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THROUGH-BOND *vs* THROUGH-SPACE INTERACTIONS

THE STABILIZATION OF CARBONIUM IONS

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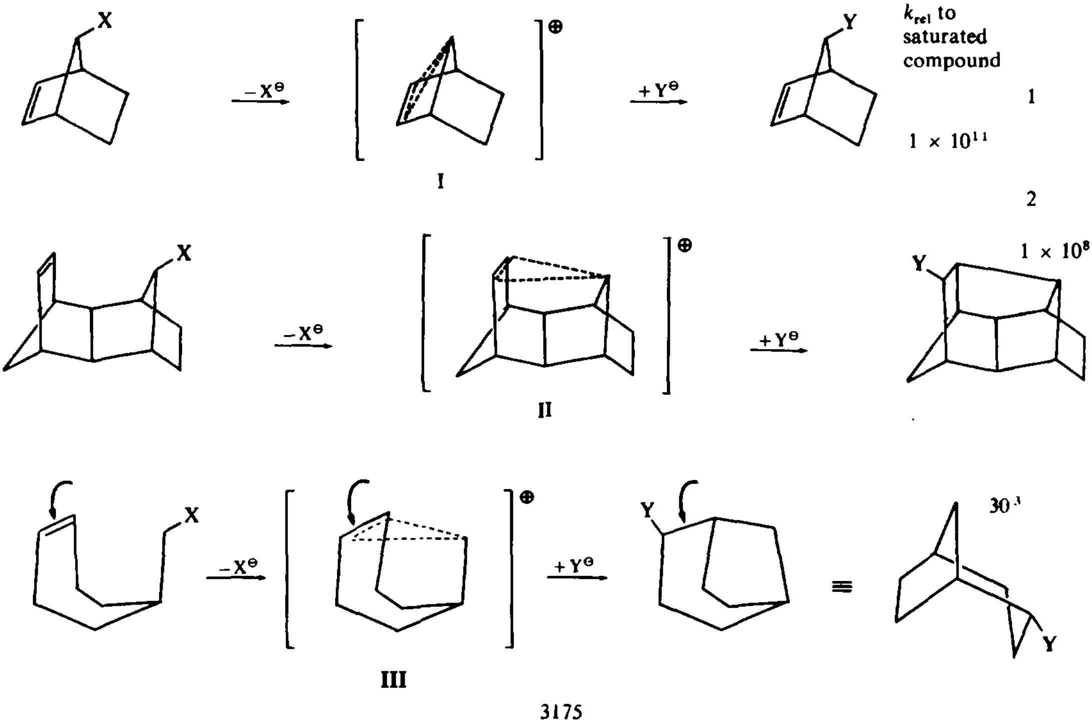
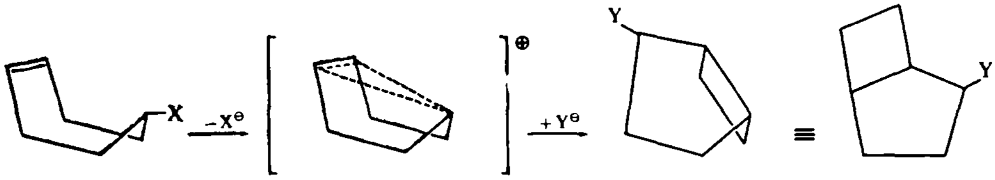
Abstract—The solvolysis technique is suggested as an investigational tool for the possible opposing effects of through-bond and through-space orbital interactions. Existing data indicate, however, that such effects are negligible. A rationalization of the results is presented.

FOR years an important part of research in organic chemistry has involved the study of delocalized carbonium ions and the effect of this delocalization on reaction rates and products. The recognition that a delocalized carbonium ion might occur in a reaction path would greatly affect predictions on the outcome of that reaction. Representative results are available from reactions leading to the 7-norbornenyl cation(I) the octahydrodimethanonaphthyl cation (II) and the 4-cyclohepten-1-methyl cation(III).



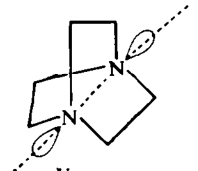
Winstein[4] predicted similar results for the formation of a delocalized 4-cyclohepten-1-yl cation(IV).



IV

One essential difference between this and the other systems is that here an odd number of σ bonds separates the p orbital from the π bond in each direction. This yields two σ bonds which are essentially parallel with the vacant p orbital and the π bond. Do these bonds cause this cation (IV) to be fundamentally different from the others or do they merely form a different insulating structure. If these bonds are involved will the effect be additional stabilization resulting from further delocalization. To help answer these questions some molecular orbital work of Hoffmann and co-workers[5] is discussed.

Hoffmann showed that orbitals within a molecule may, given the appropriate geometry, interact by other than the obvious direct through-space mechanism. That an alternate mechanism does exist is experimentally indicated in the case of triethylenediamine (TED), V.



V

If only a through-space interaction between the nitrogen lone pair orbitals were operative in V there would be a small (the orbitals are separated by 2·5–3·0 Å)[5] splitting of the levels with the symmetric combination, S, at a lower level than the antisymmetric combination, A. In contrast, a large splitting of 2·13 eV (49·12 kcal) is found with the A level below S.[6]

Fig 1 shows the interaction of the nonbonding orbitals with one of the three identical σ bonds.* It is this through-bond interaction which accounts for the unusual results found in TED. Note that the 1-2 and 3-4 bonds are not involved because they would merely add an S and A bonding pair and an S and A antibonding pair of orbitals. The effect of the two S orbitals is essentially to cancel each other out, as is also the case with the two A orbitals.

Fig 1 also shows the effect of superimposing the through-space interaction on the through-bond interaction. Since the center levels must cross as the former effect becomes stronger, it is evident that where the two interactions are of similar magnitude, the allowedness of both occuring concomitantly will depend on the number of electrons in the system. Thus, for a system with four electrons in the four orbitals

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* The signs of the AO's in each of the MO's are predictable since the linear combination of any "n" AO's in a linear configuration should yield *qualitatively* the same result.

(e.g. nitrogen at 1 and a vacant p orbital at 4) it would be desirable for electronic stability to have the *anti* orientation where the through-bond and through-space interactions, by the elimination of the latter, would not cancel one another out as they would in the *syn* conformation.*

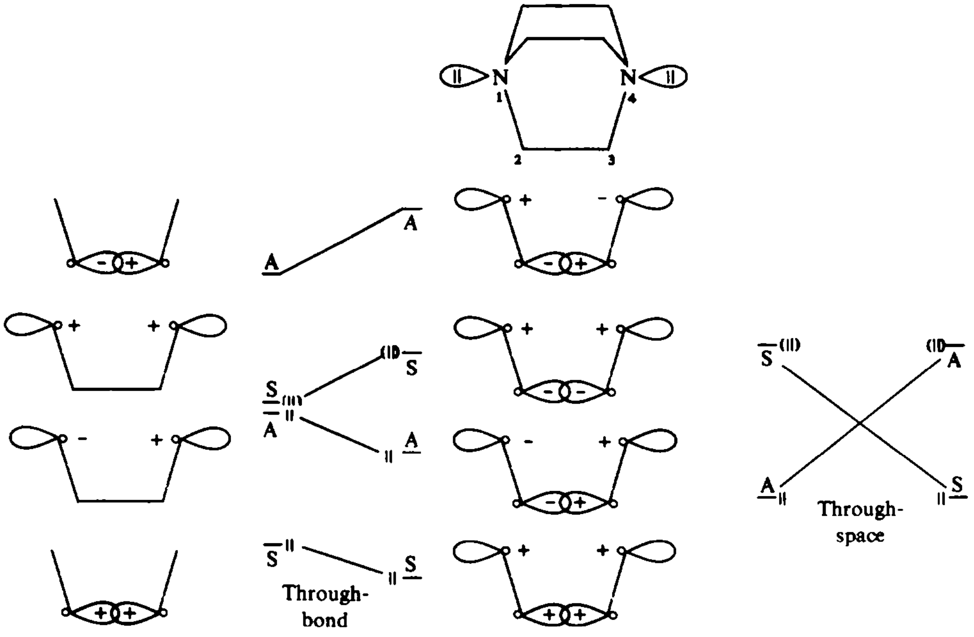
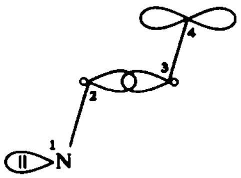
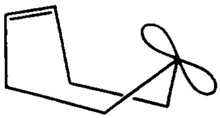


FIG. 1. 1,4 Through-bond and through-space mixing diagram



Since this discussion can be applied to carbonium ion stabilities, the rates of solvolysis of appropriate systems should be capable of probing the effect of a through-bond *vs* through-space interaction. One approach is to expand the basic four orbital system to the 4-cyclohepten-1-yl cation(VI).



VI

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* Inspection of Fig 1 indicates that the opposition of the through-bond *vs* through-space interaction for the four electron system is closely related to the disallowed [2 + 2] cycloaddition.

Fig 2 will be used to discuss the applicability of this system to the through-bond *vs* through-space argument. First the interaction of the 1-2 and 5-6 σ bonds with the π bond is shown. This is followed by the interaction of the p orbital with the closest lying orbital of the same symmetry. The result of this through-bond interaction of the p orbital is to place the bonding combination of the *through-space* interaction, $-7-3-4$, at higher energy than the antibonding combination, $+7-3-4$. Thus, the through-bond *vs* through-space opposition is in effect and the *syn* cation should be less stable relative to the *syn* hydrocarbon than the *anti* cation relative to the *anti* hydrocarbon.

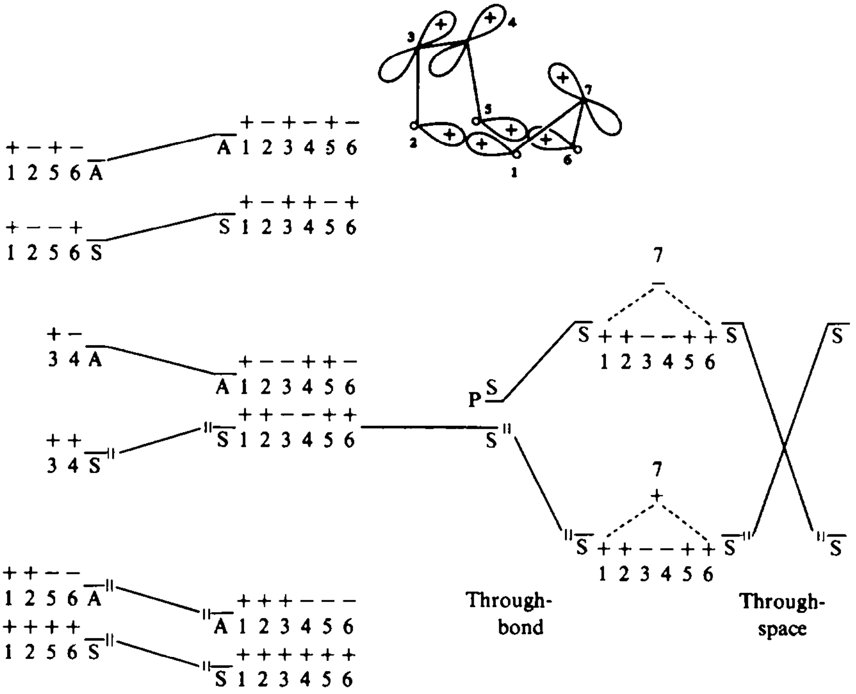

Fig. 2. 4-Cyclohepten-1-yl orbital diagram

These arguments provide the framework for a reconsideration of the prediction concerning the 4-cyclohepten-1-yl solvolysis and also raise doubts as to the stability of the delocalized cation(IV).

The brosylate of this system has been solvolyzed[7] and the predicted bicyclic products do *not* appear. Table 1 shows these results along with those of similar compounds. The lack of bicyclic products in A and the fact that *no* bicyclic products in B, C or D arise from 1,4 closure make it tempting to suggest that the through-bond and through-space interactions might indeed cancel each other out.* In B, C and D

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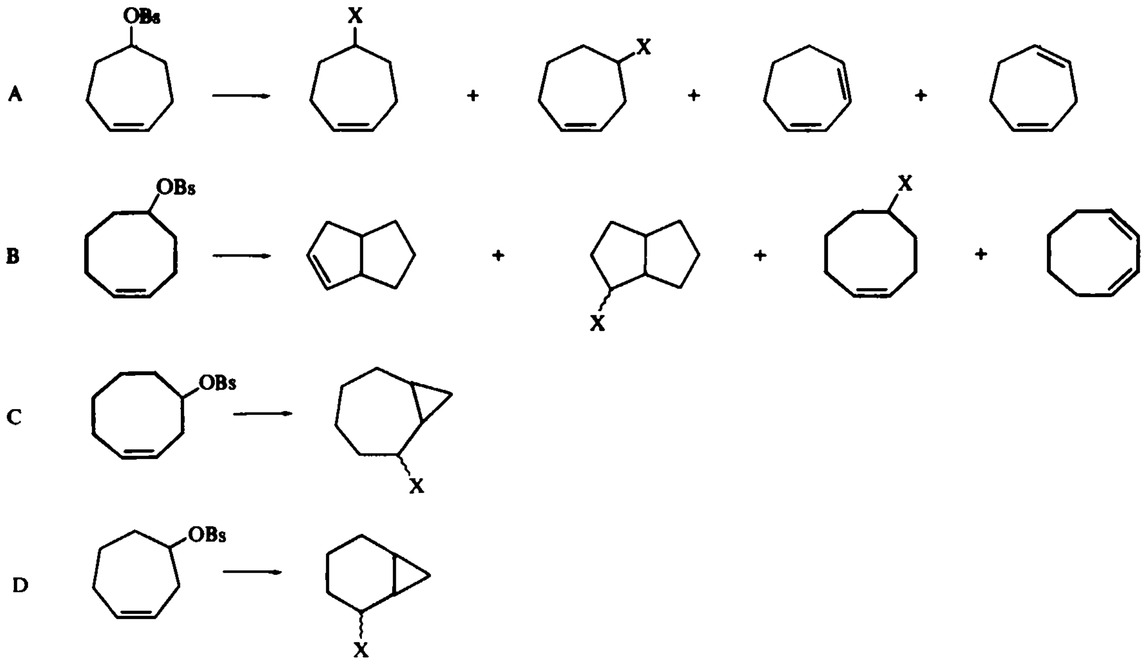
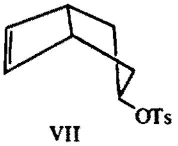
* Addition of formic acid to 1,5-cyclooctadiene results in *trans*-2-vinylcyclohexanol as a minor component.[8] Its formation appears to involve a 1,4 closure.

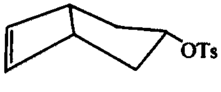
TABLE 1. ACETOLYSIS OF 4-CYCLOHEPTEN-1-YL BROSYLATE AND RELATED SYSTEMS

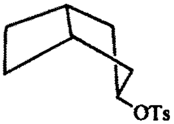


the homoallylic delocalization other than 1,4 could then be more important in determining ion stability and product direction.

Some relevant rate data are also available for the acetolysis of *exo*-(VII) and *endo*-(VIII)bicyclo[3.2.0]hept-6-en-3-yl tosylates[9] and their saturated analogues


VII


VIII


VII S


VIII S

VII S and VIII S, respectively. The interpretation of the results is based upon the assumption that the *exo* isomer would display the effects of the through-space interaction to a greater extent than would the *endo* isomer. Since the through-bond interaction should be approximately the same in both isomers the data should indicate whether or not the addition of the through-space interaction gives the usual effect of enhanced rates.

Table 2 shows that the *endo* isomer solvolyzes faster than the *exo* isomer by a factor of two. But a more important comparison is that of the *exo* ratio (i.e. the ratio of rates of the saturated to the unsaturated *exo* isomers) to the *endo* ratio. They are 7.83 and 5.83[*] respectively. Though the latter ratio is smaller, which is consistent with simultaneous through-bond and through-space interactions being destabilizing relative to either interaction alone, there are other factors to consider. If these delocalizing interactions were actually occurring to any great extent, retention of configuration would be expected. Table 2 shows that almost complete inversion is observed in both isomers of the saturated and unsaturated compounds. Actually these data are in agreement with the interpretation that the reaction is essentially bimolecular with the π bond only affecting an inductive destabilization of the transition state. Backside attack and relief of transannular interactions could explain the greater *endo* rates.[9] And of course, the *endo* and *exo* ratios are essentially the same.

A very similar situation is found in the acetolysis of *exo* (IX)- and *endo*(X)-bicyclo [3.2.1]oct-6-en-3-yl tosylates.[10] These reactions lead to a complex mixture of products. Among them, however, are no tricyclic compounds derived from the through-space delocalized cation, XI.

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[*] The *endo* ratio might actually be corrected to a smaller number because of the extra steric acceleration that will occur in the saturated *endo* compound:

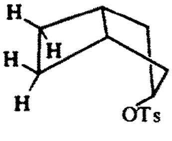
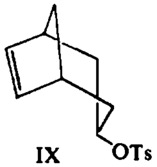
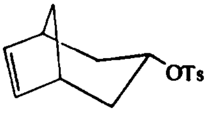


TABLE 2. ACETOLYSIS OF *exo*- AND *endo*-BICYCLO[3.2.0]HEPT-6-EN-3-YL TOSYLATES AND THEIR SATURATED ANALOGUES

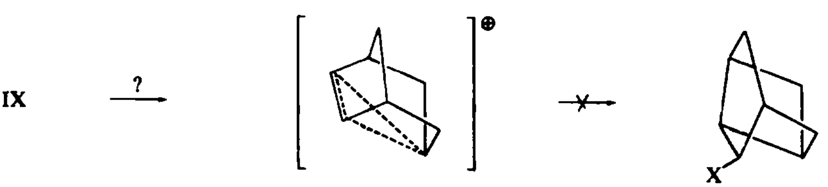
Compound	Rel. Rate	Percent Comp. *Endo*	Percent Comp. *Exo*
VII	0·023	83	17
VIII	0·048	9	91
VII S	0·18	94	6
VIII S	0·28	7	93



IX



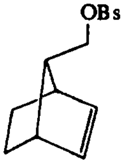
X



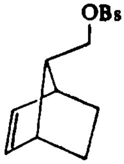
XI

Though arguments like those used for the 4-cyclohepten-1-yl system could be used here, the rate and product data are essentially the same as for the bicyclo[3.2.0] hept-6-en-3-yl system (VII and VIII).

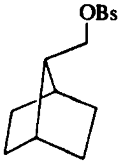
A final system is considered. It is the 2-norbornenyl-*syn* (XII)- and *anti*(XIII)-7-carbinyl[*] brosylate series.[11, 12] This is a better system to study than those previously discussed in that the molecules are more rigid. Again, as can be seen in Table 3, there



XII



XIII



XIII S

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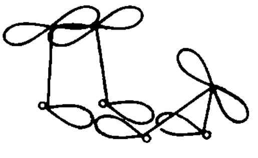
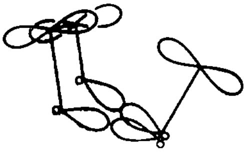
[*] In terms of the through-bond *vs* through-space problem the 3-cyclopenten-1-carbinyl unit is very much the same as the 4-cyclohepten-1-yl structure:





is no substantial effect on the rate by the position of the π bond.* There is also very little difference in rates relative to the saturated compound, XIII S.

TABLE 3. ACETOLYSIS OF 2-NORBORNENYL-*syn*- AND *anti*-7-CARBINYL BROSYLATES AND THEIR SATURATED ANALOGUE[11, 12]

Compound	$k \times 10^5$/sec.
XII	1·50
XIII	1·08
XIII S	2·64

DISCUSSION

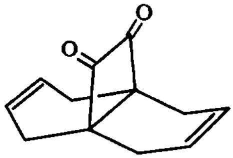
The conclusion which must be reached is that in the systems described both the through-bond and through-space interactions are not operating to any appreciable extent.

The lack of a through-space effect is apparently due to an overly large distance between the p orbitals in the 1,4 systems.[10–12] The extra carbon in the 4-cyclohepten-1-methyl system(1,5) and the loss of a carbon in the 7-norbornenyl system(1,3) allow the orbitals to have sufficient overlap. This argument could well explain the products listed in Table 1.

The failure of the through-bond interaction to appreciably affect the energy levels is apparently due to the energy difference between the unoccupied p orbital and the σ bonds. That is, as the difference between the energies of two orbitals increases, the smaller will be the changes in these energies due to their mixing. If this is the case, systems in which the energy levels are closer together should exhibit more substantial through-bond interactions.

TED accomplishes this with the use of nitrogen lone pairs.[5] These orbitals will be closer in energy to the σ bonds than would carbon p orbitals. This closer proximity of levels evidently contributes to the large splitting found in TED.

An operative through-bond interaction seems necessary to account for the bathochromic shift observed for the n → π* transition of tricyclo[4.4.2.$0^{1,6}$]dodeca-3,8-diene-11,12-dione (XIV) relative to its tetrahydro derivative.[13] Calculations which allowed for only a through-space interaction of the diene π system with the dione π system predict the opposite result. Inclusion of the σ system, however, yields results



XIV

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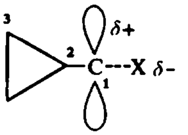
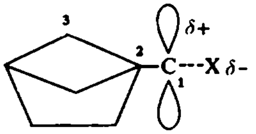
* Products resulting from 1,4 ring closure are observed from the 7-methyl derivative of XII, however, there is no significant rate enhancement relative to the saturated compound.[11]

which are in qualitative agreement with the observed spectral shift. Thus, in this molecule the through-bond interaction of the diene and the dione π systems seem to be dominating. Apparently, the energies of both π systems are close enough to that of the σ system to allow for effective coupling.

An alternative way of increasing the p-sigma component of the through-bond interaction would be to increase the energy of the σ bond. This could be done by increasing the strain involved in the bond. Thus it has been shown[14] that increasingly strained σ bonds are more capable of donating electrons to a carbonium ion center. This manifests itself as increased rates of solvolysis with increasing strain in the 2-3 σ bond. The resulting interaction of the σ bond with the p orbital is thus great enough to overcome the increased inductive withdrawal effect which would tend to decrease the solvolysis rates.



k_{rel} $6{\cdot}25 \times 10^3$



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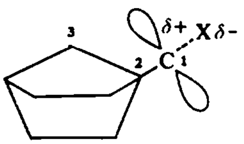

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Summary. The opposition of certain through-bond and through-space interactions led to the exciting possibility that, in comparable systems, a direct interaction of reaction site and unsaturation might actually be rate retarding while an indirect interaction could be rate enhancing. The obvious basic framework seemed to be the 4-cyclohepten-1-yl system: its 1,4 relationship providing the necessary odd number of σ bonds linking the π bond and the vacant p orbital in each path, and appearing to maximize both through-bond and through-space overlap. This system, however, is accompanied by a small 1,4 overlap. Furthermore, the energy of a p orbital (and even the hybridized precursor) appears to be too far above the level of a σ bond in energy to allow meaningful mixing. Apparently the through-bond *vs* through-space phenomenon will successfully avoid testing by the conventional solvolysis method.*

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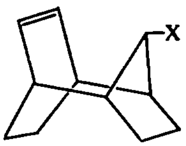
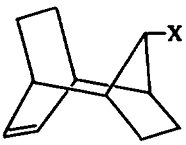
* The systems discussed above lack the structural rigidity that seems to be necessary for optimization of both through-bond and through-space interactions. The following systems, and their saturated analogue, would seem to be more appropriate for study.





This research, however, is *not* being pursued in this laboratory.

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