

The dimethyl phenylsuccinate was further purified by recrystallization from aqueous methanol. Phenylmaleic anhydride was isolated by sublimation from the reaction mixture and recrystallization from benzene-hexane rather than by distillation, and, of course, in this example, mercuric salts were removed only with water rather than with aqueous bicarbonate.

Identification of dimethyl *cis*-1,2,<sup>13</sup> and dimethyl *cis*-1,3-cyclopentenedicarboxylate<sup>14</sup> was made by nmr and glc comparison with authentic samples. Similarly methyl *trans*-2-methoxycyclohexanecarboxylate was prepared by treatment of the *trans*-2-hydroxycyclohexanecarboxylic acid<sup>15</sup> with freshly prepared silver oxide and iodomethane. *cis*-1,2-Cyclohexanedicarboxylic acid was commercially available from the Aldrich Chemical Co., and it was esterified with diazomethane to obtain an authentic sample. The authentic *dl* and meso dimethyl 3,4-hexanedicarboxylates were obtained by diazomethane treatment of the known acids.<sup>12</sup>

In carrying out reactions employing carbomethoxymercuric chloride significant pressure increases were noted. This reaction was therefore begun at 0° and allowed to warm up slowly, releasing pressure as necessary to keep the pressure at 30 psi.

**Carbomethoxylation of Phenylacetylene.** A mixture of 0.64 g (22 mmol) of carbomethoxymercuric acetate,<sup>8</sup> 10 ml of acetonitrile, and 2 ml of phenylacetylene was stirred magnetically in an ice bath, and 0.45 g (2 mmol) of powdered palladium acetate was added.

(13) W. H. Perkin, *J. Chem. Soc.*, 572 (1894).

(14) W. H. Perkin and H. A. Scarborough, *ibid.*, 119, 1405 (1921).

(15) J. Pascual, J. Sistare, and A. Regas, *ibid.*, 1943 (1949).

The mixture was stirred at 0° for 30 min and then at room temperature overnight. Gas chromatographic analysis showed the solution to be 0.07 *M* in methyl phenylpropiolate. A slightly lower yield was obtained when the reaction was carried out with 0.5 ml of tri-*n*-butylamine present.

A similar reaction with 1.28 g (4 mmol) of carbomethoxymercuric acetate and with 0.5 ml of tri-*n*-butylamine gave 0.136 *M* methyl phenylpropiolate. A sample of product was isolated from this reaction mixture by preparative gas chromatography. The analysis and nmr spectra are listed in Table II.

**Methylation of Phenylacetylene.** The reaction was carried out exactly as in the preceding experiment, substituting 1.37 g (5 mmol) of methylmercuric acetate for the carbomethoxymercuric acetate and using 1.12 g (5 mmol) of palladium acetate. After the mixture was allowed to react overnight, gas chromatographic analyses showed the solution to contain 1.3 mmol of 1-phenyl-1-propyne. A sample was isolated by preparative gas chromatography and the analyses obtained are given in Table II.<sup>10</sup>

**Phenylation of Phenylacetylene.** A reaction was carried out as in the preceding experiment, employing 1.68 g (5 mmol) of phenylmercuric acetate in place of methylmercuric acetate. After reacting overnight, the solution was found to contain 3.84 mmol of diphenylacetylene. An isolated sample was found to be essentially identical with a known sample of diphenylacetylene.

**Acknowledgment.** Laboratory assistance was provided by Mr. A. G. Fleming and nmr spectra were taken by Mr. L. Haas.

## Oxidations of Hydroaromatic Systems.

### II. 2,3-Dichloro-5,6-dicyanobenzoquinone<sup>1</sup>

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**Abstract:** Aromatic stabilization in the transition state is used to develop a new approach to the study of one- and two-electron oxidations involving hydrogen transfer. 2,3-Dichloro-5,6-dicyanobenzoquinone is shown to react with tropilidene and 1,2,3-triphenylcyclopropene 10<sup>4</sup> to 10<sup>5</sup> times faster than with simple model compound. This high reactivity is interpreted by aromatic stabilization in the transition state of the rate-limiting step and considered as additional evidence for hydride ion transfer. The high reactivity of 1,4-dihydrobenzene is discussed and interpreted as suggesting the simultaneous removal of two hydrogen atoms.

A large number of oxidation processes include the breaking of carbon-hydrogen bonds in the rate-limiting step. A fundamental question is whether this reaction occurs as a one-electron oxidation involving the transfer of a hydrogen atom, or as a two-electron oxidation with the transfer of a hydride ion.

The distinction between hydrogen atom and hydride ion transfer in oxidation processes is by no means easy to establish. Attempts have been made to classify oxidizing agents as one- and two-electron reagents based on reaction with compounds like hydrazine<sup>2</sup> or sulfurous acid;<sup>3</sup> however, electron transfer processes in these reactions and hydrogen transfers in the oxidations of organic compounds are basically too different

to allow any close analogy. The formation of free radicals in solution was often taken as a proof of hydrogen atom transfer;<sup>4</sup> however, very ambiguous results were frequently obtained. The magnitude of the kinetic isotope effect was predicted to be different for hydrogen and hydride transfers,<sup>5</sup> but this view is not generally shared and experimental support is lacking. Linear free energy relationships between oxidation and solvolytic processes were used to support the hydride ion transfer mechanism,<sup>6</sup> but the basic similarity between electronic effects in the two types of mechanisms leaves the argument not quite convincing. Similarities in relative rates between known free radical reactions and oxidation processes were suggested to support a hydrogen atom transfer,<sup>7</sup> but the

(1) (a) Part I: P. Müller, E. Katten, and J. Roček, *J. Amer. Chem. Soc.*, 93, 7114 (1971); (b) support of this work by the U. S. Army Research Office (Durham) is gratefully acknowledged; (c) presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) R. E. Kirk and A. W. Browne, *J. Amer. Chem. Soc.*, 50, 337 (1928).

(3) W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957).

(4) For instance, J. S. Littler and W. A. Waters, *ibid.*, 1299 (1959).

(5) C. G. Swain, R. A. Wiles, and R. F. Bader, *J. Amer. Chem. Soc.*, 83, 1945 (1961).

(6) F. Mareš, J. Roček, and J. Sicher, *Collect. Czech. Chem. Commun.*, 26, 2355 (1961).

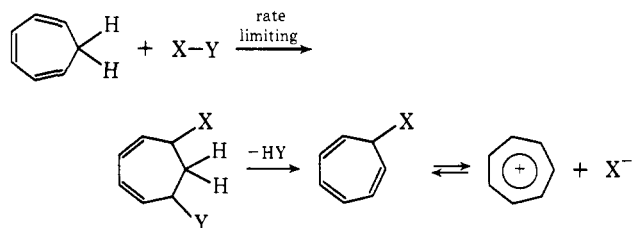
(7) K. B. Wiberg and R. J. Evans, *Tetrahedron*, 8, 313 (1960).

known variation in selectivities of different species reacting by the same mechanism makes changes in relative reactivities of limited value as long as they are not accompanied by a change in sequence of the test substrates.

In this series of papers we will employ a new approach to the problem of hydride *vs.* hydrogen ion transfer, based on the aromatic stabilization present in conjugated  $4n + 2$  electron systems but not in the corresponding  $4n + 3$  electron systems.<sup>8</sup> Consequently, the tropylium ion or the cyclopropenium ion will be stabilized far more than the corresponding radicals. We expect therefore that oxidants capable of hydride anion abstraction should react far more rapidly with tropilidene or cyclopropene than with acyclic or a nonconjugated model compound. On the other hand, we expect no large difference between these two classes of compounds for oxidizing agents capable only of hydrogen atom abstraction.<sup>9</sup>

A factor complicating this approach is the possibility that the oxidation reaction may proceed by still another route, namely, double bond attack. The mere fact that a product corresponding to hydride ion abstraction could be isolated does not, in itself, offer sufficient proof that the aromatic carbonium ion is formed directly in the rate-limiting step. It is quite conceivable that it is produced in a reaction consisting in a rate-limiting addition to the double bond followed by an elimination process (*e.g.*, Scheme I). In order to establish there-

Scheme I



fore whether carbon-hydrogen bond breaking does indeed take place in the rate-limiting step, kinetic isotope effects will be determined in all studies.

In this paper we wish to report the results of a study of the oxidation of tropilidene, triphenylcyclopropene, and a series of olefins with 2,3-dichloro-5,6-dicyanobenzoquinone. This reagent is a particularly strong oxidizing agent and shares with many other quinones the ability to dehydrogenate unsaturated systems.<sup>12</sup> It is usually assumed<sup>13</sup> that the mechanism consists in a rate-limiting hydride ion transfer to quinone,

(8) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

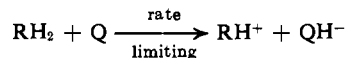
(9) A certain complication arises from the fact that the tropylium radical, though stabilized much less than the corresponding cation, still seems to be a rather stable species as can be judged from the low bond dissociation energy for the carbon-hydrogen bond of the methylene group or from the facile dissociation of ditropyl.<sup>10</sup> On the other hand, no stabilization of this type has been observed for the cyclopropenyl radical which, on the contrary, is believed to be extremely unstable.<sup>11</sup>

(10) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Amer. Chem. Soc.*, **82**, 5593 (1960); G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *ibid.*, **91**, 2823 (1969).

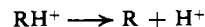
(11) R. Breslow, *Chem. Eng. News*, **43** (26), 90 (1965); *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968).

(12) D. Walker and J. D. Hiebert, *Chem. Rev.*, **67**, 153 (1967).

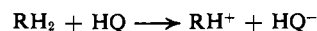
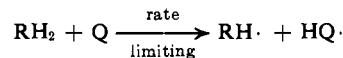
(13) Cf. particularly the extensive work by E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 3123, 3133 (1961), and references given therein.



followed by a loss of a proton in the second step if the reaction is a dehydrogenation of a hydroaromatic system



However, quinone oxidations leading to free radical products have also been observed,<sup>14</sup> and the possibility that the first step could be, in fact, a hydrogen atom transfer followed by an electron transfer has been considered<sup>14</sup>



The objective of the present work is twofold. First, using the above outlined approach we present further evidence for the hydride ion mechanism in quinone oxidations, and, second, we set up a scale of reactivities to be used as a reference point in further studies.

## Experimental Section

**Acetic Acid.** Fisher (99.7%) reagent grade was used.

**2,3-Dichloro-5,6-dicyanobenzoquinone.** Stock solutions were prepared by dissolving *ca.* 20 mg of the quinone (Aldrich Chemical Co.) in 10 ml of acetic acid. The solutions were stored in the dark in a refrigerator for no longer than 2 days.

**Olefins.** Commercially available compounds were used. The olefins were purified by preparative glpc immediately before use. In some instances they were further purified by distillation from sodium on a vacuum line; however, this procedure did not produce any noticeable effect on reaction rates.

The preparation of tropilidene-*d*<sub>8</sub> has been described elsewhere.<sup>15</sup> The sample had the following composition of the methylene group: 90.6% dideuterio, 8.3% monodeuterio, and 1.1% undeuterated (by nmr and mass spectra); the rate constant was corrected for this deuterium content.

1,2,3-Triphenylcyclopropene and 1,2,3-triphenyl-3-deuterio-cyclopropene were prepared by reduction of triphenylcyclopropenium bromide with lithium aluminum hydride and lithium aluminum deuteride, respectively.<sup>16</sup> They were purified by chromatography on silica gel.

**Kinetic Measurements.** A standard amount (0.5 ml) of a stock solution 2,3-dichloro-5,6-dicyanobenzoquinone in glacial acetic acid was diluted to 2.5 ml in a 1-cm quartz cell and equilibrated in a thermostated cell holder ( $25 \pm 0.1^\circ$ ) of a Zeiss PMQ II or Hitachi Perkin-Elmer Model 139 spectrophotometer. After 15 min the substrate was added with a syringe directly into the cell and the disappearance of the quinone was followed at 390 m $\mu$ . With triphenylcyclopropene, cyclohexane, and 1,5-cyclooctadiene, appropriate stock solutions were prepared and kept in a constant-temperature bath. The concentration of the quinone was usually kept at about  $2.0 \times 10^{-3}$  M. Substrate concentrations were varied according to reactivity from  $6 \times 10^{-3}$  to 2.5 M. As the solution of 2,3-dichloro-5,6-dicyanobenzoquinone is unstable toward light, the sample cells were always kept out of the light beam except when readings were taken. Good straight-line plots of  $\log(A_t - A_\infty)$  vs. time were obtained for 2 to 3 half-lives. With 1,4-pentadiene some polymerization was observed, leading to cloudiness and a somewhat higher infinity reading; nevertheless, a good first-order plot was obtained. While the rate of solvent oxidation was negligible with the more reactive substrates, major difficulties were encountered in the measurement of the very unreactive compounds, cyclohexene and 1,5-cyclooctadiene. With these two compounds high substrate concentrations had to be used and a considerable experimental uncertainty has to be assumed.

(14) D. H. Reid, *Chem. Ind. (London)*, 1504 (1956); *Tetrahedron*, **3**, 339 (1958).

(15) P. Müller and J. Roček, *J. Org. Chem.*, **33**, 3001 (1968).

(16) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961); R. Breslow and P. Dowd, *ibid.*, **85**, 2729 (1963).

**Table I.** Oxidation of Tropilidene with 2,3-Dichloro-5,6-dicyanobenzoquinone (Sample Run, 25°)

$t_{\min}$	$A_t - A_\infty$	$t_{\min}$	$A_t - A_\infty$
0	1.15	3.83	0.39
0.34	1.05	4.01	0.37
0.48	1.01	4.22	0.35
0.60	0.97	4.44	0.33
0.75	0.93	4.67	0.31
0.94	0.88	4.92	0.29
1.14	0.83	5.20	0.27
1.35	0.78	5.45	0.25
1.60	0.73	5.79	0.23
1.84	0.68	6.12	0.21
2.10	0.63	6.48	0.19
2.40	0.58	6.90	0.17
2.72	0.53	7.37	0.15
3.07	0.48	7.90	0.13
3.47	0.43	8.60	0.11
3.65	0.41	9.33	0.09

$k_1 = 4.73 \times 10^{-3} \text{ sec}^{-1}$ ,  $k_2 = 0.195 \text{ M}^{-1} \text{ sec}^{-1}$

Data for a representative run with 5.53 mg of tropilidene in 2.50 ml of acetic acid ( $2.43 \times 10^{-2} \text{ M}$  in substrate and  $1.97 \times 10^{-3} \text{ M}$  in DDQ) are given in Table I. Variations in the tropilidene concentration from  $1.7 \times 10^{-2}$  to  $4.0 \times 10^{-2} \text{ M}$  confirmed that the oxidation follows the usual first-order dependence on the concentration of the substrate. First-order rate constants were determined graphically. The second-order rate constants listed in Table II are averages of two to nine measurements with a standard

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

	Substrate, $M$	$10^3 k$ , $M^{-1} \text{ sec}^{-1}$	$k_{\text{rel}}$
Tropilidene	$1.7\text{--}4.0 \times 10^{-2}$	20,000	$1.74 \times 10^5$
Tropilidene- $d_8$	$2.30 \times 10^{-2}$	4,980 <sup>a</sup>	$4.34 \times 10^4$
1,2,3-Triphenylcyclopropene	$6.50 \times 10^{-3}$	5,850	$5.2 \times 10^4$
1,2,3-Triphenylcyclopropene-3- $d$	$7.00 \times 10^{-3}$	852	$7.4 \times 10^3$
1,4-Pentadiene	2.30	2.42	21
Cyclohexene	1.67	0.12	1.00
1,5-Cyclooctadiene	0.720	0.057	0.49
1,4-Cyclohexadiene	$6.50 \times 10^{-2}$	5,300	$4.6 \times 10^4$

<sup>a</sup> Corrected for 94.75% deuterium content in methylene group;  $k_{\text{exp}} = 5.78 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ .

deviation of less than 5% for the means, except for the runs with cyclohexene and 1,5-cyclooctadiene (see above).

An attempt was made to study the kinetics of 1,3-cyclohexadiene. This compound underwent a fast Diels-Alder addition. The adduct precipitated out of the solution and no rate measurements could be made.

## Results and Discussion

**Reaction Products.** The reaction of dichlorodicyanobenzoquinone with tropilidene leads to tropylium salts.<sup>17</sup> Similarly, 1,2,3-triphenylcyclopropene yields the triphenylcyclopropenium ion.<sup>17</sup>

Simple olefins are also dehydrogenated. Even though the dehydrogenation product of cyclohexene was not identified,<sup>18</sup> the related tetralin undergoes almost quantitative dehydrogenation to naphthalene.<sup>19</sup> Naphthalene is also formed smoothly by dehydrogenation of 1,4-dihydronaphthalene.<sup>20</sup> It can therefore

(17) D. H. Reid, M. Fraser, B. B. Molloy, H. A. S. Payne, and R. C. Sutherland, *Tetrahedron Lett.*, 530 (1961).

(18) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954).

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

be safely concluded that the reaction of 1,4-cyclohexadiene with dichlorodicyanobenzoquinone will yield benzene. Methylbenzenes have been shown to undergo oxidation in the methyl group.<sup>21</sup> We consider it therefore safe to assume that in all unsaturated compounds which we investigated, the oxidation consists in an allylic (or benzylic) oxidation as the primary process.

**Isotope Effects.** A large deuterium isotope effect was observed both in the oxidation of perdeuteriotropilidene<sup>22</sup> ( $k_{\text{H}}/k_{\text{D}} = 4.0$ ) and of 1,2,3-triphenyl-3-deuteriocyclopropene ( $k_{\text{H}}/k_{\text{D}} = 6.9$ ). This demonstrates clearly that the carbon-hydrogen bond is broken in the rate-limiting step of the reaction in both cases. No isotope effects have been determined for the dehydrogenation of simple olefins.

**Structure and Reactivity.** The rates for the oxidation of tropilidene and triphenylcyclopropene with dichlorodicyanobenzoquinone are compared with the oxidation rates of several other olefins in Table I. Even though it is very likely that the measured reaction rates refer to a dehydrogenation reaction with a rate-limiting breaking of a carbon-hydrogen bond, the interference of other oxidation reactions cannot be excluded in compounds for which isotope effects were not determined. The rate constants for these olefins therefore have to be regarded as upper limits for the allylic oxidation.

Inspection of the rate data demonstrated clearly that both tropilidene and triphenylcyclopropene exhibit a special reactivity and undergo oxidation by several orders of magnitude faster than simple olefins or polyenes for which the loss of a hydride ion is not connected with the formation of a stable aromatic system. Particularly significant is the low reactivity of 1,4-pentadiene which we consider the closest model compound to tropilidene. In this diene the methylene group is activated by two neighboring double bonds resulting in a 20-fold increase in reactivity compared with cyclohexene. Nevertheless, this olefin is still almost  $10^4$  times less reactive than tropilidene. We consider this difference in reactivity most significant and fully in agreement with the hydride ion mechanism.

The high reactivity of triphenylcyclopropene is perhaps even more significant. Even though we do not have in this case a good model compound, the mere fact that the compound is very reactive and does react with carbon-hydrogen bond cleavage presents in itself very strong evidence in favor of a hydride ion transfer. Hydrogen atom abstraction would lead to the unstable triphenylcyclopropenium radical where the odd electron has to be placed in an antibonding orbital.<sup>11,24</sup> The deuterium isotope effect for this

(20) E. A. Braude, L. M. Jackman, and R. P. Linstead, *ibid.*, 3548 (1954).

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

(22) Perdeuteriotropilidene was employed rather than 7,7-dideuteriotropilidene in order to avoid complications which might arise from hydrogen migration in the tropilidene molecule under the reactions conditions or from the relatively easy hydride transfer reaction between tropilidene and the tropylium ion.<sup>23</sup>

(23) Z. N. Parnes, M. E. Volpin, and D. N. Kursanov, *Tetrahedron Lett.*, 20 (1960).

(24) One of the referees brought to our attention Gal's<sup>25</sup> finding that hydrogen abstraction from triphenylcyclopropene by methyl radicals proceeds at a rate slower by only a factor of 6 than the corresponding rate of hydrogen abstraction from triphenylmethane. We therefore attempted to determine the reactivity of triphenylmethane toward DDQ and found it to be at least  $10^5$  times less reactive than the triphenyl-

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.<sup>5</sup>

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

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).

transferring 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.<sup>13,19</sup> 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.<sup>26</sup>

**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.

(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

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**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 five 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.<sup>1</sup> 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.

(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).

Scheme I

