A Molecular Orbital Study of the 1,2-Migration Reaction of Substituted Cyclohexadienyl Radicals

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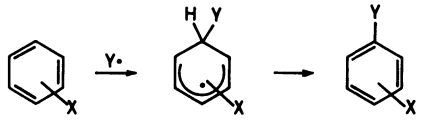
Synopsis. The 1,2-migration reaction of cyclohexadienyl radicals was examined on the basis of an open-shell restricted self-consistent field (SCF) MINDO/3 calculation. For the NO_2- and OH-substituted cyclohexadienyl radicals, the 6-substituted isomers (**1**; X=H, Y=NO_2 or OH) were calculated to be the least stable and apt to undergo a 1,2-hydrogen shift. The electron-withdrawing groups were predicted to have high migratory aptitude.

The cyclohexadienyl radical, **1**, is considered to be an intermediate in the radical aromatic substitution reaction.[1] The isomer distribution of the reaction products in the radical substitution reaction of substituted benzenes is affected by the stabilities of isomeric cyclohexadienyl radicals.[2]



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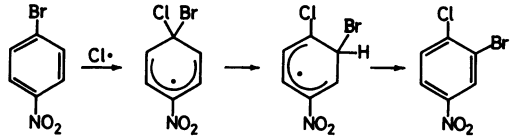
Another factor which affects the product distribution is the 1,2-migration reaction of the intermediate radical to give another cyclohexadienyl radical. *p*-Bromonitrobenzene reacts with the Cl radical to give 2-bromo-1-chloro-4-nitrobenzene.[3]



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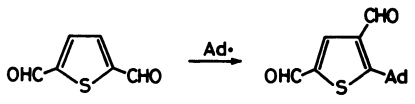
This suggests that the intermediate ipso radical, **2**, rearranges to **3** by the bromo 1,2-shift. The reaction of the adamantyl radical with **4** to give **5** also suggests the 1,2-shift of the CHO group in the intermediate ipso radical.[4]



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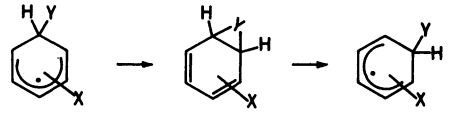
In this note the 1,2-migration reaction of cyclohexadienyl radicals is examined theoretically. The open-shell restricted SCF method[5] with MINDO/3 approximation[6] was applied to substituted cyclohexadienyl radicals, **1**, and to the bridged radicals, **6**, which are the transition states of the 1,2-migration reaction.



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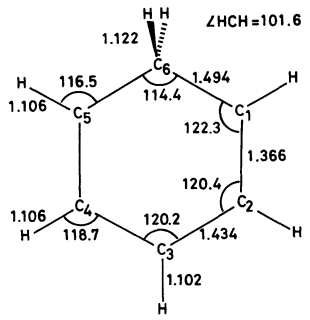
Results and Discussion

1,2-Shift of Cyclohexadienyl Radical. The structures of unsubstituted cyclohexadienyl radical, **1** (X=Y=H), and the transition state bridged radical, **6** (X=Y=H), were optimized by assuming a planar carbon skeleton,[7] C_{2v} symmetry for **1** and C_s symmetry for **6**. The structures obtained are shown in Fig. 1. Structure **II** is that of the transition state, since a small deviation of the migrating H atom out of the C_s symmetry plane results in energy lowering. The schematic representation of the singly-occupied molecular orbitals (SOMO) of **I** and **II** are shown in Fig. 2. The energy difference between **I** and **II**, 156 kJ/mol, is the activation energy of the 1,2-hydrogen shift of **I**.

Substituent Effect. The substituent effect on the 1,2-hydrogen shift was examined by using the NO_2 and OH groups as the substituent. The **I** and **II** structures were employed and partial optimization was performed for the substituent structure. The calculated heats of formation are listed in Table 1. The activation energies are shown in Fig. 3. For the NO_2- and OH-substituted cyclohexadienyl radicals, the 3-substituted isomer was predicted to be the most stable, while the 6-substituted isomer was the least stable. The stability of the 3-substituted isomer may be understood from the interaction between the SOMO of **I** (Fig. 2-a) and the substituent. The energy differences among the transition states are small in comparison with those among the reactant isomers, suggesting that the liability of the 1,2-shift is determined by the instability of the reactant radical.

Migratory Aptitude. The migratory ability of migration groups was estimated from the energy differences between **1** (X=H) and **6** (X=H) for Y=CH_3, H, NO_2, and CHO. The structure of **6** was optimized for each migration group. The calculated activation energies are listed in Table 2. The activation energies for the 1,2-shift of electron-withdrawing groups (NO_2 and CHO) are smaller than those for the H and CH_3 groups. This trend is well explained by the stability of the SOMO at the transition state. In the H shift, the unpaired electron localizes on the six-membered carbon ring (Fig. 2-b). On the other hand, in the case of the CHO shift, the unpaired electron delocalizes into the antibonding π-orbital of the carbonyl group (Fig. 4); this delocalization lowers the SOMO energy. The easy transformation of the electron-withdrawing



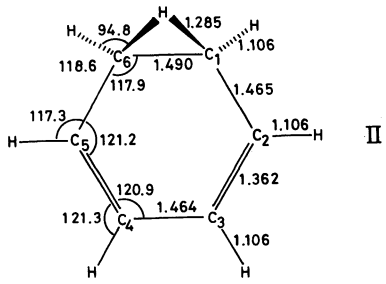


Fig. 1. The optimized structures of cyclohexadienyl radical, I, and the transition state of the 1,2-hydrogen shift, II. Bond lengths are in A and bond angles in degrees.

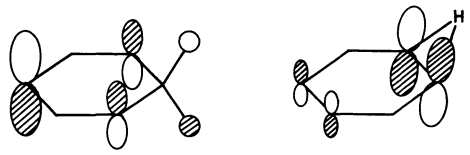


Fig. 2. Schematic representations of (a) SOMO of I and (b) SOMO of II.

group, as is observed in the **4**→**5** reaction, is caused by the stabilization of the transition state due to the delocalization of the unpaired electron into the migrating group.

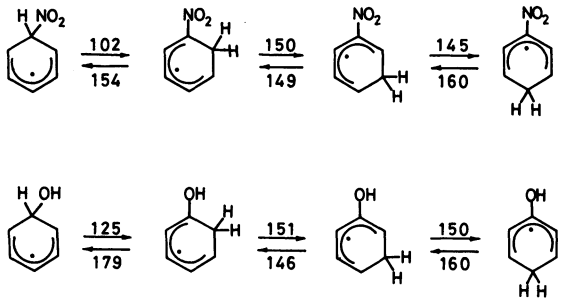


Fig. 3. Activation energies for the 1,2-hydrogen migration reactions of the NO_2 or OH substituted cyclohexadienyl radicals. Values are in kJ/mol.

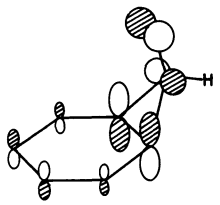


Fig. 4. Schematic representation of SOMO of the transition state of the 1,2-CHO shift.

Table 1. Calculated heats of formation (KJ/mol) of NO_2 and OH substituted cyclohexadienyl radicals and of the transition state for the 1, 2-hydrogen shift

Cyclohexadienyl[a]			
1-NO_2	124	1-OH	−59
2-NO_2	125	2-OH	−54
3-NO_2	110	3-OH	−64
6-NO_2	176	6-OH	−5
Transition state[b]			
1-NO_2	278	1-OH	120
2-NO_2	274	2-OH	92
3-NO_2	270	3-OH	96

a) Numbering is shown in I of Fig. 1. b) Numbering is shown in II of Fig. 1.

Table 2. Calculated activation energies(KJ/mol) for the 1,2-shift

Migration group	Activation energy
CH_3	181
H	156
NO_2	96
CHO	66

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