Chemists have found that a useful description of the electronic structure of organic molecules may be obtained by the following prescription. Assume an underlying framework of \( \sigma \) bonds. On top of that framework place, as needed, delocalized \( \pi \)-electron systems and lone pairs. If several nonconjugated functional groups or chromophores occur in one molecule think of them as possessing, to a first approximation, orbitals localized within each such group. These orbitals or groups of orbitals, localized to a group, perhaps delocalized within that group, confer on that functional group its characteristic physical and chemical properties.

The above picture is one that has gradually evolved in the minds of experimentalists. It is easy for a theoretician to find faults in this simplistic prescription. Indeed the points of contact between the above dogma and the product of the successful procedures for calculation of electronic structure are few. Many theoreticians have consequently given up on trying to build a bridge of understanding between their computational results and the current ways of thinking of experimentalists; instead they have fallen back on simple predictability of observables as a criterion of success of a theory. My own tastes are not in this direction. I prefer a compromise in which the calculations are carried out, as they have to be, in a delocalized way, but are interpreted starting from a semilocalized view. Modifications to operationally useful patterns of thinking should be introduced only when absolutely necessary and when the experimental evidence for these modifications can be impressively mustered. Such a case now exists, in my opinion, in our ways of thinking about the interaction of localized sets of orbitals, or chromophores, or functional groups. In particular I wish to discuss the simplest case of the interaction of just two orbitals, atomic or molecular, with each other. These orbitals may be occupied by zero to four electrons in total. The more interesting cases are those with two to four electrons, and the molecules shown below illustrate the type of question we want to ask. Typical of the four-electron problem it makes to one double bond in norbornadiene (3) that there is another nonconjugated double bond in the same molecule. Analogous questions can be asked for the three-electron case: will the radical cation of 3 tend to form a new 2-6 \( \sigma \) bond or not; in the pyridinyl free radicals, such as 4, is the most stable isomer the one with the radical lobe ortho, meta, or para to the lone pair?

Perhaps the most interesting questions are those arising for the two-electron case. Formal diradicals such as benzyne or methylenes usually have a pair of nearly degenerate nonbonding orbitals, to be occupied by two electrons. The normal consequence is a triplet ground state. If the two levels can somehow be significantly split in energy, by interaction with themselves or with other levels, then the possibility of a thermodynamically and kinetically stabilized singlet state arises. For example, we wish to inquire about the interaction of the radical lobes in p-benzyne (5) or the influence of the amino group in 6 on the stability of this phenyl cation. Still another two-orbital two-electron problem that has occupied the energies and

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talents of a fair-sized group of organic chemists is the nonclassical carbonium ion problem, here typified by the 7-norbornenyl cation (7).

**Measure of Interaction**

There are a number of chemical properties, each specifically adapted or derived for the molecule at hand, which one could use as a measure of interaction. For diazabicyclooctane one could compare the basicity of that molecule to that of a model, quinuclidine. For norbornadiene one could examine the far-ultraviolet spectrum and compare it to that of a model, norbornene. For the 7-norbornenyl cation one could and has compared the rate of solvolysis of a derivative of this molecule with that of 7-norbornyl. The various chemical measures are not as directly informative as they might seem. Solvation, in particular, often complicates the relationship between a rate or equilibrium constant and the extent of interaction.

The restriction to a set of two orbitals (or in general to a subset of the molecular levels) and our insistence on a “before–after” dichotomy of interaction force us to a measure of interaction which (1) is as direct a physical assessment of the energy of an orbital as possible, and (2) can be calculated in the theoretical absence or presence of that interaction. We are thus led to the following definition. The extent of interaction of two orbitals will be measured by the magnitude of the one-electron energy level splitting after interaction, compared to that splitting in the (theoretical) absence of such interaction. More precisely, if in the diagram below ΔE_b is the splitting between two orbitals before interaction and ΔE_a is the splitting after interaction, then the measure of the interaction will be taken to be ΔE_a - ΔE_b.

![Diagram](image)

There are a number of comments to be made about this definition. First of all it coincides with our simplest ideas of bonding. To describe molecular formation to freshmen we draw, with all their inadequacies, interaction diagrams such as the one shown. Before interaction, for H atoms separated, there is no bonding. After interaction there is bonding, measured approximately by ΔE.

The second point to be made is that our definition is basically one suited to a one-electron theory of the Hückel or extended Hückel type, where the total energy is arbitrarily taken as a sum of the individual one-electron energy levels. This is, of course, not true in self-consistent-field theory: one-electron energies do not on simple addition yield term values. The problem is partially masked in the four-electron case where both orbitals are occupied and one can compare directly their one-electron energies calculated by any method. The difficulties are magnified in the two-electron case, where in a typical closed-shell calculation one of the interacting levels is occupied but the other one is empty. The latter level is by the nature of the self-consistent-field procedure generally pushed up in energy near or above the ionization continuum. In our search for a consistent criterion that we can apply to two-, three-, or four-electron cases we have chosen to live with the inconsistency with the better methods and to discuss one-electron levels only as they come from a semiempirical theory that seems to approximate term values by direct energy differences.

The third point that should be made is that, especially for the four-electron cases, the novel development of an old technique has in recent times allowed us for the first time to probe directly the extent of orbital interaction as defined above. The technique is photoelectron spectroscopy. It allows the direct measurement, and with judicious effort the assignment, of all important valence ionization potentials of a molecule.

To recapitulate: we choose as a primary measure of orbital interaction the energy splitting between two orbitals after interaction compared to that splitting before interaction or in a model compound where that interaction is absent. Thus we want to compare the energies of the two oxygen lone pairs in glyoxal to that of a single lone pair in, say, acrolein; or the two levels of a 7-norbornenyl free radical to those of 7-norbornyl and norbornene; or those of the m-pyridinyl cation to those of pyridine and phenyl cation.

**Uses of Perturbation Theory**

In principle one could go ahead and calculate each molecule listed above by an appropriate computational method. The position of the energy levels would tell us the extent of interaction. However, if such a process had to be repeated for every new molecule, even if the results were in excellent agreement with experiment, the resultant predictability would not necessarily imply understanding. True understanding implies a knowledge of the various physical factors, the mix of different physical mechanisms, that go into making an observable. To understand an observable means to me being able to predict, albeit qualitatively, the result that a perfectly reliable calculation would yield for that observable. Accordingly we have sought out the most important factors that influence orbital inter-
action and tried to construct simple arguments transferable from molecule to molecule.

Fundamental to our procedure have been some consequences of perturbation theory. In particular we will need three simple but powerful conclusions which will now be developed.

Suppose we know the solutions of the Schrödinger equation for some Hamiltonian $H_o$, i.e., the wave functions $\psi_{o0}$ and the corresponding energies $E_{o0}$. We proceed to turn on a perturbation or interaction $H'$ between some levels in the system. It is easily shown that the energy of the $i$th level after interaction with the other levels is to second order given by $E_i = E_{o0} + \sum_{j \neq i} \frac{H_{ij}'}{E_{oj} - E_{o0}}$ (eq 1) and the interacted wave functions are given by $\psi_i = \psi_{o0} + \sum_{j \neq i} \frac{H_{ij}'}{E_{oj} - E_{o0}} \psi_{o0}$ (eq 2), where $H_{ij}' = \int \psi_{o0}^* H' \psi_{o0} d\tau$ is the matrix element of the perturbation. The above formulas apply to the nondegenerate case. Also in the derivation overlap between interacting wave functions has been neglected.

The summation in eq 1 and 2 leads to our first conclusion: (A) changes in energy levels and wave functions are pairwise additive; i.e., if we wish to know how level $j$ is affected by the perturbation, all we need to do is to consider first how it interacts with level $i + 1$, linearly add on to that how it interacts with level $i + 2$, etc.

Let us then consider the simple component case, the interaction of two levels labeled 1 and 2, with level 1 at lower energy. Writing out the level energies after interaction, we obtain eq 3. Since by assumption $E_{10} < E_{20}$, and since the numerator $|H_{12}'|^2$ is positive definite, it follows that $E_1 < E_{20}$ and $E_2 > E_{20}$. Therefore: (B) when two levels interact the lower level is stabilized and the upper level is destabilized. In other words we have the well-known conclusion that the energy levels "repel" each other. Note also the inverse dependence of the perturbation energy on the difference in energy between interacting levels.

Now we write down the form of the wave functions $\psi_1$ and $\psi_2$ after interaction (eq 4). Assume again that level 1 is at lower energy. Now the sign of $H_{12}'$ is important. Though we cannot prove it in general, we have consistently found that $H_{12}'$ has the opposite sign to the overlap $S_{12}$; i.e., $H_{12}'$ is negative for positive $S_{12}$, positive for negative $S_{12}$. This is no profound discovery; it simply says that positive overlap implies stabilization or bonding. Suppose $S_{12}$ for a given choice of basis orbitals is positive. Then $H_{12}'$ is negative and, since $E_{20} - E_{10}$ is also negative, $\psi_{20}$ mixes into $\psi_{10}$ with a plus sign; i.e., $\psi_1 = \psi_{10} + \alpha \psi_{20}$. Similarly $\psi_2 = \psi_{20} - \alpha \psi_{10}$. This leads to the third conclusion, that giving us the shape of the orbitals after interaction: (C) if two orbitals interact, then the lower energy one of the two mixes into itself the higher energy one in a bonding way, while the higher energy orbital mixes into itself the lower one in an antibonding way. This is a complicated way of saying "The upper combination takes the node."

As implied by eq 3 and 4 the extent of interaction increases with the proximity of the two interacting levels. Indeed the most prominent orbital interactions are observed when the mixing is first order, i.e., the interacting orbitals are of the same energy. In such cases procedures differing from those above are applicable though the primary features of conclusions B and C are preserved. Two degenerate orbitals $\psi_{10}$ and $\psi_{20}$, originally at energy $E_0$, mix to form two new orbitals, $\psi_1$ and $\psi_2$, with energies of $E_0 + H_{12}'$ and $E_0 - H_{12}'$ respectively. The upper orbital is noded.

With these rules we can proceed to an analysis of specific cases.

### Through-Space Interaction

When a direct spatial overlap of two functional groups or chromophores is present the interaction is simple to analyze. The splitting between the interacting levels increases (B), with the bonding combination placed at lower energy (C).

Consider, for example, norbornadiene, with its two mirror planes of symmetry identified in Figure 1. Semi-localized $\pi$ orbitals for the left and right double bonds are shown below. Significant overlap is expected between the $\pi$ orbitals beneath the carbon skeleton. The delocalized combinations after interaction are shown below, identified by their proper symmetry designations. The noded combination, SA, is expected
to lie at higher energy. The observed splitting between SS and SA is 0.5 eV.\(^6\)

The \(\pi^*\) levels mix similarly to yield an AS combination below AA. The final interaction diagram is shown in Figure 1.\(^6\) Here are some specific consequences of the interaction. (1) The ionization potential of norbornadiene should be smaller in magnitude than that of a model norbornene. This is confirmed.\(^5\) (2) The \(\pi,\pi^*\) transition (SA \(\rightarrow\) AS) should be red shifted, but it is also forbidden. (3) This excitation promotes an electron from an orbital which is 2-6 and 3-5 antibonding to one which is bonding in the same regions. Closure to quinodicycylene, a common photochemical reaction of norbornadienes, is thus promoted. (4) Either removing one electron from SA to form the radical cation or adding one to AS to form the radical anion should promote bond formation between C\(_2\) and C\(_6\) or C\(_3\) and C\(_3\). Thus the extent and sign of orbital interaction have direct chemical and physical consequences.

Let us next turn to the 7-norbornenyl cation, built up by allowing interaction of an originally empty 2p orbital at C\(_7\) with the \(\pi\) and \(\pi^*\) orbitals of the double bond. The relevant interaction diagram is shown in Figure 2. The levels may be classified as symmetric or antisymmetric with respect to the mirror plane present (plane 1 of the norbornadiene case, Figure 1).

As a consequence of the rule that only levels of like symmetry may interact with each other, the \(\pi^*\) A level is unperturbed. The \(\pi\) and 2p levels mix with each other in the predictable manner, specified by rules B and C. The consequences are: (1) The \(\pi\) orbital is stabilized by through-space interaction with 2p at C\(_7\). The carbonium ion center itself is destabilized by this interaction. In fact, if overlap is included in the calculations, then typically the upper member of an interacting pair is destabilized more than the lower member is stabilized. This is why the stabilization is problematical for the three-electron case, the norbornenyl radical, and certainly nonexistent for the four-electron case, the norbornenyl anion. (2) Note the net bonding established between 2-7 and 3-7. This can be increased, subject to the limitations of increasing strain, by bending the C\(_7\) bridge over toward the double bond.\(^8\) (3) We normally like to think that a carbonium ion is stabilized as a result of some electron transfer to the positive site. This is achieved in the MO representation in the following way. Before interaction there were two electrons in the \(\pi\) orbital at C\(_7\) and C\(_8\). After interaction there are still two electrons in this orbital, but now the orbital is delocalized over three centers, and in particular has some density at C\(_7\).

Let us now turn to a third case of through-space interaction, that in the spiroaromatic molecules. Thus a perfectly adequate, somewhat unpopular, way of viewing benzene is as two strongly interacting allyl radicals (12).
In searching for still different topologies for interaction of two allyl radicals my collaborators and I came upon the idea of incorporating the allylic moieties into a spiro system. The simplest species of this type, which we called a [3.3]spirarene is 13; [3.5]-, [5.5]-, and [3.7]spirarenes are shown in 14, 15, and 16.

16. The [3.3]spirarene is redrawn below to emphasize the perpendicularity of the spiro arrangement and to define the planes used in the subsequent analysis.

In the evaluation of the stabilization of any system two questions must be faced, in the indicated sequence. (1) Does the topology and symmetry of the system allow any stabilizing interaction? (2) If so, what is the magnitude of that stabilization? The important interaction in our case is that between the nonbonding orbitals of the two allyl groups. Using the planes defined above we can classify the individual orbitals and form the interaction diagram of Figure 3. The symmetric allyl orbitals do not interact (in fact they form a degenerate e orbital in the $D_{2h}$ geometry), but the antisymmetric nonbonding orbitals are both of symmetry $A_A$ and so may interact.\(^{(10)}\)

The middle levels of the [3.3]spirarene after interaction are shown below. The view is end on, along the $S_4$ axis of the molecule. The overlap which gives rise to the splitting of $A_A$ and $A_A^*$ is small; nevertheless it is apparently sufficient to produce a singlet ground state for 13.\(^9\)

\(\text{Figure 3. Interaction diagram for two allyl systems in [3.3]-spirarene.}\)

\(\text{Figure 4. Lone-pair combination in a cis (left) and trans (right) azo compound. Levels are classified as S or A with respect to the twofold rotation axis.}\)

Interaction diagrams similar to Figure 3 readily show that there is some symmetry-allowed interaction of nonbonding orbitals in 16, but none in 14 and 15. The generalization to an arbitrary case $[m,n]$ is simple. An interaction leading to a stabilization can only occur when the nonbonding orbital of both systems has $A_A$ symmetry which occurs for the cases $m,n = 3, 7, 11, \ldots$, i.e., both $m$ and $n$ must be $4q + 3$ where $q = 0, 1, 2, \ldots$. This stabilization rule for a spiro system is thus in interesting contrast to Hückel’s rule for a lateral interaction of two allylic fragments, which states that stabilization will occur whenever $m + n = 4q + 2$.

The last case in this section illustrates the point that, while the perturbation rules hold very well, we must apply caution in trusting our intuition on the sign of the overlap and the consequent ordering of interacted levels. Consider the cis and trans isomers of an azo compound, 17 and 18. Figure 4 shows the symmetry-adapted lone-pair combinations for both of these species. In 17 one would expect a dominant through-space interaction, with the S combination at lower energy. This is confirmed by various calculations on the system. The interesting case is 18. The first inclination is to say that the overlap between the two hybrids is small, since they are “pointing away from each other.”\(^{(11)}\) As was first pointed out by Robin and Simpson\(^{(11)}\) the actual value of this overlap is sizable, negative, and probably even somewhat larger in magnitude than the corresponding vicinal


cis overlap. A consequence of this is that the anti-
symmetric combination is at lower energy, since it
is associated with a positive overlap. The observed
photoelectron splitting is 3.3 eV. It should be noted
that were the \( S \) orbital below the \( A \) then the spectra
of trans azo compounds would be very different from
those observed.

Through-Bond Coupling

In our analysis of orbital coupling we early came
upon some cases whose splitting patterns were com-
pletely opposite to our expectations. These cases were
pyrazine (19), \( p \)-benzylene (20), and diazabicyclooctane
(21). At a separation of 2.5–3.0 Å between \( N \) lone
pairs or carbon radical lobes the direct overlap is
very small. We correspondingly anticipated that the
two delocalized combinations shown below would be
split by a small energy, with \( S \) below \( A \).

![Diagram showing through-bond coupling](image)

To our surprise extended Hückel calculations gave a
large splitting of 1.6 eV, with \( A \) below \( S \). Similar
large gaps and the identical ordering were found for
pyrazine and \( p \)-benzylene. Before I proceed to the
analysis of this phenomenon it should be said that
the presence of a large splitting in 21 (2.1 eV) and
the ordering \( A \) below \( S \) have been fully confirmed
in recent photoelectron work.

What is the source of the large interaction which
places \( A \) below \( S \)? Since it cannot be a direct inter-
action between the two orbitals it must be the result
of their interaction with some other orbitals. It is
this phenomenon we call through-bond coupling.

Consider the case of two lone pairs separated by
three intervening \( \sigma \) bonds, as in the model diamine,
22. For the moment let us single out the 2-3 \( \sigma \)-bond
orbitals and construct a "before–after" picture of their
interaction with the \( S \) (\( n_{1} + n_{2} \)) and \( A \) (\( n_{1} - n_{2} \))
combinations of the lone pairs (Figure 5). It will
be useful to classify all levels with respect to the
twofold axis which passes through the 2-3 bond
and interchanges the two lone pairs. With respect
to this axis the 2-3 \( \sigma \) orbital is \( S \) and the 2-3 \( \sigma^{*} \) level

\[ (13) \text{R. Hoffmann, A. Imamura, and W. J. Hehre, J. Amer. Chem. Soc., 90, 1499 (1968).} \]
\[ (14) \text{P. Bischof, J. A. Hashmal, E. Heilbronner, and V. Hornung,} \]
\[ \text{Tetrahedron Lett., 4025 (1969); E. Heilbronner and K. A. Muszkat,} \]
\[ \text{J. Amer. Chem. Soc., 92, 3818 (1970).} \]
would be at lower energy. (2) In a recent study of the potential surface for the fragmentation of cyclobutane to two ethylenes we have attributed our interesting finding of the absence of a true tetramethylene intermediate to the effect of through-bond coupling of two radical lobes.\(^\text{16}\)

A particularly effective coupling unit for two \(\pi\)-electron systems is a single methylene group. The relevant orbitals are the \(\pi\)-symmetry combinations of localized \(\sigma\) and \(\sigma^*\) CH bonds. These hyperconjugating orbitals are shown in Figure 6.

In some calculations of the potential surface for cyclopropane and the addition of methylene to ethylene\(^\text{19}\) we located a potential minimum for a trimethylene intermediate, 23, with an open CCC angle, terminal methylene groups in the plane of the carbon atoms. From the two 2p orbitals at the termini one could form a symmetric and an antisymmetric combination, shown below. Whether the lowest singlet state of the diradical is predominantly the configuration \((S)^2\) or whether it is \((A)^2\) has direct consequences on its chemical properties. The interaction diagram of Figure 7 shows the mixing of the \(\text{CH}_2\) orbitals of Figure 6 with the radical orbitals illustrated above. The radical A combination cannot by symmetry interact with \(\sigma\) or \(\sigma^*\) of \(\text{CH}_2\). The radical S combination is depressed in energy by mixing with \(\sigma^*\), raised by mixing with \(\sigma\). The balance is close, but the latter effect dominates.

There are probably two reasons for a stronger interaction with \(\sigma\) than with \(\sigma^*\). First, when overlap is incorporated, \(\sigma\) is closer in energy to the radical orbitals than \(\sigma^*\). Second, the lateral \(\pi\) overlap between the triply noded \(\sigma^*\) and a 2p orbital at a terminus is smaller than that for the singly noded \(\sigma\).

A further demonstration of the role of hyperconjugation is available in the case of 1,4-cyclohexadiene.\(^\text{17}\) Recall at this point the analysis given above of through-space interaction in norbornadiene. In a planar 1,4-cyclohexadiene the direct overlap of the nonconjugated double bonds would be expected to be smaller. Superimposed on this would be the mixing with the \(\text{CH}_2\) \(\sigma\) levels. The symmetry analysis presented in Figure 8 makes it clear that the hyperconjugative interaction operates in the opposite sense to the direct interaction, and detailed calculations show that the former effect dominates. The observed splitting is 1.0 eV,\(^\text{5}\) sign unknown.

(15) Azine spectra are reviewed by K. K. Innes, J. P. Byrne, and I. G. Ross, J. Mol. Spectrosc., 22, 125 (1967). The forbidden \(n,\pi^*\) transition has not been reliably located.


(17) R. Hoffmann, ibid., 90, 1475 (1968).

(18) For the story leading up to this species see R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, ibid., 92, 3029 (1970).
rotating a single methylene group by 90°. In the 90° first, it is an antiethylene, with the CH₂ groups fixed. This is the result of the rotation of the PH₃ group. Only one d orbital, dₓᵧ, can overlap with the A combination. After interaction the latter has the shape 26. There are some further remarkable consequences of this interaction. There is essentially no barrier to rotation of the PH₃ group while keeping the CH₂ groups fixed. This is the result of the rotational properties of the 3d orbitals; no matter what the orientation of the PH₃ group there will always be available some linear combination of dₓᵧ and dₓz to interact with the carbon orbitals. There is a 1.45-eV barrier to rotating a single methylene group by 90°. In the 90° form the symmetry of the P 3d orbital set and the methylenes is effectively D₄h, and the two methylene p orbitals, 2pₓ and 2pᵧ, transform as an e representation, as do dₓz and dₓᵧ. Thus both methylene p orbitals are stabilized, and no gap is produced.

In summary, species 24 may be described as possessing a partial double bond, with the attendant torsional barrier. However, it is a most peculiar double bond: first, it is an antiethylene, with the A orbital occupied; second, 24 has in the midst of it a freely rotating phosphine group. A structural formulation such as 27 would be justified.

\[
\text{CH}_2=\text{PH}_3=\text{CH}_2
\]

27

It should be noted that, though we have stressed such cases, through-bond coupling need not always work in a direction opposite to the through-space effect. A case in point is that of the trans azo compounds discussed above, where the two effects reinforce each other.¹⁹

Patterns and Consequences of Orbital Interaction

The above sections have dealt separately with direct and indirect through-bond interaction. It may be appropriate here to point out that there is no distinction in the physical mechanism operative in the two cases. Were the interaction Hamiltonian explicitly written out, it would contain similar electrostatic terms for both types of interaction. The division is one wedded to the model, which starts out with localized groups of orbitals, allows these groups to interact directly with each other (through space), and then allows them to interact with the framework on which they are held (through bond).

Indeed the general situation will feature a superposition of both direct and indirect coupling. When the two groups are forced into close proximity the through-space interaction is bound to dominate. When the groups are widely separated through-bond coupling is the only possibility. The specific mix of the two effects is usually easy to analyze; Figure 9 presents a brief outline of some common interaction patterns.¹³

In what ways are the magnitude and sign of orbital interaction felt? We have stressed the most direct effects on ionization potentials and electronic spectra. For the two-electron cases orbital interaction is, so to speak, a matter of chemical life or death. In the presence of interaction dramatic stabilization may occur. In contrast, for the four-electron case through-space interaction is always destabilizing. The ease and stereochemistry of common reactions are directly affected by whether S is below A or vice versa. For instance, we have mentioned above the case of trimethylene. If A is significantly below S we would expect a conrotatory closure to cyclopropane; if S is below A, as it is in the ring-opened form of cyclopropanone, a disrotatory closure. Still another instance is the comparison of o-benzylene and 1,8-didehydronaphthalene (28). In the former case S is below A, and in accord with orbital symmetry control the addition to an ethylene, despite great driving force, appears not to be concerted. In the latter case through-bond coupling places A below S and the ethylene addition is stereospecific.¹⁹

The sign of the interaction can make itself felt in a number of other ways as well. Consider, for instance, the conditions needed to favor the symmetric protonation of some diamine vs. the usual unsymmetric protonation. The symmetric approach may be examined by an interaction diagram for the H⁺ 1s orbital approaching 28.

(19) This reaction is discussed in greater detail in ref 13.
Regiospecific and Stereospecific Introduction of Azide Functions into Organic Molecules

ALFRED HASSNER
Department of Chemistry, University of Colorado, Boulder, Colorado 80302
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The synthetic chemist has at his disposal a variety of methods for the stereospecific introduction of oxygen functions into the carbon skeleton, e.g., via opening of epoxides, hydroboration of olefins, or reduction of ketones. Until recently the same has not been true for functional groups containing nitrogen.

Since halogens, X-X, usually add stereoselectively to multiple bonds, we envisaged a route in which X-N moieties would add across the carbon–carbon double bond. Indeed, when we explored iodine isocyanate (INCO) additions to alkenes, we found a useful route for the stereospecific synthesis of carbamates, aziridines, and oxazolidones, as well as cis or trans 2-amino alcohols.1