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Preparation of the tricyclo[5.3.1.1^{3,9}]dodeca-1,5-diyl dication: attempts to prepare a novel μ-H cation

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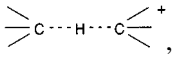
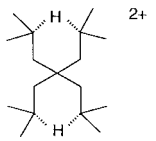
ABSTRACT: The tricyclo[5.3.1.1^{3,9}]dodeca-3,7-diyl dication (**6**) was prepared *in situ* and characterized by ^{1}H and ^{13}C NMR spectroscopy. Reaction of this dication with isopentane, $NaBH_4$ or H_2, in an attempt to prepare the μ-H cation **7**, did result in hydride transfer, but to the 'outside' face of the dication, leading to the conventional monocation **8**, or rearrangement products of this. This monocation was independently prepared, and is thermally less stable than the dication, rearranging to the 2-ethyl-2-adamantyl cation (**19**) at −60 °C, $\Delta G^{\ddagger} = 16.0 \pm 0.6$ kcal mol^{-1}. The 2-methyltricyclo[4.3.1.1^{3,7}]undec-2-yl cation (**20**), a likely intermediate in this rearrangement, was also independently prepared and shown to rearrange to **19**, $\Delta G^{\ddagger} = 14.4 \pm 0.3$ kcal mol^{-1}, consistent with a stepwise rearrangement process for **8**→[**20**]→**19**. The structures of dication **6** and monocation **8** were investigated by high-level *ab initio* calculations, and modeling studies were carried out to look at the factors that allow dications such as **6** to even be prepared. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: carbocation; μ-H-carbocation; carbodication; rearrangements; MO calculations; NMR shift calculations; bridgehead reactivity

INTRODUCTION

μ-H-bridged carbocations,  , have previously been prepared *in situ*, and have involved monocyclic,[1] bicyclic[2] and tricyclic[3] frameworks, e.g. cations **1–3**.



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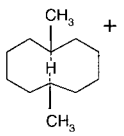

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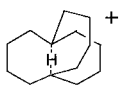

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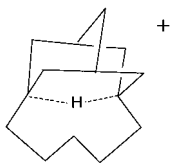
The tricyclic systems can be characterized by the sum of the carbon atoms in the three principal bridges, i.e. 12 for cation **3**. The smallest presently known framework, cation **4**, contains 11 carbon atoms. However, high-level *ab initio* molecular orbital (MO) calculations[4] suggest that even smaller frameworks, e.g. nine carbon atoms, should be possible, and that such cations would exhibit very unusual properties, e.g. record-breaking high pK_a values (*ca* +15). We describe in this paper our initial attempts to prepare such cations and these studies have focused on the possibility that one might be able to transfer a 'hydride ion' into the center of a dication structure, as shown below for the bicyclo[3.3.3]undecyl (manxyl) system **5**. However, the previously described[5] **5** has, in our experience,[6] only a limited thermal stability.



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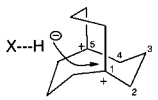

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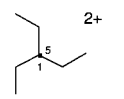

5a (view along C1-C5)

This paper describes the synthesis of a new tricyclic dication structure **6** (containing a [3.3.3]undecyl subunit), which we thought would be more rigid, and therefore less likely to rearrange. It was also thought that the $C^{+}\cdots C^{+}$ distance in **6** might be larger than in **5**, and that, unlike the symmetrical situation in **5**, the p_z orbitals from each C^{+} center might not be fully aligned along this 'shortest distance' axis. Also, **6** would have a sterically less

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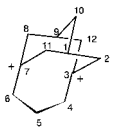
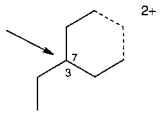
congested face (shown with an arrow in **6a**) for a hydride donor to approach the 'electrophilic core' of the dication, in contrast to **5**, which is expected to exist almost entirely in the configuration shown in **5a**.

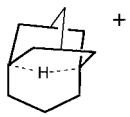


6



6a (sideview as in structure **5a**)

The choice of possible hydride donors for the conversion of **6** to **7** was unclear at this preliminary stage, since there is no precedent for this proposed reaction. The preparation of the corresponding out-H monocation **8** was also planned, since this cation would be the product of an unwanted hydride ion delivery to an 'outside' position of **6**, and therefore useful as a reference compound. The very stable 1-adamantyl cation is well known,[7] and 1-homoadamantyl cation has also been reported,[8] so that **8** would be the next member in this series.



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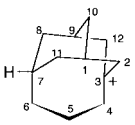

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As well as the experimental work, we planned to carry out MO calculations on **6** and **8** to obtain electronic and structure details.

RESULTS AND DISCUSSION

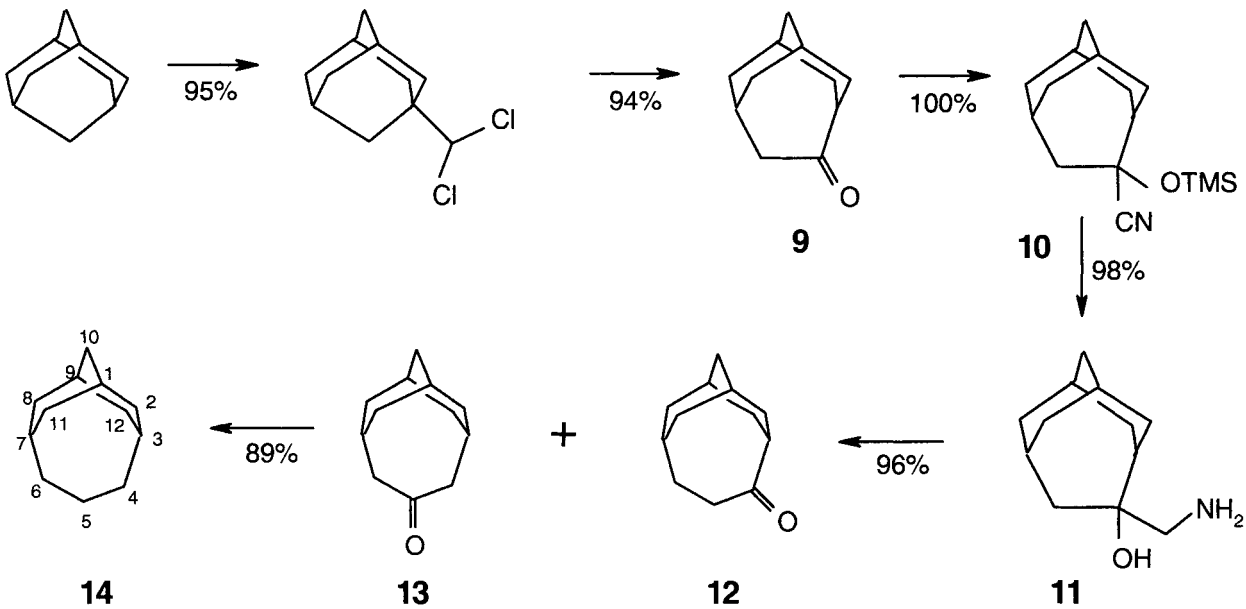
Synthesis of tricyclo[5.3.1.1^{3,9}]dodecane (14)

Tricyclo[5.3.1.1^{3,9}]dodecane (**14**) is known and has been synthesized by a twofold Tieffenau–Demjanov ring expansion of 2-adamantanone, producing first tricyclo[4.3.1.1^{3,8}]undecan-4-one (**9**) (homoadamantanone)[9] and then tricyclo[5.3.1.1^{3,9}]dodecan-4-one (**12**) (bishomoadamantanone)[10] in 48–85% and 15% yields respectively. Another method for the preparation of **9** makes use of a selective C—H insertion of dichlorocarbene into adamantane followed by a hydrolytic rearrangement[11] (63% yield). We followed the latter procedure to obtain **9** in about 90% overall yield, and then made use of trimethylsilyl cyanide followed by lithium aluminum hydride reduction to obtain the amino alcohol **11** in 98% yield from **9**.

Tieffenau–Demjanov ring expansion of the amino alcohol and Wolff–Kishner reduction of ketone mixture **12–13** yielded **14** in 75% overall yield from adamantane (Scheme 1).

The Wolff–Kishner reduction of **13–14** was superior to a sodium borohydride reduction of the corresponding tosyl hydrazones[10] in terms of number of steps and yield (89% *versus* 65%).

Functionalization of the 3- and 7-bridgehead positions in **14** could be accomplished by simply exposing the solid alkane to oxygen and then reducing the resulting mixture of alcohol and peroxide with sodium borohydride in methanol. The facile oxidation of the C3—C7 bridgehead positions was anticipated, based on the existence of similar chemistry found for the related manxane system.[12] In contrast to the latter, **14** has four bridgehead



Scheme 1

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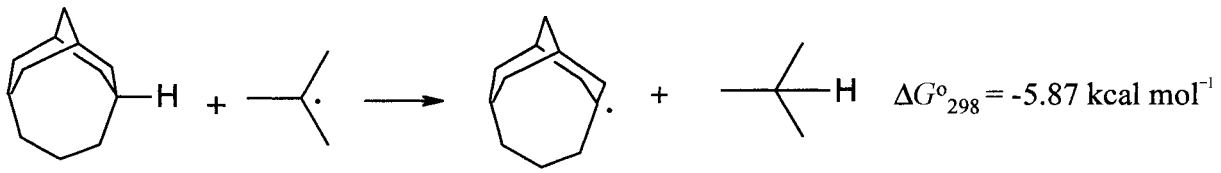

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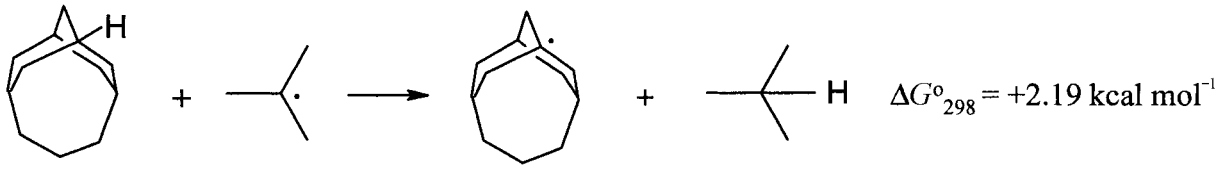


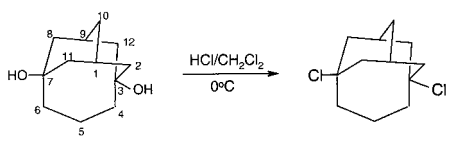
14

Scheme 2

positions, but the following homodesmic reaction calculations (Scheme 2) show that the radical formed at C3—C7 is 8.1 kcal mol^{-1} more stable than the isomeric C1—C9 species (*ca* 1×10^6 reactivity difference at 20 °C). Like the manxane system, the stability of the C3—C7 radical in **14** is related to the relief of steric strain when the sp^3 bridgehead position becomes more sp^2 hybridized.

Diol **15** was a crystalline solid, which allowed us to obtain an X-ray structure. In the tetragonal space group, there is crystallographic disorder involving atoms shown as C5, C5*, C6 and C6* (partial occupancies) in Fig. 1A, and there is a C_s symmetry plane through 'atoms' C3—C6—C5*—C5—C6*—C3*. Removal of the partial occupancy gives the ORTEP structure Fig. 1B or 1C. In IUPAC numbering, the C_s plane involves carbon atoms 9, 10, 1 and 5 (see structure **15**). The unit cell diagram of **15** shows extensive hydrogen bonding networks (Fig. 2).

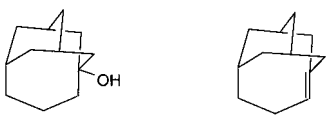
The C3···C7 distance in **15** is 3.438 Å, which compares with a calculated value of 2.81 Å for the dication **6**. A major steric distortion in **15**, as in the manxyl analog, involves the C3—C7 bridgehead hybridization. Angle O—C3—C2(4) is 104.1°, whereas the internal angle C2—C3—C4 is 113.8°. This corresponds to a partial flattening of the bridgehead sp^3 hybridization, and accounts for the previously discussed propensity of hydrocarbon **14** to form a bridgehead radical.



15 **16**

Diol **15** was converted to the dichloride **16** by treating a diol solution in dichloromethane with concentrated hydrochloric acid at 0 °C for 15 min.

The monoalcohol **17** could also be isolated from the reaction of **14** with air, using short contact times, and then separating **17** from the accompanying diol **15** and hydrocarbon. A variety of attempts to produce the corresponding chloride of **17**, either as a pure compound or as a pure *in situ* solution species, were unsuccessful. However, the known[13] alkene **18** was prepared, so that both alcohol **17** and alkene **18** were available as potential precursors of cation **8**.



17 **18**

Preparation of the tricyclo[5.3.1.1^{3,9}]dodecyl dication (6)

Careful addition of dichloride **16** to a solution of SbF_5/SO_2ClF at −116 °C generated a species whose ^{1}H NMR spectrum showed five distinct signals at δ 4.76, 4.60, 3.79, 3.40 and 2.72 (area 1:1:1:1:2), as well as an overlapping region from δ 4.2 to 4.55 (*ca* 12H). Much more revealing is the ^{13}C NMR spectrum shown in Fig. 3 (see also Table 1). There are eight signals, plausibly grouped into area ratios 2:1:1:2:2:2:1:1, from low to high field. This spectrum requires the degenerate ring shift shown below to be slow on the NMR time scale (eight peaks *versus* six for rapid exchange), and also that there is effective C_s symmetry (a plane through C5—C1—C10—C9, as also seen in the X-ray structure of diol **15**). The thermal instability of **6** (see later) prevented an NMR

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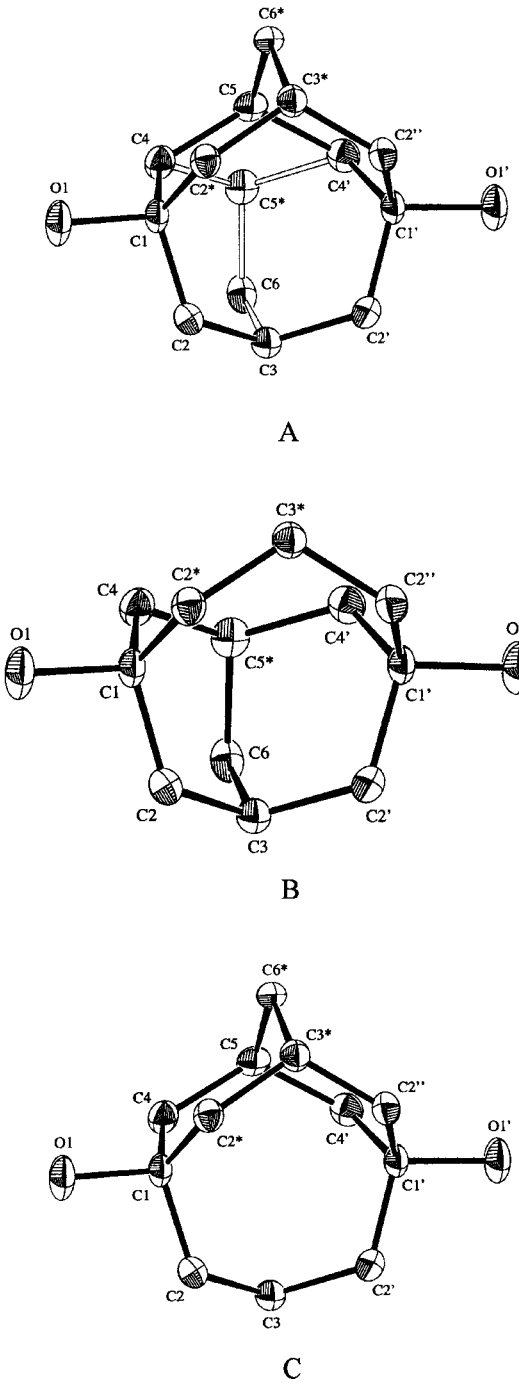


Figure 1. (A) ORTEP drawing of compound **15** illustrating the crystal symmetry [symmetry operation: ,$= -x, y, z$; ⋆$= x, \frac{1}{2} - y$; ,,$= -x, \frac{1}{2} - y, z$]. C5 and C6 are disordered over two sites. (B) ORTEP drawing of compound **15** with partial occupancies C5 and C6* removed. The crystallographic numbering system does not correspond to that used in the rest of this paper. (C) ORTEP drawing of compound **15** with partial occupancies C5* and C6 removed. The crystallographic numbering system does not correspond to that used in the rest of this paper

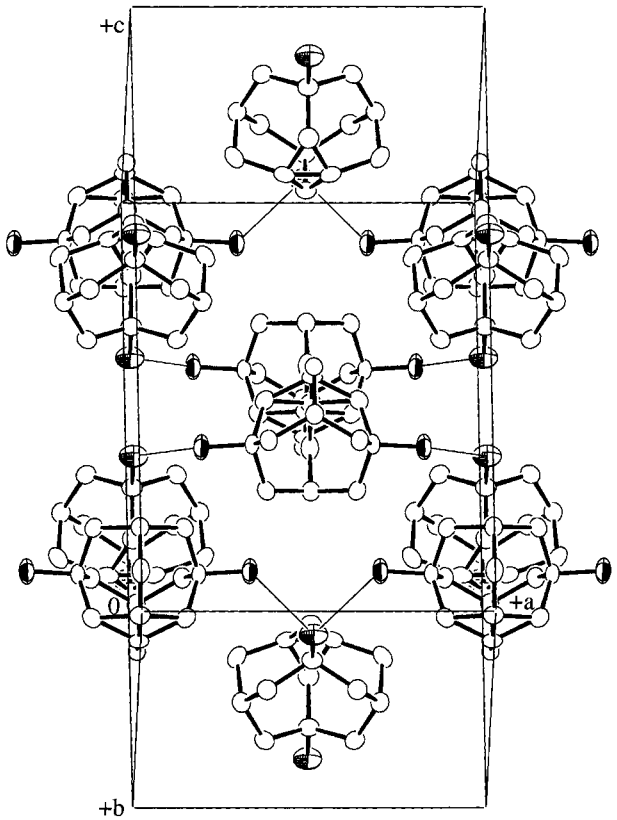
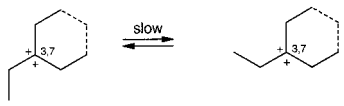


Figure 2. Unit cell for crystalline **15** illustrating the extensive H-bonding network

conformational study, but there is independent evidence that the ring flip **6a**$\rightleftarrows$**6b** would be slow at −116 °C. This fluxional behavior was studied in detail for hydrocarbon **14** (^{1}H and ^{13}C NMR data over the temperature range 243 to 363 K, 10 K increments), giving $\Delta G^{\ddagger} = 13.1$ kcal mol^{-1}. For diol **15** a similar value is obtained, based on NMR results at 240, 300 and 330 K (8C peaks → 6C peaks). In the related manxyl compounds, the manxyl dication undergoes the ring flip[5,14] with a barrier *ca* 2 kcal mol^{-1} smaller than in the hydrocarbon, so that one can estimate a ring flip barrier for **6** of about 11 kcal mol^{-1}, which at a temperature of −116 °C would correspond to a slow rate on the NMR time scale, as we indeed observe.



Further evidence for the structure of our dication **6** comes from a comparison of calculated and observed ^{13}C NMR shifts, as shown in Figure 4.

The structure of cation **6** was optimized at the B3LYP/6-31G* level of theory, and the NMR calculations were carried out at the GIAO/MP2(full)/6-31G*//B3LYP/6-31G* level. In general, the calculated δ values are somewhat lower field than the experimental ones, but

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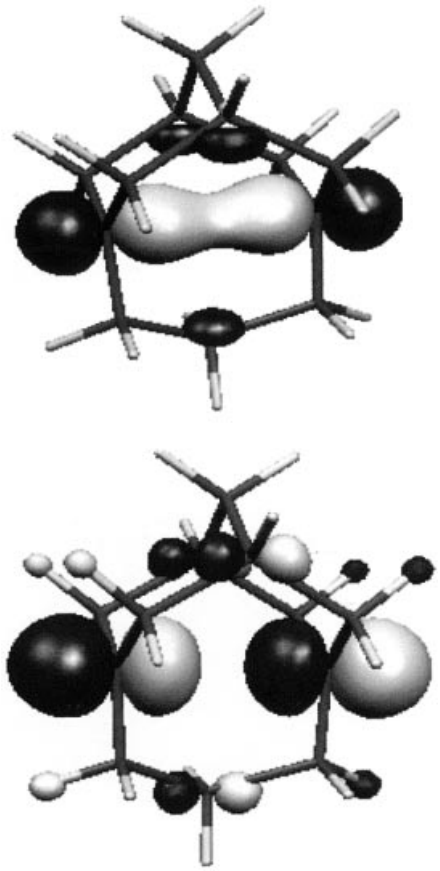

Figure 3. Plot of the LUMO (top) and LUMO−1 (bottom) orbitals calculated for dication **6**. The LUMO–LUMO−1 gap is 32.3 kcal mol^{-1}, indicating extensive interaction between the two C^+ centers (versus 3.8 kcal mol^{-1} for the extended chain conformer of 2,6-dimethylhepta-2,6-diyl dication)

the observed overall pattern is fairly similar. The NMR spectra reveal several interesting features of the dication **6** structure. (1) The lowest field ^{1}H signals observed in the experimental spectrum, δ 4.76 and 4.60, can be assigned to the bridgehead hydrogen atoms at C9 and C1, based on the calculated ^{1}H shifts. These peaks occur at a lower field position than any of the hydrogen atoms adjacent to the C^+ center. (2) In the ^{13}C NMR spectrum, the two carbon atoms at δ 72.1 and 67.1 (lowest field except for C^+) can likewise be assigned to C9 and C1.

These results suggest that C—C hyperconjugation from the C1—2, C9—12, C1—11 and C9—8 bonds is an important delocalization mechanism in stabilizing dication **6**. The situation in **6** is unique, in that C1 and C9 experience a double electron deshielding due to the combined effect of both carbocation sites. Interestingly, this analysis does not apply to the somewhat similarly situated C5 carbon, with a chemical shift of δ 27.6. In the manxyl dication **5** the three equivalent carbon atoms are found at δ 23.6, i.e. at much the same chemical shift as C5 in **6**, but, overall, cations **5** and **6** have distinct NMR shift differences in the other carbon sites.

The calculated geometry of dication **6** (C_s) shows structural features that are consistent with the C—C hyperconjugation proposed above. Bonds C1—C2 (C1—C11) and C9—C10 (C9—C8) have $d = 1.597$ and 1.595 Å respectively, but C4—C5 (C6—C5) with $d = 1.572$ Å is also quite long.

Having a computed structure of **6** also allows one to elaborate on several of the topics discussed in the Introduction. The $C^+ \cdots C^+$ distance is calculated to be 2.81 Å, *versus* 2.80 Å for the manxyl dication, i.e. these are very similar structures. The dihedral angle C2—C3—C4—C10 in **6** is 169.7°, so there is some 'outward' nonplanarity at the cation centers. Dication **6** differs, of course, from the manxyl dication in having an open face into the $C^+ \cdots C^+$ cavity, as discussed in the Introduction.

Although the $C^+ \cdots C^+$ distance of 2.81 Å in **6** is close to the van der Waals radii for carbon, there is clearly an interaction between the C^+ centers. This is seen in the energy separation of the lowest unoccupied

Table 1. ^{13}C NMR parameters for cations **6**, **8**, **19** and **20**

	Carbon number[b]											
Cation[a]	1	2	3	4	5	6	7	8	9	10	11	12
6[c,d]	67.1	60.1	327.8	57.5	27.6	57.5	327.8	65.9	72.1	35.1	60.1	65.9
8[c,d]	69.2	60.0	335.1	57.2	32.2	43.7	28.7	37.6	75.5	36.1	32.2	70.9
											CH_2–CH_3	
19	62.9	324.8	62.9	51.7	29.0	36.4	29.0	51.7	51.7	51.7	49.9	9.1
												CH_3
20	26.8	33.6 or 33.3	63.5	323.3	67.5	27.8	33.3 or 33.6	26.8	33.3	33.3 or 33.6	33.6 or 33.3	44.1

[a] For temperature and solvent, see Experimental (^{1}H NMR).
[b] Assignments augmented by DEPT spectra.
[c] Assignments augmented by GIAO NMR calculations.
[d] The numbering system being used is for the specific conformation shown in the **6** and **8** drawings.

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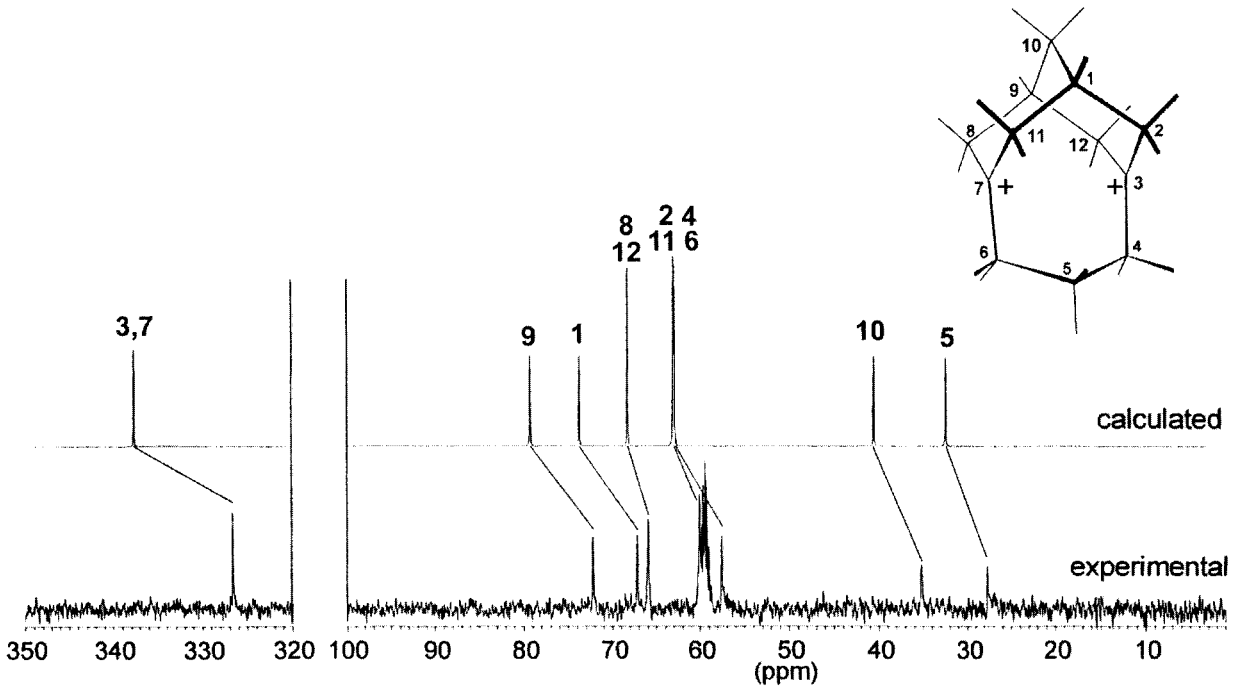

Figure 4. ^{13}C NMR spectrum of dication **6** (lower) and calculated shifts (upper). The correlations shown are our assignments, aided by knowledge of the DEPT spectrum and the number of carbon atoms in each peak. The multiplet at δ 59.4 is from a $(CD_3)_2O$ insert

MO (LUMO) and LUMO+1 (shown in Figure 3), the former showing the expected in-phase p_z orbital symmetry in the inner cavity appropriate for interaction with a hydride donor (HOMO). Of course, an interaction on the outer part of the cation is also 'allowed'.

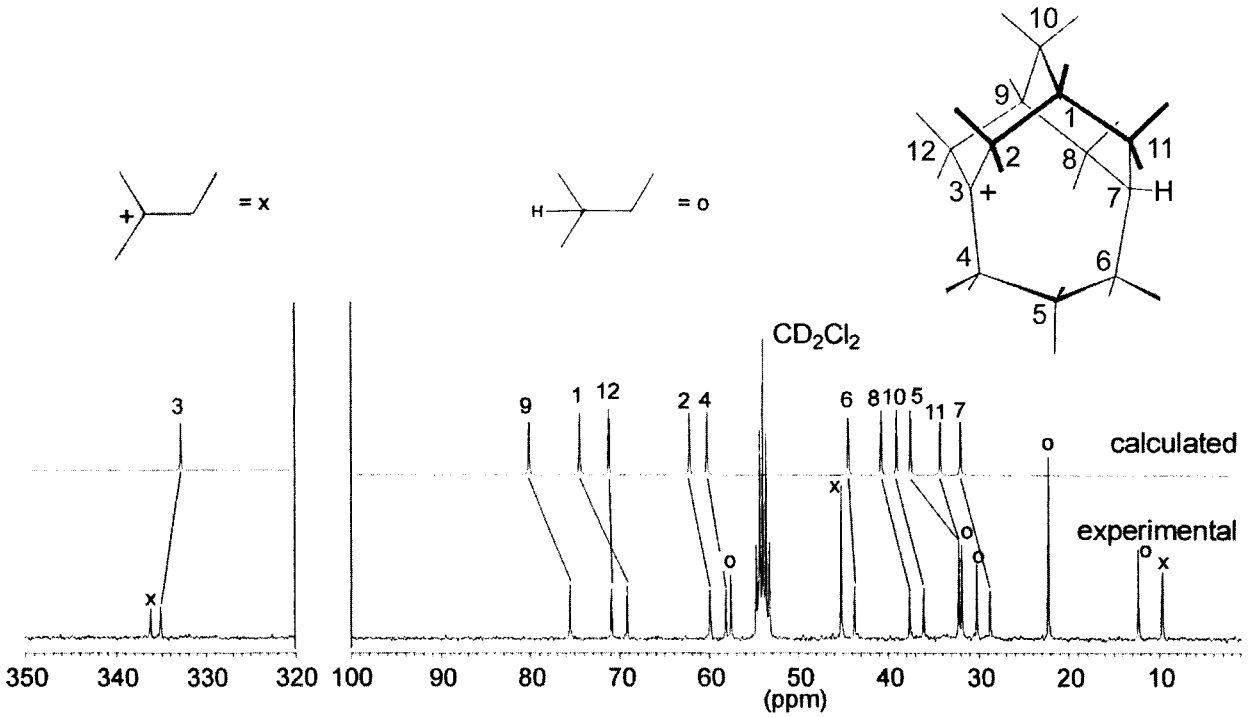

Figure 5. ^{13}C NMR spectrum of monocation **8** (lower) and calculated shifts (upper). The correlations shown are our assignments, aided by knowledge of the DEPT spectrum. The peaks marked (×) are from the t-pentyl cation and those marked (o) are from excess 2-methylbutane (isopentane). The multiplet at δ 54.0 is CD_2Cl_2

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Reaction of dication 6 with isopentane, H_2 and $NaBH_4$

The title reactions had to be conducted at very low temperatures, since **6**, contrary to our prior expectations for this structure, turned out to be about as thermally labile as the manxyl dication (slow loss of NMR signals at −70 °C, producing no defined rearrangement products). This thermal instability of **6** was not a problem for the isopentane reaction, since the addition of an excess of isopentane to the dication **6** solution, kept at −135 °C, rapidly and cleanly formed the t-pentyl cation. However, the tricyclic monocation that was formed from **6** clearly corresponded to the out-H species **8** (see ^{13}C NMR spectrum shown in Figure 5). No sign of the μ-H cation **7** was found, and it should be noted that the very high-field chemical shift predicted for the μ-H ^1H peak ($\delta = -9.5 \pm 0.5$),[4] in a region normally devoid of even spurious ^1H NMR signals, would have allowed us to detect even very small concentrations of **7**.

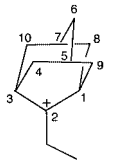
The assignment of the monocation **8** structure was based on ^{13}C chemical shift and DEPT information, augmented by a comparison of experimental and calculated ^{13}C NMR chemical shifts (Table 1 and Figure 5). Overall, the calculated shift comparisons were somewhat low field of the experimental values, but the peak pattern corresponded quite well with the experimental spectrum. Eventually (see later) a solution of authentic cation **8** (mixed with a rearrangement product) was obtained from alkene **18**. As with the dication **6**, the monocation **8** also shows a 'frozen-out' ring conformation (C4, C5, C6), with all 12 ^{13}C peaks visible in **8**, *versus* a predicted nine peaks for a rapid ring flip situation.

Sodium borohydride also reacted with the dication **6** solution, but much slower than for isopentane. After 3.5 h at −84 °C one could clearly identify ^{13}C peaks arising from monocation **8**, but other ^{13}C peaks were also present. However, no evidence for μ-H structure **7** was evident in the ^1H NMR spectrum. In these experiments, a stoichiometric excess of the hydride was used, but we have no evidence on whether the BH_4^- itself was the reducing agent, or whether H_2 gas was the actual reductant.

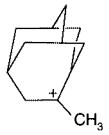
Finally, a reduction attempt was made using H_2 gas, with the hope that the small steric size of this molecule would allow reaction in the inner region of the dication. Reaction of the dication **6** solution with H_2 gas in a pressurized (8 bar) stainless steel tube at −126 °C for 12 h produced a 2:1 mixture of monocation **8** to dication **6**. In the ^1H NMR spectrum there was no sign of a μ-H peak.

Attempted generation of monocation 8 from the monoalcohol 17

Monoalcohol **17** was available as a side product of the air oxidation of the hydrocarbon **14** to diol **15**, and this material was a possible precursor for an independent preparation of monocation **8**. Attempts to prepare the corresponding chloride (a better carbocation precursor) led to complex mixtures. However, when alcohol **17** was used for the cation preparation only 2-ethyl-2-adamantyl cation (**19**) was produced (verified by starting with 2-ethyl-2-adamantanol). Cation **19** was also produced when the tricyclic monocation **8** solution (isopentane route) was allowed to warm to −52 °C (10 min for 34% rearrangement, $\Delta G^{\ddagger}$ *ca* 16 ± 0.6 kcal mol^{-1}). The same reaction was also observed in the $NaBH_4$ and H_2 reduction reactions on warming these to −63 °C for a short period.



19



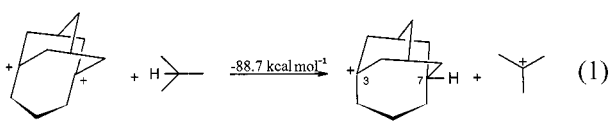
20

It appeared to us that the carbocation-forming reaction using alcohol **17** must involve a quite exothermic process and that the local heating immediately rearranges the first-formed **8** into cation **19**. The known[13] alkene **18** was also a potential precursor of **8**, and when this was carefully added to an SbF_5–FSO_3H–SO_2ClF mixture at *ca* −140 °C the monocation **8** was finally detected, accompanied by a new cationic species assigned the 4-methyltricyclo[4.3.1.1^{3,8}] undec-4-yl cation (**20**) structure (see Table 1 for NMR data).

It appears from this work that the monocation **8** is in fact best prepared from the dication **6** by hydride transfer, in preference to the direct routes, and that this procedure constitutes a novel approach to preparing some monocations.

Thermodynamics of hydride transfer to dications

Even though the μ-H monocation **7** and the conventional out-H isomer **8** are calculated to be nearly equally stable in a thermodynamic energy sense,[4] it seems clear from the present study that μ-H cations such as **7** cannot be prepared by reaction of the dication **6** with hydride donors. Before leaving this discussion, however, it was of interest to examine the dication **6** more closely, for two reasons: (1) this dication, because of the geometry, has the two C^+ centers in close proximity and (2) countering this, the steric strain in the molecule (cf. the extensively studied manxyl system[15]) should favor sp^2 centers at the C3—C7 bridgeheads. The following isodesmic reactions were therefore evaluated (B3LYP/6–31G* level):



(1)

6 **8**

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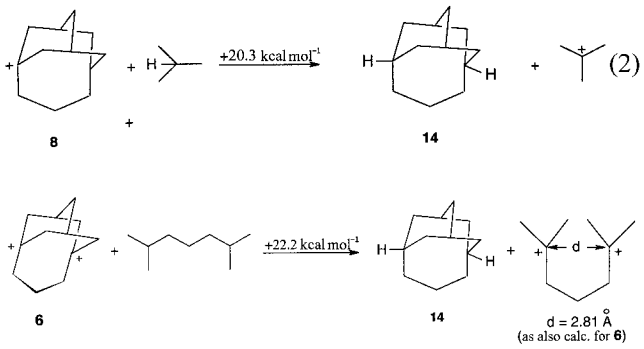


(2)

8 14

(3)

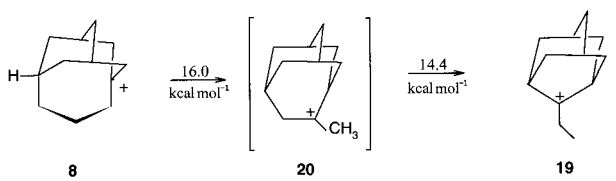
6 14

Equation (1) clearly illustrates the large charge repulsion present in the dication **6**. Even though there is expected to be some extra steric strain (at C7) generated in the Eqn. (1) 'reaction', the process is still highly exothermic as a gas-phase reaction. Equation (2) clearly shows the extra stability of the tricyclic monocation **8**, relative to the t-butyl cation, and is most plausibly attributed to the steric strain induced in the second sp^3-hybridized bridgehead in **14**. In our experimental work, the dication **6**, was reacted with a considerable excess of isopentane, and the reaction was observed clearly to proceed only to the monocation **8** stage, in agreement with the Eqn. (2) result. Equation (3) involves an imperfect isodesmic reaction, in that there is extra steric strain present in the acyclic dication not present in the alkane conformation that we employed. Nevertheless, the unfavorable energy associated with Eqn. (3) can be attributed, in the main, to the 'extra' steric strain in **14**.

In considering the double ionization of the dichloride **16** in SbF_5 solution, it seems likely that the thermodynamic factors illustrated in Eqns (1)–(3) would be crucial in allowing this dication to be formed.

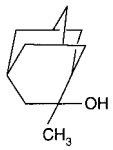
Rearrangement of monocation 8 to the 2-ethyl-2-adamantyl cation (19)

Although not directly related to this study, the monocation **8**, as discussed earlier, rearranges to the 2-ethyl-2-adamantyl cation (**19**) at about −60 °C.



8 20 19

This reaction would be expected to be a multistep process, likely involving the intermediacy of the homoadamantyl cation **20**. Since a precursor for cation **20** (alcohol **21**) was readily available from ketone **10**, we prepared this cation (initial mixing at −135 °C, NMR observations at −105 °C). The ^{13}C NMR data are reported in Table 1. At −62 °C, cation **20** cleanly rearranges to the 2-ethyl-2-adamantyl cation **19** within 20 min, $\Delta G^{\ddagger}$ *ca* 14.4 ± 0.3 kcal mol^{-1}. Since cation **20** rearranges at a faster rate than **8** ($\Delta G^{\ddagger}$ *ca* 16.0 ± 0.6 kcal mol^{-1}), the non-observation of **20** in the **8** → **19** conversion is accounted for. The observation of some cation **20**, admixed with **8**, on protonation of alkene **18** may indicate that the protonation gives both the secondary and tertiary cations, and that the former then quickly collapses to give cation **20**.



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CONCLUSIONS

The dication **6** has been prepared *in situ* and characterized experimentally and by means of theoretical calculations. It shows distinct differences in hyperconjugative delocalization modes compared with the closely related manxyl dication **5**. Dication **6** reacts with hydride donors to produce the conventional out-H cation **8** and there is no evidence that a μ-H monocation can be formed in such reactions. Neither dication **6** nor monocation **8** have much thermal stability, the latter rearranging stepwise to the 2-ethyl-2-adamantyl cation **19**.

EXPERIMENTAL

The compounds tricyclo[4.3.1.1^{3,8}]undecan-4-one[11] (**9**), 2-ethyl-2-adamantan-2-ol[16] and tricyclo[5.3.1.1^{3,9}]dodec-3-ene[13] (**18**), were prepared according to literature procedures.

General

NMR spectra were recorded on Bruker ACE 200, AMX 300 or AM 400 spectrometers. ^1H and ^{13}C chemical shifts δ were measured in $CDCl_3$ unless otherwise indicated. Superacid solutions were referenced with respect to $CDHCl_2$, δ 5.32 (^1H) or CD_2Cl_2, δ 54.00 (^{13}C). Abbreviations used: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Gas chromatography–Mass spectrometry (GC–MS) data were obtained on an HP 5890 Series II/HP 5974 spectrometer. High- and low-resolution MS spectra were measured on a Kratos MS 80 or Micromass VG 7070 spectrometer. Antimony pentafluoride was purified by heating the commercial product with SiO_2 in a thick-walled Schlenk flask to 120 °C for 20 h (***caution***: pressure) and triply distilled in high

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vacuum at room temperature. Fluorosulfonic acid was doubly distilled at *ca* 50 °C in a vacuum. Sulfuryl chloridefluoride was prepared by fluoride exchange of sulfuryl chloride (personal communication, H.U. Siehl, University of Ulm, Germany, 1995) and purified by double distillation over SbF_5.

4-Cyano-4-trimethylsiloxytricyclo[4.3.1.1^{3,8}]undecane (10)

To a mixture of tricyclo[4.3.1.1^{3,8}]undecan-4-one (**9**), 375 mg, 2.28 mmol, and zinc iodide, 50 mg, 0.16 mmol, was added 1 ml TMSCN with cooling (water bath, 10 °C). The resulting clear solution was stirred at ambient temperature for 12 h before the excess TMSCN was evaporated under vacuum (15 mmHg). The solid residue was dissolved in ether, washed twice with a sodium bicarbonate solution (5%), dried and concentrated to give 653 mg of crude product (100%), which was used without further purification. MS, *m/z* (relative intensity): 45 (50); 53 (33); 67 (30); 75 (68); 84 (100); 91 (51); 105 (20); 119 (24); 127 (17); 151 (10); 221 (58); 222 (13); 248 (77); 263 (3.5, $M^{+\cdot}$). ^{1}H NMR: 2.68 (ddd, J = 15.3, 4.3, 1.4, IH); 2.27–2.11 (m, 2H); 2.10–1.96 (m, 3H); 1.95–1.76 (m, 5H); 1.74–1.47 (m, 5H); 0.22 (s, 9H). ^{13}C NMR: 124.7 (q); 77.9 (q); 52.2 (CH_2); 43.8 (CH); 38.1 (CH_2); 36.9 (CH_2); 36.3 (CH_2); 33.1 (CH_2); 30.7 (CH); 30.1 (CH_2); 27.1 (2 × CH); 1.4 (3 × CH_3).

4-Aminomethyltricyclo[4.3.1.1^{3,8}]undecan-4-ol (11)

A solution of **10**, 2.65 g, 10 mmol, in ether (30 ml) was added dropwise to a mixture of $LiAlH_4$ (1.9 g, 50 mmol) and ether (20 ml), with stirring. After completion of addition, the mixture was refluxed for 4 h. Cautious addition of an aqueous solution of potassium hydroxide (200 g l^{-1}, 4 ml) produced a white precipitate, which was filtered off after 2 h of stirring. The resulting solution was concentrated to give 2.03 g of **11** (a waxy solid), 95% pure by ^{1}H NMR, 98% yield. ^{1}H NMR: 2.86 (d, J = 12.6, 1H); 2.55 (d, J = 13.2, 1H); 2.28 (d, br, J = 13.8, 1H); 2.07–1.95 (m, 2H); 1.94–1.79 (m, 7H); 1.79–1.48 (m, 8H); 1.42 (d, br, 11.5, 1H). ^{13}C NMR: 73.6 (q); 51.8 (CH_2); 48.2 (CH_2); 38.7 (CH_2); 38.7 (CH); 36.8 (CH_2); 36.6 (CH_2); 31.8 (CH_2); 31.4 (CH_2); 30.4 (CH); 27.7 (CH); 27.6 (CH). These data are in agreement with literature values.[10]

Tricyclo[5.3.1.1^{3,9}]dodecan-4-one (12) and tricyclo[5.3.1.1^{3,9}]dodecan-5-one (13)

The aminoalcohol **11**, 22.8 g, 117 mmol, was dissolved in a mixture of water (710 ml) and acetic acid (26.7 ml). At ambient temperature, a solution of sodium nitrite (24.2 g, 350 mmol) in water (210 ml) was added dropwise over a period of 2 h. After completion of the addition, the reaction mixture was heated to 90 °C for 2 h, before extracting with ether. The ether phase was washed with sodium bicarbonate solution, dried with magnesium sulfate and concentrated. The waxy solid obtained was purified by column chromatography (silica gel, 500 g; hexanes:ether, 95:5). Concentration of the major band eluant yielded 18.78 g of **12** and **13** (96:4 by GC), 90% yield. HRMS: M^+ calc. 178.135 765, found, 178.1343. ^{1}H NMR: 2.59 (t, J = 6.6, 2H); 2.28 (t, J = 6.9, 1H); 1.73–2.20 (m, 11H); 1.48 (t, J = 6.6, 4H). The spectral data were in accordance with literature values.[10,13]

Tricyclo[5.3.1.1^{3,9}]dodecane (14)

Using the procedure of Nagata and Itazaki,[17] a mixture of **12** and **13** (0.75 g, 4.2 mmol), hydrazine (55%, 15.7 ml, 278 mmol), hydrazine dihydrochloride (3.53 g, 33.6 mmol) and triethylene glycol (85 ml) was heated to 130 °C for 3 h. The temperature was then increased to 215 °C within 30 min, at which point it was kept for 3 h. After cooling the reaction mixture to room temperature, water (300 ml) was added and the resulting solution was extracted with ether (3 × 50 ml). The combined ether layers were dried with $MgSO_4$, filtered and concentrated to give 0.87 g of crude material. Purification on a column (SiO_2, 50 g, hexanes) yielded 0.64 g of white waxy material, 96% pure by GC, 89% yield. The following MS and NMR data were in agreement with the published data of Sasaki *et al.*[10] and Ward and Murray.[13] GC–MS, *m/z* (relative intensity): 41 (20); 55 (13); 67 (32); 79 (6); 93 (70); 107 (13); 121 (67); 136 (20); 149 (7); 164 (100). ^{1}H NMR (233 K): 2.12–1.93 (m, 4H); 1.91–1.53 (m, 9H); 1.51–1.29 (m, 5H); 1.18 (td, J = 13.8, 2.8, 2H). ^{1}H NMR (363 K): 2.22–2.05 (s, br, 2H); 2.04–1.88 (m, 4H); 1.87–1.76 (s, br, 2H); 1.75–1.39 (m, 12H). ^{13}C NMR (233 K): 39.3 (CH_2); 37.0 (CH_2); 35.4 (CH_2); 31.0 (CH_2); 36.2 (CH); 25.2 (CH); 24.9 (CH); 21.4 (CH_2). ^{13}C NMR (363 K): 37.5 (CH_2); 36.0 (CH_2); 35.7 (CH_2); 26.5 (CH); 25.7 (CH); 21.7 (CH_2).

Tricyclo[5.3.1.1^{3,9}]dodecan-3,7-diol (15) and tricyclo[5.3.1.1^{3,9}]dodecan-3-ol (17)

Method a: partial oxidation. Tricyclo[5.3.1.1^{3,9}]dodecane (**14**) (639.6 mg, 3.89 mmol) was dissolved in hexanes (40 ml), placed in a 1 l RB flask and the solvent was evaporated on a rotavapor to produce a fine solid film of the hydrocarbon on the glass wall. The flask was stoppered and stored at ambient temperature for 7 days. After 3 and 5 days, the air in the flask was replaced with fresh air. The resulting mixture of alkane, monoalcohol and diol was separated *via* column chromatography

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(silica gel, 30 g, hexanes:ether, 80:20, followed by ether) yielding 130.0 mg starting material, 172.8 mg **17** and 322.6 mg **15**, all of which were white solids (84% combined yield of **15** and **17** based on alkane consumed.

Method b: exhaustive oxidation. Tricyclo[5.3.1.1^{3,9}]-dodecane (**14**) (180 mg, 1.10 mmol) was applied as a film as described above. Oxygen was then passed into the flask at a rate of 1 to 3 ml min^{-1} for 2 weeks. The solid was then dissolved in methanol and sodium borohydride (2 g, 52.8 mmol) was added in small portions over a period of 2 h. The reaction mixture was then concentrated on a rotavapor and the diol **15** extracted with warm chloroform (50 °C, 3 × 20 ml). Purification of the diol by column chromatography (silica gel, 30 g, ether 100%) yielded 69.2 mg of pure solid diol (32% yield).

Tricyclo[5.3.1.1^{3,9}]dodecane-3,7-diol (15). GC–MS, *m/z* (relative intensity): 41 (12); 55 (12); 67 (14); 79 (38); 95 (100); 105 (32); 117 (64); 135 (45); 145 (21); 160 (89); 178 (51). HRMS (EI): calc. for M^+-H_2O, 178.135 765; found, 178.1347. ^{1}H NMR (230 K, CD_3OH): 2.27–2.13 (s × 2, br, 4H); 2.01 (dd, J = 13.9, 5.6, 2H); 1.98 (m, 1H); 1.94 (d, J = 13.6, 2H); 1.83 (m, 2H); 1.78–1.56 (m, 7H). ^{13}C NMR (240 K, CD_3OH): 71.5 (q); 49.3 (CH_2); 47.0 (CH_2); 43.1 (CH_2); 36.1 (CH_2); 32.1 (CH); 31.1 (CH); 23.4 (CH_2). ^{1}H NMR (330 K, CD_3OH): 2.24–2.12 (s, br, 2H); 2.06 (d, J = 14.1, 4H); 1.88 (dd, J = 14.1, 5.6, 4H); 1.80 (s, 6H); 1.64 (s, 2H). ^{13}C NMR (330 K, CD_3OH): 71.5 (q); 47.4 (CH_2); 46.6 (CH_2); 36.3 (CH_2); 31.9 (CH); 23.5 (CH_2).

Tricyclo[5.3.1.1^{3,9}]dodecan-3-ol (17). GC–MS, *m/z* (relative intensity): 40 (33); 53 (15); 67 (23); 79 (100); 91 (91); 105 (48); 119 (40); 133 (15); 147 (8); 162 (36); 180 (1). HRMS (EI): calc. for $M^{+\cdot}$, 180.151 415; found, 180.1514. IR (neat): 3340 (m); 2905 (s); 2847 (m); 1450 (m); 1057 (m); 926 (m); 908 (m); 732 (m). ^{1}H NMR (300 K): 2.07–1.92 (m, 5H); 1.91–1.82 (s, br, 2H); 1.82–1.58 (m, 8H); 1.58–1.45 (m, 4H); 1.44–1.37 (m, 1H). ^{13}C NMR (300 K): 71.1 (q); 46.1 (CH_2); 45.1 (br, CH_2); 37.1 (CH_2); 35.2 (CH_2); 34.5 (br, CH_2); 28.3 (br, CH); 24.8 (CH); 22.2 (CH_2).

3,7-Dichlorotricyclo[5.3.1.1^{3,9}]dodecane (16)

Tricyclo[5.3.1.1^{3,9}]dodecane-3,7-diol (**15**), 15 mg, 76 μmol, was dissolved in dichloromethane (3 ml) and the solution cooled to 0 °C. At this temperature, hydrochloric acid (concentrated, 2 ml) was added and the heterogeneous mixture was stirred vigorously for 10 min. The organic layer was then separated and dried by passing it through a column containing magnesium sulfate (2 g). The dichloromethane of the filtrate was evaporated using a stream of nitrogen. The solid obtained was directly used for carbocation preparation. GC–MS, *m/z* (relative intensity): 39 (43); 53 (31); 67 (34); 79 (95); 91 (95); 106 (100); 119 (81); 196 (17); 197 (2); 198 (4). ^{1}H NMR (273 K): 2.66 (dd, J = 14.6, 6.3, 2H); 2.60–2.45 (m, 4H); 2.37 (dd, J = 14.8, 5.5, 2H); 2.33–2.21 (m, 3H); 2.16 (s, br, 1H); 2.12–1.95 (m, 3H); 1.68 (s, br, 3H). ^{13}C NMR (273 K): 74.8 (q); 49.5 (CH_2); 47.5 (CH_2); 43.2 (CH_2); 33.8 (CH_2); 32.1 (CH); 31.1 (CH); 23.9 (CH_2).

4-Methyltricyclo[4.3.1.1^{3,8}]undecan-4-ol (21)

Tricyclo[4.3.1.1^{3,8}]undecan-4-one (**9**) 420 mg, 1.46 mmol, was dissolved in ether (20 ml) and cooled to −78 °C. At this temperature, methyl lithium, 1.5 M, 3.4 ml, 5.10 mmol, was added and the resulting solution stirred for 2 h, while warming to ambient. The reaction mixture was poured into a solution of ammonium chloride, 5%, 100 ml, 0 °C. Extraction with ether (3 × 30 mL), drying ($MgSO_4$), filtration and concentration afforded a semi-solid crude material, which was purified on a silica gel column using hexane: ether (95:5) to yield 439.3 mg of the crystalline alcohol **21**, yield 95%. GC–MS, *m/z* (relative intensity): 43 (78); 59 (50); 67 (44); 79 (100); 93 (65); 105 (33); 122 (14); 147 (16); 162 (38); 180 (2). HRMS (EI): calc. for $M^{+\cdot}$, 180.151 42; found, 180.149 61. IR (neat): 3382 (s); 2960 (s); 1444 (m). ^{1}H NMR: 2.24 (d, J = 13.2, 1H); 2.02–1.90 (m, 3H); 1.90–1.80 (m, 4H); 1.80–1.67 (m, 4H); 1.67–1.59 (m, 1H); 1.59–1.46 (m, 4H); 1.31 (s, 3H). ^{13}C NMR: 77.35 (q); 51.17 (CH_2); 45.03 (CH); 38.24 (CH_2); 37.14 (CH_2); 36.86 (CH_2); 33.85 (CH_3); 32.66 (CH_2); 31.42 (CH_2); 30.49 (CH); 27.89 (CH); 27.68 (CH).

Carbocation preparation

Dication 6. The dichloroalkane **16** (15 mg, 64 μmol) was dissolved in dichloromethane-d_2 (0.2 ml) and added to a solution of SbF_5 (100 mg, 0.46 mmol) and SO_2ClF (1.8 ml) at −116 °C. The sample was mixed with a tungsten wire, while an argon stream prevented moisture contamination. In some preparations of dication **6** the superacid solutions were prepared without CD_2Cl_2 solvent. In these cases, the solid dichloride and cold (157 K) SO_2ClF were placed in an NMR tube, and precooled SbF_5 dissolved in SO_2ClF was slowly added with stirring. ^{1}H NMR (168 K, 300 MHz): 4.9–4.1 (m, 14H); 3.75 (s, br, 1H); 3.41 (s, br, 1H); 2.70 (s, 2H); see Table 1 for ^{13}C NMR data.

Cation 8. A mixture of SbF_5 (50 mg, 231 μmol), FSO_3H (100 mg, 1 mmol) and SO_2ClF (0.3 ml) was prepared and cooled to −140 °C (the solution became very viscous). On top of this mixture, SO_2ClF (0.2 ml) was condensed, and then a solution of alkene **18** (12.3 mg, 75.8 μmol) in dichloromethane-d_2 (70 μl) was added. The dichloromethane solution immediately froze on contact with the SO_2ClF, thereby only slowly dissolving upon stirring

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with a tungsten wire. A constant stream of argon over the sample was maintained at all times to keep the sample free of moisture. The cation **8** was produced as a mixture with cation **20**.

Cations 19 and 20. Using the general procedure described for **8**, employing alcohol **21** and a temperature of −135 °C, a solution of pure cation **20** was prepared, and the spectra were measured at −105 °C. Cation **19** was prepared in a similar manner, starting from the corresponding tertiary alcohol.

Cation **19**. ^{1}H NMR (153 K, 400 MHz): 4.19 (s, 2H); 4.06 (q, $J = 6.1$ 2H); 2.99 (d, $J = 12.2$, 4H); 2.63 (d, $J = 12.2$, 4H); 2.22 (s, 2H); 2.20 (s, 2H); 1.58 (t, $J = 6.3$ 3H).

Cation **20**. ^{1}H NMR (168 K, 300 MHz): 4.27 (s, 2H); 4.16 (t, $J = 6.9$, 1H); 3.59 (s, 3H); 2.54 (s, br, 2H); 2.40 (s, 1H); 2.24 (s, 2H); 2.16–1.80 (m, 6H); 1.68 (d, $J = 13.7$, 2H).

Hydrogenation experiments with dication 6

Isopentane. The dication solution (from 16.6 mg, 71.2 μmol of **16**) was prepared as described. At *ca* −135 °C, 15 μl of isopentane was added. Stirring with a tungsten wire formed a clear, slightly yellow, solution of monocation **8**, the t-pentyl cation and excess isopentane. ^{1}H NMR (168 K, 300 MHz): 4.3–3.7 (m, 6H); 2.9 (q, 1H); 2.8–1.6 (m, 12H).

Sodium borohydride. The dication solution (from 10.0 mg, 42.9 μmol of **16**) was treated with 30 mg, 793 μmol, of the hydride salt. To get any reaction, the solution had to be warmed to −84 °C. After 3.5 h, the dication had disappeared and a mixture of monocation **8**, cation **19** and other material was present. At −63 °C, a relatively clean spectrum of cation **19** was obtained.

Hydrogen gas. The dication **6** solution, in an NMR tube, was placed in a stainless steel tube cooled with an *n*-pentane/liquid N_2 slush at −126 °C. The initial argon atmosphere was replaced with H_2 by repeated pressurization–depressurization and the sample was maintained at this temperature for 12 h (pressure, 8 bar). After depressurization, NMR studies showed that a 2:1 mixture of monocation **8** and dication **6** were present.

Computational procedures

MO calculations employed either the Gaussian 94[18] or Gaussian 98[19] suite of programs. Structures were optimized at the B3LYP/6-31G* level of theory (UHF for radicals). ZPVE corrections have been applied to all energy values using the factors recommended by Scott and Radom.[20] Thermal corrections to 298 K have also been included. GIAO MP2/6-31G* NMR calculations employed Gaussian 98 and were based on B3LYP/6-31G* optimized structures. Calculations (ground state and transition states) were carried out in an attempt to model the **8** → **20** → **19** reaction, using both MP2/6-31G* and B3LYP/6-31G* optimizations. However, these two *ab initio* methods gave conflicting results.[14]

Table 2. Crystallographic data for structure **15**

Crystal data	
Empirical formula	$C_{12}H_{20}O_2$
Formula weight	196.29
Crystal system	tetragonal
Lattice parameters	
a (Å)	10.058(4)
c (Å)	20.599(7)
V (Å^3)	2083.8(7)
Space group	$I4_1/amd$ (#141)
Z value	8
D_{calc} (g cm^{-3})	1.251
μ (Mo Kα) (cm^{-1})	0.83
Intensity measurements	
Diffractometer	Rigaku AFC6S
Radiation	Mo Kα ($\lambda = 0.710 - 69$ Å)
Temperature (°C)	−113.0
$2\theta_{max}$ (°)	55.2
No. of reflections measured	Unique: 674
Structure solution and refinement	
Structure solution	Direct methods (SIR92)
Refinement	Full-matrix least squares
No. observations [$I > 2.00\sigma(I)$]	350
No. variables	47
Coefficients used	F^2
Residuals: R; wR	0.0506; 0.1403
Goodness of fit indicator	1.006
Max shift/error in final cycle	0.000
Max. peak in final diff. map (e^- Å^{-3})	0.278
Min. peak in final diff. map (e^- Å^{-3})	−0.328

X-ray structure determination of 15

Table 2 contains a summary of important crystallographic data. The details have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 162994.

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