

## Neighbouring group participation and the tool of increasing electron demand : A review

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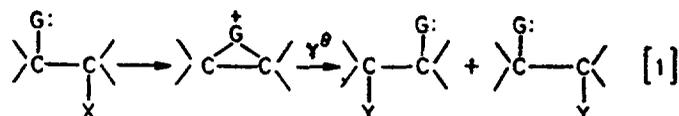
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**Abstract.** Solvolytic reactions could be greatly influenced by the presence of neighbouring groups. The tool of increasing electron demand has been successfully used to detect such participation. For example, the tool has detected the presence of major  $\pi$ -participation in *anti*-7-norbornenyl and  $\pi$ -conjugation in cyclohexen-2-yl derivatives. The changes observed in the absolute values of  $\rho^+$  with ring size in cyclic systems could be adequately explained by the I-strain concept. The tool has established major  $\pi\sigma$ -conjugation in cyclopropylcarbinyl and nortricycyl derivatives.  $\pi\sigma$ -participation in the Coates' cation has been unambiguously established. However, this sensitive probe has failed to provide evidence for  $\sigma$ -participation in the solvolysis of 2-norbornyl system. It is concluded that the tool of increasing electron demand is quite sensitive to detect the presence or absence or neighbouring group participation.

**Keywords.** Neighbouring group participation ; Hammett-Brown relationship ; increasing electron demand ;  $n$ -,  $\pi$ -,  $\sigma$ -participation ; I-strain.

### 1. Neighbouring group participation

Winstein and his co-workers (Winstein *et al* 1948; Winstein and Grunwald 1951) established that donor atoms in the  $\beta$ -position to the reactive centre could greatly enhance the rates of unimolecular solvolytic reactions. This would simultaneously



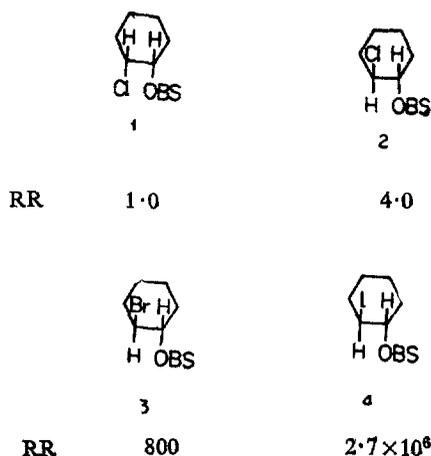
control the mechanism and stereochemistry of substitution. Transition state containing a bridged ring was proposed (equation 1).

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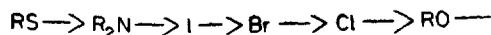
1.1. *n*-,  $\pi$ -,  $\sigma$ -participation

Neighbouring group participation in unimolecular solvolytic reactions has been broadly classified into three different types depending on the type of group involved in the participation.

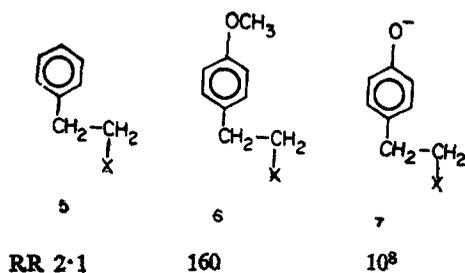
1.1a. *n*-Participation: The participating atom or groups should have available nonbonded electrons. For example, it was observed that *trans*-2-chlorocyclohexyl brosylate (2) solvolysed four times faster than the *cis* isomer (1) (Winstein *et al* 1948; Winstein and Grunwald 1951). The corresponding bromo-(3) and



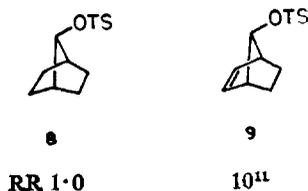
iodocyclohexyl brosylates (4) showed much larger rate enhancement over the corresponding *cis* isomers. These large rate enhancements were attributed to the driving force accompanying the formation of bridged intermediates. The following is the order of the ability of *n*-donors to serve as such bridging groups:



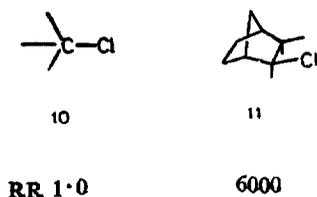
1.1b.  $\pi$ -Participation: The  $\pi$ -subdivision of neighbouring groups is known to exhibit a wide range of effectiveness in their reactivity. For example, in the solvolysis of a system like  $\alpha$ -phenylethyl derivatives, the following rate order is observed (Capon 1964). Winstein *et al* (1955) observed that *anti*-7-norbornenyl tosylate



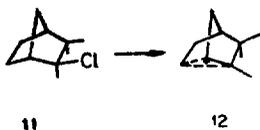
(9) solvolysed about  $10^{11}$  times faster than the saturated analogue (8). This has been attributed to the participation of the double bond facilitating the ionisation process.



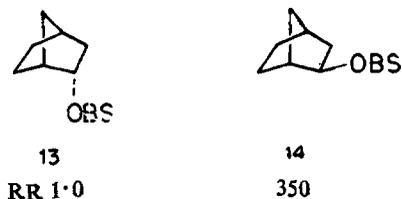
1.1c.  $\sigma$ -Participation: Brown *et al* (1951) observed that camphene hydrochloride (11) solvolysed 6,000 times faster than *tert*-butyl chloride (10). This was



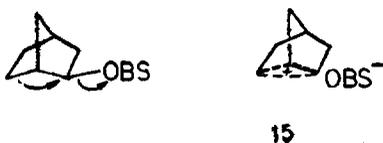
attributed to the driving force provided by the participation of the 1,6- $\sigma$ -electrons leading to the formation of a stabilised  $\sigma$ -bridged cation (12).



Winstein and Trifan (1952) observed that *exo*-norbornyl brosylate (14) underwent acetolysis 350 times faster than the *endo* derivative (13). It has been suggested



that the 1,6-bonding pair of  $\sigma$ -electrons is geometrically in an ideal position to participate in the displacement of the *exo*-OBS group, resulting in the formation of a stabilised  $\sigma$ -bridged intermediate (15)



## 1.2. Evaluation of neighbouring group effects

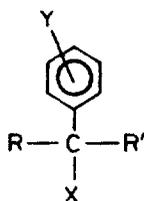
In order to evaluate the effect of a neighbouring group on the rate and products of solvolysis the correct choice of a model compound is imperative (Brown 1977). Selection of such a standard can be controversial. For example, Ingold *et al* (1951) compared the rate of solvolysis of the highly hindered camphene hydrochloride to that of *tert*-butyl chloride. This has been questioned. Therefore, there arose the need for the quantitative correlation of rate and equilibrium constants in terms of relative free energy changes. The Hammett relationship (Johnson 1973) provided the solution. This relationship is based on the fact that as the substituent is varied, the logarithms of the rate constants for aromatic side chain reactions are linearly related to one another. The relationship is as shown in equation (2), where  $k$  and  $k_0$  are the rate constants for the substituted and

$$\log \frac{k}{k_0} = \rho\sigma \quad (2)$$

unsubstituted compounds,  $\sigma$  is the substituent constant and  $\rho$  the reaction constant, a measure of the sensitivity of a particular reaction to the substituents. However, anomalies were observed when the Hammett equation was applied to the solvolysis of benzyl derivatives where a full positive charge developed. Stock and Brown (1963) considered both the inductive and resonance contributions of a substituent on the aryl group in a reaction where a full positive charge developed during the course of the reaction and formulated a more general equation,

$$\log \frac{k}{k_0} = \rho^+\sigma^+ \quad (3)$$

the Hammett-Brown relationship, *viz.*, equation (3). This modified equation has found great utility in the study of the solvolysis of various tertiary benzylic systems (16).



16.

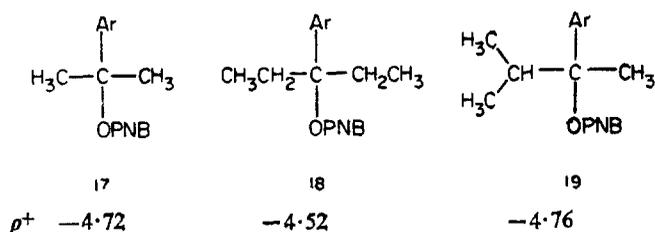
This technique works on a well-accepted theory that more stabilised the carbonium ion less demand it will make on the neighbouring groups for further stabilisation and *vice-versa*. The stability of a carbonium ion generated in a solvolytic reaction can be monitored by increasing or decreasing the electron supply to the reaction centre. This can be achieved by varying the substituent  $Y$  in the aromatic ring. The logarithm of the rate constant is plotted against the substituent constant,  $\sigma^+$ , to compute  $\rho^+$ , the reaction constant. Higher the absolute value of  $\rho^+$ , less stable is the carbonium ion and *vice-versa*. In other words, the value of  $\rho^+$ , realised in a solvolytic reaction, gives an estimate of the neighbouring group participation in the ionisation reaction.

## 2. The tool of increasing electron demand

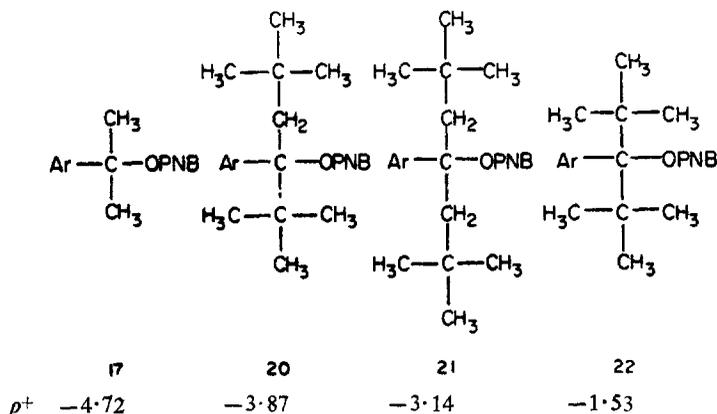
The above mentioned technique of evaluating the neighbouring group participation in a solvolytic reaction has been popularly referred to as the 'tool of increasing electron demand'. This diagnostic probe has proved to be a very powerful method in physical organic chemistry. Its use in the study of the evaluation of neighbouring group effects in solvolytic reactions will be reviewed here. Most of the available rate data is for *p*-nitrobenzoates in 80% aqueous acetone and are compared at 25°C.

### 2.1 Alkyl systems

In order to estimate the hyperconjugative stabilisation of the cationic centre by the alkyl groups, arylalkyl systems have been examined by this probe of increasing electron demand (Brown *et al* 1977; Tanida and Matsumara 1973). Simple alkyl groups such as methyl, ethyl and isopropyl do not have a significant effect on  $\rho^+$  as indicated by the values  $-4.72$ ,  $-4.52$  and  $-4.76$ , respectively. The large negative and essentially constant  $\rho^+$  values indicate that the simple alkyl groups, methyl, ethyl and isopropyl do not differ significantly in their ability to stabilize the cationic centre by hyperconjugation.



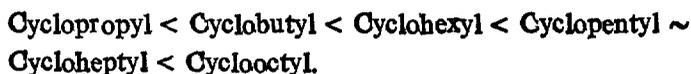
However, the solvolysis of a series of arylalkylcarbinyl *p*-nitrobenzoates (**20**, **21**, **22**) with bulky alkyl groups yields progressively decreasing  $\rho^+$  values with increasing bulk of the alkyl groups (Tanida and Matsumara 1973).



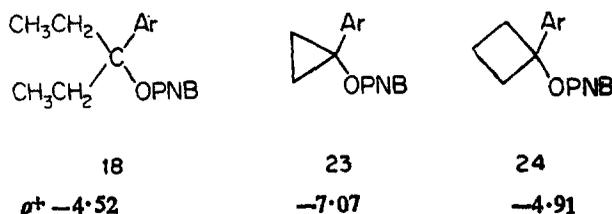
This has been attributed to steric effects, rather than to increased electronic stabilisation of the cationic centres by hyperconjugation.

## 2.2 Cycloalkyl systems

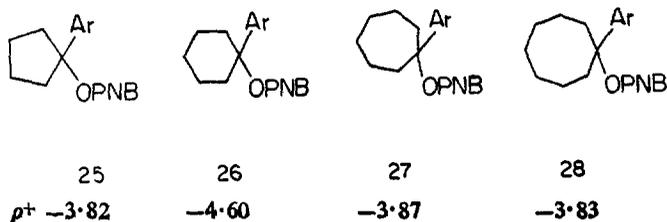
Changes in uni and bimolecular reactivities of alicyclic compounds can be related to changes in the number of carbon atoms in the ring (Brown *et al* 1977e). I-strain, the increase in internal strain in a cyclic structure resulting from alterations in bond angles and constellations accompanying a change in the coordination number of a ring atom in the course of the reaction, has been suggested to be responsible for the variation in chemical reactivity with ring size. The theory of I-strain would require the following order of reactivity:



The tool of increasing electron demand was applied to these alicyclic systems in order to detect the effects of I-strain (Brown *et al* 1977e, 1978). In comparison to the arylaliphatic system, cyclopropyl (**23**) and cyclobutyl (**24**) had large negative  $\rho^+$  values of  $-7.07$  and  $-4.91$ , respectively. The increase in I-strain in transforming a ring atom from  $\text{Sp}^3$  to  $\text{Sp}^2$  causes the developing cationic centre to become highly electron demanding and this results in a relatively large electron supply from the aryl group, which is reflected in high negative  $\rho^+$  values.



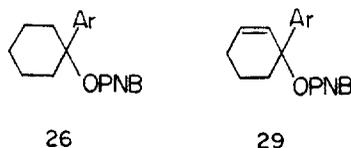
The solvolysis of cyclopentyl derivative (**25**) would involve the transformation of a ring carbon atom from  $\text{Sp}^3$  to relatively strain free  $\text{Sp}^2$  stage. This is reflected in the relatively low  $\rho^+$  value of  $-3.82$ . Similarly the more reactive cycloheptyl



(**27**) and cyclooctyl (**28**) derivatives gave  $\rho^+$  values similar to that of cyclopentyl derivatives, whereas, the situation is quite the opposite in the case of cyclohexyl (**26**), the strain free  $\text{Sp}^3$  carbon transforming into relatively strained  $\text{Sp}^2$  carbon atom. This is nicely reflected in the large negative  $\rho^+$  value of  $-4.60$ . Thus, the parallelism of the observed  $\rho^+$  values with the relative reactivities of these ring systems, accounted for in terms of I-strain effects, is truly remarkable.

## 2.3 Cycloalkenyl systems

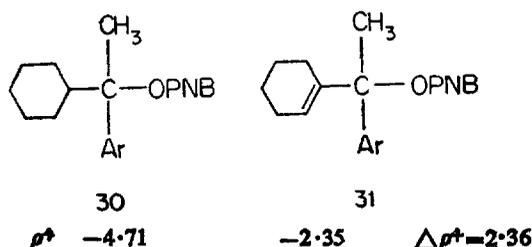
Presence of an allylic double bond in a cyclic system greatly enhances the solvolytic reactivity of the system (Streitwieser 1962). The  $\pi$ -system stabilizes the developing carbonium ion by delocalising the positive charge. The 'tool' was applied to systems possessing an allylic double bond to estimate the  $\pi$ -conjugative stabilisation of the double bond. The  $\rho^+$  values realised for cyclohex-2-enyl-1-aryl (29) and 1-( $\Delta'$ -cyclohexenyl) -1-aryl-1-ethyl (31) *p*-nitrobenzoates as compared with that of their saturated analogues (26, 30) revealed large rate-accelerating effect of the allylic double bond. The rate data indicated clearly that  $\pi$ -conjugation involving the allylic double bond increases with increasing electron demand at the cationic centre. The  $\Delta\rho^+$  observed clearly indicates the  $\pi$ -conjugative ability of the allylic double bond in these systems (Brown *et al* 1976, 1978).



Substituent in Ar

Rel. Rate

<i>p</i> -H	1.0	$1.52 \times 10^5$
<i>p</i> -CF <sub>3</sub>	1.0	$1.90 \times 10^6$
<i>m, m'</i> -(CF <sub>3</sub> ) <sub>2</sub>	1.0	$2.30 \times 10^7$
$\rho^+$	-4.60	-2.52 $\Delta\rho^+ = 2.08$



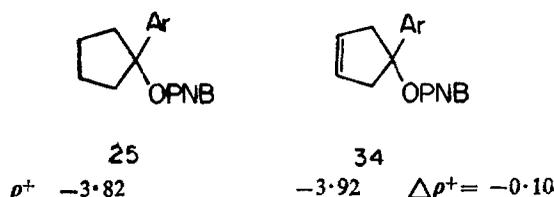
Structures with a carbon atom interposed between the cationic centre and the  $\pi$ -system are designated homoallylic. Such groups, during solvolysis, can stabilize a developing cationic centre by donating electrons through a 1,3-interaction. This type of stabilization is referred to as  $\pi$ -participation. However, it is well established that the geometry of the molecule is very important in  $\pi$ -participation. For example, anti-7-norbornenyl tosylate (9) solvolyses  $10^{11}$  times faster than the saturated analogue (8) (Winstein *et al* 1955). This rate enhancement has been attributed to  $\pi$ -participation. However, the homoallylic double bond in 4-bromocyclopentene (33) produced no rate enhancement, indeed 4-bromocyclopentene



RR 1.0

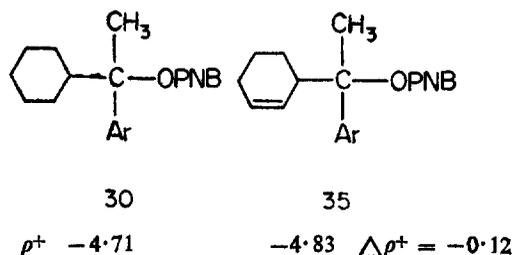
0.21

reacts slower than cyclopentyl bromide (32) (Bartlett and Rice 1963). This indicates minimum overlap of the  $\pi$ -system with the carbonium ion centre, solely because of the larger distance between the  $\pi$ -electron cloud and the developing cationic centre. The tool of increasing electron demand also indicated the absence of  $\pi$ -participation in this system (Peters and Brown 1975). The small  $\Delta\rho^+$  of  $-0.10$  is in the direction opposite to that anticipated for participation. However, from a study of the solvolysis of deuteriated cyclopent-3-enyl tosylate it has been



reported that the double bond participation in this system is quite strong (Lambert *et al* 1980).

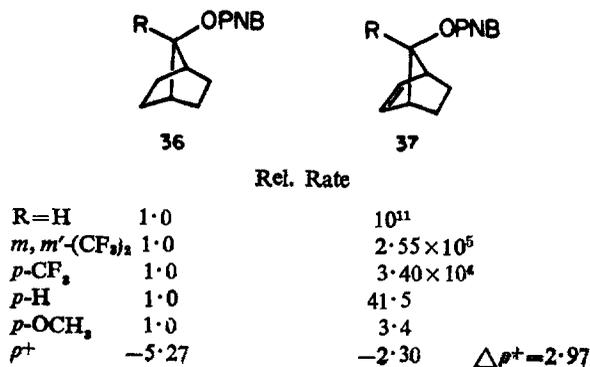
Solvolysis of 1-( $\Delta^2$ -cyclohexenyl)-1-aryl-1-ethyl *p*-nitrobenzoates (35) also revealed similar effects (Brown *et al* 1978). The similarity of  $\rho^+$  values indicates total lack of  $\pi$ -participation.



In fact, the small negative  $\Delta\rho^+$  indicates the inductive rate retarding effect of the double bond.

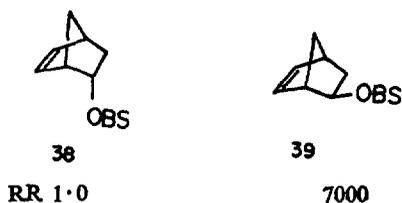
#### 2.4 Polycycloalkyl systems

The tool of increasing electron demand has been applied to a variety of polycycloalkyl systems. In fact the first application of this probe was on the 7-



norbornenyl system (Gassman and Fentiman 1970). As was pointed out earlier, *anti*-7-norbornenyl derivatives solvolyse  $10^{11}$  times faster than the saturated analogue, due to the enormous  $\pi$ -participation of the 5,6-double bond. It was observed that the large rate enhancement of  $10^{11}$  observed in the parent secondary derivatives decreased with the introduction of stabilising groups at the 7-position and effectively vanished with the *p*-anisyl group. This study effectively demonstrated the validity of the theory that the importance of the neighbouring group participation diminishes as the developing carbonium ion is stabilised by substitution. The high  $\Delta\rho^+$  observed clearly indicates the extent of  $\pi$ -participation, facilitating the solvolysis of the anti isomer.

It is often useful to compare the rate of solvolysis of the homoallylic compound with that of its saturated analogue in order to estimate the extent of  $\pi$ -participation. However, in the 2-norbornenyl system (38, 39) the observed *exo* : *endo* rate ratio of 7,000 was attributed to the  $\pi$ -participation in the *exo*-isomer (Winstein



*et al* 1950). This conclusion, based solely on the high *exo* : *endo* rate ratio is questionable especially in the light of studies indicating that steric effects may also make major contributions to high *exo* : *endo* rate ratios. In order to detect the presence of  $\pi$ -participation in these systems the tool of increasing electron demand was applied. The rate data revealed that the *exo* : *endo* rate ratio remains essentially constant when the substituent is varied from *p*-CH<sub>3</sub>O to *p*-CF<sub>3</sub>.



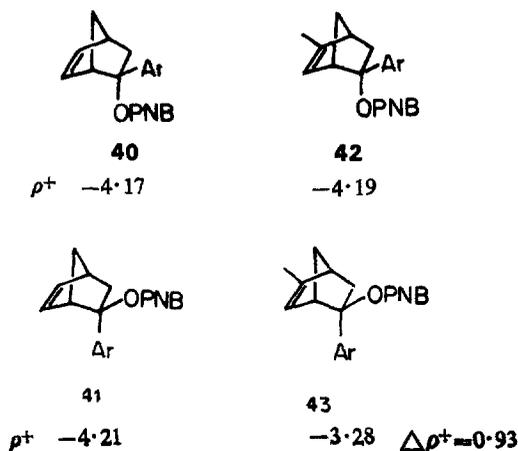
Substituent in Ar Rel. Rate

<i>p</i> -CH <sub>3</sub> O	1.0	312
<i>p</i> -H	1.0	202
<i>p</i> -CF <sub>3</sub>	1.0	283
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub>	1.0	447

indicating that with these substituents the  $\pi$ -participation is not significant. However, on further increase in the electron demand, with *m,m'*-(CF<sub>3</sub>)<sub>2</sub> derivative, there is only a modest increase in the *exo* : *endo* rate ratio to 447, thus indicating that the  $\pi$ -participation becomes a contributing factor under the influence of high electron demand by the *m,m'*-(CF<sub>3</sub>)<sub>2</sub> group (Brown *et al* 1975).

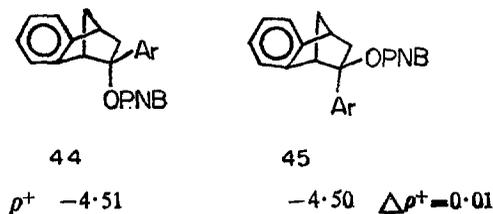
The introduction of a methyl group on a carbon carrying a double bond should greatly enhance the electron donating capacity of the  $\pi$ -system. This was observed

when the 'tool' was applied to 5-methyl-2-norbornenyl system (42, 43). The increased  $\pi$ -participation by the presence of the 5-methyl group is indicated by the  $\rho^+$  values (Brown *et al* 1974). Note the difference in value ( $\Delta\rho^+ = 0.93$ )

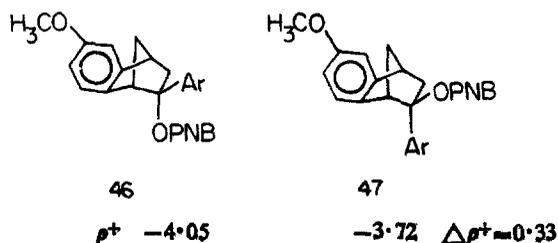


for the *exo* isomers which is in the direction anticipated for increased  $\pi$ -participation with the introduction of the 5-methyl group.

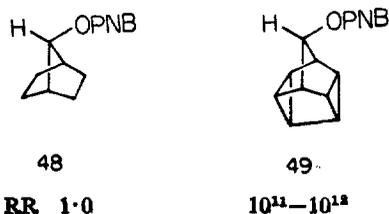
Benzonorbornenyl is a well studied system (Bartlett and Giddings 1960; Giddings and Dirlam 1963). The importance of  $\pi$ -participation in this system has been examined by introducing both activating and deactivating groups into the benzo moiety and also by introducing stabilizing substituents at the 2-position. The effect of such changes will be reflected on the rate ratios. Application of the tool of increasing electron demand to 2-aryl-benzonorbornen-2-yl *p*-nitrobenzoates (44, 45) indicated the absence of  $\pi$ -participation (Brown *et al* 1976).



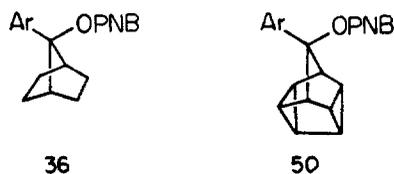
The large and essentially constant *exo* : *endo* rate ratios have been accounted for on steric grounds. The very small difference in  $\rho^+$  ( $\Delta\rho^+ = 0.01$ ) failed to reveal any differential electronic effect operating preferentially in the *exo*-derivative.



Introduction of a 6-methoxy substituent demonstrates the incursion of  $\pi$ -participation. The 6-methoxy substituent activates the aryl group towards participation (Brown and Liu 1969). Remote strained sigma bonds can also stabilize a cationic centre through electronic stabilization. For example, 9-pentacyclo [4.3.0.0<sup>2,4</sup>.0<sup>3,8</sup>.0<sup>5,7</sup>]-nonyl *p*-nitro-benzoate (**49**) solvolyses  $10^{11}$  to  $10^{12}$  times faster than 7-norbornyl *p*-nitrobenzoate (**48**) (Coates and Kirpatrick 1970). In



order to estimate this  $\pi\sigma$ -participation by the strained cyclopropyl bonds, the tool of increasing electron demand was applied to this pentacyclic system. The rate data reveals major  $\pi\sigma$ -participation with increasing electron demand at the developing carbonium ion centre. The large difference in  $\rho^+$  ( $\Delta\rho^+ = 3.22$ )

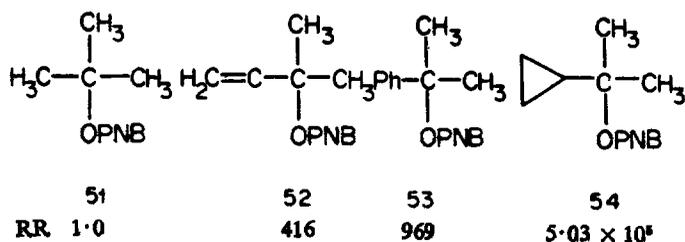


Substituent in Ar	36	50
	Rel. Rate	Rel. Rate
<i>p</i> -CH <sub>3</sub> O	1.0	$1.59 \times 10^2$
<i>p</i> -H	1.0	$5.85 \times 10^2$
<i>p</i> -CF <sub>3</sub>	1.0	$4.90 \times 10^6$
<i>m, m'</i> -(CF <sub>3</sub> ) <sub>2</sub>	1.0	$3.44 \times 10^8$
$\rho^+$	-5.27	$-2.05 \Delta\rho^+ = 3.22$

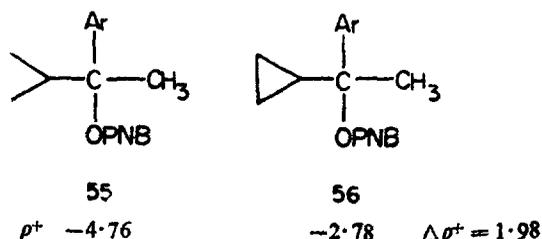
o these two systems (**36**, **50**) also indicates major  $\pi\sigma$ -participation in the pentacyclic system (Brown and Ravindranathan 1977).

### 3. Cyclopropylcarbinyl system

Cyclopropylcarbinyl derivatives are remarkably more reactive than alkylcarbinyl, allylcarbinyl or phenylcarbinyl derivatives (Brown *et al* 1977d).

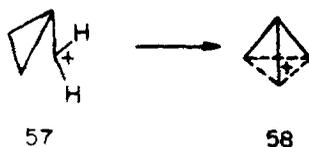


This is because of the remarkable effectiveness of cyclopropyl group to stabilize the cationic centre through electron supply by  $\pi\sigma$ -conjugation. The tool of increasing electron demand was applied to this system (Peters and Brown 1973). The rate data revealed that with increasing electron demand at the cationic centre the

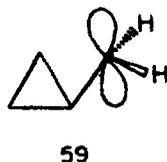


rate of solvolysis of the cyclopropyl derivative (56), relative to that of the model system (55), increases enormously. The large  $\Delta\rho^+$  indicates large stabilization provided by the cyclopropyl group to the developing carbocation. Electron supply from the cyclopropyl group to the developing carbocation can be increased or decreased by introduction of activating and deactivating substituents in the ring (Brown *et al* 1977b).

At one time, the high reactivity of cyclopropyl carbonyl derivatives in solvolytic reactions and the similarity in products from carbonium reactions of cyclopropyl-carbonyl and cyclobutyl derivatives was attributed to the formation of a stabilized intermediate involving a  $\sigma$ -bridge from the carbonium ion carbon with the cyclopropane ring (58) (Roberts and Mazur 1951).

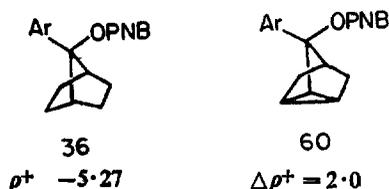


This would require the intermediate to exist in the parallel conformation to permit the  $p$  orbital of the carbonium carbon to be directed towards the ring (59). If the rate enhancement of the cyclopropyl group is solely due to such a



$\sigma$ -bridging, it was argued that the cyclopropyl group held in the bisected arrangement, a geometry in which the  $p$  orbital of the carbonium carbon cannot overlap with the ring, should greatly diminish the stabilisation provided by such interactions. The system chosen was 3-nortricycyl, the rigid geometry of the molecule forces the developing carbonium carbon to exist in the bisected arrangement

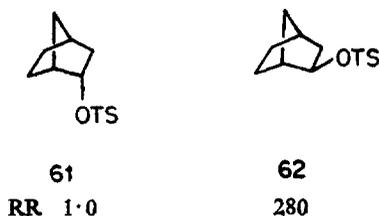
with the cyclopropyl ring. The tool of increasing electron demand was applied to this system (60) (Brown and Peters 1975).



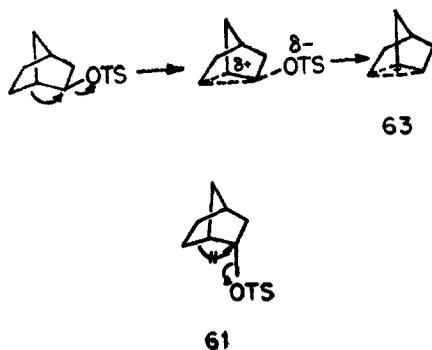
The difference in  $\rho^+$  ( $\Delta\rho^+ = 2.0$ ) of these two systems (36, 60) is similar to that of the cyclopropylcarbinyll (56) and isopropylcarbinyll (55) systems ( $\Delta\rho^+ = 1.98$ ). The similarity in  $\rho^+$  values (and  $\Delta\rho^+$ ) of these two systems indicates that the electronic contributions from the cyclopropane moiety are very similar in the two systems, in spite of the vast difference in geometries. These results confirm that the fast rates of solvolysis of cyclopropylcarbinyll derivatives are not the result of  $\sigma$ -bridging but of the stabilisation provided by  $\pi\sigma$ -conjugation of the cyclopropyl group.

#### 4. 1-Norbornyl system

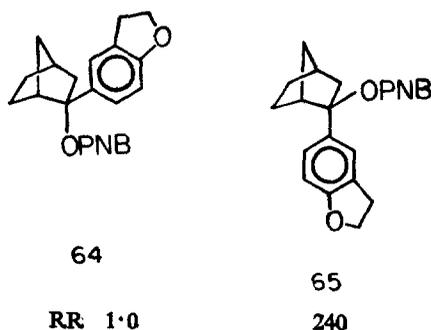
*exo*-Norbornyl tosylate (62) undergoes acetolysis at a rate 280 times faster than that of the *endo* derivative (61) (Schleyer *et al* 1965).



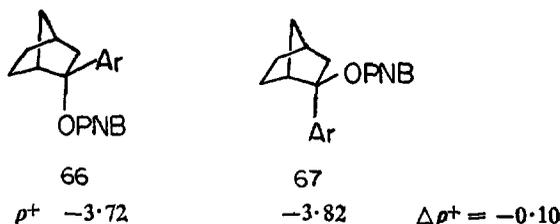
It was argued that the 1,6-bonding  $\sigma$ -electrons pair is in an ideal position to participate in the displacement of the *exo*-OTs group, leading to a stabilized  $\sigma$ -bridged cation (63). Such participation, it was argued, is stereochemically unfavourable in the *endo* derivative (Winstein and Trifan 1952).



As has been discussed earlier, the rate enhancement of  $10^{11}$  due to  $\pi$ -participation in the secondary 7-norbornenyl derivative is essentially swamped with the introduction of the *p*-anisyl group at the 7-position. Hence, a carbonium ion stabilised by a *p*-anisyl group should make a relatively little demand on the neighbouring groups for further stabilisation. Since, 5-coumaranyl ( $\sigma^+ = -0.984$ ) (Brown *et al* 1977a) group is much more electron donating than *p*-anisyl ( $\sigma^+ = -0.778$ ), it should stabilize the carbonium ion further. However, solvolysis of 2-(5<sup>t</sup>-coumaranyl)-2-norbornyl *p*-nitrobenzoates (64, 65) reveals an exo : endo rate ratio of 240 (Brown and Gundu Rao 1979). This compares with the value



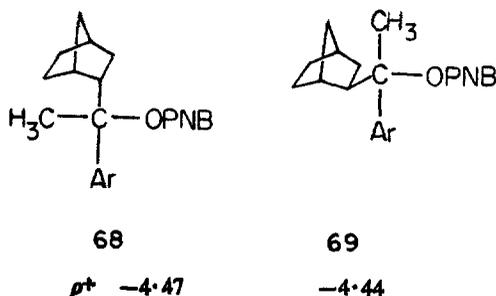
of 280 for the secondary tosylates. Application of the tool of increasing electron demand (Brown *et al* 1977f) revealed an essentially constant exo : endo rate ratio in the 2-aryl-2-norbornyl systems (66, 67).



Clearly,  $\sigma$ -participation cannot be a significant factor in the high exo : endo rate ratios in these derivatives. The similarity in the  $\rho^+$  values of the exo and endo derivatives and, hence, the small difference in  $\rho^+$  ( $-0.10$ ) which is actually in the direction opposite to that anticipated for participation, clearly rules out any such  $\sigma$ -participation in the parent system.

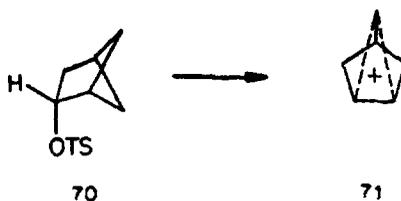
Jensen and Smart (1969) and Traylor *et al* (1971) proposed a hyperconjugative model to explain the high exo : endo rate ratios in the solvolysis of 2-norbornyl derivatives—an electronic contribution which stabilizes the exo transition state more than the endo. This interpretation differs from Winstein's nonclassical ion proposal in that  $\sigma$ -participation and  $\sigma$ -bridging are not involved in the transition state and major distortion of the structure is not essential for the operation of the electronic contribution facilitating ionisation of the exo isomer. This concept was tested by placing the developing positive charge  $\alpha$ -to the norbornyl ring system (68, 69). It was argued that the tool of increasing electron demand, when applied

to such a system, should be capable of detecting such enhanced supply in the *exo* isomer.

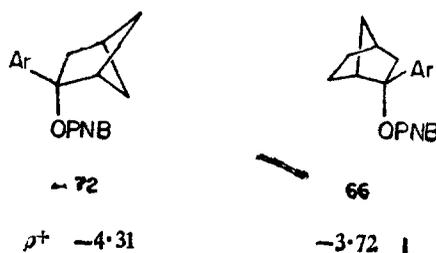


Clearly, the rates of solvolysis fail to support the proposal that there must be significant differences in the electronic contributions of the two isomeric groups (Brown and Ravindranathan 1978).

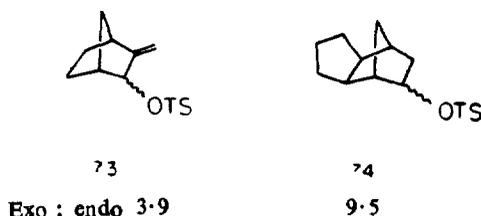
Meinwald and Gassman (1963) and Meinwald and Crandall (1966) solvolysed 2-bicyclo [2.1.1] hexyl tosylate (70) and proposed a bridged intermediate (71).



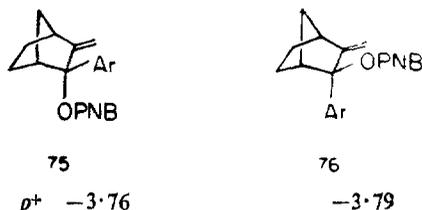
The nature of the 2-bicyclo [2.1.1] hexyl cation (71) is of special interest in view of its relationship to the norbornyl cation. Dewar (1975) has shown through calculations that the strain in 2-bicyclo [2.1.1] hexyl cation makes this an especially favourable case for  $\sigma$ -bridging. However, application of the tool of increasing electron demand to this system (72) did not support the presence of significant  $\sigma$ -participation. If the strained cyclobutane moiety facilitates solvolyses by  $\sigma$ -participation,  $\rho^+$  in this system should be more positive than in the 2-aryl-*endo*-norbornyl derivatives (66). However, this was not observed. Indeed,  $\rho^+$  is more negative, indicating the unimportance of  $\sigma$ -participation in this system (Brown *et al* 1977c).



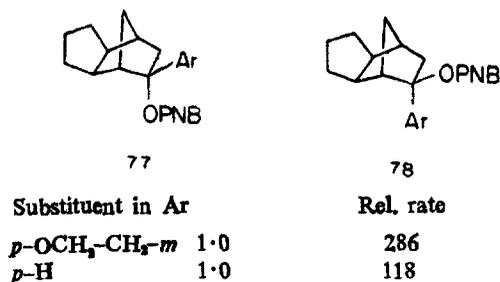
3-Methylene-2-norbornyl (**73**) (Wilcox and Jesaitis 1967) and *exo*-5, 6-trimethylene 2-norbornyl (**74**) (Takeuchi *et al* 1965) systems undergo solvolysis with relatively



low *exo* : *endo* rate ratios. It has been proposed that these systems should be considered to be models of the behaviour to be anticipated for classical 2-norbornyl systems. The unique structural features of these systems are believed to resist  $\sigma$ -bridging either because of special electronic effects (**73**) or because of steric constraints (**74**). However, the solvolysis of 2-aryl-3-methylene (**75**, **76**) (Brown and Gundu Rao 1979) and 2-aryl-*exo*-5,6-trimethylene (**77**, **78**) (Brown *et al* 1979)-2-norbornyl *p*-nitrobenzoates revealed high and essentially constant *exo* : *endo* rate



ratios. These *exo* : *endo* rate ratios are very similar to those realised for the 2-norbornyl derivatives. It is clear from these results that high *exo* : *endo* rate



ratios are not diagnostic of  $\sigma$ -bridging. Steric hindrance to ionisation provides an alternative explanation for such high *exo* : *endo* ratios in the tertiary derivatives.

The high *exo* : *endo* rate ratios, observed in the majority of the reactions of the norbornyl systems, have been attributed to the decreased rates of reaction in the sterically hindered *endo* cavity of the U-shaped norbornane structure. It appears that the high *exo* : *endo* rate ratio in the solvolysis of the tertiary 2-aryl-2-norbornyl and the parent secondary 2-norbornyl derivatives may actually be the result of a normal *exo* rate combined with a very slow *endo* rate (Brown 1977).

## 5. Conclusions

The mechanistic probe of increasing electron demand is a versatile tool for the physical organic chemist and can be used to elucidate the structure-reactivity relationships. Any change in reactivity as a result of structural change is reflected in  $\rho^+$  values. Higher the absolute value of  $\rho^+$  less favoured is the ionisation reaction and *vice versa*.

In the study of neighbouring group effect this tool has found great utility. The available data reveal that  $\rho^+$  values are very sensitive to neighbouring group effects.

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