Antiaromaticity of Cyclopropenyl Anions[1]

Ronald Breslow, John Brown, and Joseph J. Gajewski[2]

Contribution from the Department of Chemistry, Columbia University,
New York, New York 10027. Received February 17, 1967

Abstract: The base-catalyzed deuterium exchange of 1,2-diphenyl-3-benzoylcyclopropene (4) is ~6000 times slower than that of the corresponding cyclopropane 5. The effect is reflected in $\Delta H^{\pm}$, which is 6 kcal/mole higher for 4. A smaller effect, but in the same direction, is also observed in the comparison of base-catalyzed exchange of 1,2-diphenyl-3-benzenesulfonylcyclopropene (8) with the corresponding cyclopropane 10. Although Hückel MO calculations do not explain the observed effects, PPP–SCF calculations suggest that they could be due to conjugative destabilization in the cyclopropenyl anion derivatives. The possibility that various types of steric effects could play a role is also considered.

Aromaticity has been defined in many ways.[3] The earliest definitions focused attention on the kinetic stability of aromatic compounds, or on special types of reactivity. More recently a thermodynamic criterion has been applied, according to which cyclic conjugated systems are considered aromatic if cyclic delocalization of electrons makes a considerable negative contribution to their heat of formation. This is of course an idealized definition, and considerable controversy exists about the magnitude of this contribution to the energy of real molecules, such as benzene. By this definition of aromaticity, an opposite phenomenon can be imagined in which cyclic delocalization of electrons is destabilizing. Such a phenomenon could be called "antiaromaticity;"[4] an antiaromatic compound would be one in which resonance led to an increase in energy.

Sometimes aromaticity is defined in terms of the magnetic anisotropy which can be induced in planar π-electron systems, and which can be detected by nmr or magnetic susceptibility measurements.[5] Antiaromaticity could then be defined in magnetic terms, and Pople and Untch have pointed out[6] that the ring current induced in ring systems with $4n$ π electrons should cause nmr shifts in an opposite direction from those observed for aromatic $4n + 2$ π-electron systems. Such an effect has recently been observed[6,7] for some annulenes. In the present paper we wish to focus on the thermodynamic definitions of aromaticity and antiaromaticity.

The long-standing evidence for the instability of cyclobutadiene and of its various derivatives certainly shows that it is not an aromatic system, but does not distinguish between a simple lack of resonance stabilization and an actual resonance destabilization. Some evidence for the latter phenomenon is found in the observation by Blomquist and Meinwald[8] that a dimethyl-

enecyclobutene (1) fails to undergo Diels–Alder addition (to produce a cyclobutadiene) under conditions in which the related dimethylenecyclobutane reacts (to produce a cyclobutene). The chief ambiguity here is the possibility that the unreactivity is due to resonance stabilization of the starting dimethylenecyclobutene rather than conjugative destabilization of the cyclobutadienoid transition state. Other evidence of this type includes the failure of a fluorocyclobutene anion (2) to lose fluoride ion although the corresponding cyclobutane undergoes facile elimination.[9]
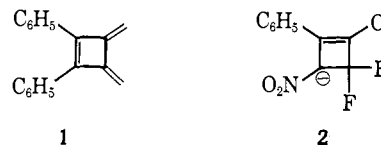
Considering aromaticity as the special stability associated with *cyclic* conjugated systems, with the linear systems taken as normal, antiaromaticity might also be defined as decreased stabilization in cyclic compared with linear conjugated systems.[10] Then the "resonance destabilization" is not absolute, but is relative to the stabilization in linear systems. The two definitions are almost equivalent for neutral polyolefins, since linear polyenes have little resonance energy. However, open-chain conjugated radicals or ions have appreciable stabilization by electron delocalization, and for such systems the two definitions of antiaromaticity (and aromaticity) differ considerably.

By a simple Hückel calculation, for instance, the cyclopropenyl anion is predicted to have $DE = 0$. This is a prediction of simple nonaromaticity on an absolute scale, but considering it relative to open-chain allyl anion (predicted $DE = 0.83\beta$), the cyclopropenyl anion is antiaromatic, since the change from linear to cyclic conjugation results in a decrease in conjugative stabilization. If one compares cyclic with open-chain compounds it seems probable that cyclopentadienyl cation is antiaromatic; the double bonds stabilize the cation, but by less than in linear pentadienyl cation. The most relevant evidence is the fact[11] that 9-phenylfluorenyl cation has a pK_{R^+} of -10.8 compared with a pK_{R^-} or -6.60 for triphenylmethyl cation. The greater planarity in the fluorenyl

(1) Support of this work by the National Science Foundation is gratefully acknowledged. Some of this work was reported at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965.

(2) National Science Foundation Postdoctoral Fellow, 1965–1966.

(3) For reviews, cf. (a) R. Breslow, Chem. Eng. News, 90 (June 28, 1965); (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(4) Reference 3a and earlier lectures; M. Dewar, Advan. Chem. Phys., 8, 121 (1965).

(5) E.g., L. Jackman, F. Sondheimer, Y. Amiel, D. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. Bothner-By, J. Am. Chem. Soc., 84, 4307 (1962).

(6) J. A. Pople and K. G. Untch, ibid., 88, 4811 (1966).

(7) G. Schröder and J. F. Oth, Tetrahedron Letters, 4083 (1966).

(8) A. Blomquist and Y. Meinwald, J. Am. Chem. Soc., 81, 667 (1959).

(9) R. Breslow, D. Kivelevich, M. Mitchell, W. Fabian, and K. Wendel, ibid., 87, 5132 (1965).

(10) R. Breslow and E. Mohacsi, ibid., 85, 431 (1963).

(11) R. Breslow and H. W. Chang, ibid., 83, 3727 (1961).

cation should make it more stable, and its instability probably reflects antiaromaticity in the central cyclopentadienyl cation ring.

We have reported elsewhere[12] evidence that triphenylcyclopropenyl anion is quite unstable. However, in this case no reasonable model was available for the steric factors which play a role, along with conjugative interaction, in determining stability. Perhaps more striking was our early observation[13] that the enolate of diphenylcyclopropenecarboxylic ester (3) forms more slowly than that of the corresponding cyclopropane ester, despite the considerably greater formal conjugation in the enolate from the cyclopropene. In this paper we wish to report further studies of such enolates.

C_6H_5 C_6H_5

H CO_2-t-Bu

3
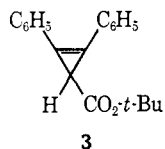
Results

Benzoylcyclopropenes and -cyclopropanes. Various 3-benzoylcyclopropenes and -cyclopropanes were synthesized by obvious procedures (see Experimental Section), and the kinetics of base-catalyzed exchange of these derivatives were determined. Thus, 1,2-diphenyl-3-benzoylcyclopropene (4) was available[14,15] from either the reaction of diphenylcadmium and 1,2-diphenyl-3-cyclopropenecarboxylic acid chloride or that of phenyllithium and 1,2-diphenyl-3-cyclopropenecarboxylic acid.

C_6H_5 H O
C_6H_5 C_6H_5

C_6H_5 C_6H_5 H
C_6H_5 =O
C_6H_5

4   **5**
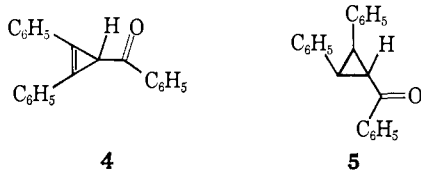
The kinetics of exchange of **4** were determined at various temperatures with potassium ethoxide (0.84 N) in 50:50 (by volume) ethanol-O-d-dimethoxyethane mixtures, the ether solvent being necessary to keep the ketone in solution. The ampoule technique was employed, and the deuterium content of the ketone was determined by mass spectrometry. In all cases the exchanges were carried to at least 60% completion, and the pseudo-first-order rate constants and activation parameters were determined (Table I).

For comparison purposes, the kinetics of exchange of cis-2,3-diphenyl-trans-1-benzoylcyclopropane (**5**) were determined using the same base–solvent system (i.e., the same batches) as used with the unsaturated ketone **4**. The saturated ketone was prepared by catalytic reduction of **4** followed by epimerization of the all-cis compound in refluxing potassium ethoxide–ethanol solution. Since the saturated ketone **5** underwent exchange very rapidly in ethoxide solution, it was dissolved in

(12) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).
(13) R. Breslow and M. Battiste, *Chem. Ind.* (London), 1143 (1958).
(14) *Cf.* Columbia University theses of (a) M. Battiste, 1960, and (b) R. Boikess, 1961.
(15) This compound has also been prepared by I. Moritani and N. Obata, *Tetrahedron Letters*, 2817 (1965).

Table I. Pseudo-First-Order Rate Constants and Activation Parameters for the Exchange of 1,2-Diphenyl-3-benzoylcyclopropene (4) and cis-2,3-Diphenyl-trans-1-benzoylcyclopropane (5) in 0.84 N Potassium Ethoxide in Ethanol-O-d-Dimethoxyethane, 50:50 by Volume

Compd	Temp, °C	k, sec^{-1} [a]	No. pts[b]	Activation parameters
4	100.83	$1.22 \times 10^{-4} \pm 2.3\%$	3	
4	87.95	$3.65 \times 10^{-5} \pm 1.5\%$	3	E(act.) = 26.01 $\pm$ 0.36 kcal
4	74.64	$8.91 \times 10^{-6} \pm 2.6\%$	3	Log A = 11.2 $\pm$ 0.2
5	31.46	$2.39 \times 10^{-4} \pm 1.3\%$	3	
5	22.50	$8.47 \times 10^{-5} \pm 3.4\%$	3	E(act.) = 20.28 $\pm$ 0.25 kcal
5	3.60	$8.39 \times 10^{-6} \pm 2.9\%$	3	Log A = 10.8 $\pm$ 0.2

[a] Deuterium analyses by mass spectrometry. Rms deviation from least-squares analysis indicated. [b] Includes a point at time zero where the per cent exchange was taken to be zero.

dimethoxyethane under nitrogen, the serum-capped flask and solution being allowed to equilibrate in a thermostat, and the appropriate volume of precooked base injected *via* syringe to begin the run. Again mass spectrometry was used to analyze the deuterium content of the ketone. The reactions were carried to at least 45% exchange giving rate constants and activation parameters which are also listed in Table I.

Besides rate comparisons between the diphenyl-substituted materials, the rate of loss of deuterium from 1-deuterio-1-benzoylcyclopropane (**6-d**) was preliminarily determined in 0.92 N potassium methoxide-methanol solution using quantitative infrared spectroscopy for the deuterium analyses; the rate of exchange of 1-deuterio-cis-2,3-diphenyl-trans-1-benzoylcyclopropane (**5-d**) was also determined under the same conditions for comparison purposes (under these conditions, $t_{1/2}$ for **4-d** at 60° was ~80 days). These rate constants are listed in Table II along with those for

Table II. Pseudo-First-Order Rate Constants for Deuterium Exchange of Various α-Deuteriobenzoylcyclopropenes and -cyclopropanes

Compd	Temp, °C	k, sec^{-1} [a]	No. pts	Conditions
4-d	70	3.19×10^{-5}	11	0.5 N potassium t-
4-d	80	7.96×10^{-5} [b]	9	butoxide in t-butyl
7-d	70	6.48×10^{-5}	7	alcohol
7-d	80	1.58×10^{-4} [c]	7	
5-d	40	1.44×10^{-5}	8	0.92 N potassium meth-
5-d	40	1.43×10^{-5}	8	oxide in methanol
6-d	40	4.20×10^{-6}	7	
6-d	60	4.80×10^{-5}	8	

[a] Deuterium analyses were performed by quantitative infrared spectroscopy. The estimated error in the rate constants is $\pm 10\%$. [b] E(act.) = 22.05 kcal; log A = 9.45. [c] E(act.) = 21.55 kcal; log A = 9.45.
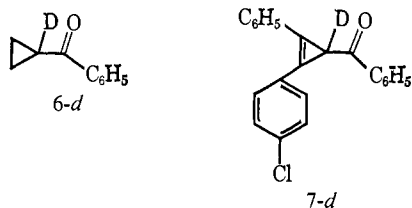
exchange of 3-deuterio-1,2-diphenyl-3-benzoylcyclopropene (**4-d**) and 3-deuterio-1-phenyl-2-(p-chlorophenyl)-3-benzoylcyclopropene (**7-d**) in potassium t-butoxide-t-butyl alcohol solution.

6-d

7-d

Diphenylbenzenesulfonylcyclopropenes and Related Sulfones.

1,2-Diphenyl-3-benzenesulfonylcyclopropene (8) was available from the reaction of 1,2-diphenylcyclopropenium fluoroborate or perchlorate with sodium benzenesulfinate in dimethylformamide. Hydrogenation of the cyclopropene gave cis-2,3-diphenyl-cis-1-benzenesulfonylcyclopropane (9) which was epimerized to cis-2,3-diphenyl-trans-1-benzenesulfonylcyclopropane (10).

8

9   10
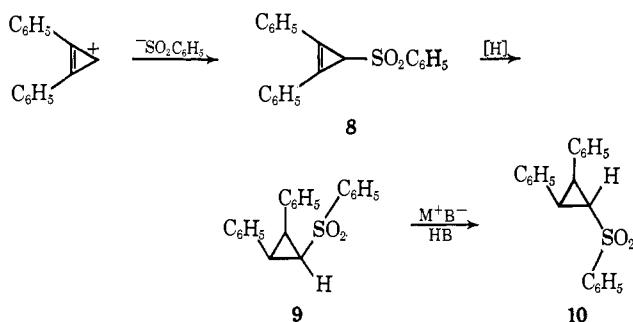
The kinetics of base-catalyzed deuterium exchange of 8 were determined as described above for the benzoyl compounds, 4 and 5. However, the mass spectrum of 8 did not have a parent peak even at low voltages so the deuterium analyses were performed on a fragment having m/e 191, this presumably being the diphenylcyclopropenium cation. A sample of 8, which according to nmr contained 50 ± 10% deuterium at C-3, had 43% of one deuterium atom as determined from the isotope distribution in the 190–195-m/e region of its mass spectrum. Thus, the use of this fragment for the analyses appears to be justified. Mass spectrometric deuterium analysis was not possible in the case of the saturated sulfone 10, since it gave no parent peak or any usable fragment. Therefore, the analyses were performed by combustion of purified, reisolated samples. The rate constants and pertinent data on the exchanges of the benzenesulfonyl derivatives are given in Table III. In addition to these data, extensive preliminary runs were performed not only with the diphenylbenzenesulfonylcyclopropene (8) and the cyclopropane (10) but also with cyclopropyl phenyl sulfone (11) and isopropyl phenyl sulfone (12) using quantitative infrared spectroscopy for the deuterium analyses. The results of these investigations are given in Table IV.
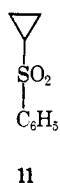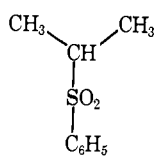
11   12

Molecular Orbital Calculations.

Hückel calculations neglecting overlap were made with a standard matrix

Table III. Pseudo-First-Order Rate Constants and Activation Parameters for Exchange of 1,2-Diphenyl-3-benzenesulfonylcyclopropene (8) and cis-2,3-Diphenyl-trans-1-benzenesulfonylcyclopropane (10) in 0.84 N Potassium Ethoxide in Ethanol-O-d-Dimethoxyethane, 50:50 by Volume

| Compd	Temp, °C	k, sec^{-1}	No. pts	Activation parameters
8	31.46	5.63×10^{-6} [a]	2[b]	E(act.) = 27.58 ± 0.26 kcal
8	56.40	1.56×10^{-4} ± 1.9%[a]	3[b]	Log A = 14.0 ± 0.02
8	63.33	3.78×10^{-3} ± 0.4%[a]	3[b]	
10	0.0	3.34×10^{-6} [c]	2	E(act.) = 24.4 ± 0.7 kcal
10	3.6	6.65×10^{-6} [c]	2	Log A = 14.9 ± 0.54
10	13.23	2.86×10^{-4} [c]	2[b]	
10	22.50	1.03×10^{-3} [c]	3[b]	

[a] Deuterium analyses by mass spectrometry. Rms deviation from least-squares analyses indicated. [b] Includes a point at time zero where the per cent exchange was taken to be zero. [c] Deuterium analyses by combustion, performed by Dr. J. Nemeth.

Table IV. Pseudo-First-Order Rate Constants for Exchange of Various Phenyl Sulfones Followed by Quantitative Infrared Spectroscopy

Compd	Temp, °C	k, sec^{-1}	No. pts	Conditions
8	40	7.7×10^{-5} [a]	7	20% diglyme–80%
8	55	4.13×10^{-4} [a]	6	0.48 N KO-i-Pr–
8	20	6.76×10^{-6}	Extrapolated	i-PrOD
11	20	6.5×10^{-4}	7	
11	20	5.7×10^{-5}	8	40% diglyme–
10	20	1.4×10^{-3}	6	60% 1.025 N KOEt-EtOD
10	20	5.4×10^{-5}	6	20% diglyme–80% 0.48 N KO-i-Pr– i-PrOD

[a] E(act.) = 23.0 kcal; log A = 11.88.

diagonalization routine. All resonance integrals including that between carbon and oxygen were set equal to β and the Coulomb integrals were set equal to α except at oxygen where it was taken to be $\alpha + \beta$ (i.e., $h_0 = 1$).[16] By this method benzoyldiphenylcyclopropenyl anion (13) was calculated to have 0.812β more resonance stabilization than its isolated components, phenacyl anion and stilbene. By the Hückel method 13 and similar cyclopropene enolates are not predicted to be antiaromatic relative to isolated olefin and enolate systems; indeed, benzoylcyclopropenyl anion has 0.206β more resonance stabilization than an open-chain analog, α-benzoylallyl anion. However, the Hückel method notoriously overemphasizes charge
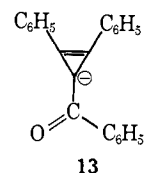

13

separation, and that is the problem here. The charge densities from Hückel calculations on 13 and related species show positively charged cyclopropenyl rings,

(16) Reference 3b, p 135.

and negative charge on both the oxygen and carbon of the carbonyl group; these cyclopropenyl anions are being calculated as cyclopropenyl *cations*.

The Pariser–Parr–Pople self-consistent field (PPP–SCF) method[17] was also applied; in this method the Hamiltonian takes account of electrostatic interaction and avoids the previous difficulty. The iterative program[18] used did not converge to self-consistent solutions for phenylated molecules such as **13**, so calculations were performed for simple cyclopropenyl enolate **15**, taking all distances as 1.40 A and the angles as expected (60 and 120°). With standard parameters, these calculations predict a loss of 0.341 ev of π-

14   15
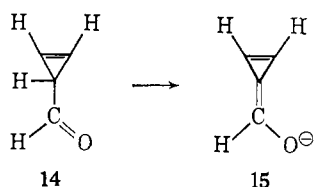
electron stability on ionization of **14** if the C=C distance in **14** is taken as 1.34 A, but a gain of 0.759 ev on ionization to **15** if the C=C distance in **14** is assigned a value of 1.40 A, all relative to the cyclopropane derivatives. Thus antiaromaticity is predicted in **15** on an absolute basis, using the assumed changes in bond lengths. On a more restricted basis antiaromaticity is fully predicted, since **15** is calculated to be 2.08 ev less stable than **16**, the open-chain analog.

16
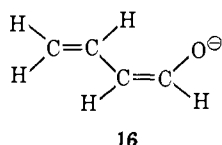
Discussion

The data in Tables I and II indicate that base-catalyzed ionization of the cyclopropenyl ketone **4** is approximately 6000 times slower than that of the saturated analog **5**; the difference is reflected in the activation energy (enthalpy) rather than the frequency factor (entropy). Since for carbon acids with pK_a between 5 and 35 the Brønsted coefficient is generally[19] of the order of 0.5, this rate difference corresponds to a pK_a difference of over 7 units. On a simple classical basis, of course, the extra double bond in **4** should acidify it, both by an inductive effect and also by conjugation of the anion with the double bond and through it with the two phenyl groups. Since the experimental result is strikingly in the other direction, some other effects must be considered.

The most interesting possibility is conjugative destabilization, "antiaromaticity." As we have pointed out above, calculations indicate that cyclopropenyl anion derivatives should be less stabilized than their open-chain allylic analogs, and our PPP–SCF calculation on a cyclopropenyl enolate indicates that it should

be destabilized even relative to a cyclopropane derivative. On a classical basis the idea that extra conjugation could be destabilizing is remarkable and should not be accepted without good evidence. We believe that the observed lower acidity of **4** relative to **5** is in fact probably due to conjugative destabilization in **13**, the enolate of **4**, although such an effect is quantitatively predicted only with PPP–SCF calculations using a specific model. However, several varieties of steric effects must also be considered.

One possibility is I strain,[20] the increased formal strain associated with a change from tetragonal to trigonal hybridization at a small-ring carbon. The comparison between a cyclopropane and a cyclopropene derivative was selected to minimize this effect; the two have roughly similar geometries, although I strain could be more important in the cyclopropene, with a 50°[21] ring angle at C-3, than in a cyclopropane, with a 60° angle. However, the I-strain effect is not dominant in benzoylcyclopropane, whose base-catalyzed ionization rate[22] is 14 times that of unstrained 2-benzoylpropane in spite of a 49.5° increase in angle strain. Apparently the I-strain effect which appears in acid-catalyzed enolizations of cyclopropyl ketones[22] is dominated in the basic ionizations by the increased acidity of the C–H bond induced by rehybridization in the small ring. It seems unlikely that this trend would be so strikingly reversed in the cyclopropene with an additional 10° strain increase. A simple calculation, using the standard[23] 17.5 cal/mole deg² which grossly overestimates[24] the strain energy of cyclopropane, indicates an I-strain effect of 19.5 kcal/mole for cyclopropyl anion and only 3.5 kcal/mole additional for cyclopropenyl anion. The possibility exists, of course, that the introduction of unsaturation into a cyclopropyl anion produces a sudden large strain effect which neither this rough type of calculation nor the simple extrapolation suggests.

Another possibility is that eclipsing interactions in a cyclopropane make it more acidic. On ionization of
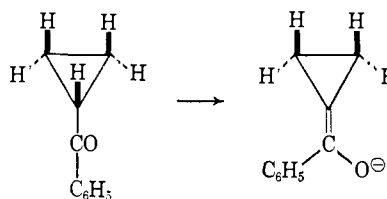
benzoylcyclopropane the eclipsing of the acidic proton with two neighboring C–H bonds and of the benzoyl group with two other protons are both relieved, and this effect might be absent in the cyclopropene. However, such an effect should generally cause results opposite to I-strain effects in cyclopropanes. It would operate to promote acid-catalyzed enolizations of cyclopropyl ketones (which are, in fact,[22] slow), and to oppose hydration of cyclopropanone (which is,

(17) *Cf.* R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963. The parameters used were as follows: $W_P{}^C = -11.42$, $W_P{}^O = -17.91$, $\beta_{CC} = -2.39$, $\beta_{CO} = -2.10$, $\gamma^{CC} = 10.53 - 2.65r + 0.2157r^2$, $\gamma^{OO} = 14.79$, $\gamma_{C-O} = 12.80 - 3.884r + 0.39r^2$.

(18) The program was a modified version of one written by E. Evleth.

(19) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 9–14.

(20) H. C. Brown, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **14**, 83 (1953).

(21) P. Kasai, R. Myers, D. Eggers, Jr., and K. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959); J. Dunitz, H. Feldman, and V. Schomaker, *ibid.*, **20**, 1708 (1952).

(22) H. Shechter, M. Collis, R. Dessy, Y. Okuzumi, and A. Chen, *J. Am. Chem. Soc.*, **84**, 2905 (1962).

(23) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12.

(24) Reference 23, p 534.

in fact,[25] strongly hydrated), for instance. Furthermore, it should show up in a heat of formation for cyclopropane even higher than that calculated on the basis of angle-strain considerations alone, whereas the experimental heat of formation is lower.[24] Thus eclipsing strain in cyclopropane has not generally played a strong role in small-ring chemistry; the reason may well be that the eclipsing strains are small since both the H–H distance and the H–C–C–H angle are larger[26] than those in ethane. The cases cited all involve a multitude of factors, though, and eclipsing strain could be playing some role in our comparison of 4 and 5.

Yet another possibility involves eclipsing in the enolate ion of benzoyldiphenylcyclopropene (13). Models show such an interaction if all the groups are planar, although it is easily relieved by a slight rotation of the phenyls. However, we find in preliminary experiments that 1,2-dimethyl-3-benzoylcyclopropene (17) is even less acidic than is the diphenyl compound; the eclipsing effect in the enolate ion of 17 should be much smaller than that in the diphenyl compound, so such eclipsing is apparently not a major factor in the rate.

Finally, it should be noted that the introduction of further unsaturation into a cyclopropyl enolate does not always cause destabilization. Bottini has found[27] that base-catalyzed exchange in methylenecyclopropyl-carboxylate (18) is ~10⁵ faster than in cyclopropyl-carboxylate (19). The 8-kcal/mole lower $\Delta H^{\ddagger}$ for 18 shows that allylic conjugation strongly stabilizes the cyclopropyl enolate. The contrast with our case is particularly striking, but consistent with the theoretical prediction that a cyclopropenyl anion should be destabilized relative to an allyl anion. Of course, the steric problems we cited for our comparison of 4 with 5 should also have come to some extent into the comparison of 18 and 19. In this latter case, however, the normal conjugative and inductive effect of a double bond predominated.
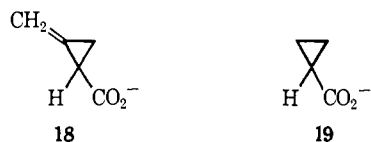
A similar but smaller effect is seen in the sulfones (Table III). Thus the ionization of the cyclopropenyl sulfone 8 is 10³ slower than that of the corresponding cyclopropyl compound 10 under the same conditions. The difference is mostly found in a difference of 3 kcal/mole in the activation energies, but some is also in the $\Delta\Delta S^{\ddagger}$. The data in Table IV show that the inductive effect of phenyls on the cyclopropyl anion is somewhat larger here than was seen for the ketones, suggesting more carbanion character in the transition state. The cyclopropyl sulfone 11 ionizes about 12 times faster than the open-chain sulfone 12, showing here as well that the I strain effect is not dominant. Destabiliza-

tion by the extra double bond has thus been observed for cyclopropenyl anions bearing ester,[13] ketone, and sulfone functions.

Clearly a proposition such as conjugative destabilization will require strong experimental support before it can be accepted without reservations. However, at the present time it seems that this phenomenon is the best explanation of the instability of cyclopropenyl anion derivatives relative both to a methylenecyclopropane anion (the allylic analog) and to the simple cyclopropyl anion. Thus the cyclopropenyl anion appears to be antiaromatic by both of our definitions.

Experimental Section[28]

1,2-Diphenyl-3-benzoylcyclopropene (4).[14,15] To 7.8 g (0.032 mole) of 1,2-diphenyl-3-cyclopropenecarboxylic acid[13] was added 25 ml of oxalyl chloride. The resulting mixture was allowed to stand at room temperature in a stoppered flask for 3 hr after which time the excess oxalyl chloride was removed under vacuum, and the residue was recrystallized from hexane giving 7.5 g (89% yield) of an acid chloride, mp 111°. The acid chloride, 7.5 g, in 70 ml of benzene was added over a period of 5 min to a cooled, stirred mixture of 0.02 m diphenylcadmium in benzene. The mixture was stirred at room temperature overnight, then heated at reflux for 1 hr. After cooling, the reaction mixture was decomposed with dilute hydrochloric acid; the benzene layer was separated, and the aqueous layer extracted twice with a benzene–ether solution. After the combined organic layers were washed with 5% sodium hydroxide solution, dried, and evaporated, a solid residue was obtained which was chromatographed on acid-washed alumina. The fraction, 6 g, which was eluted with 2:1 hexane–methylene chloride, was recrystallized from hexane–chloroform, mp 157.5–159° (lit.[14,15] melting point for 1,2-diphenyl-3-benzoylcyclopropane is 157–158°).

The ketone was also prepared by addition of 2 equiv of phenyllithium in diethyl ether to a rapidly stirred 0° ethereal solution of 1,2-diphenyl-3-cyclopropenecarboxylic acid under nitrogen over a period of 0.5 hr. After an additional 1.5 hr at 0°, a freshly prepared, aqueous, saturated solution of anhydrous sodium sulfate was added, and the resulting yellow solution was filtered, dried over anhydrous sodium sulfate, and evaporated. Chromatography of the residue on basic alumina using 3:1 hexane–methylene chloride for elution followed by recrystallization from ethanol gave a white crystalline solid, mp 156–158°.

Kinetics of Exchange of 1,2-Diphenyl-3-benzoylcyclopropene. Ethanol-O-d was prepared by the method of Streitwieser[29] and was 98.5–99.0% deuterated as determined by integration against ¹³C satellites of the methylene group. The potassium ethoxide solutions were prepared by the addition of freshly cut potassium washed in benzene to the ethanol-O-d under nitrogen. The normality of the base solution was determined by titration with standard acid, and the solution was stored under nitrogen. The normality did not change appreciably over a 4-month period. The dimethoxyethane was distilled from lithium aluminum hydride and was stored under nitrogen over sodium.

A typical kinetic run follows: 0.045 g (0.152 mmole) of 4 was dissolved in 1.0 ml of dimethoxyethane, and 1.0 ml of 0.84 N potassium ethoxide–ethanol-O-d was added at room temperature. The solution was shaken and roughly equal volumes were transferred to two Pyrex tubes. After flushing with nitrogen, the tubes were sealed under a partial vacuum and placed in an oil bath at 100.83 ± 0.10°. Time zero was taken as the time of immersion. After 3660 sec one tube was removed, placed in a beaker of cold water, broken open, diluted with water, and centrifuged. The precipitate was washed once with water and recrystallized once from ethanol giving 9 mg of crystalline solid, mp 156–158°. Mass spectral deuterium analysis indicated 37.5% of one atom d was present. The second tube was removed after 9600 sec, and 8 mg of ketone was recovered having 69.0% of one atom d. Little if any d_2 species were present in these analyses. The rate constant calculated from these two points and a third point at time zero, when it was assumed no deuterium was

(25) N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **88**, 3672 (1966).

(26) Using the electron diffraction data of O. Bastiansen and O. Hassel, *Tidsskr. Kjemi Bergvesen Met.*, **6**, 71 (1946), we calculate a distance of 2.50 A between the eclipsed hydrogens in cyclopropane compared with 2.27 A in eclipsed ethane. This is only a 10% increase, but the repulsion terms may well be very sensitive to the change.

(27) A. T. Bottini and A. J. Davidson, *J. Org. Chem.*, **30**, 3302 (1965).

(28) All melting points are corrected.

(29) A. Streitwieser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

present in the ketone, was 1.22×10^{-4} sec^{-1} $\pm$ 2.3%, correlation coefficient = 0.9997.

Since the recovery of pure ketone was about 40% and the melting point of the residue from the mother liquors melted only 5° lower than starting ketone, there was no reason to suspect that reactions were occurring other than proton removal and deuterium replacement at C-3 of 4. See Table I for a compilation of the rate constants at other temperatures.

cis-2,3-Diphenyl-*trans*-1-benzoylcyclopropane (5). 1,2-Diphenyl-3-benzoylcyclopropene, 0.850 g (0.00288 mole), was dissolved in 300 ml of diethyl ether into which was suspended 0.083 g of 10% palladium-on-carbon catalyst. After the mixture took up 65 ml of hydrogen at room temperature and atmospheric pressure, the rate of uptake decreased, and the reaction was terminated. The ethereal solution was filtered and evaporated giving 0.850 g of a white powder. One recrystallization from hexane gave 0.545 g of white needles, mp 134–136° (lit.[14b] melting point for *cis*-2,3-diphenyl-*cis*-1-benzoylcyclopropane is 133.5–134.2°).

The solid was dissolved in 10 ml of ethanol and to this solution was added 0.4 g of potassium dissolved in 10 ml of ethanol. The resulting solution was heated at reflux for 15 min. After this time the reaction mixture was diluted with an aqueous acetic acid solution and extracted with methylene chloride. The organic extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was recrystallized from hexane giving 0.445 g of white crystals, mp 90–92° (lit.[14b] melting point for *cis*-2,3-diphenyl-*trans*-3-benzoylcyclopropane, 91.2–92.4°, hexane). Recrystallization from methanol gave material, mp 90–92°.

Kinetics of Exchange of *cis*-2,3-Diphenyl-*trans*-1-benzoylcyclopropane. The dimethoxyethane and 0.84 N potassium ethoxide-ethanol-O-*d* solutions were of the same batch described in the kinetic run with the unsaturated material 4. In a typical kinetic run, 0.0361 g (0.121 mmole) of 5 was dissolved in 0.8 ml of dimethoxyethane which had been stored over sodium. The solution was prepared in a tube which was flushed with nitrogen, sealed with a serum cap, and immersed into a thermostat at 31.46°. Then 0.8 ml of the ethoxide-ethanol-O-*d* solution was injected from a calibrated syringe. The tube and contents were shaken vigorously to ensure mixing. Aliquots were removed after 1710 and 4650 sec; each was injected into water, and the resulting mixture was centrifuged, the precipitate washed with water, and the solid recrystallized from methanol giving 13 mg, mp 92–93°, and 4 mg, mp 92–93.5°, from the first and second aliquots, respectively. These samples were analyzed for deuterium *via* mass spectrometry and found to contain 34.5 and 67.2% of one atom *d*, respectively. Calculation of the rate constant, in the manner described above for that of exchange of 4, gave 2.39×10^{-1} sec^{-1} $\pm$ 1.3%, correlation coefficient = 0.99991.

For the kinetic runs at low temperatures, the base solution was precooled to approximately the temperature of the thermostat.

3-Deuterio-1,2-diphenyl-3-benzoylcyclopropene (4-*d*). To 25 ml of ethanol-O-*d* was added 0.4 g (0.001 g-atom) of potassium under nitrogen. To this solution was added 20 ml of diglyme and 2.5 g (0.0084 mole) of 4. The solution was refluxed for 72 hr and cooled; the solid collected was recrystallized from chloroform-hexane, mp 157–158°, in 58% recovery. Infrared examination in CS$_2$ indicated that the material was 85% deuterated by comparison with standard mixtures of deuterated and nondeuterated ketone.

Kinetic Measurements with 3-Deuterio-1,2-diphenyl-3-benzoylcyclopropene. The ketone was powdered and a quantity, 0.080 g (0.00027 mole), was weighed into a 10-ml volumetric flask which was flushed with nitrogen, closed with a serum cap, and evacuated. 1-Butanol, 10 ml, 0.5 N in potassium *t*-butoxide, was added by syringe; the flask was then placed in the thermostat, and the mixture was shaken until the ketone dissolved completely. Aliquots (0.5 ml) were withdrawn and quenched by addition to 1.0 ml of 10% aqueous acetic acid. The mixture was centrifuged and the liquid was removed by pipet. The precipitate was washed with 20% aqueous ethanol and centrifuged and the liquid again removed. After drying *in vacuo*, the solid was dissolved in CS$_2$ and the infrared spectrum recorded between 1300 and 1180 cm^{-1} on a Perkin-Elmer 421 instrument. The peak heights at 1255 (C–O) and 1215 cm^{-1} (C–H) were measured and compared with standard mixtures of deuterated and nondeuterated material. The rate constants for runs at 70 and 80° are given in Table II.

3-Deuterio-1-phenyl-2-*p*-chlorophenyl-3-cyclopropenecarboxylic Acid. *p*-Chlorotolan, 13 g (0.061 mole), was stirred at 130° with 2 g of copper bronze while 20 ml of 75% α-deuterioethyl diazoacetate was added over a period of 4 hr. The cooled product was filtered, dissolved in 3:1 hexane-methylene chloride, and chromato-

graphed on 1 kg of acid-washed alumina. Elution with hexane-methylene chloride gave *p*-chlorotolan, and with increasing amounts of methylene chloride a fraction was obtained which after recrystallization from hexane melted at 95–96°. This 3-deuterio-1-phenyl-2-*p*-chlorophenyl-3-carboethoxycyclopropene, 5.8 g (32% yield), was saponified without further purification.

To 4.1 g of this ester in 50 ml of ethanol was added 5 ml of 60% aqueous potassium hydroxide solution. The resulting solution was heated at reflux for 3 hr and poured into 250 ml of 0.5 N hydrochloric acid solution. Extraction of the aqueous solution with chloroform, drying, and evaporation of the organic solvent under vacuum gave a residue which was recrystallized from acetone. There was obtained 3.3 g of 3-deuterio-1-phenyl-2-*p*-chlorophenyl-3-cyclopropenecarboxylic acid, mp 226–227°. *Anal.* Calcd for C$_{16}$H$_{11.75}$O$_2$Cl: C, 70.65; H, 4.35. Found: C, 70.40; H, 4.35.

3-Deuterio-1-phenyl-2-*p*-chlorophenyl-3-benzoylcyclopropene (7-*d*). To 1.05 g (0.00385 mole) of 3-deuterio-1-2-*p*-chlorophenyl-3-cyclopropenecarboxylic acid suspended in 10 ml of ether was added 10.2 ml of 0.88 N phenyllithium in ether at room temperature over a period of 10 min with stirring. The resulting suspension was stirred for 45 min, poured into cold 2 N hydrochloric acid, and extracted with ether. The ethereal extracts were washed with an aqueous sodium carbonate solution followed by washing with water. The organic solution was dried and evaporated under vacuum giving a semisolid residue which was chromatographed on acid-washed alumina. The fraction eluted with 2.5:1 hexane-methylene chloride was recrystallized from methanol giving 0.552 g (45%) of 3-deuterio-1-phenyl-2-*p*-chlorophenyl-3-benzoylcyclopropene, mp 104.5–106°.

No loss of deuterium during the over-all synthesis was apparent from the infrared spectrum. A small sample of the protium derivative was prepared in a similar fashion; mixtures of the isomers were made for the standard infrared spectra. *Anal.* Calcd for C$_{22}$H$_{15.75}$OCl: C, 79.70; H, 4.70. Found: C, 79.35; H, 4.75.

Kinetic Runs with 3-Deuterio-1-phenyl-2-*p*-chlorophenyl-3-benzoylcyclopropene. Kinetic runs with 7-*d* were carried out in precisely the same way as with 3-deuterio-1,2-diphenyl-3-benzoylcyclopropene. The infrared absorptions were found to be at 1254 (C–D) and 1218 cm^{-1} (C–H). The rate constants at 70 and 80° are listed in Table II.

1-Deuterio-*cis*-2,3-diphenyl-*trans*-1-benzoylcyclopropane (5-*d*). The epimerization of *cis*-2,3-diphenyl-*cis*-1-benzoylcyclopropane to 5 described above was conducted in ethanol-O-*d* giving 1-deuterio-*cis*-2,3-diphenyl-*trans*-3-benzoylcyclopropane, mp 91–93° (hexane). Deuteration was apparently complete since there was no infrared absorption at 1215 cm^{-1} but instead an intense band at 1270 cm^{-1} which was not present in the protium derivative 5.

1-Deuteriobenzoylcyclopropane (6-*d*). Benzoylcyclopropane, bp 100–101° (13 mm), was prepared in 65% yield by the reaction of chlorocarbonylcyclopropane with diphenylcadmium in refluxing benzene. Deuteration was carried out by heating the material at reflux in potassium ethoxide-ethanol-O-*d* solution (0.3 N). The nmr spectrum of the product in carbon tetrachloride showed no resonances between δ 2 and 4. The infrared spectrum in carbon tetrachloride showed an absorption at 1310 cm^{-1} which was as intense as the band at 1220 cm^{-1} in the protium derivative which was no longer present in the deuterated material.

Kinetic Runs with 1-Deuterio-*cis*-2,3-diphenyl-*trans*-1-benzoylcyclopropane and with 1-Deuteriobenzoylcyclopropane. The experimental procedure for the exchange kinetics with 5-*d* followed that for 3-deuterio-1,2-diphenyl-3-benzoylcyclopropene with the exceptions that the base system used was 0.92 N potassium methoxide in methanol, and the peaks being compared in the infrared were at 1270 (C–D) and 1220 cm^{-1} (C–H). The procedure with 1-deuteriobenzoylcyclopropane was the same as that for 1-deuterio-*cis*-2,3-diphenyl-*trans*-1-benzoylcyclopropane with the exception that the aliquots were extracted with carbon tetrachloride. The organic layer was then washed with water twice, dried over molecular sieve pellets, and submitted to infrared examination. The peak heights at 1310 (C–D) and 1220 cm^{-1} (C–H) were compared with standard mixtures. The rate constants are listed in Table II.

1,2-Diphenyl-3-benzenesulfonylcyclopropene (8). To 2.0 g (0.00504 mole) of bis(1,2-diphenylcyclopropenyl) ether suspended in 200 ml of refluxing anhydrous ether was added 25 ml of 10% fluoroboric acid in acetic anhydride. The mixture was heated at reflux for 1 hr and filtered under nitrogen. Washing with ether and transfer to a sample tube under nitrogen gave 2.3 g (82%) of diphenylcyclopropenyl fluoroborate. The fluoroborate, 3.7 g (0.0133 mole), was dissolved in 50 ml of dimethylformamide. To this solution was added 2.5 g (0.0125 mole) of dried sodium benzene-

sulfinate in 50 ml of dimethylformamide over a short period of time. The solution was stirred for 1 hr, diluted with water, and extracted with methylene chloride. After the extract was washed with water and dried, the solvent was removed under vacuum. Recrystallization of the residue from hexane–methylene chloride gave 2.4 g (67% yield) of 1,2-diphenyl-3-benzenesulfonylcyclopropene, mp 139–141°. Its infrared spectrum exhibited absorptions at 1315(s), 1305(sh), 1245(w), and 1150(s) cm⁻¹. Its nmr spectrum (CDCl₃) showed peaks at δ 3.8, singlet (1 H), and 7.5, multiplet (15 H). *Anal.* Calcd for $C_{21}H_{16}O_2S$: C, 75.05; H, 4.85; S, 9.60. Found: C, 75.75; H, 4.85; S, 9.65.

3-Deuterio-1,2-diphenyl-3-benzenesulfonylcyclopropene (8-d). A sample of **8**, 0.10 g, was heated at reflux for 20 min in 2-propanol-O-d, 2 ml, 0.485 N in potassium isopropoxide. After cooling and dilution with water, the reaction mixture was extracted with methylene chloride. The organic solution was dried, the solvent removed, and the semisolid residue recrystallized from hexane giving 0.030 g of 3-deuterio-1,2-diphenyl-3-benzenesulfonylcyclopropene, mp 136–138°, which had no infrared absorption at 1240 cm⁻¹.

Kinetics of Exchange of 1,2-Diphenyl-3-benzenesulfonylcyclopropene in Potassium Ethoxide–Ethanol-O-d and Dimethoxyethane. The base solvent system used in the kinetic determinations with **8** was the same as was used for the exchange of **4** and **5**; *i.e.*, the dimethoxyethane was distilled from lithium aluminum hydride and stored over sodium; the potassium ethoxide–ethanol-O-d solution was 0.84 N, and contained 98.5–99.0% one atom deuterium on the oxygen. The technique employed was that described above for the exchange of **5**. The sulfone, 0.051 g (0.0001535 mole), was dissolved in dimethoxyethane, 1.0 ml, in a serum-capped flask under nitrogen in a thermostat at 56.4 ± 0.1°. Into this solution was injected 1.0 ml of the base solution. Aliquots were removed after 1620 and 3780 sec and quenched in water. After centrifugation and washing with water the residue was recrystallized from methylene chloride–hexane mixtures (in other runs ethanol was the recrystallization solvent). Each aliquot gave 9 mg of a white solid, mp 131–132 and 139–140° for aliquots 1 and 2, respectively.

Deuterium analyses were performed by mass spectrometry; however, since a parent peak was not obtained for the material, the analyses were performed on the foremost fragment, presumably the diphenylcyclopropenium cation, appearing in the region 191 to 195 *m/e*. The per cent d species in the first and second aliquots were 21.6 and 44.6%, respectively, giving a rate constant of 1.56 × 10⁻⁴ sec⁻¹ ± 1.9%, correlation coefficient = 0.9998 when a zero point was included. The rate constants for the other runs are listed in Table III.

Kinetics of Exchange of 8 in Diglyme–Potassium Isopropoxide–2-Propanol-O-d. Sulfone **8**, 0.050 g (0.000151 mole), was dissolved in 1 ml of dry diglyme and held at the bath temperature, and 4 ml of 0.485 N potassium isopropoxide in 2-propanol-O-d (96% O-d by nmr) was added. Aliquots, 0.5 ml, were withdrawn at intervals and quenched in 2 ml of 10% aqueous acetic acid. The resulting suspension was centrifuged; the liquid was removed by decantation, and the residue was dried *in vacuo*. The residue was dissolved in 0.6 ml of carbon disulfide, and the infrared spectrum of this solution and a solution prepared subsequently by diluting to 1 ml were taken between 1350 and 1200 cm⁻¹. The amount of deuterium incorporated was determined by comparing the peak height at 1240 cm⁻¹ with the value obtained from a curve from standard solutions of **8** of varying concentrations. The rate constants determined in this manner are given in Table IV. The order of accuracy of the rate constants is estimated as ±20%.

cis-2,3-Diphenyl-cis-1-benzenesulfonylcyclopropane (9). 1,2-Diphenyl-3-benzenesulfonylcyclopropene, 1.28 g (0.00384 mole), was dissolved in 200 ml of diethyl ether, and 0.10 g of 10% palladium on charcoal was added. The suspension was shaken under hydrogen at atmospheric pressure for 45 min. After this time the mixture was filtered, and the solvent was removed *in vacuo*. The residue was recrystallized from ethanol giving cis-2,3-diphenyl-cis-1-benzenesulfonylcyclopropane, mp 189.5–191°. The infrared spectrum showed absorptions at (CS₂) 1340(s), 1310(sh), 1260(w), 1160(s) cm⁻¹. The nmr spectrum (CDCl₃) showed peaks at δ 3.05, singlet (3 H), and 7.25, singlet (15 H). *Anal.* Calcd for $C_{21}H_{18}O_2S$: C, 75.45; H, 5.45; S, 9.57. Found: C, 75.3; H, 5.55; S, 9.39.

cis-2,3-Diphenyl-trans-1-benzenesulfonylcyclopropane (10). cis-2,3-Diphenyl-cis-1-benzenesulfonylcyclopropane (9), 0.652 g, was heated at reflux for 70 min in ethanol which was 1 N in potassium ethoxide. After this time the reaction mixture was cooled, diluted with methylene chloride, washed with water, and dried. After removal of solvent, the residue was recrystallized from methanol giving cis-2,3-diphenyl-trans-1-benzenesulfonylcyclopropane,

mp 128–129°. The infrared spectrum showed absorptions at 1320(s), 1308(sh), and 1150 cm⁻¹. The nmr spectrum showed peaks at δ 3.20, singlet with some fine structure (3 H), 7.0, multiplet (10 H), 7.6, multiplet (3 H), and 8.1, multiplet (2 H); (DMSO-d₆): doublet, J = 6 cps, 52 cps downfield from DMSO (2 H); triplet, J = 6 cps, 110 cps downfield from DMSO (1 H); singlet, 275 cps downfield from DMSO (10 H); multiplet, 315 cps downfield from DMSO (3 H); and multiplet, 340 cps downfield from DMSO (2 H). *Anal.* Calcd for $C_{21}H_{18}O_2S$: C, 75.45; H, 5.45; S, 9.57. Found: C, 75.48; H, 5.35; S, 9.35.

1-Deuterio-cis-2,3-diphenyl-trans-1-benzenesulfonylcyclopropene (10-d). 1-Deuterio-cis-2,3-diphenyl-trans-1-benzenesulfonylcyclopropene was prepared in the same manner as the protio derivative **10** with the exception that ethanol-O-d was used as the solvent for the epimerization. The triplet in the nmr of **10** 110 cps downfield from DMSO was missing.

Kinetics of Exchange of cis-2,3-Diphenyl-trans-1-benzenesulfonylcyclopropene in Potassium Ethoxide–Ethanol-O-d and Dimethoxyethane. The kinetics of deuterium exchange of cis-2,3-diphenyl-trans-1-benzenesulfonylcyclopropene (**10**) were determined using the same batches of dimethoxyethane and 0.85 N potassium ethoxide in ethanol-O-d as in the runs with **4** and **5**. Thus, 0.060 g (0.000179 mole) of **10** was dissolved in 1.2 ml of dimethoxyethane in a serum-capped flask under nitrogen, in a thermostat at 22.5°. To this solution was added, *via* syringe, 1.2 ml of 0.84 N potassium ethoxide–ethanol-O-d solution which had been equilibrated in the same thermostat. Two aliquots were removed after 510 and 1080 sec and quenched in dilute acetic acid solution. Isolation and recrystallization of the material isolated from the first and second aliquots from methanol gave 18 and 20 mg of **10**, respectively (in separate runs conducted in the same manner the recovered material invariably had mp 128–130°).

Nmr integration of the triplet at 110 cps downfield from DMSO *vs.* the multiplet 340 cps downfield from DMSO indicated that there was 51.3 and 75.6% exchange at C-1 of **10**, respectively, in the first and second aliquots. The anticipated accuracy of the integration was ±5%. The rate constants calculated from these points and a zero point was 1.30 × 10⁻³ sec⁻¹ ± 4.4%, correlation coefficient = 0.999. The rate constants at other temperatures are given in Table III.

Kinetics of Exchange of cis-2,3-Diphenyl-trans-1-benzenesulfonylcyclopropene in Potassium Ethoxide–Ethanol-O-d and Diglyme. The sulfone **10**, 0.097 g (0.00029 mole), was dissolved in 2 ml of diglyme in a 5-ml volumetric flask which was immersed in a thermostat at 20.0°. Potassium ethoxide–ethanol-O-d (1.025 N) was added by syringe to the mark. The solution was shaken in the bath, and aliquots were withdrawn over a 10-min interval and quenched in 10% aqueous acetic acid. Each aliquot was centrifuged and liquid removed by decantation. The residue was dried *in vacuo* and the infrared spectrum recorded between 800 and 1000 cm⁻¹. As the C–H absorption band at 860 cm⁻¹ disappeared, a new vibration at 960 cm⁻¹ characteristic of the C–D compound appeared.

The extent of deuterium incorporation was evaluated from the graph of peak height ratios for standard mixtures. The rate constant is listed in Table IV along with those of other sulfone exchanges.

Phenyl Cyclopropyl Sulfone (11) and Phenyl Isopropyl Sulfone (12). Phenyl isopropyl sulfone and phenyl cyclopropyl sulfone were prepared in a manner similar to that described by Zimmerman and Thyagarajan.[30] The α-deuterio sulfones were prepared by allowing the sulfone to stand for 24 hr in excess 1.025 N potassium ethoxide–ethanol-O-d followed by work-up under neutral conditions. Nmr spectra indicated that phenyl isopropyl sulfone contained 90% of one deuterium atom while the phenyl cyclopropyl sulfone contained 98% of one deuterium atom.

Kinetics of Exchange of Phenyl Cyclopropyl Sulfone and Phenyl Isopropyl Sulfone. Kinetic runs with **11** and **12** were carried out under the conditions noted in Table IV. The following experiment is typical. Phenyl isopropyl sulfone, 0.125 g (0.000727 mole), was dissolved in 2 ml of diglyme at 20° and diluted to 10 ml by addition of a 0.485 N potassium isopropoxide-2-propanol-O-d solution. The solution was shaken, and aliquots were withdrawn at suitable intervals. The aliquot was quenched in a mixture of carbon disulfide (1 ml) and 10% aqueous acetic acid (1 ml). The two layers were thoroughly mixed by pipet, the tube was centrifuged, and the aqueous layer was withdrawn. The organic layer was washed

(30) H. Zimmerman and B. Thyagarajan, *J. Am. Chem. Soc.*, **82**, 2505 (1960).

twice with water by thorough intermixing, then centrifuged, and the aqueous layer was removed by pipet. The carbon disulfide layer was decanted and its infrared spectrum recorded between 900 and 1100 cm^{-1} (C–D band at 920 cm^{-1}; C–H band at 1050 cm^{-1}),

and the deuterium content was obtained by comparison with the infrared spectra of standard mixtures. In phenyl cyclopropyl sulfone the relevant absorption bands were situated at 820 (C–D) and 920 cm^{-1} (C–H).

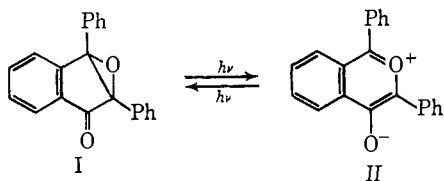# A Color Test for the Selection of Compounds Having Short-Lived Triplet States[1]

Edwin F. Ullman[2] and Wm. A. Henderson, Jr.

Contribution from the Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut. Received December 29, 1966

Abstract: 2,3-Diphenylindenone oxide (I) can be used as a color indicator for the selection of compounds with exceptionally short-lived spectroscopic triplet states. The method is simple and requires no instrumentation or degassing of solutions. The maximum lifetimes for the spectroscopic triplets of molecules that are active in the test are less than about 2.2×10^{-7} sec. Longer lived triplets cannot be detected. Rough estimates of the effective triplet energies have been made for a number of compounds with short-lived triplet states. The data suggest that triplet energy transfer for sensitizer triplets to diphenylacetylene, *cis*-stilbene, and *trans*-stilbene, and possibly other quenchers, may involve concerted geometrical changes (nonvertical excitation). The chemical processes involved in the color test are described.

In the course of our work on the mechanism of the photochemical valence tautomerization of 2,3-diphenylindenone oxide (I) to the bright red diphenylbenzopyrylium oxide II,[3] a simple color test was discovered for the identification of compounds having exceptionally short-lived triplets. Since conventional techniques for studying triplet excited states such as phosphorescence,[4a,b] triplet–triplet absorption,[4c,d] and singlet–triplet absorption induced by oxygen or heavy atom perturbation[4e,f] frequently fail when very short-lived triplet states are encountered, the method provides in some cases the only readily accessible information concerning such triplets. The color test provides a means for establishing limits on triplet lifetimes and can be used to estimate roughly both the triplet energies of conventional sensitizers and the effective triplet energies of certain quenchers.

Description of the Color Test. The indenone oxide I is known to give II both by direct absorption of light and by the use of sensitizers.[3] Only sensitizers with triplet energies greater than 64 kcal effect the reaction.

The product pyrylium oxide II is intensely colored [$\lambda_{max}^{C_6H_6}$ 544 mμ (ϵ 26,750)] and is converted by direct but not by sensitized excitation back to I.[3] On prolonged irradiation of degassed solutions of the indenone oxide I with or without sensitizers ($E_T > 64$ kcal), a steady-state concentration of II is attained. When the solutions are not degassed the concentrations of II that are reached are considerably reduced.

When nondegassed benzene solutions of I that contained sensitizers having $E_T < 64$ kcal were irradiated with 3650-A light no color was formed at all unless the concentration of the sensitizer was insufficient to absorb all the light. However, if the indenone oxide I was allowed to absorb some of the light, the intensity of color due to II rapidly reached a maximum, and then faded gradually as the reservoir of I became depleted by photo- and thermal oxidation of II (*vide infra*). By adjusting the relative concentrations of I and sensitizer the maximum concentration of II that was attained could be reduced to any desired level. In the test to be described, ratios of sensitizer to I were selected so as to obtain just visually observable maximum concentrations of II ([II] ≈ 2–4×10^{-6} M). Generally solutions about 0.5–1.0 $\times$ 10^{-2} M in I were used, and small quantities of the sensitizer were added to the solution until, by trial and error, the desired color intensity was reached. Since on irradiation of a portion (0.5–1.0 ml) of these solutions the maximum color was generally reached within 15 sec, little time was required for this procedure. Continued irradiation of solutions having these low maximum color intensities produced nearly steady-state concentrations of II.

When a compound known to have a short-lived triplet state such as *trans*-stilbene[5] was added to several

(1) A preliminary account of this work has been published: E. F. Ullman, *J. Am. Chem. Soc.*, **86**, 5357 (1964).

(2) To whom inquiries may be addressed: Synvar Research Institute, Palo Alto, Calif.

(3) E. F. Ullman and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **86**, 5050 (1964); **88**, 4942 (1966).

(4) See, *inter alia*: (a) A. Jablonski, *Z. Physik.*, **94**, 38 (1935); (b) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944); (c) G. N. Lewis, D. Lipkin, and T. T. Magel, *ibid.*, **63**, 3005 (1941); (d) G. Porter and M. W. Windsor, *J. Chem. Phys.*, **21**, 2088 (1953); (e) M. Kasha, *ibid.*, **20**, 71 (1952); (f) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(5) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Corwan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).