two observations are not mutually exclusive. Trost suggested the formation of ion-pair intermediates. We would like to postulate the same sort of explanation for the above-mentioned 1,4-dihydrobenzene aromatizations. Thus, rate-limiting hydride abstraction would occur as illustrated in Scheme I except that the resulting pentadienyl cation and hydroquinone anion would form an ion pair. For such an ion pair the subsequent rapid proton abstraction would be preferred from the same face of the original diene molecule. When such a cis elimination is impossible, as in the case of **17**, either reorganization of the ion pair or the intervention of a third species (another hydroquinone anion or solvent) is necessary. In the model systems suggested by Roček (1,4-pentadiene and 3,3-dimethyl-1,4-cyclohexadiene) there is no proton available for abstraction. Alternative pathways such as polymerization, solvent capture, or alkyl group migration might then become rate determining. The absence of good material balances or careful product identification in these cases makes them suspect as good models for the aromatization of 1,4-dihydrobenzenes which are known to be cleanly converted into the corresponding benzenes. The proposed ion-pair mechanism still allows for initial 1,4-hydride addition to the DDQ molecule, forming **18**, which would then rapidly tautomerize to the aromatic anion **19**.



18 X = Cl or CN **19**

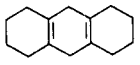
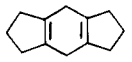
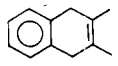
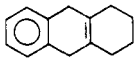
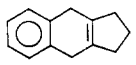
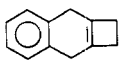
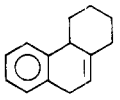
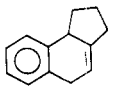
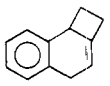
In light of the above remarks let us now direct our attention to the influence of annelation on DDQ-promoted dehydrogenations (Table II). Consider first the monoannelated dihydrobenzenes **20**, **21**, and **22** with compound **10** as the dimethyl analogue. The relative rate order is **10** > **21** > **20** > **22**. To explain the rate for **22** we must examine the pentadienyl cation **32** formed in the slow, hydride-abstraction step. The bond order between carbons one and two has been decreased in forming the cation **32**, thereby causing some relief of strain. If this factor was predominant, then **22**, experiencing the greatest relief of steric strain, should be the most reactive system. Apparently the destablizing inductive effect of the fused cyclobutene ring on the pentadienyl cation is more important. We have earlier invoked the rehybridization of bridgehead carbon atoms in cyclobutene-fused aromatic systems to explain various physical properties of such molecules.[1,11] The bridgehead carbon uses orbitals of



22 **32**

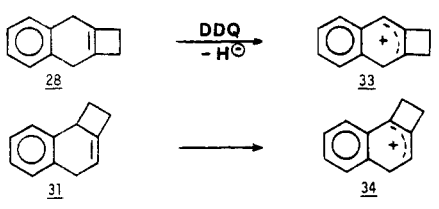
(10) B. M. Trost, *J. Am. Chem. Soc.*, **89**, 1847 (1967).
(11) A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968).

Table II. Rates of Oxidation with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone in Glacial Acetic Acid at 25 °C

substrate	no.	molarity ($\times 10^{-2}$)	$10^2 k_2$, M^{-1} s^{-1}	k_{rel}
	20	2.63	305	20
	21	2.44	447	30
	22	1.40	78.3	5.2
	23	1.87	9000	600
	24	3.13	10000	670
	25	1.85	272	18.1
	26	2.23	159	10.6
	27	1.88	219	14.6
	28	2.17	49.4	3.3
	29	2.50	64.5	4.3
	30	2.08	320	21.3
	31	2.54	12.6	0.84

higher p character in bonding to the small ring. This leaves an orbital of higher s character to bond to the adjacent carbon in the six-membered ring. The result is an inductive electron-withdrawing effect which retards formation of **32**. Conversely, the electron-donating effect of the methyl groups of **10** causes this molecule to lose a hydride most rapidly. The rates observed for the tetramethyl derivative **14** vs. the bisannelated systems **23** and **24** further support this trend.

In the case of 1,4-dihydronaphthocycloalkenes **26–31**, benzo ring fusion results in less delocalization of the positive charge generated by hydride abstraction. We assume relatively insignificant contribution from resonance forms which would perturb the existing aromatic ring. Thus **28** and **31** would generate cations **33** and **34**, respectively. The inductive effects due to ring fusion should



be nearly identical in these two systems. The formation of **33** represents a relief of strain by lessening double-bond character between the bridgehead carbons, while the formation of **34** similarly increases ring strain. The 4-fold rate difference between these two systems is explained primarily on this basis. Again, the cyclobutene-fused dihydronaphthalenes are found to react more slowly than their higher homologues, and the relative order of **25** > **27** > **26** > **28** is in excellent agreement with the order for dihydrobenzenes **20–22**, differing by a factor of about two. We have observed 1,4-dihydronaphthalene (**6**) to aromatize three times faster than 1,4-cyclohexadiene (**5**). It is difficult to explain, therefore, why the annelated dihydronaphthalenes are only one-half as reactive as the corresponding annelated dihydrobenzenes.

Experimental Section

Proton magnetic resonance spectra were obtained on a Varian Associates T-60 spectrometer, and chemical shifts are reported in parts per million downfield from Me_4Si. Infrared spectra were obtained on a Beckman IR-4250 spectrometer. Melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, AZ. High-resolution mass spectral analyses were performed by Dr. R. Grigsby at the Department of Biochemistry and Biophysics, Texas A&M University, on a CEC21-110B double-focusing magnetic sector spectrometer at 70 eV. Exact masses were determined by peak matching.

Materials. The 1,4-cyclohexadiene (Chemical Samples Co.) and 9,10-dihydroanthracene (Aldrich Chemical Co.) were commercially available samples. Other 1,4-dihydro aromatic substrates were prepared either by a dissolving-metal reduction of the corresponding aromatic molecule or by the Diels–Alder addition of an appropriate diene and benzyne. The reductions were carried out by adding a methanol solution of the benzene derivative to a solution of sodium in liquid ammonia according to a procedure recorded by Giovannini and Wagmüller.[12] The following known systems were prepared in this fashion: 1,4-dihydronaphthalene (**6**),[13] 1-methyl-1,4-cyclohexadiene (**8**),[14] 1,4-dimethyl-1,4-cyclohexadiene (**9**),[14] 1,2-dimethyl-1,4-cyclohexadiene (**10**),[15] 1,5-dimethyl-1,4-cyclohexadiene (**11**),[13,14] 1,3,5-trimethyl-1,4-cyclohexadiene (**12**),[14] 1,2,4-trimethyl-1,4-cyclohexadiene (**13**),[16] 3,5-dihydrobenzaldehyde (**15**),[17] 1,2,3,4,5,8-hexahydronaphthalene (**20**),[13] 4,7-dihydroindan (**21**),[12] and decahydroanthracene (**23**).[18] The preparation of 1,2,4,5-tetramethyl-1,4-cyclohexadiene (**14**) was carried out with lithium in ethylamine and ethylenediamine.[19] Bicyclo[4.2.0]octa-1(6),3-diene (**22**) was prepared according to a previously reported procedure.[1a] 1,4-Dihydronaphtho[*b*]cyclobutene (**28**) and 1,4-dihydronaphtho[*a*]cyclobutene (**31**) were prepared as previously described.[2]

3,6-Dihydrobenzo[1,2:4,5]dicyclopentene (24). Benzo[1,2:4,5]dicyclopentene[1a] (2.0 g, 12.6 mmol) in 20 mL of anhydrous methanol and 20 mL of anhydrous ether was added to a solution of 2.0 g of sodium metal in 100 mL of freshly distilled liquid ammonia, following the procedure of Giovannini and Wagmüller.[12] The reaction mixture was stirred at −78 °C for 2 h and then allowed to warm to room temperature, and the ammonia was evaporated. The residue was dissolved in ice water and extracted three times with ether. The ether extracts were dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure. The crude solid thus obtained was recrystallized from ethanol to provide 1.6 g (80%) of **24**: mp 90–91 °C; NMR (CCl_4) δ 2.5 (s, 4 H, H_3, H_6) and 2.4–1.8 (m, 12 H); IR (KBr) 2900 (br), 1480 (s), 1420 (s), 1340 (s), 1300 (s), 1195 (s), and 910 (m) cm^{-1}.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.61; H, 10.34.

1,2,3,4,9,10-Hexahydroanthracene (26). Treatment of 9.5 g (0.07 mol) of anthranilic acid with 14 g (0.12 mol) of isoamyl nitrite in 50 mL of dry tetrahydrofuran at 20 °C for 1.5 h provided

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benzenediazonium-2-carboxylate as a tan precipitate.[20] This material was collected by filtration and combined with 50 mL of dichloromethane to which was added 2.5 g (0.023 mol) of 1,2-dimethylenecyclohexane.[21] The mixture was refluxed for 2 h until gas evolution had ceased. It was then cooled, washed three times with saturated sodium bicarbonate solution, and dried over magnesium sulfate. Filtration and evaporation of the solvent gave an oil which was chromatographed on 30 g of silica gel, eluting with petroleum ether (bp 30–60 °C) to provide a white solid. Recrystallization from methanol gave 1.1 g (25%) of pure **26**: mp 65–66 °C; NMR ($CDCl_3$) δ 7.1 (s, 4 H, Ar H), 3.23 (s, 4 H, $ArCH_2$), 2.0 (m, 4 H, $=CCH_2$), and 1.7 (m, 4 H); IR (KBr) 2930 (s), 2860 (s), 1500 (m), 1460 (m), and 740 (s) cm^{-1}.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.99; H, 8.73.

1,4-Dihydro-2,3-dimethylnaphthalene[22] **(25).** 2,3-Dimethyl-1,3-butadiene (12.3 g, 0.15 mol) was reacted with benzyne prepared from 20 g (0.146 mol) of anthranilic acid and 20 g (0.17 mol) of isoamyl nitrite, following the procedure described above for **26**. After 2 h of reflux, the crude reaction mixture was filtered through 30 g of silica gel, and the solvent was removed under reduced pressure. The resulting oil was distilled on a Kugelrohr apparatus (70 °C (0.3 mm)) to provide 4.4 g of a liquid which showed two peaks by VPC on an 8 ft × 0.25 in. column of 10% Carbowax 20 M on Chromosorb W (60–80 mesh) at 150 °C. The shorter retention time peak (3.6 min, 75%) was isolated by preparative VPC and identified as **25**: NMR ($CDCl_3$) δ 7.0 (s, 4 H, Ar H), 3.25 (s, 4 H, $ArCH_2$), and 1.75 (s, 6 H, CH_3); IR (thin film) 2940 (br), 1700 (br), 1430 (m), 875 (s), and 740 (s) cm^{-1}.

1,4-Dihydronaphtho[*b*]cyclopentene (27). 1,2-Dimethylenecyclopentane[23] (1.0 g, 0.011 mol) was reacted with benzyne prepared from 5.3 g (0.04 mol) of anthranilic acid, following the procedure described above for **26**. Recrystallization from methanol gave 1.02 g (55%) of **27**: mp 67–68 °C; NMR (CCl_4) δ 7.02 (s, 4 H, Ar H), 3.35 (s, 4 H, $ArCH_2$), 2.40 (t, 4 H), and 2.02 (m, 2 H); IR (KBr) 2900 (s), 1500 (m), 1455 (m), and 740 (s) cm^{-1}.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.87; H, 7.94.

1,2,3,4,4a,9-Hexahydrophenanthrene (29). 1-Vinylcyclohexene[24] (5.4 g, 0.05 mol) was reacted with benzyne prepared from 9.5 g (0.07 mol) of anthranilic acid, following the procedure described above for **26**. Purification of the crude product by chromatography on 60 g of silica gel, eluting with petroleum ether (bp 30–60 °C), gave 2 g (22%) of material which was further purified by preparative gas chromatography (15 ft × 0.25 in. 10% Carbowax 20 M on Chromosorb W (60–80 mesh) at 150 °C and 30 mL/min). Collection of the major component provided pure **29**, identified by its spectral properties: NMR ($CDCl_3$) δ 7.12 (m, 4 H, Ar H), 5.51 (m, 1 H, =CH), 3.38 (m, 2 H, $ArCH_2$), 3.16 (m, 1 H, ArCH), and 2.4–1.2 (overlapping m, 8 H); IR (thin film) 3030, 2935, 2860, 1500, 1461, 1449, 811, 766, and 736 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 184 (95, parent ion), 182 (19), 156 (19), 142 (52), 141 (100), 128 (29), and 115 (23); exact mass calcd for $C_{14}H_{16}$ *m/e* 184.125200, found *m/e* 184.126060.

1,4-Dihydronaphtho[*a*]cyclopentene (30). 1-Vinylcyclopentene (5.0 g, 0.053 mol) was reacted with benzyne prepared from 21 g (0.16 mol) of anthranilic acid and 20 g (0.17 mol) of isoamyl nitrite, following the procedure described above for **26**. The crude reaction mixture was filtered through 30 g of silica gel, followed by 30 mL of dichloromethane. The solvent was removed under reduced pressure and the residue distilled [70 °C (0.1 mm)] on a Kugelrohr apparatus to give 2 mL of a yellow oil containing some solid benzoic acid. The oil showed two peaks by VPC on an 8 ft × 0.25 in. column of 10% Carbowax 20 M on Chromosorb W (60–80 mesh) at 150 °C. The shorter retention time peak (4 min) was collected and identified as **30**: NMR ($CDCl_3$) δ 7.15 (m, 4 H, Ar H), 5.70 (m, 1 H, =CH), 3.33 (m, 3 H, ArCH), 2.42 (m, 4 H), and 2.0–1.6 (m, 2 H); IR (thin film) 3070, 3030, 2965, 2880, 1496, 1461, 1440, 760, and 743 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 170 (100, parent ion), 169 (26), 142 (79), 141 (94), 129 (20), 128 (29), and 115 (26); exact mass calcd for $C_{13}H_{14}$ *m/e* 170.109550, found *m/e* 170.110041.

Kinetic Measurements. The kinetic method was essentially identical with that of Roček and Stoos.[5] Fisher (99.7%) reagent grade glacial acetic acid was utilized. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was obtained from Aldrich and recrystallized from benzene–chloroform. A fresh stock solution of DDQ (ca. 1.6×10^{-3} M) was prepared from 10 mL of glacial acetic acid and ca. 20 mg of DDQ prior to each set of kinetic runs. Kinetic samples were purified by distillation, recrystallization, or preparative gas chromatography on an 8 ft × 0.25 in. column of 10% Carbowax 20 M on Chromosorb W (60–80 mesh). Prior to use, all materials were analyzed by VPC (10 ft × 0.125 in. column of 10% Carbowax 20 M on Chromosorb W (60–80 mesh)) and NMR spectroscopy.

A Gilford 240 spectrophotometer was equilibrated and calibrated at 390 nm for a glacial acetic acid sample by using the visible source through a blue filter. The cell compartment of the spectrometer was kept at 25 °C by a flow of constant temperature water from a Haake circulation bath. Into a 1 × 1 × 3 cm cuvette was weighed ca. 2×10^{-2} mol of the substrate to be oxidized. In several cases where less substrate was utilized, the DDQ concentration was adjusted to always keep the substrate in at least 10-fold excess. To the cuvette was then added 2.0 mL of glacial acetic acid, and the substrate and acid were mixed well. The open cuvette was placed in the spectrometer and allowed to equilibrate at 25 °C. The cover plate of the spectrometer was fitted with a septum through which was inserted a syringe needle. This cover plate was aligned on the spectrometer such that the needle was in the open cuvette. While the absorbance at 390 nm was being read on a strip chart recorder with a known chart speed, 0.4 mL of the DDQ stock solution was syringed through the needle into the cuvette. An immediate deflection was noted upon addition of the DDQ. The decay of the DDQ absorption with time was recorded and followed until no further decrease in absorption was observed. This final absorption was taken as A_∞. The absorptions (A_t) at time t were read from the chart paper and the log of ($A - A_\infty$) was plotted against time. The slope of the line was determined graphically and used to calculate the pseudo-first-order rate constant (k_1 = −slope × 2.303). The second-order-rate constant was then calculated by using k_1 and the molar concentration of the substrate ($k_2 = k_1/$[substrate]).

For substrates which oxidize slowly (longer than 5 min), the above procedure was modified as follows. The stock solution was added directly to the cuvette containing the substrate. The cuvette was capped, shaken, and placed in the spectrometer. The cover plate (without the aforementioned septum and syringe needle) was placed on the spectrometer, and absorption readings were taken. The dwell time was set for 0.5 s to automatically remove the sample from the beam of light when a reading was not being taken. For slow samples this procedure is used to prevent a light-induced decrease in DDQ absorption. The above procedure is then followed to determine the rate of reaction.

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Registry No. 5, 110-83-8; **6**, 612-17-9; **7**, 613-31-0; **8**, 4313-57-9; **9**, 4074-22-0; **10**, 17351-28-9; **11**, 4190-06-1; **12**, 4074-23-1; **13**, 72985-36-5; **14**, 26976-92-1; **15**, 58836-15-0; **16**, 24560-92-7; **17**, 24560-93-8; **20**, 36231-13-7; **21**, 7603-37-4; **22**, 38325-66-5; **23**, 3485-60-7; **24**, 6555-87-9; **25**, 21564-72-7; **26**, 62690-77-1; **27**, 72985-37-6; **28**, 65957-25-7; **29**, 62690-91-9; **30**, 72985-38-7; **31**, 65957-26-8; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 84-58-2; benzo[1,2:4,5]dicyclopentene, 495-52-3; benzenediazonium-2-carboxylate, 1608-42-0; 1,2-dimethylenecyclohexane, 2819-48-9; 2,3-dimethyl-1,3-butadiene, 513-81-5; benzyne, 462-80-6; 1,2-dimethylenecyclopentane, 20968-70-1; 1-vinylcyclohexene, 2622-21-1; 1-vinylcyclopentene, 28638-58-6.

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