Verbalis facilitated this work. We thank Drs. J. E. Williams, R. C. Bingham, and G. J. Gleicher for their contributions in the development of our conformational analysis programs. We especially wish to express our gratitude to Professor K. Mislow, Professor S. Lifson, Professor N. L. Allinger, Dr. O. Ermer, and Dr. A. Warshel for stimulating discussions and helpful comments.

Supplementary Material Available. A listing of calculated Cartesian coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8005.

Substituent Effects on σ–π Conjugation. The Absence of π-Electron Transmission through Cyclopropane Rings[1,2]

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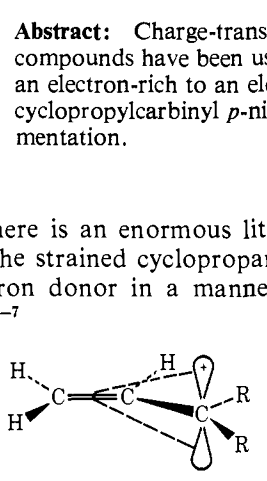
Abstract: Charge-transfer frequencies of acceptor complexes with 2-methoxy-1-phenylcyclopropane and similar compounds have been used to show that a 1,2-substituted cyclopropane does not transmit π-electron density from an electron-rich to an electron-deficient π center in the manner of a π bond. The rapid solvolysis of 2-methoxycyclopropylcarbinyl p-nitrobenzoate is interpreted as resulting from distortional stabilization in the form of fragmentation.

There is an enormous literature demonstrating that the strained cyclopropane ring acts as a simple π-electron donor in a manner similar to that of ethylene.[3–7]



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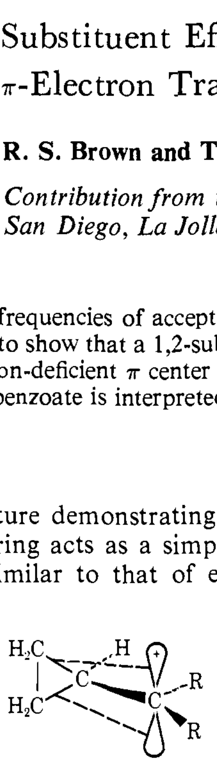

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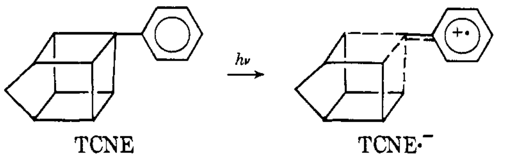
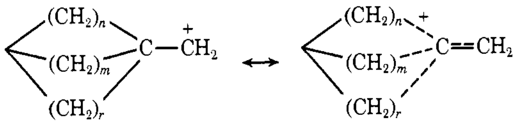
Recent evidence shows that other strained rings behave similarly, as illustrated below for the very strained homocubane group.[8a] The charge-transfer frequencies



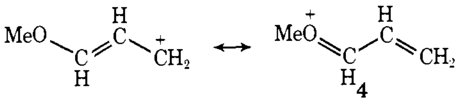
(1)

reveal a $\sigma^+_{p\text{-homocubyl}} = -0.75$ compared to $\sigma^+_{p\text{-cyclopropyl}} = -0.54$ and $\sigma^+_{p\text{-MeO}} = -0.78$. We can quite generally write σ–π conjugated forms of such strained, primary cations.



3

If this σ–π delocalization in **2** and **3** behaves like π–π delocalization in **1**, then we might reasonably expect conjugation through the strained ring as in **5**. This has been called π–σ–π conjugation[8b] or through-bond interaction[7b] (n, m, r = 0 to 2).



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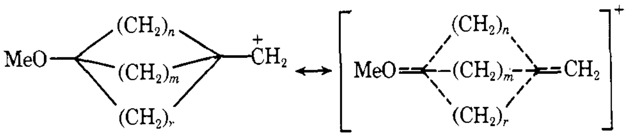
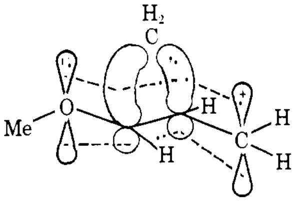


5

To apply this possible π–σ–π conjugation to cyclopropane we could fix an electron-acceptor π system (*e.g.*, CH_2) to one position and an electron-donating π group (*e.g.*, MeO) to another so as to maximize overlap of the proper Walsh orbitals to each group.



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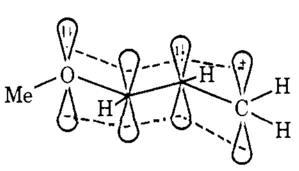

7

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(1) This work was supported by the National Science Foundation (Grant GP-27361).

(2) Presented at the Pacific Conference on Chemistry and Spectroscopy, Anaheim, Calif, October, 1971.

(3) P. v. R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, **91**, 5880 (1969). This paper contains an extensive reference list covering both experimental and theoretical treatments of cyclopropylcarbinyl derivatives.

(4) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969).

(5) W. J. Hehre, *ibid.*, **94**, 6592 (1972).

(6) D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970).

(7) (a) R. Hoffmann and R. B. Davidson, *ibid.*, **93**, 5700 (1971); (b) R. Hoffmann, E. Heilbronner, and R. Gleiter, *ibid.*, **92**, 706 (1970).

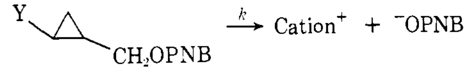
(8) (a) N. A. Clinton, R. S. Brown, and T. G. Traylor, *ibid.*, **92**, 5228 (1970); (b) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, **93**, 5715 (1971); (c) W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.*, **92**, 829 (1970); (d) T. G. Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, 30, 599 (1972).

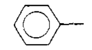
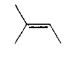
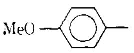
Although the oxygen lone pair and CH_2 cation orbitals are not coplanar, this system (**6**) would nevertheless lead to large stabilization if treated as a four-electron system in the manner shown in **6**.

Of the wide variety of possible spectroscopic and chemical tests for such a conduction, the most sensitive is the effect of electron-donating groups upon cation stability. For example, a methoxy group, attached to the known conducting phenyl ring, accelerates cumyl chloride solvolysis by about 10^4.[9]

Recently, solvolyses of substituted cyclopropylcarbinyl 3,5-dinitrobenzoates (*p*-nitrobenzoates, etc.) were shown to respond to resonance stabilizing groups. The data are summarized in Table I. These enhancements were interpreted in terms of delocalization of charge to these groups in the manner depicted in **6**, although fragmentation was also considered to be consistent with the results.[10]

Table I. Effects of β Substituents on the Rates of Cyclopropylcarbinyl *p*-Nitrobenzoate Solvolysis[a]



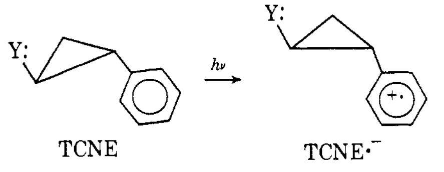
Y (trans)	k_{rel}	Ref
H	(1)	*b*
Me	11	*b*
	3	*c*, *d*
	15	*e*, *f*
	46[g,h]	*c*
MeO—	791	*b*

[a] Rates relative to cyclopropylcarbinyl 3,5-dinitrobenzoate in 75% aqueous acetone as in *b* (Schleyer and Van Dine). The leaving groups, solvents, and temperatures varied making these relative rates somewhat inaccurate. However, the value 791 for methoxy is accurate under the conditions used. [b] P. v. R. Schleyer, P. J. Stang, and D. J. Raber, *J. Amer. Chem. Soc.*, **92,** 4725 (1970); P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88,** 2321 (1966). [c] T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, **35,** 42 (1970). [d] R. Sneen, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *J. Amer. Chem. Soc.*, **83,** 4843 (1961). [e] C. D. Poulter, S. C. Molsinger, and W. W. Epstein, *Tetrahedron Lett.*, 67 (1972). [f] T. Sasaki, S. Eguchi, M. Ohno, and T. Umemuro, *Chem. Lett.*, 503 (1972). [g] A $\rho\sigma^+_p$ plot of para-substituted phenyl compounds gave $\rho = -1.48$. [h] At 130°. However, activation energies varied very little. Therefore, the relative rates are not very temperature sensitive.

We recently reported preliminary experimental evidence against such delocalization[8b] and the INDO calculations reported by Kispert, Engleman, Dyas, and Pittman[11] agreed with our conclusions. In this paper we present the details of our study on two strained systems and resolve the question of π transmission through the cyclopropane ring. Possible reasons for this failure, the significance to homoaromaticity, and the multiplicity of mechanisms for cyclopropylcarbinyl-X solvolyses will be discussed.

Results

π–σ–π Conjugation. If, as we have previously done,[8] we consider conjugation to be simple delocalization, then it should be vertical stabilization[8b] which may be demonstrated by changes in ionization potentials. We have measured charge-transfer frequencies of trans 2-substituted cyclopropylbenzenes to see whether resonance electron-donating substituents indeed stabilize the positive charge. The results are shown in Table II.



(2)

Table II. Charge-Transfer Spectra of TCNE Complexes with Trans 2-Substituted Cyclopropylbenzenes

Compd	Y	λ^{CT}_{max}, nm[a]	ν, cm^{-1} $\times 10^{-3}$	$\sigma^+{}_Y$
8	H	480	20.8	0.0[b]
9	$NH(C{=}O)CH_3$	480	20.8	−0.58[c]
10	$NH(C{=}O)Ph$	480	20.8	−0.58
11	Ph[d]	482	20.6	−0.179[d]
12	OCH_3[d]	480	20.8	−0.78[d]
13	CH_3	492	20.3	−0.31[b]

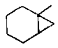
[a] Determined in CH_2Cl_2 at 25°. [b] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2,** 323 (1964). [c] T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89,** 2304 (1967). [d] Contains some cis compound. See Table III.

It is quite apparent that none of the strongly resonance stabilizing groups, *e.g.*, methoxy or acetamido groups, have any effect upon this ν_{CT}. Only the methyl group, which is inductively donating, shows stabilization of the positive charge.

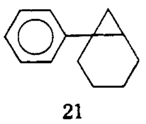
A more striking demonstration of this result may be seen in Table III where the cyclopropyl compounds are compared with the corresponding vinyl and saturated, unstrained compounds.

The conduction through bent σ bonds might conceivably increase as strain or per cent p character increases. We investigated this possibility with the more strained bicyclo[4.1.0]heptyl group. Charge-transfer frequency changes demonstrate that this group is somewhat more electron donating than is the cyclopropyl group.[8a]

σ^+  $= -0.54$

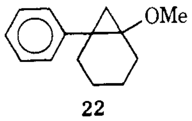
σ^+  $= -0.60$

We compare the ν_{CT} for 1-phenylbicyclo[4.1.0]heptane (**21**)[8a] and 1-methoxy-6-phenylbicyclo[4.1.0]heptane (**22**) below. Because tetracyanoethylene added very rapidly to **22**, the charge-transfer spectra of the chloranil complexes were used.



21

$\nu_{chloranil}{}^{CT} = 24{,}000\ cm^{-1}$



22

$\nu_{chloranil}{}^{CT} = 24{,}000\ cm^{-1}$

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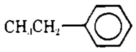
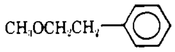
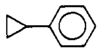
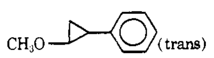
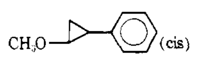
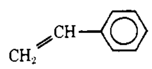
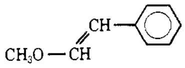
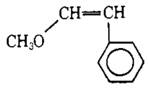
(9) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1,** 1 (1963).

(10) C. D. Poulter, S. C. Molsinger, and W. W. Epstein, *Tetrahedron Lett.*, 67 (1972).

(11) (a) L. D. Kispert, C. Engleman, C. Dyas, and C. V. Pittman, Jr., *J. Amer. Chem. Soc.*, **93,** 6948 (1971). (b) Unfortunately, there is no experimental evidence that a vinyl group has any effect on cyclopropylcarbinyl cation. Nevertheless, these calculations agree with our experimental results in the conclusion that π-electron density is not transmitted efficiently through an undistorted cyclopropane ring.

Table III. Charge-Transfer Absorption Maxima (TCNE) of Substituted Benzenes[a]

Compd		$\lambda_{\max}^{CT}$, nm	ν, cm^{-1} × 10^{-3}
14		410	24.4
15		407	24.6
16		480	20.8
12		480	20.8[b]
17		~480	~20.8[b]
18		480	20.8
19		610	16.8
20		570	17.5

[a] Determined in 10^{-2} *M* TCNE in CH_2Cl_2 at 25°. [b] A mixture of 20% cis and 80% trans compound gave a strong charge-transfer spectrum with excess TCNE with a maximum at 480 nm. The photoelectron spectrum of this mixture revealed a vertical ionization potential of 8.55 eV, compared with 8.61 eV for **16**, in good agreement with the charge-transfer spectra.

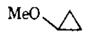
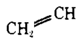
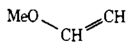
The identical charge-transfer frequencies of **21** and **22** again reveal no transmission through this strained σ bond.

Discussion

In order to establish that the effect we are investigating is one of π-electron donation which is free of inductive effect complications, we must show that inductive effects are negligible. In the measurement of ionization potentials by charge-transfer frequencies, we can easily demonstrate this by comparing the effects of the methoxy group on styrene and on ethylbenzene as shown in Table IV.

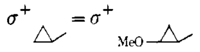
From Table IV we can see that the inductive effect of a methoxy group in $MeOCH_2CH_2$ is, within experimental error, negligible. We can therefore assume that this inductive effect is also very small in the group MeOCH=CH and then conclude that the change in the value of σ^+ from −0.58 for vinyl to −1.01 for β-methoxyvinyl is entirely due to π donation by the methoxy lone pairs. This is in keeping with the usual dominant resonance behavior of the methoxy group.

Table IV. Effects of Alkyl, Vinyl, and Cyclopropyl Groups on Benzene Ionization Potentials

Group (Y)	$\Delta\nu$, cm^{-1} [a]	σ^+_{group} [b]	$\Delta\nu_{MeO}$ [c]	$\Delta\nu^+_{MeO}$ [d]
CH_3CH_2	1800	−0.2		
$CH_3OCH_2CH_2$	1600	−0.17	−200[e]	~0
	5400	−0.58		
	5400	−0.58	0	0
 $CH_2{=}CH$	5400	−0.58		
 $MeO{-}CH{=}CH$	9400	−1.01	4000	−0.43

[a] $\Delta\nu = 26200\ cm^{-1} - \nu_{PhY}$, from ref 8c. [b] Calculated from the equation $\sigma^+ = (26200 - \nu_{PhY})/9300$ of ref 8c. The conclusions are independent of the absolute values of σ^+ calculated in this way. [c] $\Delta\nu_{MeO} = \nu_{Ph-R-H} - \nu_{Ph-R-OMe}$. [d] $\Delta\sigma_{MeO} = \Delta\nu_{MeO}/9300$. [e] The accuracy of ν_{CT} is about ±200 cm^{-1}.

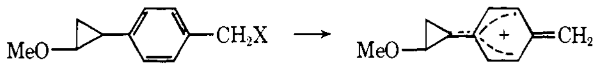
If a cyclopropyl group were behaving like a vinyl group in π transmission as shown in **6** and **7**, then we should be able to determine the extent to which such transmission of the MeÖ π density is transmitted. Because we detect no change in the first ionization potential of cyclopropylbenzene upon substitution of a methoxy group, *i.e.*

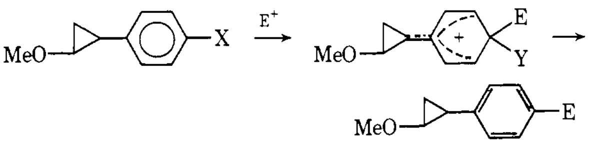


we conclude that such transmission cannot provide more stabilization than indicated by the limit of our experimental error or about 200 cm^{-1}. Compared with the 4000-cm^{-1} effect on a vinyl group this represents less than 5% of the transmission of a vinyl group.

We therefore conclude that, although cyclopropyl is at least as effective as vinyl in donating electrons, its ability to transmit π density is negligible for the groups MeO, AcNH, etc., studied here.

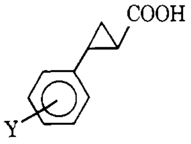
At least in terms of chemical reactions such as the following we could confidently predict little effect of a methoxy group.

 (3)

 (4)

Of course, an enormous acceleration by the methoxy group would be expected if the cyclopropyl group were exchanged for a vinyl group (see later discussion).

Many of the previous studies of transmission through cyclopropyl groups[12-16] have compared carboxylic acid acidities[12] in **23**, ^{19}F shielding parameters[13] in **24**, ir frequencies[14] in **25**, etc.



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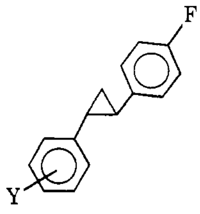

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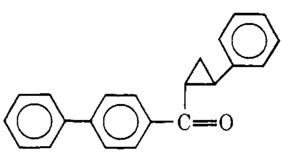

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[12] E. N. Trachtenberg and G. Odian, *J. Amer. Chem. Soc.*, **80**, 4015 (1958).

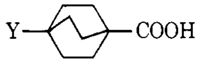
[13] R. G. Pews and N. D. Ojha, *ibid.*, **91**, 5769 (1969).

[14] R. J. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957).

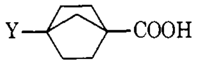
[15] L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3840 (1951).

[16] (a) R. H. Eastman, *ibid.*, **76**, 4115 (1954); (b) R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955).

In these and other similar studies, where cyclopropane was compared with the $CH_2—CH_2$ and $CH{=}CH$ groups, the differences between the alkyl and vinyl groups were not nearly so large as they are in our study. Furthermore, in none of these cases can a clear separation of inductive and π effects be made as we have done. For example, the effect of Y on fluorine chemical shift in **24** is reasonably interpreted as an inductive effect. These chemical shifts plot very accurately against σ^{I} and meta substituents have very large effects. It should also be noted that inductive ρ slopes vary as the insulating alkyl groups are changed from flexible to more rigid systems. Thus the ρ slope for acidities[17] in **26** is 2.12 compared with 2.56 for **27**.

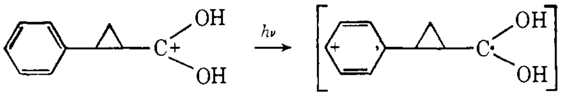


26

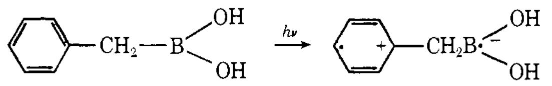


27

The results of Montaudo and Overberger[18] appear at first glance to contradict our conclusions. Protonated L-*trans*-2-phenylcyclopropanecarboxylic acid has a long wavelength absorption in the uv and cd spectra which has been interpreted in terms of conduction. However, their results do not speak to the question of stabilizing effect of the β-phenyl group on the protonated cyclopropanecarboxylic acid. What is shown in their study is that a benzene transition (reaction 5) is made easier. But this absorption could also be an internal charge-transfer transition of the type discussed by Ramsey and Das[19] for a sterically similar system, benzylboronic acid. Such charge-transfer transitions do not require conduction. In fact, the two molecular orbitals should be spacially separate for such transitions.

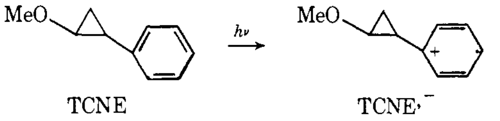


(5)



(6)

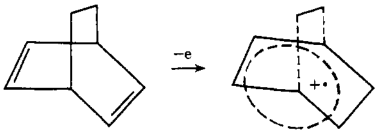
This observation should be contrasted to the ionization potential measurements which must reveal any interaction between the two orbitals adjacent to the cyclopropane ring (eq 7). That we find no appreciable interaction does not speak against the occurrence of charge-transfer transitions. The uv and cd data do not contradict our conclusions of nonconduction by the cyclopropane group. Indeed these results are in good agreement as we shall show later in this discussion.



(7)

π–σ–π Conjugation ("Through-Bond Conduction"). Although we conclude that a positive charge is not effectively delocalized through a cyclopropane ring (or other σ bonds), Heilbronner and Hoffmann[7a,b,20] discuss several systems in which "through-bond interaction" is proposed to make some contribution.

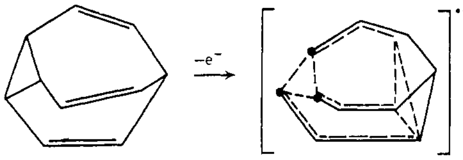
1. One-bond interaction



28

(8)

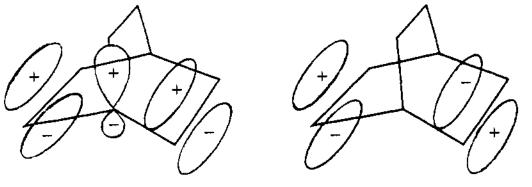
2. Two-bond interaction



29

(9)

These small effects are not directly related to the kind of π–σ–π conjugation we are discussing here. The "through-bond interaction" of Heilbronner is a case of the well-known effect of alkyl substitution on olefin, ether, amine, etc., ionization potentials. An alkyl group lowers the first ionization potential of a π bond by about 0.5 eV (compare propylene, 9.73 eV, with *cis*-2-butene, 9.24 eV). This electron donation (inductive or hyperconjugative) behaves peculiarly in the special case where there is through-space splitting of two π bonds which places the alkyl group in the node of the highest energy orbital.[20] An example of this effect is **28** in which the alkyl group repulsion raises the energy of the symmetrical orbital but has little or no effect on the higher of the two π orbitals.[20c]



repulsive   no effect

Although the through-bond interaction proposed for **28** is suggested to be a kind of σ–π conjugation, it does not necessarily follow that such an interaction would lead to conduction. Furthermore, it seems that the "through-bond interaction" is a consequence of through-space interaction.

However, if such through-bond conduction does exist, it should be enhanced by the same factors which enhance other kinds of σ–π conjugation, *i.e.*, by changing the C–C bonds in **28** to bent or polarized σ bonds. It is therefore pertinent to test for transmission of π-electron density through bent bond systems such as cyclopropane or through C–metal σ bonds.

We have used trans 1,2-disubstituted cyclopropyl compounds, which avoid through-space interactions, and the more electron-donating electron pairs of MeO and AcNH in which the π donation far outweighs the inductive effects. If through-bond conduction were

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(17) (a) R. M. Golden and L. M. Stock, *J. Amer. Chem. Soc.*, **94**, 3080 (1972); (b) C. F. Wilcox and C. Leung, *ibid.*, **90**, 336 (1968). These data are shown to be in good agreement with electrostatic models.

(18) G. Montaudo and C. G. Overberger, *J. Org. Chem.*, **38**, 804 (1973).

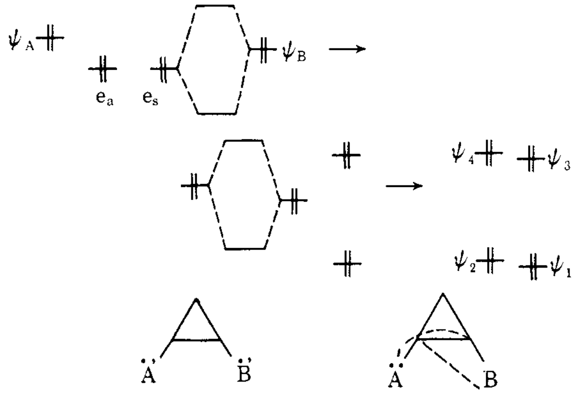
(19) B. G. Ramsey and N. K. Das, *J. Amer. Chem. Soc.*, **94**, 4233 (1972).

(20) (a) P. Bischof, R. Gleiter, E. Heilbronner, V. Horning, and G. Schroder, *Helv. Chim. Acta*, **53**, 1645 (1970); (b) P. Bischof, R. Gleiter, and E. Heilbronner, *ibid.*, **53**, 1425 (1970); (c) R. Gleiter, E. Heilbronner, and A. de Meijere, *ibid.*, **54**, 1029 (1971); (d) P. Bischof, E. Heilbronner, H. Prinzbach, and H. D. Martin, *ibid.*, **54**, 1072 (1971).

significant, it should have raised the cyclopropylbenzene highest filled orbital. This was not observed and we can therefore rule out such through-bond conduction in cyclopropane.[21,22]

We wish to understand why π bonds and the bent bonds in cyclopropane behave so similarly with respect to electron donation and completely differently with respect to what we call "π-electron transmission." We may then be able to make some predictions concerning other σ-bonded systems.

Our results seem to suggest that the two filled π-type orbitals in cyclopropane interact independently as shown in eq 10 for groups $\ddot{A}$ and $\ddot{B}$ which have slightly



(10)

different energies. Although both e_a and e_s have the correct symmetry for interacting with ψ_A and ψ_B, the perturbation of e_s by ψ_B possibly results in a stronger interaction of ψ_A with e_a. This keeps ψ_A and ψ_B in orthogonal orbitals.[22c]

Alternatively, an unoccupied antibonding Walsh orbital could interact with the ψ_A. However, because the interaction is inverse to the energy gap between two orbitals, the interaction would be very small. A similar energy gap consideration explains the failure to conduct π-electron density through a single σ bond.[21]

Such explanations are speculative and the reasons for the apparent failure of independent ψ_A and ψ_B to interact through a cyclopropane ring must await more detailed theoretical calculations than have been done.

The diagram in eq 10 also rationalizes the long wavelength absorption of protonated phenylcyclopropanecarboxylic acid.[18] Although we do not find stabilization of the cation by the electron-donating group, there is a narrowing of the orbital energy differences labeled ψ_3 and ψ_4 which would lead to a red shift. (In this compound ψ_4 is unfilled.)

Our conclusions suggest that, in general, the ability of σ-bonded systems to conduct π-electron density will be far less than their ability to supply electron density by conjugation. Studies of large and more π-electron donating σ systems such as cubane now in progress should define the generality of our nonconduction rule for σ bonds. From our analysis, we would expect that raising the energy of the filled donating orbital (ψ_A of eq 10) should increase conduction somewhat; but even 2-aminocyclopropylcarbinyl cation is not expected to be greatly resonance stabilized by the NH_2.[23]

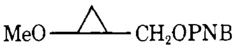
Fragmentation *vs.* Through-Bond Interaction. How can we account for the rapid solvolysis of 2-methoxycyclopropylcarbinyl *p*-nitrobenzoate without vertical stabilization? First let us use the previously established[8a] log *k* for solvolysis of RCH_2X *vs.* ν_{CT} for $RPh\cdot$

$$\log \frac{k_{RCH_2X}}{k_{t\text{-}BuCH_2X}} \cong (22600 - \nu_{RPh})0.0026 \qquad (11)$$

TCNE to estimate two things. Based upon the CT frequency for *trans*-MeOCH=CH—Ph we predict a relative rate of the reaction

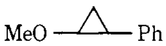
$$Me{-}OCH{=}CH{-}CH_2OPNB \longrightarrow MeOCH{=}CH{-}C^+H_2 + OPNB^- \qquad (12)$$

of 10^{10} times that of the allyl derivative. The observed k_{rel} for



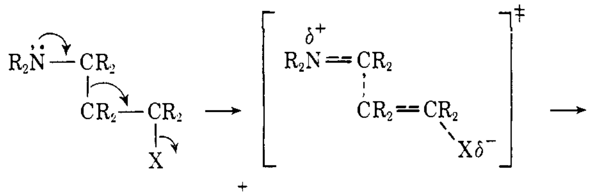
is $10^{2.9}$ over cyclopropylcarbinyl *p*-nitrobenzoate. Even though this acceleration is only 2.9/10 or about 30% of the predicted effect of a vinyl group, it is nevertheless quite easily detectable by our method.

Based upon the $10^{2.9}$ acceleration we can use eq 11 to calculate the expected ν_{CT} for



of 19,500 cm^{-1} compared with the observed value of 20,800 cm^{-1}. The apparent 30% conduction seen in solvolysis cannot be vertical (resonance) according to our test. It is apparently due to some other cause.

The most appealing rationale is fragmentation,[24-26] a process which has been previously discussed as involving distortional stabilization.[8a,b] From the series of reactions for which this phenomenon was postulated



$$R_2\overset{+}{N}{=}CR_2 + R_2C{=}CR_2 + X^- \qquad (13)$$

and from our observation that such groups as $Me_2NCH_2CH_2$ cannot provide vertical stabilization,[8b] it is clear that fragmentation requires extensive bond stretching. Frangomeric acceleration[27] is thus distortional acceleration like sigmatropic cyclopropyl tosylate ring opening.[28]

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(21) Preliminary evidence that $PhCH_2SiMe_3$, $Ph_2CHSiMe_3$, and Ph_3CSiMe_3 have the same CT frequencies with TCNE indicates that transmission through one bond is also quite negligible (H. J. Berwin, Thesis, University of California, San Diego, 1970).

(22) (a) The significant splitting of lone pair orbitals in *p*-dioxanes seems to require through-bond or through-space interaction. Our results favor through-space interaction for *p*-dioxane although through-bond interaction cannot be ruled out. (b) D. W. Turner and D. A. Sweigart, *J. Amer. Chem. Soc.*, **94**, 5599 (1972).

(22c) NOTE ADDED IN PROOF. Recent CNDO calculations of C. F. Wilcox, L. M. Loew, and R. Hoffmann (to be published) indicate that the large coefficient at C_1 and small coefficient at C_2 in the e_s of eq 10 are an important factor.

(23) J. W. Wilt and W. J. Wagner, *J. Amer. Chem. Soc.*, **90**, 6135 (1968).

(24) C. A. Grob and F. Ostermayer, *Helv. Chem. Acta*, **45**, 1119 (1962).

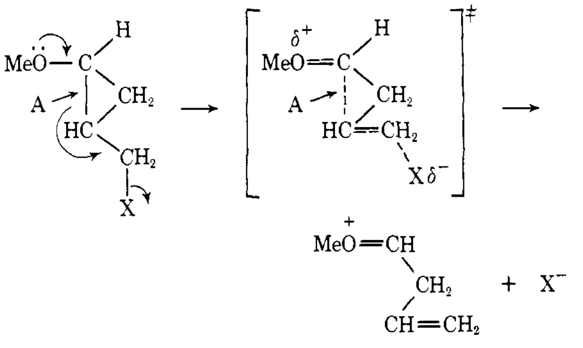
(25) C. A. Grob and P. W. Schiess, *Angew. Chem., Int. Ed. Engl.*, **6**, 1 (1967).

(26) E. M. Kosower, "An Introduction in Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 96.

(27) C. A. Grob and W. Schwarz, *Helv. Chim. Acta*, **47**, 1870 (1964).

(28) P. S. Skell and S. R. Sandler, *J. Amer. Chem. Soc.*, **80**, 2024 (1958).

Although frangomeric acceleration is not usually observed when MeO is substituted for $Me_2\ddot{N}$ in reaction 13, the combination of ring strain plus MeO electron donation makes fragmentation of the methoxycyclopropylcarbinyl system energetically favorable.

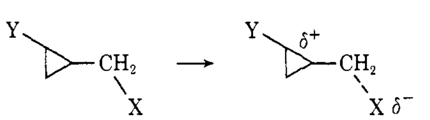


(14)

If this is the favored process, why did the calculations of Kispert *et al.*,[11] not reveal it? For convenience they assigned the bond length, A, as 1.51 Å and did not allow it to vary. Our results suggest that the "conduction" through cyclopropane might depend directly upon this bond length. Because the effect of a trans 2-phenyl or 2-vinyl group upon solvolysis of cyclopropylcarbinyl tosylate is negligible, their calculations might be expected to show no effect of this group. However, where such a group does accelerate solvolysis (*e.g.*, MeO) then we might expect that the cyclopropylcarbinyl cation will collapse without barrier to a substituted butenyl cation as in eq 14.[29]

In a chemical reaction such as solvolysis, the acceleration by resonance interactions will always involve some change in bond length within the stabilizing group, *e.g.*, in both reactions 12 and 14. Our results suggest that changes in geometry are much more requisite to the acceleration of reaction 14 than to reaction 12. It is still possible that the distorted and "resonance-stabilized" transition state of reaction 14 can lead to a similarly stabilized ion which could close to a cyclopropyl product. The extraordinary stability of methoxyalkyl cations relative to cyclopropylcarbinyl cations makes this possibility seem remote.[29]

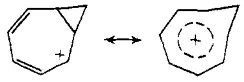
It is interesting to consider the change of mechanism of solvolysis of cyclopropylcarbinyl derivatives as Y is changed.



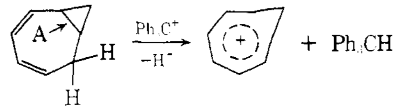
(15)

There is a wealth of evidence that the cyclopropyl ring provides only vertical stabilization if Y = H or Me, both having only inductive (vertical) effects.[3,8c] However, Y = >C=C– accelerates slightly and Y = MeO accelerates the rate almost 10^3 times. In none of these cases is there appreciable vertical stabilization by Y detectable. Therefore, it seems that the mechanism changes from resonance stabilized solvolysis (vertical stabilization) to frangomeric (distortional) acceleration as Y becomes more π-electron denoting. We are exploring both experimentally and with CNDO calculations the consequences of changes in Y upon the course of this reaction.

Homoaromaticity and Nonconduction. Our conclusion that there is no transmission through a cyclopropane ring seems to contradict the postulate of homoaromaticity in systems such as that below, for which there is evidence for ring current.[31]

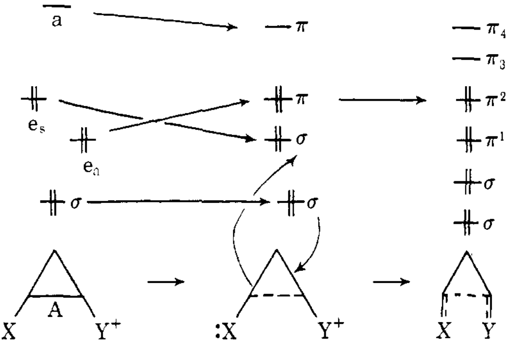


This paradox also has a solution in the idea of distortional stabilization. Consider the formation of such an ion by hydride abstraction. Our results suggest



(16)

that reaction 16 involves distortional stabilization in which the bond A is stretched as discussed by Winstein.[31] Such stretching tends to convert this bond to a stretched π bond which raises the energy of one of the filled orbitals, converts one to a lower energy σ orbital, and lowers the energy of the highest orbital.



(17)

These energy changes destroy the symmetry of cyclopropane and convert it to a σ,π system which resembles butadiene.

However, there is a much smaller overlap across the stretched A bond than there is in the usual π bond and consequently open chain or low aromaticity systems may have no minimum energy in this homoconjugated configuration. We would therefore expect that open chain systems will either have essentially the cyclopropylcarbinyl geometry or open chain configuration.[32]

Experimental Section

Charge-transfer spectra were determined with about 10 mg of donor in 3 ml of 10^{-2} *M* tetracyanoethylene in redistilled spectro quality methylene chloride (MCB) using a 1-cm path length cell and a matched reference cell containing the same solution less the donor. Tetracyanoethylene (Aldrich Chemical Co.) was purified immediately before use by two sublimations at 1 mm of pressure. Chloranil (Eastman Kodak Co.) was recrystallized before use. Nmr spectra of the charge-transfer solutions showed that reaction

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[29] Theoretical calculations indicate that both 2-vinylethyl cation[30a] and 2-phenylethyl cation[30b] collapse *without barrier* to the corresponding cyclopropylcarbinyl cations which are more stable than the primary cations. We can see no reason why the substitution of a methoxy group should change the nature of the reaction coordinate for this rearrangement although the equilibrium would be shifted entirely to the α-methoxyalkyl cation.

[30] (a) W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, **94**, 5917 (1972); (b) W. J. Hehre, *ibid.*, **94**, 91 (1972).

[31] S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

[32] The conclusions of Olah and Liang[33] and those of Hehre and Hiberty[30a] differ on this point. We interpret our results as being in closer accord with the conclusions of Hehre and Hiberty.

[33] G. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 3793 (1973).

had not occurred with most donors. Because 1-methoxy-6-phenylbicyclo[4.1.0]heptane reacted rapidly with TCNE, the spectrum of its chloranil complex was taken.

Donors were purified immediately before the charge-transfer spectra were taken. Liquid donors were purified on an 8-ft (20% D.E.G.S. on Chromosorb P) column at 150°. Solid donors were recrystallized.

Ethylbenzene (14), styrene **(18)**, and **2-phenethyl methyl ether (15)** were obtained from commercial sources and purified by distillation and/or preparative gas-liquid chromatography.

Cyclopropylbenzene (16) and **1-phenylbicyclo[4.1.0]heptane (21)** were available from a previous study.[8a]

trans-**2-Acetamido-1-phenylcyclopropane (9)** was prepared from *trans*-2-phenylcyclopropylamine by the method of Shriner, Fuson, and Curtin:[34a] mp 89–90.5°; nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.0 (m, 5 H), 2.7 (m, 1 H), 1.9, 1.0 (m, 2 H), and 1.8 (s, 3 H).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.42; H, 7.42; N, 8.56. Found: C, 75.26; H, 7.56; N, 8.34; O, 9.08.

trans-**2-Benzamido-1-phenylcyclopropane (10)** was prepared from benzoyl chloride by a procedure similar to that above,[34b] mp 122.5–123.5° (lit.[38] mp 122–123.5°). Spectral data agreed with that reported.[35]

cis- and *trans*-**β-methoxystyrene (20, 19)** were prepared by an adaptation of the methods used by Chan and Rickborn[36a] and Birch.[36b] To 20 g (1.2×10^{-2} mol) of phenylacetaldehyde dimethyl acetal (Aldrich) in a 50-ml pear-shaped flask fitted with a 10-cm distillation column filled with glass helices was added 20 mg of *p*-toluenesulfonic acid. The mixture was boiled until the theoretical amount of methanol was removed (3.85 g), at which time it was cooled and a pinch of Bromothymol Blue was added. Solid sodium methoxide was added until the solution turned blue. The vinyl ether was distilled from the mixture at reduced pressure to give 12 g (75%) of the desired product: bp 78–80° (5 mm) [lit.[36c] bp 99° (13 mm) and 210° (760 mm)]; nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.1 (m, 5 H), 3.27 (s, 3 H), 5.17 and 5.85 (dd, J = 8 Hz), 5.7 and 6.93 (dd, J = 14 Hz), in total integrating to 2 H. The pairs of doublets were derived from the cis and trans isomers and were integrated to be 1:2, respectively. The mass spectrum showed a parent ion for the mixture at m^+/e 134; no higher peaks were present. This mixture gave two long wavelength peaks with TCNE at 570 and 610 nm which we assigned to the cis and trans compounds, respectively.

trans-**2-Methoxycyclopropylbenzene (12)** was prepared along with the cis isomer **(17)** in the following manner. To 22.0 g (3.2×10^{-1} mol) of freshly prepared zinc–copper couple[37] in a flame-dried, 200-ml round-bottom flask equipped with addition funnel, reflux condenser, and magnetic stirrer was added 150 mg of iodine crystals. After the iodine color had subsided, 19.0 g of methylene iodide dissolved in 40 ml of anhydrous ether was added over a period of 1 min. After the reaction had started (as evidenced by vigorous bubbling), a solution of 6.0 g (4.35×10^{-2} mol) of β-methoxystyrene mixture (above), 40.2 g (2.6×10^{-1} mol in all) of CH_2I_2, and 50 ml of anhydrous ether were added over a period of 10 min. The mixture was stirred and refluxed for 2 days, at which time it was cooled and decomposed by the addition of 100 ml of saturated ammonium chloride solution. The ethereal layer was washed with saturated sodium bicarbonate solution and water and then dried over anhydrous magnesium sulfate. The mixture was filtered, the ether removed, and the residue distilled under vacuum to yield 2.5 g (39%) of the product: bp 76–78° (4.0 mm); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.3 to 6.8 (m, 5 H), 3.4 to 3.0 (1 m, H), 2.2 to 1.8 (m, 1 H), 1.4 to 0.6 (m, 2 H), and 3.25 (s, 3 H).

Preparative gas chromatography of the product on an 8-ft 20% DEGS on Chromosorb P column at 150° with a flow rate of 150 cm³/min yielded a broad peak which contained the cis and trans isomers.[38]

Anal. Calcd for $C_{10}H_{12}O$: C, 81.08; H, 8.11; O, 10.81. Found: C, 81.02; H, 7.93; O, 10.99.

The nmr spectrum also contained a singlet at δ 3.0 corresponding to about 20% of the cis isomer. The mass spectrum showed the parent ion of m^+/e 148; no higher peaks were present.

trans-**1,2-Diphenylcyclopropane (11).** To 18.5 g (2.85×10^{-1} mol) of freshly prepared zinc–copper couple[37] and 15 ml of anhydrous ether in a 200-ml flamed-dried, round-bottom flask equipped with reflux condenser, magnetic stirrer, and addition funnel were added 125 mg of iodine crystals and 20 g of methylene iodide in 10 ml of dry ether. After the reaction had started, a solution of 6.09 g (3.34×10^{-2} mol) of *trans*-stilbene (Eastman) and 33.5 g (2×10^{-1} mol in all) of methylene iodide in 100 ml of 1:1 di-*n*-butyl ether and ethyl ether was added over a 10-min period. The mixture was stirred and refluxed for 36 hr, cooled, and decomposed with 50 ml of saturated ammonium chloride solution. The crude mixture was filtered and the filtrate extracted with a sodium thiosulfate solution, a 5% sodium bicarbonate solution, and distilled water. After drying over magnesium sulfate and filtering the ethereal solution was distilled under vacuum to give 1.6 g (24%) of the desired product: bp 112° (1 mm) [lit.[39] bp 114° (1.2 mm)]; nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.1 (s, 10 H), 2.1 (t, 2 H, J = 8 Hz), and 1.3 (t, 2 H, J = 8 Hz).

Anal. Calcd for $C_{15}H_{14}$: C, 92.73; H, 7.27. Found: C, 92.49; H, 7.38.

trans-**2-Methylcyclopropylbenzene (13)** was prepared *via* the customary Simmons–Smith procedure described above using 6.5 g (5.46×10^{-2} mol) of *trans*-β-methylstyrene which had been redistilled at 176° (lit.[40] bp 175°) to give 3.0 g (41%) of the desired product: bp 81–83° (23–25 mm) (lit.[41] bp 78–79° (20 mm)); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.1 (s, 5 H), 1.6 (m, 1 H), 1.3 (br s, 3 H), 0.9 (m, 2 H). The mass spectrum of the product showed a parent peak of m^+/e 132; no higher peaks were present.

1,1-Dimethoxy-2-phenylcyclohexane. To 10.0 g (5.5×10^{-2} mol) of 2-phenylcyclohexanone (Aldrich) in a 100-ml, one-necked, round-bottom flask equipped with reflux condenser was added 13.0 g (8.1×10^{-2} mol) of trimethyl orthoformate (Aldrich) in 30 ml of anhydrous methanol. Dry hydrochloric acid gas was blown into the solution for 30 sec and then the entire mixture was refluxed for 30 min. After refluxing, the mixture was cooled, and solid Bromothymol Blue was added followed by enough sodium methoxide to turn the mixture blue. The mixture was filtered, the solvent removed, and the residue distilled under vacuum to yield 10.4 g (79%) of the desired product: bp 91–94° (5 mm); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.5 to 7.0 (m, 5 H), 3.1 (s, 3 H), 2.8 (s, 3 H), and 2.1 to 1.0 (m, 9 H).

1-Phenyl-2-methoxycyclohex-1-ene. To 10.0 g (4.55×10^{-2} mol) of 2-phenylcyclohexanone dimethyl ketal (prepared as above) in a pear-shaped 25-ml flask was added 20 mg of *p*-toluenesulfonic acid. The mixture was boiled until the theoretical amount of methanol was removed and cooled, and a pinch of Bromothymol Blue was added followed by enough solid sodium methoxide to turn the mixture blue. The vinyl ether was distilled under vacuum from the mixture to yield 6.3 g (74%) of the product: bp 92° (0.7 mm); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.5 (m, 5 H), 4.8 (t, 1 H, due to 3 elimination), 3.3 (s, 3 H, due to 3 elimination), 3.4 (s, 3 H), 3.6 to 1.4 (m, 8 H). From the nmr peak areas, it was discovered that there had been roughly 35% 2-methoxy-3-phenylcyclohex-1-ene produced from 3 elimination.

1-Phenyl-6-methoxybicyclo[4.1.0]heptane (22). Into a 250-ml round-bottom flask equipped with a gas inlet tube, magnetic stirrer, and reflux condenser was placed 17.0 g (2.46×10^{-1} mol) of zinc-copper couple,[37] 125 mg of iodine crystals, and 35 ml of anhydrous ether. While the solution was stirred, 20 g methylene iodide was added, and as soon as the reaction had started a solution of 1-methoxy-2-phenylcyclohex-1-ene (prepared as above), 33.5 g (2×10^{-1} mol in all) of methylene iodide and 45 ml of anhydrous ether were added over a 15-min period. The mixture was refluxed 2 days, cooled, and decomposed by the addition of 100 ml of saturated ammonium chloride solution. The mixture was filtered and the filtrate washed with two 50-ml portions of ether. The combined ether extracts were washed with 10% sodium bicarbonate solution and water and then dried over magnesium sulfate. The dry mixture was filtered and the ether removed to give a yellow oil which was

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(34) (a) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1965, p 230; (b) *ibid.*, p 260.

(35) A. Burger and W. L. Yost, *J. Amer. Chem. Soc.*, 70, 2198 (1948).

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then vacuum distilled to give 2.1 g (30%) of the desired product, bp 92–95° (0.5 mm).

After preparative gas chromatography on an 8-ft column of 20% SE-52 on Chromosorb W the sample showed the following: nmr $\delta_{TMS}^{CCl_4}$ 7.1 (m, 5 H), 3.05 (s, 3 H), 2.5 to 1.0 (m, 8 H), 0.6 and 0.7 (2 s, integrating to 2 H).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.16; H, 8.91; O, 7.92. Found: C, 82.99; H, 8.71; O, 8.13.

The mass spectrum showed a parent peak at m^+/e 202; no higher peaks were present.[42]

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[42] Preparative gas chromatography was unable to separate the desired product from those produced by addition to the nonconjugated olefin. These compounds, however, would not interfere with the charge-transfer spectrum of the desired 6-methoxybicyclo[4.1.0]-1-phenylheptane.

Lactonization of Coumarinic Acids. Kinetic Evidence for Three Species of the Tetrahedral Intermediate[1a]

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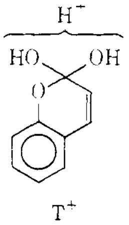
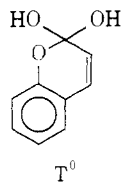
Abstract: The lactonization of four coumarinic acids substituted on the ring and side chain with methyl groups has been studied at 30° and at pH 0–7. The variation of the rate of lactonization with pH is strongly dependent on the position of the methyl substituents. With 4,6,8-trimethylcoumarinic acid, the pH–rate profile is consistent with the participation of three kinetically significant intermediates, and provides kinetic evidence for the existence of an anionic tetrahedral intermediate in the formation of a phenyl ester. The nonlinear dependence of the rate of lactonization of coumarinic acids on formate and acetate buffer concentration offers additional support for the postulation of intermediates in these reactions.

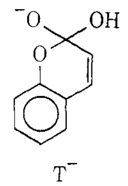
Studies of the kinetics of lactonization of coumarinic acids have led to the proposal that the reaction involves cationic and neutral tetrahedral addition intermediates.[2,3] The nature of the rate-limiting step depends on pH; for most of the compounds studied, the rate-limiting step is believed to be the formation of intermediates at low pH, and their decomposition at higher pH. This change in rate-determining step occurs because the two intermediates partition differently between reactants and products. The cationic intermediate (T^+) breaks down mainly with expulsion of water to yield the coumarin product, while the neutral intermediate (T^0) usually reverts to the reactant coumarinic acid.[4] No evidence was obtained for the existence of an anionic intermediate (T^-). If such a species is formed, it would be expected to break down generally with expulsion of phenoxide ion. The observation[3] that electron-donating substituents in the aromatic ring enhanced the departure of water relative to that of phenol from T^0 led us to consider the possibility that a suitably substituted coumarinic acid might form a neutral intermediate from which water would leave predominantly. If this coumarinic acid formed an anionic intermediate which preferred to expel phenoxide ion, the kinetics of the lactonization reaction should indicate a new change in rate-determining step, and, incidentally, provide hitherto lacking evidence for the existence of the anionic intermediate.



T^+



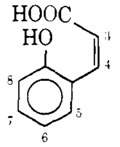
T^0



T^-

Results

The lactonization of four methyl-substituted coumarinic acids (**1–4**) was studied by spectrophotometric means in aqueous solution, μ = 1.0 (LiCl), at 30°. To avoid the necessity of extrapolating rate constants to zero buffer concentration, rate constants at pH >2.5 were determined in unbuffered solution and pH was kept constant by automatic titration with the pH-stat.[5] With **1**, some measurements were made in buffered solution; the values extrapolated to zero buffer con-



1, 4-CH_3
2, 5,8-$(CH_3)_2$
3, 4,6,8-$(CH_3)_3$
4, 4,5,7-$(CH_3)_3$

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[1] (a) This research was supported by a grant from the National Science Foundation. (b) Postdoctoral Research Fellow of the National Institutes of Health, 1971–1973.

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[4] The position of the proton in T^+ is not specified. Similarly, the structure here given for T^0 does not exclude other structures of zero net charge.

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