of benzene (200 ml.), isoprene (75 ml.), 20.2 g. of *t*-butyl perbenzoate and 0.212 g. of cuprous bromide in a 3-neck round-bottom flask was maintained under pressure (200 m.) at 68–70° for 50 hr. As the reaction progressed, the cuprous bromide went into solution and the mixture became bluer. The blue reaction mixture was extracted with dilute HCl and $NaHCO_3$. Benzoic acid did not precipitate on acidification of the $NaHCO_3$ washes. Distillation yielded 18 g. of material boiling at 106–109° (1 mm.), $n^{25}D$ 1.4908–1.4893; 3.6 g. boiling at 113–125° (1 mm.), $n^{25}D$ 1.4932–1.5040; and 2.2 g. of undistilled residue ($n^{25}D$ 1.5172). The distilled fractions each analyzed for the 1:1 adduct *t*-butoxybenzoxypentene (*Anal.* Calcd.: C, 73.25; H, 8.45; ester value, 0.382; bromine no., 61. Found: C, 73.3, 73.3; H, 8.4, 8.3; ester value, 0.394, 0.394; bromine no., 59, 62). The undistilled residue (*Anal.* Found: C, 75.1; H, 8.3) was not polyisoprene since prominent carbonyl bands (5.79, 5.85μ) were present in the infrared spectrum. The infrared spectrum of the lower boiling isomer exhibited distinctive bands at 10.1(m), 10.85(ms), 11.3(ms) and 11.75(m)μ. It was probably a mixture of 4-*t*-butoxy-3-benzoxy-2-methylbutene-1 and 4-*t*-butoxy-3-benzoxy-3-methylbutene-1. The higher boiling component showed bands in the infrared spectrum at 10.6(m) and 11.2(m)μ and is probably a mixture containing the 1,4- and 4,1-adducts of *t*-butyl perbenzoate to isoprene.

Reaction of *t*-Butyl Perbenzoate with Styrene.—In an apparatus similar to the reaction with isoprene were charged 75 g. of *t*-butyl perbenzoate, 180 g. of styrene, 200 ml. of benzene and 0.403 g. of cuprous bromide. The reaction was heated at 85–95° for 30 hours. Benzoic acid (20.8 g.) was extracted from the crude reaction mixture. In addition, 142 g. of polystyrene was precipitated with methanol (*Anal.* Calcd. for C_8H_8: C, 92.26; H, 7.74. Found: C, 91.7; H, 7.7). Approximately 10 g. of viscous oil was also obtained.

A homogeneous mixture of 60 g. of *t*-butyl peracetate, 100 g. of styrene, 10 g. of cupric acetate and 0.3 g. of cuprous chloride in 200 g. of acetonitrile was allowed to react at 75–80° for 24 hours. Analysis indicated the presence of unreacted *t*-butyl peracetate. It was reheated for an additional 24 hours at 80°. The dark green solution was decanted from approximately 20 g. of viscous oil and washed with water, and $NaHCO_3$ after dilution with a mixture of *n*-pentane and ether. After drying and distillation of the solvent, the residue was an orange-colored viscous residue. Infrared analysis indicated the presence of benzoate and *t*-butoxy end groups.

Acknowledgment.—I wish to thank Mr. Fred Rodgers for valuable technical assistance and Dr, Paul Berrigan for helpful suggestions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

The Cyclopropenylcarbinyl Cation, a Non-classical Carbonium Ion

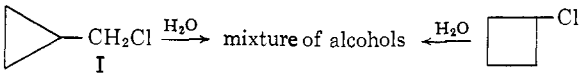
BY RONALD BRESLOW, JOYCE LOCKHART AND AUDREY SMALL

RECEIVED FEBRUARY 15, 1962

The solvolysis of diphenylcyclopropenylcarbinyl tosylate proceeds with ring expansion to diphenylcyclobutenyl cation. The rate of this process shows that a non-classical carbonium ion is involved; rate studies on *p*-anisylphenylcyclopropenylcarbinyl tosylate show that the double bond is not directly involved in the ionization, but that the process is analogous to that in the cyclopropane series, involving delocalization of a ring single bond. From the observation that neither the double bond nor the extra methoxyl group have an appreciable effect on the rate of solvolysis a transition state is deduced which resembles, both geometrically and stereoelectronically, the starting cyclopropenylcarbinyl system. This result is discussed in terms of other evidence on the structure of the bicyclobutonium ion. The expected effect of a methoxyl group on the rate as a function of the geometry of the transition state is treated by use of simple m.o. calculations.

Introduction

In recent years considerable attention has been devoted to the non-classical carbonium ions derived from cyclopropylcarbinyl derivatives. Roberts and Mazur[1] first showed that the solvolysis of cyclopropylcarbinyl chloride (I) is considerably faster than is that of β-methylallyl chloride, the cyclopropane ring being thus even more effective than a double bond in stabilizing the developing carbonium ion. They showed that cyclobutyl chloride (III) is also unexpectedly reactive, and that the same mixture of products is obtained from solvolysis of I or II.

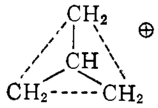


I

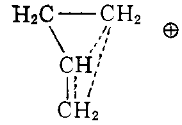
II

Shortly thereafter Bergstrom and Siegel[2] reported observations on the fast solvolysis of cyclopropylcarbinyl benzenesulfonate. To explain these high rates it was clear that transition states resembling non-classical carbonium ions must be invoked, and for a time[1,2] it was considered that a tricyclobutonium ion (III) might be the first intermediate in these solvolyses. However, subsequent studies[3–7] have demonstrated clearly that the incipient ionization of I involves the delocalization of electrons from the C_2–C_3 σ-bond, the intermediate in solvolysis being a bicyclobutonium ion (IV).

It has been found[4,8] that substituents on C-3 and C-4 have little effect on the rate of solvolysis, but that a methyl group on C-2 accelerates it fifty times.[6] Coupled with the evidence that the more stable open chain alcohol is formed to only a slight extent, this suggests that the bicyclobutonium ion has its charge distributed chiefly over C-1 and C-2. Furthermore, substituent effects[5–7] in the solvoly-



III



IV

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(1) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509, 3542 (1951).

(2) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145, 254 (1952).

(3) R. H. Mazur, *et al.*, *ibid.*, **81**, 4390 (1959).

(4) S. Borčić, M. Nikoletić and D. E. Sunko, *ibid.*, **84**, 1615 (1962), and earlier work.

(5) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959).

(6) E. Cox, M. Caserio, M. Silver and J. Roberts, *ibid.*, **83**, 2719 (1961); M. Silver, M. Caserio, H. Rice and J. Roberts, *ibid.*, **83**, 3671 (1961).

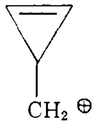
(7) R. A. Sneen and A. L. Baron, *ibid.*, **83**, 614 (1961).

(8) R. A. Sneen, K. M. Lewandowski, I. A. I. Taha and B. R. Smith, *ibid.*, **83**, 4843 (1961).

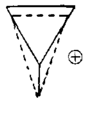
ses show that C-1 bears most of the charge in the transition state.

With the ready availability of some cyclopropenes we considered it of interest to examine the solvolytic behavior of derivatives of the cyclopropenylcarbinyl cation V. On a naive basis this might seem to be a trivial extension of the cyclopropane studies, but the double bond in the cyclopropane system presents a number of new and interesting possibilities.

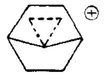
First, a non-classical carbonium ion might be formed in *this* system by interaction of the primary carbonium ion directly with the double bond. Models reveal that a symmetrical structure VI is quite similar in geometry to the 7-norbornenyl cation VII.[9]



V

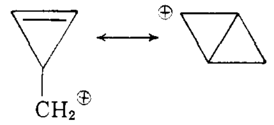


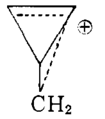
VI



VII

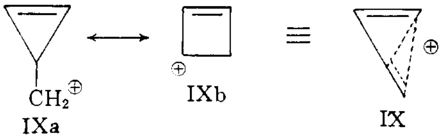
Alternatively, the interaction might involve only one end of the double bond.





VIII

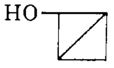
If no direct interaction with the double bond occurs and the cation, by analogy with cyclopropane compounds, simply delocalizes an adjacent ring bond, the resulting unsaturated bicyclobutonium ion IX could still have special properties. If IX has an appreciable contribution of IXb to its structure the double bond could help to delocalize charge further in the developing cyclobutenyl cation.



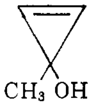
IXa IXb IX

The steric effect should also be important, for Doering and Turner[10] have shown that a cyclopropene has ~20 kcal. of extra strain energy over that in a cyclopropane, while a cyclobutene is only ~3 kcal. more strained than is a cyclobutane. Thus the expansion of a cyclopropenylcarbinyl cation to a cyclobutenyl cation should be about 17 kcal. more favorable than the analogous process in the saturated series, and if much of the ring expansion has occurred at the transition state, the strain relief will provide strong acceleration. Both of these latter factors should also strongly influence the nature of the products. While unsubstituted bicyclobutonium ion partitions with water to give almost equal amounts of cyclopropylcarbinol and cyclobutanol,[3] the partitioning can be changed by substituents.[5,6] In our case allylic conjugation and relief of strain should direct the solvolysis entirely to paths formally involving the cyclobutenyl cation.

It might even be possible that the cyclopropenyl compounds could follow a course drastically different from those already outlined. Conceivably no non-classical cation of any type would be formed. Perhaps more likely, unusual products could result because of the presence of the double bond. Two such products which come to mind are the bicyclobutanol (X) and the cyclopropenol (XI), the latter from hydride migration to form a cyclopropenium ion.



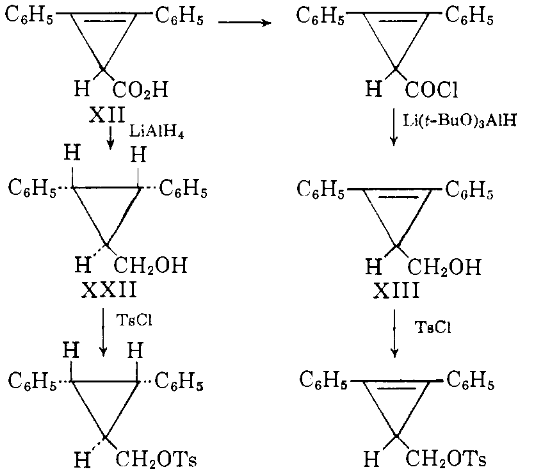
X



XI

Results and Discussion

Reactants and Products.—The availability[11] of Δ^2-2,3-diphenylcyclopropenecarboxylic acid (XII) prompted us to examine the preparation of the primary alcohol XIII and the solvolysis of its tosylate XIV.



XII XXII XIII XIV

The required alcohol was prepared by conversion of the acid to the acid chloride and reduction of the latter with an excess of lithium tri-*t*-butoxyaluminohydride. Direct reduction[12] of the acid XII or of its methyl ester with lithium aluminum hydride affords the saturated alcohol XXII. Interestingly, the unsaturated alcohol XIII is not reduced by lithium aluminum hydride under these conditions, and reduction of the acid chloride with lithium aluminum hydride instead of the milder reducing agent also yields the unsaturated alcohol, contaminated in this case by some further reduction product. Extensive investigation of these reductions has been carried out[12] and will be reported elsewhere. The tosylate XIV was solvolyzed in aqueous aceto-

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(9) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

(10) W. Doering, private communication.

(11) R. Breslow, R. Winter and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

(12) This work was first done by Robert Boikess, Ph.D. Thesis, Columbia Univ., 1961.

nitrile for product studies and the total crude product was isolated.

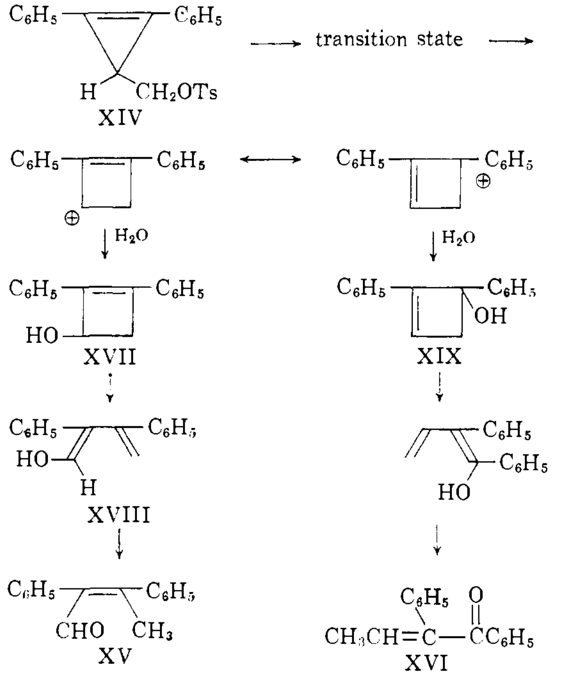
Examination in the infrared showed that a mixture of alcohols and carbonyl compounds was present; this was confirmed by n.m.r. studies (*vide infra*). One of the carbonyl compounds was identified as 2,3-diphenylcrotonaldehyde (XV). This structure follows from the analysis of the pure compound, its infrared spectrum with bands at 1680 (conjugated carbonyl) and 2750 cm.$^{-1}$ (aldehyde CH) and the ultraviolet spectrum at 275 mμ. Most convincing is the n.m.r. spectrum, with an unsplit allylic methyl group at 7.88 τ and an unsplit aldehyde peak at 0.36 τ, in addition to the phenyl hydrogens.

A second carbonyl compound was isolated as an oily chromatographic fraction and obtained as its 2,4-dinitrophenylhydrazone. This material was identified as ethylidenedesoxybenzoin (XVI) on the basis of the analysis of its DNP and the following spectroscopic information. An n.m.r. spectrum of the oily ketone showed that it was substantially pure, and that it had an allylic methyl group (doublet at 8.0 τ) adjacent to a vinyl hydrogen (quartet at 3.4 τ), in addition to the phenyl groups. The dinitrophenylhydrazone had a similar n.m.r. spectrum. The infrared spectrum of the crude ketone had absorption at 1655 cm.$^{-1}$ (conjugated carbonyl).

Examination of the crude solvolysis product mixture by n.m.r. spectroscopy showed that both of these carbonyl compounds are present, but that there is an additional major component which we identify as Δ^2-2,3-diphenylcyclobutenol (XVII) on the following basis. The n.m.r. spectrum shows a broad one-proton singlet at 6.5 τ (O–H), a complex, one-proton quartet at 5.2 τ (C_1—H) and a two-proton multiplet at 7.4 τ (C_4—H_2). The pattern of multiplets at 5.2 and 7.4 τ resembles that of styrene oxide, another ABX system.[13] The ultraviolet spectrum of the crude product had λ_{max} 295 mμ (two authentic diphenylcyclobutenes are reported[14] to have λ_{max} 285 and 288 mμ). When the mixture was warmed on the steam-bath the n.m.r. bands due to this alcohol decreased, and the n.m.r. bands due to diphenylcrotonaldehyde increased (the area due to phenyl hydrogens is used as a standard). At the same time the ultraviolet absorption at 295 mμ disappeared in favor of the aldehyde absorption at 275 mμ.

Quantitatively, again using the phenyl hydrogens as a standard, it is found that 20–25% of the product is the ketone XVI and only 5% of the aldehyde XV is present in the initial extract. However, 50–60% of the cyclobutenol XVII is detectable. After heating, this cyclobutene has disappeared, but somewhat less than half of it has been converted to the aldehyde XV. The amount of the ketone present is unchanged. These observations are easily explained if the enol XVIII which is an intermediate in the formation of the aldehyde reacts to some extent with the aldehyde in an aldol condensation. Condensed materials are detectable as an appreciable residue in the distillation of the products, and may account for the new peaks which appear in the n.m.r. when the product mixture is heated.

The cyclobutenol (XIX) which is the precursor of the ketone XVI apparently isomerizes more readily than does XVII. Considerable evidence is now available[15] that ring-opening of cyclobutenes to butadienes is accelerated when unsaturated substituents are brought into conjugation in the process; the contrast between XVII, whose phenyl groups are de-conjugated by ring opening, and XIX, where they become conjugated in the butadiene, is thus explicable. Similarly, the relative reactivity of an aldehyde XV compared to a phenyl ketone (XVI) in carbonyl condensations is consistent with chemical experience, as is the apparent preference for formation of XVII from the carbonium ion. Ignoring the problem of condensation reactions, the chief products of solvolysis are accounted for by the scheme



No trace of the cyclopropenylcarbinol XIII was found in the n.m.r., and the low intensity of the ultraviolet spectrum of the product mixture above 300 mμ showed that less than 4% of a diphenyl cyclopropene could be present.

Δ^2-2-Anisyl-3-phenylcyclopropenecarboxylic acid (XX) was converted to the primary alcohol XXI by the above sequence, involving reduction of its acid chloride with lithium tri-*t*-butoxyaluminohydride, and the three alcohols XIII, XXI and XXII were converted to tosylates in the standard way.

Kinetics and Mechanism.—For rate studies the three tosylates were solvolyzed in absolute ethanol. With the unsaturated compounds there is a difference in the ultraviolet spectra of starting materials and of product mixtures, so the rates were followed both spectrophotometrically, observing the dis-

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(13) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 49. For our spectrum, $J_{\alpha\beta'}$ = 2 c.p.s., $J_{\alpha\beta}$ = 4 c.p.s. and $J_{\beta\beta'}$ = 13 c.p.s.

(14) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959).

(15) *Cf.* E. Vogel, *Angew. Chem.*, **72**, 4 (1960), for a recent review.

appearance of the starting chromophore, and titrimetrically. Both methods of analysis gave excellent first-order plots, with good agreement between rate constants, showing that there is no significant amount of internal return. The results are listed in Table I.

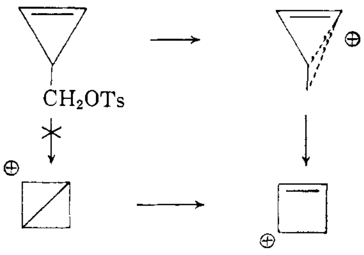
TABLE I

SOLVOLYSIS RATES IN ABSOLUTE ETHANOL AT 30°

Compound	$k_1 \times 10^4$, sec.$^{-1}$	Method	Rel. rate
Diphenylcyclopropenyl-			
carbinyl	1.36 (±0.02)	Titr.	3
tosylate (XIV)	1.29 (± .04)	Spect.	
At 18°[a]	0.233 (± .003)	Spect.	
At 40°[a]	4.0	Spect.	
Diphenylcyclopropyl-carbinyl			
tosylate	0.430 (± .02)	Titr.	1
Anisylphenylcyclopropenyl-			
carbinyl	4.50	Titr.	
tosylate (XXV)	4.78	Spect.	11
Cyclopropylcarbinyl ben-			
zenesulfonate at 20°[2]	0.60		

[a] From these data an activation energy E_a of 24.5 kcal. is estimated, and $\Delta S^{\ddagger}$ is +4.45 e.u./mole (18°) and +4.55 e.u./mole (30°).

Several points are immediately obvious from these data. First of all, the rapid rates show that the solvolyses of the cyclopropenylcarbinyl tosylates proceed through non-classical carbonium ions, just as does that of the cyclopropylcarbinyl analog. Secondly, it is seen that the double bond has a threefold effect if comparison is made between the diphenylcyclopropene and the diphenylcyclopropane compounds we have studied. Comparison with the rate for simple cyclopropylcarbinyl benzenesulfonate,[2] using the approximation[16] $k_{\text{tosylate}}/k_{\text{benzenesulfonate}} = 0.6$, and interpolating our data to 20°, shows that our unsaturated compound is 80% as reactive as is the simple cyclopropane derivative. The corollary that phenyl substituents on the cyclopropane ring have a small effect on the rate is consistent with previous work.[8] The small difference between the saturated and unsaturated compounds suggests that they solvolyze by a similar mechanism, but the possibility must be considered that the similarity of rates is a coincidence. This possibility is excluded by the data on the anisyl derivative. The extra methoxyl group adds a factor of less than four to the rate, but any process involving direct interaction of the developing carbonium ion with the double bond should be enormously accelerated by the methoxyl group. By comparison, we find that in competitive bromination studies *p*-anisylphenylcyclopropenecarboxylic ester is at least 1000 times as reactive as is diphenylcyclopropenecarboxylic ester. The contrast between this rate ratio for bromonium ion formation and our solvolytic effect of only 3.6 shows that the transition state for solvolysis does not involve addition of the primary carbonium ion to the double bond. Although it can be argued that a direct symmetric interaction with the double bond, as in the 7-norbornenyl cation, could have a small substituent effect, the absence of unrearranged carbinol in our solvolysis products also militates against this mechanism. Apparently, the process of ring expansion is exactly analogous to that in the saturated cyclopropylcarbinyl series.



The choice between two possible mechanisms for a ring expansion is certainly not unique to cyclopropenylcarbinyl compounds. The solvolytic ring expansion of 1,4-dihydrobenzyl tosylates[17] could also proceed by either σ-electron or π-electron participation. In this case a very large acceleration by a methoxyl substituent has been taken[18] to indicate that a process involving interaction with the π-electrons is involved. If this is correct, the difference from our results in the small ring reflects two factors: π-interaction in the small ring system involves greater strain, and the opportunity to realize appreciable stabilization from delocalization of σ-bonds is apparently unique to cyclopropylcarbinyl derivatives, as contrasted with larger ring analogs.

The Structure of the Carbonium Ion.—Although the interaction in the cyclopropenylcarbinyl cation is thus formally similar to that in the well-studied cyclopropylcarbinyl cation, it is striking that the extra double bond has so little effect. As predicted, of course, the double bond has a strong influence on the over-all course of the reaction, the products in the unsaturated case apparently resulting entirely from ring expansion. On the other hand, the effect of the double bond on the *rate* of solvolysis is negligible. This indicates that little of the greater over-all strain relief expected during ring expansion of the unsaturated compound is yet accomplished in the transition state.[19] Furthermore, only a small extra conjugation effect is present, so the transition state does not resemble the cyclobutenyl cation electronically either.

This is most obvious from the very small effect of the methoxyl group on the solvolysis rate. No direct evidence is available concerning the effect of a *p*-methoxyl group on the stability of diphenylcyclobutenyl cation, but a general order of magnitude can readily be estimated. It is known[20] that

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(16) A. Streitwieser, *Chem. Revs.*, **56**, 571 (1956).

(17) N. Nelson, J. Fassnacht and J. Piper, *J. Am. Chem. Soc.*, **83**, 206 (1961).

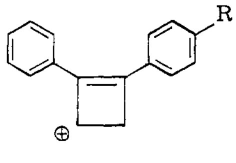
(18) O. L. Chapman and P. Fitton, *ibid.*, **83**, 1005 (1961).

(19) It is of course possible that the small net effect observed is the resultant of two opposing effects; the expected acceleration by conjugation and strain relief may be largely cancelled if the C_2–C_3 bond of a cyclopropene is less available for delocalization than is that of a cyclopropane. This would be most obviously true if appreciable charge were transferred to C_3, but previous evidence on substituent effects[4-8] and on partitioning of the bicyclobutonium ion[1] shows that the charge is shared mainly between C_1 and C_3. Accordingly, it seems unlikely that there would be a major deceleration by the double bond because of the greater electronegativity of unsaturated carbon.

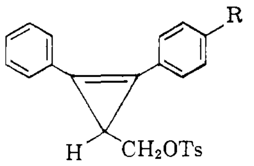
a p-methoxy group increases the pK_a of triphenylcyclopropenyl cation by 1.2 units; the ratio of equilibrium constants is therefore sixteen, and the difference in ΔF° of ionization is 1.7 kcal./mole. If the transition state for the solvolysis were identical with the cyclobutenyl cation, the effect of the methoxyl group on the $\Delta F^{\ddagger}$ should be the same as the effect on the ΔF° for the hypothetical equilibrium between a cyclopropene and a cyclobutenyl cation.

It is expected that the aromatic cyclopropenyl cation will be much less electron demanding than the cyclobutenyl cation, so that a methoxyl group will stabilize the latter much more effectively. Since the starting materials, for the two ionizations being considered, have the same conjugated system, an extra methoxyl group will affect these starting materials in the same way, so the over-all change is predicted to be much greater when cyclobutenyl cation is the product.

This qualitative prediction was made more precise by the use of m.o. calculations. The π-electron delocalization energies of the cyclobutenyl cations XXIII and XXIV and of the cyclopropenes XXV and XIV were calculated using the m.o. method with Hückel's approximations; the parameters used for methoxyl[20] are $\alpha_0 = \alpha_c + \beta$, $\beta_{co} = \sqrt{2}\beta$. The results are listed in Table II. It is seen that formation of diphenylcyclobutenyl cation from diphenylcyclopropenylcarbinyl tosylate involves a ΔD.E. of 0.88 β, while for the anisylphenyl case the ΔD.E. is 1.05β. Thus the methoxyl group favors this change by 0.17β. By contrast, ΔD.E. for ionization of triphenylcyclopropenol to the triphenylcyclopropenyl cation is 2.31β and that for ionization of anisyldiphenylcyclopropenol (the equilibrium mixture of isomers) to the anisyldiphenylcyclopropenyl cation is 2.35β.[20] Thus here the methoxyl group favors ionization by only 0.04β. Since this corresponds to a factor of sixteen in equilibrium constants, the 0.17β effect predicted for formation of the cyclobutenyl cation would be a factor of 100,000 in equilibrium constants! If the transition states in the solvolyses were identical with the cyclobutenyl cations, this would be the rate ratio as well. Although the quantitative precision of these simple m.o. calculations can certainly be questioned, clearly a large effect would be expected from the methoxyl group. The observed factor of only 3.6 shows that the transition state in the cyclopropenylcarbinyl solvolysis has essentially none of the conjugation of the cyclobutenyl cation.



XXIII, R = H
XXIV, R = OCH_3



XIV, R = H
XXV, R = OCH_3

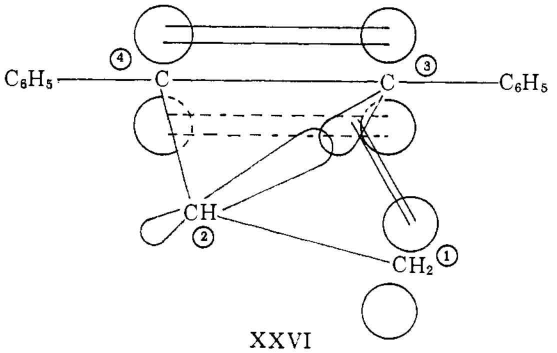
TABLE II

ELECTRON DELOCALIZATION ENERGIES BY THE HÜCKEL M.O. METHOD[a]

Compound	D.E. (β)
Diphenylcyclobutenyl cation (XXIII)	19.7577
Anisylphenylcyclobutenyl cation (XXIV)	22.8231
Triphenylcyclopropenyl cation[20]	29.1872
Anisyldiphenylcyclopropenyl cation[20]	32.1142
Diphenylcyclopropenylcarbinyl tosylate (XIV)	18.8778
Anisylphenylcyclopropenylcarbinyl tosylate (XXV)	21.7700
Triphenylcyclopropenyl[20]	26.8778
Δ^1-1-Anisyl-2,3-diphenylcyclopropenol[20]	29.7700
Δ^1-3-Anisyl-1,2-diphenylcyclopropenol[20]	29.7374

[a] Parameters: $\alpha_0 = \alpha_c + \beta$, $\beta_{co} = \sqrt{2}\beta$.[20]

These results point to a transition state (XXVI) which resembles the cyclopropenylcarbinyl system geometrically but in which σ-electrons are delocalized. Here the charge is delocalized because of overlap between the p-orbital on C-1 and the two hybrid orbitals of the σ-bond between C-2 and C-3. As the reaction proceeds, overlap of the orbitals of C-1 and C-3 increases until a full σ-bond is formed, while the hybrid orbital of C-2 changes into a p-orbital. This process results in formation of the cyclobutenyl cation. *At the instant of the transition state, the developing p-orbital of C-2 is still in the plane of the ring, and is thus orthogonal to the p-orbitals of the C-3, C-4 double bond.* Although some positive charge has been transferred to C-2, it cannot be further spread through the double bond system because of this orthogonality. This picture is of course also consistent with the idea that little strain relief has yet occurred at the transition state.



XXVI

Accordingly, these results again call attention to the remarkable stability of the bicyclobutonium ion. Although little rearrangement of the cyclopropenylcarbinyl cation has occurred by the time the transition state is reached, the slight readjustment which has occurred is sufficient to transform an unstable primary carbonium ion into a strongly stabilized species.

Acknowledgment.—This research was supported by grants from the Sloan Foundation, the Petroleum Research Fund, and the National Science Foundation. Their help is gratefully acknowledged.

Experimental

Δ^2-2,3-Diphenylcyclopropenecarboxylic acid (XII) was prepared as described previously.[11]

(Δ^2-2,3-Diphenylcyclopropenyl)-carbinol (XIII).—To 7.5 g. (0.032 mole) of Δ^2-2,3-diphenylcyclopropenecarboxylic

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(20) R. Breslow and H. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

acid in a 500-ml. three-necked flask equipped with stirrer, reflux condenser and dropping funnel, 31 g. (0.25 mole) of oxalyl chloride was added over the period of 0.5 hr. The mixture was refluxed for 2 hr. Excess oxalyl chloride was removed under reduced pressure; several 15-ml. portions of a 50–50 mixture of benzene and hexane were added and removed under reduced pressure. The product was dissolved in 100 ml. of freshly distilled diglyme, cooled in ice, and 30 g. (0.128 mole) of lithium aluminum tri-(*t*-butoxy)-hydride or tri-*t*-butoxyaluminohydride dissolved in 120 ml. of diglyme was added with stirring over the period of 1 hr. Stirring was continued for 2 hr. at 0°. The mixture was poured into 300 ml. of ice-water, stirred for 5 min. and filtered. The collected solid was repeatedly slurried in absolute ethanol and filtered. The combined ethanol filtrates (450 ml.) were concentrated to 100 ml. under reduced pressure, water was added to turbidity and the mixture was maintained at 0° overnight. The first crop of white fluffy crystals gave 4.9 g., m.p. 69–70.5°; a second crop gave 0.7 g., m.p. 67.5–69°. The total yield was 5.6 g. (78%). The ultraviolet spectrum (log ϵ) had $\lambda_{\max}$ 332 (4.24), 316 (4.37), 237 (4.08) and 228 mμ (4.19). The infrared spectrum showed bands at 3500 and 3340 cm.$^{-1}$ (hydroxyl) and 1800 cm.$^{-1}$ (cyclopropene). A sample prepared for analysis by recrystallization from ethanol–water had m.p. 71–72°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.32; H, 6.64.

(Δ^2-2,3-Diphenylcyclopropenyl)-carbinyl *p*-Toluenesulfonate (XIV).—To a solution of 1.5 g. (0.00675 mole) of the above alcohol XIII in 15 ml. of anhydrous pyridine, cooled in ice, 1.18 g. (0.0062 mole) of *p*-toluenesulfonyl chloride was added in portions. The reaction mixture was allowed to stand at 0° overnight, poured into a mixture of 15 ml. of concd. sulfuric acid and about 100 g. of ice, stirred for 15 min. and extracted three times with methylene chloride, which was then dried over magnesium sulfate. The solvent was filtered and reduced to a small volume *in vacuo;* hexane was added to turbidity and the solution was allowed to stand at 0° for several hours. There was obtained 1.2 g. (51%) of white crystals, m.p. 70–71°. The compound turned black within several hours at room temperature except when very pure. The ultraviolet spectrum (log ϵ) in hexane had $\lambda_{\max}$ 328 (4.36), 312 (4.50) and 298 mμ (4.34) and a shoulder at 303–304 mμ (4.40). The infrared spectrum showed strong bands at 1360 and 1180 cm.$^{-1}$ (sulfonate ester). The n.m.r. spectrum had a singlet at 7.6 τ (methyl on phenyl), a triplet centered at 7.6 τ (J = 6, C–H), a doublet at 5.7 τ (J = 6, CH_2) and a complex multiplet centered around 2.5 τ (phenyl hydrogens).

Anal. Calcd. for $C_{23}H_{20}O_3S$: C, 73.36; H, 5.35. Found: C, 73.67; H, 5.61.

(2^t,3^t-Diphenylcyclopropyl)-carbinol (XXII).[12]—To a dry 500-ml. three-necked flask equipped with magnetic stirring bar, dropping funnel and reflux condenser, and flushed with nitrogen, was added 6.0 g. (0.16 mole) of lithium aluminum hydride. Dry ether (200 ml.) was slowly added and then the mixture was stirred for 1 hr. To this solution was added in small portions, with stirring, 5.77 g. (0.025 mole) of Δ^2-2,3-diphenylcyclopropenecarboxylic acid (XII). The mixture was stirred for 2 hr., then wet ether and finally water was added. The ether layer was separated, washed with 10% sodium hydroxide, then water, dried over sodium sulfate and filtered. The ether was removed under reduced pressure. There remained 4.8 g. of crude material, m.p. 55–85°. One recrystallization from hexane gave 4.15 g. (74%), m.p. 86–88°. A sample prepared for analysis had m.p. 88.5–89.5°. In the ultraviolet spectrum only end absorption was significant. The n.m.r. spectrum showed a 1 proton apparent pentuplet centered at 7.2 τ (J = 6, CH), a 2 proton doublet centered at 7.0 τ (J = 6, benzylic protons), a two proton doublet centered at 5.4 τ (J = 6, CH_2), and a large multiplet centered at 2.2 τ (phenyl hydrogens).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.62; H, 7.18.

(2^t,3^t-Diphenylcyclopropyl)-carbinyl *p*-toluenesulfonate was prepared in the same manner as Δ^2-2,3-diphenylcyclopropenylcarbinyl *p*-toluenesulfonate (XIV). From 0.310 g. of saturated alcohol XXII was obtained approximately 0.3 g. (57%) of a white crystalline compound, m.p. 76–77°. The compound turned black within several hours at room temperature except when very pure. The infrared spectrum showed strong bands at 1365 and 1180 cm.$^{-1}$ (sulfonate ester) and no peaks in the hydroxyl region.

Anal. Calcd. for $C_{23}H_{22}O_3S$: C, 72.99; H, 5.86. Found: C, 72.98; H, 5.89.

***p*-Methoxytolane** was prepared from 4-methoxystilbene dibromide by the procedure previously reported.[20]

Δ^2-2-*p*-Anisyl-3-phenylcyclopropenecarboxylic acid (XX)[21] was prepared by the method used for the preparation of Δ^2-2,3-diphenylcyclopropenecarboxylic acid. From 10 g. (0.049 mole) of *p*-methoxytolane, 6 g. (0.053 mole) of ethyl diazoacetate and copper powder was obtained 2.7 g. (21%) of acid, m.p. 178–180°. A sample prepared for analysis, by recrystallization from acetone, had m.p. 179.5–181.5°. The ultraviolet spectrum (log ϵ) had $\lambda_{\max}$ 333 (4.52), 317 (4.59), 236 (4.27) and 229 mμ (4.27).

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.91, 76.69; H, 5.62, 5.77.

(Δ^2-2-*p*-Anisyl-3-phenylcyclopropenyl)-carbinol (XXI) was prepared from the above acid by the method described for the preparation of (Δ^2-2,3-diphenylcyclopropenyl)-carbinol (XIII). From 3 g. of acid, a yellow oil was obtained which upon crystallization from methylene chloride–hexane gave 1 g. (35%) of a white solid, m.p. 72.5–73.5°. The ultraviolet spectrum (log ϵ) had $\lambda_{\max}$ 340 (4.37), 324 (4.48), 238 (4.18) and 233 mμ (4.20). The infrared spectrum had bands at 3200 (hydroxyl) and 1820 cm.$^{-1}$ (cyclopropene).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.08; H, 6.65.

(Δ^2-2-*p*-Anisyl-3-phenylcyclopropenyl)-carbinyl *p*-toluenesulfonate (XXV) was prepared in the same manner as (Δ^2-2,3-diphenylcyclopropenyl)-carbinyl *p*-toluenesulfonate (XIV). From 0.350 g. of alcohol XXI, a yield of approximately 50% of white crystals was obtained. A sample prepared for analysis had m.p. 74° dec. The compound decomposes within an hour at room temperature except when very pure. The ultraviolet spectrum (log ϵ) had $\lambda_{\max}$ 337 (4.42), 320 mμ (4.53), and shoulders at 310 (4.42) and 304 mμ (4.37). The infrared spectrum has strong peaks at 1350 and 1160 cm.$^{-1}$ (sulfonate ester).

Anal. Calcd. for $C_{24}H_{22}O_4S$: C, 70.91; H, 5.45. Found: C, 71.16; H, 5.63.

Ethyl (Δ^2-2,3-diphenylcyclopropenyl)-carboxylate was prepared by the method of Breslow, *et al.*,[11] for the preparation of Δ^2-2,3-diphenylcyclopropenecarboxylic acid; however, the intermediate ester was not hydrolyzed but was isolated by the procedure of D'yakanov *et al.*[22] From 24.8 g. of diphenylacetylene was obtained 0.865 g. (3%) of white crystals, m.p. 75.5–76.5° (lit.[22] m.p. 77–78°).

Ethyl (Δ^2-2-*p*-anisyl-3-phenylcyclopropenyl)-carboxylate was prepared by the method used above. From 20 g. (0.096 mole) of *p*-methoxytolane, 6 g. (0.095 g. atom) of copper powder and 15 g. (0.113 mole) of ethyl diazoacetate was obtained, after chromatography, 3.5 g. (12%) of white crystals, m.p. 68–70°. A sample prepared for analysis by recrystallization from hexane had m.p. 69.5–71°. The ultraviolet spectrum (log ϵ) showed $\lambda_{\max}$ 324 (4.49), 313 mμ (4.55) and a shoulder at 300 mμ (4.44). The infrared spectrum showed peaks at 1855 (cyclopropene) and 1730 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.01, 77.15; H, 6.08; 6.23.

Kinetic Measurements.—All solvolyses were performed in U.S. Industrial Chem. Co. absolute ethanol, U.S.P. reagent quality. No difference in rate constant was observed when absolute ethanol prepared by the method described by Fieser[23] was used.

For the titrimetric procedure a convenient amount of the tosylate was diluted to 100 ml. with absolute ethanol (previously taken to constant temperature) in a volumetric flask and the solution was maintained in a thermostated bath. At intervals 5-ml. aliquots were removed, run into 11 ml. of a stock solution composed of 10 ml. of ethanol and

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[21] This compound was first prepared and characterized by M. Battiste, in unpublished work.

[22] I. A. D'yakonov, *et al.*, *Zhur. Obshch. Khim.*, **29**, 3848 (1959).

[23] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 359.

1 ml. of water, and titrated to maximum *p*H change (usually at *p*H 7) with standard sodium hydroxide. The time was noted at the end-point of the titration. For points taken on subsequent days the base was restandardized. The infinity titer was taken at greater than 9 half-lives for all runs. The buret was a Gilmont ultra-microburet of 0.1-ml. capacity; the *p*H meter was a Beckman model G.

The spectrophotometric procedure utilized the disappearance of a characteristic band in the ultraviolet spectrum (337 mμ for the *p*-anisyl compound and 328 mμ for the diphenyl compound). A convenient amount of the tosylate was dissolved in 25 ml. of absolute ethanol (previously taken to constant temperature). At intervals 1-ml. aliquots were removed from the thermostated solution and diluted to 10 ml. with hexane in a volumetric flask. The time was noted as the reaction was quenched with hexane. Spectra were taken immediately, since solvolysis occurred slowly even in the presence of excess hexane. The absorption at greater than 9 half-lives was less than 16% of the absorption at time zero.

The rate constants were calculated in a straightforward manner from the slope of a plot of $\log(a - x)$ *vs.* time. Good straight lines were obtained to greater than 64% completion for all runs.

Competitive Bromination Studies.—A minimum value for the relative rates of bromination of ethyl (Δ^2-2,3-diphenylcyclopropenyl)-carboxylate and ethyl (Δ^2-2-*p*-anisyl-3-phenylcyclopropenyl)-carboxylate was obtained by competitive bromination of each compound against cyclohexene in glacial acetic acid at room temperature. A freshly opened bottle of Baker analyzed reagent acetic acid was used. White label Eastman Kodak Co. cyclohexene was redistilled through a Vigreux column; a middle fraction boiling at 82–83° was collected.

A standard solution of 17.00 g. of cyclohexene diluted to 100 ml. with acetic acid in a volumetric flask was prepared. Aliquots of 25 ml. each were run into 250-ml. volumetric flasks containing enough of the cyclopropene to absorb with an optical density of 1.5 at $\lambda_{\max}$ in the ultraviolet (the peak used for the diphenyl compound was at 318 mμ, for the *p*-anisyl compound at 324 mμ). These solutions were then diluted to the mark with acetic acid. An approximately 0.2 *M* bromine solution was prepared in acetic acid. The determination of bromine by the potassium iodide–thiosulfate method showed the solution to be 0.204 ± 0.002 *M*.

To a 100-ml. aliquot of the solution containing the *p*-anisyl compound and cyclohexene (0.207 *M*) was added with stirring 2 ml. of the standard bromine solution. The solution was stoppered and stirred for 2 hours in the dark and a 50-ml. aliquot removed and run into excess potassium iodide solution. The titer with 0.102 *N* thiosulfate was 0.1 ml. The titer for a control (100 ml. of acetic acid plus 2 ml. of bromine solution) run in the same manner was 4.1 ml. The optical density of the original solution containing the mixture of olefins was 1.61, while that for the final solution after reaction was 0.87 at 324 mμ. Taking account of the 2% dilution by the bromine reagent this corresponds to 45% reaction of the cyclopropene, while from the quantity of bromine consumed less than 2% of cyclohexene has reacted. Assuming that for both olefins the reaction is kinetically first order in substrate and bromine, this corresponds to a ratio of rate constants, k_2 (anisylphenylcyclopropene derivative)/k_2(cyclohexene), of 29.

In a similar manner a 100-ml. aliquot of the solution containing the diphenyl ester and cyclohexene was mixed with 90 ml. of the bromine solution. After 2 hr., titration of an aliquot showed that the amount of bromine remaining in the solution corresponded to 0.4 ml. of the original standard bromine solution. The optical density of the original solution of olefins was 1.56 and the final optical density at 318 mμ was 0.82. Taking account of the considerable dilution by bromine solution in this case, this corresponds to less than 5% reaction of the cyclopropene, while from the quantity of bromine consumed 87% of the cyclohexene has reacted. Again assuming second-order kinetics, this corresponds to a ratio of rate constants, k_2 (diphenylcyclopropene derivative)/k_2(cyclohexene), of 0.027.

Accordingly, the relative reactivity, k_2(anisylphenylcyclopropene derivative)/k_2(diphenylcyclopropene derivative), is at least 1000. This figure assumes the 2% cyclohexene in the first experiment, and 5% cyclopropene in the second, which are upper limits to the amounts which have reacted. The ratio of reactivities becomes even larger if lower values than these limits are assumed.

Product analysis was performed on the hydrolysis products of (Δ^2-2,3-diphenylcyclopropenyl)-carbinyl *p*-toluenesulfonate (XIV).

To 0.49 g. (0.0013 mole) of the tosylate was added a mixture of 20 ml. of acetonitrile and 5 ml. of water. After 17 hr. the ultraviolet spectrum of the tosylate had disappeared and a new band appeared at 295 mμ. The acetonitrile was removed under reduced pressure and the resulting mixture was neutralized with dilute sodium hydroxide and extracted with methylene chloride; this was then dried over sodium sulfate, filtered and evaporated under reduced pressure, leaving 0.30 g. of yellow oil. Its infrared spectrum showed strong bands at 3610, 3410 and 1670 cm.$^{-1}$ (carbonyl). The oil was distilled at 0.5 mm. and 0.195 g. of oily solid was collected at 130–200°. Treatment of the material with 95% ethanol and filtration gave 0.070 g. (24%) of material, m.p. 121–124°. One recrystallization from 95% ethanol gave a pale yellow solid, m.p. 126–128°. Redistillation of the liquors gave 0.066 g. of oily solid whose infrared spectrum showed bands at 3400 and 1680 cm.$^{-1}$.

The pale yellow compound absorbs in the infrared at 1680 (aldehyde carbonyl) and 2750 cm.$^{-1}$ (aldehyde CH). The ultraviolet spectrum (log ϵ) has $\lambda_{\max}$ at 275 mμ (4.03). The n.m.r. spectrum shows a three-proton singlet at 7.88 τ (methyl), a complex ten-proton multiplet centered at 2.64 τ (phenyl) and a one-proton singlet at 0.36 τ (aldehydic H). The compound forms a 2,4-dinitrophenylhydrazone, m.p. 224–225°.

When recrystallized from benzene–hexane mixtures the white compound, m.p. 126°, apparently contains 1 mole of benzene of crystallization.

Anal. Calcd. for $C_{16}H_{14}O \cdot C_6H_6$: C, 87.96; H, 6.71. Found: C, 87.82, 87.72, 87.93; H, 6.58, 6.77, 6.53.

The sublimate of the recrystallized material had the expected analysis for 2,3-diphenylcrotonaldehyde (XV), m.p. 127–128°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.28; H, 6.53.

A similar hydrolysis experiment was run for 60 hr. The n.m.r. spectrum of the crude material isolated in the same manner showed the presence of another compound in addition to XV. That is, there was a three-proton doublet at 8.0 τ ($J = 7$, methyl), a one-proton quartet at 3.4 τ ($J = 7$, vinyl H) and a complex ten-proton multiplet at 2.6 τ (phenyl). Chromatography of the oil on alumina gave, from the hexane–benzene eluate, an oil whose n.m.r. contained only the above bands. This is assigned the structure ethylidenedesoxybenzoin (XVI). The infrared spectrum showed a band at 1655 cm.$^{-1}$ (carbonyl); the ultraviolet spectrum (log ϵ) had $\lambda_{\max}$ at 250 mμ (4.24).

A 2,4-dinitrophenylhydrazone, m. p. 185°, was prepared and recrystallized from hot ethanol–ethyl acetate.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.71; H, 4.51. Found: C, 65.67, 65.93; H, 4.97, 4.67.

The ultraviolet spectrum (log ϵ) had $\lambda_{\max}$ at 373 (4.41) and 230 mμ (4.41). The n.m.r. spectrum of a very weak solution showed a doublet at 7.8 τ ($J = 7$, methyl) and a complex multiplet centered at 2.7 τ (phenyl).

In a third hydrolysis the tosylate was solvolyzed in 15 ml. of acetonitrile with water added to turbidity. After 1 hr. the solution was strongly acidic to *p*H paper and was neutralized with 10% sodium bicarbonate. After 19 hr. the solution was still neutral and the acetonitrile was removed under reduced pressure. Water was added and the mixture was extracted three times with methylene chloride which was then dried over magnesium sulfate, filtered and removed under reduced pressure. An infrared spectrum of the yellow oil remaining showed a broad band at 3300–3450 cm.$^{-1}$ and a peak at 1660 cm.$^{-1}$. The ultraviolet spectrum (log ϵ) had $\lambda_{\max}$ at 295 mμ (2.97) and a shoulder at 247 mμ (2.97). The n.m.r. spectrum showed a singlet at 8.4 τ (unassigned), singlets at 8.0 and 0.4 τ (XV); a doublet at 8.2 and a quartet at 3.8 τ (XVI), a complex two proton multiplet centered at 7.4 τ, a broad one proton singlet at 6.5 τ and a one proton quartet at 5.2 τ (diphenylcyclobutenol, XVII), and a complex multiplet centered at 2.8 τ (phenyl hydrogens). The ratio of the area of the phenyl hydrogens to the ketone methyl hydrogens was 14.8/1; the ratio of aldehyde methyl to ketone methyl was 1/4; the ratio of ketone methyl to cyclobutene methylene was 1/1.5. The crude mixture was heated for 1 hr. on a steam-bath; the n.m.r. spectrum showed that the peaks at 8.0 and 0.4 τ (XV) were greatly enhanced at the expense of the peaks between 5.23–7.4 τ (XVI). However, some new broad peaks did appear in the latter region. In this spectrum the ratio of the area of the phenyl hydrogens to ketone methyl was 15.4/1. The ratio of aldehyde methyl to ketone methyl was 1/1. The ultraviolet spectrum showed shoulders at 275 (3.72) and 250 mμ (3.95).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

The Chromic Acid Oxidation of Aromatic Aldehydes. Some Observations Concerning the Oxidation by the Chromium Species of Intermediate Valence[1]

BY KENNETH B. WIBERG AND WILLIAM H. RICHARDSON

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The effect of substituents and the kinetic isotope effect for the oxidation of benzaldehyde by the chromium species of intermediate valence has been determined by a competition technique. The oxidation of triphenylacetaldehyde has been found to give triphenylacetic acid, triphenylcarbinol and carbon monoxide as the main products. The significance of the results is discussed in terms of the possible mechanisms for the reaction.

The first step in many chromic acid oxidations appears to involve a two-electron transfer giving chromium(IV).[2] The chromium(IV) may either react with chromium(VI) to give two chromium(V), or it may react with the organic substrate to give chromium(III) and a free radical. The latter would probably react with chromium(VI) to give the oxidized organic species and chromium(V), which would in turn effect further oxidation.[3] In either case, two-thirds of the net reaction will proceed *via* oxidation by the chromium species of intermediate valence, and one one-third involves chromium(VI).

Even if the initial step were a one-electron oxidation, the above conclusion would apply. Such a reaction would lead to chromium(V) which would effect a net two-electron oxidation. The various possibilities may be represented as follows, where AH_2 is the compound being oxidized.

$$\begin{array}{ll}
\text{(A)} & AH_2 + Cr^6 \longrightarrow A + 2H^+ + Cr^4 \\
 & Cr^4 + Cr^6 \longrightarrow 2Cr^5 \\
 & 2(AH_2 + Cr^5 \longrightarrow A + 2H^+ + Cr^3)^4 \\
\text{(B)} & AH_2 + Cr^6 \longrightarrow A + 2H^+ + Cr^4 \\
 & AH_2 + Cr^4 \longrightarrow AH\cdot + H^+ + Cr^3 \\
 & AH\cdot + Cr^6 \longrightarrow A + H^+ + Cr^5 \\
 & AH_2 + Cr^5 \longrightarrow A + 2H^+ + Cr^3 \\
\text{(C)} & AH_2 + Cr^6 \longrightarrow AH\cdot + H^+ + Cr^5 \\
 & AH\cdot + Cr^6 \longrightarrow A + 2H^+ + Cr^5 \\
 & 2(AH_2 + Cr^5 \longrightarrow A + 2H^+ + Cr^3)
\end{array}$$

Although much is known about the oxidation of organic compounds by chromium(VI), little is known about the stoichiometrically more important oxidation by the chromium species of intermediate valence. From the limited data presently available, it appears that chromium(V) may behave differently from chromium(VI). For example, whereas phenyl-*t*-butylcarbinol is oxidized to the ketone with chromium(VI), the oxidation by the chromium species of intermediate valence gives, under certain conditions, only cleavage to benzaldehyde and *t*-butyl alcohol.[5]

It is not possible to study the oxidation by chromium(IV) and -(V) directly since these species are not stable under the reaction conditions. It is, however, possible to obtain some information concerning their mode of action by studying oxidations of mixtures of organic substrates. Consider the oxidation of a mixture of benzaldehyde and *p*-chlorobenzaldehyde using chromic acid. The chromic acid will react with the two aldehydes in the ratio of the relative reactivities determined in separate kinetic runs. This initial step will lead to the formation of chromium(IV) and -(V), either one or both of which may react further with the aldehydes with the relative reactivity characteristic of that reagent. Thus, having the relative reactivity determined by competition experiments, and correcting this for the known relative reactivity toward chromium(VI), one may obtain the relative reactivity toward the chromium species of intermediate valence.

Competitive oxidations were carried out using several pairs of aldehydes labeled with carbon-14. Aliquots of the reaction mixture were removed and quenched at reasonable intervals, and known amounts of unlabeled aldehydes were added. The aldehydes were isolated and were separated by vapor phase chromatography. They were then converted to the corresponding benzoic acids, purified further by recrystallization, and analyzed for their carbon-14 content. The data for the competitive oxidation of benzaldehyde and *p*-chlorobenzaldehyde are given in Table I.

It is reasonable to assume that the oxidation of benzaldehyde by chromic acid involves an initial two-electron step. Whereas the rate of oxidation of hydrocarbons[6] and of diisopropyl ether,[7] which presumably involves a hydrogen abstraction, is proportional to the concentrations of both the acid

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[1] This investigation was supported by the U. S. Atomic Energy Commission.

[2] W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949); F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949).

[3] A reaction leading to chromium(II) is also possible, but somewhat unlikely in view of the strong reducing properties of this species.

[4] For this sequence, it has been noted[3] that if chromium(V) reacted by one-electron step, the reaction would be autocatalytic. Similar arguments may be advanced for sequences B and C. This type of behavior has not been observed.

[5] J. Hampton, A. Leo and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 306 (1956).

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

[7] R. Brownell, A. Leo, Y. W. Chang and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 406 (1960).