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# TRANSFERENCE OF CHARGE IN ORGANIC REACTIONS—I

## MODELS FOR SIMPLE ABSTRACTION REACTIONS

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**Abstract**—A simple MO model is proposed for calculating the charge or spin delocalization at the beginning of an abstraction reaction in which a single MO of some attacking agent, $B^-$ say, interacts with one of the atomic orbitals, say $\psi_{H^*}$, of the molecule $RH^*$. According to the model there should be a direct proportionality between the distribution of 'extra' charge or spin induced in $RH^*$ at the start of the reaction, and the hyperfine coupling of proton $H^*$ with other magnetic nuclei in $RH^*$.

By assuming that increased delocalization in R-- or in $RH^*$—$B^-$, as measured by the coefficients of their non-bonding orbitals, will decrease the R—$H^*$ bond strength and also will increase the ease of forming the B—$H^*$ bond, some empirical correlations between NMR coupling constants and reactivities can be explained.

The rate of a chemical reaction is determined by two main factors; one is the probability that the reactants will collide in a favourable way and the other, the activation energy of the slowest step. We shall only be concerned with the second of these factors.

To determine the height of the energy barrier which has to be overcome in a reaction, we could ideally apply the methods of quantum mechanics to a large number of static configurations of the nuclei involved, calculate the energy of each configuration, plot potential energy surfaces and finally measure the height of the lowest pass connecting the valley associated with the reactants with that associated with the products. In practice, of course, this ideal situation is not realised and we have to be content with semi-empirical theories of questionable validity.[1,2] Though often crude, such theories have greatly added to our insight into chemical behaviour, and can be classified into three types: First, the sites open to attack are considered in terms of the electron distribution in the isolated molecule,[3] Fukui's frontier orbital theory[4] is an example of this; secondly, the energy of an intermediate or transition state is either calculated or estimated,[5] the "localization energy" model[6] is an example; and thirdly, the changes in MO energies occurring as the reaction proceeds are examined in terms of perturbation theory[7,8]

Into the third category comes also the application of symmetry principles to show how the course of a reaction may be determined.[9] The advantage of this approach is that, apart from finding the order of the energy levels, one does not have to actually calculate energies, so that the method leads to predictions which are relatively insensitive to the choice of parameters. This is an important point when we are using simple MO theory, for calculated energies are very sensitive to the values chosen for the various integrals.

In this paper we, too, shall avoid explicit calculation of energies and shall examine instead how the electrons get delocalized as the reactants come together. The main question to which we shall try to find a reliable answer will be: What has to happen in a reaction involving the initial abstraction of an H atom?

*Charge delocalization in a model E2 reaction.* We start our investigation with a convenient example—a base-catalysed E2 reaction of a substituted ethylene. Suppose a single MO of base $B^-$ interacts with the hydrogen ls orbital of olefine CHZ:CXY (Fig. 1).

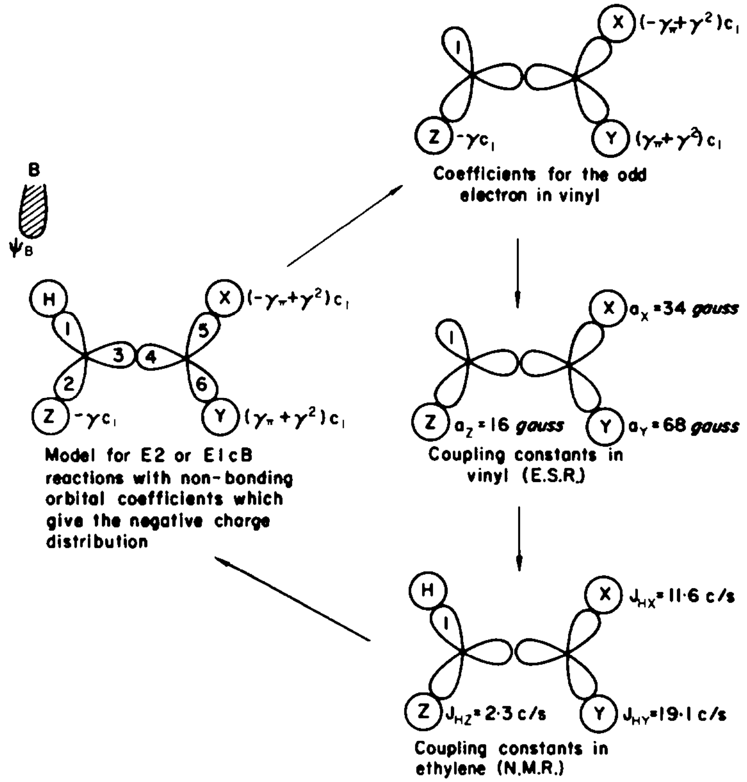


Fig. 1 Model for elimination reactions and the connection with NMR coupling constants. Parameters as in text, except that for simplicity we equate $\beta_{34}$, $\beta_{1H}$, etc., with our unit of energy.

If we equate all coulomb integrals, i.e. $\alpha_B = \alpha_H = \alpha_1$ = etc, then the distribution of negative charge is given by the squares of the coefficients of the non-bonding orbital $E = \alpha_B$. A convenient parameterization[10–12] which has been found adequate for calculating proton spin-spin coupling constants is: for the resonance integrals, $\beta_{15} = -\beta_{16} = \gamma_\pi$, $\beta_{12} = \gamma$; usually we shall equate the resonance integrals of types, $\beta_{1H}$, $\beta_{34}$ and shall let them be our unit of energy. Other "non-bonded" interactions are neglected apart from $\beta_{BH}$. For simplicity we shall neglect overlap since this makes no difference to relative charge densities in the atomic orbitals. Since the carbon orbitals in this case are $sp^2$ hybrids $\gamma$ is one third of the difference in coulomb energy of carbon 2s and 2p atomic orbitals.[10]

It is easy to calculate the coefficients of the non-bonding orbital because the diagonal terms of the secular equations are zero; for example, from appropriate rows we find immediately that coefficients $c_H$, $c_2$, $c_3$, $c_5$, and $c_6$ are all zero.

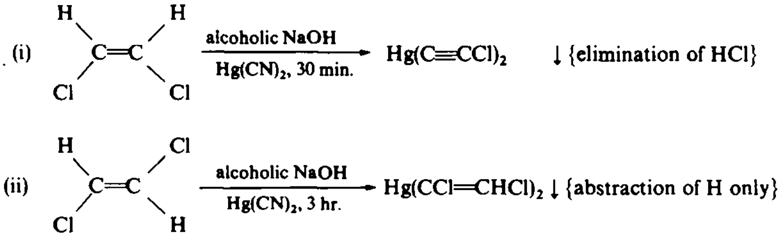
The other coefficients are as follows:

$$c_1 = -(\beta_{BH}/\beta_{1H})c_B; \quad c_2 = -(\gamma/\beta_{2Z})c_1; \quad c_4 = -(\gamma/\beta_{34})c_1;$$
$$c_X = (-\gamma_\pi + \gamma^2/\beta_{34})c_1/\beta_{5X}; \quad c_Y = (+\gamma_\pi + \gamma^2/\beta_{34})c_1/\beta_{6Y}. \tag{1}$$

The most important point to observe here is that since all of the resonance integrals have the same sign, i.e. all our parameters are negative, more negative charge drifts on to a substituent when it is *trans* than when it is *cis* with respect to the attacked hydrogen. Another point of interest is that delocalization is favoured by weak bonds, i.e. small β's, in particular, the amount of negative charge which accumulates on say, substituent X, varies with the resonance integral $\beta_{5X}$.

*Connection with reaction rates.* In order to translate our discussion about charge densities into energetic terms we have to make some further assumptions. We shall assume that the more easily the negative charge on $B^-$ is transferred to the molecule, the faster will be the abstraction, and also that the situation is most favourable when this charge is concentrated in the most electronegative orbitals, i.e. in the attacked molecule. For example, in the case of vinyl chloride, *trans* elimination of HCl is preferred because more negative charge is transmitted to the chlorine when it is *trans* than when it is *cis* with respect to the eliminated H atom.

Another point to consider is that for there to be synchronous loss of HCl, there needs to be sufficient accumulation of negative charge on the halogen atom in the perturbed molecule. The presence of other electronegative groups in the molecule will increase the total ability of a vinyl residue for holding negative charge, but also will decrease the concentration of charge in any particular orbital. This would appear to be the explanation of the ways in which *cis*- and *trans*-dichloroacetylenes behave when reacting with base in the presence of mercuric ions;[13]



Apparently the α-Cl atom reduces the excess negative charge on the vicinal chlorine in reaction (ii) so much that elimination of HCl is no longer an effectively synchronous process.

*Connection with nuclear magnetic resonance.* In view of the apparent connection with certain abstraction reactions, it would be very useful if we had some way of measuring the efficiency of negative charge transfer when a hydrogen atom is attacked by base. Fortunately such a measure is available from NMR spectra and this comes about in the following way:

Consider the fragment left when an H atom is removed from ethylene and the other nuclei are fixed in their original positions. The spin densities in the atomic orbitals of this vinyl radical are given by the squares of appropriate coefficients, which are: $c_2 = c_3 = c_5 = c_6 = 0$;

$$c_Z = -(\gamma/\beta_{2Z})c_1; \quad c_4 = -(\gamma/\beta_{34})c_1;$$

$$c_X = (-\gamma_\pi + \gamma^2/\beta_{34})c_1/\beta_{5X}; \quad c_Y = (+\gamma_\pi + \gamma^2/\beta_{34})c_1/\beta_{6Y}$$

The relative spin densities in this radical fragment are exactly the same as the negative charge densities induced when the base $B^-$ approached in our model reaction. Since the spin density in a hydrogen atomic orbital is proportional to the coupling constant between its nucleus and the odd electron, we arrive at the following results: First, the relative magnitudes of coupling constants in σ-radical will tell us the way in which negative charge from a base is distributed over the complete molecule; and secondly, the absolute value of the coupling constants give a measure of the total delocalization of the negative charge, i.e. away from the incoming base.

By itself, this connection with ESR spectra is not very useful because very few σ-radicals have been observed. We can, however, use data from NMR spectra instead, since the proton spin-spin coupling constant $J_{12}$ between protons $H_1$, $H_2$ in molecule $RH_1$, is proportional to the splitting $a_2$ of the electron spin resonance spectrum of the σ-radical R— by proton $H_2$[10, 14, 15]; i.e. if $R \equiv CX{:}CH_2H_3$, splittings in ESR spectrum are $a_2$, $a_3$; coupling constants in NMR spectrum of $RH_1$ are $J_{12}$, $J_{13}$, then $a_2/J_{12} = a_3/J_{13}$. (Fig. 1).

Using this relationship, then, we can use relatively accessible data from NMR spectra for estimating degrees of delocalizability.

Example (a): in ethylene, $J_{cis} = 11{\cdot}6$ c/s, $J_{trans} = 19{\cdot}1$ c/s; we therefore expect base attack on a hydrogen *trans* with respect halogen to be the most effective, i.e. by the same argument as that above.

Example (b): In vinyl chlorine, $J_{cis} = 7{\cdot}3$ c/s, $J_{trans} = 14{\cdot}6$ c/s[16]. If attack is on the proton *trans* with respect to the chlorine degree of delocalization relative to ethylene is $11{\cdot}6/7{\cdot}3 = 1{\cdot}59$. If attack is *cis*, degree of delocalization $= 19{\cdot}1/14{\cdot}6 = 1{\cdot}31$. We conclude that elimination should be *trans*, as in example (a) but now there are two reasons; one that more negative charge goes onto the Cl atom when it is *trans*, and two, that the total degree of delocalization is then greater.

The above relationship between ESR and NMR is only expected to apply when the nuclei in question are joined by an odd number of bonds; in other cases there is often

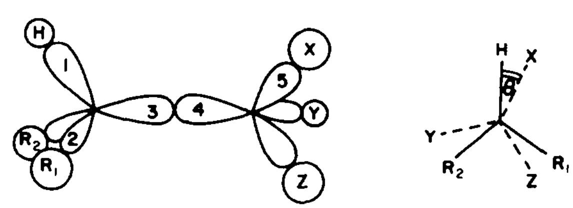


FIG. 2 Model for base-catalysed 1:2 eliminations in saturated systems.

a large negative contribution to consider also.[10] Also for nuclei other than hydrogen the situation becomes rather complicated and usually we would not expect any obvious simple connections between coupling constants and reactivities except perhaps when the H atom is bonded directly to a magnetic nucleus.

*Extension to alkane/cycloalkane systems.* In simple olefine systems the situation is simplified by the nuclear planarity; in saturated compounds, on the other hand, we have to consider a 3-dimensional problem. Let the dihedral angle of the bonds connecting the eliminated groups to the molecule be $\theta$ (Fig. 2).

The coefficient of orbital X in the non-bonding orbital is:

$$c_X = (-\gamma_\pi \cos\theta + \gamma'^2/\beta_{34})c_1/\beta_{5X}$$

where $\gamma_\pi$ is approximately the same as before[10] and $\gamma' = \frac{3}{4}\gamma$, assuming that the C atoms are tetrahedrally hybridized. Two orientations give maximum transference of charge on to X;

$$\text{(i) } \theta = 0, \quad C_X/c_1 = (-\gamma_\pi + \gamma'^2/\beta_{34})/\beta_{5X}$$

$$\text{(ii) } \theta = 180, \quad c_X/c_1 = (+\gamma_\pi + \gamma'^2/\beta_{34})\beta_{5X}$$

Using the principles put forward in the previous section we can see from Fig. 3 why it is that elimination is unlikely when atoms are *gauche* with respect to each other.

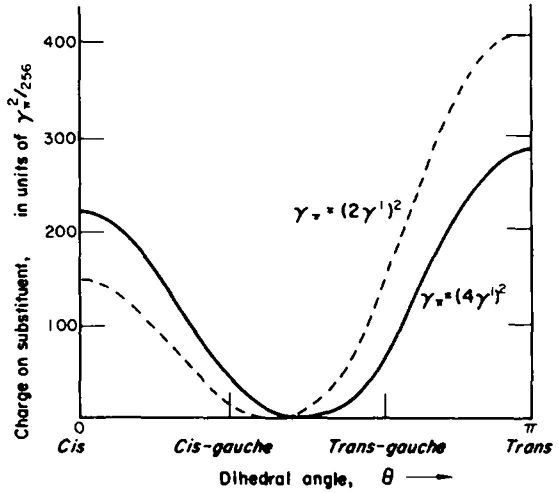


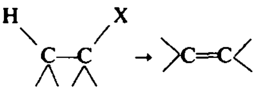
FIG. 3 Variation of induced charge on a vicinal substituent with dihedral angle. (Most probable relationship between $\gamma_\pi$ and $\gamma'$ is $\gamma_\pi \approx (4\gamma')^2$).

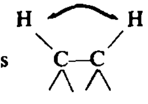
When there is relatively free rotation about the C—C bond it will be most improbable that the atoms will ever be in eclipsing positions for a significant length of time, hence we expect facile removal of a proton only when there is a strongly electronegative group *trans* with respect to it. This is due to the low degree of charge transfer on to *gauche* substituents. When substituents are held in eclipsing positions as in cyclopentyl derivatives, aromatic halides, etc, *cis* elimination will occur, i.e. according to our approach.

Once again we expect a direct connection with NMR coupling constants and this is shown in Table 1.

TABLE 1. STEREOCHEMISTRY OF SOME ELIMINATION REACTIONS AND THE CONNECTION WITH NMR DATA

Reaction is:



| | Coupling constants | |  | |
|---|---|---|---|---|
| Product | $J_{trans}$ | $J_{cis}$ | $J_{gauche}$ | Elimination[11] |
| Cyclohexene | ~ 12 c/s | — | ~4 c/s | *trans* |
| Cyclopentene | — | ~9 c/s | ~5 c/s | *cis* |
| Benzyne | — | 9 c/s | — | *cis* |
| Acetylene | 19·1 c/s | 11·6 c/s | — | *trans* |

*Effects of substituents.* Until now we have been concerned with determining which proton in a given molecule is that most likely to be removed by base. Now we shall briefly discuss the effects of replacing H atoms by Me groups in various types of molecules and their reactions.

Using either of our previous models (Figs 1 and 2) the total charge delocalization as the base approaches will increase by an amount $\frac{3}{2}\gamma_\pi^2 c_1^2$ when we replace an α-H by Me, due to the "extra" transference of charge on to the Me protons. We also expect that the average coupling constant between an α-proton and one of these Me protons, will be proportional to $c_1^2$, so that this coupling constant will give us a measure of total delocalization.

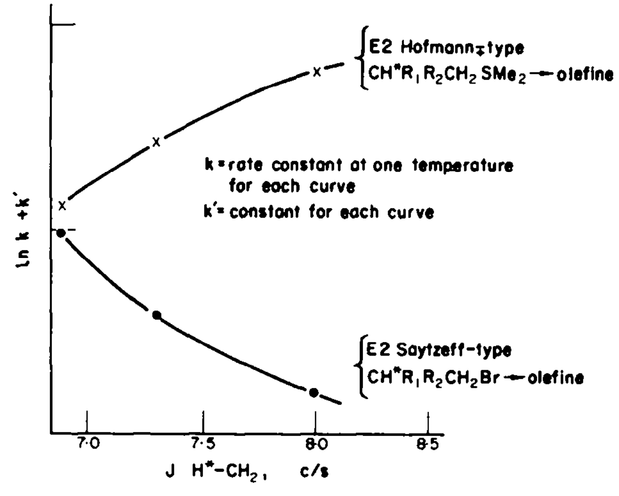
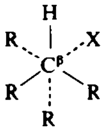


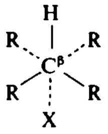
FIG. 4 Effect of β-substituents on rates of base-catalysed E2 reactions and the connection with NMR.

The curves shown in Fig. 4 show that Me substituents generally increase rates of elimination and the correlation with the NMR data indicates that this arises from increased delocalization of negative charge, i.e. the Me groups are acting as electron acceptors! This direct connection between reaction rates and proton–proton hyperfine interactions is also found in gas phase E1 reactions[1] and in various radical abstraction reactions.[11] A similar[20] correlation has been observed between $C^{13}$—H coupling constants and rates of hydrogen abstraction from molecules of type $M(CH_3)_4$.

*Effects of steric repulsions.* We have deliberately limited ourselves to considering a single orbital of the attacking species in order to keep the theory simple. Interactions of other orbitals of the two reactants come broadly under the heading of "steric effects". In most of the cases cited above it appears that the way in which the charge of the incoming group is transferred to the attacked molecule often determines, or at least, is directly connected to, the course of the reaction. In some cases, however, e.g. in Hofmann-type eliminations, the rates are governed by something else. In this connection we have to consider two factors; the size of the attacking group and the size of the leaving group. In the former case it is obvious that if the incoming base or radical is large enough, attack will be preferred on the least hindered H atom; and in the latter case, the ease of attaining a favourable conformation for transference of charge may be determined by the size of the leaving group. Consider as an example Hofmann-type eliminations ($X = NR_3$, $SR_2$, etc.). In these cases the group X is large and the reaction rates depend on how easy it is to achieve the favourable conformation of type (a),[2] which has a smaller probability when there are substituents on the site of attack. Apparently in these instances the steric repulsions of methyl groups outweigh their ability to delocalize charge.



(a)



(b)

*Abstraction of negative groups.* We shall now examine the three main ways whereby substituents can affect the rate of loss of $X^-$ from RX, that is apart from steric repulsions. First we could set up a model in exactly the same way as we did in Fig. 1, replacing the base $B^-$ by an acid $A^+$, which normally would be a solvent molecule. As this acid approaches X its positive charge becomes delocalized around the fragment R— and as before, a measure of the degree of delocalization is given by the coupling of protons in R— with $H^*$ in $RH^*$. Substituents which increase the degree of delocalization, e.g. α-Me groups, according to the NMR data, do, in fact, also increase the rates of reactions involving loss of $X^-$.

The second and third ways are related to the first and depend on the strength of the C—X bond, which is weaker when there is more delocalization around the fragment R—.[21] Since the carbonium ion $R^+_{(\pi)}$ is stabilized by delocalization of the positive charge, a group such as Me should favour dissociation in the equilibrium

$$RX \rightleftharpoons R^+_{(\pi)} + X^-$$

i.e. as in El and $S_N1$ reactions.

The third way, by means of which loss of $X^-$ could be affected by substituents, is that if the C—X bond is weakened in some way, its length could increase and the associated resonance integral decrease. From formula (1) this could increase the transference of any positive charge from the acid to the group R—.

All of these effects act in the same direction and so, if any/all of them is important, we would expect a correlation between the degree of delocalization in the fragment R—, as measured by the coupling constants in the NMR spectrum of RH*, and the rates of reactions involving breakage of the C—X bond. Such a correlation certainly exists, as we can see from Fig. 5, indicating that the stretching of the C—X bond is important even when the reaction depends on the attack on a proton by a suitable base. Steric factors appear to have little effect on the reactions considered, when we change only the α-substituents in going from one reactant to another.[18]

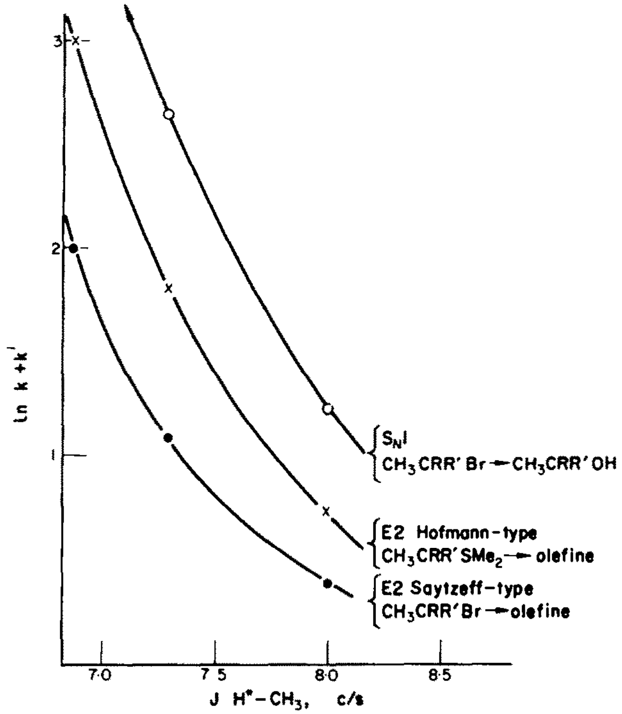


FIG. 5 Effect of α-substituents on reactivities of $CH_3CRR'X$ and the connection with the NMR spectrum of $CH_3CRR'H^{*3}$.

## RESULTS AND DISCUSSION

We have tried to make three main points in this paper. The first is that the transference of charge/spin, initially associated with a single orbital $\psi_B$ of the attacking species B, to a molecule RH, occurs largely via a non-bonding orbital. The coefficients of this non-bonding orbital tell us how this "extra" charge/spin is distributed around R, and are found by substituting $E = \alpha_B$ directly into the secular equations.

The second point is that the activation energy of the abstraction reaction is determined by the ease of forming the new bond B—H and of breaking the old one R—H, say, and that both of these processes are favoured by a large tendency for charge/spin delocalization around the fragment R— in these reactions.

The third point is that this tendency, as well as the extra charge/spin distribution in the initial stages of these reactions, can be measured by the values of certain coupling constants in the NMR spectrum of RH.

The whole model and the connection with NMR are only expected to be valid, at least in the simple form described above, when the coulomb integral to be associated with the attacking agent is not too different (i.e. by more than $\sim 1\frac{1}{2}$ eV) from that of appropriate carbon hybrid orbitals. In view of all the correlations given, it would appear that this condition is satisfied. We can justify it in the case of base-catalysed E2 reactions because the O atoms are then negatively charged at the start and are therefore less electronegative than when they are in neutral molecules, i.e. we can use a lower coulomb energy.

What we have tried to do, then, is to simplify the approach to some abstraction reactions in order better to correlate reactivities with either a simple theory or some properties of the reactant molecules. As a final example of our approach we shall compare 1:2 and 1:4 eliminations:[22, 18]

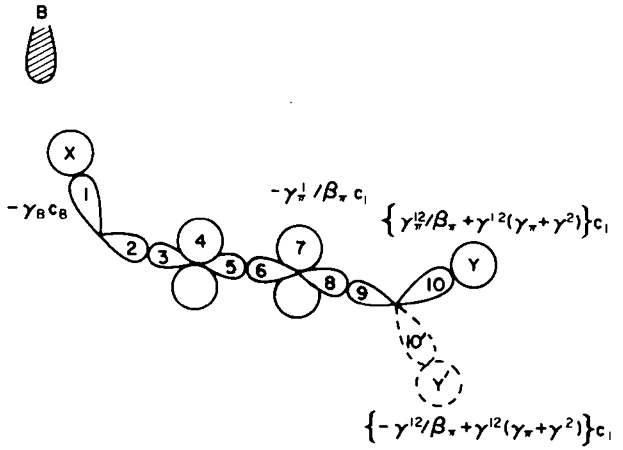


FIG. 6 Model for 1:4 eliminations of XY from *trans*-$CH_2XCH:CHCH_2Y$. The most favourable conformations are illustrated. Parameters as in previous figures with in addition: $\beta_{47} = \beta_\pi$, $\beta_{14} = \gamma'_\pi$.

The important differences between the situation in 1:4 eliminations as shown in Fig. 6, and that in 1:2 eliminations are:

(i) Even in the most favourable conformation less charge is transmitted to the leaving group Y.

(ii) Delocalized charge from the base collects on a C atom rather than on a leaving group.

(iii) One would not expect any particularly preferred conformation of the original molecule, whereas in $C_2H_4I_2$, for example, the I atoms would tend to be *trans* with respect to each other.

(iv) Because $\gamma,\gamma'$ are small, some stereospecificity of the elimination will be lost, in fact *cis* elimination would be expected to be preferred over *trans*. Gauche elimination should not occur, however.

Summing up these factors, we have to balance them against the greater delocalization of charge to estimate whether 1:4 E2 reactions should be more or less fast than corresponding 1:2 reactions. On the whole we would expect points (i) and (ii) to be the most important effects and therefore 1:4 eliminations to be the slower ones.

This example illustrates the approach and we show later how it can be applied to reactions involving initial addition, e.g. as in aromatic substitution.[12]

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