reaction deserves special attention. The value is higher ($k_H/k_D = 6.9$) than usually found for hydride ion abstractions and demonstrates that high isotope effects are not restricted to proton or hydrogen atom transfer reactions as had been suggested.[5]

Among the olefins which we have investigated, a special place is occupied by 1,4-cyclohexadiene. This hydrocarbon is 2000 times more reactive than the acyclic 1,4-pentadiene, a difference which is difficult to rationalize in terms of a simple hydride anion abstraction. It seems most likely that the high reactivity of 1,4-cyclohexadiene results from considerable aromatic stabilization in the transition state, and we are therefore forced to assume that, in this special case, two carbon–hydrogen bonds are broken synchronously in the rate-limiting step. This could be achieved either by a cyclic mechanism leading to benzene by way of transfering two cis hydrogens to the quinone, or by a mechanism involving the solvent as a proton acceptor. In this case one would expect the two trans hydrogens to be lost. The latter mechanism would represent a mechanism closely related to an E2 elimination. A change from an E1- to an E2-type mechanism could be very well understood in light of the high stability of the reaction product, benzene.

Both mechanisms have been considered earlier and rejected for the dehydrogenation of 1,4-dihydronaphthalene.[13,19] However, the evidence which was presented against these mechanisms is not entirely convincing and led us to further studies along these lines. The results of this work are published in the accompanying paper of this series.[26]

Acknowledgments. The authors wish to express their thanks to Mr. Robert A. Miller for his help in carrying out the kinetic measurements and to Mr. Elliot Katten for the synthesis of triphenylcyclopropene and triphenylcyclopropene-*3-d*.

---

cyclopropane. This difference of about six orders of magnitude in the reactivity of the two hydrocarbons toward DDQ and methyl radicals thus lends strong additional support to a hydride ion abstraction mechanism for the DDQ oxidation.

(25) P. Gal, Ph.D. Thesis, Columbia University; *Diss. Abstr.*, **13**, 2693 (1963).

(26) F. Stoos and J. Roček, *J. Amer. Chem. Soc.*, **94**, 2719 (1972).

Oxidation of Hydroaromatic Systems. III. The Effect of Aromatic Stabilization in the Dehydrogenation of 1,4-Cyclohexadienes

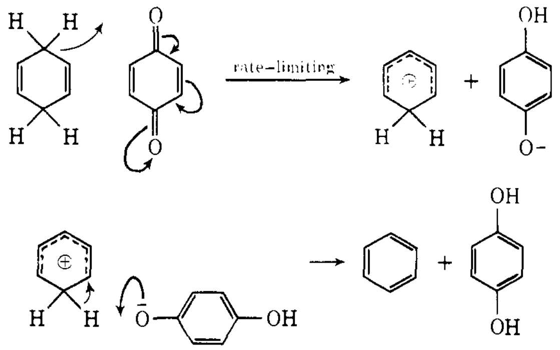
Fred Stoos and Jan Roček*

Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680.
Received September 13, 1971

Abstract: The dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) of 1,4-dihydrobenzene and *cis*-3,6-dimethyl-1,4-cyclohexadiene is by about three orders of magnitude faster than that of model dienes 1,4-pentadiene, 3-methyl-1,4-pentadiene, and 3,3-dimethyl-1,4-cyclohexadiene, which cannot form an aromatic hydrocarbon in a one-step dehydrogenation reaction. It is thus concluded that the energy of the transition state in the dehydrogenation of 1,4-dihydrobenzene is lowered by aromatic stabilization and that the dehydrogenation must therefore involve the simultaneous breaking of two carbon–hydrogen bonds. As the *cis*-3,6-dimethyl-1,4-cyclohexadiene reacts about 20 times faster than the trans isomer, the most favorable reaction path involves the transfer of both hydrogen atoms to the same molecule of the quinone, reducing it to a hydroxycyclohexadienone intermediate. While trans elimination of two hydrogens is a less favored route than cis elimination, it is still preferred to simple hydride abstraction as suggested by the reactivity of *trans*-3,6-dimethyl-1,4-cyclohexadiene, which lies in between that of the cis isomer and that of the model compound incapable of forming an aromatic dehydrogenation product. The low reactivity and different reaction mechanism in the quinone dehydrogenation of 1,2-dihydrobenzenes are discussed.

The dehydrogenation of 1,4-cyclohexadienes with a large number of quinones was extensively studied by Braude, Jackman, Linstead, and coworkers.[1] These authors came to the conclusion that the reaction consists of a rate-limiting hydride anion transfer from the dihydrobenzene to the quinone, leading to a delocalized carbonium ion, which will lose a proton in a subsequent rapid step of Scheme I.

Scheme I

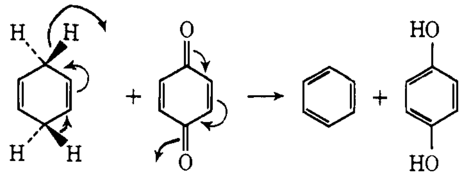


---

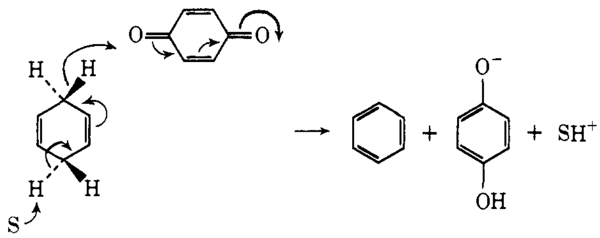
[1] E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 3123, 3133 (1960), and references given therein. For reviews, *cf.* L. M. Jackman, *Advan. Org. Chem.*, **2**, 329 (1960); D. Walker and J. D. Hiebert, *Chem. Rev.*, **67**, 153 (1967).

Braude and coworkers considered the possibility of forming benzene in a single-step reaction. They rejected a cyclic mechanism (Scheme II) in which two cis hydrogens are transferred to the quinone when they established that the dehydrogenation rate for 1,2- and 1,4-dihydronaphthalene with 1,4-benzoquinone, 1,2-naphthoquinone, and 3,3′,5,5′-tetrachloro-4,4′-diphenoquinone are insensitive to the internuclear distance of the hydrogen atoms undergoing transfer and the two quinone oxygens.[2,3] They further considered a mechanism involving a synchronous trans elimination of two carbon–hydrogen bonds involving the solvent as a proton acceptor (Scheme III), but rejected it when they found that the dehydrogenation shows little dependence on the basicity of the solvent.[2,4]

Scheme II



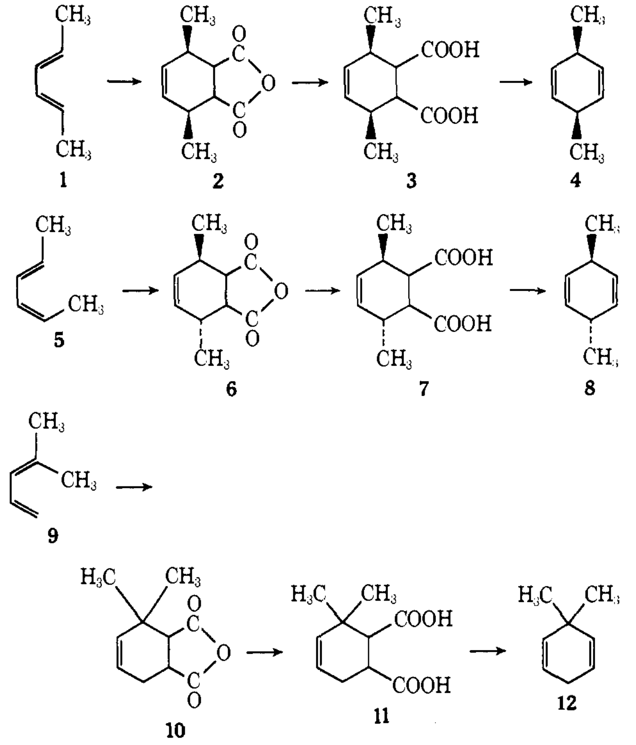
Scheme III



Müller and Roček[5] (preceding paper) made the surprising observation that 1,4-dihydrobenzene reacts with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) about 2000 times faster than 1,4-pentadiene. This result, which is difficult to reconcile with Braude's mechanism, revealed a need for the reinvestigation of the problem of the mode of hydrogen transfer from 1,4-dihydrobenzenes to quinones. We therefore studied the reactivity toward dehydrogenation of 1,4-dihydrobenzenes compared with a number of model compounds. As compounds which could not yield an aromatically stabilized transition state by the simultaneous loss of two hydrogen atoms, we chose 3,3-dimethyl-1,4-cyclohexadiene and 1,4-cycloheptadiene. To investigate the stereochemistry of the reaction, we prepared the *cis*- and *trans*-3,6-dimethyl-1,4-cyclohexadiene and compared its rate of dehydrogenation with the open-chain 3-methyl-1,4-pentadiene.

The preparation of 3,6-dimethyl-1,4-cyclohexadienes was reported by Paquette and coworkers[6] and by Frey and coworkers.[7] We used Frey's procedure in this study and applied it also to the preparation of 3,3-dimethyl-1,4-cyclohexadiene (**12**) (Scheme IV).

Scheme IV



Results and Discussion

Braude and coworkers[2] have firmly established that 1,4-dihydronaphthalene undergoes a dehydrogenation to the aromatic hydrocarbon. We assume that the same reaction takes place in the oxidation of the 3,6-dimethyl-1,4-cyclohexadienes. In those cases where no aromatic component can be formed by direct hydrogen abstraction, it is assumed that the rate-limiting step of the reaction is the abstraction of a hydride anion to form the corresponding carbonium ion,[8,9] which can then either react with the solvent (*e.g.*, form an alkyl acetate if the reaction is carried out in acetic acid) or undergo a rearrangement with a subsequent loss of a proton. Additional evidence for rate-limiting hydride ion transfer in DDQ oxidation was provided by Müller and Roček's observation of large kinetic isotope effects in the oxidation of tropilidene-d_8 and 3-deuterio-1,2,3-triphenylcyclopropene.[5,10]

Table I summarizes rate data obtained in this study. It is quite obvious that the four compounds which cannot by a simple process form an aromatic hydrocarbon in a one-step dehydrogenation, namely, 1,4-pentadiene, 3-methyl-1,4-pentadiene, 3,3-dimethyl-1,4-cyclohexadiene, and 1,4-cycloheptadiene, all react with comparable reaction rates.

---

(2) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548 (1954).

(3) E. A. Braude, A. G. Brook, and R. P. Linstead, *ibid.*, 3569 (1954).

(4) E. A. Braude, L. M. Jackman, and R. P. Linstead, *ibid.*, 3564 (1954).

(5) P. Müller and J. Roček, *J. Amer. Chem. Soc.*, 94, 2716 (1972).

(6) L. A. Paquette, D. E. Kukla, F. H. Barrett, and R. T. Haluska, *J. Org. Chem.*, 34, 2866 (1969).

(7) H. M Frey, A. Krantz, and I. D. R. Stevens, *J. Chem. Soc. A*, 1734 (1969).

(8) *Cf.* R. Foster and I. Horman, *ibid.*, *B*, 1049 (1966).

(9) R. P. Linstead, E. A. Braude, L. M. Jackman, and A. N. Beames, *Chem. Ind.* (*London*), 1174 (1954).

(10) The intermediacy of charge-transfer complexes in quinone dehydrogenations of substituted benzenes has been considered.[11] We found no indication of the formation of charge-transfer complexes in our studies. Further, even if charge-transfer complexes are formed as reaction intermediates, they are most likely formed in a rapid equilibrium preceding the rate-limiting hydrogen transfer. Their formation would therefore be of no consequence in the discussion of reaction rates which are determined by the difference between the energy of the starting materials and the transition state of the rate-limiting step. For these reasons, the possibility of charge-transfer formation is omitted from the discussion of the reaction mechanisms.

(11) R. Forter and I. Horman, *J. Chem. Soc. B*, 1049 (1966).

Table I. Rates of Oxidation with 2,3-Dichloro-5,6-dicyanobenzoquinone in Glacial Acetic Acid and Benzene at 25°

	Acetic acid			Benzene		$k_{AcOH}/k_{benzene}$
	Substrate, M	10^4k, M^{-1} sec^{-1}	k_{rel}	Substrate, M	$10^{-4}k$, M^{-1} sec^{-1}	
Cyclohexene[a]	1.67	0.011	0.04			
1,4-Pentadiene[a]	2.30	0.291	1			
3-Methyl-1,4-pentadiene	0.0592–0.471	1.22 ± 0.06	5	0.201–0.211	0.86 ± 0.003	1.4
3,3-Dimethyl-1,4-cyclohexadiene	0.0394–0.043	1.23 ± 0.09	5			
1,4-Cycloheptadiene	0.0283–0.0334	9.0 ± 2	37			
trans-3,6-Dimethyl-1,4-cyclohexadiene	0.0238–0.0424	36.3 ± 0.1	150	0.00747–0.00773	260 ± 0.5	1.4
1,4-Cyclohexadiene	0.0204–0.0281	540 ± 5	2240	0.00346–0.0136	363 ± 15	1.4
cis-3,6-Dimethyl-1,4-cyclohexadiene	0.0232–0.0274	773 ± 15	3200	0.00720–0.00948	536 ± 12	1.4
1,2,3-Triphenylcyclopropene[a]	0.0065	585	2430			
Tropilidene	0.0185	2010	8340	0.0127–0.0217	1130 ± 10	1.6

[a] Reproduced from ref 5.

On the other hand, the five compounds capable of yielding an aromatic compound in a one-step reaction all react with much faster rates. The most reactive is tropilidene, which in a one-step hydride abstraction will yield the tropilium ion. However, both 1,4-cyclohexadiene and *cis*-3,6-dimethyl-1,4-cyclohexadiene also show a high reactivity of the same order of magnitude. This suggests that in this group of compounds the high reactivity is the reflection of lowering of the energy of the transition state due to the developing of the product. In tropilidene and 1,2,3-triphenylcyclopropene the aromatic compound formed in the reaction is the corresponding carbonium ion, tropenium and triphenylcyclopropenium ions, respectively, formed by hydride ion abstraction from the substrate. Hydride ion transfer, of course, could not lead to an aromatic product in the oxidation of 1,4-cyclohexadiene or of *cis*-3,6-dimethyl-1,4-cyclohexadiene, but would produce a carbonium ion the stability of which should not differ significantly from the stability of carbonium ions formed by hydride ion abstraction from 1,4-pentadiene, 3-methyl-1,4-pentadiene, 3,3-dimethyl-1,4-cyclohexadiene, or 1,4-cycloheptadiene. In order to rationalize our results, we are thus forced to conclude that 1,4-cyclohexadiene and 3,6-dimethyl-1,4-cyclohexadiene are undergoing direct dehydrogenation to benzene and *p*-xylene, respectively. The oxidation must thus proceed with a synchronous, single-step loss of two hydrogen atoms instead of the more common two-step hydride ion transfer mechanism involving the formation of a carbonium ion intermediate.[12]

The observation that *cis*-3,6-dimethyl-1,4-cyclohexadiene is considerably more reactive than the trans isomer suggests that the preferential mechanism involves the transfer of two cis hydrogen atoms to the oxidant in a cyclic transition state. This conclusion is further supported by the insensitivity of relative reaction rates to the polarity of the solvent[2,4] observed by Braude and coworkers and also confirmed in the present study (Table I).

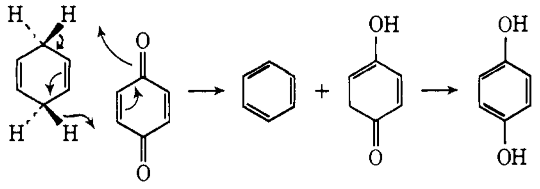
The addition of two hydrogen atoms to a molecule of quinone can take place in several ways. The addition to the two oxygen atoms (Scheme II) may seem attractive because it would lead directly to the hydroquinone. Braude and coworkers, however, argued convincingly against this mechanism, basing their arguments mostly on geometric considerations. We should like to mention two additional arguments which make this mechanism most unlikely.

The reactivity of quinones in dehydrogenation reactions increases strongly with the increasing number of electronegative substituents in the quinone molecule.[2] One can therefore assume that even when two hydrogen atoms are being transferred simultaneously, the transition state will not be symmetrical, but will resemble a hydride anion transfer. As quinones react essentially as unsaturated ketones, the hydride anion should add either to the carbonyl carbon or to a ring carbon atom, but not to the oxygen atom.[13]

Another important argument against the transfer of the two hydrogen atoms to the oxygen atoms of the benzoquinone system can be based on orbital symmetry considerations. As was pointed out by Hoffmann and Woodward,[14] thermal transfer of two hydrogen atoms to a conjugated system is symmetry-allowed if the sum of π electrons involved in the reaction is equal to $4q + 2$, when q is an integer. The 1,6 addition represented in Scheme II would involve eight interacting π electrons and is therefore symmetry-forbidden.[15]

We therefore prefer to describe the reaction as shown in Scheme V, in which the molecule of the quinone undergoes a 1,4-reduction to 2-hydroxy-1,3-cyclohexadien-5-one. Not only can it be shown from models that the transition state leading to this reaction is geometrically favored, but the reaction also involves a

Scheme V



---

[12] One of the referees suggested that steric hindrance may play an important role in the reaction. We believe that the higher reactivity of 3,3-dimethyl-1,4-cyclohexadiene as compared with 1,4-pentadiene and particularly the very high reactivity of 1,2,3-triphenylpropene make an important role of steric inhibition rather unlikely.

(13) *E.g.*, quinones react with Grignard reagents as α,β-unsaturated ketones and give 1,2 addition and 1,4 addition; *cf.* M. S. Kharasch and A. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954, Chapter 7.

(14) (a) R. Hoffmann, *Trans. N. Y. Acad. Sci.*, 475 (1966); (b) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, 1970, pp 141–144.

(15) In Zimmerman's approach[16] the 1,6 transfer would be considered as involving 12 electrons (Hückel forbidden). The predictions based on the Woodward–Hoffmann and Zimmerman approach are the same, but the latter avoids the complications stemming from lack of actual molecular symmetry.

(16) H. B. Zimmerman, *Accounts Chem. Res.*, 4, 272 (1971).

hydride transfer to the β position of an α,β-unsaturated carbonyl system and is symmetry-allowed. The reaction involves six π electrons[14] or a total of ten electrons[16] in the hydrogen transfer. Further, the reaction leads to a polar but nonionic product, which seems to be in excellent agreement with the observed solvent dependence of the reaction.[2]

A rather unexpected result was the intermediate oxidation rate for the *trans*-3,6-dimethyl-1,4-cyclohexadiene. We had originally expected that one of the dimethyl compounds would react at a rate of the same order as that of the 3-methyl-1,4-pentadiene, while the other isomer would be unreactive. The intermediate reactivity of the trans isomer seems to suggest that the possibility of aromatic stabilization is important enough to force another mechanism even when the more favorable cyclic process is ruled out.

It should be noted that the synchronous mechanism of hydrogen abstraction is probably restricted to 1,4-dihydrobenzenes and most likely does not apply to 1,2-dihydrobenzenes. 1,2-Dihydrobenzene is at least ten times less reactive than 1,4-dihydrobenzene, although the heats of formation for the two isomers differ by only 0.3 kcal/mol.[17,18] This assumption is further supported by the observation that 1,2-dihydro-1,1-dimethylnaphthalene, in which the presence of two geminal methyl groups makes direct dehydrogenation to an aromatic compound very unlikely, reacts only about 30% slower than the parent 1,2-dihydronaphthalene.[20] This stands in sharp contrast to the almost 450-fold higher reactivity of 1,4-cyclohexadiene as compared with 3,3-dimethyl-1,4-cyclohexadiene. Also, 1,2-dihydronaphthalene itself is only seven times more reactive than tetralin,[20] whereas 1,4-cyclohexadiene is almost 10^5 times more reactive than cyclohexene. Furthermore the 1,2 dehydrogenation of *cis*-1,2-dideuterioacenaphthene was shown to give a mixture of *cis*- and *trans*-acenaphthylenes. Although the cis isomer formed the larger part (63–78%) of the products, the trans isomer was always present in substantial amounts, and Trost offers good evidence for a two-step mechanism in which the rate-limiting step leads to the formation of the carbonium ion in an ion pair.[21]

We believe that the reason why 1,4-dihydrobenzenes react in a one-step concerted process, whereas 1,2-dihydrobenzenes seem to react in a two-step carbonium ion mechanism, can again be found in orbital symmetry requirements. The transfer of two vicinal hydrogens in an electrocyclic reaction to the terminal points of an α,β-unsaturated carbonyl compound would involve four π electrons (or eight electrons using Zimmerman's approach) and is therefore forbidden. The transfer of the hydrogens to the carbon and oxygen of the carbonyl group would be allowed, but is probably far less favorable, and therefore does not effectively compete with the two-step carbonium ion mechanism.[22]

Experimental Section

Melting points were determined using open capillary tubes in a Thomas Hoover capillary melting point apparatus and are uncorrected. Analytical gas chromatography (glpc) was performed with a Hewlett-Packard (F & M) instrument equipped with flame ionization detectors. A 5 ft × $^1/_8$ in. column packed with 5% Silicone Gum Rubber (Methyl) GE SE-30 on 60–80 Chromosorb N was used. The carrier gas was nitrogen. Retentiom times (t_R) are given in minutes. The compounds were identified using the peak enhancement method.

Infrared data were obtained on a Perkin-Elmer Model 521 or a Beckman IR-10 spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian Associates T-60 spectrometer; chemical shifts are given in parts per million downfield from internal tetramethylsilane (δ = 0). The multiplicity, peak areas, coupling constants, and proton assignments are given in parentheses. Ultraviolet and visible spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer. Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

Materials. *trans,trans*-2,4-Hexadiene (99%), *cis,trans*-2,4-hexadiene (99%), and 4-methyl-1,3-pentadiene (99%) were commercially available from Chemical Samples Co. Maleic anhydride (Aldrich Chemical Co.) was recrystallized from chloroform. Lead tetraacetate (Smith Chemical Co.) was recrystallized from glacial acetic acid containing *ca.* 3% acetic anhydride and was found 96% pure by iodometric titration. Methyl sulfoxide (Fisher Certified), pyridine (Fisher Spectranalyzed), toluene (Baker Instra-Analyzed), and hydroquinone (Eastman Kodak) were used as received.

Kinetic measurements were made in acetic acid (99.7% Fisher Reagent Grade or 99.9% Baker Reagent Grade) and in benzene (Fisher Spectranalyzed).

Stock solutions of 2,3-dichloro-5,6-dicyanobenzoquinone (Aldrich Chemical Co.) in acetic acid varied from 3.88×10^{-3} to 4.74×10^{-3} *M*, and in benzene from 9.84×10^{-4} to 19.72×10^{-4} *M*. The solutions were stored in the dark in a refrigerator for no longer than 2 days.

3-Methyl-1,4-pentadiene (99%), 1,4-cyclohexadiene (99%), and tropilidene (99%) were commercially available from Chemical Samples Co. and were not further purified. 1,4-Cycloheptadiene was prepared according to Doering and Roth.[24] A typical kinetic run was carried out with a mixture containing 20.1% 1,4-cycloheptadiene, 19.7% cycloheptene, and 58.7% *p*-xylene; as *p*-xylene and monoolefins react with quinones only very slowly, they did not interfere with the determination of the dehydrogenation of the diene. Hydrocarbon samples were dried before each run over calcium hydrate and sodium and distilled on a vacuum line. The purity or concentration of each sample was determined by glpc on silicone rubber. When larger amounts of inert impurities were present, the analytical determinations of diene concentration were reproducible within 2%.

***cis*-3,6-Dimethyl-1,4-cyclohexadiene (4).** *trans,trans*-2,4-Hexadiene (**1**) (45.3 g, 0.552 mol) gave with 56.9 g (0.580 mol) of maleic anhydride after recrystallization from ether 89.9 g (90%) of *cis,cis*-3,6-dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylic anhydride (**2**), mp 91–92° (lit.[7] mp 92–94°). Hydrolysis of 44.0 g (0.244 mol) of anhydride **2** with 800 ml of water afforded 45.9 g (95%) of *cis,cis*-3,6-dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylic acid (**3**), mp 169–171° dec (lit.[7] mp 170–171°). The decarboxylation of 12.9 g (65 mmol) of dicarboxylic acid **3** was carried out with 32.0 g (69 mmol) of lead tetraacetate (96% pure) in 100 ml of dimethyl sulfoxide and 10.5 ml of pyridine under nitrogen. After 10 min 250 ml of water was added and the mixture was immediately steam distilled. Separation of the two layers, drying the hydrocarbon phase with anhydrous potassium carbonate, calcium hydride, and sodium, and distillation on a vacuum line afforded 1.58 g of a colorless liquid. Glpc analysis (112°, flow rate 15 ml/min) indi-

---

[17] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

[18] In this connection it is interesting to note that the appearance potential for the formation of the benzenium ion as obtained by electron-impact studies is, in fact, slightly higher (by 0.1 eV) for 1,4-cyclohexadiene than for 1,3-cyclohexadiene.[19] To the extent that one can assume that these results reflect correctly the relative energies of the species in solutions, one would be led to conclude that the benzenium ion intermediate assumed in the two-step mechanism should be formed *more readily* from the 1,2- than from the 1,4-dihydrobenzene.

[19] J. L. Franklin and S. R. Carroll, *J. Amer. Chem. Soc.*, **91**, 6564 (1968).

[20] E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 3133 (1960).

[21] B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 1847 (1967).

[22] It is interesting to note that the far higher reactivity of 1,4-dihydrobenzene as compared with 1,2-dihydrobenzene toward quinone dehydrogenation parallels the reactivity of the two dienes in the thermal elimination of molecular hydrogen which Benson and Shaw have shown to be about 10^3 times faster for the 1,4-dihydro compounds.[23]

[23] S. W. Benson and R. Shaw, *J. Amer. Chem. Soc.*, **89**, 5351 (1967); *Trans. Faraday Soc.*, 63, 985 (1967).

[24] W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

cated *cis*-3,6-dimethylcyclohexa-1,4-diene (**4**) (52% corresponding to a yield of 11% based on dicarboxylic acid, $t_R = 1.15$), *p*-xylene (46%, $t_R = 1.5$), and pyridine (2%, $t_R = 1.0$). The nmr (CCl$_4$) spectrum showed besides the *p*-xylene bands signals at δ 1.03 (d, 6, $J = 7$ Hz, methyl), *ca.* 2.70 (m, 2, allylic H), and 5.50 ppm (d, 4, $J = 1$ Hz, olefinic H). As *p*-xylene is unreactive toward 2,3-dichloro-4,5-dicyanobenzoquinone, it was not removed from the mixture.

***trans*-3,6-Dimethyl-1,4-cyclohexadiene (8).** A solution of 22.7 g (0.276 mol) of *cis,trans*-2,4-hexadiene (**5**), 54.1 g (0.552 mol) of maleic anhydride, and 68 mg of hydroquinone (to avoid polymerization) in 133 ml of toluene was stirred for 40 hr at 100 ± 5°. After evaporation of toluene and sublimation (100° (15 mm)) of most of the excess of maleic anhydride, the residue was recrystallized[25] from petroleum ether (bp 20–40°) giving 36.9 g (74%) of *cis*-3,*trans*-6-dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylic anhydride (**6**): mp 57–62°; ir (Nujol) 1850 and 1770 cm^{-1} (anhydride C=O); nmr (CDCl$_3$) δ 1.13 (d, 3, $J = 8$ Hz, methyl), 1.27 (d, 3, $J = 8$ Hz, methyl), 2.2–3.4 (m, 4, allylic H and HC–CO), and 5.2–5.8 ppm (m, 2, olefinic H). *Anal.* Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.75; H, 6.75. Hydrolysis of 35.0 g (0.194 mol) of anhydride **6** with 640 ml of boiling water yielded 35.5 g (92%) of *cis*-3,*trans*-6-dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylic acid (**7**), mp 130–132° dec (lit.[7] mp 132–134°), which was decarboxylated as before (12.9 g of dicarboxylic acid **7** and 32.0 g of lead tetraacetate). The hydrocarbon layer was separated, dried over anhydrous potassium carbonate and calcium hydride, and distilled on a vacuum line over sodium to yield 3.7 g of a colorless liquid, which, by glpc analysis (115°, flow rate 20 ml/min), was shown to be composed of *trans*-3,6-dimethyl-1,4-cyclohexadiene (**8**) (64.5% corresponding to a 35% yield, $t_R = 1.8$), *p*-xylene (34.0%, $t_R = 2.4$), pyridine (1.3%, $t_R = 1.5$), and *ca.* three minor products (together 0.2% $t_R = ca.$ 1.2). Besides the *p*-xylene bands the nmr (CCl$_4$) spectrum exhibited signals at δ 1.03 (d, 6, $J = 7$ Hz, methyl), *ca.* 2.70 (m, 2, allylic H) and 5.53 ppm (d, 4, $J = 1$ Hz, olefinic H).

3,3-Dimethylcyclohex-4-ene-1,2-dicarboxylic acid (11). A mixture of 5.65 g (68 mmol) of 4-methyl-1,3-pentadiene (**9**), 13.5 g (137 mmol) of maleic anhydride, and 17 mg of hydroquinone in 33 ml of toluene was kept at 100 ± 5°. Monitoring by glpc (135°) showed the reaction to be practically complete after 51 hr. Toluene was evaporated under reduced pressure and the bulk of unreacted maleic anhydride was sublimed at 100° (*ca.* 25 mm). The residual crude 3,3-dimethylcyclohex-4-ene-1,2-dicarboxylic anhydride (**10**)[26] was hydrolyzed with 160 ml of boiling water for *ca.* 1 hr to yield 8.41 g (mp 172–175° dec) of 3,3-dimethylcyclohex-4-ene-1,2-dicarboxylic acid (**11**). Two recrystallizations from water gave 7.10 g (52% with respect to 4-methyl-1,3-pentadiene (**9**), mp 175–177° dec) of the acid **11** as fine white needles: ir (Nujol) 1725 cm^{-1} (C=O acid); nmr (deuterioacetone) δ 1.10 (s, 3, methyl), 1.13 (s, 3, methyl), 2.2–3.1 (m, 4, allylic H and HC–CO), 5.2–5.8 (m, 2, olefinic H), and 9.0 (s broad, 2, COOH). *Anal.* Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.57; H, 7.15.

3,3-Dimethyl-1,4-cyclohexadiene (12). Lead tetraacetate (31.4 g, 68 mmol, 96% pure) was added in 1 min to a stirred solution of 12.9 g (65 mmol) of 3,3-dimethylcyclohex-4-ene-1,2-dicarboxylic acid (**11**) in 100 ml of dimethyl sulfoxide and 10.5 ml of pyridine under nitrogen at room temperature. After 6 min from the addition of lead tetraacetate, an exothermic evolution of carbon dioxide ensued. After 13 min the temperature was 44° and began to drop. After 1 min of additional stirring, 250 ml of water was added to the mixture. Immediate steam distillation, separation of the two layers, drying the hydrocarbon phase with anhydrous potassium carbonate and calcium hydride, and distillation on a vacuum line over sodium afforded 2.7 g of a colorless liquid. Glpc analysis (112°, flow rate 25 ml/min) showed 3,3-dimethyl-1,4-cyclohexadiene (**12**) (79.4% corresponding to a yield of 30%, $t_R = 1.7$), *o*-xylene (18.4%, $t_R = 2.8$), pyridine (1.5%, $t_R = 1.55$), and minor products (0.1%, $t_R = 0.95$; 0.3%, $t_R = 2.25$; and 0.3%, $t_R = 2.5$).

As *o*-xylene is unreactive toward 2,3-dichloro-4,5-dicyanobenzoquinone, it was not removed from the above mixture: nmr (CCl$_4$) δ 1.00 (s, 6, methyl), 2.54 (t, 2, $J = 1$ Hz, allylic H), and 5.47 ppm (d, 4, $J = 1$ Hz, olefinic H).

1,1-Dimethyl-2,3,5,6-tetrabromocyclohexane. Bromine (4 g, 25 mmol) in 4 ml of CHCl$_3$ was added dropwise during 1.5 hr to a stirred solution of 1.64 g (12.4 mmol) of 82% pure 3,3-dimethyl-1,4-cyclohexadiene in 6 ml of CHCl$_3$ at 0°. The mixture was stirred for an additional hour at room temperature. After evaporation of the solvent, the residue was recrystallized three times from alcohol to give 3.11 g (59%) of tetrabromide: mp 100–102° (lit.[27] mp 102°); nmr (CDCl$_3$) δ 1.52 (s, 6, methyl), 3.03 (t, 2, $J = 5$ Hz, methylene), and 4.4–4.8 ppm (m, 4, methine). *Anal.* Calcd for $C_8H_{12}Br_4$: C, 22.45; H, 2.82; Br, 74.73. Found: C, 22.46; H, 2.84; Br, 74.78.

Kinetic Measurements. Appropriate stock solutions of the olefins were prepared. Both the substrate and DDQ stock solutions were kept in a constant-temperature (25 ± 0.1°) bath for 15–30 min. Quartz cells (1 cm, 3-ml volume) were equilibrated in the thermostated cell holder of a Zeiss PM QII or Cary 15 spectrophotometer. After mixing 2 ml of the olefin solution and 1 ml of the DDQ solution, the disappearance of the quinone was followed at 390 nm (ϵ 700 M^{-1} cm^{-1}) in acetic acid and at 404 nm (ϵ 3040 M^{-1} cm^{-1}) in benzene solution. The concentration of the quinone was kept at 1.29×10^{-3}–1.58×10^{-3} M in acetic acid and at 3.28×10^{-4}–6.57×10^{-4} M in benzene, thus giving reasonably large initial absorbances. Substrate concentrations were varied according to reactivity from 1.85×10^{-2} to 0.471 M in acetic acid and from 7.20×10^{-3} to 0.211 M in benzene and were in 7- to 600-fold excess over the quinone. Rate constants were determined from plots of log A_t or log $(A_t - A_\infty)$ *vs.* time. The correction for the infinity absorbance was used wherever possible but could not be applied in the case of 3,3-dimethyl-1,4-cyclohexadiene where decomposition occurred, or in the case of *trans*-3,6-dimethyl-1,4-cyclohexadiene where in benzene as a solvent precipitation occurred. Good first-order plots were obtained, usually over several half-lives. First-order rate constants were determined graphically. The second-order rate constants listed in Table I are averages of two to five measurements.

Acknowledgments. The authors wish to think Professor R. M. Moriarty, University of Illinois at Chicago Circle, and Professor P. Müller, Ecole de Chimie, Geneva, for helpful discussions and comments.

---

[25] We preferred to purify the anhydride 6 since it can be more easily purified than the corresponding dicarboxylic acid 7.

[26] The anhydride 10 can be purified by recrystallization from petroleum ether: mp 67–70°; ir (Nujol) 1845 and 1775 cm^{-1} (anhydride C=O); nmr (CDCl$_3$) δ 1.00 (s, 3, methyl), 1.30 (s, 3, methyl), 2.4–3.7 (m, 4, allylic H and HC–CO), and 5.73 ppm (t, 2, $J = 2$ Hz, olefinic H). Since large amounts of petroleum ether are necessary, we preferred to hydrolyze the crude anhydride 10.

[27] A. W. Crossley and N. Renouf, *J. Chem. Soc.*, **93**, 637 (1908).