

Generation of a cyclopentenyl cation labelled with a single deuterium at C-4. Rate studies of the scrambling reaction[†]

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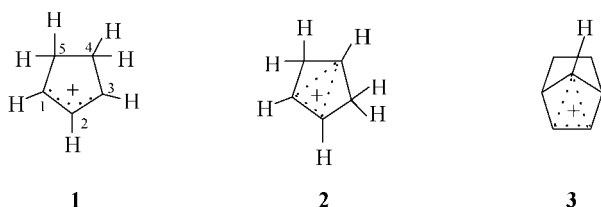
ABSTRACT: The kinetics of the hydrogen scrambling reaction in the cyclopentenyl cation **1** were studied. The pure 4-deutero derivative of **1** was prepared using superacid conditions and the activation energy ΔG^\ddagger for the rearrangement of this label to the C-1(3) position of **1** was determined using low-temperature ²H NMR spectroscopy. In addition, the sequential rearrangement of the deuterium label from C-4(5) → C-1(3) → C-2 was noted in a qualitative fashion. Based on a statistical analysis, the activation free energy ΔG^\ddagger for a single hydrogen (deuterium) migration leading to the 4-cyclopentenyl cation intermediate was determined to be 18.3 kcal mol⁻¹ (–20.8 °C), in good agreement with the less direct determination provided by an earlier NMR line-broadening and spin-saturation transfer experiment. Copyright © 2003 John Wiley & Sons, Ltd.

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KEYWORDS: carbocation; cyclopentenyl; isotope labelling; ²H NMR; hydrogen scrambling

INTRODUCTION

The superacid generation of the allylic cyclopentenyl cation **1** was first reported in 1972.^{1,2} A number of alkyl-substituted cyclopentenyl cations had been characterized even earlier,^{3,4} and one of these, the *trans*-1,2,3,4,5-pentamethyl derivative,⁵ has had its x-ray structure determined.⁶



Cation **1** was originally of interest for several reasons, including the possibility that a 1,2-hydride shift (5,1 or 4,3 in **1**) could yield a bishomocyclopropenyl cation **2**, of which several direct analogs in the bicyclo[2.2.1]heptane skeleton series had been found to be unusually stable,⁸ e.g. **3**. However, direct attempts¹ to observe cation **2** resulted only in the formation of **1**. Nevertheless, cation **2** might still serve as a favorable low-energy intermediate

which might be generated as a result of rapid reversible hydride shifts in **1**, as shown in Scheme 1, and indeed Saunders and Berger² reported ¹H NMR line-broadening and spin saturation transfer experiments which were interpreted in terms of the scrambling process shown in Scheme 1. The measured activation barrier (E_a) was 18.0 ± 0.9 kcal mol⁻¹ (1 kcal = 4.184 kJ).

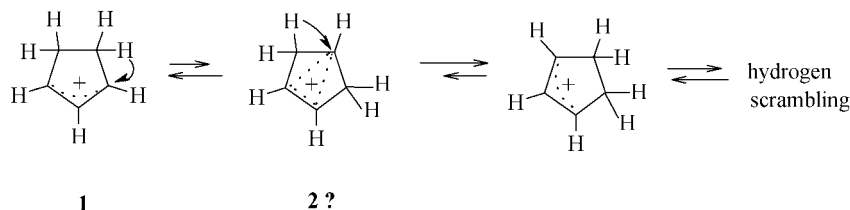
The maximum temperature reached in these line-broadening experiments was 112 °C, yielding half-widths only about twice those obtained at 42 °C. In contrast, Olah *et al.*¹ reported no line broadening at 105 °C, but in any case it would be generally conceded that superacid NMR studies at temperatures above 100 °C are experimentally challenging.

Carneiro and Schleyer (personal communication) have recently carried out *ab initio* MO calculations on a wide range of C₅H⁺ species, including various transition states. For the Scheme 1 isomerization reaction (hydrogen scrambling), their calculations at the MP2/6–311+G** and B3LYP/6–311+G** levels yield activation barriers, E_a , of 23.0 and 23.9 kcal mol⁻¹, respectively, although the mechanistic details differ somewhat in the two cases. Interestingly, cation **2** is a minimum at both levels, but is *not* directly connected with the hydrogen scrambling reaction profile. More relevant to the present study, their calculated barriers were *ca* 5 kcal mol⁻¹ higher than the reported experimental energy barrier determined by Saunders and Berger.² We were therefore encouraged to try to obtain additional experimental evidence concerning the Scheme 1 process. Given the enormous advances in NMR spectroscopy since the original work (1971), the most straightforward and unambiguous procedure for

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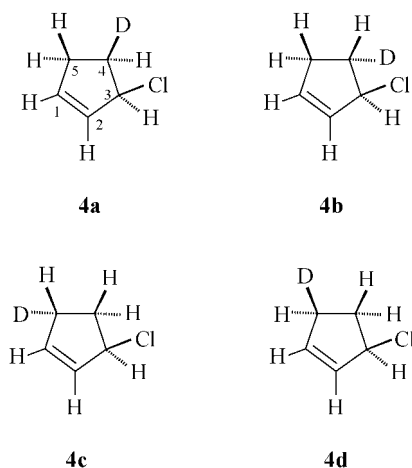


Scheme 1

verifying the Scheme 1 reactions appeared to be a deuterium labelling experiment, employing ^2H NMR spectroscopy for the kinetic measurement.

RESULTS AND DISCUSSION

Addition of DCl to cyclopentadiene⁹ yielded a mixture containing at least three of the four possible isotopomers **4a–d**, showing that competitive 1,2- and 1,4-addition of DCl was occurring. Related results have previously been reported by Nordlander *et al.* for the addition of DCl to *trans*-1,3-pentadiene¹⁰ and by Hammond and Warkentin for DBr addition to 1,3-cyclohexadiene.¹¹ The characterization of the isotopomers **4a–d**, reported in the Experimental section, is of some general mechanistic interest. For example, most of the 1,4-addition of D and Cl appears to result from a *cis* addition. However, the primary concern for us in the present study was that the deuterium label should be confined to the C-4 and C-5 positions of **4**, as indeed found. The percentage D label in **4** is expected to be high (>95%), but this incorporation is an unimportant quantity since only the labeled species is being studied.



4-Deuterocyclopentenyl cation

This cation was prepared by the careful addition of the above chloride to a solution of SbF_5 in SO_2ClF solvent, precooled to -116°C . The low-temperature (-60°C) ^2H NMR spectrum of this cation showed only one resonance,

a doublet at δ 4.0, $J = 4$ Hz, assignable to cation **1** with a D atom at C-4 (C-5). This doublet is almost certainly due to geminal C–H(D) coupling, since a 4 Hz ^2H – ^1H coupling constant translates into a 26 Hz ^1H – ^1H coupling constant, a value much larger than the normal vicinal coupling constant in five-membered rings. For control purposes, the ^1H and ^{13}C NMR spectra of the all-hydrogen ion were also obtained: ^1H NMR, δ 3.92 (4H), 8.31 (t, 4 Hz, 1H), 10.9 (b, 2H); ^{13}C NMR, δ 51.0 (CH_2), 150.5 (CH), 241.1 (CH). These ^1H NMR shifts are in reasonable agreement with the literature^{1,2} considering the different referencing techniques used.

Kinetic measurements

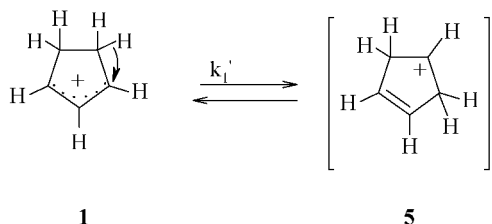
From trial runs, a temperature of -20.8°C was found to give a rearrangement rate which could be conveniently followed. Some data were also obtained at slightly lower and higher temperatures. In Fig. 1, a series of spectra are shown, the first one corresponding to a low temperature (-60°C), showing that the cation can be prepared without incurring any isotope rearrangement. The remaining spectra show 10 min progressions at -20.8°C . These have been plotted such that the C-4 deuterium peak has a constant size, which means that the total ^2H integral is slowly increasing (the small peak at *ca* δ 10 is due to traces of an ‘acid ^2H signal’ formed in the preparation and the apparent increase in size shown in Fig. 1 is because of this overall integral increase).

One can see from Fig. 1 that the ^2H signal at δ 10.9 (^2H -1- ^2H -3) appears first, followed later by the ^2H -2 signal (δ 8.3). Eventually, at the exchange equilibrium (not shown), the three ^2H peaks have the expected areas of ca 2:1:4 (equilibrium isotope effects appear to be minimal).

For the reaction $\text{A} \xrightleftharpoons[k_{-1}]{k_1} \text{B} \xrightleftharpoons[k_{-2}]{k_2} \text{C}$, where **A**, **B** and **C** refer to

the cyclopentenyl cation with deuterium atom at C-4(C-5), C-1(C-3) and C-2, one can obtain a value for rate constant k_1 by plotting $\ln(B_e - B_t)$ vs t (where B_e = the equilibrium area of the 1- ^2H cation peak) and considering only the **A** and **B** species, taking a tangential line near zero time, giving $k_1 = (1.3 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$. In order to compare this value with that for a single hydride migration step, designated k'_1 , one has to consider various statistical factors since most of these single hydride shifts

would not result in a rearrangement of the deuterium atom. If one assumes that the classical 4-cyclopentenyl cation **5** is a true intermediate in the rearrangement reaction (true for the B3LYP calculation), then one can show (see Appendix) that the actual success rate for a C-4(5)-²H atom transferring to C-1(3) is between 2/9 (0.22) and 3/16 (0.19), i.e. $k = (0.19-0.22)k_1'$, with the limiting assumptions in these two cases being ¹H hydride shift \gg ²H shift, and ¹H hydride shift = ²H shift, ignoring any secondary isotope effects (which are expected to be smaller in magnitude). Although these appear to be extreme assumptions for the shift process, there is not much real difference in the end result, and an arbitrary factor of 0.2 was decided upon, giving $k_1' = k_1/0.2 = (6.5 \pm 1) \times 10^{-4} \text{ s}^{-1}$ at -20.8°C , $\Delta G^\ddagger = 18.3 \pm 0.1 \text{ kcal mol}^{-1}$.



Comparison with the Saunders–Berger result

Using both NMR line-broadening and spin-saturation transfer techniques, Saunders and Berger² estimated E_a to be $18.0 \pm 0.9 \text{ kcal mol}^{-1}$ ($\log A = 12.2 \pm 0.6$) for the hydrogen scrambling in **1**. From transition-state theory, $(\Delta S^\ddagger)^\ddagger$ can be estimated as $-2.7 \pm 0.2 \text{ e.u.}$, giving $\Delta G^\ddagger = 18.4 \pm 1 \text{ kcal mol}^{-1}$. The statistical factor in the all hydrogen cation is somewhat larger than for our situation, but this factor has only a very marginal effect when comparing the respective ΔG^\ddagger values. Within both experimental error limits, our values for ΔG^\ddagger are identical. Nevertheless, as illustrated in Fig. 1, our experiment is clearly a more direct and ‘foolproof’ measure of hydrogen scrambling in the cyclopentenyl cation.

EXPERIMENTAL

NMR spectra were obtained using a Bruker AMX-300 instrument. ²H NMR spectra were run unlocked. The cation ²H spectra were referenced relative to internal CD₂Cl₂, and the same spectrum frequency was used for the spectra shown in Fig. 1 (no CD₂Cl₂). Temperatures were calibrated (CH₃OH) before and after each series of runs. MO calculations utilized the Gaussian 98 suite of

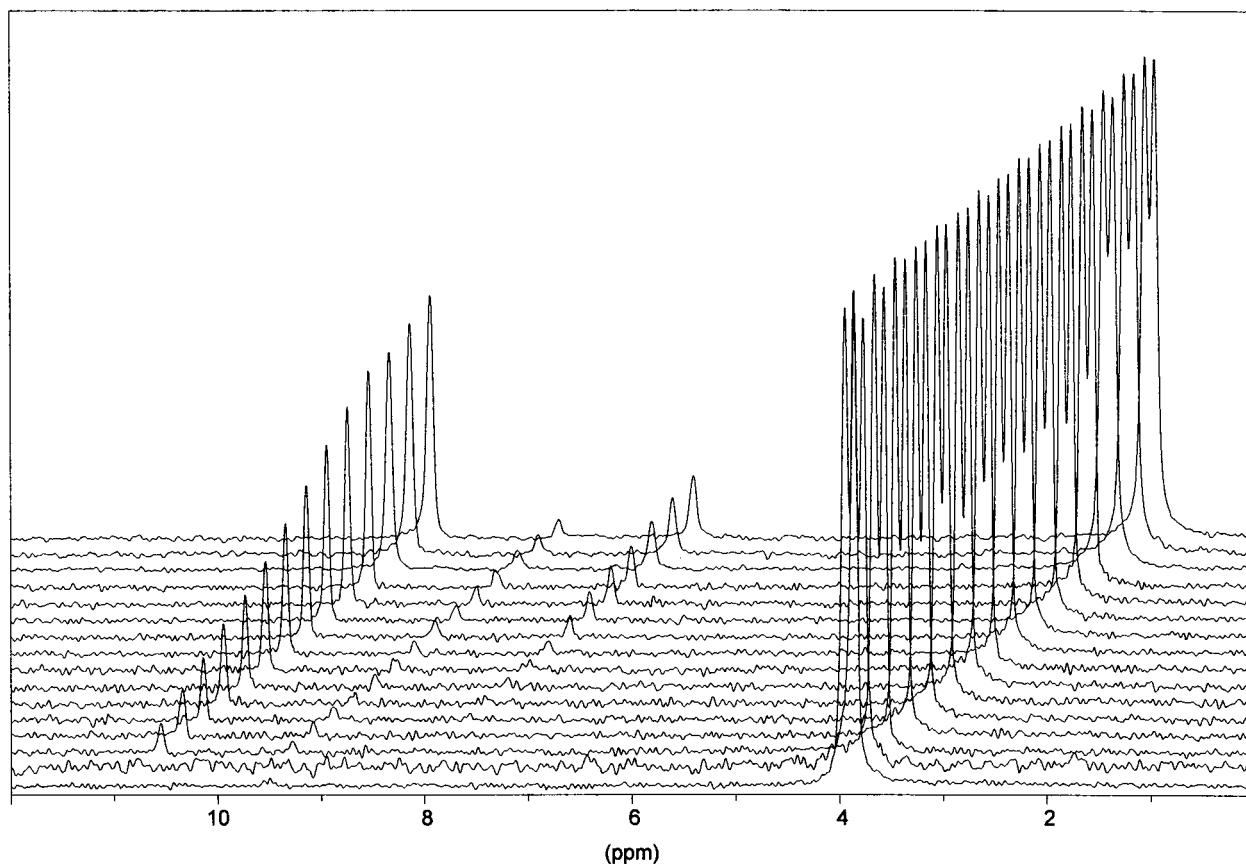


Figure 1. ²H NMR spectra starting with the 4-²H-cyclopentenyl cation. The lowest trace is a low-temperature (-60°C) run of the initially produced cation. The sequentially shown spectra were recorded at 10 min intervals at -20.8°C

programs,¹² and the optimized coordinates of **3** and calculated NMR chemical shifts are included as supplementary material, available at the epoc website at <http://www.wiley.com/epoc>.

4(5)-Deutero-3-chlorocyclopentenes **4a–d**

Deuterium chloride (generated from 98% D₂SO₄ and sodium chloride) was slowly bubbled through cyclopentadiene, the latter kept at –40 °C during the reaction,⁹ and the weight of the reaction flask was monitored to ensure nearly complete reaction. The round-bottomed flask containing the product was immediately switched to a small distillation assembly, and the title product was collected as a liquid, b.p. ca 25 °C/10 mmHg, in a dry-ice cooled receiver. The product was thermally labile and was stored at dry-ice temperature. A detailed NMR analysis (¹H, ²H, ¹³C) was carried out; the ²H spectrum shows no peaks at position 1, 2 or 3, but has three peaks at δ 2.3, 2.5 and 2.8, area ca 2:1:2, corresponding to at least three of the four possible isotopomers involving positions 4 and 5 (structures **4a–d**).

In the ¹³C {¹H} NMR spectrum, there are two high-field carbon singlets at δ 35.7 and 32.4 ppm together with associated 1:1:1 triplets which are ca 0.3 ppm to the high-field side of the singlet carbon peaks (the singlet peak at δ 32.4 is larger than that at δ 35.7). NMR chemical shift calculations on the optimized structure of **4** (C1 symmetry GIAO/B3LYP/6–311G**//B3LYP/6–31G*) yield values of 39.95 ppm for C-4 and 36.45 for C-5, suggesting strongly that δ 35.7 is C-4 and δ 32.4 is C-5. The inclusion of 1:1:1 triplets of approximately equal size with both C-4 and C-5 carbons suggests that the two major isotopomers are regioisomers rather than isomeric at a single carbon. Furthermore, the NMR calculations (¹H) suggest that the lowest field ¹H(²H) peak (observed, δ 2.8; calculated, 2.83) corresponds to the H-5 hydrogen (deuterium) *cis* to the C-3 chlorine atom (**4d**), i.e. one of the major isotopomers is formed from same-face 1,4-addition of the D and Cl to cyclopentadiene. The other large ²H peak (ca 2.2 ppm) must be from an H-4 position deuterium (1,2-addition), but the position of this relative to the chlorine atom is unassignable (from the NMR calculations H-4 *cis* and *trans* are very similar, 2.23 and 2.22). The ²H peak at δ 2.5 is probably H-5 *trans*. These

assignments are also consistent with the 300 MHz NMR spectrum of all-hydrogen **4**.

Kinetics

Data for the initial ‘concentrations’ of **B** were obtained as [area of peak B/combined area of A + B]. Plots of ln*B* vs *t* were made, resulting in a curved line from which a tangential slope near *t* = 0 was obtained.

Acknowledgements

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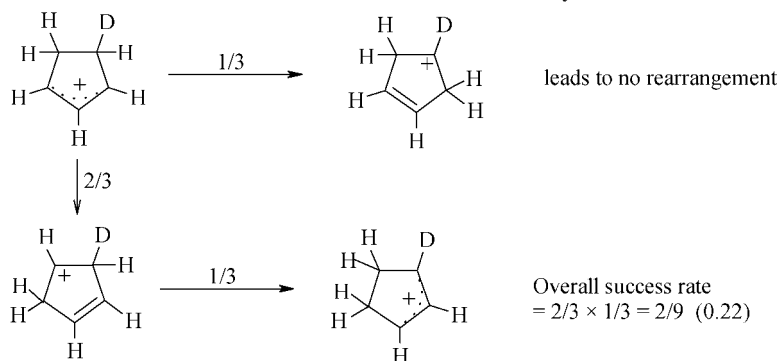
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APPENDIX

Statistical factor for a single H(D) shift vs observable rearrangement of the original cation (D at C-4) to that with D at C-1 (C-3)

Assumption No. 1 H \gg D shift (assume no D shift)
 Assume secondary isotope effects are small
 Assume classical cation **4** is an intermediate
 Assume rate is determined from a tangential line near $t=0$, i.e. no reverse reaction and no **1-2d** formed yet.



Assumption No. 2 As above but $D_{\text{shift}} = H_{\text{shift}}$

