interconversion of metallocycles need not perforce be involved.

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Distortional Stabilization in Phenyl Participations[1]

Sir:

There is a wealth of kinetic, product, and theoretical evidence for the direct formation of phenonium ions through transition states closely resembling the ions in eq 1.[2-4] This implies that the accelerated k_2 in-

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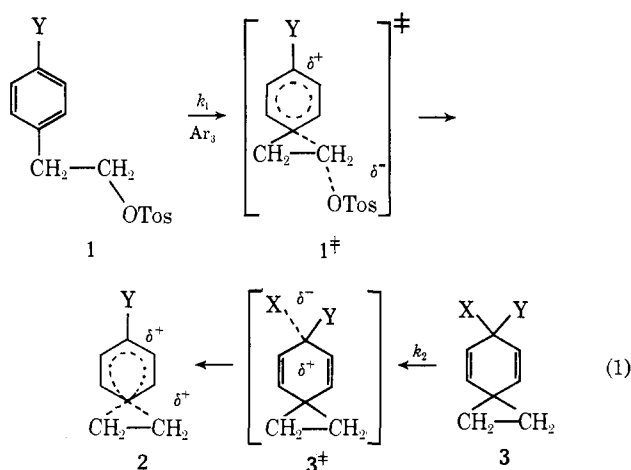
volves little change in the geometry of the three-membered ring in going to 2[5,6] and that acceleration of k_1 requires extensive movement in the direction of cyclopropane ring formation. Recent calculations of Hehre[4] on this system agree with this postulate.

An alternative suggestion of through-space[9] inter-

actions between the phenyl ring and the incipient cation center and requiring little advancement toward 2 has been made by Brown and Kim.[10]

(2)

4

Ramsey and Das[11] observed a correlation between the uv transition energy identified as reaction 3 and

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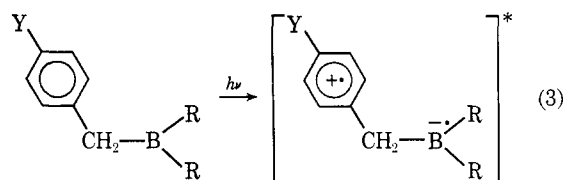
$-\log k$ of the corresponding reaction 1. This, and the fact that both these quantities were in turn proportional to the first ionization potentials of the corresponding substituted benzenes, PhY, were interpreted as evidence for the through-space stabilization suggested by Brown and Kim. It should be pointed out that such charge-transfer spectra will correlate even if the acceptor (in this case R_3B) is 3 Å away as in external charge-transfer complexes.[5a] This evidence therefore reveals little about the geometry of transition states of eq 1.

It is possible to probe directly for stabilizing interactions in such molecular geometry as that shown in 4 by using photoelectron spectroscopy.[12] If the interaction as shown in 4 is significant, then the π orbitals in 5 should reveal such interaction.[12] In fact, we can

(4)

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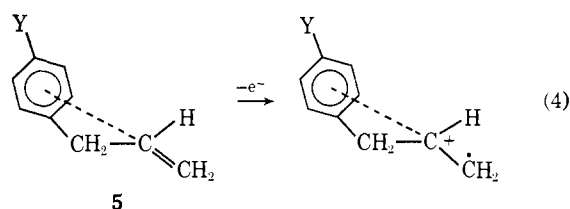
quite generally conclude that any neighboring group will interact strongly with such a π system if vertical

(1) Supported by the National Science Foundation, Grant GP 27361.

(2) (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, 74, 1113 (1952); (b) R. Heck and S. Winstein, *ibid.*, 79, 3432 (1957); (c) A. Diaz and S. Winstein, *ibid.*, 91, 4300 (1969), and references cited there.

(3) (a) C. I. Lancelot, D. J. Cram, and P. v. R. Schleyer, "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1971, p 1347; (b) D. J. Cram, *J. Amer. Chem. Soc.*, 71, 3863 (1949); (c) *ibid.*, 74, 2129 (1952); (d) J. A. Thompson and D. J. Cram, *ibid.*, 91, 1778 (1969).
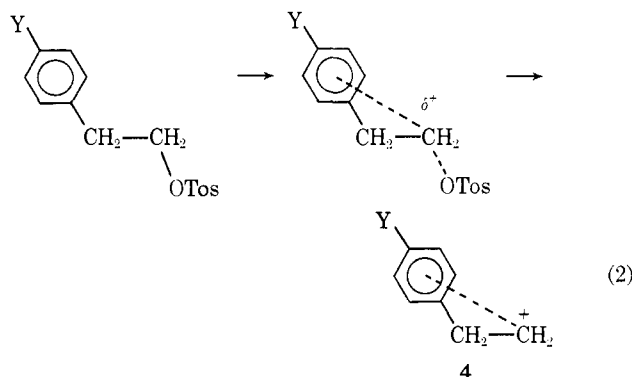
(4) W. J. Hehre, *J. Amer. Chem. Soc.*, 94, 5919 (1972).

(5) (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 92, 829 (1970); (b) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, 93, 5715 (1971); (c) K. Munk, J. Maier, D. W. Turner, and T. G. Traylor, submitted for publication; (d) J. M. Jerkunica and T. G. Traylor, *J. Amer. Chem. Soc.*, 93, 6278 (1971).

(6) Charge-transfer data[5a] and additivity effects also give excellent evidence against vertical stabilization in the phenethyl system. Two neighboring phenyl groups in $(PhCH_2)_2CHOTos$ give additive k effects[7] whereas two vertical stabilizing groups such as cyclopropyl[8] or Me_3-$SnCH_2$[5d] in $(\triangleright)_2CHX$ or $(Me_3SnCH_2)_2CHX$ give additive log k effects.

(7) C. J. Lancelot and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 91, 4291 (1969).

(8) H. Hart and G. M. Sandri, *J. Amer. Chem. Soc.*, 81, 320 (1959).

(9) R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Amer. Chem. Soc.*, 92, 706 (1970).
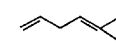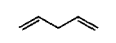
(10) H. C. Brown and C. J. Kim, *J. Amer. Chem. Soc.*, 93, 5765 (1971).

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

(12) We tentatively concluded[5a] that such an interaction as shown in eq 4 was absent in diphenylmethane, a conclusion corroborated by photoelectron spectroscopy.[13] However, the expected interaction is small, and these results are therefore rather inconclusive.

(13) S. Pugnataro, V. Mancini, J. N. A. Ridyard, and H. J. Lempka, *Chem. Commun.*, 142 (1971).

Table I. Vertical Ionization Potentials of Unsaturated Compounds Having Neighboring Groups (G̈—CH₂C═C<)

		IP$_V$^{a,b}						
G	Compound	Aromatic π₃	Aromatic π₂	Olefin π	Lone pair	k_{rel}	Ref (IP)	Ref (k_{rel})
H	Toluene	8.82, 9.1, 9.4^c				(1)	15, 16	3d
Ph	PhCH₂Ph	8.8, 9.13, 9.5^c			See ref 13	6^d, 12^e >10³ ^{f}	13, this work	
H	Propylene			9.88		(1)	15, 16	
Ph	PhCH₂CH═CH₂	9.16		9.85	11.5, 11.96, 12.39, 13.2, 14.06, 14.96, 16.50	6,^{d} 12^e >10³ ^{f}	This work	3c, 17, 18
An	MeO—⟨C₆H₄⟩—CH₂CH═CH₂	8.20	9.22	9.72	10.83, 11.40, 12.39, 14.09	80,^{d} 880^e	This work	3c, 17, 18
	MeO—⟨C₆H₄⟩—CH₃	8.17	9.17		10.75, 11.40, 12.44, 13.93		This work	
MeS	MeSCH₂CH═CH₂			9.95 (9.93)	8.65 (8.65)	10⁷	19b, this work	
	MeSMe				8.7		19b	20
	⟨diene⟩			8.70, 9.66	11.4, 12.60, 13.3		This work	
	⟨diene⟩			9.72, 10.13^g	12.04, 12.41, 13.40, 14.1		21, this work	

^{a} Photoelectron spectra were determined as previously described.²² ^{b} All compounds used here are commercial products used without purification. As a check on the purity we determine spectra on small samples several times as up to 90% of the sample disappeared. In all cases the spectra did not change during sample evaporation. ^{c} The first band of both toluene and diphenylmethane consists of a broad band centered at 9.1 eV with shoulders at 8.8 and 9.5, but this band is essentially identical for the two compounds. See ref 13 and 16 for details. ^{d} Acetolysis of substituted neophylbrosylates. ^{e} β,β,β-Trifluoroethanolysis of β-phenethyl tosylates.¹⁷ ^{f} Trifluoroacetolysis.¹⁸ ^{g} The small interaction of 1,4-pentadiene, which is the same as that in 1,6-heptadiene, disappears when the π orbital degeneracy is removed with the substitution of the two methyl groups. See also, S. A. Cowling, R. A. W. Johnstone, A. A. Gorman, and P. G. Smith, *J. Chem. Soc., Chem. Commun.*, 627 (1973).

stabilization is important. This comparison is shown in reactions 5 and 6 for the general neighboring group

(5)

vertical stabilization, transition state near starting geometry

distortional stabilization, transition state near bridged geometry

(6)

G. When G and C═C are held close together and geometrically and energetically degenerate as in norbornadiene or 1,3-dioxalane, interaction is observed¹⁴ with a resulting change in ionization potentials of both C═C and G: electrons.

In order to probe for the interaction shown in 4 in open chain compounds having nondegenerate orbitals, we have determined the vertical ionization potentials of a number of related structures, 6, using photoelectron spectroscopy. These results are compared with the

(14) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, 52, 1745 (1969).

corresponding solvolysis rates of compounds 6 in Table I.

The similarities of the phenyl group first ionization potentials in toluene and diphenylmethane and those of the vinyl group in the next three compounds make it quite clear that the 1,3-interactions implied by 4 are absent in such open chain systems.

A comparison of the π benzene orbital ionization potentials of *p*-allylanisole with *p*-methylanisole is especially informative. If there were a through-space interaction in *p*-allylanisole then the vinyl orbital (9.75 eV) and the *p*-methylanisole orbital (8.17 eV) should have split to raise the 9.75-eV orbital and lower the 8.17-eV orbital. No such splitting was observed.²³ The negligibly small changes are actually in the opposite

(15) (a) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970; (b) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968)

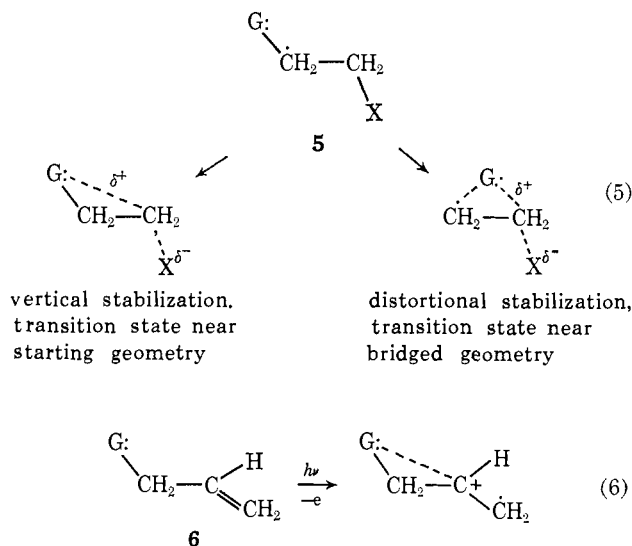(16) A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, 1, 1 (1963).

(17) W. G. Dauben and J. L. Chitwood, *J. Amer. Chem. Soc.*, 90, 6876 (1968).

(18) D. S. Noyce and R. L. Castenson, *J. Amer. Chem. Soc.*, 95, 1247 (1973).

(19) (a) U. Weidner and A. Schweig, *J. Organometal. Chem.*, 39, 261 (1972); (b) W. Shäfer and A. Schweig, *J. Chem. Soc., Chem. Commun.*, 824 (1972).

(20) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 70, 821 834 (1948).

(21) J. C. Bünzli, A. J. Burak, and D. C. Frost, *Tetrahedron*, 29, 3735 (1973).

(22) R. S. Brown, D. F. Eaton, A. Hosomi, T. G. Traylor, and J. M. Wright, *J. Organometal. Chem.*, 66, 249 (1974).

(23) Although the acceleration of acetolysis of phenethyl tosylate would correspond to an ionization potential change too small to detect, the 2-*p*-anisyl participation should be detectable if it were vertical stabilization. Our previous results for Y—CH₂X acetolysis *vs.* YCH═CH₂ ionization potentials reveals that Δ log *k* = 1 corresponds to ΔIP ≥ 0.1 eV. A factor of 80 in rate would result in a change of ionization potentials of about 0.2 eV which is several times the standard deviation of our ionization potential measurements.

directions. Similarly negligible interactions were observed for 5-methyl-1,4-hexadiene and, by Schäfer and Schweig, for allylmethyl sulfide.[19b] These results should be contrasted to the 2.2-eV interaction observed in allyltrimethyltin[22] where $\sigma-\pi$ conjugation has been demonstrated.[5a,19a]

We therefore agree with the original postulates[2,3b,c,d] and most current interpretations[3a] that β-aryl group participation leads to a transition state closely resembling a symmetrical phenonium ion as depicted in eq 1. That is, the stabilizations are: for k_1, principally distortional stabilization, and for k_2 mostly vertical stabilization. Both transition states $1^{\ddagger}$ and $3^{\ddagger}$, being similar to 2, probably derive stabilization from cyclopropyl $\sigma-\pi$ conjugation.[24]

The results with the very nucleophilic neighboring group, MeS, when compared to our previous studies of neighboring C–metal bonds,[5] suggest the following generalization for the neighboring group B: in eq 6. If the G: lone pair has a much lower ionization potential than does an orbital associated with the G–C σ bond, then the stabilization will require distortion to increase 13 overlap, whereas a lower "G–C σ bond ionization potential"[19] results in dominant stabilization by $\sigma-\pi$ conjugation which does not require such distortion.

Acknowledgment. We wish to acknowledge the assistance of Dr. Robert S. Brown and Dr. John Wright in the construction of the instrument and determination of photoelectron spectra.

(24) This development of $\sigma-\pi$ conjugation at the transition state $1^{\ddagger}$ could explain both the facts that Ar$_3$ is faster than Ar$_5$ participation and the failure of Ar$_5$ participation to accurately follow σ^+ values.[25]

(25) F. L. Schadt and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 7860 (1973).

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1,2-Dimethylhexahydropyridazine Conformations by Carbon-13 Nuclear Magnetic Resonance

Sir:

The conformations of 1,2-dimethylhexahydropyridazine (1) have been the cause of some discussion. Anderson[1] concluded that it existed solely in the equatorial, equatorial N-methyl conformation 1ee because the

| 1ee | 1ea | 1aa |
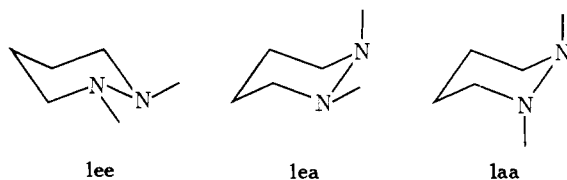
proton nmr spectrum of the N-methyl groups remained a singlet at low temperature, where he assumed both ring flipping and nitrogen inversion to be slow. Katritzky and coworkers[2] then showed that the dipole

(1) J. E. Anderson, *J. Amer. Chem. Soc.*, **91**, 6374 (1969), and references therein.

moment of 1 was too high for 1ee to be the sole conformation and, by using low temperature nmr studies of derivatives in conjunction with dipole moment studies, came to the striking conclusion that 1 exists as a 36:34:30 mixture,[2b] later revised to a 62:20:18 mixture[2d] of 1aa:1ea:1ee at room temperature. Using a diagram topologically similar to Figure 1,[2b] they made the important point that different ring flips and nitrogen inversions ought to have different activation energies, pointing out that all of the processes which cross the heavy vertical line of Figure 1 will be relatively slow because they force methyl groups to pass each other. They subsequently realized[2d] that even ring flips, which do not force methyl groups past each other, should have substantially higher activation energies than nitrogen inversions which do not force methyl groups past each other, leading to three types of barriers for 1.

We report ^{13}C nmr data for 1 which illustrate freezing out of the two lower energy barriers, and which allow a more accurate estimation of the conformational population of 1, by direct observation of the conformers.

The ^{13}C nmr spectrum of 1[3] shows three sharp lines at ambient temperature, as expected when rapid conformational interconversion occurs. These lines broaden below about $-20°$, and, by $-53°$, six lines can be observed: a set of three lines (set A) which remain sharp as the temperature is lowered further, and a second set of three lines (set B). The lines of set B sharpen until about $-85°$, but then broaden substantially and disappear into the base line near $-100°$. At still lower temperatures, a new set of five lines (set C) appears. The positions of the lines together with assignments to the three types of carbons (verified by using undecoupled spectra for the ambient temperature spectrum and set A) appear as shown in Table I.

Because steric compression will certainly cause upfield cmr shifts for any conformation containing axial N-methyl substituents, set A, which has the farthest downfield carbon signals for each type of carbon present can be confidently assigned to 1ee. By $-53°$, 1ee is already interconverting slowly enough with the other conformations to allow resolution of the mixture of interconverting conformations 1ae, 1aa, and 1ea as a second set of signals (set B). Thus the "easy" ring flip marked with dotted lines in Figure 1 is frozen out by $-53°$. A rough estimate of $\Delta G^{\ddagger}$ for this process gives *ca.* 10 kcal/mol, but line shape analysis for a more accurate figure remains to be carried out. This "easy" ring flip is thus not very much lower in energy than the processes marked by the center line in Figure 1, for which Anderson found a $\Delta G^{\ddagger}$ of about 12 kcal/mol.[1]

The only rate processes left to freeze out are those of "easy" nitrogen inversion, the unmarked equilibria of Figure 1. We attribute the five observed lines of set C, the result of freezing out these equilibria, to conformation 1ae ($= $1ea) and note that the average of each set of two lines is close to the positions for set B (and the

(2) (a) R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, *Chem. Commun.*, 644 (1971); (b) R. A. Y. Jones, A. R. Katritzky, and R. Scattergood, *Chem. Commun.*, 644 (1971); (c) R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, *J. Chem. Soc., Perkin Trans. 2*, 34 (1972); (d) R. A. Y. Jones, A. R. Katritzky, K. A. F. Record, and R. Scattergood, *ibid.*, 406 (1974).

(3) Data were collected on a Varian XL 100 instrument equipped for Fourier transform, using internal deuterium lock, and are reported in parts per million downfield from TMS.