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CONCERNING DRIVING FORCES FOR β-ELIMINATION REACTIONS

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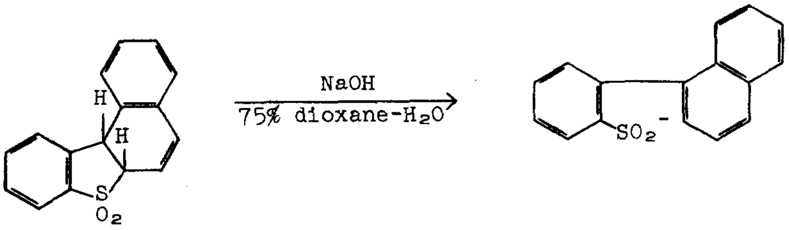
In a recent paper under the above title, Bordwell, Happer and Cooper[1] present evidence suggesting that base-promoted elimination from 1 to give 2 proceeds via the ElcB mechanism.



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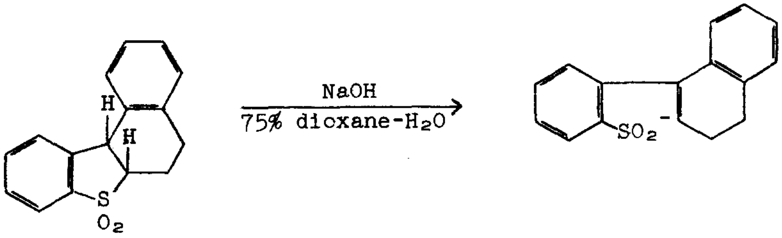
Though no exchange of the β-hydrogen was observed, the elimination was only twice as fast as the rapid exchange which accompanied the elimination 3 → 4, indicating little or no extra driving force for 1 → 2. They emphasize that 1 → 2 apparently fails to utilize the E2 pathway, even though a 21-kcal/mole gain in resonance energy due to the formation of a new aromatic ring in 2 (compared to a



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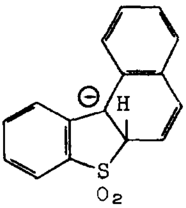
gain of only 4 kcal/mole in 3 → 4) might have been expected to result in a substantially lowered activation energy for the E2 process. They present these observations as strong support for their contention that driving forces due to concerted β-C-H and α-C-X cleavage must generally be so low that the E2 mechanism is seldom utilized.

These arguments rest upon the contention that 1 → 2 is an exceptionally favorable case for the E2 mechanism. To decide whether the E2 is favored over the E1cB mechanism by the resonance-energy gain, however, one must compare the gain from 1 to 2 in the E2 with the gain from 1 to 5 (the carbanion intermediate) in the E1cB process. Experimental resonance energies are not available, but one can approximate the necessary figures with data on closely analogous systems from simple HMO (Hückel Molecular Orbital) calculations. The process 1 → 2 converts a styrene system (RE 2.42β)[2] to a naphthalene system (RE 3.68β)[3] for a gain of 1.26β. The process 1 → 5 converts a diphenylmethane system to a diphenylmethyl anion for a 1.30β gain in resonance energy[4] (in this approximation, the same gain is expected for 3 → 6). By this criterion, the difference in resonance-energy gain between 1 → 2 and 1 → 5 is small, and slightly in favor of 1 → 5!



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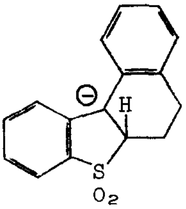

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Objections could be made to some aspects of these comparisons. The HMO method overestimates the resonance energy of styrene, which means that our figure for the 1 → 2 conversion should be somewhat higher. Similarly, electron repulsion in the diphenylmethyl anion is expected to decrease its stabilization. It is still clear, however, that the resonance-energy gains for 1 → 2 and 1 → 5 cannot differ markedly.

It should be emphasized that these resonance-energy gains will be reflected only partially in the transition states. An E2 reaction with a poor leaving group such as arylsulfonyl[5] would, in fact, be expected to have a transition state with a great deal of carbanion character and relatively little double-bond character,[6] so that only a small fraction of the resonance-energy gain in the product might contribute to transition-state stability. The fraction of the resonance stabilization of the anion which appears in the transition state for its formation would probably be larger. A transition state leading to a high-energy intermediate will in general resemble the intermediate fairly closely.[7] Incidentally, there does seem to be one noticeable effect of the aromatization occurring in the formation of **2**. The lack of exchange during the elimination reaction of **1** probably arises from facilitation of **5** → **2** (relative to **6** → **4**) by the resonance stabilization of **2**.

There are structural factors other than those producing the resonance effects, which clearly dispose **1** toward the E1cB mechanism. Arylsulfonyl is a poor leaving group in elimination reactions,[5] and poor leaving groups favor the E1cB mechanism.[8] The ring system of **1** also makes it very difficult for the β-C-H and α-C-S bonds to attain the coplanarity required if a concerted process is to gain energetic advantage over a non-concerted one.[9] Thus, an E2 mechanism for **1** → **2** would be expected to have a transition state with little double-bond character. By contrast, the two benzene rings in **5** are held by the ring system in very favorable orientations for maximum overlap with the p-orbital on the β-carbon.

From the above discussion, it is clear that there is no good reason to expect the E2 to be favored over the E1cB mechanism for **1** → **2**. The apparent utilization of the E1cB mechanism by this reaction, then, provides no basis for the contention that the E2 process is rare, or that it generally has little driving force. There is, as yet, no convincing experimental evidence that the principle of least motion[10] militates to any serious extent against concerted elimination reactions. A great deal of evidence does exist that many elimination reactions utilize the E2 pathway, and that substantial driving forces can be associated with it. For example, leaving-group effects,[11,12] leaving-group isotope effects,[13] and β-deuterium isotope effects[14] demonstrate that both the α-C-X and β-C-H bonds are partially but not completely broken in the transition states of typical reactions under E2 conditions. A more thorough discussion of the evidence is beyond the scope of this paper.

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