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1,5-Sigmatropic Shifts of Chlorine in the Cyclopentadiene Ring

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Intramolecular rearrangement due to successive 1,5-sigmatropic shifts of chlorine over a five-membered ring were found to occur in 5-chloro-1-alkyl-2,3,4,5-tetramethoxycarbonylcyclopentadienes with energy barriers to chlorine migration falling in the range 26.0–27.3 kcal mol^{-1}.

The first examples of intramolecular migration of chlorine,[1] bromine[1,2] and iodine[3] in the cyclopentadiene ring have recently been documented. However, it is only in the case of bromine migration that the mechanism of the 1,5-sigmatropic shift has been reliably established. Here we report on a study of the kinetics of displacement of chlorine over the cyclopentadiene ring in a series of 5-chloro-1-alkyl-2,3,4,5-tetramethoxycarbonylcyclopentadienes **3** using ^{1}H and ^{13}C NMR spectroscopy and present evidence in favour of the successive 1,5-sigmatropic shift mechanism of the rearrangement.

A mixture of isomers **2–4** was obtained in 85–95% yields upon coupling 5-alkyl-1,2,3,4-tetramethoxycarbonylcyclopentadienes **1** with *N*-chlorosuccinimide (SuccCl) in CCl_4 solution in the presence of catalytic amounts of benzoyl peroxide.†

In the ^{1}H NMR spectra of equilibrium mixtures of isomers **2–4** an assignment of signals to **2** has been made with accounts for the C_s-symmetry of the **2a–c** molecules and the higher-field position of the alkyl or benzyl group R^1 signals which in **2a–c** are attached to the C_{sp^3}-centres. In contrast to

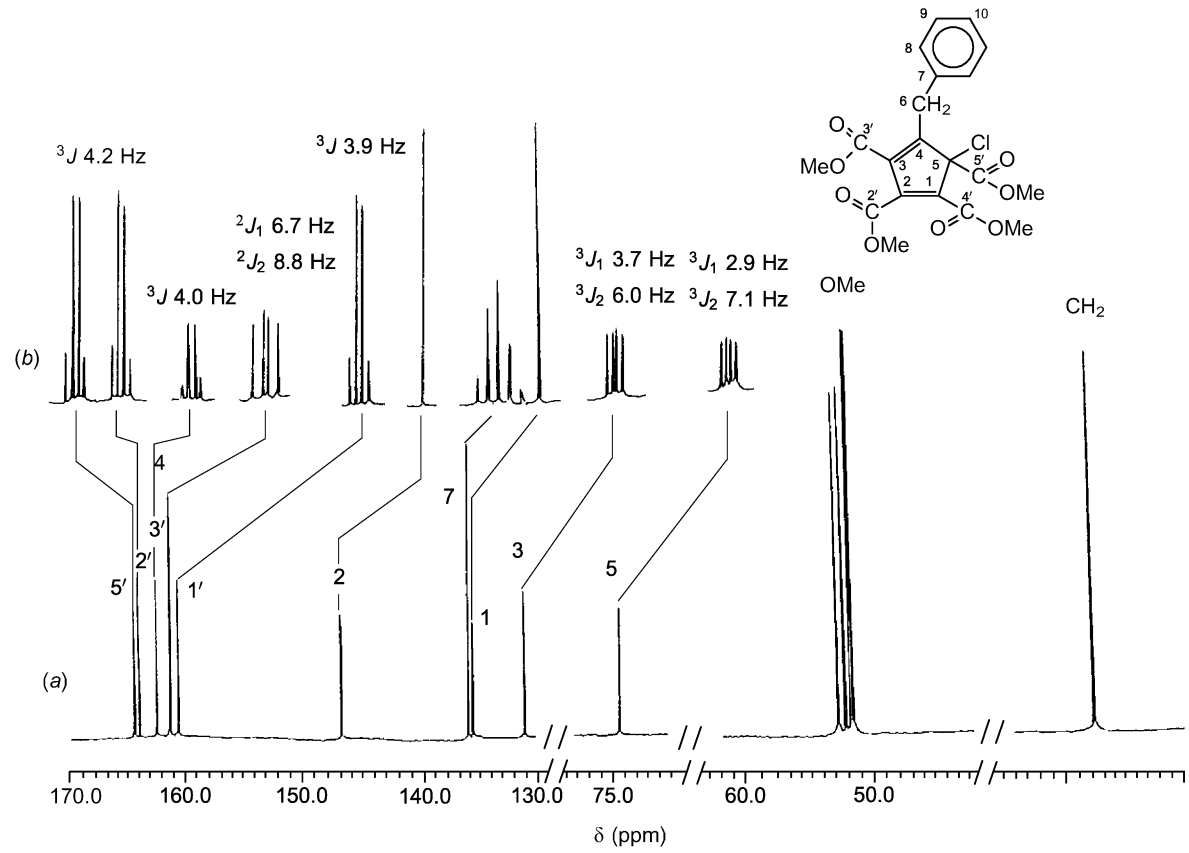
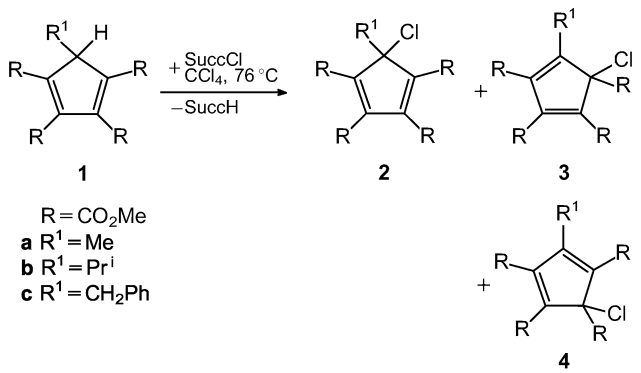


Fig. 1 ^{13}C NMR spectrum (75.47 MHz) of 5-chloro-1-benzyl-2,3,4,5-tetramethoxycarbonylcyclopentadiene (**3c**) in [$^2H_6$]benzene solution: (*a*) proton noise-decoupled; (*b*) single resonance (proton coupled) in the region of ring and carbonyl group carbon nuclei.



Scheme 1

2, the C_{sp^3}-centres in isomers **3b,c** and **4b,c** are stereogenic and their isopropyl and benzyl groups are thus prochiral displaying diastereotopic splitting of, respectively, methyl and methylene protons. Such a splitting, Δδ, should certainly be larger for isomers **3** owing to the closer, compared to **4**, proximity of their prochiral groups to the stereogenic centre. The values of Δδ (in ppm) were found to be equal to: **3b** 0.01, **4b** 0, **3c** 0.90 ($^2J_{HH}$ 14.3 Hz), **4c** 0.77 ($^2J_{HH}$ 12.5 Hz). The same approach to the assignment of ^1H NMR spectral signals to certain isomers of types **2–4** has been applied previously in the case of trifluoromethylacyloxybenzyltetraphenylcyclopentadiene, its reliability being proved by X-ray structural and ^{13}C NMR spectral studies.[4]

By repeated recrystallization from diethyl ether, it was possible to preparatively isolate isomers **3a–c**.‡ These were assigned by means of ^{13}C NMR spectroscopy, taking as indicator groups the carbon atoms of the cyclopentadiene ring and using as a basis the values of the spin-spin coupling constants of the alkyl (benzyl) group protons with the carbon (^{13}C) atoms of the ring, particularly with C_{sp^3}-centres, since the values of the spin-spin coupling constants gradually decrease with an increase in the number of bonds which

† The equilibrium ratio of the isomers **2**:**3**:**4** in CCl_4 solution at 25 °C were determined from intensities of the proton signals of the alkyl groups and found to be as follows: **2a**:**3a**:**4a** = 0.15:0.60:0.25, **2b**:**3b**:**4b** = 0.30:0.54:0.14, **2c**:**3c**:**4c** = 0.15:0.49:0.36. ^1H NMR spectral data (300 MHz, C_6D_6): **2a** δ 1.88 (3H, s, Me), 3.49 (6H, s, OMe), 3.50 (6H, s, OMe); **3a** see footnote‡; **4a** δ 2.15 (3H, s, Me), 3.42 (3H, s, OMe), 3.43 (3H, s, OMe), 3.44 (3H, s, OMe), 3.53 (3H, s, OMe); **2b** δ 1.11 (6H, d, ^3J 7.0 Hz, Me of Pr^i), 3.22–3.30 (1H, m, CH of Pr^i), 3.46 (6H, s, OMe), 3.49 (6H, s, OMe); **3b** see footnote‡; **4b** δ 1.24 (6H, d, ^3J 7.0 Hz, Me of Pr^i), 3.33 (3H, s, OMe), 3.35–3.73 (1H, m, CH of Pr^i), 3.36 (3H, s, OMe), 3.44 (3H, s, OMe), 3.57 (3H, s, OMe); **2c** δ 3.19 (6H, s, OMe), 3.30 (6H, s, OMe), 3.94 (2H, s, CH_2), 6.75–7.28 (5H, m, aromatic H); **3c** see footnote‡; **4c** δ 3.11 (3H, s, OMe), 3.23 (3H, s, OMe), 3.28 (3H, s, OMe), 3.31 (3H, s, OMe), 3.92 and 4.69 (2H, AB-spectral pattern, ^2J 12.5 Hz, benzyl H), 6.92–7.18 (5H, m, aromatic H).

‡ Compounds **3a–c** (colourless crystals from diethyl ether) gave satisfactory elemental analyses.

3a: m.p. 107–108 °C; ^1H NMR (300 MHz, C_6D_6) δ 2.14 (3H, s, Me), 3.33 (3H, s, OMe), 3.38 (3H, s, OMe), 3.41 (3H, s, OMe), 3.60 (3H, s, OMe); IR (Nujol) ν/cm^{-1} 1775, 1750, 1725 (C=O), 1630, 1590 (C=C), 1440, 1335, 1300, 1210.

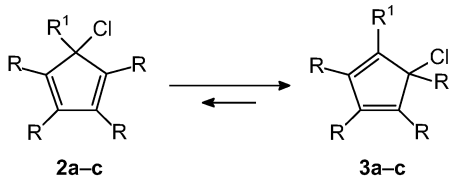
3b: m.p. 121–122 °C; ^1H NMR (300 MHz, C_6D_6) δ 1.33 (3H, d, ^3J 7.0 Hz, Me of Pr^i), 1.34 (3H, d, ^3J 7.0 Hz, Me of Pr^i), 3.30–3.58 (1H, m, CH of Pr^i), 3.26 (3H, s, OMe), 3.33 (3H, s, OMe), 3.38 (3H, s, OMe), 3.71 (3H, s, OMe); IR (Nujol) ν/cm^{-1} 1775, 1755, 1730 (C=O), 1600 (C=C), 1300, 1240.

3c: m.p. 131–132 °C; ^1H NMR (300 MHz, C_6D_6) δ 2.62 (3H, s, OMe), 3.18 (3H, s, OMe), 3.24 (3H, s, OMe), 3.68 (3H, s, OMe), 3.72 and 4.62 (2H, AB-spectral pattern, ^2J 14.3 Hz, benzyl H), 6.89–7.20 (5H, m, aromatic H); IR (Nujol) ν/cm^{-1} 1775, 1750, 1730 (C=C), 1635, 1590 (C=C), 1470, 1310, 1250, 1210.

Table 1 The ^{13}C NMR spectra of compounds **2b**, **3a–3c** (solvent C_6D_6), δ (ppm)[a].

Compound	R^1	OMe[b]	C_{sp^3}-ring	C=O
2b	35.09 (CH), 16.92 (Me)	52.01, 52.23	78.77 (C^5), 138.06 ($C^{2,3}$), 145.37 ($C^{1,4}$)	162.29, 162.35,
3a	12.50 (Me)	51.53, 51.83, 52.22, 53.56	75.03 (C^5), 130.26 (C^3), 134.76 (C^1), 147.06 (C^2), 160.30 (C^4)	160.43, 161.92, 164.07, 164.62, ($C^{1'-3',5'}$)
3b	28.88 (CH), 20.57 (Me), 20.90 (Me)	51.62, 51.86, 52.13, 53.37	75.44 (C^5), 130.56 (C^3), 134.78 (C^1), 147.05 (C^2), 168.01 (C^4)	160.38, 162.13, 164.12, 164.65, ($C^{1'-3',5'}$)
3c	32.64 (CH_2), 126.97 (C^{10}), 128.59, 129.55 ($C^{8,9}$), 136.08 (C^7)	51.89, 51.97, 52.37, 53.07	74.53 (C^5), 131.47 (C^3), 135.73 (C), 146.73 (C^2), 161.14 (C^4)	160.37 ($C^{1'}$), 162.16 ($C^{3'}$), 163.78 ($C^{2'}$), 164.15 ($C^{5'}$)

[a] The assignment of the signals in the ^{13}C NMR spectra of compounds **2b**, **3a–3c** is carried out according to the characteristic chemical shifts of carbon atoms using ^{13}C single resonance (proton coupled) spectra and the values of long range spin-spin coupling constants ^{13}C–^1H.
[b] The chemical shifts of OMe group carbons are not assigned and are given in ascending order.



Scheme 2

separate the interacting nuclei.[1,5] The isomer **3a** shows its C_{sp^3}-ring signal at δ 75.03 ppm (C_6D_6 solution) which is split into a quartet (J_{CH} 3.9 Hz) in the single resonance (proton coupled) ^{13}C NMR spectrum. The ^{13}C NMR spectrum of the equilibrium mixture of isomers **2a–4a** contains, apart from a signal δ 75.03 ppm, two additional signals in the region characteristic of the C_{sp^3}-ring centres, at 78.12 and 77.44 ppm. Whereas the former less intense peak transforms into a quartet (J_{CH} 5.2 Hz) in the single resonance ^{13}C NMR spectrum, the latter does not show splitting under the same conditions (J_{CH} 0 Hz). Taking into account the fact that $^2J_{CH} > {}^3J_{CH}$ and $^4J_{CH} \simeq 0$ and that the content of isomer **2a** in the equilibrium mixture is, judging from the ^1H NMR spectral data, smaller then those of **3a** and **4a**, an assignment was made of the δ 78.12 ppm signal to **2a**, the δ 77.44 signal to **4a** and the δ 75.03 signal to isomer **3a**. In the single resonance ^{13}C NMR spectra (C_6D_6 solution) of compounds **3b** and **3c** C_{sp^3}-ring signals appear as a doublet at δ 75.44 ppm ($^3J_{CH}$ 3.8 Hz) and doublet of doublets at δ 74.53 ($^3J_{1,CH}$ 2.9 Hz, $^3J_{2,CH}$ 7.1 Hz). Fig. 1 shows the ^{13}C NMR spectra of **3c**. Assignments for signals observed in the ^{13}C NMR spectra of **3c**, **3a**, **3b** and compound **2b** for which preparative isolation was also possible are given in Table 1.

When *o*-dichlorobenzene solutions of individual isomers **3a–c** were heated at 70–100 °C, the gradual appearance in the ^1H NMR spectra of a signals due to the respective isomers **2a–c** was observed, equilibria being established, regardless of

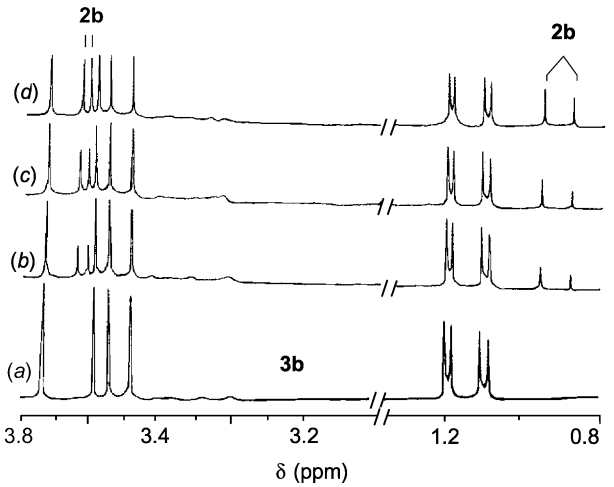


Fig. 2 ^1H NMR spectra (100 MHz) of 5-chloro-1-isopropyl-2,3,4,5-tetramethoxycarbonylcyclopentadiene (**3b**) in *o*-dichlorobenzene solution: (*a*) at 25 °C; (*b*) after heating for 14 min at 80 °C (**2b**: **3b** = = 0.13: 0.87); (*c*) after heating for 28 min at 80 °C (**2b**: **3b** = = 0.22: 0.78); (*d*) after heating for 1.5 h at 80 °C (**2b**: **3b** = = 0.35: 0.65), equilibrium mixture of isomers.

concentration of the solution, in 0.5–2.5 h. Fig. 2 portrays spectral changes occuring during the equilibration reaction.

Such a spectral behaviour is caused by the reversible intramolecular 1,5-sigmatropic shifts of chlorine over the cyclopentadiene ring which result in interconversion of the type **3** and **2** isomers. By studying the time dependence of the intensities of the proton signals of the rearranging isomers, kinetic and activation parameters of the reactions **2** ⇆ **3** were calculated. These are listed in Table 2.

No formation of measurable amounts of isomer **4** has been detected over the temperature range 70–100 °C upon equilibration (2) started from either **2** or **3**. Heating the equilibrium

Table 2 Equilibrium content of isomers **2a–c**, **3a–c** in *o*-dichlorobenzene solution at 80 °C. Kinetic and activation parameters of the rearrangement **2** ⇆ **3**.

Ratio of isomers	Rearrangement	k_{298}/ s^{-1}	$\Delta H^{\ddagger}$ /kcal mol^{-1}	$\Delta S^{\ddagger}$ /e.u.	$\Delta G^{\ddagger}_{298}$ /kcal mol^{-1}
0.11:0.89	**2a** ⟶ **3a**	4.3×10^{-7}	25.1 ± 0.2	-3.5 ± 0.3	26.1
	3a ⟶ **2a**	5.6×10^{-8}	26.1 ± 0.2	-5.7 ± 0.3	27.3
0.35:0.65	**2b** ⟶ **3b**	5.0×10^{-7}	23.9 ± 0.4	-6.9 ± 0.5	26.0
	3b ⟶ **2b**	2.6×10^{-7}	24.1 ± 0.3	-7.6 ± 0.5	26.4
0.25:0.75	**2c** ⟶ **3c**	9.1×10^{-7}	24.1 ± 0.3	-5.5 ± 0.4	25.7
	3c ⟶ **2c**	3.2×10^{-7}	24.3 ± 0.4	-6.6 ± 0.6	26.3

mixture of isomers **2** and **3** in *o*-dichlorobenzene solution at higher temperature gives rise instead to formation of another type of isomer, the 1-chloro-5-alkyl(benzyl)-2,3,4,5-tetramethoxycarbonylcyclopentadienes. This rearrangement is caused by 1,5-sigmatropic shift of the geminal methoxycarbonyl group of **3a–c**.[1]

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References

1 V. I. Minkin, I. E. Mikhailov, G. A. Dushenko, J. A. Yudilevich, R. M. Minyaev, A. Zschunke and K. Mügge, *J. Phys. Org. Chem.*, 1991, **4**, 31.
2 I. E. Mikhailov, V. I. Minkin, G. A. Dushenko, A. A. Klenkin and L. P. Olekhnovich, *Zh. Org. Khim.*, 1988, **24**, 1179 [*J. Org. Chem. USSR (Engl. Transl.)*, 1988, **24**, 1061].
3 R. Breslow and W. Canary, *J. Am. Chem. Soc.*, 1991, **113**, 3950.
4 I. E. Mikhailov, G. A. Dushenko, I. A. Kamenetskaya, O. E. Kompan, Yu. T. Struchkov and V. I. Minkin, *Mendeleev Commun.*, 1991, 83.
5 P. E. Hansen, in *Progress in NMR Spectroscopy*, eds. J. W. Emsley, J. Feeney, L. H. Sutcliffe, Pergamon Press, New York, 1981, vol. 14, p. 175.

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