Table III. Volumes of Activation for the Acid- and Base-Catalyzed Hydrolysis of Carboxylic Acid Esters and Amides in Water

Compd	Catalyst	Temp, °C	$\Delta V^{\ddagger}$, ml	Ref
Methyl acetate	NaOH	25	−9.9	*a*
	HCl	30.5	−8.3	*b*
	HCl	14	−10.1	*c*
	HCl	35	−9.1	*d*
Ethyl acetate	NaOH	2.4	−4.5	*e*
	NaOH	25	−8.8	*a*
	NaOH	20	−5.6	*f*
	NaOH	30	−6.4	*f*
	HCl	14	−8.4	*c*
	HCl	35	−9.3	*g*
	HCl	0	−7.9	*g*
Isopropyl acetate	NaOH	20	−5.6	*f*
Butyl acetate	NaOH	20	−5.6	*f*
Isobutyl acetate	NaOH	20	−6.3	*f*
tert-Butyl acetate	HCl	60	0.0	*g*
Amyl acetate	NaOH	20	−5.8	*f*
Acetamide	NaOH	25	−14.2	*a*
	$HClO_4$	55	−9.4	*h*
Propionamide	NaOH	25	−16.9	*a*

[a] K. J. Laidler and D. Chen, *Trans. Faraday Soc.*, **50**, 1026 (1958). [b] A. Bogojawlensky and G. Tammann, *Z. Phys. Chem.*, **23**, 13 (1897). [c] V. Rothmund, *ibid.*, **20**, 168 (1896). [d] B. T. Baliga, R. J. Withey, D. Poulton, and E. Whalley, *Trans. Faraday Soc.*, **61**, 517 (1965). [e] E. Cohen and H. F. G. Kaiser, *Z. Phys. Chem.*, **89**, 338 (1915). [f] B. Anderson, F. Grønlund, and J. Olsen, *Acta Chem. Scand.*, **23**, 2458 (1969). [g] A. R. Osborn and E. Whalley, *Can. J. Chem.*, **39**, 1094 (1961). [h] A. R. Osborn, T. C.-W. Mak, and E. Whalley, *ibid.*, **39**, 1101 (1961).

evidence suggests that in these cases the transition state is reached during generation of a tetrahedral intermediate.[24] The base-catalyzed hydrolysis of acetamide, on the other hand, shows an unusually large negative volume of activation. In this exceptional case the breakdown of a tetrahedral intermediate, rather than its formation, appears to be rate limiting.[24] The present findings thus appear to provide some support for earlier mechanistic interpretations[3,4] of volumes of activation observed for nonenzymatic hydrolysis of carboxylic acid esters. Substituent effects are, however, quite marked, and need to be examined more extensively if volumes of activation are to serve as a more exact basis for speculation concerning reaction mechanisms. Since these effects appear to be exerted through solvent, it appears that particular caution should be exercised in comparing volumes of activation for enzymatic reactions (proceeding in the chemically unique environment of the active site) with volumes of activation for nonenzymatic model reactions in aqueous solution.

Some diving mammals encounter a considerable range of environmental hydrostatic pressures; in an extreme case, a whale was found trapped in the Pacific Ocean at a depth of 1135 m.[25] Pressure effects on aldehyde hydration might in principle constitute a serious problem in metabolic control, since changes in the state of hydration of simple aldehydes are known to affect their activities in several enzymatic reactions.[26] The present results suggest that these effects are not biologically significant. Even in the case of the aldehydes most sensitive to pressure, the effect of submersion to such depths would be to change the equilibrium constant for hydration by 5% or less.

Acknowledgment. We are grateful to Drs. Adam Zipp and Walter Kauzmann for familiarizing us with the high-pressure apparatus used in this work.

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(24) S. Johnson, *Advan. Phys. Org. Chem.*, **5**, 237 (1967), and references cited therein.

(25) L. H. Matthews, "The Whale," Simon and Schuster, New York, N. Y., 1968.

(26) S. J. Reynolds, D. W. Yates, and C. I. Pogson, *J. Biochem.*, **122**, 285 (1971).

Quantitative Assessment of the Antiaromaticity of Cyclobutadiene by Electrochemical Studies on Quinone Derivatives

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received May 15, 1973*

Abstract: Precursors of cyclobutadienonaphthoquinone derivatives have been prepared by novel procedures, utilizing photochemical additions. These may be oxidized electrochemically to the quinones, generating cyclobutadiene rings or models which help to correct for strain and inductive effects. The electrochemical potentials, obtained by extensive cyclic voltammetric studies, may be analyzed to indicate the conjugation energy of the cyclobutadiene system. The data indicate that cyclobutadiene is destabilized by at least 12–16 kcal/mol, and is thus clearly antiaromatic. Substituent effects on the thermodynamic and kinetic stability of cyclobutadiene have also been explored.

Cyclobutadiene has fascinated chemists ever since the early evidence that, contrary to simple expectations, it did not share the stability of benzene.[2] Many studies have been devoted to detecting this molecule, and preparing various stabilized derivatives, in the past

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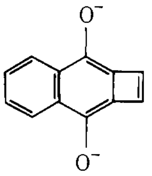
(1) (a) Taken principally from the Ph.D. Thesis of Dennis R. Murayama, Columbia University, 1973. (b) Taken in part from the Ph.D. Thesis of Robert Grubbs, Columbia University, 1969.

(2) M. P. Cava and M. L. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

few years. The properties of cyclobutadiene itself[3] certainly leave no doubt about the fact that it is not an aromatic system in the sense of being significantly resonance stabilized by cyclic delocalization of π electrons.

Some time ago[4] we called attention to the fact that the cyclic delocalization of π electrons is actually destabilizing for at least some species with $4n$ π electrons. We suggested the term "antiaromaticity" to describe the property, in such a molecule, of being destabilized by cyclic delocalization of π electrons relative to suitable reference compounds without such cyclic π-electron delocalization. Two types of reference systems can be selected: linear analogs in which the same conjugated units are simply in a linear rather than cyclic arrangement, or alternatively fragmented analogs in which the conjugated units of the antiaromatic compound are completely separated in the analog. By the first definition, cyclobutadiene is to be compared with linear 1,3-butadiene, while by the second definition it is to be compared with two isolated ethylene units. Since linear delocalization of π electrons in 1,3-butadiene is not significantly stabilizing, the antiaromaticity of cyclobutadiene should be more or less equivalent with either choice of reference system.

The serious experimental problem in this field is concerned with obtaining thermodynamic data which reflect the conjugation energy in a proposed antiaromatic system as distinct from other kinds of energy such as that of angle strain. As an example, it would not be sufficient (if this were possible) to determine the heat of hydrogenation of cyclobutadiene and use this to assess the π-electron energy of the system unless there were a reliable way to correct for the strain energy associated with the incorporation of unsaturated carbons into a four-membered ring. The solution to this problem would be to find some way to "turn on" the cyclobutadiene conjugative interaction by an electronic rearrangement while maintaining as closely as possible the same geometry, and thus presumably the same strain energy, throughout the transformation. This seemingly impossible problem of turning on an electronic interaction without moving any atoms can be approached by the oxidation of species such as **1**.



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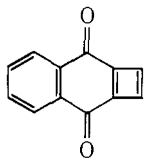

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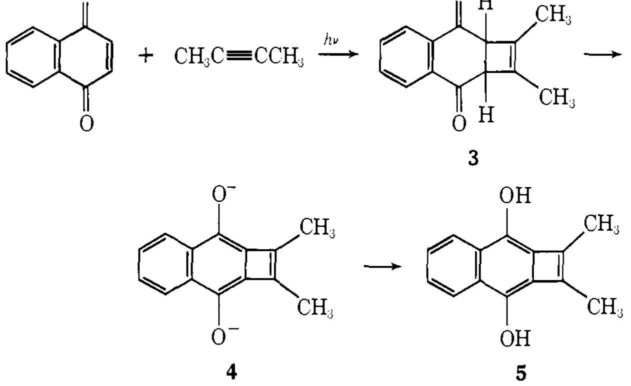
In species **1** the four-membered ring has only partial cyclobutadiene character, since the π-bond order in a naphthalene ring between C-2 and C-3 is less than one-half.[5] By contrast, in the oxidation product **2** the four-membered ring is essentially a full cyclobutadiene ring, since now there is a double bond between C-2 and C-3 of the naphthalene system. By this oxidation we have not turned on a cyclobutadiene interaction, but we have considerably increased it. Thus, the oxidation potential associated with the conversion of **1** to **2** contains information about the delocalization energy of cyclobutadiene.

In a preliminary communication[6] we have reported an examination of derivatives of **1** and other related compounds in an attempt to extract the (antiaromatic) delocalization energy of cyclobutadiene from a series of such oxidation potentials. In this paper we report a more detailed exploration of this problem.

Results and Discussion

A. Synthesis of Naphthoquinone Derivatives. Systems of the type symbolized in structure **1** are in principle accessible from the photoadducts of acetylenes with naphthoquinone. Our earliest work in the series[6] involved the photoaddition of 2-butyne to naphthoquinone to produce compound **3** which could be converted to its dienolate **4** by treatment with sodium hydride. On protonation of **4** the hydroquinone **5** was produced, but it proved to be very unstable with respect to rapid dimerization. Stability was better[6] with the corresponding diphenyl derivative **13**, and most of our studies have been concerned with this system and some close analogs.



Photoaddition of naphthoquinone **6** to diphenylacetylene affords the cyclobutene derivative **7**, but in poor yield. As has been described elsewhere,[7-9] this reaction is accompanied by a considerable amount of cycloaddition at the carbonyl group of the quinone rather than at the double bond. Such photoadditions are strongly affected by substituents on the naphthoquinone system, and in particular 2-methoxynaphthoquinone (**8**) affords the corresponding cyclobutene **9** in good yield[8-11] on photolysis with diphenylacetylene. We find that **9** can be conveniently converted to the corresponding chloro derivative **10** with BCl_3, and that this represents a better route to the compound than direct photoaddition[6] to 2-chloronaphthoquinone. Similarly, with BBr_3, **9** is converted to the bromide **11**,

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[3] L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965); C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972); O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Amer. Chem. Soc.*, **95**, 614 (1973); S. Masamune, M. Suda, H. Ona, and L. M. Leichter, *J. Chem. Soc., Chem. Commun.*, 1268 (1972); G. Maier and B. Hoppe, *Tetrahedron Lett.*, 861 (1973).

[4] R. Breslow, *Chem. Eng. News*, 43, 90 (1965); R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967); R. Breslow, *Angew. Chem., Int. Ed. Engl.*, 7, 565 (1968).

[5] This is the basis of the relative stability of the naphthocyclobutadienes first prepared by M. P. Cava, B. H. Wang, and J. P. van Meter, *J. Amer. Chem. Soc.*, **85**, 4032 (1963).

[6] R. Breslow, R. Grubbs, and S. I. Murahashi, *ibid.*, **92**, 4139 (1970).

[7] R. H. Grubbs, Ph.D. Dissertation, Columbia University, 1968.

[8] S. Farid, W. Kothe, and G. P. Pfundt, *Tetrahedron Lett.*, 4147, 4151 (1968).

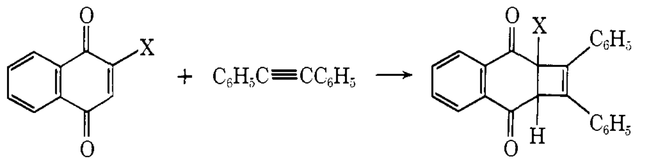
[9] S. P. Pappas and N. A. Portnoy, *J. Org. Chem.*, **33**, 2200 (1968).

[10] S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *ibid.*, **34**, 520 (1969).

[11] S. P. Pappas and N. A. Portnoy, *Chem. Commun.*, 597 (1969).

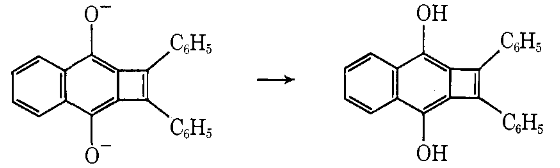
and this is easily reduced to the unsubstituted derivative **7**. The indirect route from **8** to **9** to **11** to **7** is actually better from a preparative standpoint.

On treatment with potassium *tert*-butoxide **7** is converted to the dienolate **12**, and this can be neutralized to afford the naphthohydroquinone **13**. This diphenylcyclobutadiene derivative is somewhat unstable with respect to dimerization, although it seems to be considerably less reactive than is the dimethyl analog **5**. If the dienolate **12** is instead treated with acetic anhydride it is smoothly converted to the diacetate **14**, a relatively stable compound. By contrast, methylation of the dienolate **12** occurs on carbon, not oxygen, to afford the derivative **15** which is identical with the photoadduct[8] of diphenylacetylene with 2,3-dimethylnaphthoquinone.



6, X = H
8, X = OCH_3

7, X = H
9, X = OCH_3
10, X = Cl
11, X = Br



12

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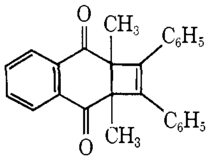

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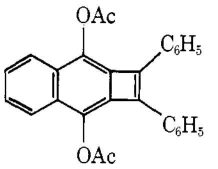

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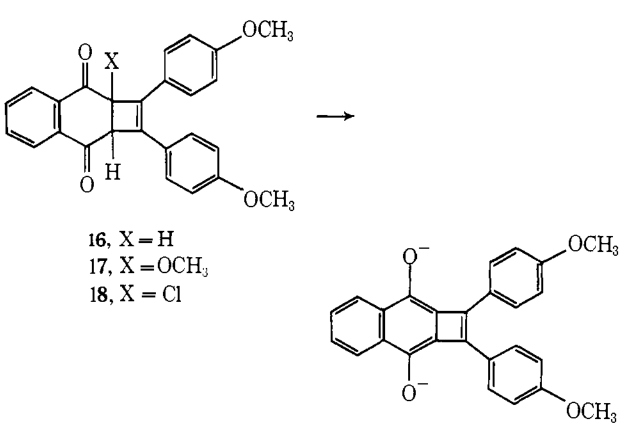
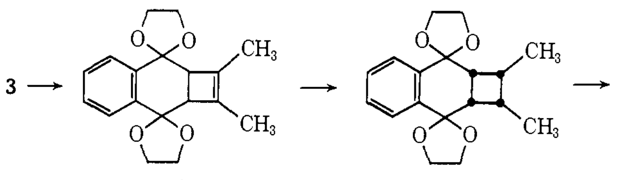
Related compounds can be prepared starting with di-*p*-anisylacetylene. The indirect route again proved most attractive, and methoxynaphthoquinone (**8**) was used to produce **17**. This could also be converted to the stable chloro derivative **18**. The corresponding bromide was too unstable for easy handling, however, so it was produced from **17** and then directly reduced to afford the unsubstituted derivative **16**. Again this could be converted to the dianion **19**, and again on treatment with acetic anhydride the corresponding diacetate was produced.



16, X = H
17, X = OCH_3
18, X = Cl

19

Various reference compounds were also prepared to assist in the interpretation of the oxidation potentials of the derivatives of structure **1**. Thus compound **23** was prepared[6] as a cyclobutene analog of the cyclobutadiene systems of interest. Since it turned out that direct hydrogenation of the double bond in **3** was not selective, **3** was first converted to its bisketal **20** with ethylene glycol. This bisketal was then hydrogenated to reduce the four-membered ring, and the product **21** was hydrolyzed to the corresponding dione **22** again. This dione could be enolized to **23**, and the corresponding diacetate of **23** could also be prepared. On standing, the cyclobutene derivative **23** was completely stable in contrast to the cyclobutadiene derivatives **5** and **13**.



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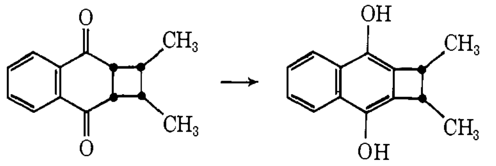
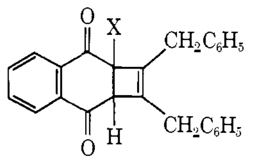


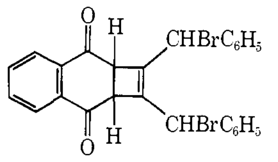
22

23

We also prepared the dimethylenecyclobutene derivative **29** as an even closer analog of our cyclobutadiene systems. The first step was photoaddition of methoxynaphthoquinone (**8**) to dibenzylacetylene to afford the adduct **24**; remarkably, the product actually isolated from this photoreaction was **25**, in which the methoxyl



24, X = OCH_3
25, X = H



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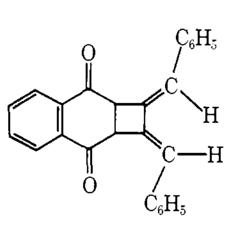

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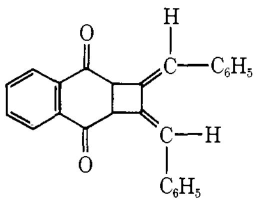

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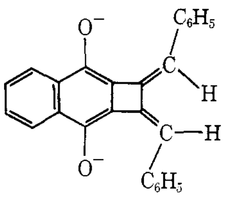
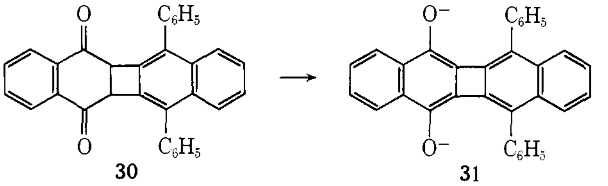


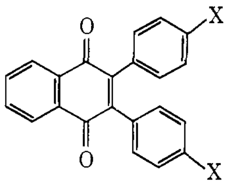
29

had been replaced by a hydrogen. Of the various possible explanations of this transformation, the most reasonable involves photochemical attack by the carbonyl group of **24** on the hydrogen of the methoxyl. The resulting diradical should fragment to produce formaldehyde and the enol of **25**, which would ketonize. In any case, this happy result considerably shortens the sequence, and **25** could be converted with *N*-bromosuccinimide to a mixture of dibromides symbolized by **26**. This mixture was directly reduced with stannous chloride to afford a mixture of stereoisomers of the diene, principally **27** and **28**. This could be fractionated to afford pure **27**, which was converted to its dienolate ion **29**.

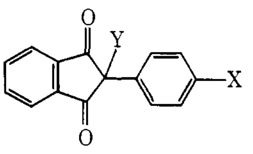
Another analog of our cyclobutadiene systems was prepared (**31**) in which again all of the carbons of the four-membered ring are trigonal but in which the oxidation product would have only a partial cyclobutadiene ring. Compound **30** has recently been described,[12] and is conveniently prepared from the photodimer of naphthoquinone; its dienolate ion **31** was examined in the present work. Finally, 2,3-diphenylnaphthoquinone (**32**) was prepared as was 2,3-dianisylnaphthoquinone (**33**). These compounds could be synthesized from the corresponding indan diones **34** and **35** by oxidative dimerization to **36** and **37** and base cleavage to afford **32** and **33**, as has been described[13] for **32**.



30 **31**

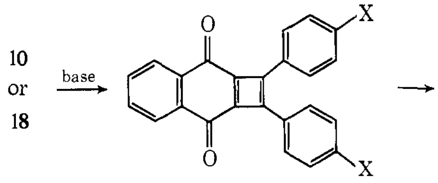


32, X = H
33, X = OCH_3

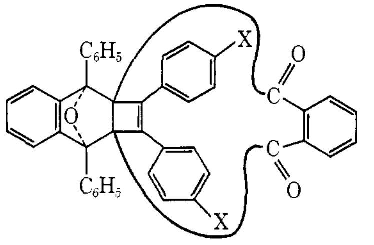


34, X = Y = H
35, X = OCH_3; Y = H
36, X = H; Y = $)_2$
37, X = OCH_3; Y = $)_2$

The main purpose of this work was to prepare compounds for the electrochemical studies to be described in the next section. However, we have done some studies on the cyclobutadiene derivatives related to structure **2** which can be generated chemically from some of these compounds. Thus, treatment of the chlorodiphenylcyclobutene derivative **10** with base affords the diphenylcyclobutadienonaphthoquinone (**38**). This elimination of HCl occurs readily, but **38** is not stable under the reaction conditions, even at fairly high dilution. If the elimination from **10** is run in the presence of diphenylisobenzofuran then the adduct **40** is produced, but this adduct is not formed if the diphenylisobenzofuran is added after the elimination from **10** is complete; **38** does not have enough lifetime to be trapped in this latter experiment.



38, X = H
39, X = OCH_3



40, X = H
41, X = OCH_3

Even more extensive studies were done with the dianisylchlorocyclobutene (**18**). On treatment with base under a variety of conditions this underwent an elimination; again the resulting cyclobutadiene derivative **39** could be trapped, if it were generated in the presence of diphenylisobenzofuran, to afford adduct **41**. However, under all conditions of high dilution and low temperature it proved impossible to perform the elimination before adding the trapping reagent and still obtain any of adduct **41**. Apparently, the cyclobutadiene derivative **39** is also quite unstable to these reaction conditions. This is striking because **39** bears two electron-attracting carbonyl groups and two electron-feeding *p*-anisyl groups, and is thus a "push,push,pull,pull" substituted cyclobutadiene. Of course, the conjugating groups involved are not as effective as are those in the stable push,pull substituted cyclobutadiene prepared by Gompper.[14] Furthermore, our substitution pattern may be somewhat less effective than the alternating pattern in the Gompper compound. It is, however, somewhat surprising that a highly substituted cyclobutadiene such as **39** is still extremely reactive. This same high reactivity is revealed in the electrochemical studies in which species **38** and **39** are generated oxidatively.

B. Electrochemical Studies. Our early work[6] involved the polarographic oxidation of hydroquinone derivatives. These undergo a two-electron oxidation to afford the corresponding quinone in a process which also involves the ionization of the two hydroxylic protons. Such a process is of course chemically complicated, and in a case such as ours in which the product is rapidly removed by chemical reactions the potentials obtained will in general not be good thermodynamic potentials. Although the dimethylcyclobutadiene derivative **5** was too reactive to be examined by this technique, we did examine the diphenylcyclobutadiene derivative **13** and the dimethylcyclobutene model compound **23** as well as 1,4-naphthohydroquinone by this technique. The data obtained are listed in Table I.

When hydroquinone dianions are oxidized, then two one-electron waves are in general observed. We have reported[6] a preliminary study of the polarographic oxidation of the diphenylcyclobutadiene dianion derivative **12** as well as of 1,4-naphthohydroquinone dianion as a

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(12) D. P. Venter and J. Dekker, *J. Org. Chem.*, 34, 2224 (1969); N. P. du Pereez, P. J. van Vuuren, and J. Dekker, *ibid.*, 35, 523 (1970); N. P. du Pereez, D. P. Venter, P. J. van Vuuren, G. J. Kruger, and J. Dekker, *ibid.*, 36, 485 (1971).

(13) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, 28, 3250 (1963); see also P. Auburn, *Ann. Chim. (Paris)*, 9, 359 (1964).

(14) R. Gompper and G. Seybold, *Angew. Chem., Int. Ed. Engl.*, 7, 824 (1968).

Table I. Preliminary Polarographic Data[a]

	$E_{1/2}$, V *vs.* sce at dme
Hydroquinone Derivative[b]	
Diphenylcyclobutadiene derivative **13**	+0.163
1,4-Naphthohydroquinone	−0.113
Dimethylcyclobutene derivative **23**	−0.153
Hydroquinone Dianions[c]	
1,4-Naphthohydroquinone	−1.32, −0.63 (−1.42, −0.65)[d]
Diphenylcyclobutadiene derivative **12**	−0.86, −0.40

[a] Reference 6. [b] In aqueous ethanol at pH 5.6 with acetate buffer. [c] In dimethylformamide with tetrabutylammonium perchlorate. [d] From reduction of the quinone.

reference. These preliminary data are also listed in Table I. Both kinds of data indicate that it is much more difficult to oxidize **12** or **13** than to oxidize appropriate model compounds. From these data we had concluded that the cyclobutadiene system in the oxidation product **38** is destabilizing by 12–16 kcal/mol, and that this was a lower limit to the antiaromaticity of cyclobutadiene itself.

Several factors made it important to improve on these preliminary studies. It was clear that the cyclobutadienonaphthoquinone derivative **38** was extremely unstable, and should undergo rapid chemical reaction on formation by oxidation of either **12** or **13**. The product removal makes the oxidation occur more easily than it would for a truly reversible process, and thus leads to an underestimate of the instability of the cyclobutadiene system. This kind of problem is best approached by using cyclic voltammetry,[15–28] in particular of dianions such as **12**. Furthermore, it seemed desirable to examine a number of other model compounds so as to correct as well as possible for the inductive effects and strain effects on the **12** to **38** conversion and thus to isolate as well as possible that part of the energy change which corresponds to the cyclobutadiene conjugation energy. Thus in our recent work we have concentrated on cyclic voltammetric oxidation of dianions prepared in dimethylformamide with a K^+ counterion.

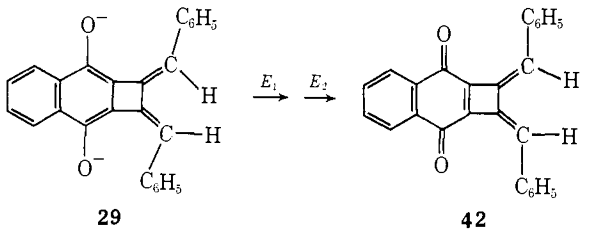
Previous studies[29] have demonstrated that the reduction waves of naphthoquinones are unaffected by potassium perchlorate in dimethylformamide, although they are perturbed by Na^+, Li^+, or a variety of other coordinating cations. Accordingly, we considered that ion-pairing effects would be minimal in our system with the choice of K^+ as counterion. In general, the dianions (such as **12**) were prepared from the corresponding diketones (such as **7**) by treatment with potassium *tert*-butoxide, and after addition of appropriate electrolyte the resulting solutions were directly examined electrochemically in a standard[15,16] cyclic voltammetry apparatus. For all of the dianions examined, two one-electron waves were observed. The best values for the corresponding oxidation potentials are listed in Table II.

Table II. Half-Wave Oxidation Potentials for Hydroquinone Dianions[a]

Compd[b]	E_1	E_2	$E_1 + E_2$	$\Delta(E_1 + E_2)$[c]
Naphthohydroquinone	−1.50	−0.68	−2.18	
Diphenylcyclobutadiene derivative **12**	−0.90	−0.25[d]	−1.15	1.03
Dianisylcyclobutadiene derivative **19**	−1.00	−0.38[d]	−1.38	0.80
Dibenzylidenecyclobutene derivative **29**	−1.22	−0.45	−1.67	0.51
Binaphthylene derivative **31**	−1.17	−0.36	−1.53	0.65

[a] Concentration ≤0.5 m*M* in DMF at 20° with 0.5 *M* tetrabutylammonium perchlorate using a Pt working electrode. Potentials are reported in V *vs.* a Ag|AgCl reference electrode. [b] As the dipotassium salt. [c] The total energy change in eV on two-electron oxidation relative to that for the naphthohydroquinone dianion system taken as a standard. [d] Irreversible potentials, taken at peak potentials at 10 V/sec. See text for a discussion of the errors involved.

These compounds were in general more poorly behaved the more closely their structures were related to cyclobutadiene. Thus, for simple naphthohydroquinone dianion a classic reversible pattern was obtained and the corresponding potentials agree with those we have also observed (*vide infra*) by reduction of naphthoquinone. The cyclic voltammogram of the dibenzylidenecyclobutene derivative **29** was also essentially classical. As Figure 1 shows, both waves were reversible at modest scan rates. Thus, the quinone oxidation product **42** derived from **26** was stable in solution at least for the duration of the electrochemical scan.



29 **42**

This was not true in the case of the binaphthalene derivative **31**. As Figure 2 illustrates, the first wave is reversible but the cathodic portion of the second wave could be seen only with rather fast scan rates and low concentrations of **31**. This is consistent with the expected behavior if the quinone **43** is chemically unstable

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(17) J. E. B. Ruadles, *Trans. Faraday Soc.*, **44**, 327 (1948); A. Sevcik, *Collect. Czech. Chem. Commun.*, **13**, 349 (1948); P. Delahay, *J. Amer. Chem. Soc.*, **75**, 1190 (1953); H. Matsuda and Y. Ayabe, *Z. Electrochem.*, **59**, 494 (1955); **61**, 489 (1957); W. H. Reinmuth, *Anal. Chem.*, **32**, 1891 (1960); W. H. Reinmuth, *J. Amer. Chem. Soc.*, **79**, 6358 (1957).

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(25) M. L. Olmstead, R. G. Hamilton, and R. S. Nicholson, *ibid.*, **41**, 260 (1969).

(26) M. L. Olmstead and R. S. Nicholson, *ibid.*, **41**, 862 (1969); M. Mastrogostino, L. Nadjo, and J. V. Saveant, *Electrochim. Acta*, **13**, 721 (1968).

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(29) T. Fuginaga, K. Izutsu, and J. Nomura, *J. Electroanal. Chem.*, **29**, 203 (1971).

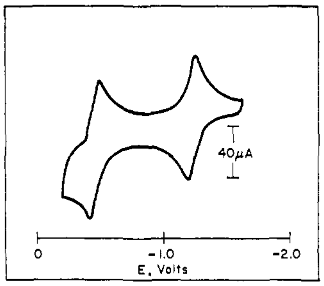
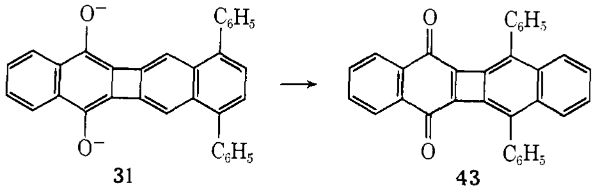


Figure 1. Steady-state stationary electrode polarogram of dibenzylidenecyclobutenonaphthohydroquinone dianion (**29**) ($\leq$0.5 m*M*) in DMF, 0.5 *M* TBAP, at a platinum disk electrode at 20°, for a sweep rate of 0.54 V/sec.



31 **43**

with respect to either a dimerization or a reaction with **31** itself. In either case, the reduction of the quinone must compete with this chemical destruction, and this is only possible if the chemistry is slowed by utilizing low concentrations of **31** and the reduction is accelerated by scanning at faster rates.

The most poorly behaved compounds were those of greatest interest, the dianions **12** and **19** whose oxidation products are the cyclobutadiene derivatives **38** and **39**. Even the starting dianions are relatively unstable; with careful exclusion of moisture and oxygen it is possible to maintain their solutions for 3 hr or so with a negligible decay in their concentrations, as judged by the corresponding electrochemical currents. The first oxidation wave is almost reversible in both cases, as Figure 3 indicates. However, if relatively slow scan rates were used and the dianions were present in high concentration then some asymmetry was observed even for the first wave, in the sense that the anodic current was then larger than the corresponding cathodic current. This kind of asymmetry is consistent with some chemical destruction of the intermediate anion radical in competition with its electrochemical rereduction, but this can be easily suppressed by the use of lower concentrations and higher scan rates. Apparently the intermediate anion radical either dimerizes or disproportionates fairly rapidly.

The second wave was irreversible at all scan rates and concentrations for both **12** and **19**. This irreversibility is indicated in Figure 3 by the absence of a cathodic peak for the second wave. However, the electrochemical behavior of this wave indicated clearly that it was in fact the second oxidation wave of our starting dianions, rather than any electrochemistry associated with other chemical products. Thus at low scan rates the current associated with the second anodic wave was very small, but it increased to a value comparable to the anodic current for the first wave if the scan rate was increased. This behavior is of course parallel to that just discussed for the other electrochemical process involving the intermediate anion radical, namely the rereduction in the cathodic portion of the first wave. Thus, this behavior indicates clearly that the intermediate anion radical is undergoing a chemical process which competes with the rate of either of its two electrochemical processes: the cathodic rereduction at E_1 discussed above and the anodic oxidation at E_2 to afford the quinone **38** or **39**. As expected from this interpretation, the ratio of second wave anodic current to first wave anodic current was also a function of the original concentration of the dianion, since this also would determine the rate of disappearance of intermediate anion radical by any second-order process. The ratios of currents as a function of scan rate at two different concentrations for anions **12** and **19** are shown in Figures 4 and 5.

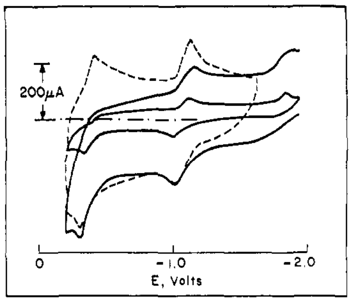


Figure 2. Stationary electrode polarogram of diphenyldibenzobiphenylenehydroquinone dianion (**31**) in DMF at a platinum disk electrode at 20°. Full lines are for a concentration of >1 m*M*, with 0.2 *M* TBAP at sweep rates of 0.108 and 1.08 V/sec. The dashed lines correspond to a concentration of $\leq$0.5 m*M*, with 0.5 *M* TBAP, for a sweep rate of 11.2 V/sec. The current scale is shown for the latter experiment.

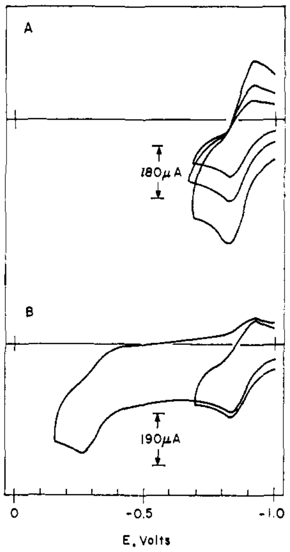


Figure 3. Cyclic voltammetry of diphenylcyclobutadienonaphthohydroquinone dianion (**12**) (~0.8 m*M*) in DMF, 1.0 *M* TBAP, at a platinum disk electrode at 20°: (A) first wave isolated for sweep rates of 1, 4, and 9 V/sec; (B) extension of the potential sweep to include the second anodic process at 4 V/sec.

The more serious chemical complication is the disappearance of the product cyclobutadiene quinone derivatives **38** and **39** so rapidly that we could not detect their rereduction under any circumstances. As we have pointed out above, this kind of chemical process occurring after the electrochemical process has the effect of making the electrochemical step easier, thus leading to an underestimate of the oxidation potential required for the removal of the second electron. With faster scan rates the electrochemical step competes better with the subsequent chemical destruction of

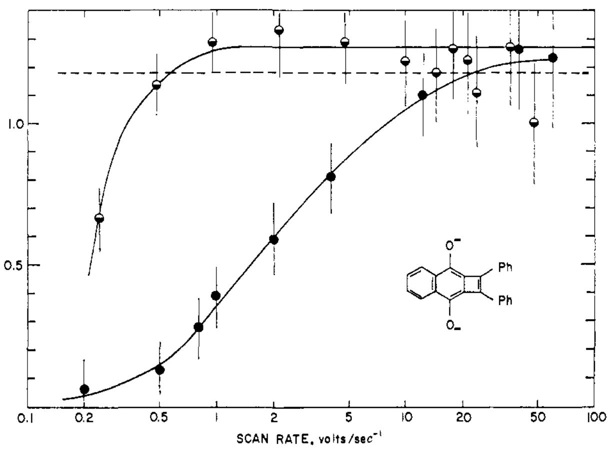


Figure 4. The ratio of the second- to the first-anodic peak current as a function of scan rate and concentration for diphenylcyclobutadienonaphthohydroquinone dianion (**12**) in DMF, 1.0 *M* TBAP at 20°: (⊖) 0.3 m*M*; (●) 1.5 m*M*.

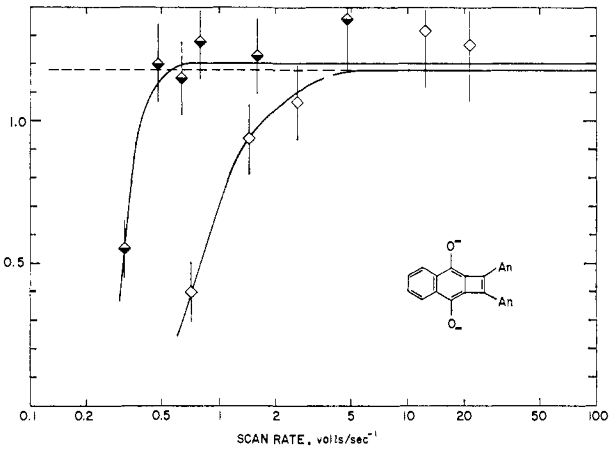


Figure 5. The ratio of the second- to the first-anodic peak current as a function of scan rate and concentration for dianisylcyclobutadienonaphthohydroquinone dianion (**19**) in DMF, 1.0 *M* TBAP at 20°: (⬖) 0.25 m*M*; (◇) 0.5 m*M*.

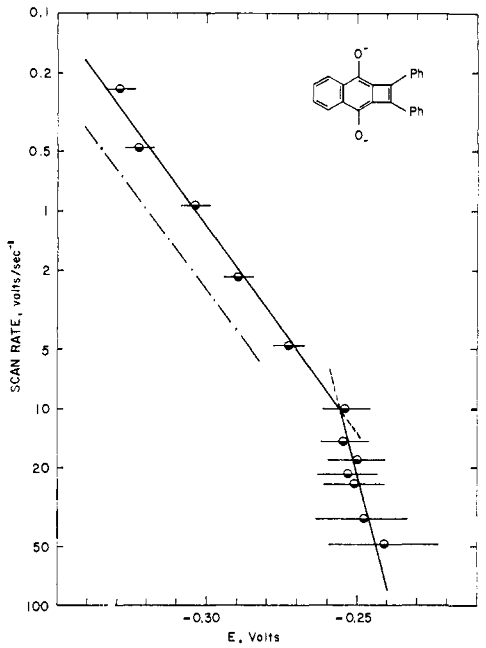


Figure 6. The behavior of the second anodic peak potential of diphenylcyclobutadienonaphthohydroquinone dianion (**12**) with increasing scan rate, at 20° for a concentration of about 0.3 m*M*.

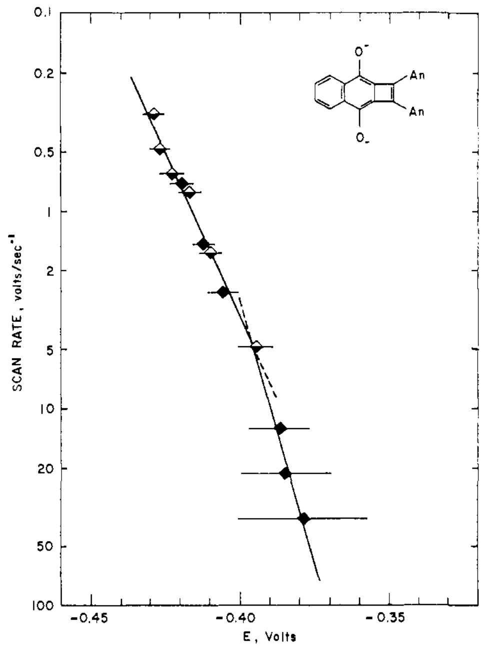


Figure 7. The behavior of the second anodic peak potential of dianisylcyclobutadienonaphthoquinone dianion (**19**) with increasing scan rate, at 20° for concentrations of about 0.25 and 0.5 m*M*: (⬖) 0.25 m*M*; (◆) 0.5 m*M*.

product, and the potential observed is thus closer to the true reversible potential. However, as Figures 6 and 7 illustrate, the peak potential for the second wave of both anions shifts to more positive values with faster scans, and at no point did the potential become independent of the scan rate. Therefore, at the highest velocities used we had not yet reached the reversible potential, and the potentials we observed are thus still underestimates of the true potential required to remove the second electron from anions **12** and **19**. It should also be mentioned that some studies were done at very high scan rates at temperatures at low as −40° in an attempt to slow down the chemical complication, but even at low temperature no cathodic rereduction peak was ever observed for the second wave.

Another indication of the effect of subsequent chemical reaction is a decrease in breadth in a peak, since negative potential shift by chemical removal of the products is more significant in the last half of the oxidation wave than it is in the first half. The separation between the peak and half peak potentials at moderate frequencies was in the region of 46 ± 6 and 41 ± 8 mV for the second anodic waves of the diphenyl dianion **12** and the dianisyl dianion **19**, respectively. By contrast, the separations between peak potential and half-peak potential for the first oxidation waves of these compounds under reversible conditions were approximately 55–59 mV. For conditions in which the cathodic portion of the first wave was absent (*e.g.*, for 1.5 m*M* concentrations of **12** with a slow 0.2 V/sec sweep) the separation between peak and half-peak potential was approximately 40 mV. On the other hand, it should be noted that the first waves under these irreversible conditions, which are apparently similar to the sort of irreversibility we observe for our second waves, were not *strongly* displaced from the true reversible potentials which we could achieve at higher frequencies and lower concentrations.

We can also make a more direct estimate of the quantitative effect that the chemical reactions of **38** and **39** may be having on the observed potentials. For a process in which **38** or **39** is being removed by simple dimerization, the peak potential is related to the formal oxidation potential by eq 1.[24,25,27] If we use the value

$$E_{\mathrm{p}} = E^{0\prime} + 0.058 - 0.0197 \log (kC^0/v) \qquad (1)$$

of 10^{-4} *M* for the bulk concentration of the substrate C^0, a diffusion controlled second-order rate constant of 10^{10} M^{-1} sec^{-1} for the rate constant k, and a scan rate of 10 V/sec for the scan velocity v, then it is calculated that the peak potential is approximately 40 mV more negative than the true formal potential. This would correspond to a 1 kcal/mol underestimate of the energy increase accompanying the oxidation. With other mechanisms for disappearance of the quinones **38** and **39** a different equation applies, but the estimate of the error is of a similar magnitude.

Another estimate of the error can be derived from a consideration of the data in Tables II and III. For the dianion–quinone pairs which give good reversible potentials for both waves, the separation between the first and second wave ranges from 0.71 to 0.83 V. By contrast, the separation of the two waves for **12** is only 0.65 V, while for **19** it is 0.62 V. The separation should be roughly constant among these compounds, since it reflects chiefly electrostatic repulsion effects as two successive electrons are fed into the same orbital (in the simple MO theories). By this criterion the true E_2 for **12** and **19** may be 60–200 mV more positive than the values in Table II, with the smaller value being more likely. Thus the potentials for the second waves of compounds **12** and **19** are in fact lower limits to the potential required for the oxidation, but the error is probably not more than a few kcal/mol.

Table III. Half-Wave Reduction Potentials for Quinones[a]

Compd	E_1	E_2
1,4-Naphthoquinone (**6**)	−0.68	−1.51
2,3-Diphenyl-1,4-naphthoquinone (**32**)	−0.73	−1.52
2,3-Dianisyl-1,4-naphthoquinone (**33**)	−0.78	−1.55
9,10-Anthraquinone	−0.96	−1.67

[a] In dimethylformamide at 20° with 0.5 *M* tetrabutylammonium perchlorate using a Pt working electrode. Potentials are reported in V *vs.* a Ag|AgCl reference electrode.

Finally, some reference compounds were examined by cyclic voltammetric reductions of the corresponding quinones. These data are listed in Table III. In all cases, good classical behavior was obtained, and it should be noted in particular that the data for reduction of 1,4-naphthoquinone correspond exactly to those obtained by oxidation of the corresponding hydroquinone anion as listed in Table II. The interpretation of these oxidation potentials is the subject of the next section.

Interpretation and Conclusions

As Table II indicates, dianion **12**, whose oxidation generates cyclobutadiene derivative **38**, is the most difficult to oxidize (its oxidation waves come at the most positive potentials). The difference in overall energy change for the oxidation of **12** relative to naphthohydroquinone dianion is at least 1.0 eV (23 kcal/mol), and it may be as large as 1.2 eV (27 kcal/mol) in view of our estimate of the effect of the chemical irreversibility of the second wave for **12** on its observed potential. Three general classes of factors may be involved in this difference. First of all, there is the general group of inductive effects. Secondly, there are any changes in strain energy associated with the oxidation. Finally, there are the changes in conjugation energy which are of interest in our present investigation.

It is quite difficult to separate these effects in simple models, since it usually turns out that any model differs in several ways from the system for which it is an analog. Thus one might wonder whether the substitution on a naphthalene hydroquinone by two vinyl carbons in **12** will change the oxidation potential of **12** appreciably by their simple inductive electron-withdrawing effect.[30] In general, electron-feeding groups will make such oxidations occur at more negative potentials while electron-attracting groups move them to more positive potentials. A model suggesting that inductive effects are small is found in diphenylnaphthoquinone (**32**), whose reduction potentials are only very slightly affected by the substitution of phenyl groups; and for that matter, they are affected in the negative direction. However, the substitution of two phenyl groups on the naphthoquinone system adds not only the inductive effect of two unsaturated carbons, but also whatever conjugative effects the phenyls may have in stabilizing the quinone structure by conjugative electron donation. One can argue that this compensating conjugative effect is not expected to be very large here, since the phenyl groups are rather strongly twisted out of planar conjugation. Further evidence that the conjugative effects are quite small is found in the very small incremental stabilization of the naphthoquinone system when phenyl groups are replaced by *p*-anisyl groups. The conclusion is thus that the inductive effect of the vinyl carbons in **12** is probably also small. Some of our other models are designed to incorporate appropriate corrections for the possible inductive effects of a vinyl carbon substituent.

Our whole system was designed to minimize the change in strain energy on increasing the cyclobutadiene interaction, but strain energy changes cannot be completely eliminated. To the simplest approximation there is no change in hybridization in the atoms when **12** is oxidized to **38**, but real hybridizations in small strained rings are not simple. There will in fact be a Mills–Nixon effect[31] which destabilizes **38** relative to **12** on the basis of some change in strain energy. Rieke has done a series of studies[32] of the first reduction wave of some naphthoquinones with fused rings, and his data are presented in Table IV. It is apparent that the cyclobutene derivative has its first reduction potential at a value comparable to that of simple naphthoquinone itself, but more positive than the potentials for larger ring fused systems. We had also observed (Table I)

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(30) For general discussion of substituent effects on quinone reductions, see P. Zuman, *Collect. Czech. Chem. Commun.*, 27, 2035 (1965); "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967.

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

(32) R. D. Rieke, W. E. Rich, and J. H. Ridgeway, *J. Amer. Chem. Soc.*, **93**, 1962 (1971).

Table IV. First Reduction Waves of Some 1,4-Naphthoquinones[a]

Derivative	$-E_{1/2}$ (dme)[b]	$-E_{1/2}$ (hmde)[c]
Unsubstituted	0.685	0.68
2,3-Dimethyl-	0.846	0.85
2,3-Cyclobuteno-	0.695	0.70
2,3-Cyclopenteno-	0.748	0.74
2,3-Cyclohexeno-	0.854	0.84

[a] Reference 32. [b] Polarography at a dropping mercury electrode. [c] Cyclic voltammetry at a hanging mercury drop electrode.

that a fused cyclobutene ring had no net effect on the oxidation potentials of a naphthohydroquinone dianion.

In these cyclobutene models there is obviously a compensating combination of strain and inductive effects. The difference between the cyclobutene derivative and the cyclohexene derivative in Table IV also contains both the obvious change in strain energy and also a difference in inductive effects, since a cyclobutane carbon will have a different ability to donate or accept electrons inductively than a cyclohexane carbon does. Although the strain effects seem to be small relative to the very positive oxidation potential increment in compound **12**, it is important to correct for them as well as possible.

The dimethylenecyclobutene derivative **29** incorporates many features of interest for such corrections. The energy change on oxidation of **29** is essentially halfway between that for oxidation of simple naphthohydroquinone and for oxidation of the cyclobutadiene derivative **12**. If we should select **29** as a model for the inductive and strain energy changes associated with the oxidation of **12**, then we would conclude that there is still 0.52–0.70 eV (12–16 kcal/mol) to be accounted for in terms of conjugation energies.

Of course, with the introduction of all the unsaturation in **29**, one now has to wonder about whether there are any special conjugation features associated with its oxidation. The corresponding quinone **42** is a dimethylenecyclobutene derivative. Simple Hückel calculations suggest that dimethylenecyclobutene systems will be conjugatively stabilized, and Pullman has suggested[33] that this stabilization plays a significant role in the quinone oxidations we are discussing. However, the stabilization predicted for dimethylenecyclobutenes by simple Hückel calculations is not supported by the properties of these compounds. A Hückel calculation (in which electrostatic repulsion is ignored) derives most of the stabilization in this system from heavy mixing of charge separation into the ground-state structure. Other calculations suggest that the dimethylenecyclobutene system is not appreciably stabilized, and both Dewar[34] and Schaad and Hess[35] calculate that it is mildly destabilized by conjugation. Thus, we suggest that there is no strong stabilization in **42** as a result of the presence of a dimethylenecyclobutene system. The same question must be addressed again in connection with the energy of species **12** itself; its rather positive oxidation potential could be reflecting stabilization in **12** rather than destabilization in the cyclobutadiene product **38**.

The naphthocyclobutadiene **12** is a derivative of cyclobutadiene, but it is also a derivative of dimethylenecyclobutene. Consideration of the bond orders in naphthalene indicates that **12** should have less than half cyclobutadiene character, and more than half dimethylenecyclobutene character. However, its properties indicate that it is still appreciably destabilized, as least judged by its chemical reactivity and that of the dimethyl analogs **4** and **5**. The aggregate effect of unsaturation in system **12** is thus destabilizing, although the destabilizing effect is much greater in the quinone **38** derived from it. This is essentially a full cyclobutadiene, perturbed by substituents, and the oxidation of **12** to **38** has thus involved a considerable increase in the cyclobutadiene character of the system. Taking the dimethylenecyclobutene **29** as a model for the expected potential in the absence of this special conjugative interaction, the cyclobutadiene system in **38** is 12–16 kcal/mol more destabilizing by a conjugative effect than is the fused ring system in **12**. Since **12** is already conjugatively destabilized, the full conjugative destabilization effect of a cyclobutadiene ring must be even larger than this estimate of 12–16 kcal/mol.

The results with the binaphthalene derivative **31** are consistent with these interpretations. Thus, **31** is **29** with an extra ring fused on, and oxidation of **31** to the corresponding quinone **43** creates a new system which now has some cyclobutadiene character to it (since there is *some* C_2–C_3 π-bond order in naphthalene). We thus expect that the oxidation potential of **31** should lie between that of **29** and that of **12**; that is what we see in Table II. The sum of the oxidation potentials for **31** is -1.53 V *vs.* the -1.67 V for **26** and the -1.0 to -1.15 V for **12**. The minor extra destabilization in **43** compared with **42** again suggests that in systems with a cyclobutadiene ring fused to the 2,3 positions of a naphthalene there is rather low double bond order between carbons 2 and 3 of the naphthalene, and thus only modest cyclobutadiene character to the system.

Finally, we can consider the dianisylcyclobutadiene derivative **19** which is oxidized to the corresponding quinone **39**. The sum of the oxidation potentials in this system is -1.2 to -1.38 V. This rather positive value also shows that the cyclobutadiene system in **39** is destabilizing, although the conjugative effect of the anisyl groups helps to stabilize it by 0.23 eV (5.3 kcal/mol). Formally the effect is simply on the energy difference between dianion **19** and quinone **39**, but there can be no doubt that the substituent effect is principally on the energy of the quinone **39**. This stabilization of the system by electron donation from the anisyl groups and electron acceptance by the quinone carbonyl groups is, however, not able to make **39** really stable, as judged either by our electrochemical studies or by the attempts at isolation or detection of free **39** described above.

It has been suggested[36] that push–pull conjugation should be particularly effective in stabilizing cyclobutadiene systems. This is related to the proposition that the cyclobutadiene system itself is conjugatively destabilized relative to any perturbed structure in which some electron density is shifted out of the ring by conjugation of appropriate substituents. Of course if push–pull stabilization is particularly effective for cyclo-

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[33] A. Pullman, *J. Amer. Chem. Soc.*, **93**, 1825 (1971).

[34] N. C. Baird and M. J. S. Dewar, *ibid.*, **91**, 352 (1969).

[35] L. J. Schaad and B. A. Hess, Jr., *ibid.*, **93**, 305 (1971); **94**, 3068 (1972).

[36] J. D. Roberts, *Chem. Soc., Spec. Publ.*, No. 12, 111 (1958); S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1336 (1959).

butadienes, then by the same token a cyclobutadiene ring between two substituents should amplify any push–pull conjugation effect they might have.

Our data contain some evidence for this amplification. Table III shows that the effect of replacing the phenyls on diphenylnaphthoquinone with *p*-anisyl groups is only a 0.08-eV change in the oxidation energy, but the replacement of two phenyl groups on **12** by the two *p*-anisyl groups in **19** has three times the effect. The conversion of **33** to **39** involves separating a conjugating *p*-anisyl group from the naphthoquinone with which it interacts by the interposition of a cyclobutadiene ring. Usually the separation of two conjugating groups, as in vinylogs or even more so in phenylogs of conjugated systems, leads to diminished effectiveness of conjugation. In our system the interposition of a cyclobutadiene ring by contrast amplifies the substituent effect of the anisyl group on the quinone oxidation potentials. This is consistent with the expectation that the cyclobutadiene system might be such an amplifier of push–pull effects. However, the phenyl and anisyl groups in all of these compounds are twisted out of plane. We must also consider the possibility that there are different amounts of nonplanarity of the substituents in the **38**, **39** cyclobutadiene series and in the corresponding simple **32**, **33** naphthoquinone derivatives.

It is thus apparent that the oxidation of systems such as **12** or **19** whose corresponding quinones have significant cyclobutadiene character requires considerably more energy than does the oxidation of various other systems which can be considered as models for the process. There seems to be no doubt that most of this extra energy is a reflection of conjugative destabilization, antiaromaticity, in the cyclobutadiene system itself. Reasonable estimates of the magnitude of this destabilization can be based on our data, and these estimates are not inconsistent with theoretical predictions.[37] However, in common with all other determinations of conjugation energy, the precise quantitative assignment of an exact value to the resonance destabilization in cyclobutadiene is complicated by the question of whether our model systems perfectly correct for any strain or inductive effects also involved in the energy.

Experimental Section

1,2-Dimethyl-3,4-phthaloylcyclobutadiene (3). This compound was prepared in 6% yield by photolysis of naphthoquinone with dimethylacetylene in benzene, a procedure subsequently described in the literature.[8] A better preparative procedure[38] involved photolysis of a deoxygenated solution of 20 g of 2-chloronaphthoquinone and 55 g of dimethylacetylene in 600 ml of acetonitrile for 6 hr with a Hanovia 450-W medium-pressure mercury lamp through a Pyrex filter. Removal of the solvent and chromatography on silica gel afforded a 25–30% yield of the 3-chloro derivative of the title compound, mp 98–99.5° (*m/e* 246). Treatment of a solution of 1.5 g of this chloro compound and 1.5 g of potassium azodicarboxylate in 100 ml of ethanol with 0.6 ml of acetic acid for 4 hr afforded, after work-up and chromatography, 0.815 g (62%) of the title compound **3**.

The Dienolate (4) and Dienol (5) of 3. A suspension of 100 mg of NaH in 15 ml of dimethoxyethane was stirred with 106 mg of the dione **3** for 12 hr under an inert atmosphere. A deep purple solution was formed, but the color was quenched on addition of saturated aqueous ammonium chloride solution. When the reaction was run with sodium hydride as above, but using a gas buret, 22.2 ml of gas (99% of 2 mol/mol of **3**) was collected in 10 hr. Work-up of the quenched solution afforded 30 mg of a very high melting solid. This is assigned the structure of a 2 + 2 dimer of the napthohydroquinone **5** on the basis of its mass spectrum, with *m/e* 424, its nmr methyl signals at δ 1.18 indicating methyls on saturated carbon, and its ultraviolet spectrum with λ_{max} 330 nm (3.61), 242 (4.43), and 220 (4.39). Ultraviolet spectroscopic studies of the quenched solution revealed an additional chromophore which disappeared with time and which we assign to the monomer **5**.

1,2-Dimethyl-3,4-phthaloylcyclobutane (22). The cyclobutene dione **3** was converted to its diketal **20** in the normal fashion on treatment with ethylene glycol and *p*-toluenesulfonic acid. Diketal **20**, mp 178–180°, showed the expected nmr and infrared spectrum. It was hydrogenated with platinum in ethyl acetate to afford the diketal **21**, mp 134–136°, with *m/e* 302 and the expected nmr spectrum. This was hydrolyzed with hydrochloric acid and tetrahydrofuran to afford the dione **22**, mp 78–80°. The dione had *m/e* 214 with isotope peaks in the expected ratios and an nmr spectrum with the methyl groups at δ 0.90. The infrared and uv spectra were also as expected.[38] On treatment of 0.4 g of **22** with 1.5 g of anhydrous sodium acetate in 60 ml of acetic anhydride at 130° for 5 hr, a 53% yield of the diacetate, mp 114–115°, of the dienol **23** was obtained. *Anal.* Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.02; O, 21.45. Found: C, 72.31; H, 6.20; O, 21.45. The other spectroscopic data[38] were also consistent with this structure. On treatment with acetic anhydride and sodium acetate under the same conditions, the unsaturated dione **3** was recovered unchanged.

1,4-Dihydroxy(3,4-dimethylcyclobuteno)naphthalene (23). A solution of 100 mg of dione **22** was stirred with 83 mg of NaH in 50 ml of tetrahydrofuran for 13 hr. On quenching with acid and the usual work-up the dihydroxynaphthalene derivative **23** was obtained, mp 163–166°, as 30 mg of a colored solid. The mass spectrum had peaks at *m/e* 214 (15%) and 213 (100%) and the ultraviolet spectrum showed maxima at 335, 247, and 211 nm. This crude hydroquinone derivative was somewhat unstable on standing, but it could be oxidized with N_2O_4 in CCl_4 to the quinone corresponding to **23**. This quinone, mp 99–100°, had *m/e* 212 with isotope peaks in the expected ratio.

1,2-Diphenyl-3,4-phthaloylcyclobutenes 7, 9, 10, and 11. The methoxy derivative **9** was prepared as described[9] by photolysis of methoxynaphthoquinone **8** with diphenylacetylene in acetonitrile. The product, mp 129–130° (lit.[9] mp 128–129°), was obtained in 74% yield. To a stirred solution of 1.34 g of **9** in 7 ml of dry CH_2Cl_2 at −78° was added 0.3 ml (condensed at −78°) of BCl_3. The red solution was allowed to warm to 0° over a period of 1.5–2 hr and the resulting green reaction mixture was washed with saturated Na_2CO_3 solution and worked up in the standard fashion. Chromatography afforded a 33% yield of the chloro derivative **10**, mp 157–157.5° (lit.[6] mp 157–158°), identical with the material which can be prepared by the reported[6] photoaddition of diphenylacetylene to chloronaphthoquinone. Treatment of the methoxy compound **9** with BBr_3 under similar conditions afforded the bromodione **11**, mp 158–158.5° on recrystallization from benzene–hexane. *Anal.* Calcd for $C_{24}H_{15}O_2Br$: C, 69.41; H, 3.64; Br, 19.24. Found: C, 69.60; H, 3.96; Br, 18.73. The spectra were as expected.[39] Direct photolysis of bromonaphthoquinone with diphenylacetylene afforded this material in less than a 1% yield.

A solution of 104 mg of the bromodione **11** in 8 ml of CCl_4 and 1 ml of absolute methanol was degassed with argon for 0.5 hr. Then, 100 mg of triphenylphosphine was added, followed by 0.25 ml of trifluoroacetic acid, and the reaction mixture was stirred for 1 hr at room temperature under an argon atmosphere. After addition of 1 g of anhydrous potassium carbonate the solution was filtered and evaporated to dryness, and the product was chromatographed on silica gel to afford 74 mg (88%) of the dione **7**, mp 179–179.5° (lit.[8] mp 179–180°), identical with material produced by direct photolysis of naphthoquinone with diphenylacetylene.

Preparation and Quenching on the Dianion 12. A solution of 67 mg (0.2 mmol) of dione **7** in 25 ml of dimethyl sulfoxide with 60 mg of potassium *tert*-butoxide was stirred for 2 hr under argon. This resulted in a green solution of the dianion **12**. Addition of excess acetic anhydride to this solution, followed by the normal work-up,

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[37] M. J. S. Dewar, M. C. Kohn, and N. Trinajstic, *J. Amer. Chem. Soc.*, **93**, 3437 (1971); B. A. Hess, Jr., and C. J. Schaad, *Tetrahedron Lett.*, 5113 (1972).

[38] For further details, see R. Grubbs, Ph.D. Thesis, Columbia University, 1969.

[39] For further details, see D. R. Murayama, Ph.D. Thesis, Columbia University, 1972.

afforded 78 mg (0.19 mmol, 95% yield) of the diacetate **14** as a chromatographically pure material, mp 237–238.5° after recrystallization from hexane–benzene. *Anal.* Calcd for $C_{28}H_{20}O_4$: C, 79.98; H, 4.80. Found: C, 79.86; H, 4.66. The ultraviolet spectrum had bands at 476 nm (3.54), 444 (3.71), 4.2 (3.74), 303 (4.91), 292 (4.86), 260 (4.67), and 212 (4.70). When the dianion solution was instead treated with methyl iodide and allowed to stand for 12 hr, chromatography yielded the C-methylation product **15** in 36% yield, mp 164–165° (lit.[8] mp 165–166° from photoaddition of dimethylnaphthoquinone to diphenylacetylene). The nmr was also consistent with that reported,[8] and the nmr of the crude methylation product revealed no other significant components. Solutions of the naphthohydroquinone **13** were prepared by treating the dianion solution with NH_4Cl. On standing **13** was converted to a mixture of dimers with mp 217–218, 239–241, and 229–231° in 78% overall yield.

Preparation of the 1,2-Dianisyl-3,4-phthaloylcyclobutenes 16, 17, and 18. A solution of 565 mg of 2-methoxynaphthoquinone (**8**) and 5.0 g of di-*p*-anisylacetylene in 150 ml of benzene was purged with N_2, then irradiated through a uranium glass filter with a Hanovia 450-W high-pressure mercury lamp for 2 hr at room temperature. Column chromatography followed by preparative layer chromatography and crystallization from benzene–hexane afforded 515 mg of the photoadduct **17**, mp 131–132°. *Anal.* Calcd for $C_{27}H_{22}O_5$: C, 76.04; H, 5.20. Found: C, 75.99; H, 5.34 The spectra were as expected.[39] Treatment of a solution of 1.18 g of this methoxydianisyldione **17** in 25 ml of pure CH_2Cl at −78° with 1 ml of BCl_3 for 1.5 hr, during which the temperature was allowed to rise from −78 to −20°, afforded a deep blue reaction mixture which was quenched with water and sodium carbonate solution. Isolation in the usual fashion afforded 879 mg (73%) of the chlorodione **18**, mp 131–131.5°, on crystallization from ether. *Anal.* Calcd for $C_{26}H_{19}O_4Cl$: C, 72.48; H, 4.44; Cl, 8.23. Found: C, 72.57; H, 4.62; Cl, 8.44. The spectra were as expected.[39] Similar treatment of the methoxydianisyldione **17** with BBr_3 afforded a crude unstable bromo derivative which was directly treated with triphenylphosphine as above to afford the unsubstituted dianisylcyclobutenedione **16**, in 50% overall yield from the methoxydione **17**. Crystallized from benzene–hexane, the dione **16** had mp 162–163°. *Anal.* Calcd for $C_{26}H_{29}O_4$: C, 78.77; H, 5.09. Found: C, 78.83; H, 5.39. The spectra were as expected.[39] A solution of 20 mg of the dianisyldione **16** in 7 ml of dry dimethylformamide and 25 mg of sublimed potassium *tert*-butoxide was stirred for 5 min at room temperature, and quenched by the addition of 0.1 ml of acetic anhydride. The solution was stirred for an additional hour, then worked up in the normal fashion to afford 8 mg (33%) of the diacetate of **19**, mp 233–235°, *m/e* 480. The other spectra were as expected.[39]

1,2-Dibenzyl-3,4-phthaloylcyclobutene (25). Irradiation of a solution of 2.00 g of 2-methoxynaphthoquinone (**8**) and 15.5 g of dibenzylacetylene in 330 ml of benzene for 2 hr through a uranium glass filter under argon gave directly the unsubstituted derivative **25**, presumably *via* the simple adduct **24**. After chromatography and recrystallization from benzene–hexane 892 mg of **25** was obtained, mp 144–145°. *Anal.* Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.61; H, 5.73. The spectra were as expected.[39]

1,2-Dibenzylidene-3,4-phthaloylcyclobutane (27). A mixture of 182 mg of the dibenzyldione **25** and 200 mg of *N*-bromosuccinimide in 30 ml of CCl_4 was irradiated with a sunlamp at 0° for 1 hr. The resulting crude material, apparently the dibromo compound **26**, exhibited singlet nmr resonances at δ 3.94 and 5.53 whose relative integrated areas were 1:1. This unstable dibromide was quickly dissolved in 30 ml of acetone, and 300 mg of $SnCl_2 \cdot 2H_2O$ and 100 mg of oxalic acid were added. The reaction mixture was stirred for 1 hr at room temperature and then refluxed for 0.5 hr. Standard work-up and chromatography afforded 83 mg (46%) of a mixture of **27** and **28** (and possibly the syn, syn isomer) as a yellow band with R_f 0.37 to 0.45 on preparative chromatography on a silica gel plate with 20% methylene chloride–benzene as eluent. Fractional crystallization from ether separated 33 mg (18%) of the *anti,anti*-dibenzylidene isomer **27** as bright yellow needles, mp 197–198°, on recrystallization from benzene–hexane; *m/e* 362.13038 ± 0.00036 (calcd for $C_{26}H_{18}O_2$, *m/e* 263.13067). The pmr spectrum of **27** had signals at δ 4.68 (d, $J < 1$ Hz, 2 H), 6.68 (d, $J < 1$ Hz, 2 H), and 7.16–7.9 (m, 14 H). The ultraviolet spectrum had λ_{max} 227 nm (4.63), 246 sh (4.47), 260 sh (4.37), 3.32 sh (4.51), 3.51 (4.56), and 3.71 sh (4.54). In the mother liquors from the fractional crystallization signals could be observed in the nmr at δ 4.28 (dd, J = 2.5 and 8 Hz), 4.63 (dd, J = 2.5 and 8 Hz), 6.67 (d, J = 2.5 Hz), and 6.31 (d, J = 2.5 Hz) in relative intensity of 1:1:1:1, assigned to the anti,syn isomer **28**. Some probable traces of the syn,syn isomer were evidenced by the observation of singlet resonances at δ 4.37 and 6.64 with relative intensity of 1:1.

2,3-Di-*p*-anisyl-1,4-naphthoquinone (33). A solution of 5.05 g of 2-anisylindan-1,3-dione[40] (**35**) in 60 ml of CH_2Cl_2 was stirred for 0.5 hr with 20 ml of 1 *N* sodium hydroxide solution in 35 ml of water, and a solution of 6.9 g of potassium ferricyanide in 20 ml of water was added over a period of 20 min at room temperature with vigorous mechanical stirring. After an additional 10 min of stirring, the layers were separated and the aqueous portion was extracted with 30 ml of CH_2Cl_2. The combined organic layers were treated in the usual fashion and concentrated to afford 4.92 g (98% yield) of the dimer **37**, mp 253–245°, on recrystallization from chloroform–ethyl acetate. *Anal.* Calcd for $C_{32}H_{22}O_6$: C, 76.48; H, 4.42. Found: C, 76.27; H, 4.52. The spectra were as expected.[39] A solution of 1.00 g of this dimer **37** and 0.50 g of potassium *tert*-butoxide in 40 ml of dimethyl sulfoxide was heated at 110–115° for 2 hr. The precipitated potassium phthalate was collected and the filtrate was then treated in the usual fashion affording 183 mg of 2,3-di-*p*-anisylnaphthoquinone (**33**), mp 169.5–170°, after rough chromatography, crystallization from ethanol, and sublimation at 150° (0.1 mm). *Anal.* Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.88; H, 4.92. The spectra were as expected.[39]

Generation of the Cyclobutadienes 38 and 39 by Basic Elimination of HCl from the Chlorodiones 10 and 17. A suspension of 80 mg of washed NaH in 80 ml of tetrahydrofuran containing 101 mg of diphenylisobenzofuran was deoxygenated. Then 139 mg of the diphenylchlorodione **10** was added and the mixture was stirred for 18 hr under an inert atmosphere. The usual work-up afforded 108 mg (50% yield) of a 1:1 adduct **40**, mp 289–291°. The mass spectrum had a parent at *m/e* 604 and the infrared spectrum had the carbonyl absorption at 1685 cm^{-1}. The ultraviolet spectrum had λ_{max} 233 nm (4.18) and 300 (3.59).[41]

Similar treatment of the chlorodianisyldione **17** afforded the corresponding adduct **41**, mp 237–237.5°. *Anal.* Calcd for $C_{46}H_{32}O_5$: C, 83.11; H, 4.85. Found: C, 82.89; H, 5.01. The infrared spectrum had the carbonyl band at 1687 cm^{-1} while the ultraviolet spectrum (ethanol) had λ_{max} 232 nm (4.77), 250 sh (4.52), 298 (4.26), 3.36 sh (4.02), and 400 sh (3.38).[41] The same adduct was formed in 28% yield when sublimed potassium *tert*-butoxide was used as base.

Adduct **41** could not be detected in reactions in which the diphenylisobenzofuran was added subsequent to the base reaction. In the most careful experiment, a Schlenk apparatus with two parallel tubes connected by a glass frit was used.[39] One arm was charged with 3 mg of diphenylisobenzofuran while the other arm was charged with 4 mg of NaH and 3 mg of the chlorodianisyldione **17**. The apparatus was flushed with argon and immersed in a bath held at −60 to −65°. Using a gas-tight syringe, 5 ml of pure dry dimethoxyethane was added to the tube containing the chlorodione, and the yellow reaction mixture was submitted to magnetic stirring. After approximately 20 min, the mixture had developed a deep turquoise color. One-half of the solution was then filtered into the second tube which contained the diphenylisobenzofuran and the apparatus was then allowed to warm slowly to room temperature. Chromatography of the two separate solutions, after normal work-up, revealed no trace of adduct **41** and no detectable difference in the complex mixture of products from either half of the reaction apparatus except for the presence of unchanged diphenylisobenzofuran in the second solution. In a control, using the same procedure except that the diphenylisobenzofuran solid was placed with the other solids in the same arm of the apparatus before cooling and addition of solvent, the expected adduct **41** was obtained.

Electrochemistry. The initial polarography was done using a standard apparatus. Cyclic voltammetry was performed using a Princeton Applied Research Corporation Model 173/176 potentiostat driven by a Hewlett-Packard low frequency function generator (Model 202A) with the results displayed on a Tekronix Model 5103/D11 single-beam storage oscilloscope. The electrochemical cell was adapted from a 50-ml round-bottomed flask

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(40) S. L. Shapiro, K. Geiger, Y. Youlus, and L. Freedman, *J. Org. Chem.*, **26**, 3580 (1961).

(41) The spectra indicate addition to the quinone, rather than stilbene, double bond.

and contained a Ag|AgCl reference electrode separated from the solution by an asbestos fiber junction placed as close as possible to the working electrode, a working electrode consisting of a smooth platinum disk (Beckman No. 39273), and a platinum wire auxiliary electrode separated from the solution by a medium porosity sintered glass frit which was placed just opposite the reference electrode. In addition, the cell was flushed through a port with inert gas. The reference electrodes were calibrated by periodic checks against the known reduction potentials of naphthoquinone, and appropriate corrections for iR drop were also made. The cell itself was immersed in a temperature-controlled bath. Additional details of the apparatus and techniques used are reported elsewhere.[39]

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A Study of Substituent Effects on Nuclear Magnetic Resonance Spectral Parameters of N-Substituted Methylamines[1]

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Abstract: A method is presented that allows primary and secondary amines to be dried sufficiently for the observation of H–N–C–H pmr spin–spin coupling. By means of this method the values of J_{HNCH} were examined for a series of N-substituted methylamines and were found to be quite dependent on the N substituent. A correlation is presented between the value of J_{HNCH} and the chemical shift of the *N*-methyl group extrapolated to infinite dilution in carbon tetrachloride. Large solvent shifts are shown to occur for the *N*-methyl group in aromatic methylamines but not for aliphatic systems. One possible explanation for this is presented.

Small traces of water or acid catalyze hydrogen exchange in relatively basic primary and secondary amines such that H–N–C–H spin–spin coupling is normally not observed. This hydrogen exchange is thought to occur through the following equilibrium[2]

$$\mathrm{R_2NH + H_2O \rightleftharpoons R_2NH_2^+ + OH^-}$$

In recent years several reports of H–N–C–H coupling have appeared, but in almost all cases the conditions were such that slow hydrogen exchange would be expected either because of substituents present on the nitrogen which reduce its basicity or because the nitrogen site is blocked by coordination to a Lewis acid. Indeed, Rae has reported that the ability to observe coupling in ring-substituted *N*-methylanilines is dependent on the base strength of the amine,[3] with coupling being easily observed for weakly basic systems. Coupling was also reported for methylaminobis(trifluoromethyl)phosphine.[4]

The possibility of cross nitrogen–proton coupling was alluded to by Meek and Springer in the case of complexes in which the fourth coordination site of the nitrogen atom was occupied by a boron derivative.[5] Similar phenomena have been observed for boron complexes of other strong bases, *e.g.*, $\mathrm{BF_3 \cdot NH_2CH_3}$, $\mathrm{BF_3 \cdot NH(CH_3)_2}$,[6] and $\mathrm{B(CH_3)_3 \cdot NH_2NHCH_3}$.[7] It is of interest to note here that in the last case, a solution of the uncomplexed methylhydrazine exhibited no pmr coupling even though the substance was dried over anhydrous barium hydroxide and carefully distilled under vacuum.

Most attempts to observe H–N–C–H coupling in strongly basic amines have been futile with typical examples being the study of neat monomethylamine in the condensed phase[8] and work with substituted hydrazines in solution.[9]

Bichlmeir and West observed coupling in the spectra of *N*,*N*-bis(trimethylsilyl)methylhydrazine and *N*,*N*-bis(ethyldimethylsilyl)methylhydrazine[10] because, they postulated, the method used in the preparation of compounds rigorously excluded all traces of moisture.

Because of the limited number of systems studied, little work has been done on the correlation of the magnitude of J_{HNCH} with the nature of nitrogen substituents. Rae has studied the magnitude of J_{HNCH} as a function of substitution in a series of N-substituted benzylamines[11] and he found that the magnitude of J decreased with an increase in the electronegativity of the N-substituent, but only a small range of electronegativities was examined. Because of the previously mentioned limitation on base strengths, only strongly electron withdrawing groups could be used as substituents.

One of us recently reported[12] a method of drying samples sufficiently to allow for the observation of H–N–C–H coupling in strongly basic systems. This method involved the exhaustive drying of the amine samples by refluxing the commercially available amines over sodium–potassium alloy (NaK) for several days in a vessel attached to a high vacuum system. (Caution, hydrogen gas is produced in this process and care

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(1) Presented in part at the American Chemical Society 5th Central Regional Meeting, Cleveland, Ohio, 1973.

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