BIMOLECULAR ELIMINATION REACTIONS: STEREOCHEMISTRY AND THE SCOPE OF CONFORMATIONAL ANALYSIS

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ABSTRACT

The ratio of *trans*- to *cis*-olefin, $R \cdot CH{=}CH \cdot R'$, formed in bimolecular eliminations from substrates of the type $R \cdot CH(X) \cdot CH_2 \cdot R'$, is frequently used as a criterion of 'the extent of double bond development' in the transition state of olefin formation. This reasoning is based on the assumption that the elimination reaction proceeds exclusively by the *anti*-elimination mechanism. It is shown that for many bimolecular elimination reactions (particularly those involving trimethylammonium as the leaving group) this assumption is not valid, *anti*- as well as *syn*-elimination taking place side by side. Before *trans*- to *cis*-olefin ratios can be meaningfully discussed, it is therefore necessary to make an assignment of the relative contributions of *syn*- and *anti*-elimination to *trans*- and *cis*-olefin formation. Once such an assignment has been made one finds (particularly for elimination reactions of 'onium bases) that there is a distinct tendency for the *trans*-olefin to be formed by *syn*-elimination and the *cis*-olefin by *anti*-elimination. In some cases, the 'stereoselectivity' of the two reaction paths is so pronounced that the *trans*- to *cis*-olefin ratio corresponds closely to the *syn*- to *anti*-elimination ratio. Possible interpretations of this 'stereoselectivity' of *syn*- and *anti*-elimination are considered.

Conformational analysis is a method applicable to ground and transition state alike[1]: indeed, nowadays, a conformational analysis of one kind or another forms part of most mechanistic discussions. Our Symposium has the task of assessing the scope and the limitations of conformational analysis; it is therefore appropriate that a discussion of a mechanistic problem—from this particular angle—be on the agenda. The process I shall deal with is the bimolecular elimination reaction[2].

Conformational argumentation in mechanistic discussions frequently takes on the form of attempts at deducing information about the geometry of the transition state from the isomer composition in the product: an isomer composition which is close to equilibrium composition is—crudely speaking—taken to indicate a transition state of a product like structure. As applied to elimination reactions, the argument runs somewhat as

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follows. Consider an elimination reaction such as (1) which can give rise to a mixture of *cis*- and *trans*-olefin:

$$R \cdot CH(X)CH_2 \cdot R' + B^- \rightarrow R \cdot CH{=}CH \cdot R' + X^- + BH \qquad (1)$$

The ratio of *trans*- to *cis*-olefin in the product is, according to this reasoning, a criterion of the extent of C—H and C—X bond-breaking in the transition state: the closer the ratio of *trans*- to *cis*-olefin in the product approaches the equilibrium value for the *trans–cis* pair, the more nearly product, i.e. olefin-like, is the transition state of the elimination believed to be. This is a standard argument and as long as it was applied with due reserve it appeared to be unobjectionable. At any rate, it has been very frequently employed[3].

Let us now, however, consider some experimental results from reactions of the type (1). I have, in *Table 1*, assembled data on the *trans–cis* isomer composition for bimolecular eliminations in two systems, the open-chain 5-nonyltrimethylammonium base and the cyclic cyclodecyltrimethylammonium base[4]. Both these compounds on elimination can give rise to a mixture of *trans*- and *cis*-isomers: *trans*- and *cis*-4-nonene, and *trans*- and *cis*-cyclodecene, respectively.

Table 1. Per cent *trans*-olefin in *trans–cis* isomer mixture*

	Cyclodecyl NMe_3	*5-Nonyl* NMe_3
t-BuOK/*t*-BuOH	98	74
i-PrOK/*i*-PrOH	96	46
EtOK/EtOH	80	26
MeOK/MeOH	67	20
	ΔG^0_{t-c}	
Stability of olefins	1·9	−1·0

* cf.: Závada and Sicher, *Coll. Czech. Chem. Commun.* **32**, 3701 (1967).

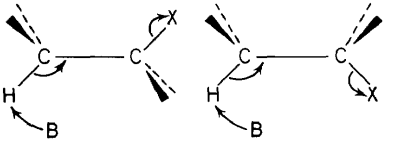
Note that in the open-chain system the *trans*-olefin is more stable than the *cis*, whereas in the cyclic system the reverse order is found, the *trans*-isomer being less stable than the *cis*. The reaction has been carried out using different base–solvent combinations and this, as can be seen, greatly affects the *trans–cis* composition of the product. What we have to note is that as we go down the columns, i.e. to the weaker base and the more polar solvent, the proportion of the *trans*-isomer decreases in both the substrates. Thus, the proportion of the *trans*-isomer decreases in the case of the 4-nonenes, where it is the more stable isomer, but it also decreases in the cyclodecenes, where it is the less stable isomer. In other words, the same change in reaction conditions thus leads in the one case to a decrease in the proportion of the more stable isomer and in the other to an increase. It should also be noted that in seven out of the eight runs listed the reaction gives rise to an excess of the less stable product!

The conclusion we must draw from these results is that product composition bears no relationship—or at any rate no simple relationship—to

product stability. It is clear that an application of the very crude conformational arguments of the kind I mentioned earlier to data such as these could hardly be meaningful. We analysed these and related results and came to the conclusion that since the conformational reasoning cannot be fundamentally unsound, we may have to look for an inconsistency somewhere else. In this way we were led to the idea that some of the accepted mechanistic concepts themselves could be at fault.

The key feature of the mechanism of concerted 1,2-elimination processes is the torsion angle about the $-C_\alpha-C_\beta-$ bond in the activated complex. It is amply supported, by experiment as well as theory, that the arrangements which are preferred are those in which the four atoms concerned lie in a single plane[5]. This arrangement can obviously be attained in two different ways: either by placing both the groups which are going to be eliminated on the same side of the developing double bond, or by placing them on opposite sides of this bond (*Scheme 1*). We speak of *syn*-elimination in the

Scheme 1



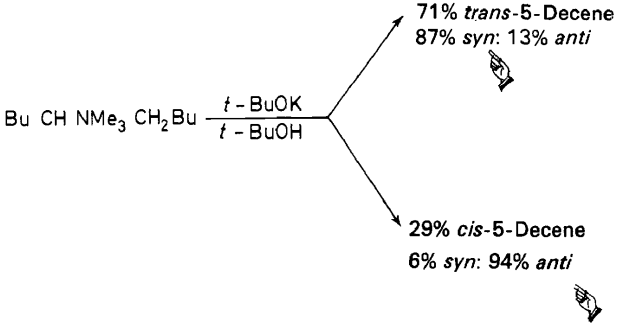
anti *syn*

former case and of *anti*-elimination in the latter. The view has been generally accepted that in base-catalysed bimolecular eliminations the *anti*-elimination route is greatly superior to the *syn*-route so that eliminations, in general, proceed by this mechanism; the only exceptions are systems in which the bonds cannot become *anti*planar, as, e.g. the norbornyl system[6]. You will find statements to this effect in all textbooks and monographs[2] and it is on this view that the conformational arguments which we have been considering are, of course, based. The origin of this view, formalized in the so-called E2 Rule of *Anti*-elimination[7], goes back to the last century[8] and has over the years, assumed the qualities of a dogma. We felt, nevertheless, that it should be subjected to a re-examination, particularly after a study of the literature had convinced us that the evidence on which it is based, though strong, is not necessarily compelling.

Time does not permit me to discuss our investigations[9] in any detail. Suffice it to say that the methods which we employed involved the application of β-deuterium labelled substrates and that conclusions as to the steric course—*syn*- or *anti*—were drawn from the deuterium content in the isolated olefins and from deuterium isotope effect data. An alternative approach was based on rate comparison studies involving reactions on homologous series of cycloalkyl derivatives[9a, c, g, h].

Just to illustrate the situation, let me give you one example out of several dozen reactions of open-chain and alicyclic substrates already investigated. Consider the reaction of 1-butylhexyltrimethylammonium base with *tert*-butoxide in *tert*-butanol[9k] (*Scheme 2*). This reaction gives rise to a mixture of *cis*- and *trans*- 4- and 5-decenes. We shall consider only the latter. The

Scheme 2

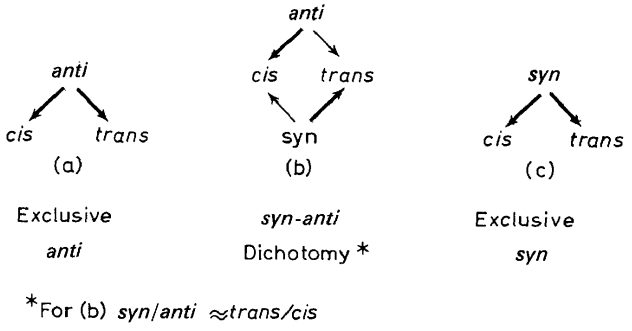


mixture of the 5-decenes consists of 71 per cent of the *trans*- and 29 per cent of the *cis*-isomer. Now, as can be seen, contrary to what the E2 Rule of *Anti*-elimination predicts, the reaction does not proceed homogeneously by *anti*-elimination. The *trans*-olefin is indeed formed predominantly by *syn*-elimination; by contrast, in *cis*-olefin formation *syn*-elimination plays only a minor role.

Sufficient facts are now available to permit the following generalizations regarding the steric course to be made.

In bimolecular eliminations leading to a pair of *cis–trans* isomers of the type R · CH=CH · R′ both *anti*- as well as *syn*-elimination can take place; the view that *anti*-elimination is generally favoured over *syn*-elimination must be abandoned. Either *anti*- or *syn*-elimination may be preferred, depending—in a way which is now in part known and perhaps understood—on the nature of all the 'variables', i.e. the base, the solvent, the leaving group, and the alkyl structure of the substrate. Under conditions in which the contribution of *syn*-elimination is extensive, a more or less strict stereoselectivity of the two alternative elimination modes is frequently found, the *trans*-olefin being formed predominantly by *syn*-elimination, the *cis*-olefin by *anti*-elimination.

Scheme 3



*For (b) *syn/anti* ≈*trans/cis*

The possible alternative combinations are depicted in *Scheme 3*. Exclusive *anti*-elimination for both *cis*- as well as *trans*-olefin formation, as shown in (*a*), is, as we now know, by no means as general as had hitherto been believed; we must, however, be careful not to go to the other extreme of believing that

such a situation is never found. Such behaviour is, indeed, encountered; most likely so in eliminations involving good leaving groups, e.g. OTs, and solvents of high dissociating capacity. *Scheme 3*(*c*) depicts a situation which presumably never occurs in simple bimolecular eliminations leading to a pair of *cis–trans* isomers, i.e. one in which *both* isomers are formed by *syn*-elimination. This mode operates, as is well known, in intramolecular elimination reactions, such as the amine oxide (Cope) elimination[13]. Finally, (*b*) depicts the newly discovered situation for which we have proposed the term *syn-anti elimination dichotomy*: in this reaction mode, the *trans*-olefin is formed, mainly or even exclusively, by *syn*-elimination; the *cis*-isomer, again mainly or even exclusively, by *anti*-elimination. This behaviour is most frequently found for eliminations involving poor leaving groups ('onium groups), using strong bases and relatively non-dissociating solvents.

I should like to add at this point that the conclusions reached by us have lately been corroborated, and in some important respects extended, by work in the laboratories of W. H. Saunders Jr.[10], J. L. Coke[11] and D. H. Froemsdorf[12].

We can now return to our original topic, namely that of the *cis–trans* olefin ratios in bimolecular elimination reactions and their mechanistic significance. Clearly, this problem now appears in an altogether new light. We are concerned with two distinct—yet interrelated—features: the steric course (*syn-* or *anti-*) and the stereochemical composition of the product (*trans* or *cis*). Knowledge of the steric course is a prerequisite for any interpretation of the *trans–cis* isomer composition.

Only where both the *trans-* and the *cis*-olefins arise by the same route, that is both *anti* or both *syn*, can the *trans–cis* ratios serve as a starting point for simple conformational argumentation of the type mentioned at the beginning of this article. To what extent such reasoning will lead to useful conclusions is another question; but at least the basic requirements for such speculations are fulfilled under such circumstances.

Where the elimination proceeds according to the *syn-anti* dichotomy pattern we are clearly faced with a different situation: since here *syn*-elimination leads to the *trans*-olefin and *anti*-elimination to the *cis*-olefin, the *trans–cis* ratio becomes a function of the propensity of the system to react by the one or the other steric pathway. Moreover, even for cases intermediate between (*a*) and (*b*) (*Scheme 3*), that is, for processes in which the *trans*-olefin is only in part formed by *syn*-elimination, a correlation between *trans–cis* isomer composition and preferred steric course may be shown to exist. *Figure 1* shows a plot of the percentage of *trans*-olefin in the *trans–cis* isomer mixture against the percentage of *trans*-olefin formed by *syn*-elimination; the reaction is the pyrolysis of five open-chain 'onium hydroxides†.

It is clear from the plot (*Figure 1*) that the processes in which the percentage of *trans*-isomer is high are also those in which the *trans*-isomer is formed by

† Except for the compounds R=M and R′=Pr, where the data relate to a reaction with *tert*-pentoxide in *tert*-pentanol[10]. The inclusion of the results of this reaction into the plot appeared to be justified since there is evidence, from reactions of quaternary ammonium bases of related alkyl structure, that the reaction course using a *tert*-alkoxide–*tert*-alkanol system and under pyrolytic conditions is closely similar, both with respect to *trans–cis* composition and steric course.

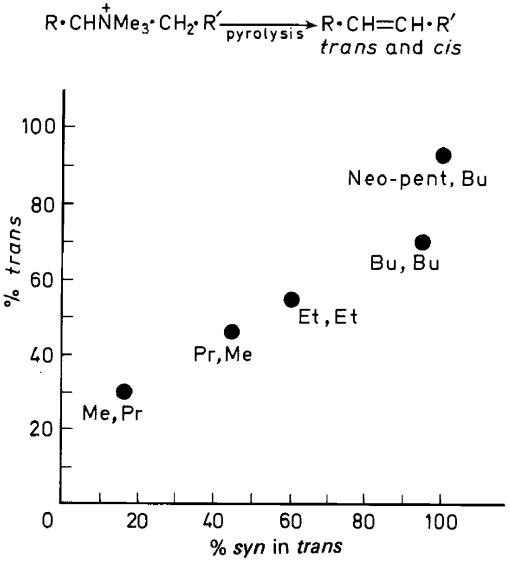
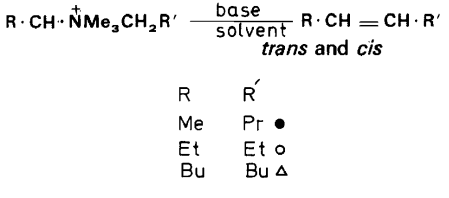


Figure 1

syn-elimination; by contrast, in the substrates which give only a low proportion of *trans*-olefin, this is formed by *anti*-elimination predominantly. In other words, the preponderance of *cis*-olefin is a consequence of the preponderance of *anti*-elimination.

Here we considered a series of substrates reacting under identical



R	R′
Me	Pr ●
Et	Et ○
Bu	Bu △

Refs: Bailey, *Thesis*, U. of Rochester (1969); Pánková, Závada and Sicher, *Chem. Commun.* 1142 (1968); Bailey and Saunders, *ibid.*, in press.

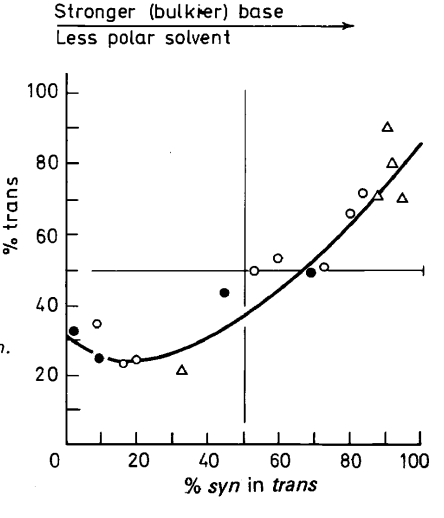


Figure 2

conditions. An analogous correlation may be shown to exist for reactions using different base–solvent systems. *Figure 2* shows such a correlation, for three substrates (again 'onium bases) reacting with primary, secondary and tertiary alkoxides in the corresponding alcohols or in aprotic solvents (benzene or DMSO) or under pyrolytic conditions.

As can be seen in *Figure 2*, a high proportion of *trans*-olefin in the elimination product is due to a great contribution of *syn*-elimination; a low proportion of *trans*-olefin to a great contribution of *anti*-elimination. This is shown very clearly by the fact that all the points fall practically exclusively into the lower left and the upper right quadrants.

It is in this way that we have to account for the—at the time—puzzling finding that the change in *trans–cis* isomer composition with change in base and solvent in the elimination of 5-nonyl and cyclodecyltrimethylammonium bases go in parallel, even though the *trans–cis* order of stabilities of the olefins produced from the two substrates is not parallel (*Table 1*). The parallel shift towards a lesser proportion of *trans*-olefin simply reflects the decreasing tendency towards *syn*-elimination as we go from the stronger base and relatively non-polar solvent towards weaker base and more polar solvent.

I might mention in passing that the discovery of these correlations also has some practical, that is preparative, significance. Since the way in which the percentage of *syn*- and *anti*-elimination is affected by factors such as base, solvent and leaving groups is now fairly well known, in suitable cases it is possible, by proper choice of these variables, to prepare mixtures highly enriched in the one or the other isomer. This is rather strikingly demonstrated by the following example[14]. Cyclodecyl chloride with dicyclohexylamide in hexane (strong base, non-polar solvent) gives practically pure *trans*-cyclodecene, presumably by *syn*-elimination, while with *tert*-butoxide in DMSO (polar solvent) it gives predominantly *cis*-cyclodecene, presumably by *anti*-elimination.

By the discovery of the *syn-anti*-elimination dichotomy we have thus, at least in part, been able to account for some puzzling trends in *trans–cis* isomer composition in bimolecular elimination reactions. We realize, of course, that by having done so, we have simultaneously raised a new question, i.e. given that the observed trends in *trans–cis* isomer composition may be ascribed to the tendency for stereoselectivity of the two elimination modes, how then do we account for this stereoselectivity, that is, for the fact that *syn*-elimination gives preferentially the *trans*-olefin and that *anti*-elimination—frequently—gives preferentially the *cis*-olefin? It is to this problem that we must now turn our attention.

We begin by considering the nature of the steric effects which may operate in these processes. Two findings may be of significance in this context. The first concerns the fact that eliminations leading to medium ring cycloalkenes possess an exceptionally strong tendency towards *syn*-elimination and, hence, *trans*-olefin formation, as is evident from the data given in *Table 1*. The second relevant finding is the already noted dependence of the steric course of eliminations leading to olefins of the type $R \cdot CH{=}CH \cdot R'$ on alkyl structure and, in particular, on the nature of the group R.

With regard to the first of these observations, we considered some time ago the following conformational arguments, using 7-substituted derivatives

of 1,1,4,4-tetramethylcyclodecane as suitable models. The methyl groups in this system serve as conformation holding groups, the most probable conformation being that in which all the four methyl groups occupy the energetically favourable extra-annular positions (*Figure 3*). Elimination in this system can give rise to four olefins, i.e. two-position isomeric pairs of *trans–cis* isomers. The reaction of the trimethylammonium base (*Figure 3*)

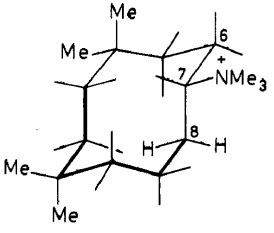


Figure 3

with methoxide in methanol—conditions generally very unfavourable for *syn*-elimination—gave 49 per cent *trans*-7,8-ene, 6 per cent *cis*-7,8-ene and 36 per cent *trans*-6,7-ene, 9 per cent *cis*-6,7-ene. It could be shown by suitable deuterium labelling that the *trans*-7,8-ene was formed by *syn*-elimination, the *cis*-7,8-ene by *anti*-elimination. Consider the two alternative paths which can lead to the *trans*-7,8-cyclodecene; clearly, *anti*-elimination involves reaction of the intra-annular hydrogen, *syn*-elimination reaction of the extra-annular hydrogen. The intra-annular hydrogen is located in the overcrowded inside of the ring and the approach of a molecule of the base to it can well be imagined to be hindered; by contrast, the extra-annular hydrogen sticks out of the ring and is thus open to attack by the base. The point can be made that these features are responsible for the observed high proportion of *syn*-elimination in this reaction. Steric effects of the same magnitude can hardly be expected in simple open-chain systems, and this could explain why the preference of *syn*- over *anti*-elimination is more pronounced in the medium rings than in the large ring or open-chain compounds.

We now come to consider the second of the stereochemically relevant findings, namely the dependence of the steric course on the alkyl structure of the substrate, in particular on the nature of the alkyl group R. The following interpretation has been proposed by Bailey and Saunders[10]. In the preferred conformation of an open-chain quaternary 'onium base of the type $R \cdot CH\overset{+}{N}Me_3CH_2 \cdot R'$ set up for *anti*-elimination (*Figure 4*) the alkyl chain R′ is *anti*planar to the sterically dominating 'onium group, irrespective of whether the reaction leads to the *trans*- or the *cis*-olefin. The attack by the base on the *anti*planar hydrogen to be eliminated may be subject to steric hindrance through the group R′ in a way reminiscent of the situation of an intra-annular hydrogen in the cyclodecyl derivatives just considered. The ease of *anti*-elimination should thus depend, *inter alia*, on the steric characteristics of this group. When R′ = H, i.e. R = Me, steric hindrance towards the approach of the base should be small and *anti*-elimination

should take place smoothly, as indeed it does. When R′ = Pr (i.e. R = Bu), hindrance should be larger, and hence the contribution of *anti*-elimination smaller, and this is again the case. Finally, when R′ = *t*-Bu (i.e. R = neopent) steric hindrance should be massive and, in fact, the contribution of *anti*-elimination in this case is negligible.

In summary, the high *syn-anti* ratio, both in the case of the medium ring and certain open-chain derivatives, is here ascribed to steric hindrance of approach of base to the *anti*planar hydrogen. In this view, *syn*-elimination is still regarded as a kind of a 'substitute' process which operates when *anti*-elimination is impeded by some specific steric feature. This feature can be torsional constraint, as in the case of the exo-nor-bornyl derivatives[6] which I mentioned earlier, or it can be hindrance towards the approach of base to the *anti*planar hydrogen†.

This view implies that the trend in *syn-anti* ratios is determined by variations in the rates of *anti*-elimination, the rates of *syn*-elimination not being sensitive to the steric factors in question. We are somewhat sceptical as to whether this is a completely satisfactory description of the actual situation. Clearly, rate ratios alone cannot decide this and rates for the individual processes are required. These are available, for a variety of elimination conditions, for reactions leading to cycloalkenes[9a, c, g, h]. In all cases, these data show that *anti*-elimination in the medium rings is indeed slower than in the large rings or open-chain derivatives, in accordance with the conformational analysis here presented; at the same time, however, the rate data show that *syn*-elimination in the medium rings is substantially accelerated relative to other systems.

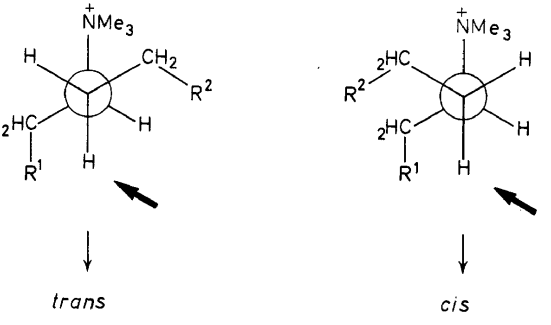
Having now considered the possible operation of steric effects we may approach the question of the stereoselectivity of the alternative elimination modes.

A plausible explanation, in conformational terms, for the observed tendency of the *syn*-elimination component to lead preferentially to *trans*-olefin can readily be provided. Since *syn*-elimination, by definition, involves a transition state with a near to eclipsed arrangement about the C_α and C_β carbon atoms, eclipsing effects between R and R′ will here be of particular importance. The fact that these interactions are clearly smaller in the activated complex leading to the *trans*-isomer could account for the fact that in *syn*-elimination this isomer is formed in a predominant amount.

It is much less simple to give a corresponding explanation for the complementary observation, i.e. that the *anti*-elimination component leads preferentially to the *cis*-olefin. Bailey and Saunders[10] claim that this stereoselectivity can be explained on the basis of the model shown in *Figure 4*. They suggest that in the *anti*-elimination transition state leading to the *trans*-olefin, the *anti*planar hydrogen on C_β is, so to speak, shielded on both sides, by R^1 on the one and by R^2 on the other. In the corresponding transition state leading to the *cis*-olefin the hydrogen on C_β is again shielded by R^1 but—if 'non-linear approach' of the base is possible—it should be open to

† Steric hindrance of access of base to the hydrogen to be eliminated has already been claimed as an important feature determining the outcome of elimination reactions, in particular by H. C. Brown[15] in conjunction with the Hofmann–Saytzeff orientation problem.

anti



cf.: Bailey and Saunders, *Chem. Commun.* 1598 (1968)

Figure 4

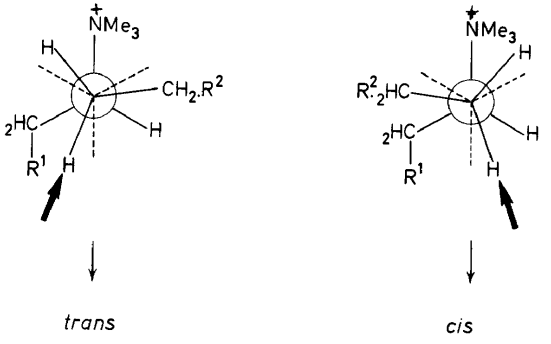


Figure 5

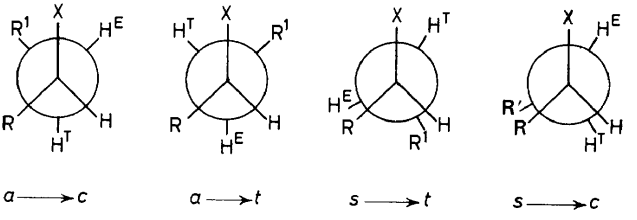


Figure 6

attack from the other side, the consequence of this being that by *anti*-elimination *cis*-olefin should form faster than *trans*.

A more detailed conformational analysis of the situation leads to a somewhat modified picture of the transition state which may make this purely steric interpretation more acceptable†. Additionally, in this analysis (*Figure 5*) we take into account the dominating *gauche* interaction in the system, i.e. that between C_β—R^2 and C_α—NMe_3 and the fact that this interaction can, in part, be relieved by making the dihedral angle between the two bonds somewhat greater than 60°. It is true that this change necessarily involves a corresponding deviation from *anti*-periplanarity but it can be argued that, since one is presumably dealing with a transition state with relatively little double-bond development, the *anti*-periplanarity requirements should not be particularly strict anyway. Now, as is evident from *Figure 5*, this rotation has opposite consequences in the transition states leading to the *trans*- and the *cis*-olefins respectively; in the former, this rotation moves the hydrogen further into the congested environment about C_α—CH_2—R^1, in the latter the rotation moves the hydrogen out of this congested environment: the hydrogen in the arrangement leading to the *cis*-olefin is thus more open to attack by the base.

We have suggested[9m] an alternative interpretation of the stereoselectivity of the two elimination modes, based on the following arguments. An inspection of the four alternative rotameric arrangements (*Figure 6*), corresponding to the *anti*- and *syn*-elimination transition states, shows that both the arrangements $a \rightarrow c$ and $s \rightarrow t$, through which the greatest part of the dichotomous elimination process proceeds, involve reaction of the hydrogen labelled H^T, whereas both the unreactive arrangements, $a \rightarrow t$ and $s \rightarrow c$, involve removal of the other hydrogen, H^E. This may, of course, be mere coincidence; however, it is clear that the two hydrogens on C_β are non-identical (diastereotopic) and one may argue that hence they could differ in reactivity, both as a result of conformational factors as well as intrinsically. If H^T is indeed more reactive than H^E, then this fact would result in *syn*-elimination leading preferentially to *trans*-olefin and *anti*-elimination to *cis*-olefin. Differences in the reactivity of diastereotopic hydrogens have been noted previously[16].

I should like to express my sincerest gratitude to my co-workers whose skill, ingenuity and perseverance enabled us to carry out the studies of which I have given a partial survey. They are, in alphabetical order, Drs Magdalena Pánková, Miroslav Svoboda and Jiří Závada.

I would also like to acknowledge my warmest appreciation of the support and encouragement which I received over many years from my teacher and mentor Professor František Šorm, Director of the Institute of Organic Chemistry and Biochemistry of the Czechoslovak Academy of Sciences, Prague, where the work which I discussed has been performed.

Last but not least I should like to thank Professors Hans Schmid, André Dreiding and my other colleagues at the Chemical Institute of the University of Zürich whose generous hospitality I have enjoyed during the past academic year.

† These ideas have been suggested to us in discussion by Dr Hugh Felkin, Gif-sur-Yvette.

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