JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 4, 31–47 (1991)

# 1,5-SIGMATROPIC SHIFTS OF BROMINE OVER A CYCLOPENTADIENE RING

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**The intrinsic mechanism of circumambulatory rearrangements of 5-bromo-5-methyl-1,2,3,4-tetramethoxycarbonylcyclopentadiene, 5-bromo-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene and 5-bromo-1,2,3,4,5-pentaphenylcyclopentadiene due to sigmatropic shifts of bromine over the cyclopentadiene ring was proved, using the dynamic $^{13}C$ and $^{1}H$ NMR technique, to be governed by successive intramolecular 1,5-sigmatropic shifts. Semi-empirical AM1 and MINDO/3 calculations of reactions paths performed for fluoro-, chloro- and bromocyclopentadienes are in accord with the conclusion of a preference for a 1,5- over a 1,3-shift reaction path of halogen migration over a cyclopentadiene system. Intramolecular 1,5-sigmatropic shifts of chlorine in 5-chloro-5-methyl-1,2,3,4-tetramethoxycarbonylcyclopentadiene with the free energy barrier of $\Delta G^{\ddagger}_{298} = 26 \cdot 1$ kcal mol$^{-1}$ were studied using $^{1}H$ NMR spectroscopy.**

## INTRODUCTION

The discovery in 1956 of the migration of certain organometallic groups along the perimeter of the cyclopentadiene ring[1] served as the basis for the development of the fundamental concept of the fluctuating (structurally non-rigid) molecular systems.[2,3] Later it was found that migrants with a Main Groups (III–VI) central atom also show an aptitude for fast, intramolecular sigmatropic shifts over a cyclopentadiene system occurring on the NMR time scale (for reviews, see Refs 4–6). Recently, sulphur–[7–10] and selenium-containing groups[11,12] and bromine[13] were added to the number of migrants circumambulating the cyclopentadiene ring, which made it possible to involve the elements of all groups (except Group VIII) of the Periodic System in the process of dynamic sigmatropic rearrangements (of the 'merry-go-round' type) of cyclopentadiene derivatives.

The overall scheme of the mechanism of intramolecular migrations of the substituents X in the cyclopentadiene ring (Scheme 1) includes intermediates or transition states of the $\eta^2$-type (1,2- or 1,5-shift), $\eta^3$-type (1,3-shift) or $\eta^5$-type (randomization due to the formation of a $\pi$-complex or ion-pair structure). In addition to these routes, also possible are randomization mechanisms in which tight or solvent-separated ion pairs (e.g. migration of arylazo groups[14,15]) and radical pairs (by-product of bromotropic rearrangements in the series of pentaarylbromocyclopentadienes[13]) are formed, and also intermolecular mechanisms[13,16].

It has been shown using the dynamic NMR method[6,17] and by performing quantum chemical calculations[18–20] that most intramolecular rearrangements of cyclopentadiene derivatives **1** proceed by the mechanism of 1,2-(1,5)-shift **1a** ⇄ **2** ⇄ **1b**. According to expectations based on the eight-electron rule,[21,22] the $\eta^5$-structures can be realized for those migrants which are derivatives of the Group II elements (BeR, MgR). MINDO/3 calculations of the critical parts of the potential energy surface for the circumambulatory rearrangement of still unknown $\eta^1$-nitrosocyclopentadiene showed that the 1,3-shift of the nitroso group is nearly equivalent in energy to the alternative 1,5-shift reaction path.[23,24] The 1,3-shift of the SSR group with the formation of a type **3** transition state structure is, according to MINDO/3 and AM1 calculations (X = SSH),[25] the most favoured in the case of pentamethoxycarbonylcyclopentadienylsulphane.[26]

The experimental identification of the intrinsic

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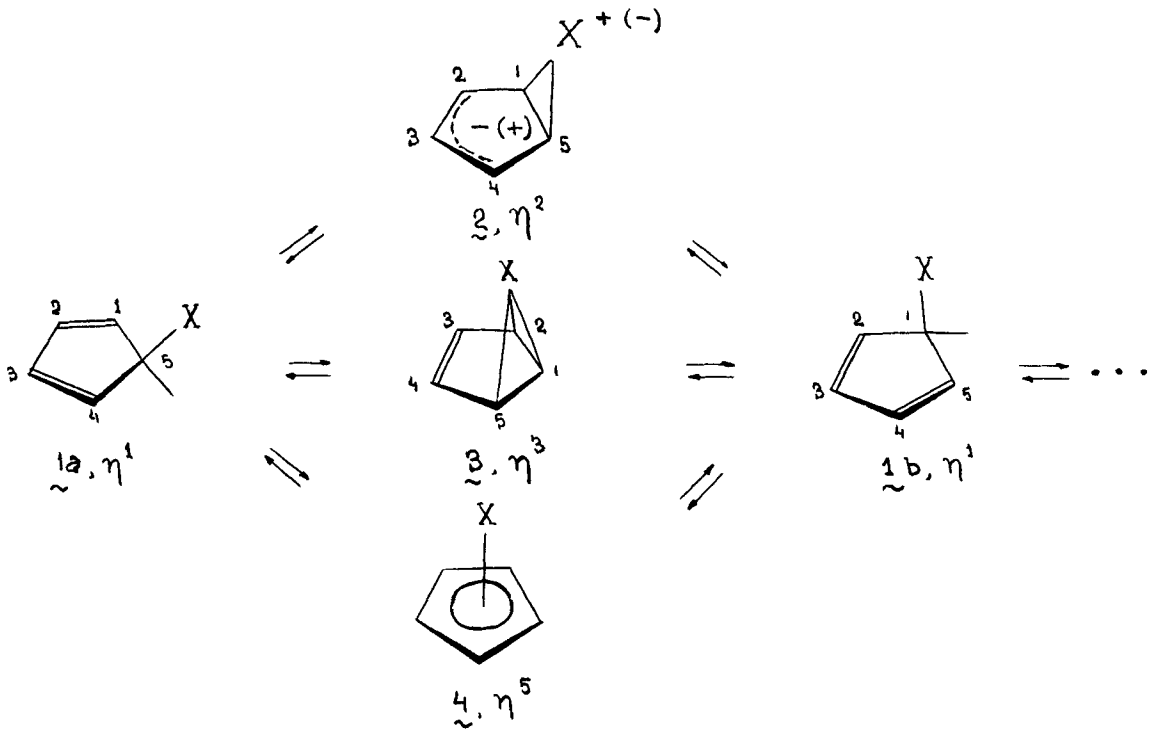
0894–3230/91/010031–17$08.50


*Received 18 October 1989*
*Revised 17 March 1990*



Scheme 1

mechanism of rearrangement[27] is commonly based on the line-shape analysis of the variable-temperature NMR spectrum of the rearranging compound. It requires the strict assignment of signals belonging to certain carbon atoms of the five-membered ring which only in rare cases could be done completely unambiguously.

In this work, a fairly reliable assignment of the $^{13}C$ NMR signals for the isomers **7**–**9** of bromomethyltetramethoxycarbonylcyclopentadiene was made in which a sufficiently fast migration of bromine in the cyclopentadienyl ring was established by the dynamic $^{1}H$ NMR method.[13] Based on this assignment and employing the dynamic $^{13}C$ NMR method, the mechanism was proved to involve successive 1,2-shifts (1,5-sigmatropic shifts) of bromine along the perimeter of the cyclopentadiene ring, **1a** ⇄ **2** ⇄ **1b**. In the same system, by means of the $^{1}H$ NMR method, the intramolecular 1,5-sigmatropic shifts of chlorine with a free activation energy ($\Delta G^{\ddagger}_{298}$) of 26·1 kcal mol$^{-1}$ were observed for the first time.

Using the semi-empirical AM1[28] and MINDO/3[29] methods, model calculations were performed of possible reaction paths for intramolecular shifts of fluorine, chlorine and bromine in the unsubstituted cyclopentadiene. The selection of mechanisms was based on the analysis of the nature of stationary points on the potential energy surface (PES) of the reactions which correspond to the structures **2**–**4** and estimations of their relative energies.

## RESULTS AND DISCUSSION

Whereas chlorine in 5-chloro-1,2,3,4,5-pentaphenylcyclopentadiene displayed a very low migration aptitude,[30] both 5-bromo-1,2,3,4,5-pentaphenyl- (**5**) and 5-bromo-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes (**6**) were found to be fairly fluxional in solution owing to five-fold degenerate rearrangements involving circumambulation of bromine over the cyclopentadienyl rings.[13] The line-shape analysis of the temperature-dependent $^{13}C$ NMR spectra of **5** and $^{1}H$ NMR spectra of **6** allowed any randomization mechanism, i.e. **1** → **4** or ion-pair pathways to be ruled out. However, uncertainty remained about the 1,2- or 1,3-shift mechanism of circumambulation of bromine because of ambiguity in the assignment of spectral signals to C-2 or C-3 positions, the problem often encountered in studies of the dynamics of fluxional $\eta^1$-cyclopentadienyl compounds.[31–33] To obviate this problem and thus to distinguish between the routes **1** → **2** and **1** → **3** (Scheme 1), we investigated in some detail the $^{13}C$ and $^{1}H$ NMR spectra of isomers of $C_5(COOMe)_4MeBr$, in which the perturbation of

degeneracy of the circumambulatory rearrangement is achieved through the replacement of one of the methoxycarbonyl groups.

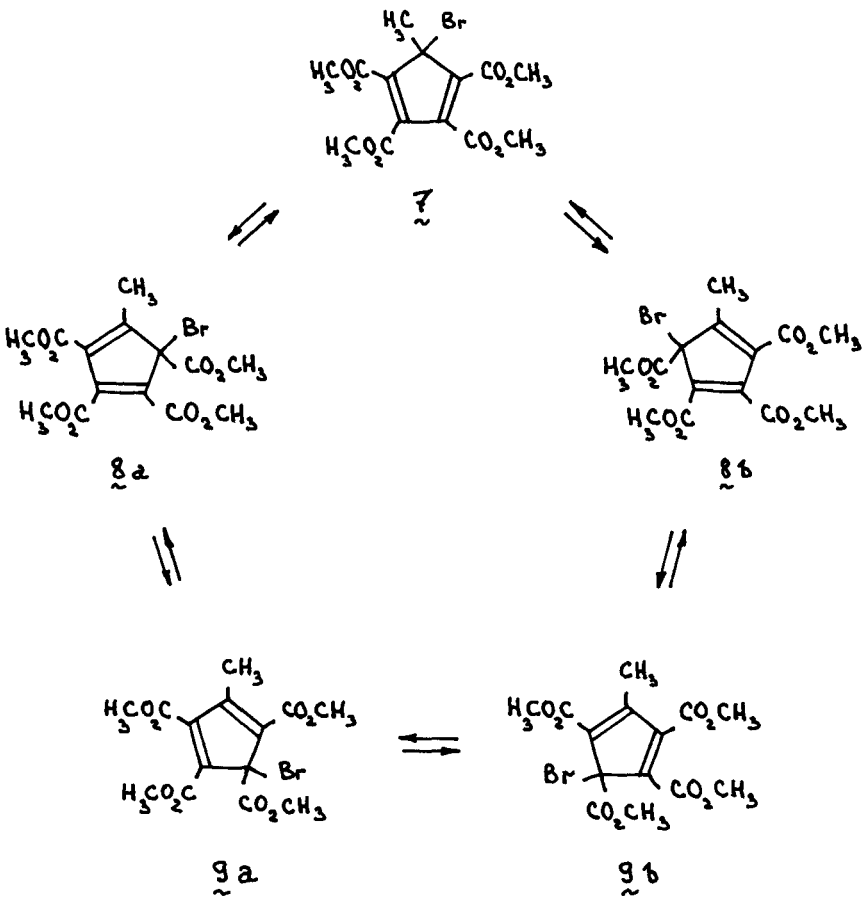
The reaction of 5-methyl-1,2,3,4-tetramethoxycarbonylcyclopentadiene with *N*-bromosuccinimide gives rise to an equilibrium mixture of bromocyclopentadiendes **7** (6%), **8** (54%) and **9** (40%) (the assignment was made according to Ref. 13) which could not be separated preparatively. (Scheme 2).

$^1$H NMR spectra of the mixture of the isomers of $C_5$-(COOMe)$_4$MeBr in the *o*-dichlorobenzene-$d_4$ solution in the temperature range 30–160 °C are shown in Figure 1. Whereas the isomer **7** can readily be identified owing to its $C_s$ symmetrical structure [$\delta$ 3·66 (6H), 3·67 (6H), 1·97 (3H)], the choice between the isomers **8** and **9** on the basis of the $^1$H NMR spectrum is complicated. Nevertheless, a good evidence in favour of the circumambulatory rearrangement can be obtained.

On increasing the temperature of the solution from 50 to 160 °C, three successive dynamic processes, with rates independent of concentration (0·01–0·3 mol l$^{-1}$), are revealed in the $^1$H NMR spectra. These are associated with the bromine migration over the cyclopentadiene ring as portrayed in Scheme 2. The processes are as follows.

(i) In the temperature range 50–100 °C, a reversible broadening of the proton signal ($\delta$ 1·97) belonging to the methyl group of **7** is seen, followed by its coalescence at 110 °C with simultaneous broadening of proton signal of the methyl group with $\delta$ 2·30 (Figure 1). This process may be assigned to the **7** ⇌ **8** exchange, $\Delta G^{\ddagger}_{298}$ (**7** → **8**) = 18·9 kcal mol$^{-1}$.

(ii) At temperatures higher than 120 °C, another exchange process is manifested in a broadening of the non-coalesced proton signals related to methoxycarbonyl groups. A pairwise coalescence of signals ($\delta$ 3·52, 3·60 and $\delta$ 3·62, 3·70) is observed at 140 °C, the width of the methyl group




Scheme 2

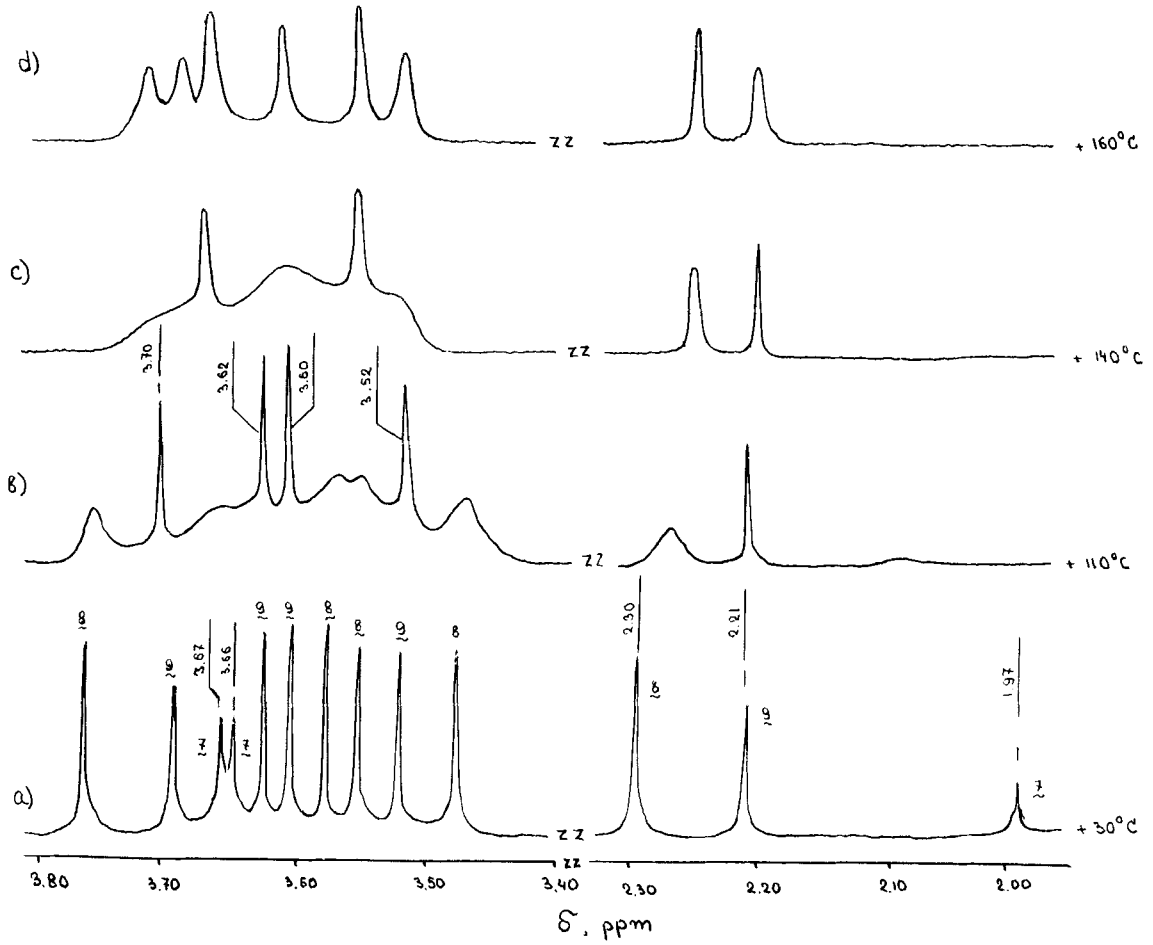



Figure 1. 100 MHz $^1$H NMR spectrum of a mixture of bromomethyltetramethoxycarbonylcyclopentadiene isomers (**7**–**9**) in *o*-dichlorobenzene-$d_4$ at (a) 30, (b) 110, (c) 140 and (d) 160 °C

signal (δ 2·21) being unaffected by the above exchanges. The only dynamic process compatible with such a spectral behaviour is the 1,2-shift of bromine, **9a** ⇄ **9b**, the energy barrier of which is $\Delta G^{\ddagger}_{298} = 20{\cdot}3$ kcal mol$^{-1}$.

(iii) Short-term (3–5 min) holding of the solution at 145–160 °C (prolonged heating at this temperature results in gradual decomposure of the compound) allows an additional exchange process to be detected, which is seen in the reversible broadening of the methyl proton signals (δ 2·21). This may be associated with the **8** ⇄ **9** rearrangement, with its energy barrier $\Delta G^{\ddagger}_{298} = 25$ kcal mol$^{-1}$.

These assignments (Scheme 2) were definitely supported by the $^{13}$C NMR spectral study of isomers **7**–**9**. In order to identify the isomers **7**–**9**, we made use of the $^{13}$C NMR spectra of these compounds, taking as indicator groups the carbon atoms of the cyclopentadiene ring. One could expect that a precise enough assignment would be achieved by examining the values of the spin–spin coupling constants of the methyl group protons with the carbon ($^{13}$C) atoms of the cyclopentadiene ring, particularly with $C_{sp^3}$,[34] since the values of the spin–spin coupling constants decrease with increase in the number of bonds which separate the interacting nuclei. The $^{13}$C NMR spectrum was determined for 5-methyl-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene (**10**) serving as a model for isomer **7**, and is shown in Figure 2. Applying the complete proton noise-modulated [Figure 2(a)] and off-resonance [Figure 2(b)] decoupling conditions and taking into account the characteristic difference in the chemical shifts for sp$^3$- and sp$^2$-hybridized carbons, it was poss-

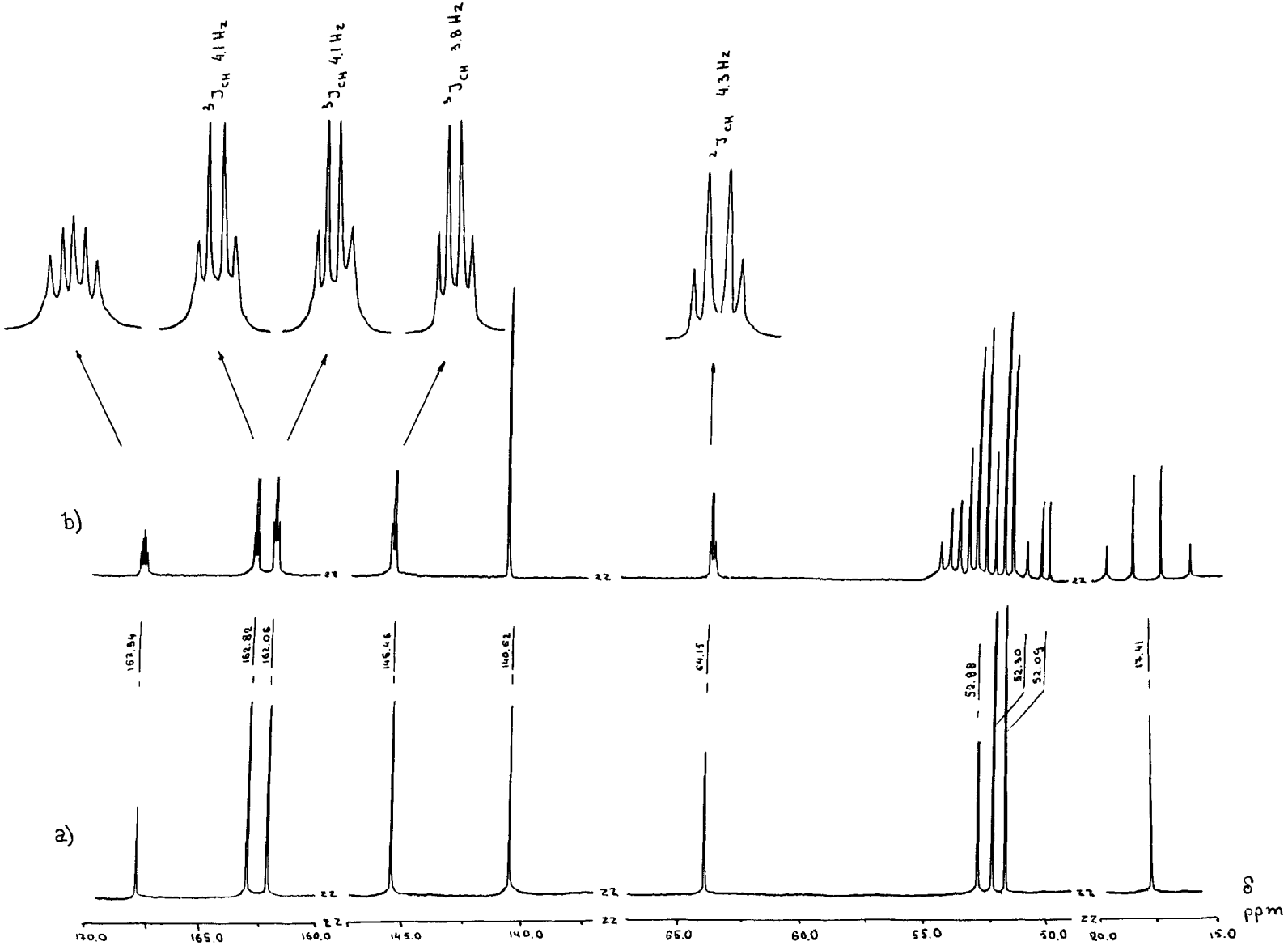
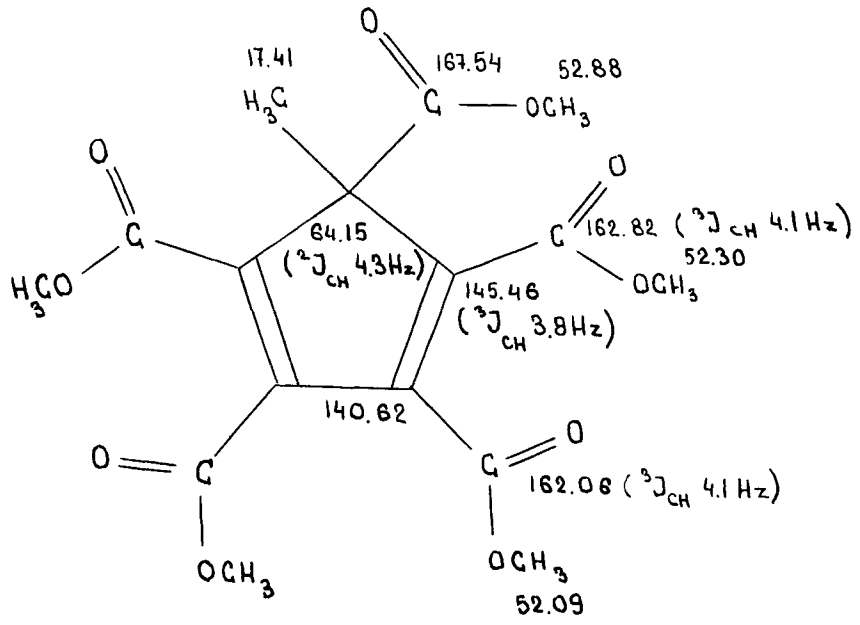



Figure 2. $^{13}C$ NMR spectrum of 5-methyl-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene (**10**) in benzene-$d_6$ solution, (a) proton noise-decoupled and (b) off-resonance decoupled

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Scheme 3. Assignment of carbon atom signals in 5-methyl-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene (**10**).

ible to assign the signals from the $^{13}C$ NMR spectrum of this compound as indicated in Scheme 3.

From the spectrum in Figure 2 it follows that the C-5 atom of the cyclopentadiene ring whose signal is observed in the region characteristic of the $sp^3$-hybridized carbons shows spin–spin coupling ($^2J_{CH}$ 4·3 Hz) with the protons of the *C*-methyl group. The $sp^2$-hybridized C-1,4 are observed at $\delta$ 145·46 ($^3J_{CH}$ 3·8 Hz) and C-2,3 at $\delta$ 140.62 ($^4J_{CH}$ 0 Hz). The carbonyl carbon atoms attached to the C-1,4 and C-2,3 atoms of the cyclopentadiene ring under off-resonance decoupling conditions show the signals split as quadruplets owing to coupling with the methoxyl protons ($^3J_{CH}$ 4·1 Hz). The carbonyl carbon attached to C-5 atom ($\delta$ 167·54) can readily be identified by its relative intensity and an additional splitting caused by spin coupling with the protons of the neighbouring *C*-methyl group. These couplings are seen in Figure 2(b).

Thus, in the 5-methyl-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene system (**10**) the geminal two- and three-bond spin–spin H–C couplings are available ($^2J_{CH} > {}^3J_{CH}$), whereas four-bond H–C coupling is not observed. This makes it possible to identify unambiguously all three isomers **7**–**9** from the $^{13}C$ NMR spectrum of their mixture.

Figure 3 shows the proton noise (a) and off-resonance (b) decoupled spectra of the equilibrium mixture of bromomethyltetramethoxycarbonylcyclopentadienes (**7**–**9**). The assignment of the signals of the cyclopentadiene ring carbons was made for all isomers (Scheme 4) taking into account that $^2J_{CH} > {}^3J_{CH}$ and $^4J_{CH} = 0$, and that the content of isomer **7** in the equilibrium mixture is, according to the $^1H$ NMR data, much smaller than those of **8** and **9**.

The $^{13}C$ NMR spectrum of the equilibrium mixture of isomers **7**–**9** in nitrobenzene-$d_5$ is shown in Figure 4(a); it is similar to the spectrum in benzene-$d_6$ solution. It can be seen from Figure 4(b) that the signal $\delta$ 59·47 belongs to isomer **7** whereas those at $\delta$ 65·44 and 62·07 are associated with isomers **8** and **9**. Raising the temperature of the solution to 120 °C leads to reversible broadening of all $^{13}C$ resonances belonging to isomers **7** and **8** whereas the shapes of those related to isomer **9** remain unaffected. This is illustrated in Figures 4(c)–(e) by the spectral pattern pertaining to $C_{sp^3}$ peaks of **7**–**9**. Hence the interconversion occurs between the isomers of **7** and **8** associated with a 1,5-sigmatropic shift of the bromine atom.

Further, we observed a migration of chlorine in the system of methyltetramethoxycarbonylcyclopentadiene. On interaction between methyltetramethoxycarbonylcyclopentadiene and *N*-chlorosuccinimide a mixture of isomers **11**, **12** and **13** formed (15, 60 and 25% respectively) (Scheme 5). After repeated recrystallization of the mixture of reaction products from diethyl ether, the isomer **12** could be isolated as an individual compound.

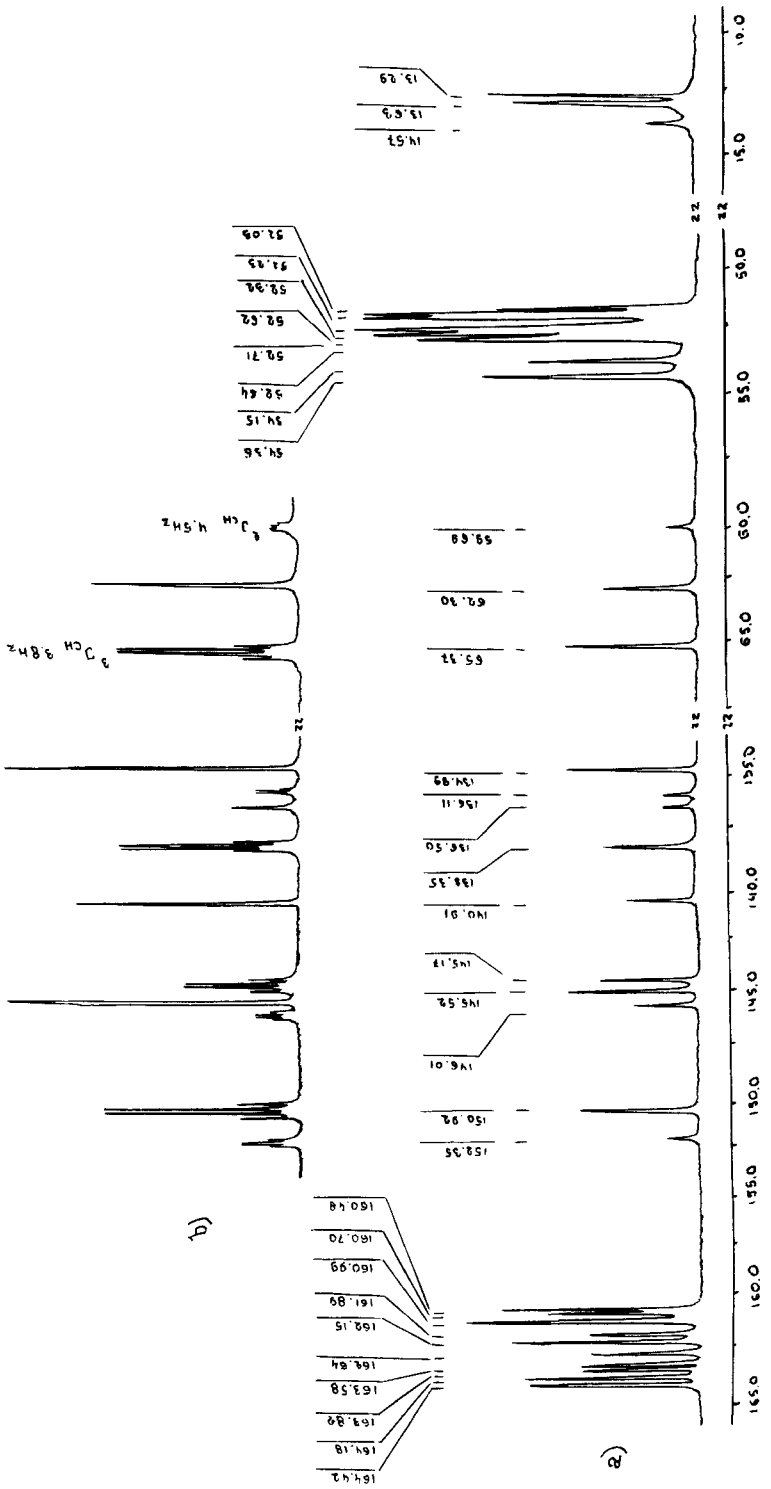
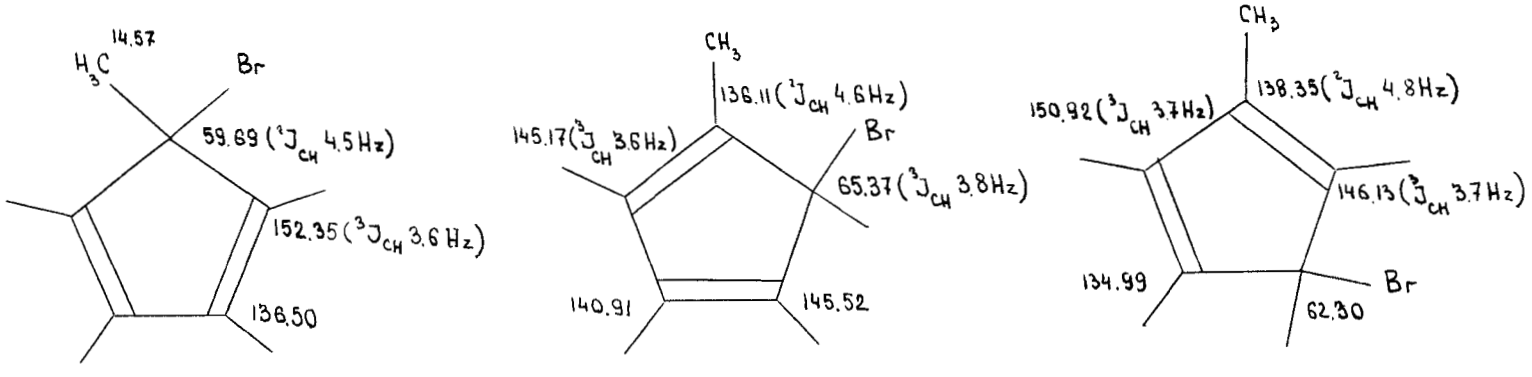



Figure 3. $^{13}C$ NMR spectrum of a mixture of bromomethyltetramethoxycarbonylcyclopentadiene isomers (**7–9**) in benzene-$d_6$ solution, (a) proton noise-decoupled and (b) off-resonance decoupled in the region of ring carbon atoms. In range 50–55 ppm partial superposition of signals of carbons from $OCH_3$ groups occurs




7 8 9

Scheme 4. Assignment of carbon atoms signals in the cyclopentadiene ring in bromomethyltetramethoxycarbonylcyclopentadiene (7–9).

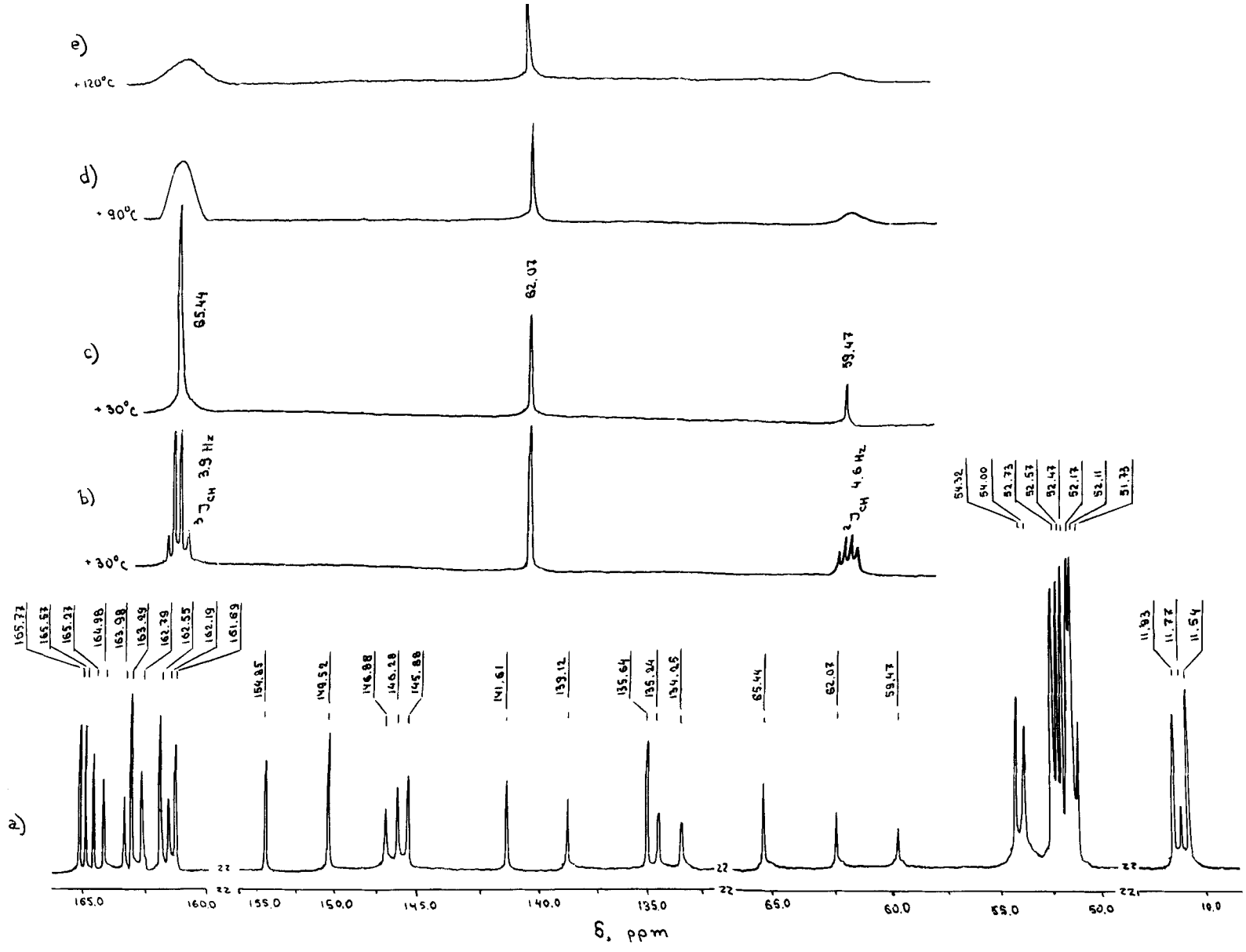
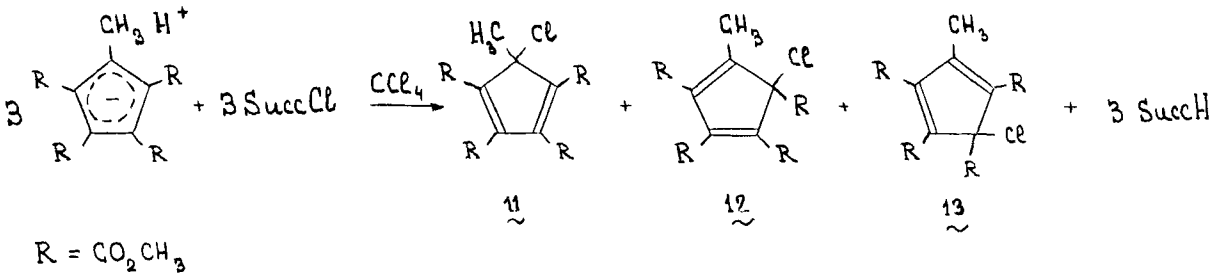



Figure 4. $^{13}C$ NMR spectrum of a mixture of bromomethyltetramethoxycarbonylcyclopentadiene isomers (**7**–**9**) in nitrobenzene-$d_5$ solution, (a) proton noise-decoupled,



Scheme 5

The spectral characteristics of compounds **11**–**14** are given in Table 1.

Heating an *o*-dichlorobenzene-$d_4$ solution of isomer **12** at 70–100 °C leads to the gradual appearance in the $^1$H NMR spectra of signals of the isomer **11** up to an equilibrium **12**:**11** ratio of 0·89:0·11 (Figure 5) (see Scheme 6). This indicates the 1,5-sigmatropic shift of the chlorine atom in the cyclopentadiene system **11** ⇌ **12** whose kinetic and activation parameters are listed in Table 2. The time dependence of the logarithmic difference between the current and the equilibrium intensities of the proton signals of **11** and **12** in the $^1$H NMR spectra has a linear character in the temperature range under study, which points to the first-order kinetics of the rearrangement. Moreover, the rate of the rearrangement **11** ⇌ **12** does not depend on the solution concentration (0·01–0·3 mol l$^{-1}$), which also indicates an intramolecular character of chlorine migration in the methyltetramethoxycarbonylcyclopentadiene system.

Heating the *o*-dichlorobenzene-$d_4$ solution of the equilibrium mixture of isomers **11** and **12** above 100 °C does not lead to the formation of the isomer **13**, but rather isomer **14** is formed as a result of the 1,5-sigmatropic shift of the methoxycarbonyl substituent (at 145 °C the equilibrium **11**:**12**:**14** = 0·05:0·30:0·65 is established in 1·5 h). Chemical shifts of **14** in the $^1$H NMR spectrum are given in Table 1 and the kinetic and activation parameters of the shift of the methoxycarbonyl substituent in Table 2. A similar 1,5-sigmatropic shift of the methoxycarbonyl group was observed by Hoffmann and Backes[35] in 5-chloro-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene at 140–160 °C.

Hence the migrational aptitude of chlorine in the methyltetramethoxycarbonylcyclopentadiene system is lower by nearly 7 kcal mol$^{-1}$ than that of bromine in the same system.

The calculations carried out are fully consistent with the conclusion as to the preference of the mechanism of the 1,5-sigmatropic shift of halogen, **1a** ⇌ **2** ⇌ **1b**, over the 1,3-shift and randomization via an intermediate $\eta^5$-structure. As can be seen from the data in Tables 3–5, both the $\eta^2$- and $\eta^3$-structures **2** and **3** represent genuine transition states for different reaction paths for the migration of halogen, i.e. on the potential energy surface (PES) of $C_5H_5X$ (X = Br, Cl, F) they correspond to the saddle points of the first order ($\lambda$ = 1). In contrast, the $\eta^5$-structures **4** are the hill-tops on the PES, through which no reaction trajectories pass. This conclusion is in accord with a qualitative analysis of haptotropic shifts in cyclopentadienyl compounds based on a division of $C_5H_5X$ MOs into their fragment orbitals.[36] As is evident from the calculation data, the structures **4** are triplet-unstable. This can be understood from the fragment MO analysis of the 12-electron $C_{5v}$ pyramidal system **4** (X = Cl, Br),[22] which possesses a half-occupied antibonding MO of 2e symmetry.

Table 1. $^1$H NMR spectra of compounds **11**–**14** in *o*-dichlorobenzene-$d_4$ solution at 25 °C

| Compound | Proton signals of $CO_2Me$ groups, $\delta$ (ppm) | Proton signals of Me group at Cp ring, $\delta$ (ppm) |
|---|---|---|
| **11** | 3.50 (s, 6H), 3·49 (s, 6H) | 1.88 (s, 3H) |
| **12** | 3·60 (s, 3H), 3·41 (s, 3H) | |
| | 3·38 (s, 3H), 3·33 (s, 3H) | 2·14 (s, 3H) |
| **13** | 3·53 (s, 3H), 3·44 (s, 3H) | |
| | 3·43 (s, 3H), 3·42 (s, 3H) | 2·15 (s, 3H) |
| **14** | 3·57 (s, 3H), 3·45 (s, 3H) | |
| | 3·44 (s, 3H), 3·30 (s, 3H) | 1·55 (s, 3H) |

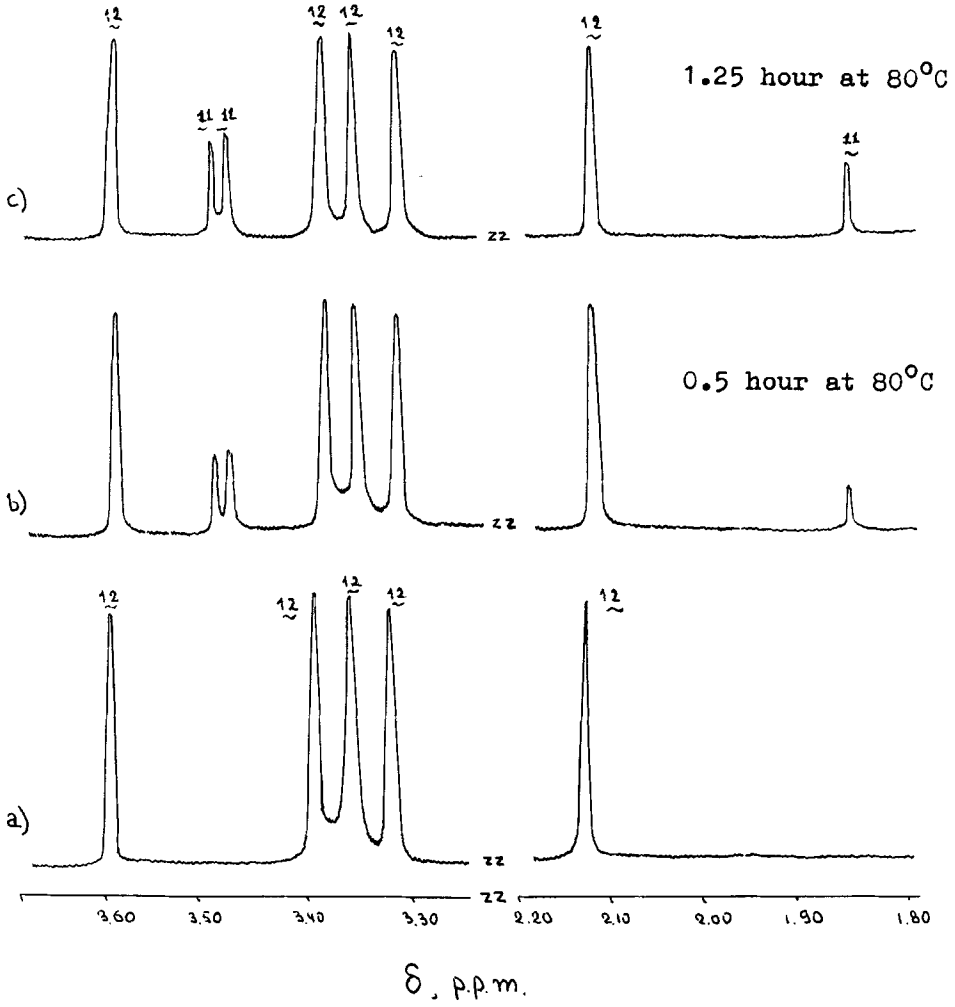
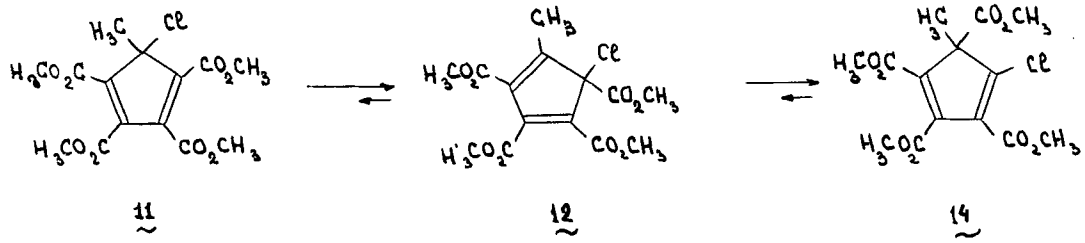



Figure 5. $^1$H NMR spectrum of 5-chloro-1-methyl-2,3,4,5-tetramethoxycarbonylcyclopentadiene (**11**) in *o*-dicholorbenzene-$d_4$ solution, (a) at 25 °C, (b) after heating for 0·5 h at 80 °C and (c) after heating for 1·25 h at 80 °C



Scheme 6

Table 2. Kinetic and activation parameters of the **11** ⇌ **12** and **12** ⇌ **14** rearrangements (solvent, *o*-dichlorobenzene-$d_4$)

| Rearrangement | Temperature (°C) | $k_t$ ($s^{-1}$) | $\Delta H^{\ddagger}$ (kcal $mol^{-1}$) | $\Delta S^{\ddagger}$ (cal $K^{-1}$ $mol^{-1}$) | $\Delta G^{\ddagger}_{298}$ (kcal $mol^{-1}$) | $k_{298}$, ($s^{-1}$) |
|---|---|---|---|---|---|---|
| **11** → **12** | 80 | $6{\cdot}6 \times 10^{-4}$ | 25·1 ± 0·2 | −3·5 ± 0·3 | 26·1 | $4{\cdot}3 \times 10^{-7}$ |
| | 90 | $1{\cdot}9 \times 10^{-3}$ | | | | |
| | 100 | $4{\cdot}7 \times 10^{-3}$ | | | | |
| **12** → **11** | 80 | $8{\cdot}4 \times 10^{-5}$ | 26·1 ± 0·2 | −5·7 ± 0·3 | 27·3 | $5{\cdot}6 \times 10^{-8}$ |
| | 90 | $2{\cdot}4 \times 10^{-4}$ | | | | |
| | 100 | $6{\cdot}0 \times 10^{-4}$ | | | | |
| **12** → **14** | 130 | $1{\cdot}9 \times 10^{-4}$ | 26·7 ± 0·3 | −10·6 ± 0·4 | 29·9 | $6{\cdot}9 \times 10^{-10}$ |
| | 145 | $6{\cdot}4 \times 10^{-4}$ | | | | |
| | 155 | $1{\cdot}1 \times 10^{-3}$ | | | | |
| **14** → **12** | 130 | $8{\cdot}7 \times 10^{-5}$ | 25·0 ± 0·2 | −16·2 ± 0·3 | 29·8 | $8{\cdot}1 \times 10^{-10}$ |
| | 145 | $2{\cdot}9 \times 10^{-4}$ | | | | |
| | 155 | $5{\cdot}2 \times 10^{-4}$ | | | | |

Table 3. Heats of formation ($\Delta H_f$), ionization potentials ($I$), dipole moments ($\mu$), atomic charges ($q$), rank of stationary points ($\lambda$) and imaginary frequencies of transition vectors ($\nu_{im}$), calculated by the AM1 method for the $\eta^1$– $\eta^5$-structures of bromo-1,3-cyclopentadiene (numbering of atoms is given in Scheme 1)

| | Structures | | | | |
|---|---|---|---|---|---|
| Property | $\eta^1$, $C_s$, **1b** | $\eta^2$, $C_s$, **2** | $\eta^3$, $C_s$, **3** | $\eta^5$, $C_{5v}$, ($S_0$), **4** | $\eta^5$, $C_{5v}$, ($T_1$), **4** |
| $\Delta H_f$ (kcal $mol^{-1}$) | 43·9 | 74·8 | 119·5 | 130·6 | 116·8 |
| $I$ (eV) | 9·42 | 8·67 | 8·24 | 8·56 | 5·62 |
| $\mu$ (D) | 1·30 | 1·07 | 2·30 | 3·48 | 3·49 |
| $q$ (C-1) | −0·134 | −0·039 | −0·312 | −0·295 | −0·095 |
| $q$ (C-2) | −0·176 | −0·264 | 0·079 | 0·080 | −0·095 |
| $q$ (C-3) | −0·135 | −0·075 | −0·155 | −0·171 | −0·095 |
| $q$ (H-1) | 0·149 | 0·148 | 0·165 | 0·164 | 0·160 |
| $q$ (H-2) | 0·156 | 0·157 | 0·154 | 0·156 | 0·160 |
| $q$ (H-3) | 0·148 | 0·171 | 0·161 | 0·161 | 0·160 |
| $q$(Br) | −0·004 | −0·088 | −0·330 | −0·319 | −0·321 |
| $\lambda$ | 0 (min.) | 1 (TS[a]) | 1 (TS[a]) | 2 (hill) | 2 (hill) |
| $\nu_{im}$ ($cm^{-1}$) | — | i 830·4 | i 1816·8 | — | — |

[a] Transition state.

Table 4. Heats of formation ($\Delta H_f$), ionization potentials ($I$), dipole moments ($\mu$), atomic charges ($q$), rank of stationary points ($\lambda$) and imaginary frequencies of transition vectors ($\nu_{im}$), calculated by the AM1 and MINDO/3 methods (values in parentheses) for the $\eta^1$– $\eta^5$-structures of chloro-1,3-cyclopentadiene (numbering of atoms is given in Scheme 1)

| | Structures | | | | |
|---|---|---|---|---|---|
| Property | $\eta^1$, $C_s$, **1b** | $\eta^2$, $C_s$, **2** | $\eta^3$, $C_s$, **3** | $\eta^5$, $C_{5v}$, ($S_0$), **4** | $\eta^5$, $C_{5v}$, ($T_1$), **4** |
| $\Delta H_f$ (kcal $mol^{-1}$) | 32·4(33·8) | 74·4(55·8) | 110·3(83·6) | 121·0(101·5) | 108·1 |
| $I$ (eV) | 9·45(9·13) | 8·81(8·14) | 8·95(7·66) | 8·78(7·54) | 5·80 |
| $\mu$ (D) | 1·44(2·05) | 1·78(1·56) | 4·44(2·46) | 4·66(3·42) | 4·61 |
| $q$ (C-1) | −0·037(0·315) | 0·006(0·210) | −0·315(−0·228) | −0·298(0·273) | −0·073 |
| $q$ (C-2) | −0·182(−0·080) | −0·301(−0·216) | 0·147(0·313) | 0·127(−0·021) | −0·73 |
| $q$ (C-3) | −0·133(0·018) | 0·007(0·179) | −0·154(−0·025) | −0·158(0·176) | −0·073 |
| $q$ (H-1) | 0·138(−0·040) | 0·170(0·002) | 0·169(0·054) | 0·168(−0·006) | 0·164 |
| $q$ (H-2) | 0·155(0·032) | 0·159(0·043) | 0·164(−0·025) | 0·160(0·024) | 0·164 |
| $q$ (H-3) | 0·149(0·010) | 0·148(−0·016) | 0·167(0·027) | 0·165(0·040) | 0·164 |
| $q$(Cl) | −0·082(−0·235) | −0·226(−0·244) | −0·503(−0·408) | −0·459(−0·405) | −0·455 |
| $\lambda$ | 0 (min.) | 1 (TS[a]) | 1 (TS[a]) | 2 (hill) | 2 (hill) |
| $\nu_{im}$ ($cm^{-1}$) | — | i 937·9(714·7) | i 969·6(676·4) | — | — |

[a] Transition state.

Table 5. Heats of formation ($\Delta H_f$), ionization potentials ($I$), dipole moments ($\mu$), atomic charges ($q$), rank of stationary points ($\lambda$) and imaginary frequencies of transition vector ($\nu_{im}$), calculated by the AM1 method for the $\eta^1$– $\eta^5$-structures fluoro-1,3-cyclopentadiene. The bond lengths $l$ are in Å and angles $\alpha$ in degrees (numbering of atoms is given in Scheme 1)

| | Structures | | | | |
|---|---|---|---|---|---|
| Property | $\eta^1$, $C_s$, **1b** | $\eta^2$, $C_s$, **2** | $\eta^3$, $C_s$, **3** | $\eta^5$, $C_{5v}$, ($S_0$), **4** | $\eta^5$, $C_{5v}$, ($T_1$), **4** |
| $\Delta H_f$ (kcal mol$^{-1}$) | −4·3 | 73·2 | 131·3 | 142·3 | 127·5 |
| $I$ (eV) | 9·53 | 8·12 | 9·19 | 8·87 | 9·15 |
| $\mu$ (D) | 1·68 | 1·51 | 3·53 | 3·52 | 3·11 |
| $q$ (C-1) | 0·092 | 0·060 | −0·289 | −0·294 | −0·085 |
| $q$ (C-2) | −0·203 | −0·388 | 0·177 | −0·159 | −0·085 |
| $q$ (C-3) | −0·129 | 0·016 | −0·145 | 0·112 | −0·085 |
| $q$ (H-1) | 0·113 | 0·159 | 0·163 | 0·162 | 0·157 |
| $q$ (H-2) | 0·155 | 0·156 | 0·152 | 0·155 | 0·157 |
| $q$ (H-3) | 0·148 | 0·141 | 0·158 | 0·159 | 0·157 |
| $q$(F) | −0·147 | −0·134 | −0·438 | −0·402 | −0·358 |
| $\lambda$ | 0 | 1 | 1 | 2 | 2 |
| $\nu_{im}$ (cm$^{-1}$) | — | i 1073·9 | i 1014·5 | — | — |
| $l$(C-1—C-2) | 1·532 | 1·402 | −1·496 | 1·429 | 1·429 |
| $l$(C-2—C-3) | 1·353 | 1·439 | 1·414 | — | — |
| $l$(C-3—C-4) | 1·476 | 1·529 | 1·363 | — | — |
| $l$(C-1—F) | 1·378 | 1·580 | 2·330 | 2·426 | 2·425 |
| $\alpha$[a] | 130·8° | 103·7° | — | — | — |
| $l$(C-1—H-1) | 1·129 | 1·089 | 1·086 | 1·088 | 1·088 |
| $l$(C-2—H-2) | 1·087 | 1·084 | 1·088 | — | — |
| $l$(C-3—H-3) | 1·090 | 1·100 | 1·087 | — | — |

[a] $\alpha$ is the angle between the Cp ring plane and the migrating atom.

Table 6. Energy barriers calculated by the AM1 and MINDO/3 (in the parentheses) methods for 1,5- and 1,3-sigmatropic shifts of halogens in cyclopentadiene derivatives **1**, compared with the experimental data for compounds **1**

| | $\Delta G^{\ddagger}$ (kcal mol$^{-1}$) | | |
|---|---|---|---|
| X | 1,5-Shift (**2**, $\eta^2$) | 1,3-Shift(**3**, $\eta^3$) | Experimental |
| F | 77·5 | 135·6 | — |
| Cl | 42·0(22·0) | 77·9(49·8) | 26·1–27·3[a] |
| Br | 30·9 | 75·6 | 16·2–22·9[b] |

[a] Chlorine migration in corresponding methyltetramethoxycarbonyl cyclopentadiene derivatives (this work).
[b] Bromine migration in corresponding tolyltetraphenyl- and alkyltetramethoxycarbonylcyclopentadiene derivatives.[13]

Table 6 lists some results for the calculation of the energy barriers of intramolecular migrations of halogens in the cyclopentadiene ring in comparison with the experimental data obtained for solutions of tetra- and pentasubstituted $\eta^1$-halogencyclopentadienes. It can be see that the route of the 1,5-sigmatropic migrations is more favourable than that of the 1,3-halogen shift in all cases. Even though the direct comparison between the energy barriers calculated for cyclopentadiene derivatives **1**, unsubstituted in the ring, and those for tetra- and pentamethoxycarbonyl- and aryl-substituted cyclopentadienes is somewhat arbitrary, it is clear that the AM1 method overestimates the absolute values of the energy barriers. A similar overestimation is also typical of the analogously parameterized MNDO, as was shown by calculations[25] of the reaction paths for circumambulation of the thiol and dithiol (X = SH, SSH) groups. As with sulphur-containing compounds, the use of the MINDO/3 method, while retaining the order of relative energies, gives a fairly good agreement with experimental barriers.

Figures 6 and 7 present geometry characteristics, calculated by the AM1 method, of the ground-state $\eta^1$-structures of chloro- and bromocyclopentadienes and $\eta^2$- and $\eta^3$-structures of the transition state for 1,5- and 1,3-shifts, respectively, of halogens. From the charge distributions and the dipole moment values given in Tables 3–5, it may be inferred that the transition-state structures for 1,5-sigmatropic shifts are weakly polarized and structure **2** represents only one of the complete set of conceivable resonance forms that adequately describe the electron distribution in the transition state. It is evident from Tables 3–5 that passing from the $\eta^1$- to the $\eta^2$-structure hardly disturbs the original electron distribution. It may be expected that the

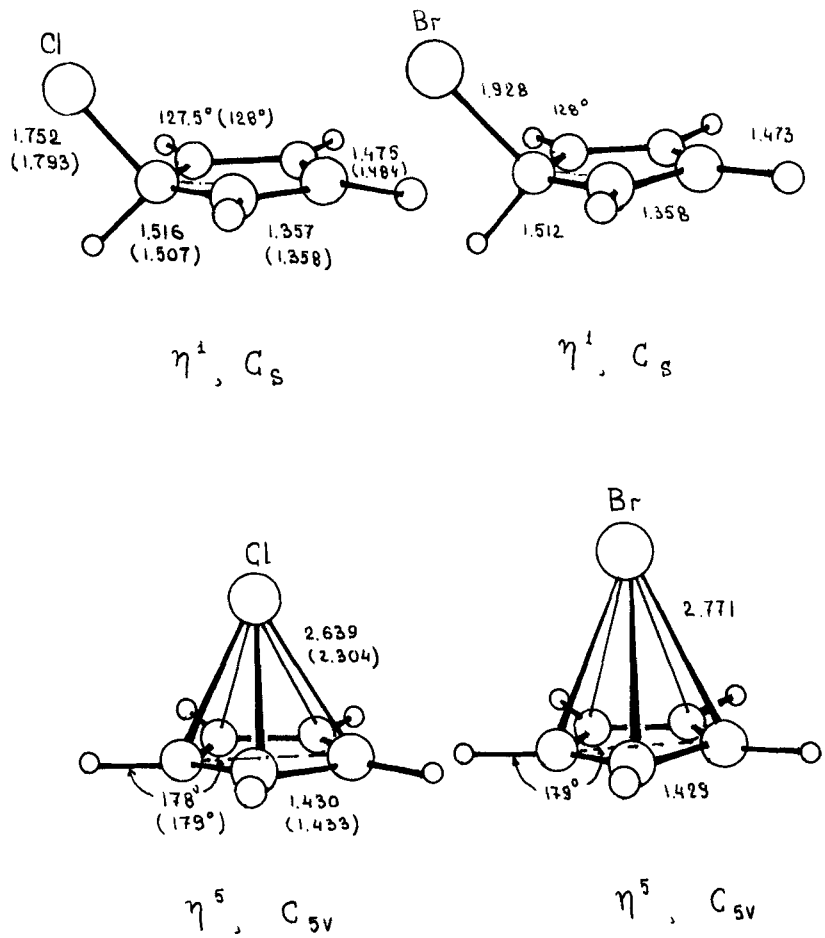
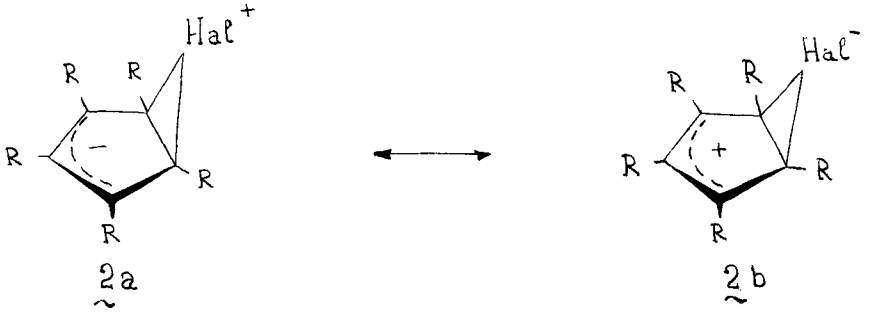



Figure 6. Geometric characteristics of the $\eta^1$- and $\eta^5$- structures of bromo-1,3-cyclopentadiene and chloro-1,3-cyclopentadiene calculated by the AM1 method. The bond lengths are in Å. Numbers in parentheses are the data from the MINDO/3 calculation




Scheme 7

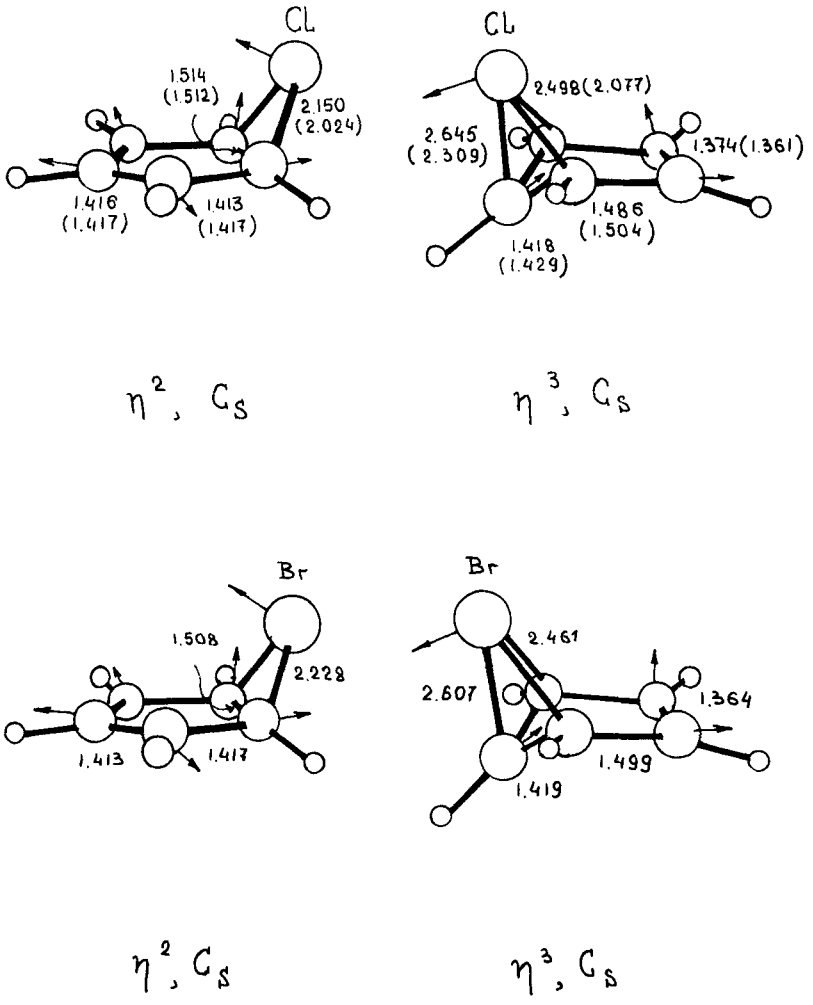



Figure 7. Geometric characteristics of the $\eta^2$- and $\eta^3$-structures of transition states of bromo-1,3-cyclopentadiene and chloro-1,3-cyclopentadiene calculated by the AM1 method. Arrows show the direction of the components of the transition vector corresponding to imaginary frequency. The bond lengths are in Å. Numbers in parentheses are the data from the MINDO/3 calculation

balance of contributions from the two most important structural forms describing the transition state for the 1,5-sigmatropic shift will depend strongly on the character of the substituent in the ring (Scheme 7). This question will be dealt with in a separate publication.

## CONCLUSION

In the 5-methyl-1,2,3,4-tetramethoxycarbonylcyclopentadiene system, the migration of bromine occurs as a result of successive intramolecular 1,5-sigmatropic shifts. The migrational aptitude of chlorine in analogous chlorine derivatives is lower by nearly 7 kcal mol$^{-1}$ than that of bromine. It has been shown using the semi-empirical AM1 and MINDO/3 methods that the route of the 1,5-sigmatropic migrations of fluorine, chlorine and bromine in unsubstituted cyclopentadiene is preferred over that of the 1,3-halogen shift. The $\eta^5$-structures (randomization mechanism) represent on the PES the hill-tops through which no reaction trajectories pass.

## EXPERIMENTAL AND CALCULATIONS

The $^{13}C$ NMR spectra were recorded on Bruker AM instruments (frequency for $^{13}C$, 125·76 and 50·33 MHz) and Tesla BS-567A (25·14 MHz) in benzene-$d_6$ and nitrobenzene-$d_5$ solutions at concentra-

tions of 0·1–0·4 mol $l^{-1}$. $^1$H NMR spectra (100 MHz) in *o*-dichlorobenzene-$d_4$ solutions at concentrations of 0·01–0·3 mol $l^{-1}$ were recorded on a Varian XL-100 spectrometer. IR spectra were recorded on a Specord IR-75 instrument with Nujol films.

The rate constants of the shifts of chlorine and the methoxycarbonyl group were calculated as for the reversible first-order reactions based on the time dependence of the intensities of the signals in the $^1$H NMR spectra of the respective compounds at three temperatures.

All calculations by the AM1 and MINDO/3 methods were carried out using the AMPAC set of programs[37] *adapted* for an ES-1061 computer. Complete optimization of all independent geometry parameters was performed. The identification of the nature of the stationary points was achieved by calculating the Hess matrices. Inclusion of the configuration interaction does not have any appreciable effect on the energies of the calculated structures.

Bromomethyltetramethoxycarbonylcyclopentadienes (**7**–**9**) and 5-methyl-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene (**10**) were obtained as described previously.[13,38]

To prepare 5-chloro-1-methyl-2,3,4,5-tetramethoxycarbonylcyclopentadiene (**11**), 1-methyl-2,3,4,5-tetramethoxycarbonylcyclopentadiene[38] (0·002 mol) was suspended in 10 ml of dry $CCl_4$ and 0·002 mol of *N*-chlorosuccinimide and a catalytic amount of activated benzoyl peroxide were added. After refluxing the mixture for 30 min, a precipitate of succinimide formed and was filtered off. The residual solution was evaporated to dryness under vacuum and the residue of raw compound **11** was recrystallized three times from diethyl ether to give colourless rhomboidal crystals, m.p. 107–108 °C (60% yield). IR (Nujol), $\nu_{C=O}$ 1775, 1750, 1725 $cm^{-1}$, $\nu_{C=C}$ 1630, 1590, 1440, 1355, 1300, 1210, 1170, 1150, 1075, 1020, 1000, 980, 965, 900, 865, 800, 700, 670 $cm^{-1}$. $^1$H NMR data for **11** are given in Table 1. Elemental analysis: C 48·52, H 4·38, Cl 10·26; calculated for $C_{14}H_{15}ClO_8$, C 48·50, H 4·36, Cl 10·23%.

ACKNOWLEDGEMENTS

The authors are grateful to Dr Yu. E. Chernysh and Dr E. V. Sukholenko for their assistance with the NMR experiments and useful discussions.

REFERENCES

1. T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.* **2**, 32–38 (1956).
2. F. A. Cotton, in *Dynamic NMR Spectroscopy*, edited by L. M. Jacman and F. A. Cotton, pp. 377–440. London, Academic Press (1979), and references cited therein.
3. V. I. Minkin, L. P. Olekhnovich and Yu. A. Zhdanov, in *Molecular Design of Tautomeric Compounds*, p. 280. Reidel, Dordrecht, (1988), and references cited therein.
4. C. W. Spangler, *Chem. Rev.* **76**, 187–217 (1976).
5. R. F. Childs, *Tetrahedron* **38**, 567–608 (1982).
6. P. Jutzi, *Chem. Rev.* **86**, 983–996 (1986).
7. I. E. Mikhailov, V. I. Minkin, A. A. Klenkin, G. A. Dushenko, L. P. Olekhnovich and Yu. A. Zhdanov, *Dokl. Akad. Nauk SSSR* **287**, 1404–1406 (1986).
8. I. E. Mikhailov, A. A. Klenkin, V. I. Minkin and L. P. Olekhnovich, *Zh. Org. Khim.* **22**, 865–867 (1986).
9. I. E. Mikhailov, V. I. Minkin, A. A. Klenkin, G. A. Dushenko, O. E. Compan, Yu. T. Strychkov, A. I. Janovski, L. P. Olekhnovich and N. I. Borisenko, *Zh. Org. Khim.* **24**, 2301–2309 (1988).
10. I. E. Mikhailov, V. I. Minkin, A. A. Klenkin, G. A. Dushenko, O. E. Compan, Yu. T. Struchkov and A. I. Janovski, *Zh. Org. Khim.* **26**, 28–40 (1990).
11. G. I. Borodkin, E. P. Susharin and V. G. Shubin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1687 (1986).
12. I. E. Mikhailov, V. I. Minkin, A. A. Klenkin and L. P. Olekhnovich, *Zh. Org. Khim.* **22** 1331–1332 (1986).
13. I. E. Mikhailov, V. I. Minkin, G. A. Dushenko, A. A. Klenkin and L. P. Olekhnovich, *Zh. Org. Khim.* **24**, 1179–1189, (1988).
14. I. E. Mikhailov, G. A. Dushenko, V. I. Minkin, L. P. Olekhnovich, N. I. Borisenko and Yu. A. Zhdanov, *Dokl. Akad. Nauk SSSR* **270**, 891–893 (1983).
15. I. E. Mikhailov, G. A. Dushenko, V. I. Minkin and L. P. Olekhnovich, *Zh. Org. Khim.* **20**, 2306–2311 (1984).
16. V. A. Mironov, A. D. Fedorovich and A. A. Akhrem, *Usp. Khim.* **50**, 1272–1303 (1981).
17. P. Jutzi and H. Saleske, *Chem. Ber.* **117**, 223–233 (1984).
18. C. A. Schembelov and Yu. A. Ustynyuk, *J. Am. Chem. Soc.* **96**, 4189–4191 (1974).
19. V. I. Minkin, R. M. Minyaev, J. A. Yudilevich and M. E. Klezski, *Zh. Org. Khim.* **24**, 2241–2251 (1988).
20. W. W. Schoeller, *J. Am. Chem. Soc.* **97**, 1978–1980 (1975); W. W. Schoeller, *J. Chem. Soc., Dalton Trans.* 2233–2236 (1984).
21. V. I. Minkin and R. M. Minyaev, *Zh. Org. Khim.* **15**, 1569, (1979).
22. V. I. Minkin, R. M. Minyaev and Yu. A. Zhdanov, in *Nonclassical Structures of Organic Compounds*, p. 311 Mir, Moscow (1987).
23. V. I. Minkin, R. M. Minyaev and J. A. Yudilevich, *Zh. Org. Khim.* **23**, 1137–1148 (1987).
24. V. I. Minkin, J. A. Yudilevich and R. M. Minyaev, *Zh. Org. Khim.* **23**, 717–730 (1987).
25. V. I. Minkin, R. M. Minyaev and J. A. Yudilevich, *J. Mol. Struct., THEOCHEM.* **186**, 293–304 (1989).
26. I. E. Mikhailov, V. I. Minkin and A. A. Klenkin, *Zh. Org. Khim.* **27** in press (1991).
27. V. I. Minkin, B. Ya. Simkin and R. M. Minyaev, in *Quatum Chemistry of Organic Compounds, Mechanisms of Reaction*. Springer, Heidelberg (1990).
28. M. J. S. Dewar, E. G. Zoebsch and E. F. Nealy, *J. Am. Chem. Soc.* **107**, 3902–3909 (1985).
29. R. G. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.* **97**, 1294–1301 (1975).
30. Ch. Janiak, M. Schwichtenberg and F. E. Hahn, *J. Organomet. Chem.* **365**, 37–46 (1989).
31. A. Bonny, R. D. Holmes-Smith, G. Hunter and S. R. Stobart, *J. Am. Chem. Soc.* **104**, 1855–1859 (1982).

32. N. M. Sergeyev, *Prog. Nucl. Magn. Reson. Spectrosc.* **2**, 71–144 (1973).
33. B. E. Mann, in *Comprehensive Organometallic Chemistry*, edited by G. Wilkinson, A. G. F. Stone and W. E. Abel, Vol. 3, Chapt. 20, pp. 90–168. Pergamon Press, New York (1982).
34. G. C. Levy and G. L. Nelson in *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, p. 295 Wiley, New York (1972).
35. R. W. Hoffmann and J. Backes, *Chem. Ber.* **109** 1928–1941 (1976).
36. N. T. Anh, M. Elian and R. D. Hoffmann, *J. Am. Chem Soc.* **100**, 110–116 (1978).
37. *Quantum Chemistry Program Exchange*, Prograr No. 706. Department of Chemistry, Indiana University Bloomington, IN, USA.
38. R. C. Cookson, J. B. Henstock, J. Hudec and B. R. D Whitear, *J. Chem. Soc. C* **70**, 1986–1993 (1967).