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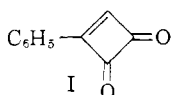
## Small-Ring Compounds. XXV. Phenylcyclobutadienoquinone and Related Compounds<sup>1</sup>

BY EDGAR J. SMUTNY, MARJORIE C. CASERIO AND JOHN D. ROBERTS

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Thermal addition of phenylacetylene to trifluorochloroethylene and tetrafluoroethylene followed by hydrolysis of either product with concentrated sulfuric acid has led to the formation of phenylcyclobutene-1,2-dione (phenylcyclobutadienoquinone). This compound proved to be quite stable and displayed some unusual properties. A number of its substitution products have been prepared and their properties are described. Of these, 4-hydroxy-3-phenylcyclobutene-1,2-dione was of special interest in being a remarkably strong acid with  $pK_a$  of 0.37. The stability of phenylcyclobutadienoquinone and the acid strength of the 4-hydroxy derivative are discussed and correlated with delocalization energies calculated by the LCAO method.

We recently reported the preparation of a compound which may be regarded as the quinone of phenylcyclobutadiene and which is herein accordingly referred to as "phenylcyclobutadienoquinone" (I).<sup>2</sup> In contrast to the apparent instability of



cyclobutadienes,<sup>3,4</sup> which bear a formal resemblance to I by virtue of the expected  $sp^2$ -hybrid character of the four-ring carbon atoms, phenylcyclobutadienoquinone is a remarkably stable compound. Therefore, it was with considerable interest that we undertook a comprehensive investigation of the chemistry of I, which is now described in more detail than previously.<sup>2</sup>

Other closely related quinones of comparable stability are now known. Thus Cava and Napier<sup>5</sup> have prepared benzocyclobutadienoquinone, and, very recently, Blomquist and LaLancette<sup>6</sup> reported the synthesis of diphenylcyclobutadienoquinone.

**Synthesis.**—The cycloadducts of perhaloethylenes with phenylacetylene were the starting materials for the preparation of phenylcyclobutadienoquinone and related compounds. These adducts are easily obtained by simple thermal reactions.<sup>7</sup> Thus, from trifluorochloroethylene and phenylacetylene in a sealed tube held at 125° for 20 hours, there was obtained 1,1,2-trifluoro-2-chloro-3-phenylcyclobutene (II) in yields up to 79%. Tetrafluoroethylene adds similarly to phenylacetylene giving 1,1,2,2-tetrafluoro-3-phenylcyclobutene (III). The structures of these adducts were separately established from their subsequent reactions, which will be described.

(1) (a) Supported in part by the National Science Foundation; (b) presented in part at the XIV National Organic Chemistry Symposium of the American Chemical Society, Lafayette, Ind., June, 1955.

(2) E. J. Smutny and J. D. Roberts, *THIS JOURNAL*, **77**, 3420 (1955).

(3) See chapter by W. Baker and J. F. W. McOmie, in *Chemical Society Symposia*, Bristol, 1958, Special Publication No. 12, London, The Chemical Society, p. 49.

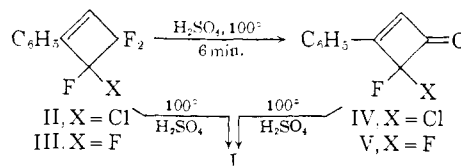
(4) It has been reported very recently that cyclobutadiene may be isolated as a complex with silver nitrate [M. Avram, E. Marica and C. D. Nenitzescu, *Ber.*, **92**, 1088 (1959)].

(5) M. P. Cava and D. R. Napier, *THIS JOURNAL*, **79**, 3606 (1957).

(6) A. T. Blomquist and E. A. LaLancette, Abstracts A.C.S., Division of Organic Chemistry, April, 1959, p. 54-O.

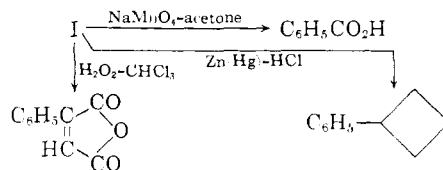
(7) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *THIS JOURNAL*, **75**, 4765 (1953).

The *gem*-difluoro group of II was readily hydrolyzed with concentrated sulfuric acid at 100°. The product (IV) was a white crystalline solid which contained chlorine, possessed a strong infrared absorption at 5.6  $\mu$  characteristic of cyclobutenones<sup>7</sup> and gave normal carbonyl reactions. The proton and fluorine magnetic resonance spectra further established the structure of IV as 2-fluoro-2-chloro-3-phenylcyclobutenone. Under more vigorous conditions, namely heating II



or IV with concentrated sulfuric acid for about 20 minutes at 100°, phenylcyclobutadienoquinone (I) was formed. Similarly, hydrolysis of the tetrafluorocyclobutene (III) gave initially 2,2-difluoro-3-phenylcyclobutenone (V), which on further heating with sulfuric acid furnished I.

The structure of I was rigorously established in the following manner. Microanalysis and molecular weight measurements suggested the formula  $C_{10}H_6O_2$ . Oxidation with sodium permanganate in acetone gave benzoic acid, and oxidation with 30% hydrogen peroxide gave phenylmaleic anhydride. The latter type of oxidative cleavage is a diagnostic test for  $\alpha$ -diketones. The presence of the four-membered ring was demonstrated by the reduction of I with amalgamated zinc and hydrochloric acid to phenylcyclobutane. The phenylcyclobutadienoquinone structure for I satisfactorily accounts for all the experimental data, and the proton magnetic resonance spectrum of I is entirely in accord with this assignment. A study of the crystal structure of I by X-ray diffraction has further confirmed the molecular structure and has demonstrated that the molecule is planar.<sup>8</sup>



(8) C. Wong, Ph.D. Thesis, California Institute of Technology Pasadena.

**Physical and Chemical Properties.**—The quinone separates from acetone as brilliant yellow crystals which melt with decomposition at 152–153° forming carbon monoxide and polymeric material. The crystalline solid possesses an appreciable vapor pressure and can be purified easily by slow sublimation at reduced pressure. The infrared spectrum of I has a *single* strong absorption maximum at 5.58  $\mu$ , which is ascribed to the carbonyl stretching vibration; there are also intense bands at 6.21, 6.42, 6.72 and 6.87  $\mu$ , which may be associated with the double bond and the phenyl ring. The primary absorption of I in the ultraviolet is at 287  $m\mu$  in ethanol which is resolved into a major peak at 281  $m\mu$  and a shoulder at 295  $m\mu$  in isoöctane (*cf.* Fig. 1). In the visible region, I possesses no absorption band but rather has a long absorption tail extending from the ultraviolet into the visible, which accounts for its distinct yellow color.

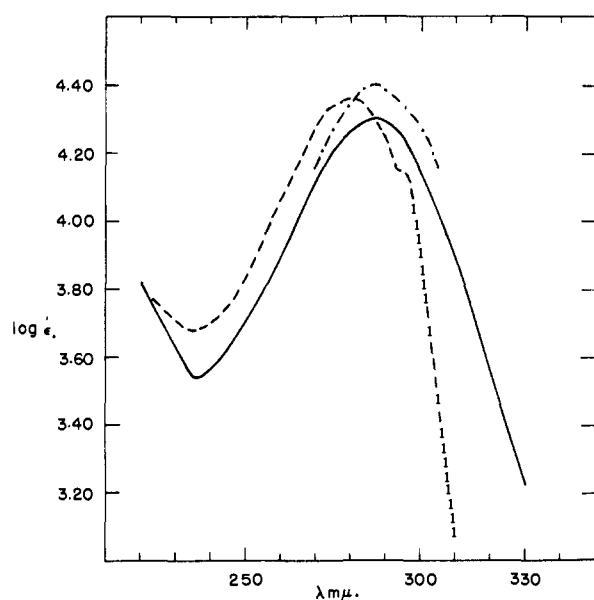
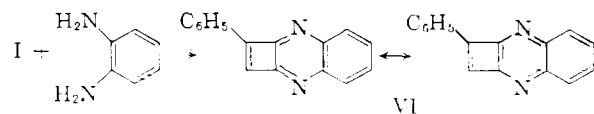
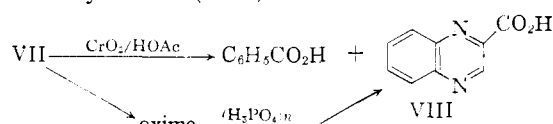


Fig. 1.—Ultraviolet spectrum of phenylcyclobutadienoquinone: solid line, in ethanol; dashed line, in isoöctane; dashed and dotted line, in chloroform.

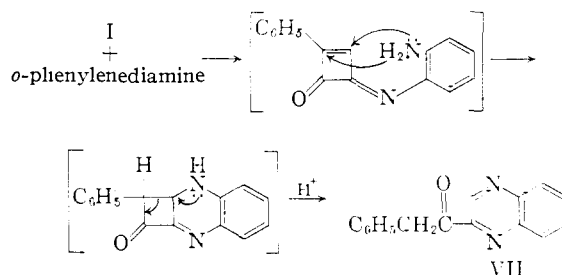
As an  $\alpha$ -diketone, Compound I would be expected to condense with *o*-phenylenediamine and, if the condensation were to follow a normal course, the product would be the quinoxaline VI having a fused cyclobutadiene ring system. A condensation indeed took place and therefore it was of some consequence to establish the structure of the product. It was no surprise that the product was not



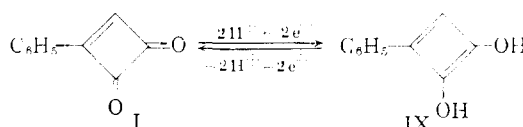
VI but a monoketone VII which gave quinoxaline-2-carboxylic acid (VIII) on oxidation with chromic



acid. The same acid VIII was obtained from a Beckmann rearrangement of the oxime from VII. An independent synthesis of VIII<sup>9</sup> from tribromo-methylquinoxaline confirmed the assigned structure. The condensation product is 2-phenylacetylquinoxaline (VII), therefore, which possibly may form according to the scheme



The reluctance of I to form a cyclobutadiene derivative is further evident in its resistance to catalytic hydrogenation. Thus, the quinone could not be reduced to the hydroquinone IX with catalysts such as platinum oxide, 5% palladium-on-charcoal, Raney nickel or ruthenium metal. Apparently, the quinone or some reduction product poisoned the catalyst since introduction of a reducible species, such as cinnamic acid, produced



no further uptake of hydrogen. Further, quinhydrone formation, which is generally characteristic of quinones, was not observed when Compound I was refluxed with catechol in toluene. A preliminary polarographic study suggests that the quinone is not reversibly reduced and that its reduction is *pH* dependent.

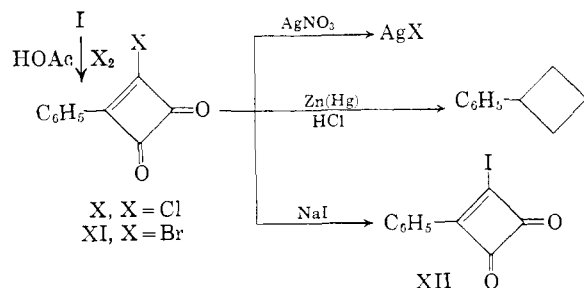
The quinone is sensitive to base, and it has been shown in a recent study<sup>10</sup> that the ring is cleaved by the action of hot methanolic sodium hydroxide to give benzaldehyde and benzylidenepyruvic acid.

Perhaps the most remarkable chemical feature of phenylcyclobutadienoquinone is the ease with which it undergoes substitution at the 4-position. Thus, elementary chlorine and bromine attacked the quinone in acetic acid to give 4-chloro- and 4-bromo-3-phenylcyclobutene-1,2-dione, X and XI, respectively. The nature of the solvent appears to be an important factor in this reaction since, in carbon tetrachloride, no reaction took place. While a substitution mechanism of addition-elimination cannot be ruled out, attempts to isolate an addition product were unsuccessful and it seems reasonable that substitution occurs by direct electrophilic attack of halogen.

The halogen-substituted quinones X and XI displayed unusual properties in that the halogens proved to be exceptionally labile for vinyl-type halides. In fact, their reactivity suggests they

(9) B. R. Brown, *J. Chem. Soc.*, 2577 (1949).

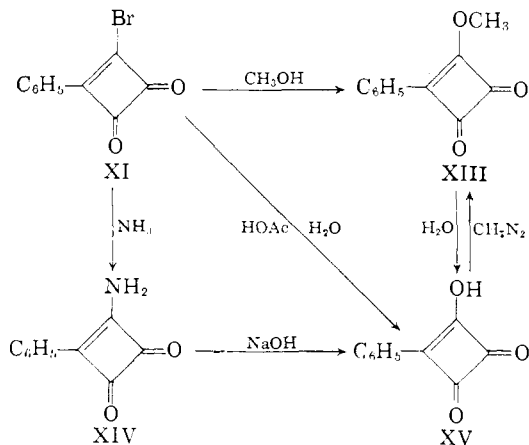
(10) L. Skattebøl and J. D. Roberts, *THIS JOURNAL*, **80**, 4085 (1958).



should be regarded as vinylogs of acid halides—a point which will be demonstrated more vividly in succeeding discussion. Thus, Clemmensen reduction of X and XI gave phenylcyclobutane; alcoholic silver nitrate produced an immediate precipitate of silver halide, and nucleophilic displacement occurred with sodium iodide in acetone to give 4-iodo-3-phenylcyclobutene-1,2-dione (XII).

The view that 4-substituted phenylcyclobutadienoquinones are to be regarded as vinylogs of carboxylic acids is supported by numerous reactions which parallel those of the carboxyl function. Thus, the methyl "ester" (XIII) was prepared from the 4-bromoquinone (XI) by gently heating the latter with absolute methanol; passage of dry ammonia gas into a benzene solution of XI precipitated the "amide" XIV as a colorless high melting solid. The parent "acid" itself, 4-hydroxy-3-phenylcyclobutene-1,2-dione (XV), was prepared by the hydrolysis of the "acid bromide" XI, the "methyl ester" XIII and the "amide" XIV under appropriate conditions, and proved to be a colorless high melting solid. Like carboxylic acids, the 4-hydroxyquinone XV was readily methylated with diazomethane to the ester XIII, and, like most enols, XV gave an intense magenta coloration with ferric chloride. The ultraviolet spectrum of XV and its enolate anion is shown in Fig. 2, and Table I records the principal absorption maxima for the derivatives of XV.

As reported previously,<sup>10</sup> the four-membered ring of XV, like that of phenylcyclobutadienoquinone, is cleaved by the action of alkali. In boiling 10% aqueous sodium hydroxide, XV decomposes to phenylpyruvic acid and 1,3-diphenylpropene.



The acid strength of 4-hydroxy-3-phenylcyclobutene-1,2-dione (XV) is so considerable that it

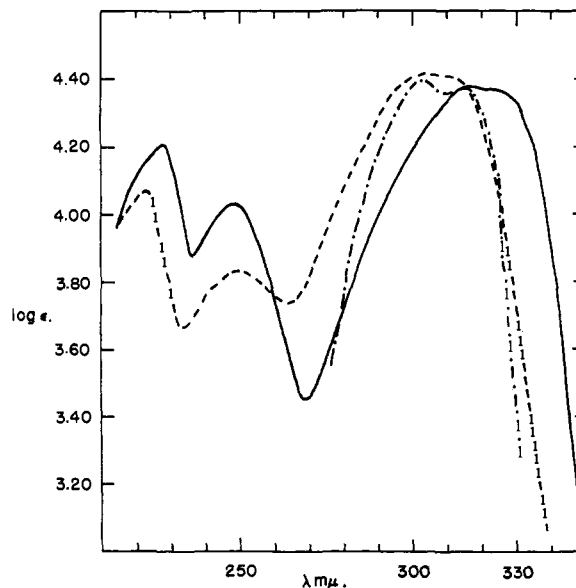


Fig. 2.—Ultraviolet spectrum of 4-hydroxy-3-phenylcyclobutadienoquinone: solid line, in water; dashed line, in 10 *N* sulfuric acid; dashed and dotted line, in chloroform.

merits particular attention. The  $pK_a$  value was determined as  $0.37 \pm 0.04$ , and XV must therefore be present almost entirely in the form of the enolate anion in aqueous solution. In order to appreciate the exceptional acid strength of this enol, it is

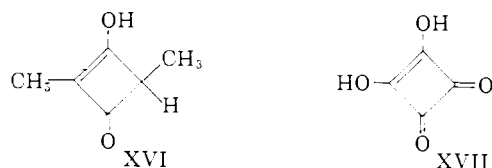
TABLE I  
ULTRAVIOLET SPECTRA OF SUBSTITUTED  
PHENYLCYCLOBUTADIENOQUINONES<sup>a</sup>

X	Solvent	$\lambda_{max}$ , mμ	$\epsilon$
H	Ethanol	287	20,000
	Isooctane	281	23,000
Cl	Chloroform	295	14,200
		299	26,200
	Isooctane	306	20,800
Br	Chloroform	304	23,900
	Isooctane	296	26,300
I	Chloroform	309	20,400
		315	17,900
	Isooctane	308	14,500
OCH <sub>3</sub>	Chloroform	320	11,800
		302	28,100
	Ethanol	316	26,200
		314	22,500
		301	19,200
NH <sub>2</sub>	Ethanol	328	26,000
		315	25,800

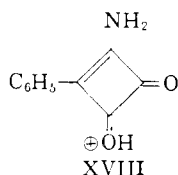
<sup>a</sup> Cary recording spectrophotometer, model 11M, with 1-cm. quartz cells.

instructive to compare its  $pK_a$  value with the  $pK_a$ 's of enols of related structure as shown in Table II. Dihydroresorcinol, 2-hydroxy-1,4-naphthoquinone

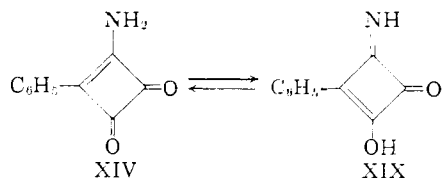
and 2-hydroxy-3-phenyl-1,4-naphthoquinone are in themselves of comparable acid strength and are vinylogous with typical carboxylic acids; yet they are far weaker acids than 4-hydroxy-3-phenylcyclobutene-1,2-dione (XV). The high acid strength of XV seems to be related to the enolizable  $\beta$ -diketone system being incorporated within a four-membered ring. Significantly, dimethylcyclobutenolone (XVI) is also a strong acid<sup>11</sup> and is also a cyclic  $\beta$ -ketoenol of four carbon atoms. Nevertheless, XV is still stronger than XVI by a factor of two hundred and fifty. The compound diketocyclobutenediol (XVII) is also closely related to XV, and its synthesis has been reported very recently.<sup>12</sup> This interesting compound is a strong acid which has a  $pK_2$  of 2.2 ( $pK_1 \sim 1$ ). A rational explanation of these facts is required, but it is convenient to further this discussion in a later section.



In keeping with the high acidity of XV, 4-amino-3-phenylcyclobutene-1,2-dione (XIV) is a very weak base. It was found to be insoluble in concentrated hydrochloric acid, although solution was effected with concentrated sulfuric acid. No benzoyl derivative could be prepared. An attempt to measure the base strength of XIV in concentrated sulfuric acid was unsuccessful since species other than the free amine and its conjugate acid absorbing in the ultraviolet were present. One such species could be XVIII in which the proton resides on oxygen. That the amine may largely be the tauto-



mer XIX is unlikely since it gave no ferric chloride test.



**The Heat of Combustion and Resonance Energy of Phenylcyclobutadienoquinone.**—The experimentally determined heat of combustion,  $\Delta H^\circ_c$  of phenylcyclobutadienoquinone is  $-1125.35 \pm 0.17$  kcal./mole.<sup>13</sup> The heat of sublimation,  $\Delta H^\circ_{(s)}$ , is

(11) R. B. Woodward and G. Small, Jr., *THIS JOURNAL*, **72**, 1297 (1950).

(12) S. Cohen, J. R. Lacher and J. D. Park, *ibid.*, **81**, 3840 (1959).

(13) We are indebted to Dr. Robert E. Krall for these measurements. Combustion experiments were conducted at the Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla. Concordant

TABLE II  
 $pK_A$  VALUES OF SOME ORGANIC ACIDS AND CYCLIC  $\beta$ -KETOENOLS

Compound	$pK_a$
4-Hydroxy-3-phenylcyclobutene-1,2-dione (XV)	$0.37 \pm 0.04$
Picric acid	$0.8^a$
Dimethylcyclobutenolone (XVI)	$2.8^b$
2-Hydroxy-1,4-naphthoquinone	$4.0^c$
2-Hydroxy-3-phenyl-1,4-naphthoquinone	$4.35^c$
Benzoic acid	$4.2^d$
Dihydroresorcinol	$5.25^e$
Tropolone	$7.00^f$
Cyclohexane-1,2-dione	$10.3^g$

<sup>a</sup> L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 583. <sup>b</sup> See ref. 11. <sup>c</sup> M. G. Ettlinger, *THIS JOURNAL*, **72**, 3085 (1950). <sup>d</sup> F. G. Brockman and M. Kilpatrick, *ibid.*, **56**, 1483 (1934). <sup>e</sup> G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1162 (1940). <sup>f</sup> J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, *J. Chem. Soc.*, 503 (1951). <sup>g</sup> G. Schwarzenbach and CH. Wittwer, *Helv. Chim. Acta*, **30**, 663 (1947).

$13.00 \pm 0.10$  kcal./mole.<sup>13</sup> Thus, the heat of combustion of the quinone in the vapor state is  $-1138.35 \pm 0.27$  kcal./mole. Using Klages' table of bond energies,<sup>14</sup> a value of  $\Delta H^\circ_c$  for the reference structure was calculated as  $-1160$  kcal./mole which, if corrected for 36 kcal./mole of stabilization due to the phenyl ring, reduces to  $-1124$  kcal./mole. Thus, the cyclobutadienoquinone ring is less stable than the reference structure by  $-14$  kcal./mole. This figure includes the extent to which the four-membered ring is stabilized by resonance and destabilized by ring strain. It implies that the strain energy exceeds the resonance energy by 14 kcal./mole. Unfortunately, there is considerable uncertainty in the value of the strain energy. Calculations made by Weltner,<sup>15a</sup> Coulson and Moffitt<sup>15b</sup> and Dauben<sup>15c</sup> for cyclobutadiene place the strain energy over a wide range, 45–74 kcal./mole. If the strain energy is about the same in the quinone, then the resonance energy of the cyclobutadienoquinone ring would lie between 31 and 60 kcal./mole. Thus, the resonance stabilization of phenylcyclobutadienoquinone (I) is probably appreciable even though the absolute value in kcal./mole is quite uncertain.<sup>16</sup> Accordingly, Compound I may be described as a resonance hybrid of these structures.

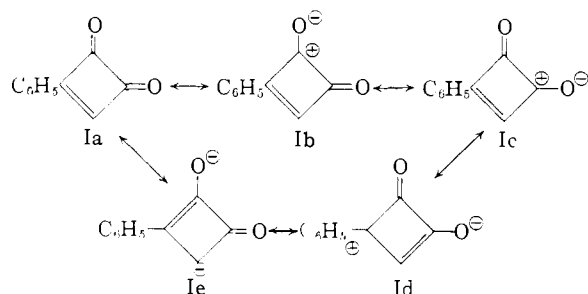
A rational explanation of the stability of I is suggested by the results of some simple molecular orbital calculations<sup>17</sup> made for certain open-chain combustion data were obtained earlier by Professor R. M. Badger and his students at the California Institute of Technology, Pasadena.

(14) F. Klages, *Chem. Ber.*, **82**, 358 (1949); see also, G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 88.

(15) (a) W. Weltner, Jr., *THIS JOURNAL*, **75**, 4224 (1953); (b) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949); (c) private communication from Professor H. J. Dauben.

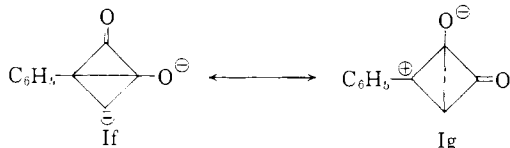
(16) Dr. R. E. Krall (private communication) has concluded that total angular and torsional strain in I is much smaller than would be expected from earlier estimates<sup>15</sup> and, in fact, might be only 18 kcal. If this were true, the resonance energy of I would be essentially negligible. The arguments pertinent to the low value of the strain energy will be discussed in a later paper.

(17) For a description of the LCAO method employed, see C. A. Coulson, "Valence," Oxford Press, New York, N. Y., 1952. All coulomb integrals for carbon were assumed equal to  $\alpha$ ; the coulomb



and cyclic diketones and their isoconjugate hydrocarbons. Calculated delocalization energies (D. E.)<sup>17</sup> are listed in Table III, and it will be noticed that the open-chain and six-ring ketones are predicted to be *less* stable than the corresponding hydrocarbons—and the 3- and 4-membered ring ketones to be *more* stable. These theoretical results may be correlated with Hückel's  $(2 + 4n)$   $\pi$ -electron rule; the ketonic functions of the six-membered ring of six  $\pi$ -electrons will tend to reduce the number of electrons operating over these centers to below six, and will thus destabilize the system; the same type of electron withdrawal in a four-membered ring of four  $\pi$ -electrons can only stabilize the system since the effective number of electrons is reduced from four toward the much more favorable configuration of two. Hybrid structures Ib–Ie clearly show this.

Two additional structures, If and Ig, may well contribute to the ground state of the molecule. Here, additional stabilization is attained by elec-



tronic cross-ring interaction between the orbitals of the 1,3- and 2,4-positions. The type of non-bonded interaction visualized is similar to that described by Simonetta and Winstein<sup>18</sup> for the homoallylic cation where the  $\pi$ -electrons of the double bond are delocalized by interaction with an otherwise vacant orbital which is two carbon atoms removed. Molecular orbital calculations do predict a substantial stabilization of the cyclobutadienoquinone ring due to cross-ring interaction.<sup>19</sup> The



integral for oxygen was taken as  $\alpha + 2\beta$ . The resonance integrals for each C—C bond and for each C—O bond were set equal to  $\beta$  and  $\sqrt{2}\beta$ , respectively [R. D. Brown, *Quart. Revs.*, **6**, 63 (1952)]. Delocalization energies were computed by subtracting  $2(\alpha + \beta)$  for each pair of electrons in a localized double bond and  $2(\alpha + 2.73\beta)$  for each pair of electrons in a localized carbonyl bond from twice the sum of the energies of the lowest occupied molecular orbitals as found from the secular equation.

(18) M. Simonetta and S. Winstein, *THIS JOURNAL*, **76**, 18 (1954).

(19) In estimating the overlap and resonance integral for non-bonded cross-ring interaction, it was necessary to calculate the diagonal interatomic distance; for this, the four-membered ring was assumed to be planar with bond angles of  $90^\circ$  and single and double bond distances of 1.54 and 1.34 Å., respectively. The overlap integral ( $S_{1,2}$ ) was then evaluated from Kopineck's tables [H. J. Kopineck, *Z. Naturforschung*, **5A**, 420 (1950)] and a resonance integral ( $\beta_{1,2}$ ) of 0.43 $\beta$  was subsequently obtained with the aid of Mulliken's approxima-

delocalization energy is increased from 1.24 $\beta$  (22–25 kcal./mole) to 1.99 $\beta$  (36–40 kcal./mole) by inclusion of non-bonded energy terms (cf. Table III). These figures may be compared with the resonance energy of 31–60 kcal./mole estimated from heat of combustion data for I after appropriate corrections for phenyl resonance and strain energy. However, there is too much uncertainty in the quoted figures to permit any conclusions as to the importance of cross-ring interaction. In a related system, 1,3-dimethylenecyclobutane, no experimental evidence was found for 1,3-electronic interaction which theory predicts.<sup>20</sup>

TABLE III

CALCULATED DELOCALIZATION ENERGIES FOR SOME DIKETONES AND THEIR ISOCONJUGATE HYDROCARBONS

Compound	D.E. <sup>a</sup>	
	Y = CH <sub>2</sub>	Y = O
Y=CHCH=Y	0.47 $\beta$	0.20 $\beta$
Y=CHCH=CHCH=Y	0.99 $\beta$	0.89 $\beta$
	1.95 $\beta$	1.58 $\beta$
	1.21 $\beta^b$	1.24 $\beta^c$
	1.42 $\beta^c$	1.99 $\beta^c$
	0.96 $\beta^b$	1.36 $\beta$

<sup>a</sup> See ref. 17 and 19 for method of calculation. <sup>b</sup> Calculations made by J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *THIS JOURNAL*, **74**, 4579 (1952). <sup>c</sup> Electronic cross-ring interaction included in the calculated D. E. value.

**Dipole Moment Data.**—The dipole moment of phenylcyclobutadienoquinone could not be measured directly owing to its limited solubility in benzene. However, the moments of cyclohex-1-enylcyclobutadienoquinone and some related compounds<sup>21</sup> are given in Table IV.<sup>22</sup> Since there is a difference of 0.3 D. between the corresponding cyclohexenyl and phenyl derivatives, it is inferred that the dipole moment of phenylcyclobutadienoquinone is about 5.3 D. The resultant moment due to the chlorine dipoles in the dichloroketones XX and XXI may be roughly calculated if one assumes coplanarity of the six- and four-membered rings, a tetrahedral bond angle between substituents at the 4-position of a square four-membered ring, and a contribution of 1.5 and 2.0 D. from the C—Cl dipoles at the 2- and 4-positions, respectively. From the data obtained, the contribution made by the phenylcyclobutenone ring system in XX and XXI, and hence in phenylcyclobutadienoquinone itself, was estimated as 4.6 D. Since the resultant dipole moment of I is about 5.3 D., the cross-

tion (see ref. 18). However, in order to simplify solution of the secular equation, a value of 0.5 $\beta$  was adopted.

(20) F. F. Caserio, Jr., S. H. Parker, R. Piccolini and J. D. Roberts, *THIS JOURNAL*, **80**, 5507 (1958).

(21) C. M. Sharts and J. D. Roberts, *ibid.*, in press.

(22) Dipole moments were kindly measured by Professor R. M. Badger and his students. The interpretation of the results is essentially that given by C. M. Sharts, Ph.D. Thesis, California Institute of Technology, 1958.

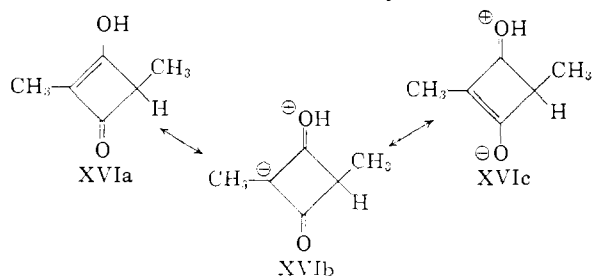
conjugated carbonyl must therefore contribute a vector moment of approximately 2.7 D., which is just about equal to the dipole moment of an isolated carbonyl group.<sup>23</sup> Hence, not much can be said about the relative contributions made by structures Ib, Ie, If and Ig, including additional structures which extend resonance to the phenyl ring. In connection with extended conjugation between the two rings, it has been shown by an X-ray diffraction study<sup>8</sup> that the bond bridging the two rings is shorter than a single bond by 0.08 Å.; this information cannot be considered as reliable evidence for extended conjugation since as Dewar and Schmeising<sup>24</sup> have emphasized most clearly, the contraction may be due to the change in covalent radius of carbon with the change in hybridization from  $sp^3-sp^3$  to  $sp^2-sp^2$ .

TABLE IV  
DIPOLE MOMENTS OF SOME PHENYL AND CYCLOHEXYNYL-SUBSTITUTED CYCLOBUTENONES AND CYCLOBUTADIENOQUINONES IN BENZENE<sup>22</sup>

Compound	$\mu$ , D.	Compound	$\mu$ , D.
	5.46		5.62
	5.46		5.16
	—		5.17
	—		4.75
			5.3 <sup>d</sup>

<sup>a</sup> Estimated, see text.

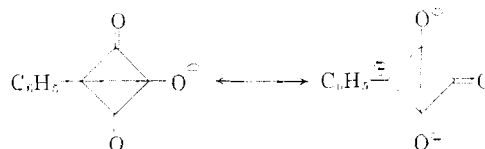
**The Acid Strength of 4-Hydroxy-3-phenylcyclobutadienoquinone.**—An explanation is required of the enhanced acid strength of a  $\beta$ -ketoenol system when incorporated within a four-membered ring, as exemplified by dimethylcyclobutenolone (XVI) and 4-hydroxy-3-phenylcyclobutadienoquinone (XV). The acidity of the 4-hydroxyquinone would, of course, be expected to be greater than XVI because of the potent electron-withdrawing influence of the second carbonyl group. Woodward and Small<sup>11</sup> have suggested that the abnormally high acidity of XVI may result from greater contributions by the ionic structures XVIb and XVIc to the ground state than ordinarily obtains in like systems. Presum-



(23) W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. II, Elsevier Publishing Co., New York, N. Y., 1958, p. 100.

(24) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

ably, a structure such as XVIb would be relatively favored because of a net release of ring strain inherent in the cyclobutene structure XVIa. The same type of stabilizing influence can be formulated for the 4-hydroxyquinone (XV), but we prefer to explain the acidity of this enol (and XVI as well) by the aforementioned cross-ring, non-bonded electronic interaction. Such interaction may be an important stabilizing influence in the case of phenylcyclobutadienoquinone, and consistently may also be important in stabilizing the enolate anion of the 4-hydroxyquinone substantially over what might be expected for corresponding larger ring anions. This idea is supported by LCAO theory which predicts as improvement arising from inclusion of cross-ring interaction in the calculated delocalization



energy for the anion of 4-hydroxycyclobutadienoquinone from  $6.11\beta$  to  $6.94\beta$  (*cf.* Table V). Similarly, the D.E. value for the cyclobutenone enolate anion increases from  $5.42\beta$  to  $5.72\beta$  (*cf.* Table V). As expected, the stabilizing effect of 1,3-interaction is predicted to fall off with increasing ring size, and this is reflected by the decreasing D.E. values<sup>25</sup> of the four-, five- and six-membered cyclic  $\beta$ -ketoenolates, respectively (*cf.* Table V). However,

TABLE V  
CALCULATED DELOCALIZATION ENERGIES OF SOME CYCLIC  $\beta$ -KETOENOLATES

Compound	D.E. <sup>a</sup>	Compound	D.E. <sup>a</sup>
	$5.42\beta^b$		$6.12\beta$
	$5.72\beta^c$		$6.11\beta^b$
	$5.55\beta^c$		$6.94\beta^c$
	$5.52\beta^c$		

<sup>a</sup> See footnotes 17, 19 and 25 for method of calculation. <sup>b</sup> Cross-ring electronic interaction neglected. <sup>c</sup> Cross-ring electronic interaction included as indicated by dotted line.

the importance, if any, of non-bonded interaction within small rings awaits further experimental justification.

### Experimental

**1,1,2-Trifluoro-2-chloro-3-phenylcyclobutene (II).**—Phenylacetylene (30 g., 0.29 mole) and trifluorochloroethylene (34 g., 0.29 mole) were heated in a sealed tube at  $100^\circ$  for 7 hr. and at  $125^\circ$  for 20 hr. The tube had been flushed with nitrogen prior to addition of reactants, and the halogenated ethylene was dried before condensing it at  $-45^\circ$  in the phenylacetylene. The crude product was distilled at reduced pressure from some polymeric material and then fractionated through a 1-m. Vigreux column. The yield of 1,1,2-trifluoro-2-chloro-3-phenylcyclobutene was 50.8 g. (79%), b.p.  $52-54^\circ$  (0.4 mm.),  $n_D^{25}$  1.5117.

(25) The D.E. values were evaluated using 0.50 $\beta$ , 0.25 $\beta$  and 0.20 $\beta$  as the cross-ring resonance integrals ( $\beta_{1,2}$ ) for the four-, five- and six-membered ring systems, respectively (see ref. 19).

*Anal.* Calcd. for  $C_{10}H_8F_3Cl$ : C, 54.94; H, 2.77. Found: C, 54.83; H, 2.89.

In contrast to the behavior of the cycloadduct from 1,1-difluoro-2,2-dichloroethylene,<sup>7</sup> reaction in the presence of triethylamine did not afford the allylic isomer, 1,1,2-trifluoro-4-chloro-3-phenyl-2-cyclobutene. Compound II did not react with silver nitrate, sodium iodide in acetone or with bromine in carbon tetrachloride. It rapidly decolorized potassium permanganate solution.

A sample of 1,1,2,2-tetrafluoro-3-phenylcyclobutene (III) from phenylacetylene and tetrafluoroethylene was kindly supplied by Dr. J. J. Drysdale.

**2-Fluoro-2-chloro-3-phenylcyclobutenone (IV).**—Trifluorochlorophenylcyclobutene (10 g.) was added to 20 ml. of concentrated sulfuric acid which was rapidly stirred in a large test-tube. A water-bath maintained at 85° was used periodically to heat the mixture until it became homogeneous. At this point, the mixture was immediately poured into an ice-water slurry. The precipitate was collected by filtration, dissolved in ether, dried over Drierite and the solvent evaporated. The residue was distilled in a two-bulb flask at 1 mm. pressure. The pale yellow distillate was recrystallized from ethanol to yield 6 g. (67%) of 2-fluoro-2-chloro-3-phenylcyclobutenone as pale yellow crystals of m.p. 39.6–42.6°. Further crystallizations from ethanol and fractional sublimation gave an analytical sample as white needles, m.p. 42.8–43.8°.

*Anal.* Calcd. for  $C_{10}H_8FCIO$ : C, 61.09; H, 3.08. Found: C, 60.86; H, 3.06.

On heating IV with triethylamine, rearrangement to its allylic isomer did not take place.<sup>7</sup>

**Phenylcyclobutadienoquinone (I).**—Trifluorochlorophenylcyclobutene (5 g.) was added to 20 ml. of 90–92% sulfuric acid which had been preheated on a steam-cone. Hydrogen halide evolution began at once. The mixture was heated and mechanically stirred for 20 min. and then quickly quenched by pouring into an ice-water slurry. The precipitate was filtered, washed with water and crystallized from acetone. The yield of phenylcyclobutadienoquinone was 3.1 g. (86%), m.p. 149–152° dec. Sublimation and further crystallizations gave bright-yellow crystals of m.p. 152.4–153.2° dec.

*Anal.* Calcd. for  $C_{10}H_8O_2$ : C, 75.94; H, 3.82; mol. wt., 158.15. Found: C, 76.00; H, 3.85; mol. wt. (Rast), 151.

The mono-oxime had m.p. 165–166.8° after crystallization from ethyl alcohol.

*Anal.* Calcd. for  $C_{10}H_7O_2N$ : C, 69.36; H, 4.07. Found: C, 69.42; H, 3.98.

The mono-2,4-dinitrophenylhydrazone was obtained as an orange crystalline powder from dioxane and had m.p. 212.0–213.4° dec.

*Anal.* Calcd. for  $C_{16}H_{10}N_4O_6$ : C, 56.81; H, 2.98; N, 16.56. Found: C, 56.60; H, 3.09; N, 16.43.

Oxidation of 106 mg. of I in acetone with sodium permanganate gave, after destruction of the manganese dioxide with sodium bisulfite, 48 mg. of benzoic acid which was identified by melting point and mixed melting point with an authentic sample.

**2,2-Difluoro-3-phenylcyclobutenone (V).**—Tetrafluorophenylcyclobutene [III, 5 g., b.p. 65–78° (6–7 mm.),  $n_D^{25}$  1.4810] was added to 20 ml. of concentrated sulfuric acid and the mixture was heated gently with stirring on a steam-bath for 15 min. The deeply colored mixture was poured into ice-water and the precipitate separated by filtration. Fractional crystallization of the solid from dilute ethanol gave 2.5 g. (59%) of 2,2-difluoro-3-phenylcyclobutenone as white prisms of m.p. 60.5–61.5° and 0.4 g. of phenylcyclobutadienoquinone.

*Anal.* Calcd. for  $C_{10}H_8OF_2$ : C, 66.67; H, 3.36. Found: C, 66.63; H, 3.37.

Hydrolysis of either 2,2-difluoro-3-phenylcyclobutenone or 2-fluoro-2-chloro-3-phenylcyclobutenone to phenylcyclobutadienoquinone was accomplished by heating 0.5 g. of the ketones with 10 ml. of concentrated sulfuric acid at 95° for 30 min. The product (~350 mg.) after crystallization from acetone was identified as I by melting point and mixed melting point with an authentic sample.

**Oxidation of I with Hydrogen Peroxide.**—A mixture of 66 mg. of phenylcyclobutadienoquinone (I), 15 ml. of chloroform and 2 ml. of 30% hydrogen peroxide was shaken in a

50-ml. heavy-walled bottle at room temperature for 24 hr. More hydrogen peroxide was added periodically until the chloroform solution was clear. The organic layer was separated, washed with ferrous sulfate solution, and with water, and then dried over anhydrous magnesium sulfate. The solvent was removed and the residue (57 mg.) when recrystallized from chloroform-petr. ether gave crystals of m.p. 119.2–120.2°. The product gave no depression of melting point on admixture with an authentic sample of phenylmaleic anhydride.<sup>26</sup> Its infrared spectrum was identical with that of the authentic sample.

**Reduction of I to Phenylcyclobutane.**—A mixture of 5 g. of phenylcyclobutadienoquinone, 50 g. of amalgamated zinc, 50 ml. of distilled water and 50 ml. of concentrated hydrochloric acid was refluxed for 13–14 hr. The reaction mixture was cooled and the supernatant liquid decanted. The zinc amalgam was extracted with ether and these washings were used to extract the aqueous portion of the reaction mixture. The ethereal extract was washed with 5% sodium bicarbonate solution, water, and dried over anhydrous magnesium sulfate. The solvent was removed and the residue fractionated under reduced pressure in a 30-cm. spiral-wire column. The phenylcyclobutane (1.31 g.) collected had b.p. 38–40° (1.8–2.0 mm.),  $n_D^{25}$  1.5267 [lit.<sup>27</sup> 101–102° (41 mm.),  $n_D^{25}$  1.5277] and had an infrared spectrum identical with that of an authentic sample.

**2-Phenylacetylquinoxaline (VII).**—An intimate mixture of *o*-phenylenediamine (1.08 g., 0.01 mole) and phenylcyclobutadienoquinone (1.58 g., 0.01 mole) was warmed in a test-tube on a steam-bath until the solid became a dark brown liquid. Crystallization of the mixture from ethanol gave 1.3 g. of 2-phenylacetylquinoxaline as yellow needles having m.p. 83.2–84°, which gave a deep blue solution in concentrated sulfuric acid and a deep red solution in alkaline dioxane.

*Anal.* Calcd. for  $C_{18}H_{12}N_2O$ : C, 77.40; H, 4.87; N, 11.28. Found: C, 77.01; H, 4.96; N, 11.67.

The oxime crystallized as white needles from ethyl alcohol and had m.p. 210–211.6° dec.

*Anal.* Calcd. for  $C_{18}H_{12}N_2O$ : C, 72.99; H, 4.98; N, 15.96. Found: C, 72.89; H, 4.95; N, 16.07.

A monobromo derivative was prepared by adding bromine (0.129 g., 0.008 mole) to 2-phenylacetylquinoxaline (0.2 g., 0.008 mole) in 5 ml. of glacial acetic acid. The solution was heated to reflux, hydrogen bromide was evolved and the bromoketone of m.p. 115.6–116.5° separated on cooling.

*Anal.* Calcd. for  $C_{18}H_{11}N_2OBr$ : C, 58.73; H, 3.39; N, 8.56. Found: C, 58.77; H, 3.38; N, 8.58.

This compound produced a reddish-brown solution in sulfuric acid and a pink solution in alcoholic alkali; it reacted with silver nitrate only on standing.

**Oxidation of 2-Phenylacetylquinoxaline.**—Compound VII (0.9 g.) was dissolved in 5 ml. of glacial acetic acid, and there was added 1.5 g. of chromic anhydride in 5 ml. of 50% acetic acid. The mixture was allowed to stand at room temperature for 30 min. and then was diluted with water and extracted with ether. A bicarbonate wash of the ethereal solution gave, after neutralization with acid, about 200 mg. of mixed acids. Benzoic acid (0.12 g.) was removed by sublimation at reduced pressure, while crystallization of the residue from water gave 40 mg. of quinoxaline-2-carboxylic acid (VIII), m.p. 201–201.50° dec. The infrared spectrum of the product was identical with that of an authentic sample<sup>9</sup> and had m.p. 200–201° dec.

*Anal.* Calcd. for  $C_9H_6O_2N_2$ : C, 62.07; H, 3.47; N, 16.09. Found: C, 62.06; H, 3.51; N, 16.05.

**Beckmann Rearrangement of Oxime of VII.**—The procedure outlined by Horning and Stromberg<sup>28</sup> was followed. A mixture of 1.0 g. of the oxime of 2-phenylacetylquinoxaline in 30 g. of polyphosphoric acid was heated on a steam-cone at 95–100° for 10 min. The mixture was poured into water and extracted with ether. An alkaline wash of the ethereal solution gave, after neutralization, quinoxaline-2-carboxylic acid as tan crystals of m.p. 200–202° dec. having an infrared spectrum identical with VIII obtained by chromic acid oxidation of VII.

(26) L. E. Miller, H. B. Staley and D. J. Mann, *THIS JOURNAL*, **71**, 374 (1949).

(27) F. H. Case, *ibid.*, **56**, 715 (1934).

(28) E. C. Horning and V. L. Stromberg, *ibid.*, **74**, 2680 (1952).

*Anal.* Calcd. for  $C_9H_6O_2N_2$ : C, 62.07; H, 3.47; N, 16.09. Found: C, 62.43; H, 3.61; N, 15.82.

**4-Chloro-3-phenylcyclobutadienoquinone (X).**—Phenylcyclobutadienoquinone (1 g.) was dissolved in 15 ml. of glacial acetic acid and chlorine gas passed through the solution for 15 min. A crop of 0.2 g. of 4-chloro-3-phenylcyclobutadienoquinone as lemon-yellow crystals separated on cooling, which, after recrystallization from carbon tetrachloride, had m.p. 113.8–114.8°. An additional 0.65 g. (70%) of X was isolated from the mother liquor.

*Anal.* Calcd. for  $C_{10}H_5O_2Cl$ : C, 62.36; H, 2.62. Found: C, 62.20; H, 2.54.

The chloroquinone X gave an immediate precipitate with alcoholic silver nitrate, decolorized permanganate, reacted with sodium iodide in acetone, was sensitive to base and gave a positive 2,4-dinitrophenylhydrazine test.

**4-Bromo-3-phenylcyclobutadienoquinone (XI).**—Phenylcyclobutadienoquinone (3 g.) was dissolved in 15 ml. of glacial acetic acid containing 1 ml. of acetic anhydride, and 3.03 g. of bromine was added. The solution was heated on a steam-cone until it became pale yellow. Crystals of 4-bromo-3-phenylcyclobutadienoquinone separated on cooling and, after recrystallization from carbon tetrachloride or benzene-petroleum ether, melted at 128–129°. The yield was 2.4 g. (53%).

*Anal.* Calcd. for  $C_{10}H_5O_2Br$ : C, 50.66; H, 2.13. Found: C, 50.64; H, 2.13.

The bromoquinone XI reacted immediately with permanganate, gave a precipitate with alcoholic silver nitrate, was sensitive to base and reacted with 2,4-dinitrophenylhydrazine.

**Reduction of 4-Bromo-3-phenylcyclobutadienoquinone.**—Amalgamated zinc was prepared by successive treatments of 25 g. zinc dust with dilute hydrochloric acid, water and a solution of 2.5 g. of mercuric chloride in 50 ml. of water. The amalgam was washed with water and then placed with 1.5 g. of 4-bromo-3-phenylcyclobutadienoquinone in a flask with 25 ml. of distilled water and 25 ml. of concentrated hydrochloric acid. The mixture was heated under reflux for 15 hr., after which the supernatant liquid was decanted. The zinc residue was washed with ether and the washings used to extract the aqueous mixture. The combined extracts were washed with water, bicarbonate solution, water and dried over anhydrous magnesium sulfate. The solvent was removed and the residue distilled at reduced pressure through a 30-cm. spiral-wire column. The first fraction gave 0.21 g. of phenylcyclobutane, b.p. 52–53° (3.8–3.9 mm.). The infrared spectrum of this material was identical with that obtained from other sources.<sup>7</sup>

**4-Iodo-3-phenylcyclobutadienoquinone (XII).**—4-Bromo-3-phenylcyclobutadienoquinone (250 mg.) was dissolved in 10 ml. of dry acetone and treated with a solution of sodium iodide in acetone. When precipitation was complete, the solution was filtered, the solvent removed in a stream of nitrogen and the residue crystallized from benzene to give material of m.p. 162.5–165.5° dec.

*Anal.* Calcd. for  $C_{10}H_5O_2I$ : C, 42.28; H, 1.77. Found: C, 42.38; H, 1.87.

**4-Methoxy-3-phenylcyclobutadienoquinone (XIII).**—4-Bromo-3-phenylcyclobutadienoquinone (250 mg.) was dissolved in 10 ml. of absolute methanol and refluxed on a steam-cone for 30 min. Concentration of the solution furnished 140 mg. (71%) of product, m.p. 151–152.2°.

*Anal.* Calcd. for  $C_{11}H_8O_3$ : C, 70.21; H, 4.29. Found: C, 70.04; H, 4.09.

Compound XIII (23 mg.) readily hydrolyzed on heating in 1 ml. of water. When solution was complete, the solvent was removed in a stream of nitrogen and the solid residue crystallized from a mixture of ether and benzene. The product, 4-hydroxy-3-phenylcyclobutadienoquinone (XV), had m.p. 200–205° dec.

**4-Hydroxy-3-phenylcyclobutadienoquinone (XV).**—Phenylcyclobutadienoquinone (1 g.) was dissolved in 15 ml. of glacial acetic acid, and bromine (1 g.) was added dropwise. When the bromine color had faded and hydrogen bromide fumes were no longer evident, 5 ml. of water was added and the mixture heated to reflux for several minutes. This treatment was repeated. The solvent was removed in an air stream, the residue dissolved in ether and the product removed by continuous extraction with water. Concentration of the aqueous extract gave 0.9 g. (82%) of 4-hydroxy-

3-phenylcyclobutadienoquinone which crystallized from ether-benzene to give colorless crystals of m.p. 208–211° dec.

*Anal.* Calcd. for  $C_{10}H_8O_3$ : C, 68.96; H, 3.47. Found: C, 68.87; H, 3.61.

With aqueous ferric chloride, XV produced a magenta coloration. Permanganate solution was decolorized, and XV was recovered unchanged from 10% sodium hydroxide solution after acidification and extraction. The 2,4-dinitrophenylhydrazine test was positive and XV formed a copper salt with cupric acetate.

**Methylation of XV with Diazomethane.**—4-Hydroxy-3-phenylcyclobutadienoquinone (0.35 g.) was dissolved in 30 ml. of dry ether. The flask was cooled and an ethereal solution of diazomethane added in small amounts until the reaction mixture failed to give a ferric chloride test. The solvent was removed and crystallization of the residue from methanol gave 0.27 g. of 4-methoxy-3-phenylcyclobutadienoquinone, m.p. 151–152.2°, which value was not depressed on admixture of the product with the material prepared as described above.

**4-Amino-3-phenylcyclobutadienoquinone (XIV).**—4-Bromo-3-phenylcyclobutadienoquinone (250 mg.) was dissolved in 10 ml. of dry benzene and ammonia gas bubbled through the solution for one minute. The solvent was removed and the solid residue was recrystallized from dilute ethanol or acetic acid. The product, 150 mg. (82%), was a white crystalline solid of m.p. 282–283° dec.

*Anal.* Calcd. for  $C_{10}H_7O_2N$ : C, 69.36; H, 4.07; N, 8.09. Found: C, 69.37; H, 4.04; N, 8.08.

Compound XIV was insoluble in the usual hydrocarbon solvents, sparingly soluble in 50% sulfuric acid and soluble in concentrated sulfuric acid. It did not give a ferric chloride test in dioxane and did not form a benzoyl derivative. On warming with 10% sodium hydroxide, XIV dissolved and ammonia was evolved. A positive ferric chloride test was obtained on neutralizing the mixture, from which it was inferred that XIV had hydrolyzed to XV.

$pK_a$  of 4-Hydroxy-3-phenylcyclobutadienoquinone.—The procedure employed in the determination of the dissociation constant for XV was that of Flexser, Hammett and Dingwall.<sup>29</sup> A stock solution of XV in water ( $6.9 \times 10^{-4} M$ ) was prepared. A 5-ml. aliquot was then diluted to 50 ml. with water containing enough sulfuric acid to bring the final solution to the desired acidity. In this fashion, ultraviolet absorption curves for the free anion (in water), its conjugate acid (in  $\sim 10 N$  sulfuric acid), were obtained at various acidities. Calculation of the acid strength was then made by employing the equation

$$pK_a = H_{\ominus} - \log [C_{A\ominus}/C_{HA}]$$

where  $H_{\ominus}$  is the Hammett acidity function which measures the tendency of a solution to transfer a proton to a singly charged base<sup>30</sup> and was determined at each acid concentra-

TABLE VI

$pK_a$  OF 4-HYDROXY-3-PHENYLCYCLOBUTADIENOQUINONE

$\lambda$ , m $\mu$	$\epsilon_{H_2O}$	$\epsilon_{1N}$	$\epsilon_{2N}^a$	$\epsilon_{4N}^a$	$pK_a^{2N}$	$pK_a^{4N}$
220	13,450	11,250	12,660	12,240	0.488 <sup>b</sup>	0.304
230	14,750	5,770	11,660	9,350	.362	.396
240	8,920	5,770	7,820	7,050	.371	.382
250	10,800	6,850	9,500	8,570	.333	.330
270	2,520	6,640	3,885	4,892	.337	.349
280	4,750	12,275	7,340	9,210	.362	.379
290	9,350	19,700	12,960	15,540	.371	.389
300	15,680	25,550	18,940	21,510	.335	.376
310	21,880	25,700	23,100	24,040	.313	.331
320	24,400	18,750	22,250	20,710	.430	.491 <sup>b</sup>
330	22,400	5,120	16,400	11,880	.368	.400
340	9,060	866	5,980	3,815	.422	.467

Av.  $pK_a$ , 0.37  $\pm$  0.04

<sup>a</sup>  $H_{\ominus}$  was determined as 0.642 in 2 *N* sulfuric acid and 0.217 in 4 *N* sulfuric acid. <sup>b</sup> Omitted from average.

(29) L. A. Flexser, L. P. Hammett and A. Dingwall, *THIS JOURNAL*, **57**, 2103 (1935).

(30) L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932).



tion employed for XV by using a strong acid of known dissociation constant such as picric acid. The indicator ratio  $C_{A\ominus}/C_{HA}$  can be determined from the relationship

$$\left[ \frac{C_{A\ominus}}{C_{HA}} \right] = \frac{\epsilon - \epsilon_{HA}}{\epsilon_{A\ominus} - \epsilon}$$

where  $\epsilon_{HA}$  is the extinction coefficient for the conjugate acid

at high acid concentration;  $\epsilon_{A\ominus}$  is the extinction coefficient for the free anion in water and  $\epsilon$  is the extinction coefficient at some intermediate acidity. The results are given in Table VI, which records the  $pK_a$ 's computed from  $\epsilon$ -values measured at twelve different wave lengths for each of 4 solutions of XV of different acid strength.

PASADENA, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

## Ozonation of Carbon-Nitrogen Double Bonds. I. Nucleophilic Attack of Ozone<sup>1</sup>

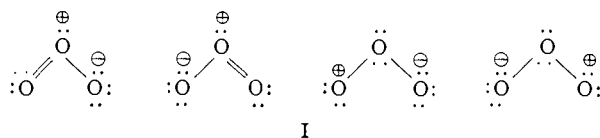
BY ALEXANDER H. RIEBEL, RONALD E. ERICKSON, CLAUDE J. ABSHIRE AND PHILIP S. BAILEY

RECEIVED MARCH 30, 1959

Contrary to reports in the literature, carbon-nitrogen double bonds, at least in Schiff bases and nitrones, are attacked by ozone. Evidence is presented that in these cases ozone behaves as a nucleophilic reagent, whereas in most other cases it acts as an electrophilic reagent. Ozonation of *N*-benzylidene-*t*-butylamine yielded the corresponding amide and oxazirane as non-cleavage products and benzaldehyde or benzoic acid and ammonium-type salts or other nitrogen-containing materials as cleavage products. Cleavage was the major reaction with *N*-benzylideneaniline and *N*-cyclohexylideneisobutylamine. Ozonation of *N*-phenylbenzaldoxime and *N*-*t*-butylbenzaldoxime gave initially benzaldehyde and the corresponding nitroso compounds. The latter were further oxidized by ozone to the corresponding nitro compounds.

### Introduction

Agreement seems to have been reached that the ozone molecule has an obtuse angle ( $116^\circ 45' \pm 30'$ ) and two oxygen-oxygen bonds of equal length ( $1.278 \pm 0.002 \text{ \AA.}$ )<sup>2-4</sup>



and can be described as a resonance hybrid of structures I. On this basis one would expect ozone to behave either as an electrophilic or as a nucleophilic reagent in its initial attack. The electrophilic attack appears to be established as the type involved in the ozonolysis of carbon-carbon unsaturated bonds<sup>4,5</sup> and in the reactions of ozone with amines<sup>4,6,7</sup> and sulfides.<sup>4,7-9</sup> Ozone is able to react as a radical reagent in autoxidation initiations,<sup>4,10,11</sup> probably because of a low lying excited state of the ozone molecule.<sup>11</sup> Although the possibility of ozone behaving as a nucleophilic reagent has been suggested,<sup>4,12</sup> no definite example has heretofore been pointed out.

The best opportunity for a nucleophilic ozone

(1) This work was included in a paper presented at the Symposium on Ozone Chemistry, Organic Chemistry Division, 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

(2) R. Trambarulo, S. N. Ghosh, C. A. Burrus, Jr., and W. Gordy, *J. Chem. Phys.*, **21**, 851 (1953).

(3) R. H. Hughes, *ibid.*, **24**, 131 (1956).

(4) P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

(5) P. S. Bailey, S. B. Mainthia and C. J. Abshire, to be published.

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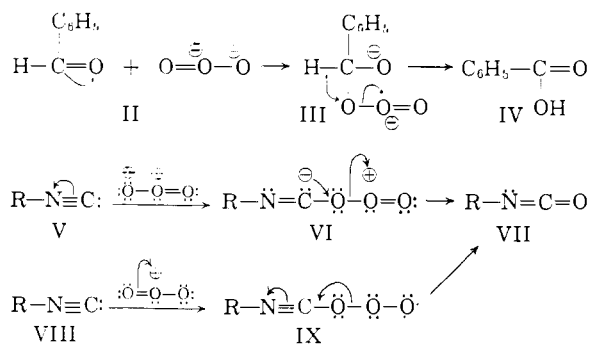
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attack would appear to be with carbonyl groups or with carbon-nitrogen double or triple bonds. Briner<sup>10,13</sup> has shown that whereas ozone-oxygen mixtures oxidize benzaldehyde to a mixture of benzoic and perbenzoic acids, ozone-nitrogen mixtures carry the oxidation only to benzoic acid. The first reaction largely is an ozone-initiated autoxidation and undoubtedly goes by a radical mechanism.<sup>4</sup> The second reaction, however, must involve a nucleophilic attack of ozone followed by loss of oxygen, as shown in the changes II→III→IV.<sup>4</sup> Ketones are less easily attacked by ozone than are aldehydes and the reaction appears to be radical in nature.<sup>4</sup> The reaction between ozone and isonitriles (V) to give isocyanates has been described recently.<sup>14</sup> This could result from either a nucleophilic (V→VI→VII) or an electrophilic (VIII→IX→VII) attack of ozone.



It has been stated and/or assumed in the literature that carbon-nitrogen double bonds do not react with ozone, at least in pyridine,<sup>4,15</sup> quino-

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