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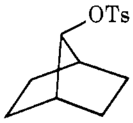
Structural Effects in Solvolytic Reactions. 15. Solvolysis of 1-Arylcyclohexyl and 1-Arylcyclohex-2-enyl *p*-Nitrobenzoates. Effect of Increasing Electron Demand on the Contributions of an Allylic Double Bond in the Solvolysis of Tertiary Cyclohex-2-enyl Derivatives

Herbert C. Brown,* M. Ravindranathan,[1a] and Morris M. Rho[1b]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received September 28, 1975.*

Abstract: 1-Arylcyclohexyl *p*-nitrobenzoates containing representative substituents in the aryl ring were synthesized and their rates of solvolysis in 80% aqueous acetone determined. The corresponding cyclohex-2-enyl derivatives were also synthesized and their rates of solvolysis measured in this solvent. The value of ρ^+ for the 1-arylcyclohexyl system is −4.60 and that for the 1-arylcyclohex-2-enyl derivatives is −2.52. This remarkable change in ρ^+ is attributed to increased π conjugation, involving the allylic double bond, with increasing electron demand at the cationic center. Consequently, the tool of increasing electron demand can detect both π participation, as in the 7-aryl-*anti*-norbornenyl derivatives, and developing π conjugation, as in the 1-arylcyclohex-2-enyl derivatives.

The effect of certain homoallylic double bonds in enhancing the rates of solvolysis reactions is well documented.[2,3] For example, the rate factor of 10^{11} observed in *anti*-7-norbornenyl tosylate (**2**) is attributed to π participation.[2] From a study of the solvolysis of 7-aryl-*anti*-norbornenyl *p*-nitrobenzoates (**3**) and the corresponding saturated derivatives (**4**), Gassman and Fentiman established that the contribution of the π electrons to the stabilization of the electron-deficient center increases with increasing electron demand.[3] On the other hand, the tool of increasing electron demand establishes the absence of π participation in the cyclopent-3-enyl system[4] (**5**).



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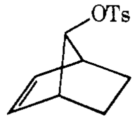

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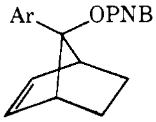
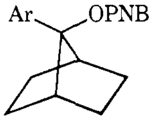
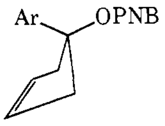
Rel rate (25°) 1.0 10^{11}



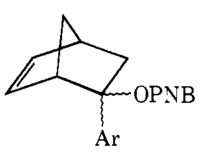
3 (ρ^+ −2.30)



4 (ρ^+ −5.27)



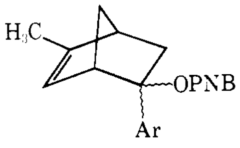
5 (ρ^+ −3.92)



6 (*exo*: ρ^+ −4.21)
(*endo*: ρ^+ −4.17)

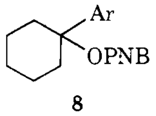
In contrast, the 2-aryl-2-norbornenyl system (**6**) appears to be a borderline case.[5] With the less electron-demanding substituents (*p*-CH_3O, *p*-H, *p*-CF_3) the exo:endo rate ratio remains sensibly constant, indicating the absence of π participation. However, with the more deactivating 3,5-$(CF_3)_2$ substituent, there is observed a modest increase in the exo:endo rate ratio, suggesting the initiation of π participation. Steric hindrance to ionization of the endo isomers arising from the π cloud of the double bond has been proposed for the relatively high, essentially constant exo:endo rate ratio observed in the 2-aryl-2-norbornenyl derivatives.[5,6]

Activation of the double bond by a methyl group (**7**) converts the system (**6**) from a borderline case to one that clearly involves π participation.[7]



7 (*exo*: ρ^+ −3.27)
(*endo*: ρ^+ −4.19)

It was of interest to examine the question of whether the tool of increasing electron demand could detect π conjugation as well as π participation. To this end we undertook a study of the solvolysis of the 1-arylcyclohexyl (**8**) and the 1-arylcyclohex-2-enyl (**9**) *p*-nitrobenzoates.



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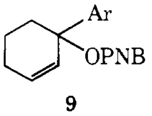

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Table I. Solvolysis of 1-Arylcyclohexyl and 1-Arylcyclohex-2-enyl *p*-Nitrobenzoates in 80% Aqueous Acetone

System	Substituent in aryl	$k_1 \times 10^6$ s^{-1}			$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
		T$_1$ °C	T$_2$ °C	25°		
Cyclohexyl	p-CH$_3$O			67.3[a]		
	p-H			0.0146[b]		
	p-CF$_3$	19.6 (125)	1.35 (100)	3.05×10^{-5} [c]	30.7	−2.8
	3,5-(CF$_3$)$_2$	124 (175)	11.9 (150)	2.66×10^{-7} [c]	34.7	0.43
Cyclohex-2-enyl	p-H			2200[a]		
	p-CF$_3$			57.9		
	3,5-(CF$_3$)$_2$	99.6 (50)		5.41	21.7	−9.8

[a] Calculated from the rate constant for the benzoate by multiplying by the factor 20.8 (ref 9). [b] E. N. Peters, Final Report, Purdue University, 1973. [c] Extrapolated from data at higher temperatures.

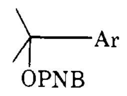
Results

Synthesis. The Grignard reagents prepared from *p*-bromoanisole, bromobenzene, *p*-bromobenzotrifluoride, and 3,5-bis(trifluoromethyl)bromobenzene were added to cyclohexanone or cyclohex-2-en-1-one. The tertiary alcohols were converted into *p*-nitrobenzoates by treating their lithium salts with *p*-nitrobenzoyl chloride in THF. The properties of the *p*-nitrobenzoates are listed in Table II.

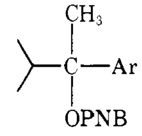
Rate Studies. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone. 1-Phenylcyclohex-2-enyl *p*-nitrobenzoate and 1-anisylcyclohexyl *p*-nitrobenzoate proved too unstable to isolate. Hence, the benzoates were synthesized and the rate constants for the *p*-nitrobenzoates were calculated from the benzoate by multiplying the rate constants by the factor 20.8.[8] The pertinent rate data are summarized in Table I.

Discussion

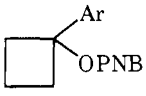
Sufficient data are now available to examine the differences in the abilities of various saturated alicyclic and bicyclic systems to stabilize an electron deficient center as measured by the tool of increasing electron demand. Thus, a detailed study of the tertiary cumyl (**10**),[9] 2-aryl-3-methyl-2-butyl (**11**),[10] 1-arylcyclobutyl (**12**),[11] and 1-arylcyclohexyl (**8**) derivatives



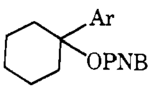
10 (ρ^+ −4.72)



11 (ρ^+ −4.76)

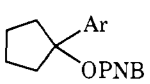


12 (ρ^+ −4.66)



8 (ρ^+ −4.60)

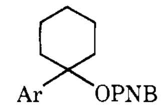
reveal a close similarity in the ρ^+ values, indicating no significant difference in the electronic contributions to an electron-deficient center of the methyl, isopropyl, cyclobutyl, and cyclohexyl groups. On the other hand, ρ^+ for cyclopentyl (**13**)



13 (ρ^+ −3.82)

is considerably less negative, −3.82.[4,12] Consequently, the cyclopentyl group is far better than the other groups examined (**8, 10, 11, 12**) in supplying electrons to an electron-deficient center. Possibly this is the result of superior hyperconjugative contributions.[13]

In the present study the tool of increasing electron demand has been applied to cyclohexyl (**8**) and cyclohex-2-enyl *p*-nitrobenzoates (**9**) to estimate their relative electronic contributions. The rate of solvolysis of cyclohex-2-enyl derivatives increases compared with the corresponding cyclohexyl derivative. The data not only reveal the large accelerating effect on the rate of the allylic double bond, but also reveal clearly that π conjugation involving the allylic double bond increases with increasing electron demand at the cationic center.



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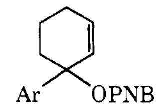

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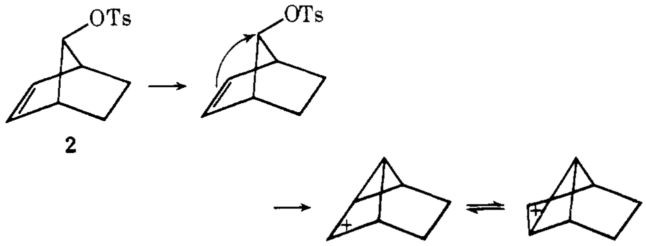
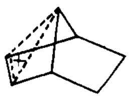
Substituent in Ar	Rel rate	
p-H	1.0	1.52×10^5
p-CF$_3$	1.0	1.9×10^6
3,5-(CF$_3$)$_2$	1.0	2.3×10^7

A major increase in the electronic contributions from the cyclohex-2-enyl system, as compared to the cyclohexyl system, is likewise revealed by comparing the value of ρ^+ with that for the cyclohexyl system. The data for **8** provides a value of ρ^+ of −4.60 (correlation coefficient 0.9997), quite comparable with the values for the methyl (**10**), isopropyl (**11**), and cyclobutyl (**12**) derivatives, whereas **9** provides a value of −2.52 (correlation coefficient 0.999). Hence the stabilization provided by the double bond is a linear function of the electron demand of the incipient carbonium ion center.

It is highly desirable to distinguish between π bridging and π conjugation. The enormous rate enhancement observed in the solvolysis of *anti*-7-norbornenyl tosylate (**2**) has been attributed to π participation. There is no question but that solvolysis proceeds with participation of the π electrons in the transition state. The problem is that of defining the precise nature of the intermediate—a pair of rapidly equilibrating cyclopropylcarbinyl cations (**14**) involving a stabilized transition state (**15**) for this equilibrating pair, or a π bridged ion (**15**) sufficiently stable so that we need no longer consider the equilibrating pair (**14**).





15

The decrease in ρ^+ observed in the solvolysis of 7-aryl-*anti*-norbornenyl *p*-nitrobenzoates (**3**) compared with their saturated derivatives (**4**) ($\Delta\rho^+ = 2.97$) suggests major π participation increasing with increasing electron demand. Consequently, there is no question at present that there is π participation in **2** and related derivatives. However, it is not yet established whether the intermediate is **15**, involving π bridging

Table II. Preparation of 1-Arylcyclohexyl and 1-Arylcyclohex-2-enyl *p*-Nitrobenzoates

System	Substituent in aryl	% yield	Mp, °C	Analyses
Cyclohexyl	*p*-CH_3O[a]	87	104-105	C, H
	p-CF_3	70	135	C, H, N, F
	3,5-$(CF_3)_2$	78	124.5-125	C, H, N, F
Cyclohex-2-en-1-yl	*p*-H[a]	26	101-101.5	C, H
	p-CF_3	31	98-99	C, H, N, F
	3,5-$(CF_3)_2$	39	122-122.5	C, H, N, F

[a] Benzoate.

or **14**, not involving π bridging. In the solvolysis of 1-arylcyclopent-3-enyl *p*-nitrobenzoates (**5**), no π participation is observed, and hence there would appear to be no reason in this case to postulate π bridging either in the transition state or in the intermediate.

π conjugation should be clearly distinguished from π participation. The introduction of an allylic double bond into the cyclohexane ring causes ρ^+ to change from −4.60 to −2.52. This major change is clearly the result of π conjugation.

Consequently, it appears that the tool of increasing electron demand can detect unambiguously either π participation, when it occurs in homoallylic systems, or π conjugation when it occurs in allylic systems.

It is of major interest to establish unambiguously in various systems the presence and magnitude of σ bridging and σ conjugation (hyperconjugation). Consequently, we are continuing our exploration in appropriate systems with this tool to test its ability to detect σ participation and σ conjugation in such systems.

Experimental Section

Preparation of 1-Arylcylcohexyl (8) and 1-Arylcylcohex-2-enyl *p*-Nitrobenzoates (9). 1-Arylcyclohexanols and 1-arylcyclohex-2-enols were obtained by the addition of the appropriate Grignard reagents to cyclohexanone or cyclohex-2-en-1-one. The alcohols were purified by distillation or crystallization. The *p*-nitrobenzoates were prepared by treating the lithium salt of the alcohols with *p*-nitrobenzoyl chloride. The physical and analytical data are listed in Table II.

Kinetic Procedure. The procedure employed in determining the rate constants of *p*-nitrobenzoates followed that described earlier.[14]

References and Notes

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(12) Cyclopropyl is superior to cyclopentyl in supplying electrons to an electron-deficient center (ref 10).
(13) Both *exo-* (ρ^+ −3.83) and *endo*-norbornyl (ρ^+ −3.75) are similar to cyclopentyl in their electronic contributions to the electron deficient center: H. C. Brown, M. Ravindranathan, K. Takeuchi, and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 2899 (1975).
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Low-Energy Singlet–Triplet and Singlet–Singlet Transitions in Cycloalkenes

Isidor Sauers, Loretta A. Grezzo, Stuart W. Staley,* and John H. Moore, Jr.†

Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20742.

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Abstract: The lowest energy singlet-triplet and singlet-singlet transitions of cis cycloalkenes, ranging from cyclopropene to cyclooctene, as well as *trans*-cyclooctene, have been investigated using the technique of ion-impact energy-loss spectrometry. In the cis cycloalkenes the maximum of the T ← N transition occurs at 4.2 eV regardless of ring size. The V ← N transition energy decreases from 7.2 to 6.5 eV with increasing ring size. The T ← N maximum for *trans*-cyclooctene decreases to 3.85 eV in agreement with predictions of the Franck-Condon principle.

The electronic spectra of ethylene and its alkyl derivatives have the potential of providing much valuable information about the structural and chemical nature of the carbon-carbon double bond. The spectra associated with the electrons in the double bond are often diffuse and of anomalous intensity and the interpretation of these spectra is currently a problem of considerable interest.

The lowest energy olefinic transition is a π → π* transition from the ground state (the N state) to the lowest triplet state (T) which lies about 4.2 eV above the ground state. Ground-state ethylene is planar, whereas the molecule in the triplet state is relatively free to twist about the double bond and is most stable in the 90° twisted conformation. For this reason the T ← N transition is of importance in photochemical isomerization processes requiring rotation about the C=C bond. The corresponding singlet-singlet π → π* transition in ethylene is identified as the V ← N transition and lies about 3.5 eV above the T ← N transition. However, the V ← N transition in many substituted ethylenes is only 3.0 eV or less above the T ← N.[1] Much of the intensity in the V ← N absorption spectrum of ethylene has been ascribed[2-5] to transitions to excited states in which the molecules are significantly twisted from the planar conformation (so-called nonvertical transitions). It has also been

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[†] 1975–76 JILA Visiting Fellow, University of Colorado and NBS, Boulder, Colo. 80309.