The structural requirement in vinylpyrroles and the reaction condition for the formation of 3a,6-dihydroindole compounds are currently under investigation in this laboratory.

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(8) Other spectral data: **2b**; IR (neat) 3050 w, 2975 w, 2825 w, 1730 vs, 1620 m, 1445 ms, 1300 s, 1160 s, 1010 s, 820 ms cm^{-1}; mass spectrum, m/e (%) 263 (5, M$^+$), 261 (12), 232 (20), 204 (52), 203 (100), 202 (98), 188 (24). **3b**; IR (neat) 3030 w, 2975 w, 2820 w, 1748 s, 1685 s, 1612 ms, 1450 ms, 1275 ms, 1035 m, 970 s, 800 ms cm^{-1}; mass spectrum, m/e (%) 263 (24, M$^+$), 232 (96), 204 (100), 203 (94), 172 (21), 145 (15).

Sigmatropic Hydrogen Rearrangements in the Gas-Phase Decarboxylation and Isomerization of But-3-enoic Acid

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Sigmatropic rearrangements have attracted considerable interest in recent years, especially in connection with orbital symmetry rules.[1] A number of quantitative studies at both the semiempirical[2] and *ab initio*[3] levels of MO calculations using simple model compounds have been reported. The calculated barriers for the rearrangements have shown that 1,3-hydrogen shifts are in general considerably higher than 1,5-H shifts[3d] in agreement with expectations based on orbital-symmetry considerations.

The gas-phase decarboxylation and isomerization of but-3-enoic acid (I) provide a very interesting and convenient example in which various types of such sigmatropic hydrogen rearrangements are involved. Experimental studies on these processes[4] have led to the following conclusions: (a) direct interconversion of the acid (I) and its isomer crotonic acid (III) is a negligibly slow process, proceeding only *via* the intermediacy of the enolic form (IV) and isocrotonic acid (II); (b) direct decarboxylation occurs only from (I).

In this work we report the MO theoretical thermodynamic energy profile obtained for the complex system, scheme 1, where the specific types of process involved in each transition state (TS) are shown.

All geometries were optimized and heats of formation were calculated using MINDO/3 RHF method.[5] Transition state geometries were deduced by fixing the forming and breaking
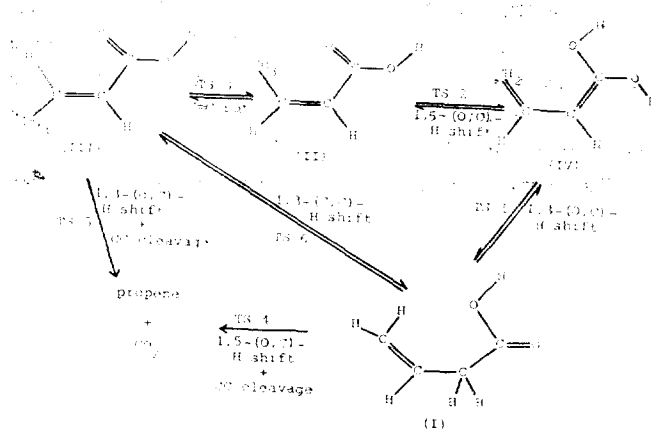
Scheme 1.

bonds at the appropriate lengths varying in steps of 0.005Å and minimizing the energy of the system with respect to the remaining variables. Smoothed plots were obtained by quadratic interpolation.

All the TS (1-6), except the TS3 where a double-bond rotation is involved, had some types of sigmatropic hydrogen rearrangements.

In view of the considerable barrier height differences involved according to the terminal atoms to which the moving hydrogen is simultaneously bonded,[3d] introduction of a notation specifically designating the two atoms is convenient;
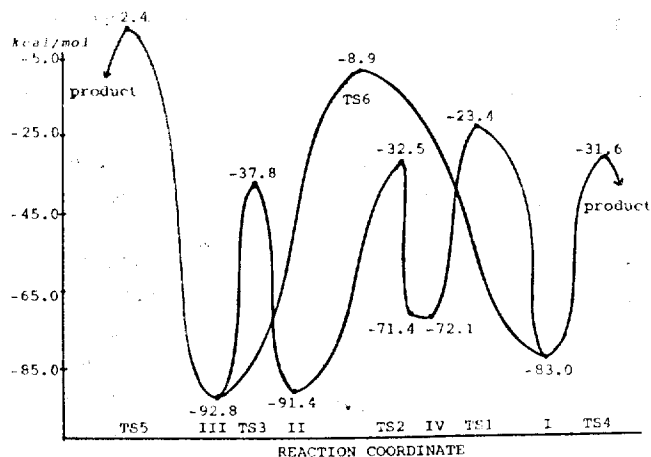
Figure. 1. Thermodynamic energy profile for the complex system shown in Scheme 1.

1,3-(C,C)-H and 1,5-(O,C)-H shifts denote 1,3-H and 1,5-H shifts between two C atoms and between O and C atoms respectively.

Following are the notable features of our results: (i) The TS1 and TS6 proceed *via* the simple 1, 3-H shift but the former involves a 1,3-(O,C)-H whereas the latter a 1,3-(C,C)-H type. As it has been shown by more sophisticated calculations on simple models,[3d] the 1,3-(C, C)-H shift has a considerably higher energy barrier compared with the 1,3-(O, C)-H shift. (ii) The TS5 is also a 1,3-(O,C)-H rearrangement process but here the H atom being transferred is required to take the place of the leaving carbon atom which is breaking away in a synchronous manner. Obviously this process of synchronous bond cleavage and formation at the same direction should be a high-energy barrier process as we found. (iii) In the TS2 and TS4,[6] the same type of H shifts are involved, a 1,5-(O,C)-H shift. However in the latter, a synchronous bond cleavage occurs away from the reaction center; this seems to interfer in no way with the moving H atom at the reaction center, if not make it facile.

The overall thermodynamic energy profile is presented in the Figure. Reference to this figure shows that our MINDO/3 results provide a clear vindication of the feasibility of the experimental conclusions[4]: (a) Direct interconversion of (I) and (III) should be a slow process due to the high-energy barrier involved in a 1,3-(C,C)-H shift. This path can be avoided by alleviating to the successive low-energy barrier processes, 1, 3-(O,C)-H, 1, 5-(O,C)-H and double-bond rotation, of the TS1, 2 and 3, respectively. (b) Direct decarboxylation from other isomers, (II)-(IV), involves a costly process of 1, 3-(O,C)-H shift coupled with a synchronous bond cleavage and formation at the same direction in the TS5.

Full details will be reported elsewhere.

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