

QUANTITATIVE STUDIES ON AROMATICITY AND ANTIAROMATICITY

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ABSTRACT

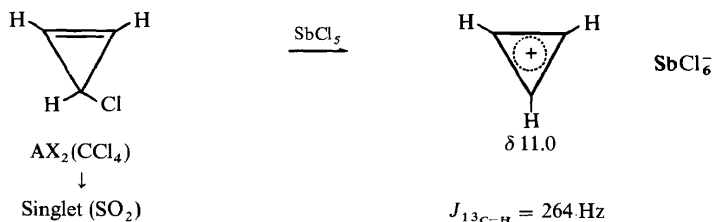
The properties of the simplest aromatic compound, $C_3H_3^+$, are fully consistent with expectations. Spectroscopic studies show that it is a symmetric cation with approximately the stability expected from simple quantum mechanical considerations. Various studies on cyclopropenyl anions reveal that they are undoubtedly resonance destabilized. Thus, the kinetic studies which have been done on rates of hydrogen exchange in this system can be shown to be consistent only with electronic destabilization in the antiaromatic cyclopropenyl anion. Direct thermodynamic determinations of the stability of cyclopropenyl anions can also be performed using a novel electrochemical procedure, and using this method very high pK_a s are found for some of these anions, indicating great stability. Resonance destabilization in cyclobutadiene can also be demonstrated by examining the basicity of a cyclobutadienocyclopentadiene anion and also by electrochemical studies on a fused naphthalenecyclobutadiene derivative. 1-Chloro-bicyclo[2,2,0]hexadiene has been prepared. On treatment with strong base it apparently eliminates HCl to generate transient butalene (cyclobutadienocyclobutadiene), which is then trapped by the medium.

Since the first synthesis of a cyclopropenyl cation, the triphenyl derivative synthesized in 1967¹, work in our laboratory and in a number of others has been devoted to a study of this simplest aromatic system. Of course, the description of the cyclopropenyl cation ring as 'aromatic' involves some assumptions about a definition of the term aromaticity, and I would like to focus first on this problem. There are a number of things which are special about the compounds which have been called aromatic, but the one which is certainly at the root of most of their unusual properties concerns their energies. Aromatic compounds are thermodynamically more stable, that is, they contain less energy than related non-aromatic reference compounds. We would like to focus on this particular definition of aromaticity, namely the possession by a cyclic conjugated system of less energy, because of its conjugation, than an open chain analogue. By logical extension, the property which we have referred to as antiaromaticity² would be the possession by a cyclic system of more energy than would be expected by analogy with an open chain linear analogue. Thus the open chain compounds are considered to be normal, and the cyclic compounds are referred to them.

This all seems so straightforward that it is hard to believe it requires

repetition, but it is an interesting fact that there are still chemists who deny that aromaticity or antiaromaticity can be defined in a meaningful way. The definition we have just described is meaningful if it becomes possible to measure the energies of suitable systems, and if it is possible to correct for any of the differences between the cyclic and the linear systems which are not due to conjugation effects. Thus, in this lecture I would like to discuss the question of the energies of some cyclic aromatic and antiaromatic systems, and to try to see the extent to which the properties of these systems are consistent with the predictions of molecular quantum mechanics.

Quantitative studies on derivatives of the cyclopropenyl cation have been reported and discussed in detail over the past thirteen years³. For this reason, I want to focus here simply on the properties of the parent cyclopropenyl ion itself, a species whose preparation we have reported only recently⁴. The reaction below indicates the procedure by which this species was prepared, and it is straightforward once a synthesis of 3-chlorocyclopropene has been achieved. The preparation of this latter was, of course, the principle obstacle to the synthesis of the parent cyclopropenyl cation, and we have described the studies⁵ which led to successful synthesis of 3-chlorocyclopropene and



the properties of some of these halocyclopropenes. As illustrated, the chloro compound is not a salt and it has a normal covalent n.m.r. spectrum in carbon tetrachloride. Even in sulphur dioxide as solvent it is essentially completely covalent; the n.m.r. signal at δ 6.5 is a simple average of the signals from the three congruent isomers⁵ of covalent 3-chlorocyclopropene. However, on treatment with Lewis acids such as antimony pentachloride, or with some silver salts, it is possible to convert this halo compound to a salt of the parent cyclopropenyl cation. This species has a single signal in the n.m.r. strongly shifted downfield to δ 11.0 by both the hybridization effects and the positive charge effect. The very large ^{13}C —H coupling in the n.m.r. corresponds to sp hybridization at the carbon.

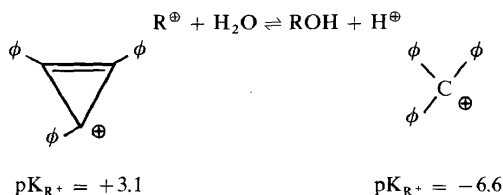
Table 1. Infra-red spectra, cm^{-1}

Principal component	C_3H_3^+	C_3D_3^+	C_3Cl_3^+	C_3Br_3^+	D_{3h}	D_{6h}	C_6H_6	C_6D_6
C—X stretch	3105	2327	735	575	E'	E_{1u}	3099	2293
C—C stretch	1276	1239	1312	1276	E'	E_{1u}	1485	1333
C—X of-plane bending	908	665	(200)		E'	E_{1u}	1037	813
C—X out-of-plane bending	736	542			A_2''	A_{2u}	671	503

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Table 1⁴ shows the infra-red frequencies observed for these cyclopropenyl salts and also for the corresponding trideutero cation. Also included in the table are the data of Robert West⁶ on the trichloro and tribromocyclopropenium ion as well as some relevant data for benzene and hexadeutero-benzene. The presence of only four infra-red transitions for cyclopropenyl cation is uniquely consistent with a threefold symmetric regular triangular structure, that is D_{3h} symmetry. The positions of the infra-red bands in the deutero compound are as expected for vibrations in which carbon-carbon and carbon-hydrogen motions are coupled to some extent, and the assignments we list are only those of the principal component of the vibration. As is apparent from the table, both the deuterium isotope effects and in fact the positions of the four allowed bands are close to those for the four strongest vibrational bands in the spectrum of benzene. The D_{6h} point group to which benzene belongs contains the D_{3h} symmetry in it, so that the correspondence of these signals is not surprising.

Of course, the simple fact of our having produced a salt of cyclopropenyl cation does not by any means define it as an aromatic system. Thus, some sort of energy measurement is the first requirement of the kind of evidence we are looking for. Although neutral aromatic substances, such as benzene, were classically characterized by heat of combustion or heat of hydrogenation measurements, these are unsatisfactory if instead it is possible to get thermodynamic measurements which result in a smaller alteration of the compound than a complete oxidation of it or even a complete hydrogenation. There is always a problem in trying to remove factors such as strain energy from the interpretation of our energy measurements, so we would prefer a transformation which converts an aromatic into a non-aromatic system with the minimum total change in structure. For carbonium ions this is most conveniently done by neutralizing them into alcohols in which the conjugation has been interrupted by the production of a saturated carbon, and determining the acid strength required to establish the equilibrium between carbonium ion and alcohol.



The type of equilibrium we are concerned with is shown above, and some data from our earlier work⁷ show the sort of evidence one can obtain. The fact that triphenylcyclopropenyl cation has a pK_{R^+} of +3.1, requiring only pH 3 in order to establish a 50 per cent carbonium ion-alcohol equilibrium, while triphenylmethyl cation has a pK_{R^+} of -6.6 and requires 50 per cent sulphuric acid to establish the 1:1 equilibrium, is a thermodynamic fact indicating something about the energy of the triphenylcyclopropenyl cation system. In this case, the cyclic system is being compared against an open chain analogue which is not a complete one. The triphenylmethyl cation has, of course, the three phenyl groups stabilizing the charge, but it does not have

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an allylic cation system as an analogue of the cyclic cyclopropenyl cation. However, the essential point here is that the position of such carbonium ion equilibria gives thermodynamic data which will be at least as easy to interpret as heats of hydrogenation or of combustion. Table 2 shows a set of such data

Table 2. pK_{R+} s of some cyclopropenyl cations

Compound	Medium ^a	Method ^b	pK_{R+}
Dipropylcyclopropenyl perchlorate	A	a	2.7
Tripropylcyclopropenyl perchlorate	A	a	7.2
Trianisylcyclopropenyl bromide	A	a	6.5
	B	b	6.4
Dianisylphenylcyclopropenyl bromide	A	a	5.2
	B	b	5.2
Triphenylcyclopropenyl bromide	A	a	3.1
	B	b	2.8
Diphenylcyclopropenyl bromide	B	b	-0.67
	C	b	0.32
Propyldiphenylcyclopropenyl fluoroborate	B	b	3.8

^a A, 50% aqueous acetonitrile; B 23% aqueous ethanol; C, water.

^b a, potentiometric titration; b spectrophotometric titration.

which we had accumulated a number of years ago⁸ and, for our present purposes, I simply want to draw attention to the possibility of extrapolating these data back to the pK_{R+} of the parent cyclopropenyl cation. If we assume that the effects of phenyls are additive, we can extrapolate from triphenyl through the diphenyl cation back to a pK_{R+} of -5.5 for the parent cation, while if we assume that the effects of propyl groups are additive, we can extrapolate from the tripropyl through the dipropyl cation back to the parent and arrive at a pK_{R+} of -6.3.

The determination of this pK_{R+} was considerably more difficult than for any of the compounds shown in this table. Thus, the aromatic cyclopropenyl cation pK s were determined by using u.v. spectral changes, but in the case of the parent cyclopropenyl cation or the alkyl derivatives no spectroscopic changes occur in the region of the u.v. spectrum accessible to normal techniques. This is as expected since the cyclopropenyl cation has a transition from a strongly bonding to a strongly antibonding orbital and should have its u.v. maximum at even higher energy than that for a simple olefin. Of course, the pK_{R+} s of the tripropyl and dipropyl cation were determined, but since the pK s came in the normal pH region in water, it was possible to do this by simple titration techniques. However, for the determination of the pK_{R+} of the simple cyclopropenyl cation we were forced to devise a technique using n.m.r. changes. In the case of a covalent cyclopropene, such as the cyclopropenol, the n.m.r. is either an AX_2 pattern or, instead, a single signal in the average position of the covalent hydrogen signals if the covalent compound is equilibrating rapidly among its congruent isomers. This is what is observed when the cation is dissolved in weak sulphuric acid, since the sulphuric acid catalyses the equilibration among the congruent isomers

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of cyclopropenol. As the acid strength is increased, the signal moves to greater and greater chemical shift until finally in strong sulphuric acid a single peak is seen at δ 11.0 corresponding to the cyclopropenyl cation. In the intermediate acid regions the covalent cyclopropene is equilibrating not only among its congruent isomers but as well with an equilibrium concentration of the cation; the line position is an average weighted by the fraction of the material which is present in each of these two forms. Thus, with an internal calibration to correct for changes in the medium it is straightforward to monitor the acid strength required to shift the signal exactly halfway between its position for equilibrating covalent compounds and its position

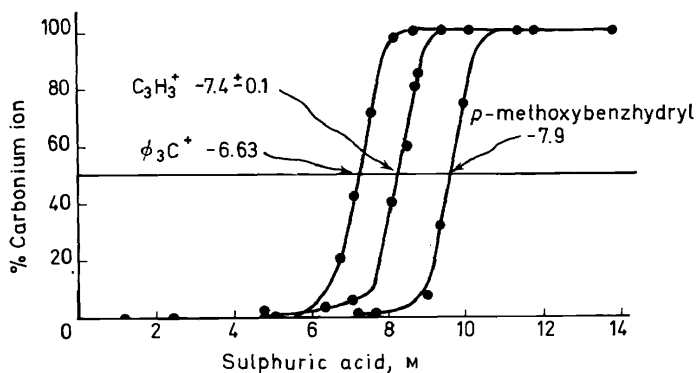


Figure 1.

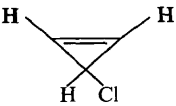
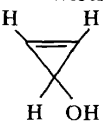
for the cation. These are the data which are plotted in Figure 1 for the cyclopropenyl cation system. Alongside it are plotted spectroscopic data obtained in the same medium for triphenylmethyl cation, of known pK_{R+} , and para-methoxybenzhydryl cation, whose pK_{R+} has also been determined⁹. As you can see, these titration curves are quite parallel, and it is easily possible to interpolate the cyclopropenyl cation pK_{R+} between those of the two known indicators. In this way we have determined that the pK_{R+} of this parent cation is -7.4 , not far from but lower than either of the values we got by simple two-point extrapolation from the derivatives.

As Table 3 shows, it is not easy to make a direct comparison of this value of -7.4 for the pK_{R+} of cyclopropenyl cation with a pK_{R+} for the open chain analogue, allyl cation. The value for allyl is only approximately known. Thus, Deno has reported a value of about -19 for benzyl cation⁹, and since allyl cation seems to be between 1 and 2 powers of 10 less stable than benzyl¹⁰, one can estimate a value of -20 or -21 for the pK_{R+} of allyl cation. A difference of the order of 13 pK units corresponds to an energy difference of 18 kcal/mole. This energy difference, of course, is the result of a four-way comparison. The energy change involved in converting a covalent allyl compound to its cation is used as our reference point for the measured energy of conversion of a covalent cyclopropene to its cation. Thus, the measured number

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contained not only whatever resonance energy comes in because of the aromaticity of the cyclopropenyl cation; it also contains whatever new strain energy arises on conversion of a covalent cyclopropene into its cation, with resulting rehybridization in a small strained ring. We have pointed out¹¹

Table 3.

	$\longrightarrow \text{C}_3\text{H}_3^+ + \text{Cl}^\cdot + \text{e}$	$10.20 \pm 0.05 \text{ V}$
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$	$\rightarrow \text{C}_3\text{H}_3^+ + \text{Cl}^\cdot + \text{e}$	11.04 V
		0.84 V
J. Groves, F. P. Lossing		
Cyclopropene $\rightarrow \text{C}_3\text{H}_3^+ + \text{H}^\cdot + \text{e}$		11.15 V
Propylene $\rightarrow \text{C}_3\text{H}_3^+ + \text{H}^\cdot + \text{e}$		11.95 V
		0.80 V
Wiberg, Bartley and Lossing, <i>J. Am. Soc.</i> 84 , 3980 (1962)		
	$+ \text{H}^+ \rightleftharpoons \text{C}_3\text{H}_3^+$	$\text{pK}_{\text{R}^+} = -7.4$
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$	$+ \text{H}^+ \rightleftharpoons \text{C}_3\text{H}_3^+$	$\text{pK}_{\text{R}^+} \approx -21$
13.6 pK units = 19 kcal/mole		
0.84 V = 19.3 kcal/mole		

that the simple calculation which is reasonably successful in predicting small strain energies predicts that this extra strain energy on ionization of the cyclopropenyl system could be as much as 20 kcal/mole. Thus, the extra aromatic stabilization in the cyclopropenyl cation may be only 18 kcal/mole or it may be as much as 40 kcal/mole of which half went to compensate for the increased strain energy.

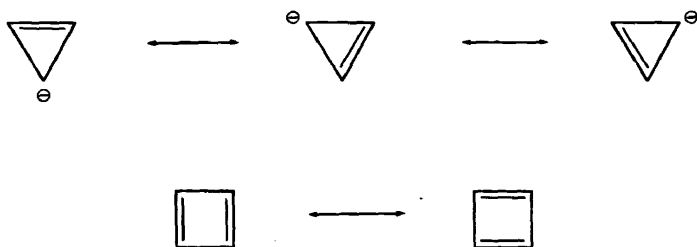
It might also be wondered how either of these numbers corresponds to the predictions of simple MO theory. By simple Hückel theory the cyclopropenyl system should gain 1.2β s more stabilization on conversion to the cation than the allyl system should. If the simple empirical value of 18 kcal/mole is used for β , this would correspond to a predicted value of the order of 22 kcal/mole; while if values for β which are used in spectroscopy or electrochemistry are invoked, the prediction is in the region of 40 kcal/mole for the resonance contribution of the aromaticity. Thus in any case the general magnitude of stabilization which is being observed in the cyclopropenyl system is more or less that which is predicted by simple MO theory.

There is an independent way of determining the stabilization in the cyclopropenyl and allyl systems, and that is illustrated at the top of Table 3. In collaboration with Professor Lossing we have determined the appearance potential for m/e 39 from chlorocyclopropene and for m/e 41 from allyl chloride. The difference between these two appearance potentials is a number

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closely related to the thermodynamic difference derived from solution pK measurements. Again, cyclopropenyl cation turns out to be formed more easily, in this case by 0.84 V. Since 0.84 eV corresponds to 19.3 kcal/mole, this determination is in very good agreement with the determination using pK_{R^+} s in solution. It is also in good agreement with the earlier report by Lossing and Wiberg¹² that m/e 39 and m/e 41 appearance potentials from cyclopropene and propylene respectively corresponded to a difference of 0.80 V. These data strongly help to confirm the identity of the m/e 39 peak in the mass spectrum of these substances as being cyclopropenyl cation; it is interesting that the differences between gas phase and solution data in a comparison of these two systems are largely cancelled, so that very similar values are obtained.

By contrast to the situation in the cyclopropenyl cation, in which both theory and now experiment have clearly indicated that it is strongly resonance stabilized compared to an open chain analogue and thus can be considered to be aromatic, theory predicted that cyclopropenyl anion and cyclobutadiene would be members of a class of antiaromatic compounds. That is, it was predicted that the resonance interaction shown below would



be destabilizing to these systems. The prediction from Hückel calculations is straightforward: both cyclopropenyl anion and cyclobutadiene are predicted to have no resonance stabilization, whereas the corresponding open chain analogues, allyl anion and butadiene, are both predicted to have some resonance stabilization. Thus, in the comparison of a cyclic with a linear analogue the prediction from simple Hückel calculations was quite clear. The results of a configuration interaction calculation using appropriate integrals are shown below, and they also indicate that allyl anion should



Singlet: -61.443
(1 $\bar{1}$ 2 $\bar{3}$: -61.167)
Triplet: -62.290
S-T gap: 0.842 (1.123)



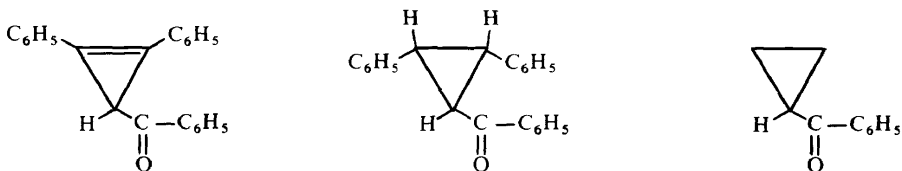
Singlet: -61.903
(1 $\bar{1}$ 2 $\bar{2}$: -61.670)
[Triplet: -59.164]
Core correction: 1.60

Antiaromaticity: Triplet: 1.2 Singlet: 2.0

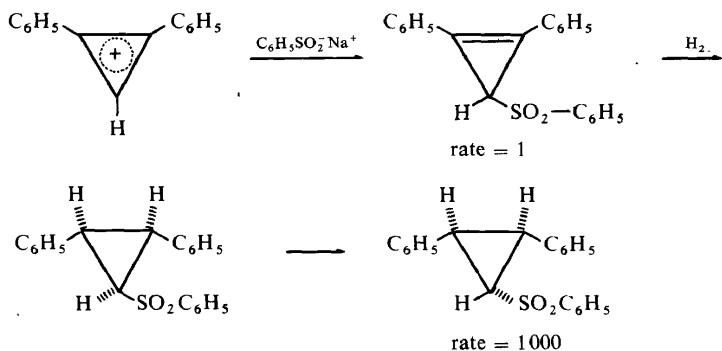
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be strongly stabilized compared with cyclopropenyl anion, in this case by 2 eV (46 kcal/mole) for the singlet states of the two systems.

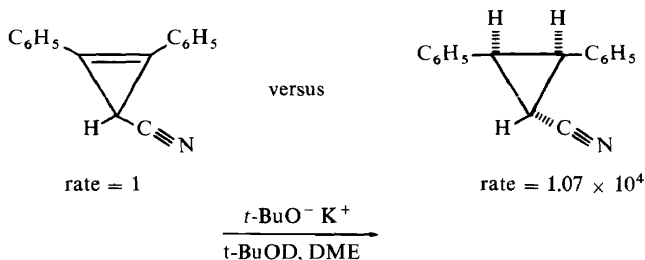
Our early kinetic studies on systems which generate derivatives of cyclopropenyl anion have been thoroughly described¹³, so I will simply mention

		
Rate of exchange:	1	6000
E_a	26 kcal/mole	20.3 kcal/mole
log A	11.2	10.8
		2000

here the results and their interpretation. As shown above, the rate of base-catalysed deuterium exchange in a cyclopropenyl derivative is much slower than that in the corresponding cyclopropane, even though the anion derived from cyclopropene should receive extra stabilization by conjugation through the double bond with the phenyl groups and also by inductive effects from the vinyl carbons. The essential point, of course, is that its other interaction with the double bond, the conjugative interaction, is the sort of antiaromatic interaction for which we are looking. The magnitude of the effect is certainly not enormous here, corresponding to only about 5 kcal/mole in the activation energy. However, we only expect a modest fraction of the antiaromaticity of cyclopropenyl anion to show up in this comparison since, of course, the carbanion we are forming is also an enolate ion with substantial charge out of the three-membered ring and on the oxygen atom. We have described related studies¹³ in which the activating group is a sulphone instead of a ketone, and as shown below, an apparent destabilization of the cyclopropenyl anion is again observed by a factor of 10^3 , or a little over 4 kcal/mole. When the activating group is a cyano group, as also shown below, there is an apparent destabilization in the cyclopropenyl anion system by a factor of 10^4 , or 5.5 kcal/mole.



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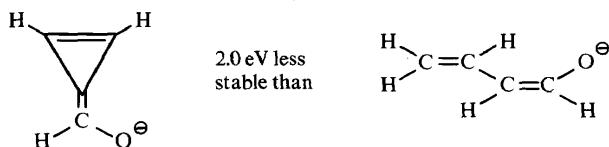


Factors slowing the cyclopropene exchanges

1. Antiaromaticity

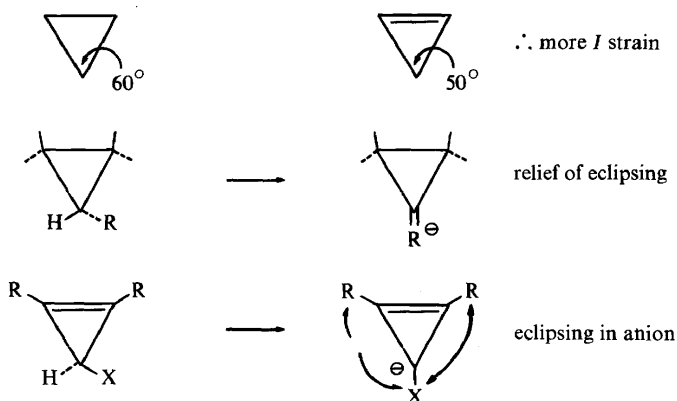


Loss of 0.34 eV of stabilization by PPP-SCF calculation.



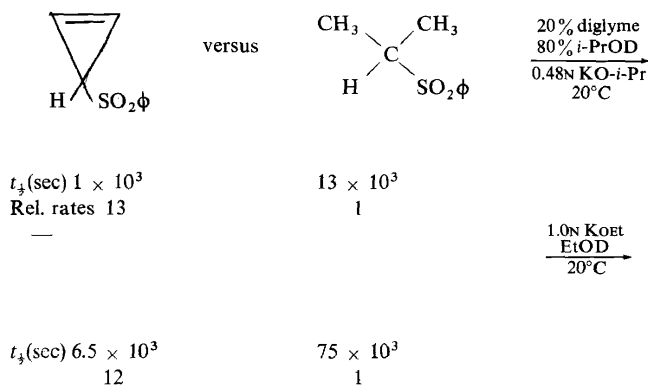
As we have discussed elsewhere¹³, there are two general classes of effects which can be invoked to explain these observations. As set out above, antiaromaticity is shown as the electronic factor; our self-consistent field calculation on an enolate ion of a cyclopropene carbonyl system indicates that it could be destabilized relative to the cyclopropane analogue by one-third of an electron volt or approximately 7 kcal/mole. Thus, the magnitudes of the effects we have been seeing in these cyclopropenyl derivatives are not inconsistent with the predictions of such⁹ a calculation. The small magnitude of the antiaromatic effect predicted here results because so much of the negative charge in such an enolate ion is out of the three-membered ring. I should also point out that the comparison we are making here is between a cyclic conjugated system and its individual components, in this case between a cyclopropenyl anion derivative and the component isolated double bond and isolated enolate ion system. That is, of course, the experimental comparison involved in using cyclopropanes as models for cyclopropenes, and it is different from the original definition of antiaromaticity in which allylic systems would be used as the reference compounds for cyclopropenyl anions. It is expected that ordinary allylic resonance should stabilize an enolate ion, as Bottini has shown¹⁴ that it does in a methylene-cyclopropane system, and the calculation by the s.c.f. method indicates that if the cyclopropenyl anion were compared with this allylic analogue, a much greater destabilization is predicted.

2. Steric effects



The second general class of effects which could be responsible for our observations includes various forms of steric effect, illustrated above. Thus, the angle strain in a cyclopropenyl anion may be greater than that in the corresponding cyclopropane, even though the latter was chosen as a close model for the strain problem in our cyclopropenyl system. Furthermore, various kinds of eclipsing strain relief could be invoked to explain our observations. We have explored the arguments against these alternative explanations¹³, but I would like to mention two critical pieces of evidence here.

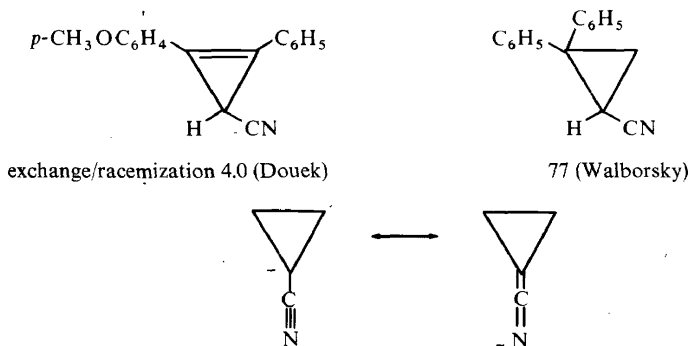
One argument against *I*-strain being the factor which is slowing cyclopropenyl exchange relative to cyclopropyl is the observation that our destabilization is observed with activating groups such as benzenesulphonyl and cyano for which *I*-strain effects are not important, as well as for the benzoyl group in which *I*-strain has been observed to be a factor. Thus, our data¹³ below illustrate that a cyclopropyl phenyl sulphone undergoes base-catalysed deuterium exchange more rapidly than does the corresponding open chain case in spite of the greatly increased angle strain in the three-membered ring, and the work of Walborsky¹⁵ shows that a related situation



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is observed for cyanocyclopropane. By contrast, it has been shown¹⁶ that benzoylcyclopropane undergoes base-catalysed deuterium exchange much more slowly than does the corresponding isobutyrophenone. Since our destabilization in the cyclopropenyl system was observed with all three of these activating groups, it seems very unlikely that it is due to angle strain, and that this angle strain effect did not show up for two of these activating groups in the comparison of a strainless open chain derivative with the cyclopropyl derivative.

A second general kind of evidence that we are not dealing with strain effects in our cyclopropene rate studies comes from our studies on the rate of racemization of optically active cyclopropenyl derivatives. Walborsky¹⁵ had studied the competition between base-catalysed deuterium exchange and racemization in optically active cyclopropane derivatives. He had observed that $k_{\text{exchange}}/k_{\text{racemization}}$ can be very high for cyanocyclopropanes under some conditions, but that the corresponding benzoylcyclopropanes racemize more readily, although they still undergo base-catalysed exchange more rapidly than racemization.



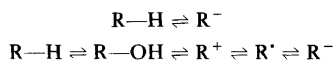
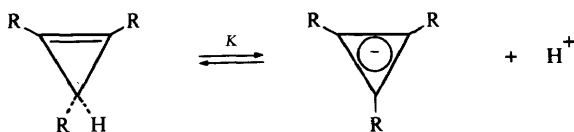
The situation is illustrated above. In the case of a cyanocyclopropyl anion there are two contributing resonance forms and the two forms have different optimal geometry. The carbanion form on the left would prefer pyramidal hybridization at the ring carbon so that angle strain could be minimized, but the nitrogen anion resonance form on the right would prefer a flat trigonal carbon in the ring so that the carbon-carbon double bond would have its normal geometry. The real system will adopt a compromise geometry somewhere between the two, and the positions of this compromise will be determined by the relative contributions of the two resonance forms. Thus, if the enolate type of resonance form is the major contributing structure, then the carbon will tend to flatten in the three-membered ring, while if there is a large contribution from a carbanion form then it will tend to remain puckered or pyramidal. The energy barrier to racemization of an anion should then be related to the electron distribution between two resonance forms of the type we have drawn for cyanocyclopropyl anion. Walborsky's observation that exchange proceeds much more rapidly than racemization in the cyanocyclopropane thus indicates that the anion is to a considerable degree non-planar, and that the planar form is of high enough relative energy

that it furnishes a barrier to racemization. By contrast, when the activating group is a benzoyl group he finds that the optically active cyclopropane racemizes much more readily, although exchange still proceeds somewhat faster. In the case of the benzoyl activating group one would expect much more of the charge to be removed from the three-membered ring in favour of an enolate structure in which the ring carbon is flattened. Thus, the hybrid structure will much more favour the right hand form and the barrier for racemization will be lower.

In the case of the cyclopropenyl anions all of the steric effects we have invoked as possible explanations for the decreased rate of deuterium exchange would predict that racemization would be even more difficult than in the cyclopropane analogues. Thus, the steric effects supposedly appeared when the cyclopropenyl anion was flattened; if they are indeed more severe in the cyclopropenyl than in the cyclopropyl series, flattening should be even more difficult for the unsaturated ring. This is precisely the opposite of what we have observed¹⁷, since in fact an optically active cyanocyclopropane racemizes with a much greater rate relative to deuterium exchange than Walborsky observed for the corresponding cyclopropane. These results are precisely the opposite of those predicted if the cyclopropenyl anion has steric difficulties.

If, on the other hand, there is antiaromaticity in the cyclopropenyl anion, then we would expect a greater rate of racemization relative to exchange in the unsaturated ring. The resonance form in which the charge is left behind on the ring carbon is the one which should be seriously destabilized by antiaromatic conjugation, and the result is that the charge should be forced into the activating group with consequent flattening of the ring carbon. Thus, it seems that antiaromatic interaction in the ring uniquely predicts what we have observed, that racemization is much more facile in this ring system than it is in the saturated cyclopropane analogues. These data seem to indicate quite strongly that the antiaromatic destabilizations of 4 to 6 kcal/mole which we have observed are in fact due to a conjugative interaction.

Of course, it is expected that the antiaromatic effects in the cyclopropenyl anion system should become much more extreme if the activating groups on the three-membered ring remove less of the charge. Thus, it was of great interest to try to determine, preferably with some equilibrium method, the acidity of the hydrogen on a cyclopropene carrying only simple substituents rather than strongly activating groups such as ketone and cyano functions. A number of studies made it quite clear that even with such activating substituents as phenyl groups it was not possible to establish an equilibrium with the cyclopropenyl anion derivative. In fact, triphenylcyclopropene is so



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non-acidic that no hydrogen exchange of the ring-hydrogen has been detected under any base-conditions¹⁸. Nonetheless, as illustrated above, we were able to devise a method¹⁹ of determining the equilibrium acidity of a compound of this type in which the direct equilibration between the hydrocarbon and its anion is impossible.

The technique involved recognized that the direct conversion of a hydrocarbon to its anion could be duplicated for thermodynamic purposes by an alternative sequence, in which the hydrocarbon is reversibly converted to the corresponding carbinol, and from this to the carbonium ion, the radical, and finally the anion. This is, of course, only a thermodynamic cycle, not a real chemical process, but it turns out that it is possible to use it to derive the pKs of compounds like triphenylcyclopropene which are such weak acids

Table 4.

	ϕ_3C	ϕ_3C_3	Δ
$R-OH \rightleftharpoons R^+$	$pK_{R^+} = -6.6$	+3.1	9.7 pKs
$R^+ \xrightleftharpoons{e^-} R^\cdot$	$E_3 = -0.08 \text{ V}$	-1.11 V	-1.0 V
$R^\cdot \xrightleftharpoons{e^-} R^-$	$E_3 = -0.83 \text{ V}$	-1.56 V	-0.7 V
$R-H \rightleftharpoons R^-$	$pK_a = +33$	X	Y
$R-H \rightleftharpoons R-OH$	assumed the same		~ 0

1.7 eV = 39 kcal/mole = 28 pK units

$\therefore X = 33 + 28 - 9.7 = 51$

that they cannot be directly ionized under any accessible conditions. Table 4 shows the essential form of the thermodynamic arguments used. The conversion of the carbinol to the carbonium ion is a reversible equilibrium which we have defined by the thermodynamic constant called the pK_{R^+} , and the data for triphenylcyclopropenyl and for the reference compound triphenylmethyl are listed in Table 4. We have been able to carry out the reversible electrochemical reduction of each of these cations to the corresponding radical with the potentials listed in Table 4 and also to determine reversible electrochemical potentials for the reduction of triphenylmethyl and triphenylcyclopropenyl radicals to the corresponding anions. The only missing leg in the thermodynamic cycle is the conversion of a hydrocarbon to the corresponding alcohol, and for this energy we used triphenylmethane as the model compound for triphenylcyclopropene and assume that these two energy changes are the same. As it turns out this is not likely to be precisely so, but the direction of the error is such as to slightly underestimate the antiaromaticity of cyclopropenyl anion. Since the pK_a of triphenylmethane is known, it is a simple matter to convert these other thermodynamic quantities in such a way as to solve for the missing value, namely the pK_a of triphenylcyclopropene, and when this is done it is seen that cyclopropene is 18 pK units less acidic than is triphenylmethane, so its pK_a is 51. Thus, even though the triphenylcyclopropenyl cation was considerably more stable than was the triphenylmethyl cation relative to their corresponding covalent compounds, the next two electrons were added to much higher energy orbitals in the cyclopropenyl case so that the anion ended up at a much higher energy than did triphenylmethyl anion.

Since this is a new technique for determining pK_s , it was important to establish that it actually works. As Table 5 shows, a series of triphenylmethyl cations was studied¹⁹ with this technique; these particular examples should lead to anions of approximately the same pK_a , since the substituents present on these rings should modify anion stability only slightly while they strongly affect the stability of the cations. The electrochemical technique does in fact lead to a series of pK_a s of these substituted triphenylmethanes which are in very close agreement, starting from cations whose original pK_{R+} are over seventeen units apart. Using the same technique, we have determined a pK_a for cycloheptatriene which is in agreement with the literature value. Thus, this technique is a valid measure of the pK_s of very weak hydrocarbon acids.

Table 5. Triphenylmethyl cations and anions

4,4',4''-Substituents	pK_{R+}	E_a (first electron)	Calculated pK_a
none	-6.63	+0.27	33.00
trichloro	-7.74	+0.38	32.3
monomethoxy	-3.40	+0.07	33.1
trimethoxy	+0.82	-0.20	33.4
tris(dimethylamino)	+9.36	-0.79	34.7
trimethyl	-3.56	+0.05	33.6
tri-isopropyl	(-6.51)	+0.07	(36.2)
tri- <i>t</i> -butyl	(-6.5)	+0.13	(35.2)

At first sight a difference of 18 pK units between the acidity of triphenylcyclopropene and that of triphenylmethane would seem to indicate an enormous antiaromatic destabilization in the cyclopropenyl anion. However, it must be remembered that this comparison between a cyclopropenyl system and the corresponding simple open chain case contains as well a difference in *I*-strain on ionization. This is the same problem we faced in trying to analyse the pK_{R+} of the cyclopropenyl cation; there all we could do was point out that a simple strain-energy calculation comes up with a number of 20 kcal/mole, and this is undoubtedly quite an overestimate. Thus, of the 25 kcal/mole which 18 pK units corresponds to, an undetermined fraction is due to changes in *I*-strain and the rest of it is due to the antiaromaticity of triphenylcyclopropenyl anion.

Table 6.

Cyclopropenyl derivative	E_1	E_2	pK_a
Tripropyl	-1.29	-1.65	65
Trimethyl	-1.19	-1.50	62
Tri-isopropyl	(-1.16)	(-1.54)	(62)
Tri- <i>t</i> -butyl	-1.39	-1.74	69
Dipropyl	-1.17	-1.52	66

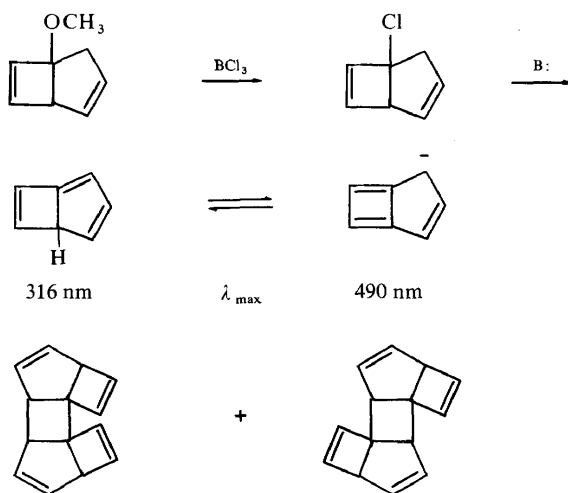
(Methane pK values from literature: 40, 48, 58)

We have also examined^{19c} the electrochemistry of some alkyl-substituted cyclopropenyl cations, and the results are listed in Table 6. Again, a combination of these reversible reductions with the pK_{R+} s of the cations leads to pK_a s

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for the hydrocarbons. The remarkably high values of these pK_a s—ranging from 62 to 69—are well above any of the estimates²⁰ for the pK_a of methane. However, they do not seem out of line with the pK_a of 51 for triphenylcyclopropene, with its three stabilizing phenyl groups.

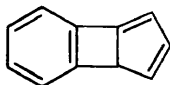
All these studies have been concerned with antiaromaticity in the cyclopropenyl anion system, but there are other conjugated systems which are also expected to be antiaromatic. The very high reactivity of cyclobutadiene has often been considered to indicate that it is resonance destabilized but, of course, it is difficult to distinguish between instability of starting materials and stability of transition state when we talk about reaction rates. We have recently reported two studies in which thermodynamic measurements on cyclobutadiene derivatives seem to indicate that they are indeed resonance destabilized.



W. Washburn
R. Bergman

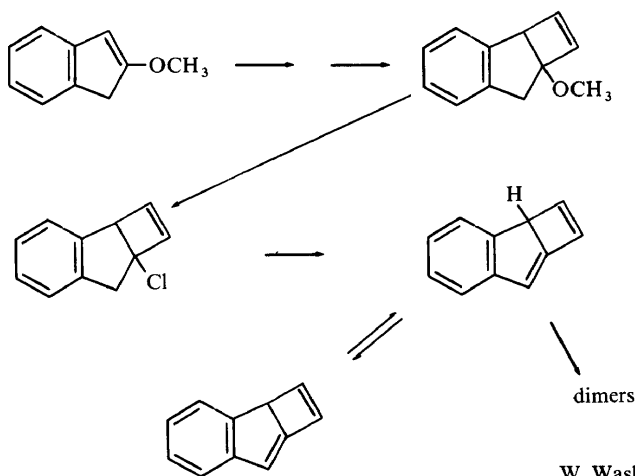
The first one²¹ is indicated above and is concerned with the properties of the [3,2,0]bicycloheptatrienyl anion. This very reactive species was prepared by the sequence indicated. The parent hydrocarbon, the bicycloheptatriene, is extremely reactive in solution and forms two dimers of the structure shown below. However, it is possible to carry out equilibrium studies on the acidity of this hydrocarbon and these indicate that it has a pK_a of approximately 29. We have determined that cyclopentadiene itself has a pK_a of a little over 18 in our system, so the bicycloheptatriene is 11 pK units less acidic. Of course, it contains a cyclopentadiene ring, but production of the anion results in a species which has a number of cyclobutadiene resonance forms. One way to look at this is that the starting hydrocarbon has no unusual conjugation properties but the product anion is a cyclopentadienyl anion system destabilized by some contribution from the antiaromaticity of cyclobutadiene. Since 11 pK units correspond to over 15 kcal/mole, a substantial destabilization has been detected. Although some of this might be the result

of increased strain in the anion, it seems likely that a substantial portion of it is due to the cyclobutadiene conjugation. Since only some of the resonance forms of the anion have a cyclobutadiene ring in them, this seems to indicate that the cyclobutadiene full antiaromatic destabilization would be quite high, possibly of the order of 20 kcal/mole.



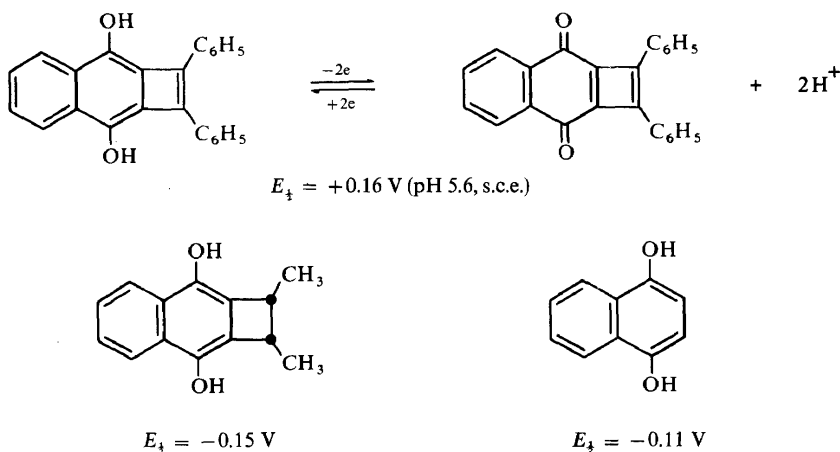
M. P. Cava, K. Narasimhan, W. Zieger, L. J. Radonovich and M. D. Glick, *J. Am. Chem. Soc.* **91**, 2379 (1969)

Other derivatives of this interesting bicyclic anion have been described more recently. Thus, Cava²² has prepared the anion shown above, and we have detected the alternative benzo derivative shown below. However, quantitative studies on these species do not yet add anything more to our understanding of the balance between conjugation and strain energy in determining the stability of the anion.



We felt it was quite important to find a system in which the electronic interactions in cyclobutadiene could be detected in the absence of any appreciable change in strain, so we undertook an examination²⁴ of the electrochemical oxidation system shown next. The hydroquinone at the top left is a cyclobutadiene derivative, but the cyclobutadiene contribution to the hybrid structure is quite small. In a naphthalene system the β - β' bond order is less than one-half, so the cyclobutadienonaphthohydroquinone is less than 50 per cent a cyclobutadiene system. On the other hand, in the naphthoquinone on the upper right the bond order in the four-membered ring is now very high, approximately one, so that this is essentially a full cyclobutadiene ring. Thus, the net result of the oxidation of the hydroquinone

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is to generate greatly increased cyclobutadiene character, and if this is a higher energy situation, it should be reflected in the oxidation potentials of this reaction.

Fortunately, there are almost no geometric changes involved since fundamentally this amounts to an electron reorganization and the removal of two remote hydrogens. There are the same number of trigonal carbons in the four-membered ring on both sides of the equation, and only very small changes in bond-angle are expected. Studies on a variety of quinone derivatives with small fused rings do indicate that steric effects in these systems from angle strain are very small²⁵, much smaller than the sorts of energies we will be talking about momentarily. For our model compound we used the substance on the bottom left, a cyclobutene rather than cyclobutadiene derivative. This should mirror most of whatever strain effects there are in the top equation, and in reality it turns out that the bottom compound has an oxidation potential slightly lower than that of simple naphthohydroquinone itself, so the strain effects turn out to be quite small. The observation is that it is approximately 0.3 V more difficult to oxidize the top hydroquinone than the bottom one, which corresponds to 14.2 kcal/mole by which the top process is more difficult than oxidation of the bottom compound.

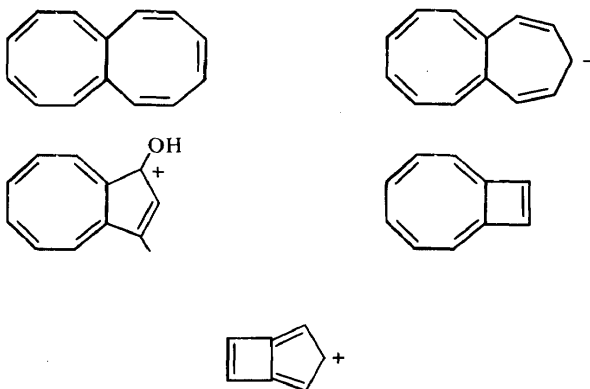
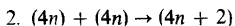
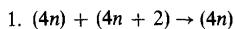
We have also prepared the dianions corresponding to the cyclobutadienonaphthohydroquinone and to simple naphthohydroquinone itself and looked at the oxidation, which in this case turns out to be two sequential one-electron oxidation steps. In this latter case there is a 16 kcal/mole greater energy requirement for the oxidation which produces a cyclobutadiene ring. Again, in this case small strain and substituent effects must be playing some role, but the bulk of the effect is certainly a reflection of the high energy of a cyclobutadiene ring. As in our studies on bicycloheptadienyl anion, only part of the entire antiaromaticity of cyclobutadiene is being observed in this case, since the starting material has a certain amount of cyclobutadiene character as well. This study also seems to suggest that the antiaromaticity in the cyclobutadiene system may be of the order of 20 kcal/mole of destabilization.

We have been discussing systems in which a cyclobutadiene ring is fused to an aromatic ring, such as a benzene or cyclopentadienyl anion system. As indicated below, in such systems the overall result is still a system with $4n$ π electrons, so it still retains antiaromaticity. There is a theoretically interesting class of substances in which two antiaromatic rings are fused together and the result, as indicated below would be conversion into an overall system which has $4n + 2$ π electrons and which might be aromatic. There is no time to discuss the history of this class of substances, but a number of studies have been carried out by us and by others in the field, and the result so far is still ambiguous. No strikingly stabilized substances have been prepared but there are some indications that these systems may be more stable than simple unfused antiaromatic rings.

In the list of structures below there is one missing which has excited considerable interest, the compound with two cyclobutadienes fused together, which has been given the trivial name butalene. Our work on this substance is still preliminary, and we cannot yet report in full detail on the most interesting question: does the molecule 'notice' the two antiaromatic cyclobutadiene rings, or does it notice the overall aromatic content of six π -electrons? However, it seems virtually certain that we²⁶ have generated butalene in solution.

The synthetic sequence is modelled on van Tamelen's synthesis²⁷ of

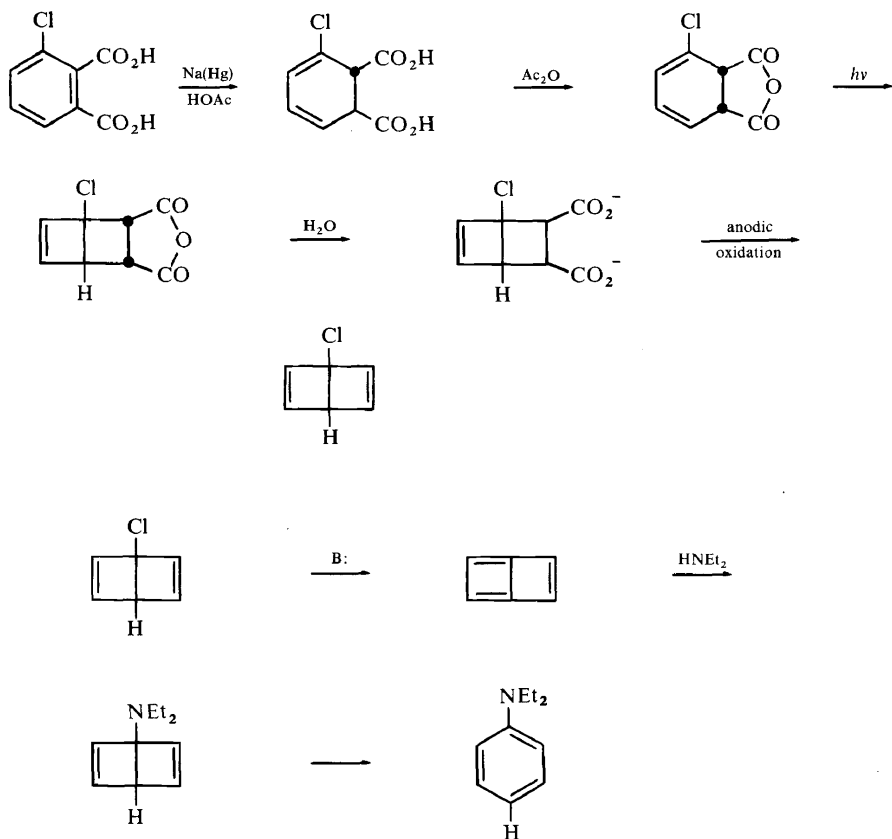
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[2,2,0]bicyclohexadiene (sometimes called 'Dewar benzene'). Under carefully controlled conditions it proves possible to carry out the conversions shown below. The first reduction step leads to some dechlorinations as well, but after that all goes fairly smoothly except for the anodic decarboxylation. This step produces a 50/50 mixture of the 1-chlorobicyclohexadiene shown, together with chlorobenzene. However, we find that the chloro-Dewar-benzene undergoes thermal rearrangement to chlorobenzene quite readily. Thus, further precautions may improve this last step.



We indicate above our evidence that butalene can be formed from this chloro compound. HCl elimination is actually quite difficult, and requires very strong base. This suggests that butalene is not strongly stabilized, although we will need further work to correct for strain effects. However, with LiNEt_2 in HNEt_2 the chloro-Dewar-benzene is converted to diethylaniline. Under our conditions chlorobenzene itself is less reactive, and it is recovered after base treatment of the original mixture.

We believe that the sequence shown above has occurred. If the solvent is DNEt_2 , the product diethylaniline contains deuterium. Our data suggest

that butalene can be generated with difficulty in solution, and that it is extremely reactive. Even at this preliminary stage, it seems clear that butalene is not a strongly stabilized aromatic system.

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