

## Full Articles

### Mechanisms of circumambulatory rearrangements of 5-halogeno-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes\*

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Possible paths of halogen atom migration in 5-halogeno-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes were studied using the density functional theory. The calculations revealed preferential 1,5- (in comparison with 1,3-) sigmatropic shifts of halogen atoms along the perimeter of the five-membered ring with the energy barriers  $\Delta E^{\ddagger}_{ZPE} = 42.9, 26.9, 19.8,$  and  $15.4 \text{ kcal mol}^{-1}$  for the fluoro-, chloro-, bromo-, and iodosubstituted derivatives, respectively. The calculated charges of halogen atoms in the structures of transition states for 1,5-shifts change from negative for the fluorine atom to positive for the iodine atom ( $-0.356$  (F),  $0.019$  (Cl),  $0.052$  (Br),  $0.184 e$  (I)). The migration capacity increases in the order  $F < Cl < Br < I$  with an increase in the atomic radius of halogen.

**Key words:** halocyclopentadienes; fluoro-, chloro-, bromo-, and iodopentamethoxycarbonylcyclopentadienes; rearrangements; density functional theory.

Halocyclopentadienes form one of the most important classes of precursors of cyclopentadienyl compounds and their metal complexes.<sup>1,2</sup> Intramolecular migrations of halogen atoms along the perimeter of the five-membered ring result in the formation of several isomers in non-

degenerate systems and can affect the direction of subsequent reactions.<sup>3–6</sup> There are known reactions of hexabromocyclopentadiene accompanied by the intermolecular transfer of the bromine atom to the activated nucleophilic carbon atoms. This reagent selectively brominates aromatic amines and alcohols, furans, thiophenes, and ketones with activated  $\alpha$ -carbon atoms.<sup>7</sup> 5-Halosubstituted pentamethoxycarbonylcyclopentadienes also exhibit the

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properties of halogenating agents due to the ability of the cyclopentadienide anion stabilized by five electron-acceptor methoxycarbonyl substituents to act as a readily leaving group.<sup>8</sup>

A restricted number of examples is described for intramolecular rearrangements of halocyclopentadienes caused by halogen atom migration over the five-membered carbocycle. We have earlier<sup>9–14</sup> detected by dynamic <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy intramolecular migrations of chlorine and bromine atoms along the perimeter of rings of pentamethoxycarbonyl- and alkyltetramethoxycarbonylcyclopentadienes (Alk = Me, Pr<sup>i</sup>, Bn, CH<sub>2</sub>CO<sub>2</sub>Me) that occur with energy barriers ( $\Delta G_{25C}^\ddagger$ ) of 25.7–27.3 (Hal = Cl) and 16.2–22.9 kcal mol<sup>-1</sup> (Hal = Br). It was also shown that in the pentaphenylcyclopentadiene cycle the chlorine and bromine atoms migrate over the five-membered carbocycle with energy barriers of 25.9 and 17.0 kcal mol<sup>-1</sup>, respectively.<sup>10–12</sup> The circumambulatory rearrangement of 5-iodocyclopentadiene was found using experiments on magnetization transfer,<sup>15</sup> which revealed that at room temperature the iodine atom migrates over the ring very rapidly: this process can be "frozen" in the NMR time scale only at -40 °C. We calculated the reaction paths of this circumambulatory rearrangement of 5-iodocyclopentadiene using DFT and found that on the application of a rotating electrical field a halocyclopentadiene molecule behaves as a prototype of a rotor-type engine with the fast ( $k_{298} = 630 \text{ s}^{-1}$ ) unidimensional migration of the iodine atom along the perimeter of the five-membered ring.<sup>16</sup> Bromine and iodine atoms are among the fastest migrant-elements of IV–VII Groups of the Periodic table in cyclopolyene systems.<sup>13,14,17–22</sup>

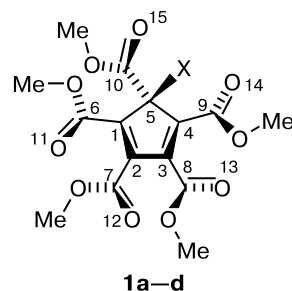
In this work, we studied possible paths of halogen atom migrations in 5-halo-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes **1** in the gas phase using DFT calculations with the B3LYP/6-311++G(d,p) and B3LYP/Gen, 6-311++G(d,p)/SDD (for the bromine and iodine derivatives) basis sets. Pentamethoxycarbonylcyclopentadiene is interesting due to stability, enhanced solubility of the related metal complexes, and the possibility of using the pentamethoxycarbonylcyclopentadienide anion for the synthesis of charge-transfer complexes with organic cations and radical cations and dopants in molecular electronics.<sup>1,23–25</sup> Available experimental data do not allow one to establish exact mechanisms of the fluctuating behavior of 5-halopentamethoxycarbonylcyclopentadienes that could be due to 1,5- and 1,3-sigmatropic shifts of halogen atoms or the intermediate formation of a tight ion pair of the halogen cation and cyclopentadienide anion and to elucidate the influence of the nature of the full series of halogens on the barriers and character of their migrations in the five-membered ring. We performed the corresponding quantum chemical calculations for the solution of the stated questions.

## Calculation Procedure

Quantum chemical calculations were performed by the DFT method<sup>26</sup> with the three-parameter B3LYP potential in the split valence basis 6-311++G(d,p) and Gen, 6-311++G(d,p)/SDD (for the bromine and iodine derivatives) in the gas phase using the Gaussian-03 program package. All stationary points were identified by the calculation of the Hesse matrix. Charges on atoms were obtained using the NBO calculations.

## Results and Discussion

According to the calculations in the gas phase, structures **1a–d** correspond to minima on the corresponding potential energy surfaces (PES) (Table 1, Fig. 1). The conformation of compounds **1a–d** is the most energetically favorable if the oxygen atom of the methoxycarbonyl group at the sp<sup>3</sup>-hybridized C(5) carbon atom is turned to the halogen atom (X = Br, torsion angle C(1)C(5)C(10)O(15) 113.5°) and the CO<sub>2</sub>Me groups at C(1) and C(4) (X = Br, torsion angles C(2)C(1)C(6)O(11) 26.5° and C(5)C(4)C(9)O(14) -6.2°) and at C(2) and C(3) (X = Br, torsion angles C(4)C(3)C(8)O(13) -102.8° and C(3)C(2)C(7)O(12) 46.4°) are in transoid conformations relative to each other (see Fig. 1). This is in agreement with the X-ray diffraction data for the covalent compounds of pentamethoxycarbonylcyclopentadiene.<sup>13,14</sup> The charges on the halogen atoms in structures **1a–d** corresponding to minima on the PES change from negative on the fluorine atom to positive on the iodine atom (-0.372 (F), 0.017 (Cl), 0.103 (Br), and 0.223 *e* (I)).



**1**: X = F (**a**), Cl (**b**), Br (**c**), I (**d**)

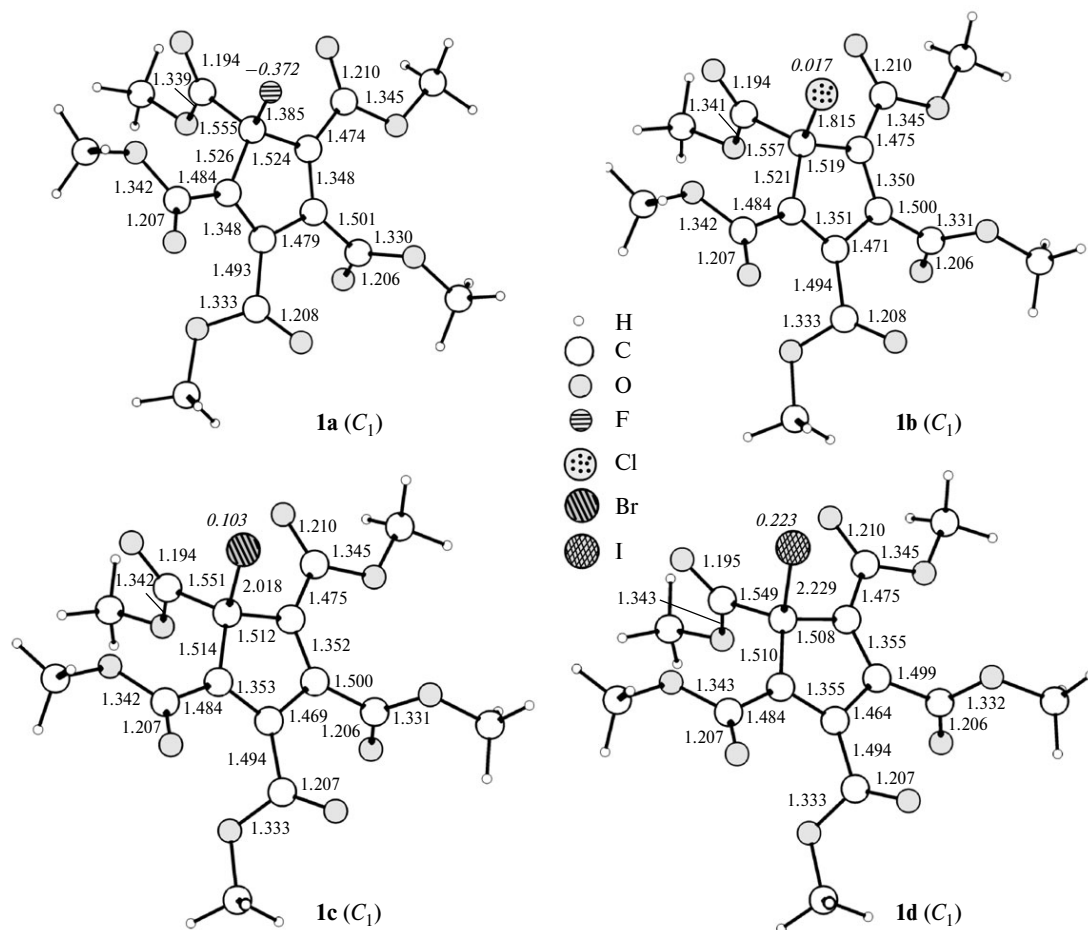
The structures of transition states TS **2** and TS **3** (see Table 1) corresponding to the sigmatropic 1,5- (Scheme 1, Fig. 2) and 1,3-shifts (Scheme 2, Fig. 3) of the halogen atoms along the perimeter of the five-membered ring were found on the PES of halocyclopentadienes **1**. No structures corresponding to the randomization mechanism through the formation of a tight ion pair were found on the PES for migrations of halogen atoms in compounds **1**.

In the structures of transition states of 1,5-shifts TS **2a–d** (Scheme 1, Fig. 2), the distances between the migrating halogen and nearest two carbon atoms of the cyclopentadiene ring elongate on going from F to I: 1.791

**Table 1.** Total energies of the ground states of **1a–d** and transition states TS **2a–d** and TS **3a–d** and the activation energies of 1,5- and 1,3-shifts of halogens in the gas phase calculated using the B3LYP/6-311++G(d,p) or B3LYP/Gen, 6-311++G(d,p)/SDD (for X = Br, I) functionals

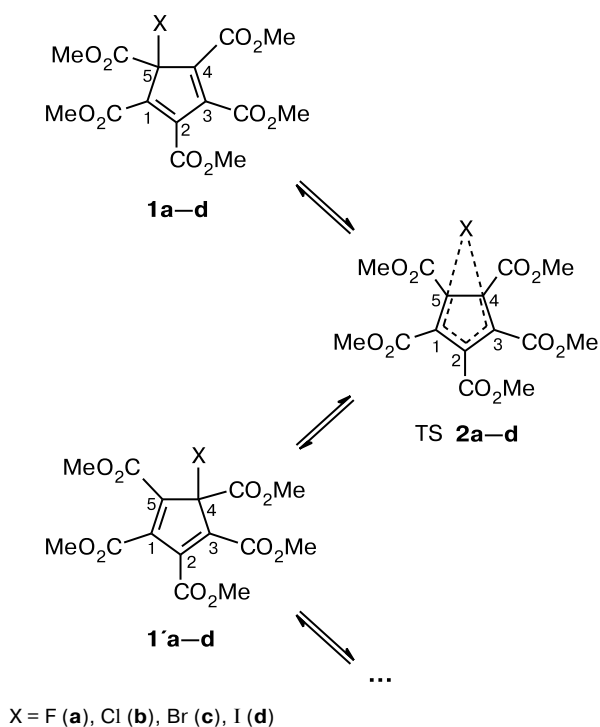
Structure	$-E_{\text{tot}}/\text{au}$	$\Delta E_{\text{ZPE}}^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G_{25\text{C}}^{\ddagger}$	$\omega_1/\text{cm}^{-1}$
<b>1a</b>	1433.11239	0	0	0	20
TS <b>2a</b>	1433.04164	42.9	42.7	43.5	-676
TS <b>3a</b>	1433.00510	65.4	65.5	65.6	-389
<b>1b</b>	1793.46859	0	0	0	23
TS <b>2b</b>	1793.42388	26.9	26.7	27.4	-450
TS <b>3b</b>	1793.39023	47.6	47.7	47.4	-266
<b>1c</b>	1346.61950	0	0	0	22
TS <b>2c</b>	1346.58652	19.8	19.6	20.3	-327
TS <b>3c</b>	1346.55659	38.1	38.1	38.1	-241
<b>1d</b>	1344.65988	0	0	0	25
TS <b>2d</b>	1344.63409	15.4	15.1	16.0	-252
TS <b>3d</b>	1344.60322	34.2	34.2	33.7	-264

Note.  $E_{\text{tot}}$  is the total energy, 1 au = 627.5095 kcal mol $^{-1}$ ;  $\Delta E_{\text{ZPE}}^{\ddagger}$  is the relative energy taking into account the zero-point energy of harmonic vibrations,  $\Delta H^{\ddagger}$  is the activation enthalpy,  $\Delta G_{25\text{C}}^{\ddagger}$  is the free energy of activation at 25 °C, and  $\omega_1$  is the lowest value of the harmonic vibrational frequency or the value of the single imaginary harmonic vibrational frequency;  $E_{\text{ZPE}} = -1432.81602$  (**1a**),  $-1793.17359$  (**1b**),  $-1346.32528$  (**1c**), and  $-1344.365876$  au (**1d**).



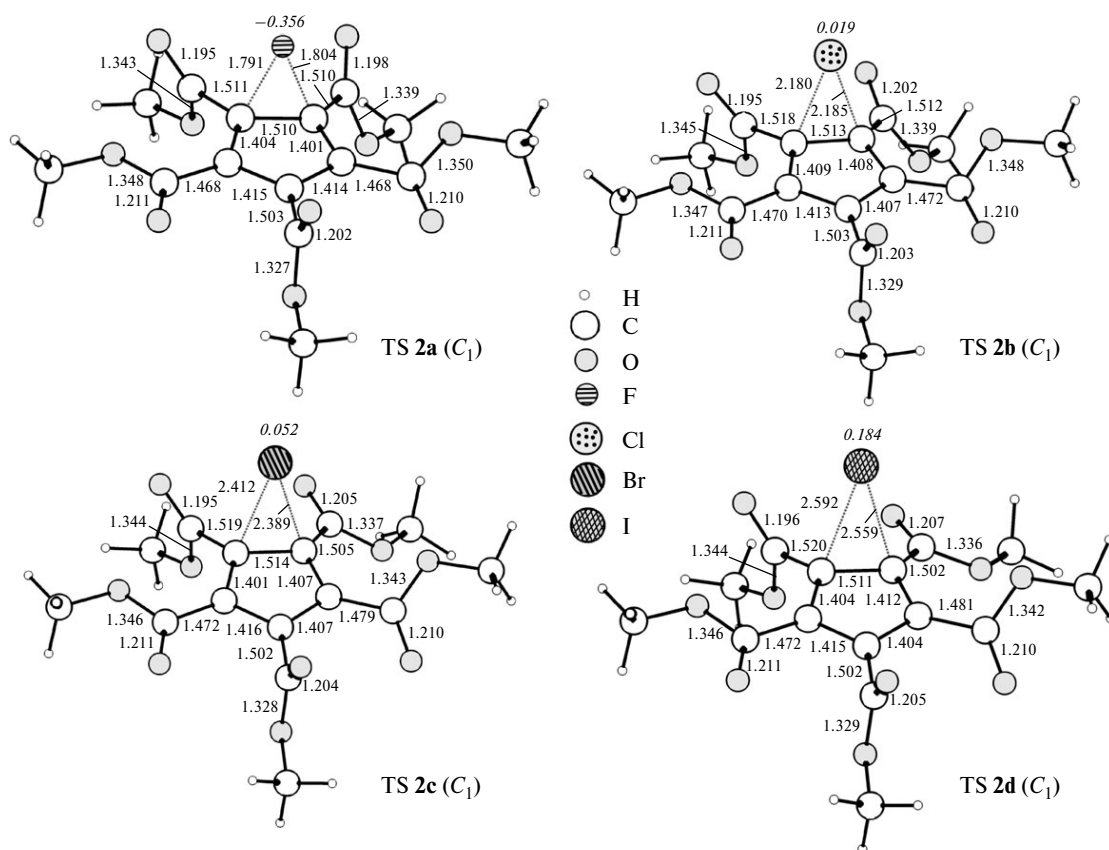
**Fig. 1.** Geometric parameters of the ground states of **1a–d** calculated by the B3LYP/6-311++G(d,p) (**1a,b**) or B3LYP/Gen, 6-311++G(d,p)/SDD (**1c,d**) method and the charges on the halogen atoms (NBO, italicized). Here and in Figs 2 and 3, bond lengths are given in Å.

Scheme 1



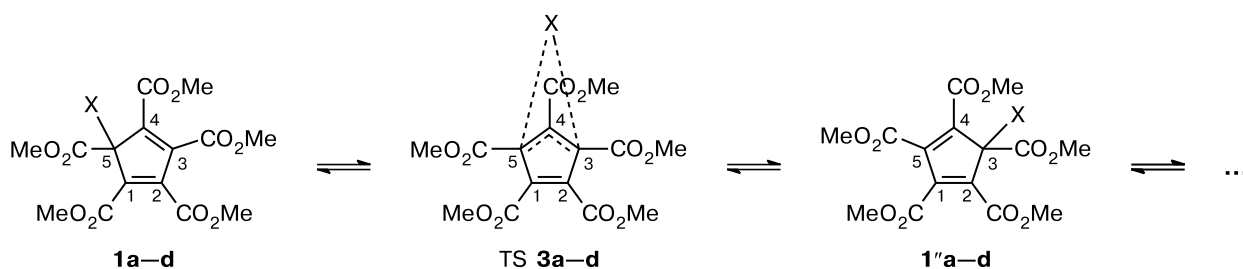
and 1.804 Å (X = F), 2.185 and 2.180 Å (X = Cl), 2.389 and 2.412 Å (X = Br), 2.559 and 2.592 Å (X = I). The cyclopentadiene ring is planar, and the  $\pi$ -electron density is delocalized over the whole ring, which is indicated by the closeness of the C(5)C(1), C(1)C(2), C(2)C(3), and C(3)C(4) bond lengths. The methoxycarbonyl groups are inclined to the plane ring at different angles. The calculated charges on the halogen atoms in TS **2a–d** change from negative on the fluorine atom to positive on the iodine atom (–0.356 (F), 0.019 (Cl), 0.052 (Br), 0.184 *e* (I)). For the chlorine and bromine derivatives, there is almost no charge separation between the migrant and system, which is typical of sigmatropic shifts.

In the structures of transition states of 1,3-shifts TS **3a–d** (see Scheme 2, Fig. 3), the migrating halogen atom is more remote from the cyclopentadiene ring than that in TS **2a–d** and the distances between the halogen and nearest two carbon atoms of the cyclopentadiene ring are 2.304 and 2.274 Å (X = F), 2.959 and 2.917 Å (X = Cl), 3.145 and 3.105 Å (X = Br), 3.390 and 3.355 Å (X = I). In TS **3a**, the C(4) atom of the ring is shifted from the plane (torsion angle C(1)C(2)C(3)C(4) –9.2°). In TS **3b–d**, the cyclopentadiene ring is nearly planar. In TS **3a–d**, charge separation between the halogen atoms and pentamethoxycarbonylcyclopentadiene system is more significant



**Fig. 2.** Geometric parameters of the transition states of the 1,5-shifts of halogens in TS **2a–d** calculated by the B3LYP/6-311++G(d,p) (**2a,b**) or B3LYP/Gen, 6-311++G(d,p)/SDD (**2c,d**) method and the charges on the halogen atoms (NBO, italicized).

Scheme 2

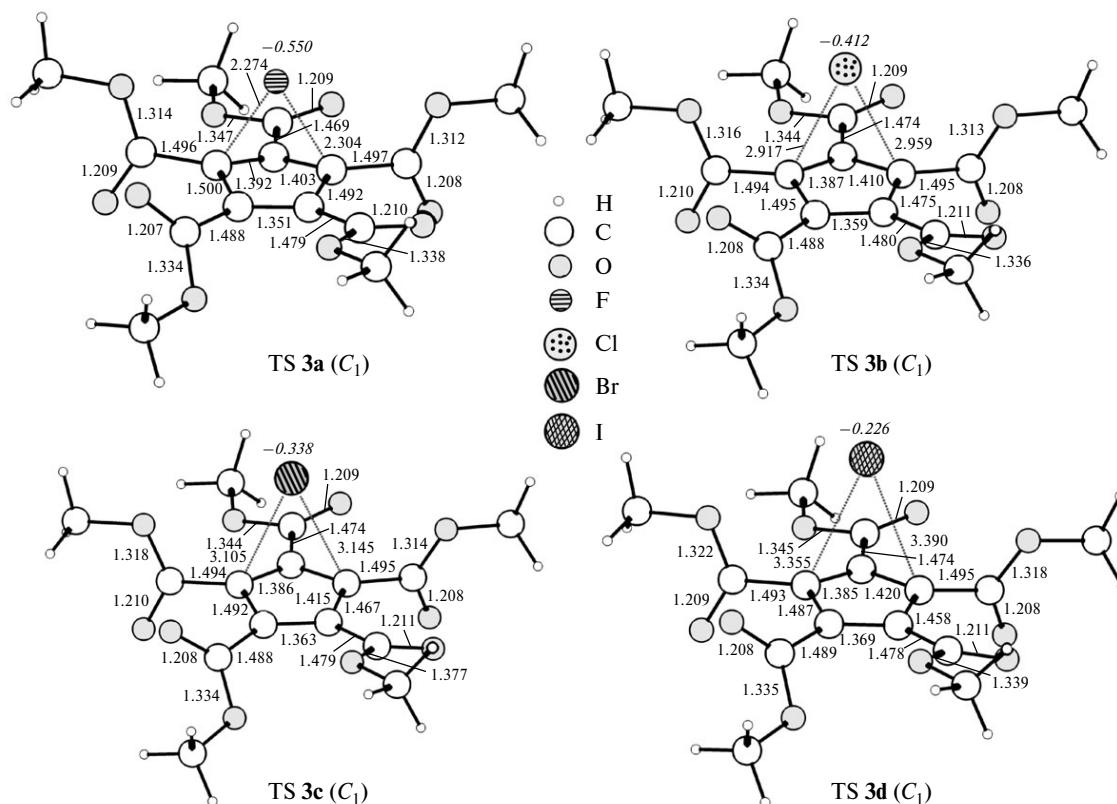


X = F (**a**), Cl (**b**), Br (**c**), I (**d**)

than that in TS **2a-d** and all halogen atoms bear a negative charge increasing on going from iodine to fluorine ( $-0.550$  (F),  $-0.412$  (Cl),  $-0.338$  (Br),  $-0.226$  (I)).

The calculations showed that the energy barriers of symmetry-allowed 1,5-shifts of halogens occurring *via* TS **2a-d** ( $\Delta E_{\text{ZPE}}^{\ddagger} = 42.9, 26.9, 19.8,$  and  $15.4$  kcal mol $^{-1}$ , respectively) were substantially lower than those for 1,3-shifts through TS **3a-d** ( $\Delta E_{\text{ZPE}}^{\ddagger} = 65.4, 47.6, 38.1,$  and  $34.2$  kcal mol $^{-1}$ , respectively) and their values were well consistent with available experimental data.<sup>9–16</sup> Therefore, the rearrangements of 5-halo-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes should proceed *via* the

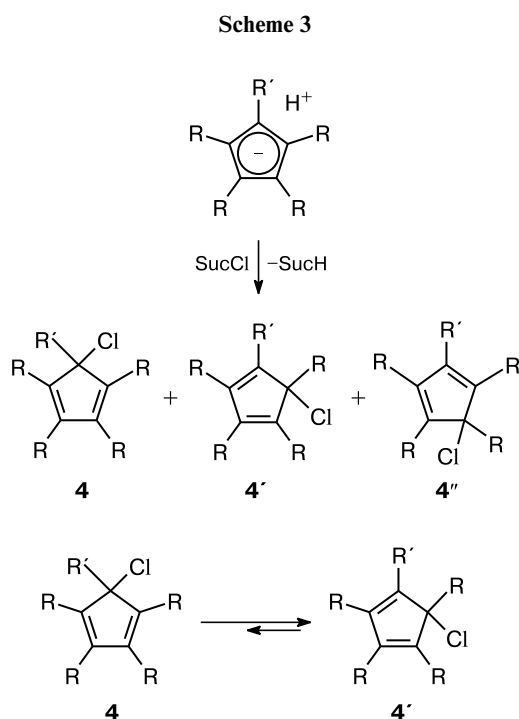
mechanism of 1,5-sigmatropic shift of halogens along the perimeter of the five-membered ring according to the Woodward–Hoffmann rules of conservation of orbital symmetry. The difference in energy barriers for the 1,5-shifts compared to the 1,3-shifts is rather substantial being  $\Delta(\Delta E_{\text{ZPE}}^{\ddagger}) = 22.5, 20.7, 18.3,$  and  $18.8$  kcal mol $^{-1}$  for X = F, Cl, Br, and I, respectively. The migration capacity increases in the order F < Cl < Br < I with increasing the atomic radius of halogen. The calculated barriers of shifts for bromine and iodine atoms ( $\Delta E_{\text{ZPE}}^{\ddagger} = 19.8$  and  $15.4$  kcal mol $^{-1}$ ,  $\Delta G_{25\text{C}}^{\ddagger} = 20.3$  and  $16.0$  kcal mol $^{-1}$ ) show that these atoms can rapidly migrate over the cyclopenta-



**Fig. 3.** Geometric parameters of the transition states of the 1,3-shifts of halogens in TS **3a-d** calculated by the B3LYP/6-311++G(d,p) (**3a,b**) or B3LYP/Gen, 6-311++G(d,p)/SDD (**3c,d**) and the charges on the halogen atoms (NBO, italicized).

diene ring, and these processes can be detected by dynamic NMR spectroscopy, which is confirmed by the works on migrations of the bromine atom in 5-bromoalkyltetramethoxycarbonyl- and pentamethoxycarbonylcyclopentadienes ( $\Delta G^\ddagger_{25C} = 16.2\text{--}22.9$  kcal mol $^{-1}$ )<sup>10,11</sup> and iodine atom in 5-iodocyclopentadiene ( $\Delta G^\ddagger_{25C} \approx 14$  kcal mol $^{-1}$ ).<sup>15</sup>

We have earlier<sup>16</sup> calculated in the similar approximation the barrier of 1,5-shifts of the iodine atom in the ring of unsubstituted cyclopentadiene ( $\Delta E^\ddagger_{ZPE} = 15.4$  kcal mol $^{-1}$ ), which coincides with the barrier for the pentamethoxycarbonylcyclopentadiene system due to an insignificant charge separation in transition states of these intramolecular reactions. The chlorine atom in the pentamethoxycarbonylcyclopentadiene ring should migrate more slowly (calculated barrier of 1,5-shifts  $\Delta E^\ddagger_{ZPE} = 26.9$  kcal mol $^{-1}$ ,  $\Delta G^\ddagger_{25C} = 27.4$  kcal mol $^{-1}$ ). We have previously experimentally detected similar processes by the equilibration method.<sup>9</sup> A mixture of all three isomers **4**, **4'**, and **4''** was obtained by the reaction of 5-alkyl-1,2,3,4-tetramethoxycarbonylcyclopentadienes with *N*-chlorosuccinimide (Scheme 3). Upon storage of solutions of each preparatively isolated isomer **4** or **4'** at 70–100 °C in *o*-dichlorobenzene, equilibrium **4**  $\rightleftharpoons$  **4'** is established (see Scheme 3), which requires to surmount the barriers with  $\Delta G^\ddagger_{25C} = 25.7\text{--}27.3$  kcal mol $^{-1}$ .



The degenerate process of 1,5-shifts of the chlorine atom in the pentamethoxycarbonylcyclopentadiene ring cannot be detected in the time scale of dynamic NMR, but the calculated value of the barrier indicates the possibility of competition of shifts of the chlorine atoms and

substituent CO<sub>2</sub>Me; the barrier of non-degenerate shifts for the latter was determined experimentally<sup>27</sup> ( $\Delta G^\ddagger_{100C} = 31.1$  kcal mol $^{-1}$ ). The calculated barrier of 1,5-shifts of the fluorine atom in this system ( $\Delta E^\ddagger_{ZPE} = 42.9$  kcal mol $^{-1}$ ,  $\Delta G^\ddagger_{25C} = 43.5$  kcal mol $^{-1}$ ) indicates their very low probability. Thus, the calculations revealed that the fast intramolecular 1,5-sigmatropic shifts of chlorine, bromine, and iodine atoms along the perimeter of the cyclopentadiene ring resulted in five degenerate isomers, which would lead to a mixture of isomers for similar non-degenerate systems, and the changing position of the halogen atom in the ring can affect the direction of subsequent reactions in the synthesis of the target products. Interestingly, in the halosubstituted derivatives of related cyclopropene and cycloheptatriene,<sup>28–31</sup> whose ionization is facilitated by the formation of stable aromatic cations, migration of the halogen atoms can occur *via* both the mechanism of ionization–recombination through the formation of tight ion pairs and the mechanism of sigmatropic shifts depending on the solvent polarity.

Thus, the migration routes of halogen atoms in 5-halo-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes were studied in this work by the DFT method. The calculations revealed the preference of the 1,5-sigmatropic shifts of halogens along the perimeter of the five-membered ring compared to the 1,3-shifts. The calculated energy barriers of the 1,5-shifts are  $\Delta E^\ddagger_{ZPE} = 42.9, 26.9, 19.8,$  and  $15.4$  kcal mol $^{-1}$  for the fluorine, chlorine, bromine, and iodine, respectively, which are well consistent with available experimental data. The calculated charges on the halogen atoms in the structures of transition states of the 1,5-shifts change from negative on the fluorine atom to positive on the iodine atom ( $-0.356$  (F),  $0.019$  (Cl),  $0.052$  (Br),  $0.184 e$  (I)). In this case, there is almost no charge separation between the migrant and system for the chlorine and bromine derivatives. The migration capacity increases in the order  $F < Cl < Br < I$  with increasing the atomic radius of the halogen atom. The fast change in positions of the chlorine, bromine, and iodine atom in the cyclopentadiene ring can exert effect on the direction of reactions in the subsequent syntheses.

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