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ON THE α-KETOL AND RELATED REARRANGEMENTS

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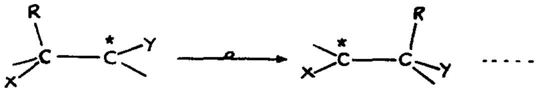
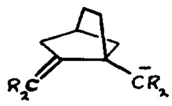
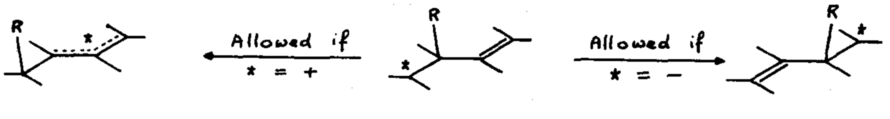
Concerted [1,2]-shifts occur very easily in carbonium ions, (1), $X = Y = H$ or CR_3, $* = +$,[1] but not in radicals (1), $* = \cdot$, or carbanions, (1), $* = -$. This is readily explained[2] by considering the 3-centre orbitals of the transition state. However concerted [1,2]-shifts with retention of configuration in the migrating group do also occur readily in a number of other situations where X and Y are heteroatoms possessing lone-pair electrons. The most familiar examples[3] are rearrangements of tertiary α-ketols in acid, (1), $X = Y = OH$, $* = +$, or base, $X = Y = O^-$, $* = +$, and the benzilic acid rearrangement. The molecular orbitals in the transition state for rearrangements of this type may be derived by interaction of the three centre orbitals, $\phi_1 - \phi_3$, with the A' and A'' combination orbitals, ω_1 and ω_2, derived from the lone-pair orbitals on X and Y (Fig. 1). Three bonding orbitals, $\psi_1 - \psi_3$, are then obtained for all likely relative energies for $\phi_1 - \phi_3$ on the one hand and ω_1 and ω_2 on the other. A low energy transition state is therefore available for a whole spectrum of situations with changes in X and Y having only a second order effect on the ease of rearrangement. This is observed in practice, examples of rearrangements being known where $X = Y = OH$[3] or OR;[4] $X = Y = O^-$;[3] and $X = NHR$, $Y = O^-$.[5] The case where $X = Y = R_2C^-$ is interesting but has not yet been observed; but-3-enyl anions undergo an alternative rearrangement *via* cyclopropylcarbinyl anions.[6] An interesting system which should avoid this is (2).



..... (1)



(2)



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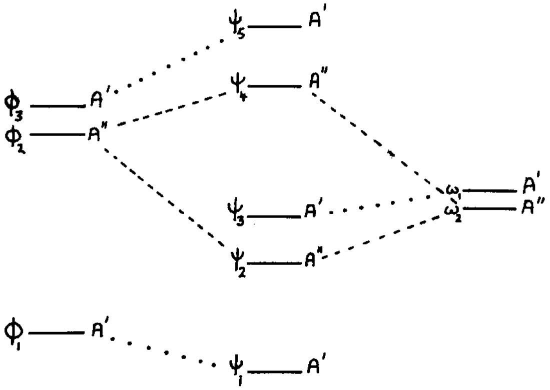

Figure 1

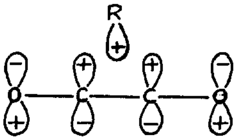

Figure 2

The transition state for the α-ketol rearrangement may alternatively be formulated[7] as a combination of a carbon radical and a semidione radical anion. The half-occupied orbitals of these combine as in Fig. 2, leading to strong bonding. Reaction through this transition state should occur readily. On this simple analysis alkyl shift to carbon is allowed but shift to oxygen to give an enolate anion is forbidden. Similar considerations apply to a but-3-enyl anion but in the corresponding cation a $C_2 \rightarrow C_1$ shift is allowed but a $C_2 \rightarrow C_3$ shift is forbidden (3). Notice that a [1,2]-shift (with retention) is always toward the more electron-deficient centre. This appears to be generally true for concerted [n,m]-shifts with retention where $n + m = 4n - 1$; the converse applies when $n + m = 4n + 1$.

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