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CONCERNING DRIVING FORCES FOR β-ELIMINATION REACTIONS

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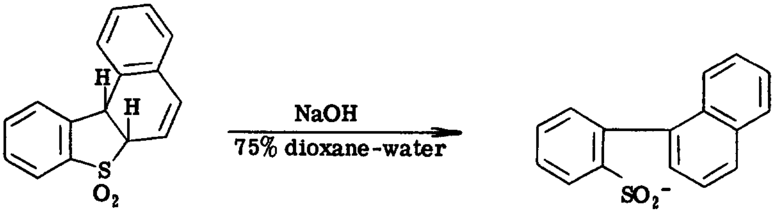
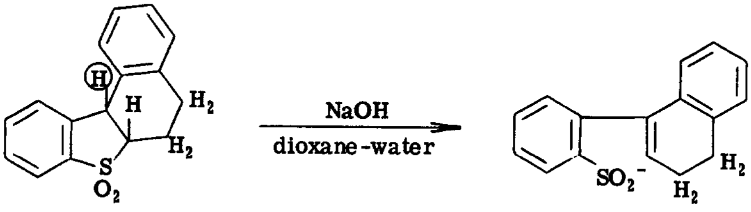
The idea of Evans and Polanyi (1) that part of the energy released in bond formation can be utilized in (simultaneous) bond breaking so as to provide a driving force for chemical reactions has been widely accepted. There is qualitative evidence to support this idea in β-eliminations from comparisons of reactions to form C=O *vs* C=C double bonds. Eliminations to form the stronger (by *ca* 30 kcal/mole) C=O bonds by attack of base on H-O-C-Y systems can easily eject strongly basic Y^- anions, such as CN^-, $SO_3^=$, HO^-, $CH_3COCH_2^-$, $C_6H_5CO^-$, etc. (reversals of carbonyl addition reactions), whereas eliminations to form C=C bonds cannot. In eliminations to form C=O bonds one bond is broken and one is formed in the rate-limiting step, which is the ionization of Y^- from the Y-C-O^- anion. On the other hand, two bonds are formed and two bonds are broken simultaneously in the base-initiated concerted eliminations with H-C-C-Y systems. For reasons given elsewhere (2) we have become skeptical of the significance and, in many instances, the very existence of concerted reactions involving the formation and breaking of as many as four bonds. If we are to accept concerted mechanisms for such complex reactions it is important to establish the presence of a driving force wherein bond making aids bond breaking. Otherwise, the question of whether or not a reaction is "concerted" is reduced to one of mere semantics, since it will be difficult to decide whether bonds are breaking simultaneously or *almost* simultaneously.

Early studies on benzenehexachloride isomers appeared to establish a strong driving force (9.6 to 12.5 kcal/mole) favoring one-stage anti eliminations over two-stage syn eliminations (3). Investigations on other systems have failed to support this view, however, and examples where syn eliminations occur as readily, or moreso, than anti eliminations are not uncommon (4). Eliminations wherein the C=C bond is formed as part of an aromatic system should provide a strong driving force for one-stage eliminations. But studies of meso-dihydroanthracene derivatives have shown that such aromatizing eliminations probably follow a two-stage pathway (5). We wish to report the results of a comparison of an aromatizing elimination with sulfone 1 and a nonaromatizing elimination with its dihydro derivative 2.



1

21 kcal/mole of resonance energy released



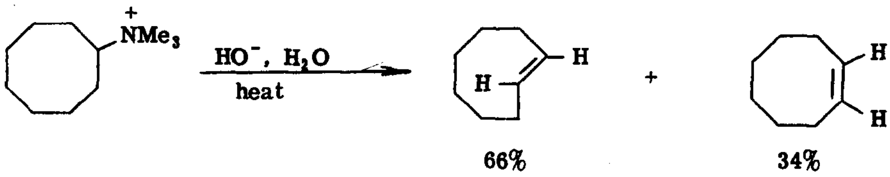
2

4 kcal/mole of resonance energy released

The mechanism for the nonaromatizing elimination from 2 was established as pre-equilibrium carbanion by the observation of complete exchange of the β-hydrogen (circled in the formula) under conditions where little or no elimination occurred. No detectable amount of exchange of the β-proton occurred during the aromatizing elimination from 1, but the rate of elimination from 1 was only twice as fast, under comparable conditions, as was deuterium exchange from 2. We conclude that the aromatizing elimination is occurring by a two-stage, carbanion mechanism. The two-fold faster rate of elimination than exchange can be accounted for by the inductive effect of the C=C bond and/or by less internal return from a hydrogen-bonded carbanion intermediate.

The results with *1* show that even a potential driving force of *ca* 17 kcal/mole is insufficient to make the H-C and C-Y bonds break in concert. Instead, the reaction follows the principle of least molecular deformation (6), i.e., *that mechanism will be preferred which demands the least structural reorganization*. If we consider β-elimination reactions as a whole, that is, those to form C=O, C=N, N=N, N=O, C≡N, C≡C, and N≡N bonds, as well those to form C=C bonds, there is no question but what most β-eliminations abide by this principle. The basis for this conclusion is that β-eliminations with H-O-C-Y, H-N-C-Y, H-O-N-Y, H-N-O-Y, H-N-N-Y, H-N=N-Y, and H-N=C-Y systems, which are legion, must nearly always follow two-stage mechanisms in view of the rapidity of cleavage of H-O and H-N bonds by bases (7). Of the remaining β-eliminations, wherein H-C_β bonds are broken, activation at the β-carbon atom by an electron-withdrawing group will often cause the reaction to adopt a (two-stage) carbanion mechanism (8), while activation at the α-carbon atom by an electron-releasing group (in H-C_β—C_α-Y systems) will often cause the reaction to follow a (two-stage) E1 mechanism. In the latter systems in protic solvents a second-order component can usually be introduced into the rate expression at high lyate ion concentrations, but in our opinion this is more likely to be caused by attack of lyate ion on an ion pair (9, 10) than on the covalent substrate (i.e., a two-stage, rather than a one-stage mechanism). A relatively small number of β-eliminations remain for which the one-stage, concerted mechanism can operate. We conclude that this mechanism is rare and can have but little driving force.

If the formation of even strongly stabilized C=C bonds in β-eliminations can often provide no assistance for H-C bond breaking because a two-stage mechanism is operative, as the present results suggest, it follows as a corollary that we can expect strongly destabilized C=C bonds to be formed by two-stage mechanisms. A striking example is the *preferential* formation of *trans*-cycloöctene (66% trans *vs* 34% cis) by Hofmann elimination from cycloöctyltrimethylammonium hydroxide (11); *trans*-cycloöctene is known to be less stable than its cis isomer by 9.3 kcal/mole (12). Other highly strained alkenes formed by Hofmann eliminations



include bicyclo[3.3.1]non-1-ene (13) and 1,3-diethylcyclopropene (14). It seems likely, then, that these reactions occur by two-stage rather than one-stage mechanisms.

We conclude that the available evidence offers no support for a driving force by which the formation of two bonds can aid the breaking of two bonds in base-initiated β-eliminations, and that mechanisms for these and similar reactions wherein as many as four bonds are represented as being formed and broken in concert are suspect.

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