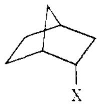
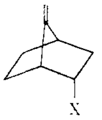
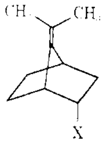
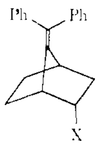
DePuy[13] found that homoallylic endo tosylate I (X = OTs) acetolyzes 270 times faster than the saturated endo tosylate II (X = OTs), which he took as a reference. The rate enhancement was attributed to formation of a σ-delocalized cyclopropylcarbinyl transition state. Consistent with this formulation the acetolysis product was exclusively endo acetate.

In order to explore further the stabilization of the cyclopropylcarbinyl transition state by methyl and phenyl substituents alcohols III (X = OH) and IV (X = OH) were prepared and characterized.[1] Acetolysis of the related tosylates (X = OTs) gave the kinetic results listed in Table I.

Table I. Rates of Acetolysis of Some Bicyclo[2.2.1]heptyl Tosylates (X=OTs)

Compound	T, °C	Rate	Rel rate	$\nu_c = 0$, cm^{-1}
 II	101.0 25	6.3×10^{-4} 8.4×10^{-8}	22	1751
 III	125.1 101.0 (25.0)	5.32×10^{-4} 5.43×10^{-5} (3.76×10^{-9})	1	1752
 I	50.1 50.0 (25.0)	3.32×10^{-4} 3.24×10^{-4} (2.26×10^{-5})	6000	1751
 IV	120.0 101.0 (25.0)	9.39×10^{-4} 1.56×10^{-4} (1.25×10^{-8})	3	1756

The 22-fold rate retardation produced by the 7-methylene group agrees precisely with the factor of 18–23[14–17] estimated for a simple inductive effect. The essential identity of the carbonyl stretching frequencies of the ketones corresponding to II and III indicates that internal angle strain effects[18] make an insignificant contribution to the rate ratio.

Using now the tosylate III as reference the acetolysis of tosylate I shows a rate enhancement of 6000. This value agrees well with the ratio of 4500 for the formolysis of 4-methyl-3-pentenyl tosylate to 3-butenyl tosylate[9] and reinforces DePuy's thesis that a σ-delocalized transition state is involved. Still more convincing is the observation that the products from the slow tosylate III were about 90% rearranged, in significant contrast to DePuy's observation of retention of configuration for the products of solvolysis of the rate enhanced tosylate. The formation of rearranged products from III suggests that little neighboring group stabilization exists in III and the products are controlled by steric factors.

Given this internal consistency we were initially surprised to observe that the benzhydrylidene compound, IV, showed almost no rate enhancement. The inductive retardation calculated for IV amounts to a factor of 2.1–2.2,[19] or an expected solvolysis rate relative to III of about 10. When the observed relative rate of IV is corrected upward for angle strain using the Foote–Schleyer recipe[18] the rate ratio is, in fact, close to 10. Isolation of the unaltered tosylate IV after 16% acetolysis excluded rapid addition of solvent to the 7-double bond as an explanation of the low rate. This was confirmed by preparing the *p*-nitrobenzoate of IV and determining its (slow) solvolysis rate in 90% acetone–water, a less acidic solvent in which addition to the double bond is therefore unlikely.

The lack of rate enhancement with IV is particularly striking given that naive application of the "one phenyl equals two methyls" rule would have led to an expected rate enhancement of *ca.* 10^7. Preparation and acetolysis of 4,4-diphenyl-3-butenyl tosylate gave a similar small rate factor,[20] demonstrating the probable generality of the result by excluding steric hindrance arguments peculiar to the norbornyl system.

A portion of the loss of phenyl rate enhancement may be caused by resonance stabilization of the ground state.[9] While the proper estimation of this effect is too complex to analyze here it seems apparent that even after correction the diphenyl compounds are too slow by a factor of at least 10^4. This is not as dramatic as the loss observed for more symmetrical σ-delocalized transition states but its origin may be related. We are continuing our study of this problem.

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[13] C. H. DePuy, I. A. Ogawa, and J. C. McDaniel, *J. Amer. Chem. Soc.*, **83**, 1668 (1961).

[14] From the Taft[15] $\rho\sigma^*$ relationship using $\sigma^* = +0.65$ for $(CH_2{=}C<)$.[16] The lower ratio was obtained using Gassman's[17] ρ of -1.94 based on five 7-substituted *endo*-norbornyl tosylates; the higher ratio based on $\rho = 2.09$ derived from Gassman's data but with only those (three) compounds with 7 substituents anti to the C-2 position.

[15] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 556.

[16] J. Hine and W. C. Bailey, *J. Amer. Chem. Soc.*, **81**, 2075 (1959).

[17] P. G. Gassman, J. L. Marshall, J. G. Macmillan, and J. M. Hornback, *ibid.*, **91**, 4282 (1969).

[18] C. S. Foote, *ibid.*, **86**, 1853 (1964); P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964).

[19] Based on the ρ values described in ref 14. The σ^* for $(Ph_2C{=}CH)$ was estimated as the difference between the σ^* for vinyl[16] and twice the difference between the σ^* values for vinyl and $(PhCH{=}CH)$.[15]

[20] Under conditions where the dimethyl analog gave a rate ratio of 4500 the diphenyl compound gave a ratio of only 19 (unpublished work of Mrs. M. Magde).

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On the Lack of Stabilization of σ-Delocalized Cyclopropylcarbinyl Ions by π Participation[1,2]

Sir:

Attention has been drawn to the remarkable lack of stabilization of the transition state from exo norbornyl derivatives by a phenyl substituent at C_1.[3,4] Previous

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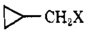
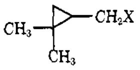
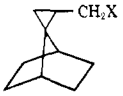
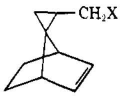
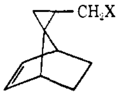
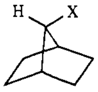
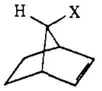
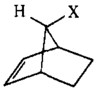
[1] Taken from the Ph.D. Dissertation of J. N. C. Hsu, Cornell University, 1970.

[2] Supported, in part, by the National Science Foundation.

[3] C. F. Wilcox, Jr., R. G. Jesaitis, and S. Belin, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. ORGN 8.

Table I. Solvolysis Data for 3,5-Dinitrobenzoates in 70% (Vol) Acetone–Water

Compd	T, °C	k, sec^{-1}	Rel rate	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
	125.0	2.55×10^{-6}	1.0		
	(125.0)	2.91×10^{-4a}	114		
 I	25.0 100.0 125.0	$0.37 \times 10^{-9\,b}$ 2.79×10^{-6} 2.62×10^{-5}	10.5 (1.0)	25.6	−15.6
 II	25.0 100.0 125.0	$1.03 \times 10^{-9\,b}$ 2.33×10^{-6} 1.61×10^{-5}	6.4 (0.61)	22.1	−25.4
 III	25.0 100.0 125.0	$1.44 \times 10^{-9\,b}$ 4.95×10^{-6} 3.82×10^{-5}	15.3 (1.46)	23.3	−20.7
			(1)		
			(4100)		
			(1.4×10^{11})		

[a] Calculated from data in ref 10 for solvolyses in 60% acetone at 100°, and the rates observed from solvolyses of cyclopropylcarbinyl dinitrobenzoates in 60% acetone at 100° (ref 10) and in 60 and 70% acetone at 125° (present work). [b] Extrapolated. [c] Based on acetolysis of tosylates cited in ref 15.

explanations for this negative result included: (1) that the transition state was classical and therefore without delocalizable charge at C_1,[5] (2) that the phenyl group exerted a fortuitously cancelling blend of conjugative stabilization and inductive retardation,[6] and (3) that the transition state leading to such a highly stabilized (bridged) intermediate comes too early on the reaction path to properly reflect the charge delocalization of the intermediate.[4b,7]

Extended Hückel calculations[8] on a variety of model σ-bridged ions indicated[3] that while inductively stabilizing groups might enhance the rate, conjugatively stabilizing groups would show only about 10% of the effect found in classical ions. Accordingly, it was proposed[3] that this low sensitivity might be a characteristic property of σ-bridged ions and hence of the related transition states. In support of this proposal it was pointed out in a recent communication[9] that whereas methyl substituents at C_8 in 7-methylene *endo*-2-norbornyl tosylate markedly stabilize the transition state (6000 times rate enhancement) that after a small correction for angle strain and inductive effects phenyl substituents at C_8 gave no rate enhancement.

We report here a study of the stabilization of cyclopropylcarbinyl transition states by remote conjugating groups for which inductive retardation is not a factor. The study is based on the supposition that the cumulative tenfold rate enhancement of the solvolysis rates observed on substitution of methyls at C_2 in cyclopropylcarbinyl derivatives[10] reflects the development of charge at C_2, as has been assumed by previous workers and is supported by model calculations.[11]

We have prepared and characterized a series of cyclopropylcarbinols and 3,5-dinitrobenzoate derivatives[12] in which one of the C_2 atoms was a spiro junction at the C_7 position of a bicycloheptane skeleton. These included the esters in which the bicyclic skeleton was (a) saturated, I, (b) unsaturated with the double bond syn to the carbinyl carbon, II, and (c) unsaturated with the anti arrangement, III.[14]

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(4) (a) P. v. R. Schleyer and D. C. Kleinfelter, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 43P; (b) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1246 (1964).

(5) For a summary and many leading references see: H. C. Brown, *Chem. Ind.* (*London*), **2**, 199 (1966).

(6) G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20**, 301 (1966).

(7) S. Winstein, *J. Amer. Chem. Soc.*, **87**, 381 (1965).

(8) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).

(9) C. F. Wilcox, Jr., and H. D. Banks, submitted for publication.

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

(11) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); H. S. Tremper and D. D. Shillady, *J. Amer. Chem. Soc.*, **91**, 6341 (1969).

(12) The syntheses, which will be described in detail elsewhere, involved the Diels–Alder addition of spiro[2.4]hepta-4,6-dienyl-2-carbinol[13] to either *cis*- or *trans*-dichloroethylene followed by appropriate functional group transformations.

(13) H. Schaltegger, *Helv. Chim. Acta*, **45**, 1368 (1962).

The anticipated rate of I relative to 2,2-dimethylcyclopropylcarbinyl 3,5-dinitrobenzoate is unclear because of the simultaneous operation of uncertain strain and inductive effects associated with the bridgehead methines in I. However, the rates of II and III relative to I can be estimated with more certainty because these effects are relatively constant. The calculation uses the rate enhancement of syn and anti double bonds in 7-substituted norbornenes relative to the saturated 7 derivative[15] combined with the observation that sufficient charge is developed at C_2 in cyclopropylcarbinyl solvolyses to produce one-fifth of the 10^5 methyl rate enhancement found in comparing secondary and tertiary solvolyses.[5,16] Taking the rate of I as 1.0 the expected[17] rate of II is $10^{3.7/5} = 10^{0.74} = 8.7$ and the expected rate of III is $10^{11.1/5} = 10^{2.2} = 160$.

The observed rate data are presented in Table I along with data for the appropriate reference compounds. It is apparent that the expected rate enhancements by the double bond are unambiguously absent. Thus in yet another σ delocalized transition state a resonance stabilizing group fails to provide the rate enhancement that would have been anticipated on the basis of enhancements afforded by methyl substituents. In the present example there is no question of steric inhibition of resonance. The blend of resonance and inductive influence of the remote double bond is markedly different from that presented by a phenyl substituent. It seems inescapable that an appeal to a fortuitous balance of resonance and induction is unacceptable.

The present solvolyses cannot distinguish between the proposal that resonance stabilizing groups are ineffective at stabilizing σ-delocalized ions and the Brown null hypothesis that in cyclopropylcarbinyl there is no delocalized charge to be stabilized. Acceptance of the latter, however, then requires a separate explanation for the rate enhancements arising from methyl substitution. A detailed discussion of such possibilities will be presented elsewhere.

(14) The syn and anti assignments were made on the basis of the synthetic path and were largely confirmed by an ir study of the alcohols. A single inconsistency in the latter results leaves open the possibility that the assignments of II and III should be reversed. As described later in the text the main thrust of the argument is not affected by the assignment.

(15) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

(16) H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5008 (1964).

(17) If Foote–Schleyer angle strain corrections[18] are made the expected rate ratios become 20 and 600, respectively.

(18) C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964).

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Zero-Field Transitions of Triplet Excimers from Phosphorescence–Microwave Double Resonance Spectroscopy

Sir:

Since the first reported detection of excimer fluorescence in concentrated pyrene solutions,[1,2] evidence has been accumulating which indicates that excimer emission from many aromatic molecules can be observed provided the right conditions of temperature, pressure, and concentration are met.[3] Initially the excimer binding energy was interpreted as arising from either an excitation resonance[4,5] or a charge resonance[6] between the monomers. However, models[7–9] taking into account the configuration interaction between exciton resonance and charge resonance states were found to come much closer to correctly interpreting the magnitude of the experimentally observed red shift of the excimer emission relative to the monomer emission.

Conclusive evidence of the existence of stable triplet excimers is of considerable theoretical interest. Recently, excimer phosphorescence was reportedly observed in several molecules including halogenated benzenes,[10–12] phenanthrene,[13] naphthalene,[13] and pyrene.[14] For triplet excimers, the coulombic terms of the excitation resonance interaction vanish due to spin orthogonality, leaving only the relatively small exchange terms. The contribution of charge resonance interactions, resulting from mixing charge-transfer functions[8] with triplet wave functions of the dimer, might then become the important factor leading to the stability of triplet excimers.

Using phosphorescence–microwave double resonance (PMDR) techniques,[15] the zero-field (zf) transitions of the triplet state of the monomer or of the excimer of hexachlorobenzene (HCB) at 1.6°K could be observed by monitoring the sharp phosphorescence bands of the monomer or the broad excimer emission, respectively. The results show that the broad emission has zero-field transitions and thus confirms its origin as a triplet state. Furthermore, it is found that the excimer of HCB at 1.6°K is formed only at crystal defects that are created by introducing small amounts of other chlorobenzenes whose lowest triplet states are at higher energies than that of HCB. A qualitative comparison of the *D* and *E* values of the excimer and the monomer is made in terms of the excimer structure as well as the charge-transfer mechanism of its stabilization.

Hexachlorobenzene (HCB), *sym*-tetrachlorobenzene (TCB), 1,3,5-trichlorobenzene (Tri-CB), and *p*-dichlorobenzene (DCB) were recrystallized four times from CCl_4, zone refined for 50 passes under nitrogen atmosphere, and chromatographed over Al_2O_3. Samples of pure HCB, HCB doped with 1.0×10^{-3} *M* of TCB, Tri-CB, and DCB were prepared and sealed in quartz ampoules under helium atmosphere and were placed inside a copper helix with the proper characteristics for the desired microwave frequency. The 3130-Å band of a

(1) Th. Förster and K. Kasper, *Z. Phys. Chem.* (*Frankfurt am Main*), 1, 19 (1954).

(2) Th. Förster and K. Kasper, *Z. Elektrochem.*, **59**, 976 (1955).

(3) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970.

(4) Th. Förster, *Pure Appl. Chem.*, 4, 121 (1962).

(5) Th. Förster, *ibid.*, 7, 73 (1963).

(6) J. Ferguson, *J. Chem. Phys.*, **28**, 765 (1958).

(7) E. Konijnenberg, Thesis, University of Amsterdam, 1962.

(8) J. N. Murrell and J. Tanaka, *Mol. Phys.*, 1, 363 (1964).

(9) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, 41, 3131 (1964); T. Azumi, A. T. Armstrong, and S. P. McGlynn, *ibid.*, 41, 3839 (1964).

(10) G. Castro and R. M. Hochstrasser, *ibid.*, **45**, 4352 (1966).

(11) E. C. Lim and S. K. Chakrabarti, *Mol. Phys.*, **13**, 293 (1967).

(12) G. A. George and G. C. Morris, *Mol. Cryst.*, 10, 187 (1970).

(13) J. Langelaar, R. P. H. Rettschnick, A. M. F. Lambooy, and G. J. Hoytink, *Chem. Phys. Lett.*, **1**, 609 (1968).

(14) O. L. J. Bijzeman, J. Langelaar, and J. D. W. van Voorst, *ibid.*, **5**, 269 (1970); 11, 526 (1971).

(15) For a review, see M. A. El-Sayed, *Accounts Chem. Res.*, 4, 23 (1971).