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A deepseated carbodication rearrangement. Limited paths because of charge repulsion

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Abstract—The 1,5-manxyl dication undergoes a very specific skeletal rearrangement to give the 3,7-dimethylbicyclo[3.3.1]nona-3,7-diyl dication. The corresponding manxyl monocation is also labile but forms an apparent myriad of rearrangement products. This result is an indication that the dication rearrangement involves many fewer branching reactions.

Productive rearrangement cascades involving carbocations are commonplace, the best known example being the high yield formation of adamantane from the isomeric tetrahydrodicyclopentadiene.[1] In spite of the above generalization, there are also numerous examples of non-productive rearrangement cascades. Germane to the present discussion is the $C_{11}H_{19}^{+}$ manxyl cation **1**, first reported by Olah et al. When solutions of **1** are warmed to ca. −60°C, the NMR peaks essentially disappear, suggestive of the formation of many individual rearrangement products. This in turn suggests that there are a number of irreversible branching pathways in the rearrangement cascade(s). In complete contrast, we describe in this paper a deepseated rearrangement cascade involving the manxyl dication **2**, wherein a single dication rearrangement product is eventually produced. Contrary to the monocation situation, there are few examples of carbodication→carbodication rearrangement cascades.

1 **2**

The observable manxyl dication **2** was prepared in situ as described,[2] starting from the corresponding 1,5-dichloride, and the ^{13}C NMR spectrum of **2** (Fig. 1

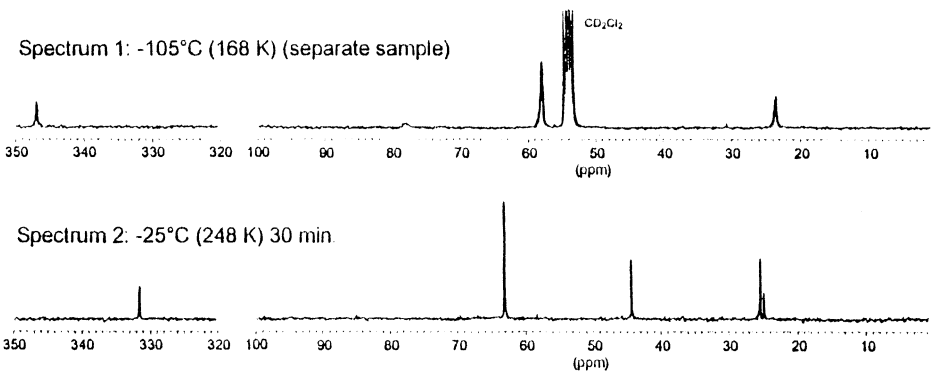

Figure 1. Upper: ^{13}C NMR spectrum of dication **2**. Lower: ^{13}C NMR spectrum of dication **3** produced from the rearrangement of **2** (without use of CD_2Cl_2).

Keywords: carbodication; cation rearrangements; superacid solutions; manxyl; bicyclo[3.3.1]nonyl; MO calculations.

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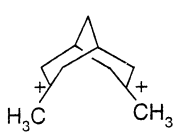
Table 1. Calculated ^{13}C NMR shifts for dications **4** and **5** versus experimental

Carbon type	CH_2					CH		CH_3		C^+	
Experimental	51.3	55.9	57.5	63.2	64.1	32.8	65.4	46.8	46.9	323.6	329.3
Atom center for **4**	3	8	9	6	4	5	1	11	10	2	7
Calcd for **4**[a]	51.5	55.9	57.5	63.2	64.1	35.5	64.3	46.1	46.3	310.2	321.8
Atom center for **5**	8	9	4	2	7	1	5	11	10	3	6
Calcd for **5**[a]	26.3	39.3	59.9	66.1	64.1	35.6	59.6	46.9	49.0	326.5	335.8

[a] GIAO NMR/B3LYP/6–31G*, using optimized geometries, shifts relative to calculated TMS value.

upper) is in good agreement with the published spectrum.[†] Our intent was to use this dication as a possible starting material for a μ-H cation preparation but **2** was found to be thermally labile above −60°C. In the initial preparation of **2**, and on subsequent warming, a very clean rearrangement product was seen in the ^{13}C NMR spectum, as shown in Fig. 1 (lower). However, this result could not be obtained reproducibly, since in some cases ^1H and ^{13}C NMR peaks for **2** disappeared without any sign of this new product (featureless NMR spectra). This problem was traced to the use of CD_2Cl_2 (lock-reference) as a component of the superacid solution (SbF_5-SO_2ClF). When **2** was prepared in the absence of CD_2Cl_2 and allowed to rearrange, the lower ^{13}C NMR spectrum in Fig. 1 was obtained reproducibly.[‡]

The ^1H NMR spectrum of this rearrangement product showed a low field doublet (4H) at 4.6 ppm, a doublet of doublets (4H) at 4.3 ppm, and a quintet (6H) at 3.7 ppm. Higher field singlets were found at 3.1 and 2.3 ppm, each of area two. The ^{13}C NMR spectrum showed only five signals, whose relative areas were determined using gated decoupling. The five signals were found at 332.3 ($2C^+$), 64.0 ($4CH_2$), 45.3 ($2CH_3$), 27.3 (2CH) and 26.7 (CH_2). The presence of four identical methylene groups in a molecule with a total of eleven carbons requires at least two symmetry planes. Arrangement of three more pairs of identical carbons in a system with two planes of symmetry apparently leaves only one possible structure, 3,7-dimethylbicyclo-[3.3.1]nona-3,7-diyl dication **3**. Subsequently a more controlled ^{13}C NMR study of the rearrangement was carried out, and an intermediate dication was seen to build up and decrease as **2** rearranged to **3** (at −52°C, $\Delta G^{\neq} = 16.0 \pm 0.4$ kcal/mol for loss of **2**, and $\Delta G^{\neq} = 17.4 \pm 0.4$ kcal/mol for intermediate→**3**). This intermediate dication had eleven ^{13}C NMR peaks, as listed in Table 1. With no symmetry element and $2CH_3$ groups, two structures were possible, dication **4** or **5**. MO calculations and calculated NMR shifts for these are shown in Table 1, and the calculated shifts for **4** are in



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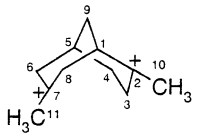

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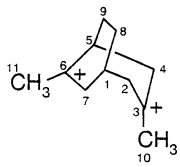

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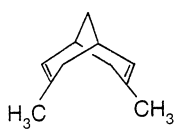
better agreement with experiment, particularly in the comparison of CH_2 carbons. Furthermore, **4** was found to be 4.0 kcal/mol more stable than **5**, and **4** is also a more obvious intermediate leading to **3**.

Independent preparation of dication 3

Dihalides are ideal reactants for preparing dications, e.g. **2**. However, we were unable to prepare a suitable dichloride precursor of **3**, and use of various diols or ene–ols led to protonated cyclic ethers or protonated alcohols. However, a mixture of dienes **6** and **7**[3] could be diprotonated with SbF_5–FSO_3H/SO_2ClF to give a messy ^{13}C NMR spectrum in which the five peaks of **3** were dominant. Clearly the best way to prepare **3** is to rearrange **2**.



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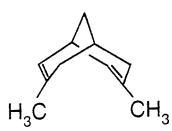

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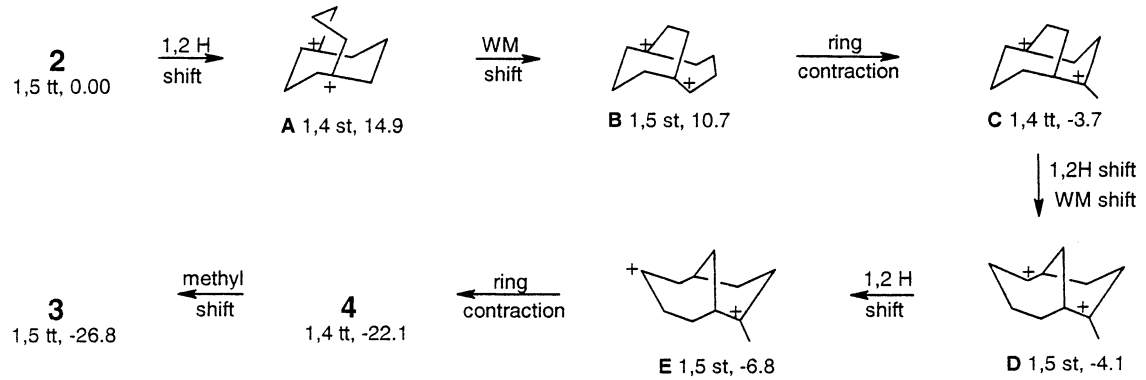
Rearrangement mechanisms

In carrying out this analysis, we use the same cation rearrangement mechanisms that are applied to monocation cascades, with two important provisos: (1) the two cation centers of dication intermediates should maintain at worst a 1,4–dication separation,[4] and (2) intermediates with two secondary cation centers would be of too high energy to be important. With these two restrictions there is a large decrease in the number of 'allowable' branching pathways, since the cation centers 'need to keep their distance'. A plausible sequence is shown in Scheme 1, where 1,4st, for example, is shorthand for a secondary–tertiary dication in which the closest C^+–C^+

[†] In the 400 MHz ^1H NMR spectrum of **2** one can now determine a value for the three-fold ring flip barrier, $\Delta G^{\neq} = 9.4 \pm 0.5$ kcal/mol.

[‡] A hydride abstraction to give a monocation intermediate is a possibility for the failed reactions, e.g. dication^{2+}·$2SbF_6^-$+CH_2Cl_2→ monocation$^+$·SbF_6^-+$CHFCl_2$+SbF_5.



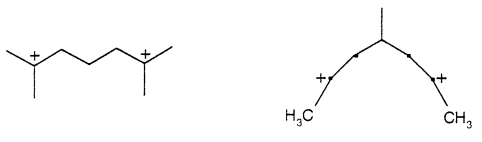
Scheme 1.

bond connection is a 1,4 relationship, and the second number in this Scheme 1 is the calculated energy relative to **2**=0.00 kcal/mol. The rearrangement path in Scheme 1 is unbranched up to the intermediate **C.** From **C** to **E** there is some possible variation, but the route shown gives the intermediate **4** (as observed experimentally). All of the rearrangement steps have well-known examples from superacid monocation rearrangement studies, e.g. **B**→**C** and **E**→**4** represent ring contractions of secondary *n*-cyclic cations to (*n*-1)-CH_3 tertiary cations.[5]

Like **2**, monocation **1** is a strained ring system, so it is not surprising that this cation is easily rearranged. Since neither of our 'dication rules' applies, there are many possible branching points on the road to more stable bicyclic structures.

Structural features of 3

In the calculated structure of dication **3** (a 1,5–dication), the key C^+–C^+ distance has increased from 2.80 Å (calcd) in **2** to 3.58 Å in **3**. However, compared to an open chain analog, the 2,6–dimethyl–2,6–diyl dication **8**, with d=5.21 Å, dication **3** still has considerable through space charge repulsion. This shows up clearly in the calculated structure, with each six-membered ring approaching a planar five-carbon geometry (**3A**) to maximize the C^+–C^+ separation. As expected for this geometry[6] there is no sign of C–C hyperconjugation (C_α–C_β=1.548 Å) and the ring C–H hyperconjugation involves all four hydrogens on each side.



8 **3A**

Experimental

Commercial SbF_5 was purified by pretreatment with SiO_2, followed by a triple distillation. Commercial FSO_3H was doubly distilled and SO_2ClF was distilled from SbF_5. All cation solutions were prepared under argon. All calculations (G98, revision A3, Gaussian Inc., Pittsburgh, PA, 1998) involved optimization at the B3LYP/6–31G* level, and ZPVE and thermal corrections were made to all energies.

Acknowledgements

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