

92. Orbital Theory of Heterolytic Fragmentation and Remote Effects on Nitrogen Inversion Equilibria

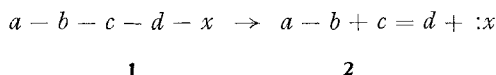
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Summary. From a molecular orbital study of model systems we derive the electronic requirements for the *Grob* fragmentation. The necessary condition for an allowed fragmentation in an X-C₁-C₂-C₃-N system, or the amino cation ⁺C₁-C₂-C₃-N is the level ordering **A** below **S**. This in turn is set by maximal through-bond coupling of the empty cation orbital and the nitrogen lone pair. The conformational dependence of through-bond coupling is exactly that derived by *Grob*, namely parallel orientation of the cation orbital (or the C-X bond), the C₂-C₃-σ-bond, and the N-lone-pair. When the C₁-C₂-C₃ and C₂-C₃-N angles are small, the through-space interaction dominates, reversing the level ordering to **S** below **A**, and consequently makes the fragmentation forbidden even though the conformational requirements for it are met. Ring closure becomes allowed. Some examples exploiting this result are presented, as well as procedures for enhancing through-bond coupling and thus fragmentation. The through-bond-effect has also kinetic consequences, allowing the definition of a new type of remote neighbouring group participation operative through bonds and not by direct overlap. The position of equilibria in nitrogen inversion processes should also be influenced by remote substituents which are π-acceptors or donors.

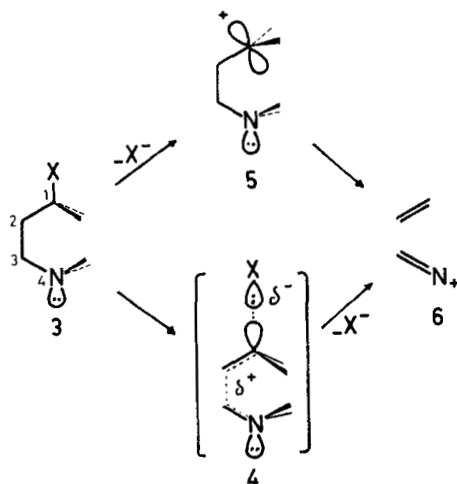
Heterolytic fragmentation, **1** → **2**, is a widely spread reaction in organic chemistry which in recent years has been extensively studied by *Grob* and coworkers [1] [2].



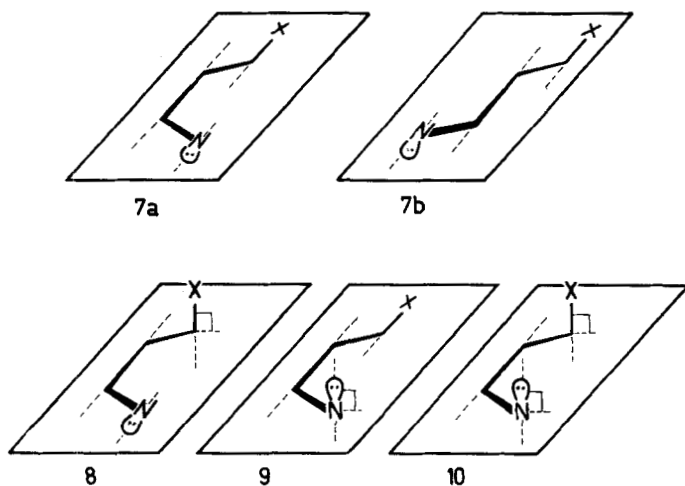
Fragmentations of this type, e.g. of γ-haloamines **3** to olefins and immonium salts **6** can in principle take place either in a concerted manner or via a two-step mechanism. In the concerted fragmentation both the C₁-X bond and the C₂-C₃ bond are broken synchronously utilizing the transition state **4**. In the two-step reaction the intermediate cation **5** is formed and subsequently undergoes fragmentation in competition with other typical cationic reactions such as interception by nucleophiles, proton elimination and ring closure¹⁾.

Grob concluded, on both theoretical and experimental grounds, that the concerted fragmentation should only take place if the orbitals involved obey strict conformational requirements: the lone pair lobe at the nitrogen, the σ-bond C₂-C₃ and the σ-bond C₁-X must be approximately parallel to each other. This means that conformation **7a** and all conformations derived from **7a** by rotation around C₂-C₃, like **7b**, are capable of undergoing a concerted fragmentation. In contrast conformations such as **8**, **9** and **10**, derived from **7** by rotation around C₁-C₂ and/or C₃-N by approxi-

¹⁾ There is a rare third mechanism also, where first a positive unit leaves the parent system **3**. Compare footnote 20 in [1f].



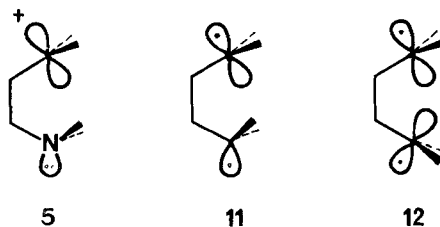
mately 90° , should not undergo the concerted fragmentation, but rather form the cation **5**, which might then fragment in a subsequent step.



In this paper these stereoelectronic conclusions, elegantly confirmed by numerous examples [1], are rationalized and extended within the framework of molecular orbital theory²⁾.

We begin with an analysis of the fragmentation of cation **5**, returning later to the concerted reaction via transition state **4**. As a model for **5** (see below) we select the homopolar carbon diradical **11**, which in turn is related by a depyramidalization to the symmetrical diradical **12**. The last-mentioned species has been the subject of an

²⁾ For a stimulating discussion of spectroscopic interactions and their relationship to the *Grob* fragmentation see [3].



extensive study by our group [4], thus simplifying our examination of the related molecules.

Fig. 1 shows extended *Hückel* calculations [5] for the model species **11**³⁾. The $C_1-C_2-C_3$ and $C_2-C_3-C_4$ angles α are bent equally. The dihedral angle defined by bonds

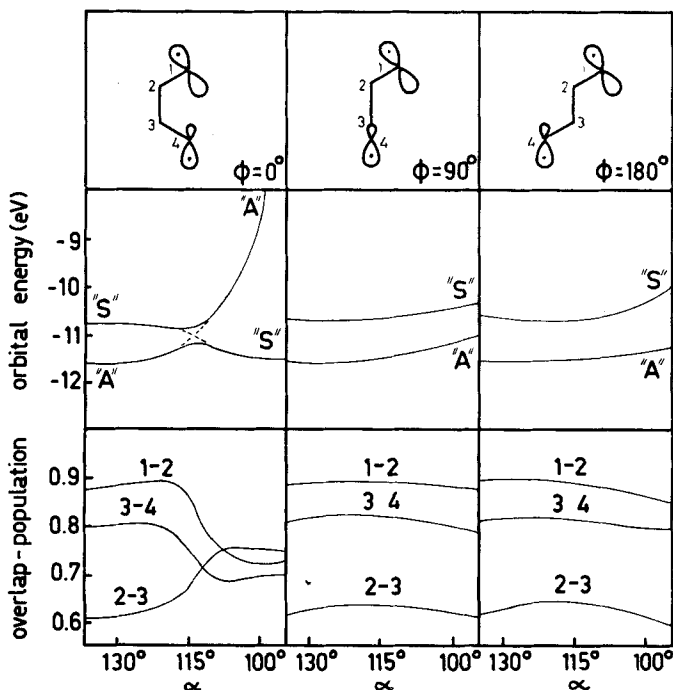


Fig. 1. HOMO and LUMO ordering (top) and overlap populations (bottom) in the diradical **11**. The variation with $C_1-C_2-C_3$ angle α is shown for three values of ϕ , the dihedral angle defined by bonds C_1-C_2 and C_3-C_4

C_1-C_2 and C_3-C_4 is denoted by ϕ ($\phi = 0^\circ$ *cis*, $\phi = 180^\circ$ *trans*). The figure shows *Mulliken* overlap populations as well as energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. These computed quantities are illustrated as a function of α for three values of $\phi = 0, 90$ and 180° .

³⁾ The model geometry has all C-C = 1.54 Å, all C-H = 1.10 Å, CH₂ groups at C₁ trigonal, at C₄ tetrahedral, and at C₂ and C₃ in the plane bisecting the respective CCC angle and with a tetrahedral HCH angle.

The salient features of the calculation are the following:

1) In the case of *cisoid* geometry, $\phi = 0^\circ$, one notes the expected and well understood [4] [6] crossing of HOMO and LUMO. Except in this case the C_1 and C_4 ends of the diradical are nonequivalent. The symmetry operation which interchanges these atoms, and which in **12** allows a crossing of HOMO and LUMO, is no longer present in **11**. Nevertheless there is an approximate interchange symmetry, a pseudosymmetry which allows us to classify levels as approximately symmetric, «**S**» or approximately antisymmetric «**A**». The real level crossing of **S** and **A** in **12** obviously becomes an avoided crossing of «**S**» and «**A**» in **11**. At small α , i.e. C_1 close to C_4 , we have the level ordering «**S**» below «**A**», whereas at larger α this order is reversed, and «**A**» moves below «**S**». The reversal, as explained elsewhere [4] [6], stems from a large through-bond coupling superimposed on a diminishing through-space interaction.

2) In the case of *cisoid* geometry, the level crossing as a function of α is accompanied by a striking overlap population (bond order) change. For small α all bonds are of approximately equal strength. But at large α , where «**A**» is below «**S**», the 1–2 and 3–4 bonds are strengthened and the 2–3 bond weakened drastically. The analysis of this phenomenon has been given elsewhere [4], and we will return shortly to it.

3) In the $\phi = 90^\circ$ and *trans*, $\phi = 180^\circ$ forms «**A**» is below «**S**» at all α . This is as expected – the through-bond interaction dominates and C_1 and C_4 are too far from each other to reverse this trend by direct overlap. The bond order differentiation noted for $\phi = 0^\circ$ and large α persists for all α in these two geometries.

4) Qualitatively all of the above features of Fig. 1, which pertain to the carbon diradical **11**, are retained in calculations on the amino-cation **5**. In fact the conclusions may hold more strongly for the amino-cation because the «**S**»-«**A**» splitting is greater than in the diradical. This follows from a more detailed consideration of the states involved. For instance we have until now described **11** by the pure configurations («**S**»)² or («**A**»)². The true wave function will be a mixture of both configurations $c_1(\text{«S»})^2 + c_2(\text{«A»})^2$. The smaller the gap between «**S**» and «**A**», the more equal the configurational mixing in the ground state and the less pronounced the bond alternation and specificity of concerted reactions will be [7] [8].

5) The conformational requirements for optimal through-bond coupling over three σ -bonds, the achievement of the pattern «**A**» below «**S**», are precisely those formulated by *Grob* [1], namely conformations **7a** or **7b** or any geometry related to these by twisting around the 2–3 bond [6].

We now come to the crucial point of our argument. From a molecular orbital point of view, *the necessary condition for a symmetry-allowed fragmentation is the level ordering «A» below «S»* in the diradical, or in the corresponding amino cation **5**. This is demonstrated most easily by the level correlation diagrams for ring-closure and fragmentation of **12**. These are drawn in Fig. 2 for the two alternate level orderings of **12**.

Another way to realize the importance of the level ordering is the following. Recall how the reversed order **A** below **S** was created [4] [6]: One starts out, as shown in Fig. 3 at the very left, with the σ - and σ^* -levels of the bond C_2 - C_3 , as well as with the two combinations **S** and **A** of the two orbitals at C_1 and C_4 . The latter are – as a

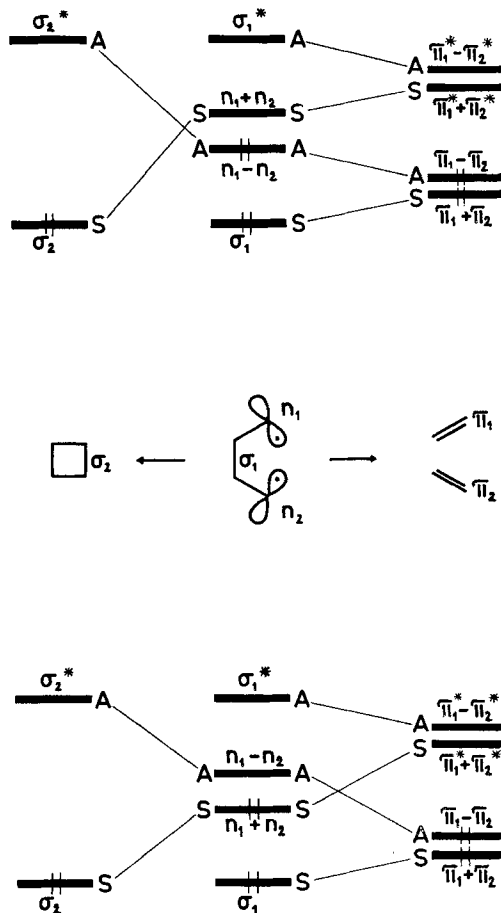


Fig. 2. Level correlation diagrams for fragmentation (right) and ring closure (left) of the diradical **12**. At top the level ordering **A** below **S** prevails, while at bottom the order is reversed

consequence of their large separation – approximately equal in energy. The symmetric combination **S** mixes with the symmetric orbital σ , creating the two new combinations $\sigma + \lambda\mathbf{S}$ and $\mathbf{S} - \lambda\sigma$, whereas **A** forms with σ^* the two combinations $\mathbf{A} + \lambda\sigma^*$ and $\sigma^* - \lambda\mathbf{A}$. From these four combinations it follows that by a simple stretching of the bond $\text{C}_2\text{-C}_3$, while maintaining the nodal properties of the orbitals, the diradical is continuously and smoothly transformed into the fragmentation product.

Fig. 3 illustrates an additional fact: There is a very interesting charge-transfer involved in the mixing of the orbitals described above. If $\mathbf{S} - \lambda\sigma$ is occupied, then the interaction between **S** and σ does not create a net charge-transfer of electrons. But in our case, where the $\mathbf{S} - \lambda\sigma$ -combination is empty, electron-transfer from the occupied σ -level into the unoccupied **S**-combination results. Similarly we obtain an electron-transfer from the occupied **A**-combination into the σ^* -orbital. Both electron transfers of course diminish the bond-strength of $\text{C}_2\text{-C}_3$ and increase the bond-strength of

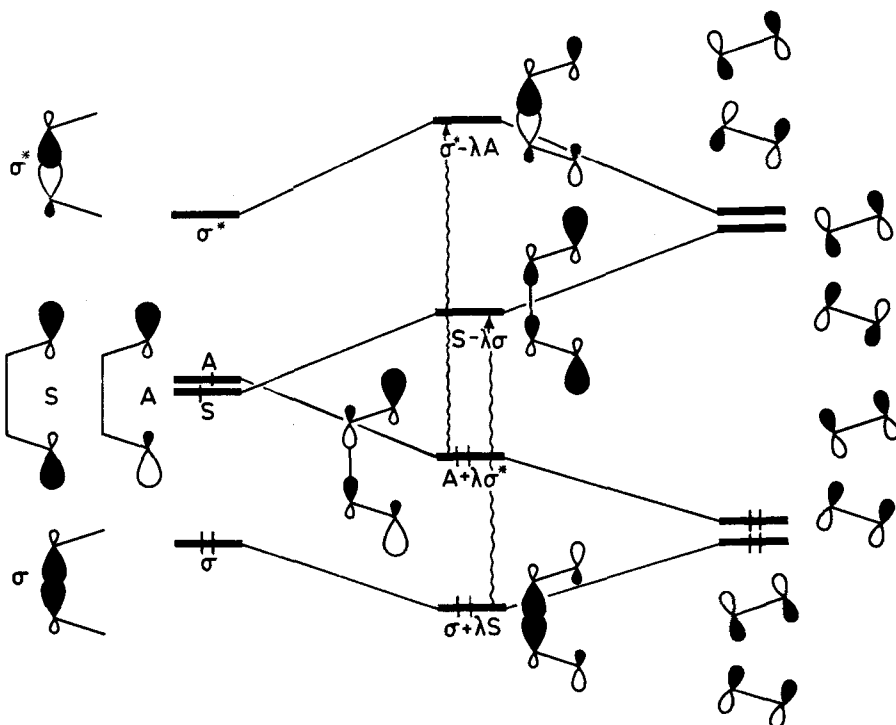


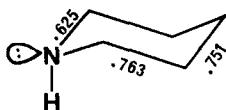
Fig. 3. Interaction diagram showing how the ordering **A** below **S** (center) is derived from the mixing of the diradical **S** and **A** levels with the C_2-C_3 σ and σ^* levels (left).

At right the fragmentation to two ethylenes is followed

C_1-C_2 and C_3-C_4 . This is precisely what may be observed in Fig. 1 for the *cisoid* form. Near the level-crossing we have the discontinuity of the bond orders just mentioned: transforming the two electrons from the **S**-level into the **A**-level strongly decreases the order of the C_2-C_3 bond and increases the order of the 1-2 and 3-4 bonds. Thus the diradical already shows the bond alternation which culminates in fragmentation, if, and only if, **A** is below **S**.

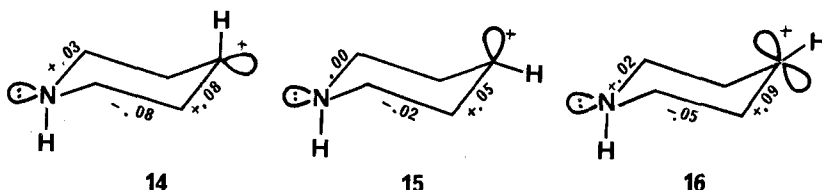
We summarize our conclusion at this point: In order to undergo a heterolytic fragmentation, a molecule not only needs to adopt a conformation which allows optimal overlap of the involved orbitals, as in conformations **7a** or **7b**. It also needs to meet an additional electronic requirement: The **A**-level must be below the **S**-level. Only then is the electron-transfer achieved which results in the strong bond-alternation described above and only then is the fragmentation symmetry-allowed.

Let us now turn from a model to a real molecule. **13** is a chair-form of piperidine, with an equatorial lone-pair. The calculated overlap populations are also indicated.

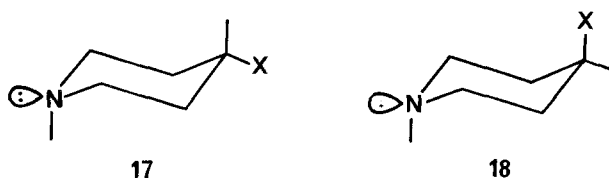


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We next calculate the electronic distributions in three cations related to **13**: Two pyramidal cations **14** and **15** obtained by removal of an equatorial and axial hydride ion from the 4 position of piperidine **13**, and a trigonal cation **16**. The numbers next to the bonds are the *differences* between their respective overlap populations and those in the parent compound **13**. Negative values mean that the bond in the cation is weakened, positive values indicate that it is strengthened with respect to the parent compound.

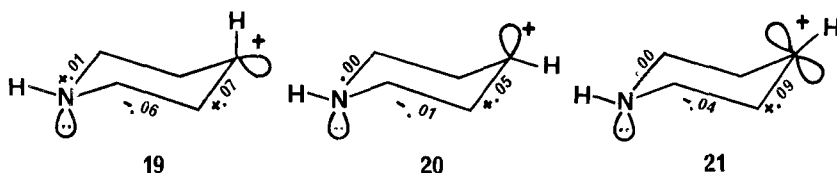


It is immediately noted that the maximum alternation of bond order occurs in the optimally aligned cation **14**. The sign of the alternation, i.e. weakened 2-3, strengthened 1-2 and 3-4 bonding is, of course, in accord with our expectation that the substituted species **17**, for which **14** is a model, should fragment easily.



In **15**, a model for the axial compound **18**, there is less bond alternation than in **14**. Presumably, whatever alternation is present is due to the partial alignment of the 2-3 bond with the empty orbital of the cationic center at position 4 (dihedral angle 60°). We would not expect **18** to fragment by a concerted mechanism but to generate instead the cation **16**, which once again possesses a favorable orbital alignment for fragmentation⁴).

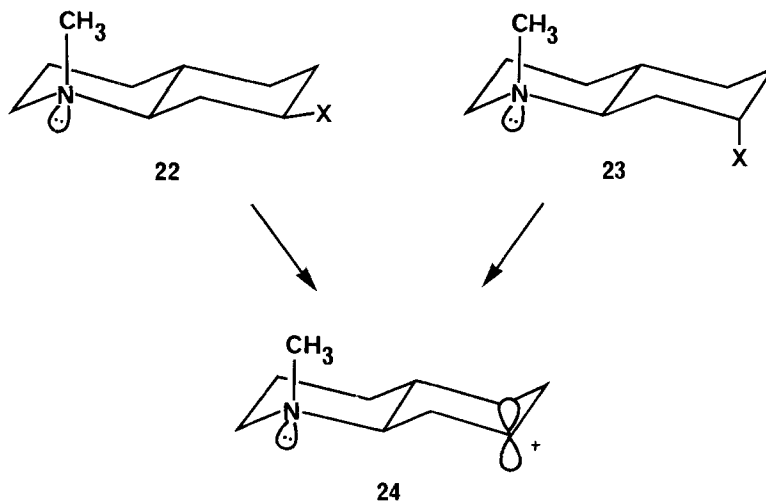
If we place the N-lone-pair in an axial position we generate cations **19**, **20** and **21**. Of these **20** and **21** show some bond alternation in accord with the favorable alignment of the empty orbital at the carbenium ion center with the central σ -bond. In no case,



⁴) It is conceivable that the optimal through-bond coupling might make itself felt in the very geometry of 4-cation of piperidine, in that the favored conformation of **16** might not be perfectly trigonal but slightly pyramidalized, toward **14**. This would represent a compromise between the through-bond effect and the normal tendency of carbenium ions to favor a trigonal geometry.

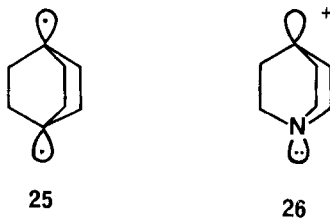
however, does the bond alternation approach that in the optimally aligned cations **14** and **16**. On the basis of these calculations, a given cation will only fragment if a threshold value of alternation of the intervening three bond orders is achieved.

An interesting experiment by *Grob* and coworkers [9] is in accord with our conclusions. These authors demonstrated that neither one of the stereoisomeric compounds **22** and **23**, nor the common cation **24** derived from them, fragment, since in none of these compounds is the N-lone-pair parallel with respect to the central σ bond. This condition also applies if the N-methyl group and the lone-pair are interchanged by nitrogen inversion.



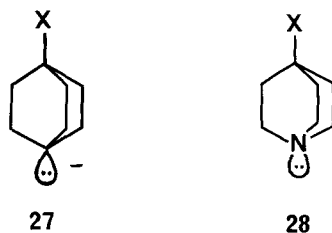
We conclude in agreement with *Grob* [1] that systems which do not undergo a concerted fragmentation because their C-X bond is not properly aligned may often undergo fragmentation via the intermediate cation; this does not, however, apply to systems in which the lone electron-pair at the nitrogen atom is improperly aligned, since they continue to violate the *Grob* rule.

We next turn our attention to those conclusions concerning the fragmentation which go beyond the simple conformational argument. It will be recalled that the electronic prerequisite for fragmentation is the level ordering **A** below **S**. There are conformations for the cation **5** or the diradical **11** where this is not obeyed, namely for the cisoid geometry with angles $\alpha < 110^\circ$ (see Fig. 1). In this region the through-space interaction dominates and ring closure rather than fragmentation is to be expected. If several through-bond coupling paths are available, the **S-A** crossing

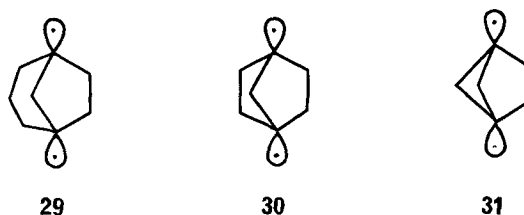


moves to still smaller values of α . In the diradical **25** [10] it is at 103° , in the amino cation **26** the angle where crossing is avoided is approximately 100° .

In the case of normal bond angles (α approx. 110°), as is present in amine **28** [1], fragmentation occurs⁵⁾ as expected.

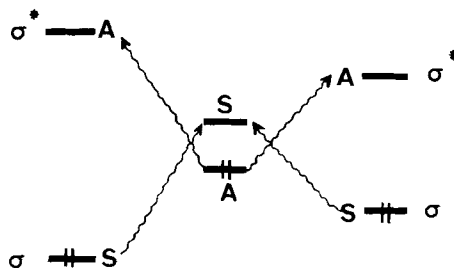


Further spatial constraints must be imposed in order to create compounds which do not fragment although they obey the conformational requirements. The diradicals **29**, **30** and **31**, as we have recently shown [10] do have at all reasonable C_1-C_4 distances **S** below **A**. In agreement with this fact **29** and probably **30**, generated from



suitable precursors, do not fragment but undergo ring closure to the corresponding highly strained propellane [10] [11] [13]⁶⁾.

Quantum mechanical analysis also indicates how to improve prospects of fragmentation. The pattern **A** below **S** with resultant bond alternation derives from an interaction of the 2–3 σ bond with the **S** diradical combination and of the corresponding σ^* with **A**, as indicated at the left of the following scheme. The strength of that

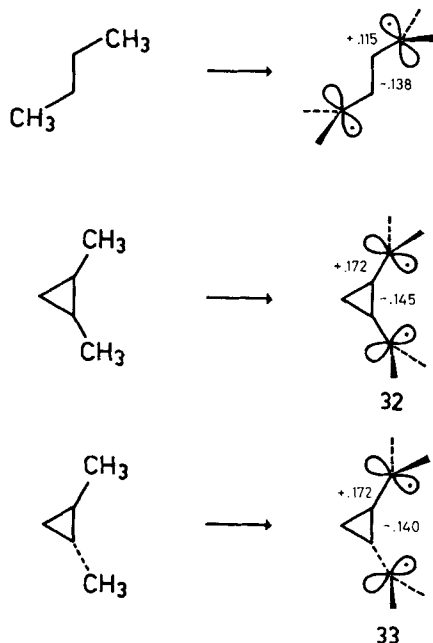


interaction, as estimated in a perturbation theoretic analysis [14], will increase with diminishing $S-\sigma$ and $A-\sigma^*$ energy gap, as shown at the right.

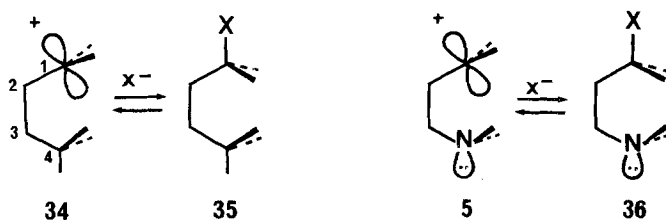
⁵⁾ Another system with a fixed cisoid conformation which fragments and for which a similar argument applies may be found in [12].

⁶⁾ In the case of **30** the evidence for the intermediate formation of the propellane is indirect [10] [11] [13].

The reduction of the σ - σ^* gap is most easily achieved by incorporating the relevant σ -bond into a strained system, e.g. a three or four membered ring. The σ - and σ^* -levels there assume the role of high-lying occupied and low-lying unoccupied Walsh-type orbitals [15]. Shown below is the change in overlap population in *cis*- and *trans*-1,2-dimethylenecyclopropane diradicals **32** and **33**, relative to their saturated counterparts, *cis*- and *trans*-1,2-dimethylcyclopropane. The tetramethylene diradical is included for a comparison.



We now return to a problem to which we referred at the beginning of the paper, namely the formation of the amino cation **5** and the alternative concerted pathway of fragmentation. The formation of the amino cation is most easily analyzed by considering the reverse process⁷⁾, the addition of a nucleophile X^- to the cation **34**,



as contrasted to its addition to the amino cation **5**. At the left of Fig. 4 we see the transformation of the nucleophile lone-pair, into the C-X σ -bond, by mixing with the empty orbital at C_1 , while the cation orbital becomes the corresponding σ^* -level.

⁷⁾ The reasoning here is analogous to that pursued in a recent study of phenyl cation stabilization [16].

At the right of Fig. 4 we see the interaction of the nucleophile with the through-bond coupled amino cation. The important feature here is the transformation of the A-orbital into a «pure» nitrogen lone pair, with a consequent energy loss which we can call ΔE . Since the σ -bond formation is the same in both cases it follows that in the dissociation of **36** there is a net energy gain due to the presence of the nitrogen.

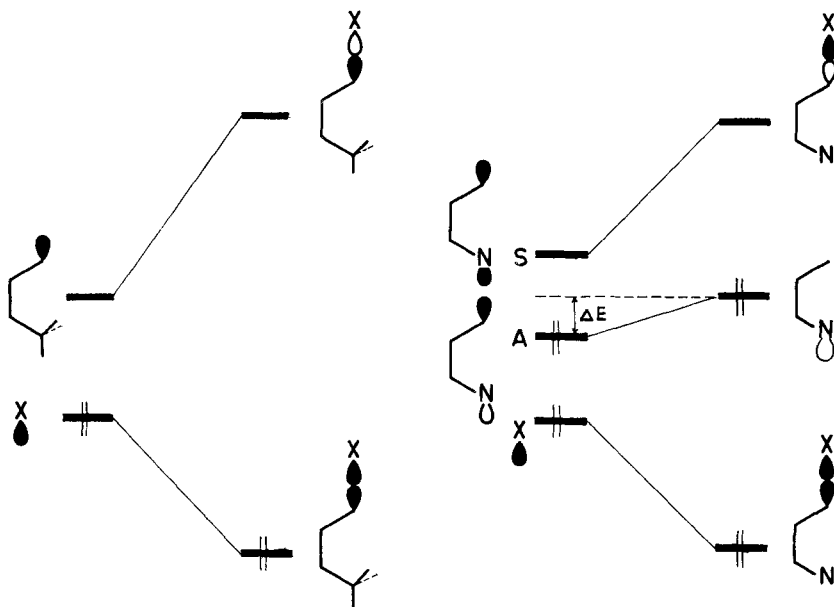
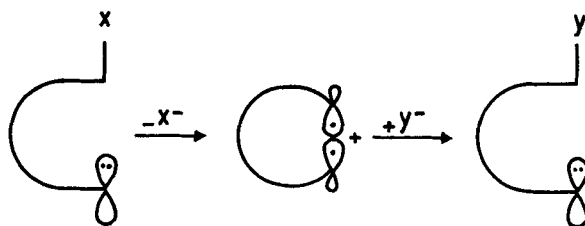


Fig. 4. Interaction diagram for a nucleophile X^- adding to cation **34** (left) and amino cation **5** (right).
See text for discussion

The effect should be of kinetic as well as thermodynamic significance. The lone-pair electrons in the 4-position accelerate the dissociation of the C-X bond. This is the acceleration referred to by *Grob* as the frangomeric effect [1f].

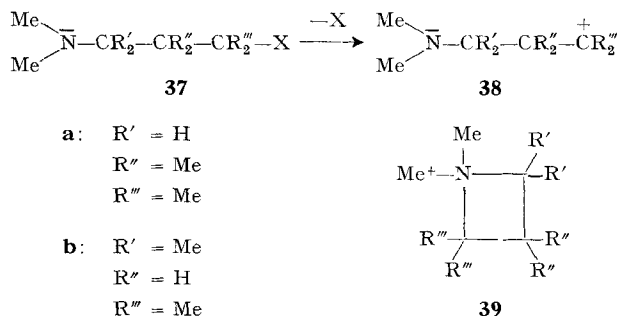
It is of course a well established fact that lone-pair electrons of a neighbouring nucleophilic substituent are able to accelerate the departure of a nucleophile X^- . The phenomenon is usually called neighbouring group participation [17] and is rationalized implicitly by direct overlap of the orbital of the lone-pair and that of the breaking C-X bond, resulting in effective ring closure:



To this phenomenon we can now add a novel type of participation, specific to electron supplying substituents which are three σ -bonds removed from the leaving group, and which operate through bonds rather than through space.

There is a related experimental result in the literature which is difficult to understand on classical grounds, but is easily rationalized on the basis of this postulate of through-bond neighbour-group participation.

Compounds **37 a** and **37 b** react unexpectedly rapid to form an intermediate cation **38**, which then undergoes fragmentation and elimination but not ring closure [18]. Obvious explanations for the observed accelerated reaction, e.g. classical neighbouring group participation via the intermediate ring **39** could be excluded by *Grob*



and coworkers [1f]. In order to explain the increased reaction speed, *Grob* suggested some years ago that the dissociation might be promoted by the lone electron pair of the nitrogen atom without formation of a real σ -bond between cationic center and nitrogen, but rather by the formation of an internally solvated carbonium ion for which structure **40** was suggested.

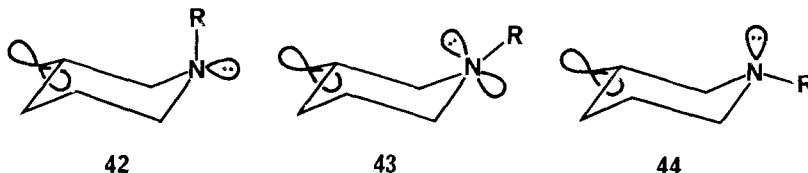


In our opinion this stabilization due to internal solvation without bond formation can be interpreted as through-bond coupling. Though little is gained by drawing dashed lines, a notation less likely to be confused with direct participation might be **41**.

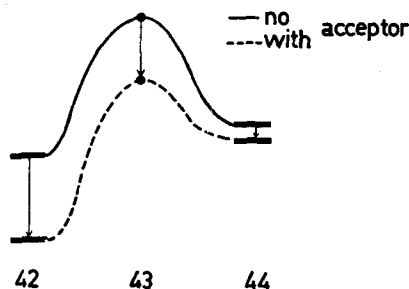
Interaction diagrams similar to those of Fig. 4 and Ref. [16] can be drawn for the concerted fragmentation **3** \rightarrow **4** \rightarrow **6** or the concerted ring closure. The results may be summarized as follows: The conformational requirements and the orbital rules for the concerted process are the same as those for the non-concerted process. If the cation **5**, derived from **3** by simple removal of X^- to infinity, has the proper conformation and level ordering (**A** below **S**) required for fragmentation the concerted fragmentation *via* transition state **4** is allowed as well. If the cation **5** is not properly disposed for fragmentation, or if it has the incorrect level ordering, then the related concerted fragmentation is forbidden. Since the conformational and electronic requirements for concerted and non-concerted fragmentation are the same we think that in the absence of special circumstances the concerted path will be followed and indeed accelerated.

Nitrogen Inversion Equilibria

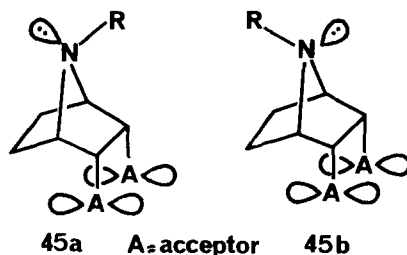
Just as lone pairs can influence cationic centers far removed, so cations may influence the behaviour of lone-pairs. To make the problem a realistic one we must replace the carbenium center by an electronically equivalent substituent i.e. a good π -electron acceptor such as $-\text{CN}$, $-\text{COOR}$, $-\text{NO}_2$, $-\text{NO}$. Consider for instance a 3-substituted piperidine in the two pyramidal N conformations **42** and **44** as well as the transition state for nitrogen inversion.



While it is difficult to make a clear decision as regards the extent of through-bond coupling in **42** vs **43** (compare the bond alternation in **14** and **16**) it is clear that there is little such coupling in **44**. Thus we would expect the nitrogen inversion potential energy curve to be modified as shown below from that in a sterically similar piperidine lacking the acceptor function⁸⁾. Axial 3-substitution by an acceptor should have the



same effect, provided that the acceptor π system can attain the proper alignment with the crucial $\text{C}_2\text{-C}_3$ bond. Piperidines are not the best examples to study this effect. Polycyclic systems containing conformationally fixed amine and carbonyl functions of the type discussed by Hudec [3] or azadecalines offer better prospects. Another example is provided by the nitrogen inversion process in the 7-azanorbornane **46**.



⁸⁾ The diagram assumes that the N-lone-pair prefers to be equatorial, but the differential stabilization due to A is of course independent of this hypothesis.

We would clearly predict that the favored conformation is **45a** and not **45b**. These examples are illustrative rather than exhaustive. It is also clear that the ionization potentials and basicities of amines can be affected by the same phenomenon, as can the electronic transitions [3]. We can thus look forward to photoelectron spectroscopic and chemical tests of our theory as well.

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