determined using a Varian A-60A nmr spectrometer with tetramethylsilane as an internal standard and CCl_4 as a solvent.

^{19}F Nmr Measurements. Fluorine nmr spectra were recorded on a Varian Model HA 56/60 operating at 56.445 MHz in the frequency sweep mode.[33] Measurements were made on approximately 5% (v/v) solutions of the substituted fluorobenzene in a 2% (w/w solution of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFCB) used as the standard in CCl_4, using a sealed capillary containing trifluoroacetic acid as an internal lock. These solutions are a permissible approximation for infinite dilution.[1] The chemical shifts were referenced to fluorobenzene by adding 1.2 ppm to the observed shift (relative to TCTFCB).

Infrared Measurements. The infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer. Quantitative studies were done using spectroscopic grade CCl_4 and cyclohexane as solvents. The technique used was identical with that described by Katritzky; absorbance values were measured directly and by varying solution concentrations between 0.30 and 1.30 *M* appeared in the desired range of 0.05–0.60.

Materials. Spectroscopic grade CCl_4 and cyclohexane (Mallinckrodt, Inc.) were used as solvents for both infrared and nmr measurements. TCTFCB was used as obtained from Peninsular Chemresearch, Inc. Commerically available anhydrous KF was rigorously dried in a vacuum oven at 120° for at least 24 hr and was finely crushed before use. Technical grade ethylene glycol was distilled beofre use and the fraction with bp 90° (1.1 mm) collected.

α-Chloro-*m*- and *p*-fluorotoluenes, *m*- and *p*-fluorotoluenes, and benzotrifluoride were purchased from Pierce Chemical Co.

Benzyl bromide (British Drug Houses, Ltd.) was used without purification.

α,α-Dichloro-*m*-fluorotoluene and α,α,α-trichloro-*m*-fluorotoluene were prepared by the method of Fukui[34] by chlorination of *m*-fluorotoluene (25.0 g, 0.23 mol) in the presence of 1.0 g of PCl_3. The reaction was monitored by nmr and terminated when all the *m*-fluorotoluene had reacted. Distillation through a 45-cm spinning band column gave 10.0 g (24%) of the dichloro derivative (n^{20}D 1.5278; nmr δ 6.60 (s, $CHCl_2$, J_{CH} = 179.0 Hz)) and 12.1 g (25%) of the trichloro derivative (bp 75° (5 mm); n^{20}D 1.5366).

α,α-Dichloro-*p*-fluorotoluene (n^{20}D 1.5282; nmr δ 6.60 (s, $CHCl_2$, J_{CH} = 179.0 Hz)), and **α,α,α-trichloro-*p*-fluorotoluene** (n^{20}D 1.5360) were prepared as above, by chlorination of *p*-fluorotoluene.

α-Bromo-*p*-fluorotoluene and **α-bromo-*m*-fluorotoluene** were prepared by the method of Hudlicky,[35] from the corresponding *m*- and *p*-fluorotoluenes.

Benzyl fluoride was prepared according to a method adapted from the procedure of Fukui.[34] Benzyl bromide was added dropwise over a period of 2 hr to a vigorously stirred, saturated solution of anhydrous KF in ethylene glycol at 170°. Continuous distillation of any volatile material was maintained during the time of the addition. A 1:1 mixture of *toluene* and of benzyl fluoride (nmr δ 5.30 (d, J_{HF} = 48.0 Hz)), was obtained in 10% yield, and separated at 100° by preparative glpc using a column packed with QF-1 on 60–80 Chromosorb W.

α,*m*-Difluorotoluene (n^{20}D 1.4645; nmr δ 5.28 (d, CH_2F, J_{HF} = 47.5 Hz, J_{CH} = 152.0 Hz)), and **α,*p*-difluorotoluene** (n^{20}D 1.4648; nmr δ 5.28 (d, CH_2F, J_{HF} = 48.0 Hz, J_{CH} = 152.0 Hz)) were prepared as above.

Anal. Calcd for $C_7H_6F_2$: C, 65.65; H, 4.68; F, 29.70. Found for meta: C, 65.93; H, 4.92; F, 29.41.

α,α,*m*-Trifluorotoluene (n^{20}D 1.4420; nmr δ 6.57 (t, CHF_2, J_{HF} = 56.5 Hz)), and **α,α,*p*-trifluorotoluene** (n^{20}D 1.4412; nmr δ 6.57 (t, CHF_2, J_{HF} = 56.5 Hz, J_{CH} = 187.0 Hz)), were prepared by treating the corresponding α,α-dichlorofluorotoluenes with SbF_3 following procedures described for similar compounds.[36]

Anal. Calcd for $C_7H_5F_3$: C, 57.51; H, 3.42; F, 39.09. Found for meta: C, 57.23; H, 3.56; F, 39.39.

Benzal fluoride was prepared from benzal chloride using the procedure outlined above.

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(33) We acknowledge the assistance of Dr. T. W. Johnson in recording the ^{19}F nmr spectra.

(34) K. Fukui, H. Kitano, T. Osaka, Y. Inamoto, and H. Shirai, *Nippon Kagaku Zasshi*, **79**, 1428 (1958); *Chem. Abstr.*, **54**, 5518 (1959).

(35) M. Hudlicky, *Collect. Czech. Chem. Commun.*, **25**, 1199 (1960).

(36) A. L. Henne, *Org. React.*, **2**, 49 (1944).

Vertical Stabilization of Cations by Neighboring σ Bonds. General Considerations[1-3]

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Abstract: A theory for stabilization of carbonium ions or other cations, by delocalization of neighboring σ bonds, is described. Such delocalization is available without changing the reactant geometry and is termed "vertical stabilization." The stabilizing influence is contrasted to the bridged-ion theory of neighboring group participation, in which the neighboring group moves toward the reaction center as the transition state is approached, and to frangomeric acceleration, in which the neighboring group moves away from the reaction center as the transition state is approached. The effects of structural changes on the magnitude of (vertical) σ–π conjugation are discussed. In addition, further evidence is offered against significant effects of C–H hyperconjugation on bond lengths.

Delocalization of σ bonds was first discussed in detail by Mulliken[5] in his treatment of carbon–hydrogen hyperconjugation as an explanation of certain properties of hydrocarbons.[6–8] Variations in such delocalizations with the nature of the hyperconjugated group were

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(1) Supported by the Air Force Office of Scientific Research, Grants AFOSR-69-1639 and AFOSR-69-1639A.

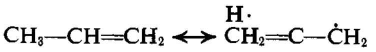
(2) The effects of σ–π conjugation on singlet neutral molecules, on free radicals, and on carbanions will be considered in subsequent papers.

(3) The major part of these ideas was presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 39. Previous discussions of σ–π conjugation in cations are found in ref 4a–g.

(4) (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970); (b) T. G. Traylor and J. C. Ware, *Tetrahedron Lett.*, 1295 (1965); (c) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967); (d) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967); (e) J. A. Mangravite and T. G. Traylor, *ibid.*, 4457 (1967); (f) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968); (g) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969); (h) N. A. Clinton, R. S. Brown, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 5228 (1970); (i) T. T. Tidwell and T. G. Traylor, *ibid.*, **88**, 3442 (1966); (j) W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.*, **92**, 7476 (1970); (k) W. Hanstein, unpublished results.

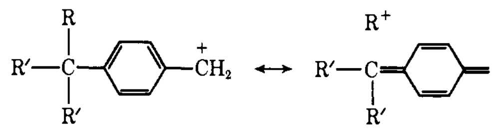
(5) (a) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); (b) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959).

(6) Ground-state properties of hydrocarbons such as bond lengths and heats of formation are better explained in terms of hybridization or repulsion effects.[7,8]



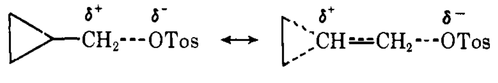
$$CH_3{-}CH{=}CH_2 \leftrightarrow CH_2{=}\overset{H\cdot}{C}{-}\dot{C}H_2$$

suggested in the Baker–Nathan effect[9] in which the

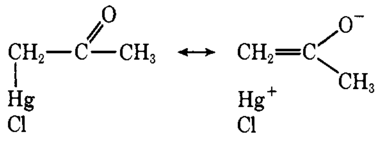


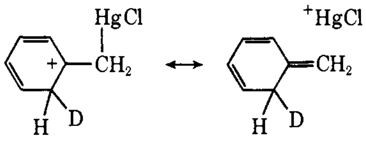
cation seemed to be more stable for R = H than for R = CH_3.[10]

Highly exalted hyperconjugation (σ–π conjugation) has been suggested to result from increased bond strain[12]



or from increased bond polarity.[13,14]

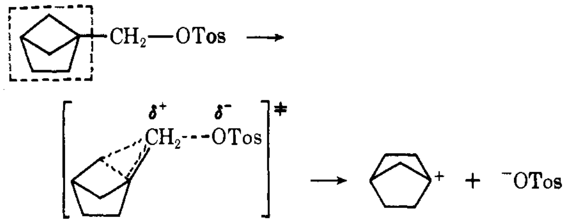




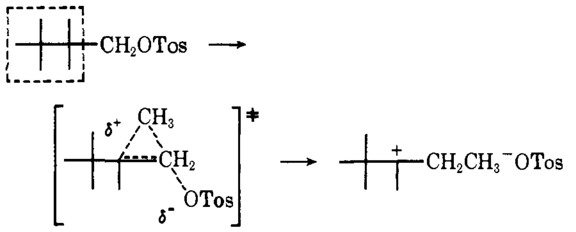
Although the previous authors did not discuss the geometrical restrictions, other than coplanarity of overlapping p orbitals, for these σ–π delocalizations, the use of the term "conjugation" implies such restriction since the Born–Oppenheimer approximation is assumed.

These ideas were not explicitly[15] included in the explanations of stabilization of carbonium ions because the proposal of neighboring group participation (essentially internal displacement) seemed to provide such a beautiful rationale for both the stereochemistry and rearrangement in many complex carbonium ion reactions.[20] Neighboring group participation has also been incorporated intact into organotransition metal chemistry and called the β effect.[21]

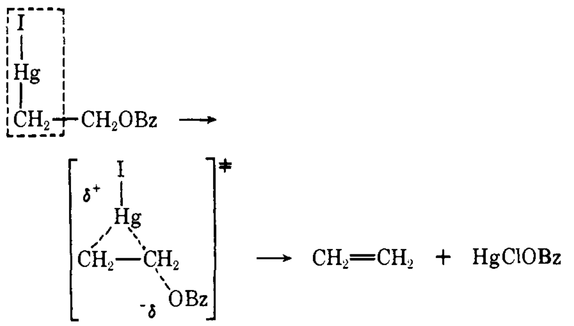
The four disparate examples of eq 1–4 illustrate this tendency to write bridged structures for the transition states and intermediates in accelerated solvolyses.



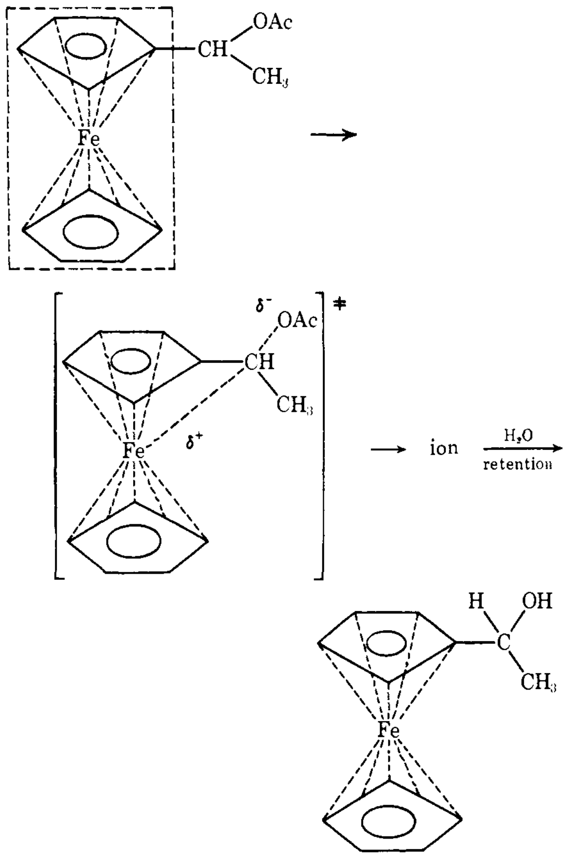
(1)[22]



(2)[23]



(3)[24]



(4)[25]

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(7) M. J. S. Dewar, "Hyperconjugation," Ronald Press New York, N. Y., 1962, p 48.

(8) R. A. Alden, J. Kraut, and T. G. Traylor, *J. Phys. Chem.*, **71**, 2379 (1967); *J. Amer. Chem. Soc.*, **90**, 74 (1968).

(9) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(10) This effect, like that of bond-length variations, has attractive alternative explanations.[4a,11]

(11) W. M. Schubert and D. F. Gurka, *J. Amer. Chem. Soc.*, **91**, 1443 (1969).

(12) J. D. Roberts and R. H. Mazur, *ibid.*, 73, 2509 (1951).

(13) A. N. Nesmeyanov and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, **59**, 707 (1948).

(14) Yu. G. Bundel, N. D. Antonova, and O. A. Reutov, *ibid.*, **166**, 1103 (1966).

(15) The σ–π overlap is usually included in any extensive molecular orbital calculation of stabilities of strained cations.[16–20]

(16) M. Simonetta and S. Winstein, *J. Amer. Chem. Soc.*, 76, 18 (1954).

(17) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

(18) C. Trindle and O. Sinanoğlu, *J. Amer. Chem. Soc.*, **91**, 4054 (1969).

(19) (a) J. E. Williams, Jr., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Nathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970); (b) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **92**, 6380 (1970), and references therein.

(20) See A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 103, for a review.

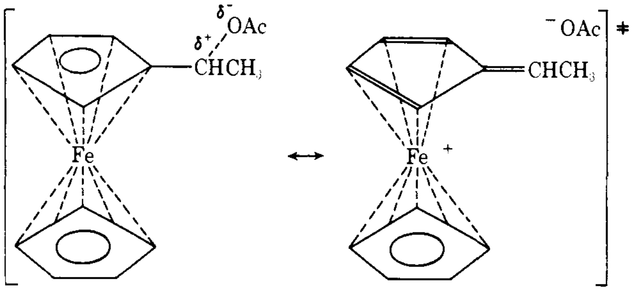
(21) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. II, Methuen and Co., London, 1968, p 211, and references quoted therein.

(22) K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.*, **85**, 3188 (1963).

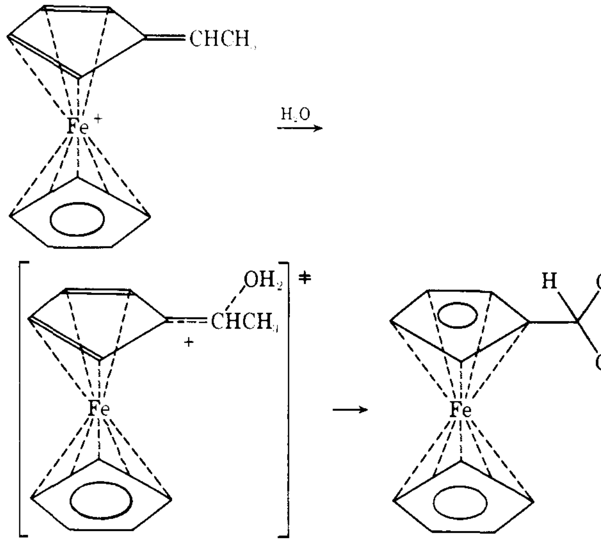
(23) E. N. McElrath, R. M. Fritz, C. Brown, C. Y. LeGall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960).

Both the transition-state structures written for reactions 1 and 2 and statements that there is "relief of steric strain at the transition state" imply that structure alteration in moieties which are enclosed in the dotted lines provides the driving force for the accelerated reactions.[26]

It has been suggested,[4b] with some evidence,[4a,c] that reactions such as 3 and 4 derive much, if not all, the driving force for acceleration as well as their stereochemistry from σ–π conjugation without significant change in the geometry of the group within the dotted lines. For example, the transition state for reaction 4 was written as follows



If the transition state for ionization has the geometry shown because of σ–π conjugation, then the transition state for the reaction of the ion must have the same geometry unless the ion rearranges. That is, microscopic



(5)

reversibility demands that σ–π conjugation have the same effect on the stereochemistry of the product-forming step as it had in the ionization step. The result is retention of configuration.[27]

Despite several suggestions of σ–π conjugation based on chemical[4a,c,e,f,32] and spectroscopic[31,33,34] evidence, this idea met with considerable skepticism.[38–40] Such cation-stabilizing groups as $-\mathrm{CH_2SiMe_3}$ and ferrocenyl continued to be discussed in terms of inductive[41,42] or d orbital[21] effects. However, the recently reported activating influence of the $\mathrm{PhCH_2HgCH_2}$ group ($\sigma^+_{\mathrm{CH_2HgCH_2Ph}} = -1.1$)[4d] toward both aromatic electrophilic substitution[4d,14] and electron removal[4a] is simply too large for any imaginable inductive effects. Consequently, σ–π conjugation appeared to be established.[4d] Recent results from several laboratories[28,43–46] seem to support it. In fact, the postulate of exalted hyperconjugation of strained C–C bonds[12,46,47] has recently received considerable experimental support[4a,f,g,47b,48] which will be discussed below.

Because effects attributable to σ–π conjugation seem to exceed in magnitude[4a] effects for which neighboring group participation has been postulated, it is pertinent to discuss the details of this effect, to summarize the influences of structural changes upon σ–π conjugation, and to present some general methods of differentiating between these two effects.

Discussion

Vertical Stabilization in a Nonvertical Process. We may describe quite accurately as "vertical stabilization"[49] the effect which makes anisole or dibenzyl mer-

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(24) M. M. Kreevoy and G. B. Bodem, *J. Org. Chem.*, **27**, 4539 (1962).

(25) E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 3840 (1961).

(26) However, the calculations in ref 16–18 seem to indicate considerable stabilization of the cation without appreciable rearrangement of the groups involved.

(27) The way in which exalted σ–π conjugation (hyperconjugation) serves as an alternative explanation for the effects attributed to neighboring group participation was set forth in some detail in ref 4c. Some of these ideas have also been discussed recently by Jensen and Smart[28] with reference to strained bonds. Free-radical stabilizations[4c,28–31] by β-metal groups have also been observed.

(28) F. R. Jensen and B. F. Smart, *J. Amer. Chem. Soc.*, **91**, 5686 (1969).

(29) F. R. Jensen and H. E. Guard, *ibid.*, 90, 3250 (1968).

(30) N. S. Vyazankin, E. N. Gladyshev, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **153**, 104 (1963).

(31) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 6161 (1969).

(32) C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

(33) B. G. Ramsey, "Electronic Transitions in Organometalloids," Academic Press, New York, N. Y., 1969, p 77. This review, while referring briefly to C–metal σ–π conjugation, unfortunately omits the discovery and most of the extensive studies of the spectroscopic effects of σ–π conjugation in the USSR from 1948[13] to the present.[14,34,35–37]

(34) (a) A. N. Nesmeyanov and I. I. Kritskaya, *Dokl. Akad. Nauk SSSR*, **121**, 477 (1958); (b) A. N. Nesmeyanov, I. F. Lutsenko, and S. V. Ponomarev, *ibid.*, 124, 1073 (1959); (c) A. N. Nesmeyanov, *Tetrahedron*, **21**, 687 (1965), and references cited there.

(35) A review of σ–π conjugation is in preparation and will be presented elsewhere.

(36) Yu. P. Egorov, L. A. Leites, and V. F. Mironov, *Zh. Strukt. Khim.*, **2**, 562 (1961); *Chem. Abstr.*, **59**, 12322c (1963).

(37) A. D. Petrov and V. F. Mironov, *Angew. Chem.*, **73**, 59 (1961).

(38) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Lett.*, 1695 (1966).

(39) M. Cais, *Organometal. Rev.*, **1**, 435 (1966), and references cited therein. See also ref 40 for more recent discussions on this point.

(40) M. J. Nugent, R. E. Carter, and J. H. Richards, *J. Amer. Chem. Soc.*, **91**, 6145 (1969). Note that the structure II in this paper is incorrectly transcribed from ref 4c.

(41) (a) R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometal. Chem.*, 2, 154 (1964); (b) D. R. M. Walton, *ibid.*, **3**, 438 (1965); (c) C. Eaborn and K. C. Pande (*J. Chem. Soc.*, 1566 (1960)) stated that "hyperconjugation of the C–PbEt3 bond should certainly not be more effective than that for the C–H bond."

(42) (a) H. Bock and H. Alt, *Angew. Chem., Int. Ed. Engl.*, 6, 942 (1967), and references cited there; (b) H. Bock and H. Alt (*J. Amer. Chem. Soc.*, **92**, 1569 (1970)) still attribute the cation stabilization by the $-\mathrm{CH_2SiMe_3}$ group to an inductive effect.

(43) E. A. Hill, S. G. Engel, J. R. Pociask, and A. Komornicki, Abstracts of the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, ORGN 169.

(44) (a) C. Eaborn, ref 32, considered C–metal hyperconjugation, and then abandoned it in favor of inductive effects.[40] Recently[42] he has explained stabilization by $-\mathrm{CH_2SiMe_3}$ or $\mathrm{(CH(SiMe_3)_2}$ in terms of hyperconjugation; (b) A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometallic Chem.*, 20, 49 (1969).

(45) D. Seyferth, S. S. Washburne, C. J. Attridge, and K. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 4405 (1970).

(46) E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962).

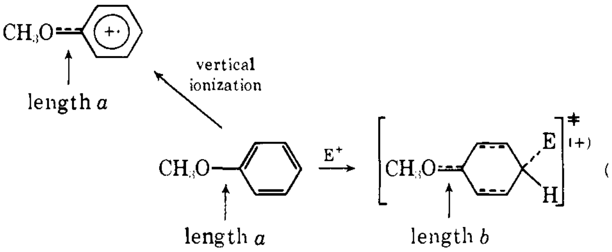
(47) (a) R. C. Hahn, T. F. Corbin, and H. Shechter, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, p 35-O; (b) *J. Amer. Chem. Soc.*, 90, 3404 (1968).

(48) L. B. Jones and V. K. Jones, *Tetrahedron Lett.*, 1493 (1966).

(49) Vertical stabilization has been defined[4a] as that stabilization in $\mathrm{Y{-}CH_2^+}$ or $\mathrm{Y{-}CH_2\cdot}$ which is afforded while the internal geometry of Y and the Y–C bond length remain essentially as they were in the reactant. The term "σ–π conjugation"[50] as used here is intended to be synonymous with "hyperconjugation."

cury have lower ionization potentials than does benzene.

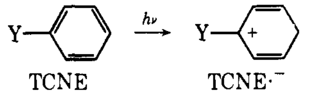
However, the term "vertical stabilization" to describe the effect which makes anisole undergo electrophilic substitution faster than does benzene is not exact. This is because the attack of an electrophilic reagent E^+ on anisole is slow and the methoxy group will change its bond length to minimize the energy. If the length b is significantly shorter than length a then the use of the term "vertical stabilization" for reactions will be inexact.



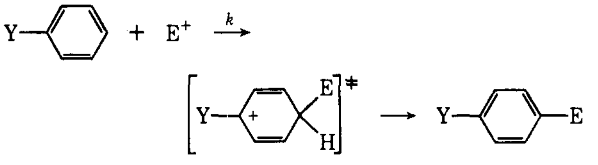
(6)

However, $p\pi$–$p\pi$ overlap integrals are not very sensitive to distance and the (C–O) σ bond will still be dominant in determining bond length. We conclude that, for the methoxy group, the distances a and b are not sufficiently different to contribute greatly to the stabilization energy and that the methoxy group provides vertical resonance stabilization. The fact that vertical ionization potentials correlate with log (reaction rate) for aromatic electrophilic substitution suggests that this conclusion is at least approximately correct.

If we assume that methoxy groups provide vertical stabilization in aromatic substitution reactions, then it follows that we may test any group attached to a benzene ring for vertical stabilization by comparing these two groups in the vertical process of ionization (charge transfer) and in the reaction in question.



(7)



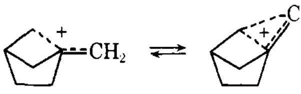
(8)

$$\log k/k_0 = \rho_8\sigma_Y{}^+ \qquad (9)$$

$$\bar{\nu} - \bar{\nu}_0 = \rho_7\sigma_Y{}^+ \qquad (10)$$

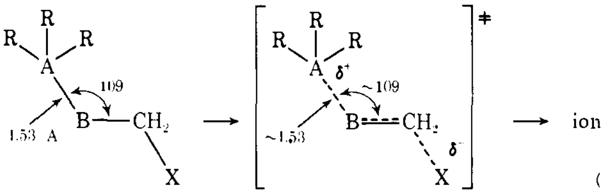
If we find that a given group Y fits both eq 9 and 10 with one value of $\sigma_Y{}^+$ then we may conclude that the group Y provides the same fraction of vertical stabilization in reaction 8 as does the methoxy group, *whatever that fraction is.* The fact that group Y lowers the ionization potential of benzene is definite evidence for vertical stabilization by the group Y. Such stabilization must be available in other reactions as well. We predict a reaction rate (*e.g.*, for reaction 1) assuming only vertical stabilization and find that it is identical with the observed rate. The conclusion is that no other stabilization (such as bridging, fragmentation, etc.) is significant. For example, the high reactivity in reaction 3 is reflected in the very low ionization potential of $RHgCH_2Ph$ whereas the high reactivity of $H_2NCH_2CH_2Cl$ is not seen in the ionization potential of benzylamine.[52] Therefore the $RHgCH_2$ group provides vertical stabilization to cationic centers whereas the stabilization by the H_2NCH_2 group is nonvertical.

We do not say that cations cannot be bridged but that, because most of the stabilization energy may be provided without nuclear movement, very little is gained by moving atoms. For example, we might write the intermediate for reaction 1 as a σ–π conjugated or as a bridged species. These are not resonance forms since the geometry changes. However, we argue that the energies of I and Ia differ very little and that the actual geometry looks more like I than Ia at the transition state.



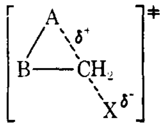
I Ia (11)

Definition of a σ–π Conjugation. As the word "conjugation" implies, simple σ–π conjugation will be interpreted as a vertical stabilization in which the σ bond is delocalized without changing its bond length or angle. For example, the cation $R_3ABCH_2{}^+$ might be formed as shown below.

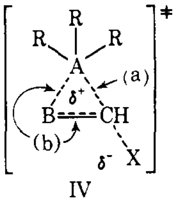


II (12)

It is obvious that the formulation II represents a limiting behavior achieved only in vertical processes, and that, between this and the formulation III which attributes all the driving force to internal displacement, there are various intermediate cases having contributions from both kinds of driving force.[4c] For example, the formulation IV implies contributions from both σ–π conjugation (b) and from internal displacement (a), but this stabilization is not vertical because A has moved. However, the b contribution need not depend highly on the ABC angle and we therefore might loosely



III



IV

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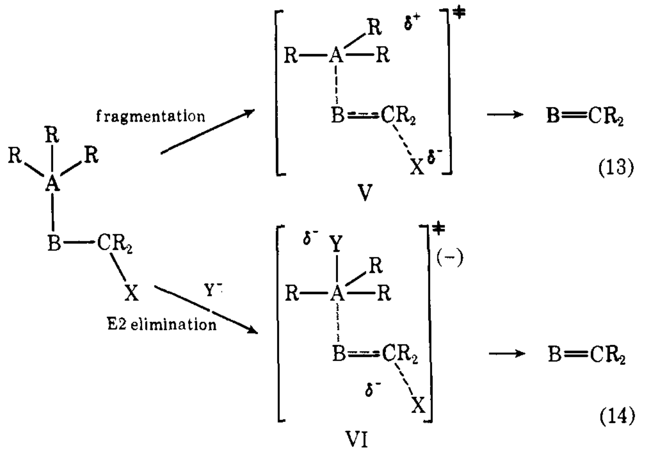
(50) A. N. Nesmeyanov[34c] has used this term more loosely than we have, including such nonvertical processes as fragmentation.[51] We prefer to differentiate breaking of a σ bond from simple delocalization of a σ bond.

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

(52) D. W. Turner, *Advan. Phys. Org. Chem.*, 4, 57 (1966).

call b the "contribution from vertical stabilization."[53-55] We expect this contribution to reveal itself in such Franck–Condon processes as electronic excitation.

A second kind of nonvertical acceleration of solvolysis reactions is fragmentation (or other eliminations) in which the AB bond lengthens and considerable rehybridization occurs at A. These processes, like internal displacement, should not correlate with any actual vertical processes.



V (13)

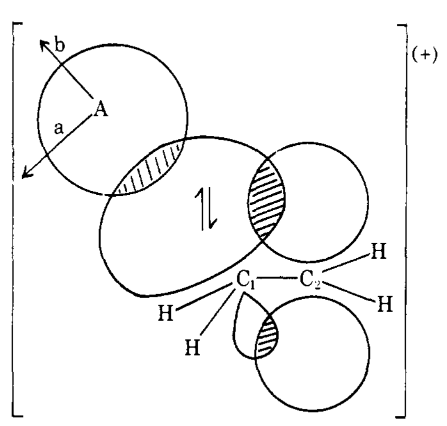
VI (14)

If we can develop a test which demonstrates that all the stabilization of a transition state which could be II, III, IV, V, or VI is available in a Franck–Condon process then we conclude that the stabilization is "limiting vertical" as in II. If such vertical stabilization is undetectable we would conclude that the stabilization is "limiting nonvertical" as in III, V, or VI (*e.g.*, $H_2NCH_2CH_2Cl$). We may expect a spectrum of merging[51] transition states varying from solvent-induced E2 elimination to fragmentation to hyperconjugation to participation (bridging).

The limiting formulation II appears to be approached in several cases and an experimental probe for such conjugation is now available.[4a]

Factors which Influence σ–π Conjugation. Since the stabilization provided to the transition state II accrues from delocalizing the AB σ bond and from formation of a $B{=}CH_2$ π bond, we expect this conjugation to be enhanced by any structural change which makes the AB σ bond more delocalizable (polarizable) or increases the strength of the $B{=}CH_2$ π bond.

The possible σ–π conjugation effects are easily visualized in the atomic orbital diagram for $ACH_2CH_2^+$ shown in VII.[27] The sp^3-hybrid orbital on C_1 may overlap with the p orbital on C_2 but the extent of this interaction will depend upon the position and electronegativity of A. The σ orbital will overlap less with A and more with C_2 if A is, by some geometrical restraint (*e.g.*, as in cyclopropylcarbinyl cation), forced away from a normal equilibrium position. Either bending (direction a) or stretching (direction b) the AC bond should have this effect. Alternatively, lowering the electronegativity of A decreases the probability that the electrons (↿⇂) will be near A and results in better C_1C_2 π bonding.



VII

Changing C_1 or C_2 to atoms having different inherent π overlap would also be expected to alter the extent of σ–π conjugation when other things are not changed.

To illustrate the effects which enhance σ–π conjugation, consider the solvolysis of a substance R_3ABCH_2X. (An example might be $Me_3SiCH_2CH_2Cl$ in which the AB bond is delocalizable.) The effects contributing to vertical σ–π conjugation in this reaction are enumerated in Chart I and discussed below.

Chart I

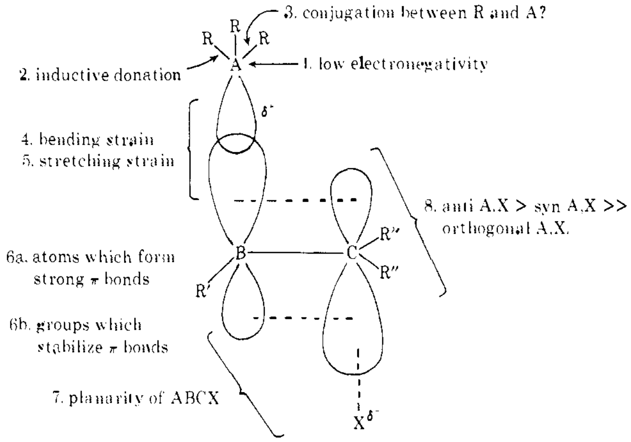


Chart I summarizes expectations for σ–π conjugation derived from a large number of empirical observations in studies of E2 elimination,[56] solvolyses,[19,57] electrophilic additions,[53,58] and deuterium isotope effects,[46] as well as molecular orbital calculations.[16-19,59,60] In order to show all the geometrical effects we have chosen to illustrate σ–π conjugation in a transition state for carbonium ion formation. However there are a wide variety of other processes, some of them Franck–Condon processes, which respond to this kind of delocalization. For example, carbonyl stretching frequencies,[33b] uv maxima,[33b] charge-transfer maxima,[4a] and aromatic

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(53) The possibilities of transition-state structures similar to II were considered by Winstein[54] in his statement "Participation amounts to delocalization of the C$_\beta$–R bonding electron pair as electron deficiency is created by ionization. Now in hyperconjugation involving β-linkages, there is also delocalization. Whether in general hyperconjugation and participation should be considered to merge depends upon the still unsettled preferred geometry in hyperconjugation." The very large effects of C–metal hyperconjugation have allowed us to settle this question and we show in this series of papers that participation and hyperconjugation do, in fact, merge.

(54) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, 74, 1113 (1952). See footnote 19.

(55) See also V. J. Shiner, *ibid.*, **82**, 2655 (1960).

(56) (a) D. V. Banthorpe, "Elimination Reactions," Elsevier, New York, N. Y., 1963, p 54; (b) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, 1, 225 (1962).

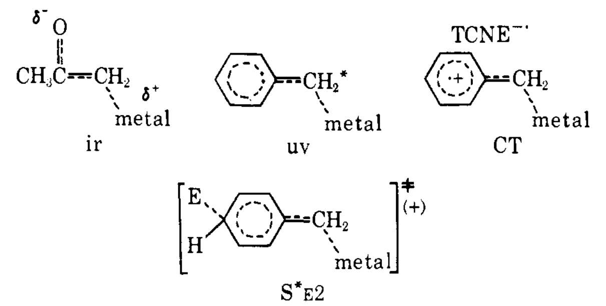
(57) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965, p 6.

(58) R. C. Fahey, *Top. Stereochem.*, 3, 237 (1968).

(59) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

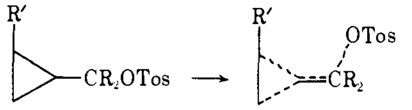
(60) R. M. Pitzer, *J. Chem. Phys.*, 41, 2216 (1964).

electrophilic substitution rates[4d,14] respond to σ–π conjugation as illustrated by the excited-state or transition-state structures below. Examples of these processes will be chosen to illustrate some of the effects of Chart I.

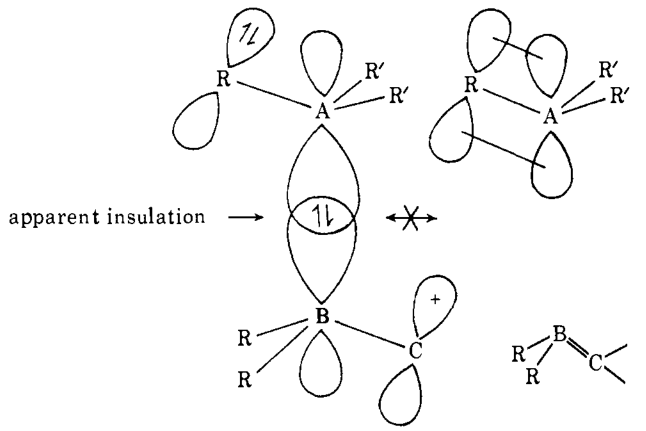


Description of the Effects Shown in Chart I. (1) Low Electronegativity of A. The polarization of the A^+–B^- bond in this sense is brought on by having the electronegativity of A lower than that of B. For example, the Pb–C bond is much more polar than the H–C bond and thus more delocalizable. Correspondingly, the ionization potential of $(C_6H_5)_3PbCH_2C_6H_4$ is lower than that of $HCH_2C_6H_5$ by about 1 eV. Details of this effect are shown in ref 4a and j.

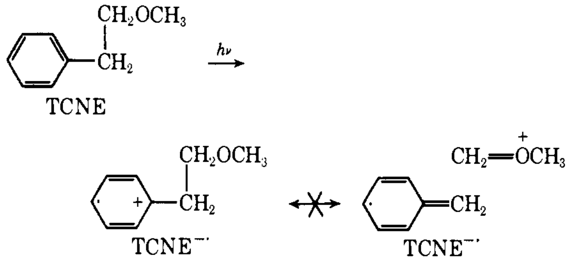
(2) Inductive Donation. It follows from (1) that donation to A by the groups R, which lowers the electronegativity of A, will increase the polarity of the A–B bond (if B is C, N, or O) and thus increase delocalization. The ionization potential of the series $C_6H_5CH_2HgX$ increases rapidly[4j] with inductive withdrawal (σ_I) of X. Similarly, the rates of solvolysis of the cyclopropylcarbinyl compounds below increase as R′ = H is changed to R′ = CH_3.[61] Correspondingly,[4a,h] ionization potentials of 1-phenyl-2,3-dialkylcyclopropanes are lower than that of phenylcyclopropane.[4h]

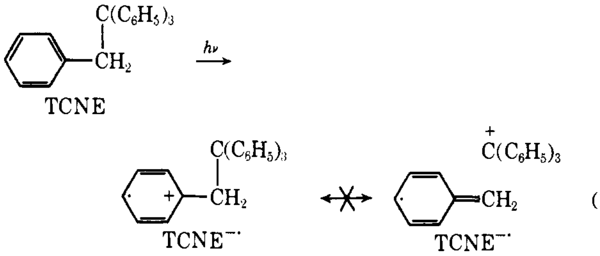

(15)

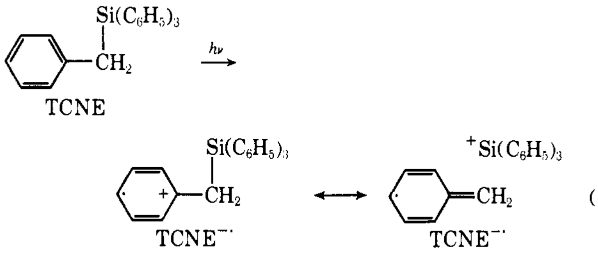
(3) Absence of Conjugation between A and R. Although there is still some argument about cross-conjugation through cyclopropyl groups,[62] cross-conjugation through σ bonds has been shown to be absent in other systems.[63] There is apparently no delocalization from one π system to another through an ordinary σ bond in the situation shown below. One reason why this might not be observed in the case of Chart I is the requirement of a rehybridization of the R_3A system to achieve good R_3A^+ delocalization.[28] Such rehybridization is a nonvertical process. However, this rehybridization may be built into the system when the σ bond is bent. We will discuss such a case in a following section.



An illustration that delocalization in R_3A^+ cannot be a factor in A–B σ–π conjugation is seen in the charge-transfer spectra of the complexes shown below.[4a,k]

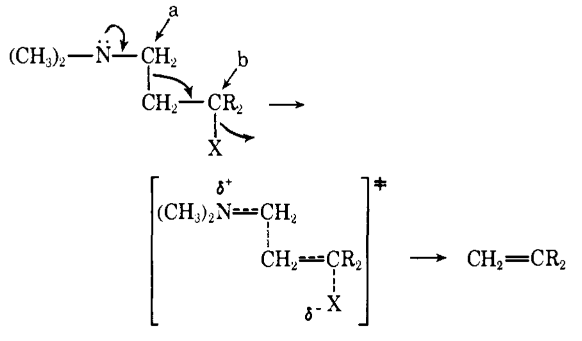

(16)


(17)


(18)

Even though there is much evidence that free $^+CH_2OCH_3$ and $(C_6H_5)_3C^+$ are more stable than $(C_6H_5)_3Si^+$, the ionization potentials reflected in eq 16 and 17 are similar to that of ethylbenzene whereas that of reaction 18 is lower than the ionization potential of ethylbenzene.[4k] These results strengthen the argument that the former ions require planarity for stability and thus cannot provide vertical stabilization.

It is for this reason that the fragmentation reactions discussed by Grob[51] are considered to be nonvertical and therefore not σ–π conjugation effects. Apparently, considerable rehybridization occurs at both points a and b. However, this needs further experimental verification.


(19)

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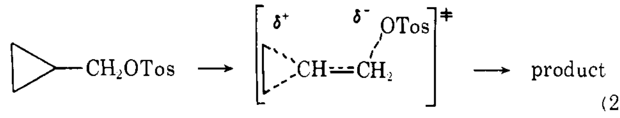
(61) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).

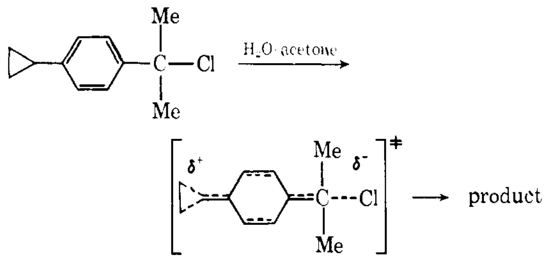
(62) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *ibid.*, 83, 4838 (1961). Other references are given there.

(63) (a) M. Rosenblum, J. O. Santer, and W. G. Howells, *ibid.*, **85**, 1450 (1963); (b) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Wiley, New York, N. Y., 1965.

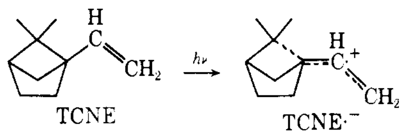
(4) **Bending Strain.** As mentioned above, one of the earliest suggestions of exalted hyperconjugation was that of Roberts and Mazur[12] (eq 20). More recently this effect has been suggested for other more complex strained systems. We have recently demonstrated



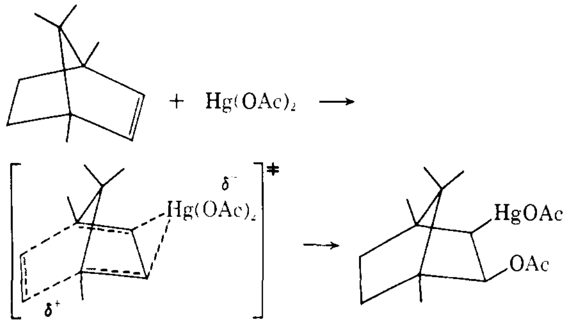
(20)



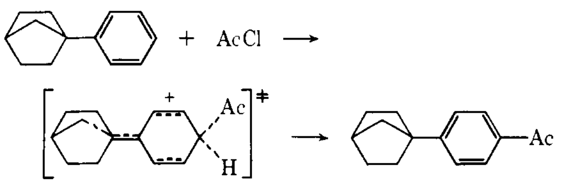
(21)[47,48]



(22)[4a]



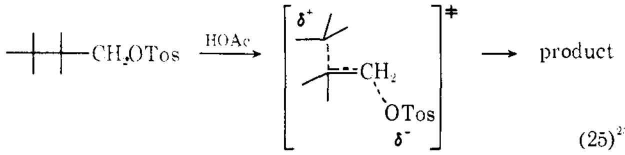
(23)[4f]



(24)[28]

vertical stabilization by a variety of angle strained systems,[4a,h] indicating a similarity between strained rings and carbon–metal bonds in such stabilization.

(5) **Stretching Strain.** The central bond length in hexamethylethane[64] is 1.578 Å compared to 1.57 Å for the 1,7 bond and 1.55 Å for the 1,2 bond in norbornane.[8b] Therefore, the central bond in hexamethylethane should be delocalizable and the accelerated solvolysis below[23] (eq 25) might be attributed in part to



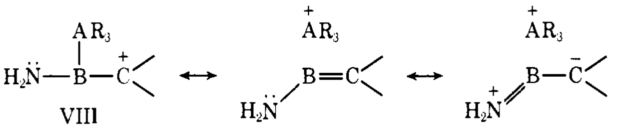
(25)[23]

this delocalization. This is in contrast to the "relief of steric strain" usually proposed.[26b] Strained systems delocalize readily and should provide considerable stability to cations without changing their geometry.

(6) **Atoms B and C Should Form Good π Bonds.** This statement needs little amplification for such delocalization depends upon good overlap between the A–B σ bond and the p orbital on C of CR_2. Therefore, for maximum σ–π conjugation, B should be C, N, or O. Hyperconjugation will be much less effective if B is a second or higher row element.

Such compounds as $Me_3SiOC_6H_5$ do not show this effect because the lone pairs on oxygen may delocalize and these same lone pairs backbond to Si.[42a] Thus, the N and O systems are much more complex than those with B = CR_2. Nevertheless, $XMgOC_6H_5$ and $LiOC_6H_5$ would probably show σ–π conjugation.

The effects of substituents on B should be considered. Since such substituents do not bear the positive charge, we might expect that they should have about the effect expected for stabilization of a simple double bond. In



VIII IX X

this example n–π conjugation and σ–π conjugation are not really cooperative but the NH_2 group might stabilize this structure slightly, if at all, as it might stabilize a double bond in, *e.g.*, an enamine. The negligibly small effects of substituents on the α position of benzyl metal compounds seem to bear this out.[4k]

(7) **Planarity of ABCX.** We know from the work on E2 elimination, additions, β-deuterium isotope effects, etc., that coplanar arrangement is preferred for all concerted processes making or breaking two adjacent bonds, *e.g.*, Diels–Alder reaction, hydroboration, xanthate pyrolysis, etc. It follows that the kind of conjugation we have written should have this requirement. Any other arrangement reduces the B–C π overlap.

(8) It is furthermore well known that ionic processes such as electrophilic addition,[58] eliminations,[56] etc., proceed from 10^4 to 10^6 times faster when the two leaving or entering groups are anti than when they are syn. It is thus expected that σ–π conjugation will have the same preferred geometry. Various calculations on stabilities of interacting radical lobes[59] or on such things as rotation barriers in ethane[60] agree with the empirical observations.

This geometry has been treated in detail for carbon–metal σ–π conjugation.[4a,j,k,65] However, the stereochemical consequences of strain-induced delocalization have only been touched upon previously.[4f,g]

Just as in the metallocenylmethyl systems of reaction 4, there are a wide variety of "two-sided" strained carbon systems which show stereochemical behavior similar to the metallocenes or other organometallic compounds. Three examples illustrate this similarity (eq 26–28[57,66,67]).

In all three cases a delocalizable bond is approximately anti coplanar with the leaving group. Wiberg[67] has attributed a major driving force for reaction 27 to be due to the stretching of this bond in the transition

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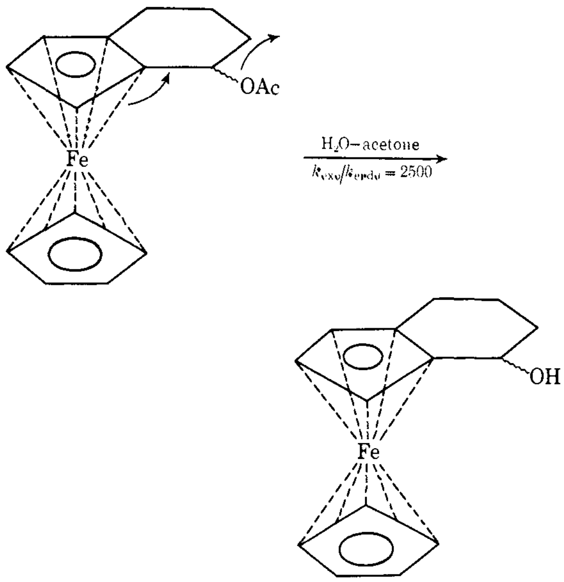
[64] L. S. Bartell, *Trans. Amer. Crystallogr. Ass.*, **2**, 134 (1966).

[65] G. G. Pitt, *J. Organometal. Chem.*, **23**, C35 (1970).

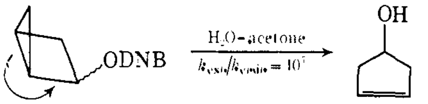
[66] E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 4216 (1961).

[67] K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *ibid.*, **90**, 5338 (1968).

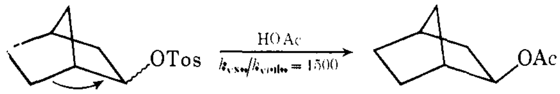
Traylor, et al. / Stabilization of Cations by σ Binds



(26)[66]



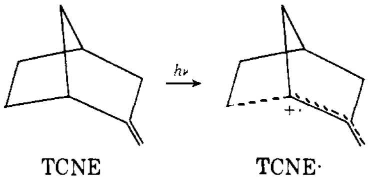
(27)[67]



(28)[67]

state and we have suggested[68] stretching of the C_1–C_6 bond in reaction 28. This stretching could be important, but such bonds are also delocalizable without movement, as we have shown.[4h]

A comparison of the ionization potentials (charge-transfer maxima) of methylenecyclohexane with 2-methylenenorbornane[69] indicates that there is probably some vertical stabilization available at the 2 position in norbornane. But the studies discussed above are not sufficiently quantitative to establish the extent to which vertical stabilization contributes to the stability of the transition state in the solvolysis of norbornyl tosylate.



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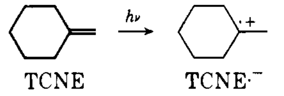
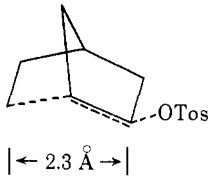
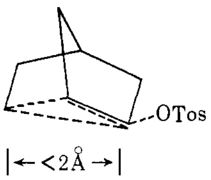


(30)

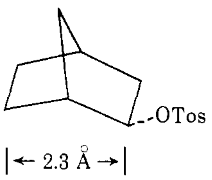
Relationship of σ–π Conjugation to Classical and Nonclassical Cations. The description which we have given for σ–π conjugation[4c] does not invoke significant bridging. And yet we must call it nonclassical for it is an electronic effect and involves nearly the same overlap integrals used in calculating stabilities of nonclassical ions,[16–19] except for overlap between, for example, atoms 2 and 6 in the norbornyl cation.



nonclassical
σ-π conjugation
XI



nonclassical,
bridged structure
XII

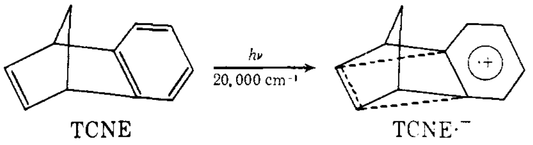


classical
XIII

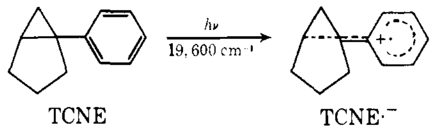
The important point is that either σ–π conjugation or nonclassical bridged structures make it unnecessary to seek steric[70] or other effects to explain the "two-sided" behavior of such systems.

The suggestion of Dewar[71] that all the language and symbolism of nonclassical or bridged ions be changed to π complex terminology does not clarify the norbornyl cation problem. His "π complex" accents the symmetrical nature of the intermediate and does not take cognizance of the possible importance of hyperconjugation.

On the other hand Brown's suggestion that there is no evidence for resonance stabilization (nonclassical resonance)[70] in strained cations or the preceding transition states must now be questioned. We are able to show strong interactions between positive centers and neighboring σ bonds or π bonds where steric effects cannot be involved. Some examples are shown below and in eq 29.

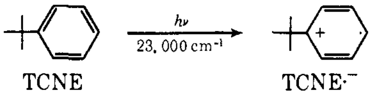


(31)[69]



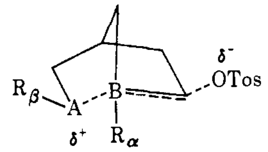
(32)[4b]

These processes, and many other similar examples, reveal lower ionization potentials for such strained systems than for their unstrained counterparts. For example, eq 32 involves a lower frequency than does eq 33. Clearly there is "resonance stabilization" of the cations formed in eq 29, 31, and 32. The conclusion that strained C–C σ bonds may be delocalized into positive centers seems inescapable.

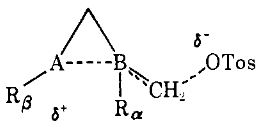


(33)

It is instructive to consider the effects of substitutions on various positions on the rates of norbornyl and cyclopropylcarbinyl tosylate solvolyses in terms of Chart 1. Based on considerations of Chart 1 we



XIV



XV

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[68] T. G. Traylor and C. L. Perrin, *J. Amer. Chem. Soc.*, **88**, 4934 (1966).

[69] K. A. Munk and R. S. Brown, unpublished work.

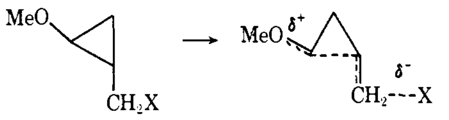
[70] H. C. Brown, *Chem. Soc., Spec. Publ.*, **16**, 140 (1962).

[71] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 354.

would expect inductively donating groups (*e.g.*, CH_3) to have slight accelerating effect at R_α or R_β in XIV and XV.

Resonance stabilizing groups (*e.g.*, R = C_6H_5, MeO, NH_2) showed no acceleration at R_β (π–σ–π delocalization) in XIV or the unstrained systems of eq 16 and 17. These effects are expected whether A and B are both carbon or if A is a metal such as Si. Most of the results for substitution of R_α and R_β when A and B are carbon[61,72–74] clearly are consistent with σ–π delocalization.

There is one exception to this behavior when the σ bond is highly strained. The observations that β-anisyl[75] or β-methoxy[76] groups accelerated the more strained cyclopropylcarbinyl–X solvolyses whereas these groups do not accelerate norbornyl tosylate solvolysis[76] might be attributed to fragmentation or to π–σ–π delocalization.[76] None of this acceleration is vertical since a methoxy group does not lower the ionization potential in cyclopropylbenzene.[69] Such π–σ–π delocalization apparently does not occur. Reaction 34 is therefore a nonvertical fragmentation process. The absence of acceleration by the methoxy group in reaction 35 shows that neither fragmentation nor π–σ–π delocalization occurs in this case. The possible occurrence and the nature of π–σ–π conjugation are under study. These results are also consistent with the bridged ion or π complex views, contrary to the views of Brown.[70,77] This point is made particularly clear by Dewar.[71]



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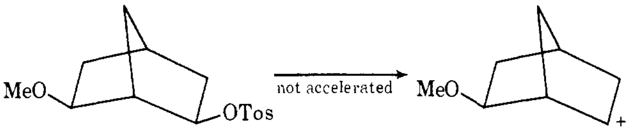
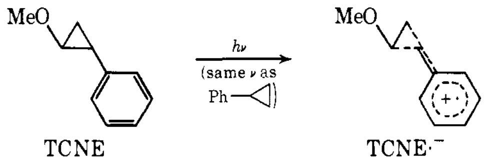
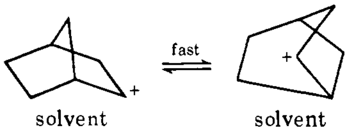


(35)

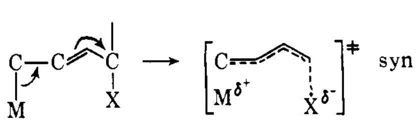


(36)

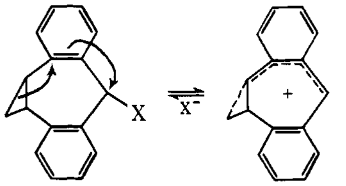
It is important to reiterate the stereochemical demands of σ–π conjugation for the norbornyl system because much confusion has resulted from the assumption that endo attack must be "prevented." Thus, even though Brown has argued against bridging, he apparently felt the need to postulate rapid migration as a way of preventing endo attack.[70] We would suggest that there is no need to "prevent" endo attack. As we illustrated above for α-ferrocenylalkyl cations, collapse anti to the hyperconjugated bond is simply faster by microscopic reversibility and is a result of electronic effects as we have previously suggested.[4f,g] In order to establish the extent of bridging, fragmentation, and σ–π conjugation in strained systems it will be necessary to study vertical processes in these systems (for example, processes like eq 29, 31, and 32).



Remote Control of Stereochemistry. The σ–π conjugation in such extended systems as phenylferrocene, cyclopropylbenzene, or dibenzylmercury suggests a novel stereochemical control which is quite outside the steric explanation.[70] For example, if the two-sided nature of 2-norbornenyl or ferrocenylalkyl cations results from σ–π conjugation or n–π homoconjugation we might expect this exo/endo reactivity ratio to be effective in vinylogs of these structures at some distance from the activating group. This is illustrated below for a C–metal bond. A possible example of these effects is shown below (eq 38). A cis/trans rate ratio of 200 was observed in reaction 38 by Childs and Winstein[78] consistent with the σ–π formulation shown above. However, the optically active compound below, although solvolyzing about 50,000 times faster than the α-phenethyl derivative, gave complete racemization in 50% aqueous dioxane.[79] Therefore, the stereochem-



(37)



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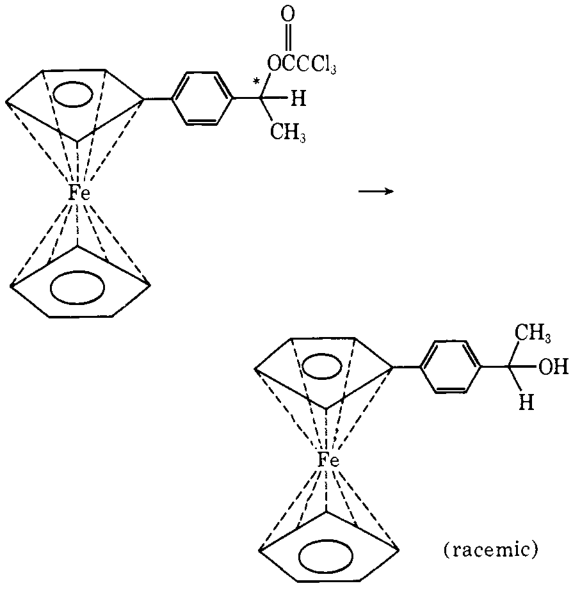

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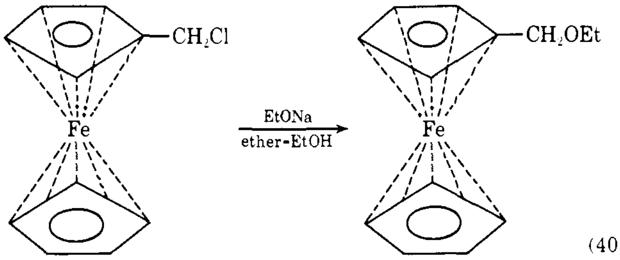
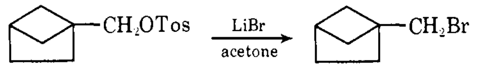
ical control in the α position on ferrocenylalkyl cations does not extend through a benzene ring. Other possible examples of remote stereochemical effects of $\sigma-\pi$ conjugation are being studied.

Acceleration of SN2 Reactions. We have previously observed that SN2 reactions of ferrocenylmethyl chloride are highly accelerated and have used this as evidence that the acceleration was provided by $\sigma-\pi$ conjugation rather than by neighboring nucleophilic participation.[4i]

Generally we expect highly accelerated SN2 reactions to respond to $\sigma-\pi$ conjugation in a manner similar to their response to other kinds of delocalization whereas internal displacement reactions would be competitive with external (SN2) displacements. The ease of the following reactions agrees with this idea.



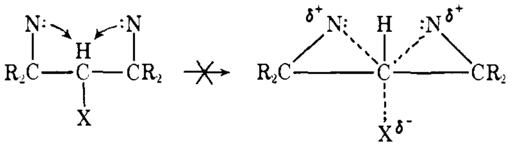
(40)[4i]



(41)[21]

It will be most interesting to compare the rates of reactions such as 41 with the corresponding displacement on *n*-butyl tosylate.

Multiple Hyperconjugating Groups. Internal nucleophilic displacement would be competitive in reactions such as 42 because steric effects prevent significant simultaneous attack by the two nucleophiles. However, there is no such severe restriction on $\sigma-\pi$ conjugation and such groups will act cooperatively (eq 43) as do other conjugating groups. Thus a reaction



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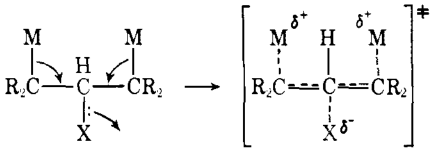


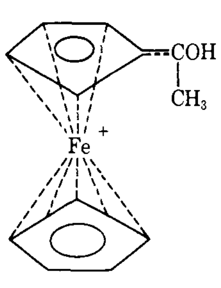
(43)

such as

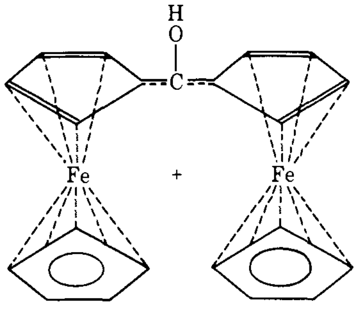
$$(MCH_2)_n(CH_3)_{3-n}CX \longrightarrow (MCH_2)_n(CH_3)_{3-n}C^+ + X^- \quad (44)$$

would be expected to accelerate approximately by $n\Delta$ for an internal nucleophile (*e.g.*, M = NH_2, OCH_3, anisyl) and by about $(\Delta)^n$ for a $\sigma-\pi$ conjugating group (*e.g.*, M = RHg, R_3Si, etc.) where Δ is the acceleration for one such group.

The observations that aryl groups (M = aryl) accelerate[80] such reactions by $n\Delta$ whereas cyclopropyl[81] groups accelerate the reaction by $(\Delta)^n$ are consistent with this postulate. The fact that diferrocenyl ketone is protonated much more easily than is ferrocenyl methyl ketone[82] is also consistent with $\sigma-\pi$ conjugation.[4a,60b]



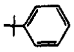
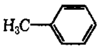
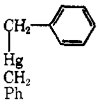
XIX



XX

On the Question of Hyperconjugation and Ground-State Properties. We have recently concluded[8] along with Dewar[7] that hyperconjugation does not affect bond lengths in hydrocarbons such as propylene. Since C–metal hyperconjugation in cations is very large compared to C–H hyperconjugation (see below) we may test this conclusion further. The rates shown in Table I indicate a σ^+ for the $C_6H_5CH_2HgCH_2$ group of −1.1. Yet the σ_R values[83] as measured by the chemical shift of a para fluoro group[84] do not reveal this extremely large hyperconjugation. The latter measures properties of the ground state and strongly suggests that $\sigma-\pi$ conjugation contributes very little to the stabilities of neutral molecules. This implies that C–H hyperconjugation, trivially small in, *e.g.*, para methylbenzyl cations, is indeed negligible in ground-state hydrocarbons.

Table I. Rates of Proton Exchange on Aromatic Compounds

				Ref
Rel rate	(1)	2	10^7	4d
σ^+	−0.28	−0.31	−1.1	4a
σ_R	−0.15	−0.12	−0.24	83, 84

That the effect of $\sigma-\pi$ conjugation on free-radical stabilities,[30,31] although important, is much less than on cation stabilities[4a] is consistent with the idea that $\sigma-\pi$ conjugation operates more upon demand than do other kinds of delocalization.[2] In other words, although $\sigma^+_{p\text{-}CH_2\text{-metal}}$ might be as large as $\sigma^+_{p\text{-}NH_2}$, $\sigma^R_{p\text{-}CH_2\text{-metal}}$ will be about as large as $\sigma^R_{p\text{-}CH_3}$ and *much smaller* than $\sigma^R_{p\text{-}NH_2}$.

Conclusions

We have described a mechanism whereby polarizable σ bonds may stabilize neighboring cationic centers *without altering the length or angles around such bonds as the transition state is approached* (vertical stabilization). Thus, for example, a cyclopropyl group may stabilize a cation by vertical delocalization just as

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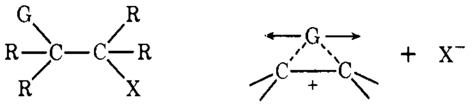
does a vinyl group. The "strain" in both the cyclopropyl and vinyl groups makes the electrons more delocalizable, but these systems need not be "relieved" by nuclear movement in order to afford stabilization or stereochemical control. We therefore see that σ–π conjugation is not simply an excuse for drawing different dotted lines but is phenomenologically very different from either internal displacement or fragmentation.

It is not suggested that the cations which are intermediates in solvolysis reactions are not bridged. The important point of this paper (and our other papers on this subject) is that because all, or nearly all, of the stabilization of cations as measured by solvolysis reactions is also seen in vertical processes, such bridging contributes very little to the stabilization at the transition state. Therefore, if a bridged ion were formed it would have a low vibration frequency for the vibration shown. Prevention of such bridging does not alter the stabilization.



While we have previously demonstrated the importance of vertical stabilization by both polarized and strained σ bonds, we have not shown that these effects act to the exclusion of bridging except in a few cases.[4a] Having established the expectations and requirements for vertical stabilization we may further probe experimentally for its importance as we do in subsequent papers on this subject.

Acknowledgment. We gratefully acknowledge the support of this work by the Air Force Office of Scientific Research, and the helpful advice from Professors Charles Perrin, Paul D. Bartlett, Edward Kosower, G. Dann Sargent, and Paul v. R. Schleyer.

Electrostatic Catalysis. IV. Intramolecular Carboxyl Group Electrostatic Facilitation of the A-1-Catalyzed Hydrolysis of Alkyl Phenyl Acetals of Formaldehyde. The Influence of Oxocarbonium Ion Stability

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Abstract: The hydrolysis of a series of alkyl phenyl acetals of formaldehyde has been studied (H_2O, 30°, μ = 1.0) as a function of pH. Rate constants are derived for specific acid-catalyzed hydrolysis of compounds with o-$COOCH_3$, o-COOH, and o-COO^- substituents on the phenyl ring. All second-order rate constants are correlated by the Taft $\rho^*\sigma^*$ relationship utilizing the σ^* values of the alkyl substituents. The rates of o-COO^--substituted compounds exhibit a 500-fold positive deviation but the ρ^* value for all three series is -3.0 ± 0.05. The identical sensitivity to oxocarbonium ion stability suggests the carboxyl facilitated reaction may best be described as an electrostatically stabilized A-1 reaction. The hydrolysis of a system possessing two bulky ortho groups was investigated in an attempt to observe intermolecular general acid catalysis in the hydrolysis of a formal. The failure to observe either a rate enhancement over a nonhindered system or buffer catalysis is attributed to a decrease in pK_a of the conjugate acid and the instability of the oxocarbonium ion.

Interest in the mechanism of hydrolysis of acetals was greatly stimulated by the elucidation of the tertiary structure of crystalline hen egg white lysozyme.[2,3] In particular, due to the proximity of the protonated carboxylic acid group of glutamic acid **35** at the point of C–O bond cleavage of the substrate, several studies have been directed toward carboxylic acid group facilitation of the hydrolysis of glycosides and acetals.

Fife and coworkers[4–7] and Capon and his associates,[8,9] have delineated the structural requirements for the observation of intermolecular general acid catalysis of hydrolysis in a number of systems. Studies from this laboratory,[10–12] from Fife's group,[13] and from Capon's group[14–16] have probed the structural, electronic, and steric origins of facilitated acetal hydrolysis in intramolecular models.

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