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3,3-Sigmatropic Shift Mechanism for Circumambulation of Acyloxy Groups around the Cyclopentadiene Ring

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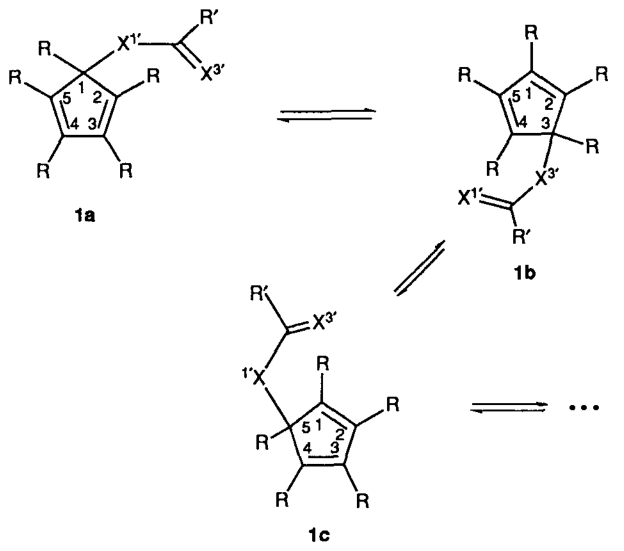
^{1}H NMR spectral data and an X-ray structural analysis of 5-acyloxy-5-benzyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene have elucidated the 3,3-sigmatropic shift pathway of circumambulation of the acyloxy group around the cyclopentadiene ring.

It has been found previously that intramolecular circumambulatory rearrangements of amidinyl (X = NAr) and acyloxy (X = O) groups occur in cyclopentadiene derivatives of type **1** (Scheme 1).[1-4]

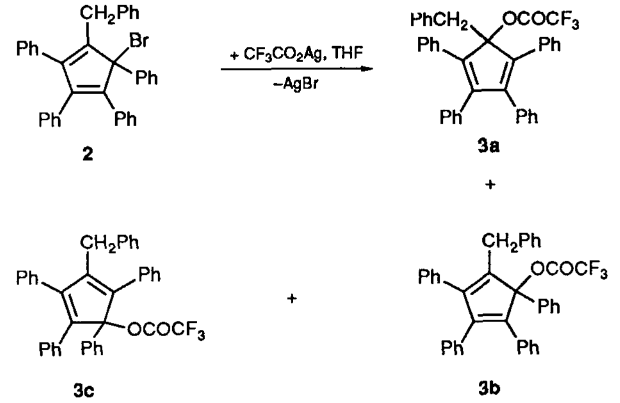


X = O, NAr; R = Ph, CO$_2$Me; R′ = Ar,Alk

Scheme 1

While a 3,3-sigmatropic shift pathway was shown by ^{1}H NMR studies[1,2] to be energetically favourable in the case of amidinyl migration (X = NAr), energy barriers to their displacement around the cyclopentadiene ring falling into the range of 20–23 kcal mol^{-1},† no unambiguous conclusion as to the preference of 1,5- or 3,3-sigmatropic shift pathways could be drawn in the case of the slower ($\Delta G^{\ddagger}_{298}$ = 27.6–35.8 kcal mol^{-1}) acyloxy group (X = O) migrations. One way to distinguish between the two possibilities is to apply ^{17}O dynamic NMR spectroscopy, whose potential in an investigation of some similar mechanistic problems has been recently demonstrated.[5] We report here on another approach based on a study of the equilibration process in compounds with a slight disturbance of the five-fold degeneracy of the circumambulatory rearrangement.

By treatment of 1-benzyl-5-bromo-2,3,4,5-tetraphenylcyclopenta-1,3-diene **2**‡ with silver trifluoroacetate in tetrahydrofuran (THF) at − 7 °C (with stirring for 1 h) a mixture of isomers **3a**, **b** and **c** in the ratio 65 : 15 : 20 was obtained in almost quantitative yield (Scheme 2.).



Scheme 2

Owing to the presence of a stereogenic C$_{sp^3}$-centre in the ring of **3b** it is easily identified on the basis of its ^{1}H NMR spectrum [Fig. 1(*d*)] in which the methylene protons of the benzyl substituent show diastereotopic splitting characteristic of a prochiral group [AB-spectral pattern, δ 2.88, 3.97 (^2J 14.5 Hz) solvent *o*-dichlorobenzene]. No diastereotopic splitting of the

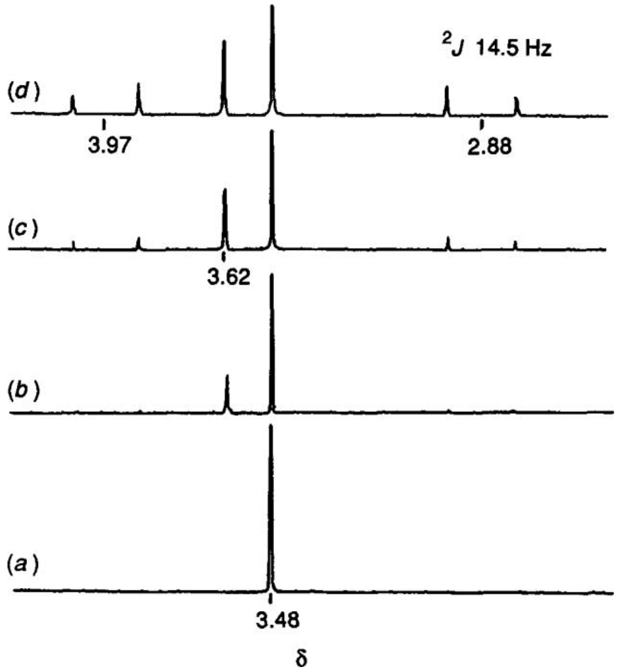


Fig. 1 Time-dependent ^{1}H NMR spectra (100 MHz) of compound **3a** in *o*-dichlorobenzene solution in the benzyl proton region (δ 2.50–4.30) (*a*) at 25 °C, (*b*) after 0.5 h heating at 80 °C, (*c*) after 1 h heating at 80 °C, (*d*) after 2 h heating at 80 °C

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† 1 kcal = 4.184 kJ.

‡ Compound **2** [m.p. 173–175 °C, ^{1}H NMR (CCl$_4$) δ 3.33, 3.73 (2H,1,^2J 4.1 Hz, benzyl H), 6.48–7.51 (25H,m,aromatic H); IR (nujol) ν/cm^{-1} 1600, 1510, 1495, 1150, 1075, 1020] was prepared by reaction of *N*-bromosuccinimide and 1-benzyl-2,3,4,5-tetraphenylcyclopenta-1,3-diene [m.p. 117–119 °C, ^{1}H NMR (C$_6$D$_6$) δ 3.25, 3.95 (2H,q,^2J 14.0 Hz, benzyl H), 4.65 (1H,s, C$_p$-ring proton), 6.39–7.47 (25H,m,aromatic H); IR (nujol) ν/cm^{-1} 1600, 1490, 1150, 1070, 1020] in CCl$_4$. The latter was obtained by reduction of 5-oxy-5-benzyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene [m.p. 153–154 °C, ^{1}H NMR (C$_6$D$_6$) δ 1.74 (1H,s,hydroxy group H), 3.67 (2H,s, benzyl H), 6.92–7.85 (25H,m,aromatic H); IR (nujol) ν/cm^{-1} 3540, 1700, 1600, 1500, 1145, 1080, 1040, 1005], which was prepared by the action of benzylmagnesium bromide on tetraphenylcyclopentadienone according to the standard method.[6]

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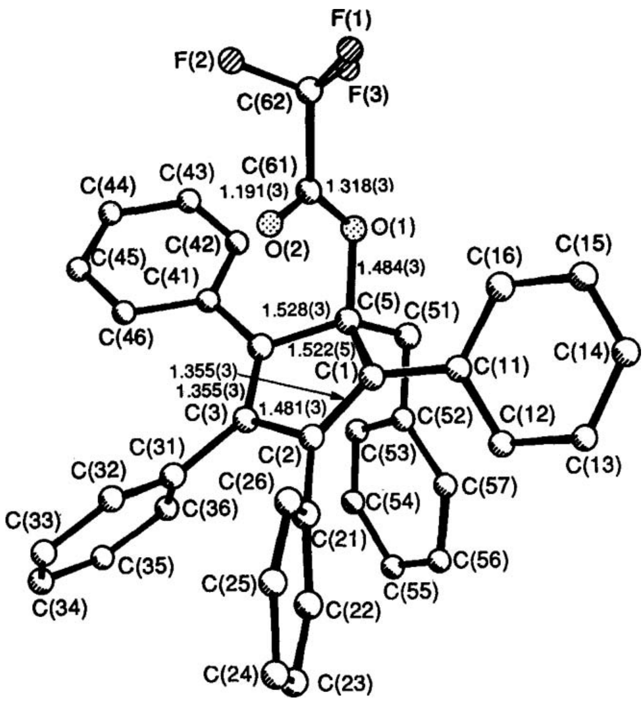

Fig. 2 Molecular structure of compound **3a**. The distances O(2)···C(3) and O(2)···C(4) are 3.393 and 3.481 Å respectively. The trifluoroacyloxy group is slightly twisted about the O(1)—C(6) bond [the O(2)C(6)O(1)C(5) torsion angle is 9.8°]. This indicates that the transition state (or intermediate) probably has a structure of type **Ia,c**

methylene protons has been observed, however, in the ^{1}H NMR spectrum of **3c** in which the stereogenic C_{sp^3}-centre is much further from a prochiral group. In order to assign the methylene proton singlet peaks at δ 3.48 and 3.62 to isomers **3a** (possessing C_s-symmetry) and **3c** respectively, one isomer (δ_{CH_2} 3.48) was isolated by repeated crystallization from benzene–hexane (2:1) and its structure was determined using X-ray analysis. As shown in Fig. 2 this isomer proved to possess the symmetrical structure **3a**.§¶

Having assigned the ^{1}H NMR spectra of all the possible isomers of **3**, the preferable reaction pathway of their interconversion may be traced by studying the temperature dependence of the ^{1}H NMR spectra. When the *o*-dichlorobenzene solution of **3a** was held at 80 °C a second singlet peak (δ 3.62) from the methylene protons of **3c** was observed whose intensity was growing with time [Fig. 1(*b*)]. With prolonged heating a slower process resulting in the accumulation in the reaction mixture of isomer **3b** manifests itself through the appearance in the ^{1}H NMR spectrum of the characteristic AB-quartet signal of the methylene group [Fig. 1(*c*)]. Equilibrium between the interconverting isomers of **3** was attained after holding the *o*-dichlorobenzene solution at 80 °C for 2 h.|| It results in a 65:13:22 ratio of the isomers **3a**, **3b** and **3c** [Fig. 1(*d*)]. No dependence on the concentration of the solution of **3** has been observed for either this ratio or the rate with which the equilibrium was established.

Such spectral behaviour unambiguously indicates the following sequence of steps for the interconversion of the isomers of **3** which conforms to a 3,3-sigmatropic shift pathway for the circumambulatory rearrangement of 5-trifluoroacetoxy-5-benzyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (Scheme 3).**

The free energies of activation ($\Delta G^{\ddagger}_{353}$) and the rate constants (k) for the 3,3-sigmatropic shifts of the trifluoroacyloxy group in compounds **3** were calculated by studying the time dependence of the intensities of signals in the ^{1}H NMR spectra of the isomers **3a**, **3b** and **3c** at 80 °C. They are: $\Delta G^{\ddagger}_{353}$/kcal mol^{-1} 27.2, 26.5, 27.0, 26.7† and $10^4\,k/\mathrm{s}^{-1}$ 1.0, 2.8, 1.3, 2.0 for **3a**→**3c**, **3c**→**3a**, **3c**→**3b**, **3b**→**3c** respectively.

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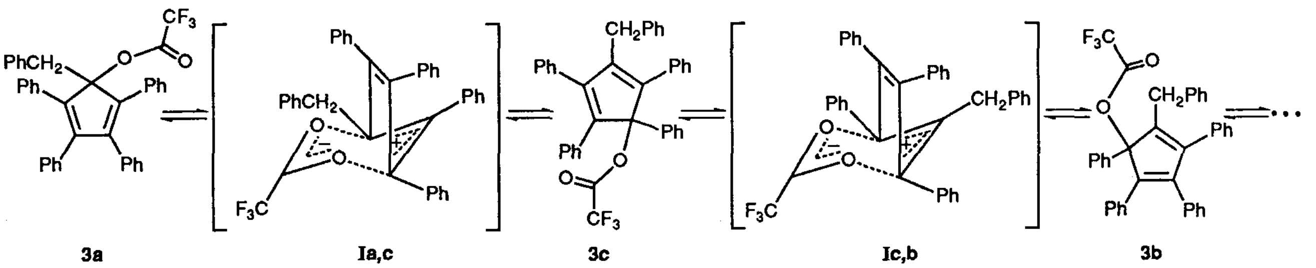

3a **Ia,c** **3c** **Ic,b** **3b**

Scheme 3

References

1 V. I. Minkin, I. E. Mickailov and G. A. Dushenko, *J. Chem. Soc., Chem. Commun.*, 1988, 1181.
2 I. E. Mikhailov, G. A. Dushenko and V. I. Minkin, *Zh. Org. Khim.*, 1987, **23**, 1109 (Engish translation in *J. Org. Chem. USSR*, 1987, **23**, 1001).
3 I. E. Mikhailov, V. I. Minkin, G. A. Dushenko, I. A. Kamenetskaya and L. P. Olekhnovitch, *Dokl. Akad. Nauk SSSR*, 1988, **299**, 1399.
4 I. E. Mikhailov, G. A. Dushenko, I. A. Kamenetskaya, L. P. Olekhnovitch and V. I. Minkin, *Zh. Org. Khim.*, 1988, **24**, 1988 (English translation in *J. Org. Chem. USSR*, 1988, **24**, 1801).
5 M. Oki, *Pure Appl. Chem.*, 1989, **61**, 699.
6 W. Broser, H. Kurreck and P. Siegle, *Chem. Ber.*, 1967, **100**, 788.
7 P. Jutzi, *Chem. Rev.*, 1986, **86**, 983.

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§ Compound **3a**: yellow crystals [from benzene–hexane (2:1)], m.p. 182–183 °C. ^{1}H NMR (CDCl$_3$) δ 3.65 (2H,s,CH$_2$), 6.73–7.32 (25H,m, aromatic H); IR (nujol) ν/cm^{-1} 1780, 1600, 1500, 1220, 1160, 1075, 1030. Compound **3a** gave satisfactory elemental analyses.

¶ *Crystal data* for **3a**: $C_{38}H_{27}O_2F_3$, rhombohedral, space group *Pbca*, $a = 11.643(5)$, $b = 16.857(7)$, $c = 29.665(10)$ Å, $V = 5822(7)$ Å^3, $Z = 8$, $D_c = 1.31$ g cm^{-1}. 3378 Independently observed reflections with $I > 2\sigma(I)$ were measured using an automatic four-circle diffractometer Syntex P2$_1$ [λ (Mo) = 0.178Å, θ–2θ scan technique, 2θ < 50°, $T = -120$ °C]. The structure was solved by direct methods and refined by least squares to a final value of $R = 0.049$ and $R_w = 0.046$. The PC SHELXTL program was employed in all calculations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, *J. Chem. Soc., Chem. Commun.*

|| No direct interconversion of the isomeric forms **3a** and **3b** has been observed when either of these were allowed to stay for 1–2 h in *o*-dichlorobenzene solution at 160 °C. Thus the **3a**$\rightleftharpoons$**3b** 1,5-sigmatropic shift, if it occurs, involves surmounting an energy barrier exceeding 33–34 kcal mol^{-1}.† Heating compound **3a** results in its decomposition.

** An alternative mechanism that could also explain the experimental results is that associated with a series of 1,3-sigmatropic shifts of the trifluoroacetoxy group. It seems, however, to be highly improbable because the relevant transition state structures are energetically unfavourable. Such a mechanism has never been shown to operate in the circumambulation of any main-group element centred migrating group, see ref. 7 for a comprehensive review.