the normal manner occurred with attack of the reagent from both the β (compound **11,** 50% yield) and α (compound **12,** 25% yield) sides of the molecule. The major component **11,** with the undesired stereochemistry at positions 5 and 6, is convertible to the desired **12** by oxidation and equilibration. The desired alcohol **12,** after removal of the ethylene ketal and reduction of the 3-ketone, provides verticine (**13**) identical in all respects with a sample of the natural alkaloid.

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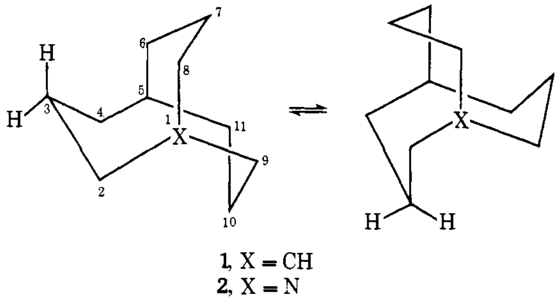
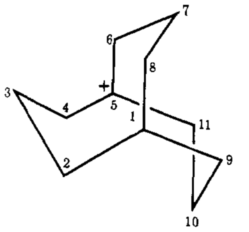
The Bridgehead Bicyclo[3.3.3]undecyl (Manxyl) Mono- and Dications[1]

Sir:

The intriguing bridge flipping process which interverts "in" and "out" hydrogens in bicyclo[3.3.3]undecane (**1**) (manxane) has recently been shown to require about 11 kcal/mol of free energy of activation.[2,3] Similar observations also have been extended to 1-azabicyclo[3.3.3]undecane (**2**) (manxine) and its salt **3**.[4] The enhanced rate of 1-chloromanxane (**4**) (10^4 greater than that of the *tert*-butyl chloride)[5] in solvolytic reactions reflects the great stability of carbocation **5**. According to empirical force field calculations,[3b,6] the rate enhancement of **4** is due largely to the relief of angle strain during ionization. The flattening at the bridgehead, at which a trigonal, planar atom is readily accommodated,[7] reduces the repulsive nonbonded interactions involving the C(3), C(7), and C(10) methylene groups. The calculations also show that in going from the hydrocarbon **1** to the monocation **5**, the C(1)···C(5) nonbonded separation diminishes from 3.322 to 2.990 Å. On this basis C(1)···C(5) distance in dication **6** would be expected to be even shorter. Having prepared previously the pseudoaromatic 1,4-bicyclo[2.2.2]octyl dication (**7**),[8] we wish to report now the preparation of the stable 1-bicyclo[3.3.3]undecyl cation (**5**) and 1,5-bicyclo[3.3.3]undecyl dication (**6**) and their spectroscopic study.



1, X = CH
2, X = N
3, X = $\mathrm{N}^{\pm}$—H
4, X = CCl
5, X = C^{+}



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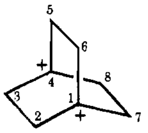

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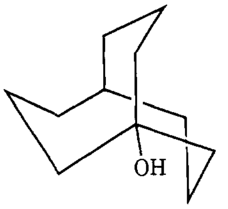
Addition of solutions of 1-chloro- (**4**) and 1-hydroxybicyclo[3.3.3]undecane (**8**) in sulfuryl chloride fluoride to a solution of SbF_5 in the same solvent at −78 °C resulted in the formation of the same carbocationic species whose ^1H NMR spectrum (Figure 1A) shows three deshielded absorptions at δ 4.15 (t, 6 H), 3.20 (br, 7 H), and 2.19 (b, 6 H) corresponding to the expected manxyl monocation **5**. The structure of **5** is further confirmed by its FT ^{13}C NMR spectrum (Figure 1B) which consists of *five* carbon resonances[9] at $\delta_{^{13}C}$ 356.3 (s), 57.9 (t, J_{CH} = 134.3 Hz), 37.0 (t, J_{CH} = 126.1 Hz), 32.7 (t, J_{CH} = 123.2 Hz), and 35.7 (d, J_{CH} = 120 Hz), which are assigned to C(1), C(2), C(3), C(4), and C(5), respectively. The solution of **5** does not show appreciable change between −135 and −30 °C, and it slowly decomposes at high temperatures.



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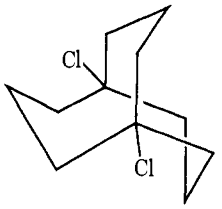

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The temperature-independent behavior of the manxyl monocation **5** seems to suggest either a rapid ring flipping process with a lower energy barrier than that of the parent hydrocarbon **1**[2,4] (faster than can be detected on the NMR time scale) or a very slow inversion of conformation due to the introduction of sp^2 hybridized carbon at C(1) causing additional strain to raise the energy barrier so that the ring flipping process is not detectable at the highest attainable temperature (−30 °C) before the ion starts to decompose. Either behavior is surprising in comparison with that exhibited by **1** and by **6**.

The bridgehead manxyl dication **6** was prepared from 1,5-dichloromanxane (**9**)[10] in SbF_5-SO_2ClF solution at −78 °C. **6** was found stable below −50 °C. It is found to be in conformation equilibrium at −60° as indicated by the ^1H NMR spectrum, which consists of two broad absorptions at δ 4.50 and 3.50 in a ratio of 2:1. The process, however, is *frozen* out at −80 °C, as shown in the 100-MHz spectrum observed at this temperature (Figure 1C), indicating the non-equivalency of the six β-methylene protons, being resolved into two sets of broad absorptions centered at δ 3.70 and 3.30 in a ratio of 1:1. The 12-proton α-methylene absorption apparently is not affected. The natural abundance FT ^{13}C NMR (proton noise decoupled, Figure 1D) spectrum of **6** is in accordance with the proton NMR study. At −85 °C, there are three carbon resonances at $\delta_{^{13}C}$ 346.2 (s), 58.7 (t, J_{CH} = 137.2 Hz), and

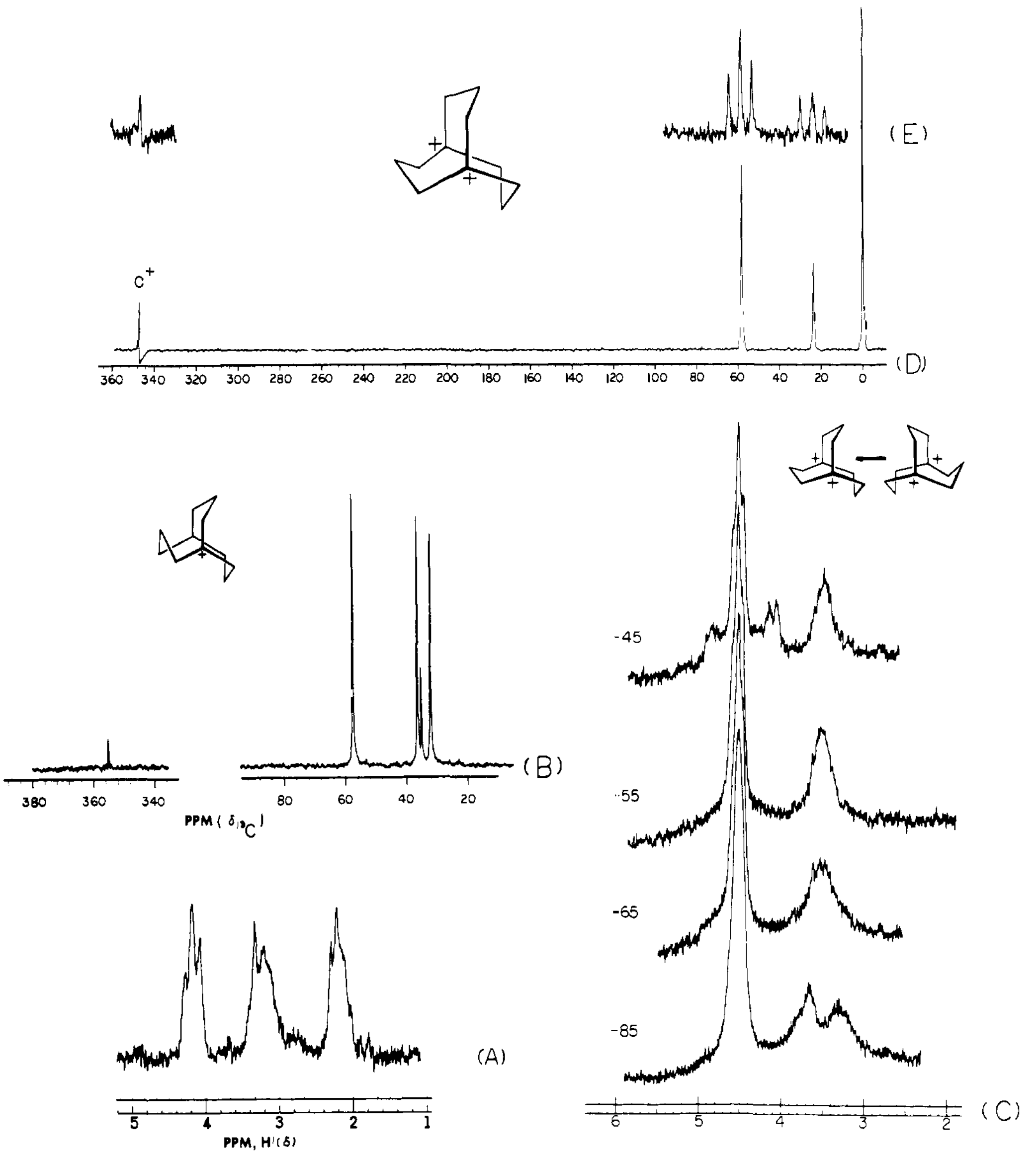

Figure 1. (A) ^{1}H NMR spectrum of 4 in SbF_5-SO_2ClF at −80 °C. (B) Proton noise decoupled ^{13}C NMR spectrum of 4. (C) Temperature dependent ^{1}H NMR (100 MHz) spectra of 5 in SbF_5-SO_2ClF. (D) Proton noise decoupled ^{13}C NMR spectrum of 5. (E) Proton coupled ^{13}C NMR spectrum of 5.

23.5 (d-d, J_{CH} = 148.5 and 148.7 Hz), which are assigned to C(1), C(2), and C(3), respectively, according to the proton coupled ^{13}C NMR spectrum (Figure 1E).

The direct observation of a doublet of doublets for the methylene carbons (C(3), C(7), and C(10)) and the resolution of methylene protons seems to indicate that the bridge flipping process has been frozen out at this temperature (−85 °C), which is very close to that previously reported for the parent hydrocarbon **1** (−80 °C).[2b] The energy barrier for the interconversion of "in" and "out" hydrogens is therefore of similar magnitude for both the hydrocarbon and its dication. The geometries of both **1** and **6** might be very similar. The $C_1 \cdots C_5$ distance, instead of being shortened, might be comparable in **1** to **6** due to the unfavorable electrostatic repulsion between the two cationic centers. As seen from the nmr data, the bridgehead carbons C_1 and C_5 in **6**, instead of being further deshielded, are ca. 10 ppm shielded relative to C_1 of the monocation **5**. The chemical shift of C_3 in **6** is also upfield from the corresponding signal of **5**. The presence of one or two carbocation centers in the manxyl system must generate subtle and complex conformational variations, as is borne out by the energy barrier for ring flipping in the monocation **5** which differs from both the dication **6** and the hydrocarbon **1**.

The flattening of the bridgehead carbon C(1) in the monocation **5** does not seem to affect the conformation of the second bridgehead carbon C(5) significantly in view of its small coupling constant J_{CH} (120 Hz). J_{CH} was estimated to be 121 ± 5 Hz for the hydrochloride **3**.[4a] Carbon shifts of the carbocationic centers for both **4** and **5** are further deshielded from those of the *tert*-butyl (329), 1,4-bicyclo[2.2.2]octyl (308),[8] 1-bicyclo[3.2.2]nonyl (322),[11] 1-adamantyl[12] (299.8), and 3-homoadamantyl[12] (304.7) cations. The extremely short bridgehead–bridgehead distance (calculated, 1.99 Å) in **7** arises from the hyperconjugative electron donation to the cationic centers, which then participate in symmetry-allowed 1,4 bonding. Such hyperconjugative interaction seems to contribute little in the case of manxyl dication **6**.

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(10) The dichloride **8** (X = Cl) is prepared just before use from diol **8** (X = OH) and thionyl chloride (in dry chloroform). The ionization of diol in SbF_5–SO_2ClF or FSO_3H–SbF_5–SO_2ClF solutions only provides the 5-hydroxy-1-manxyl monocation, which does not further ionize to give the dication **5**. Ion **5** slowly rearranges at −45 °C to give a species whose structure is under further investigation.

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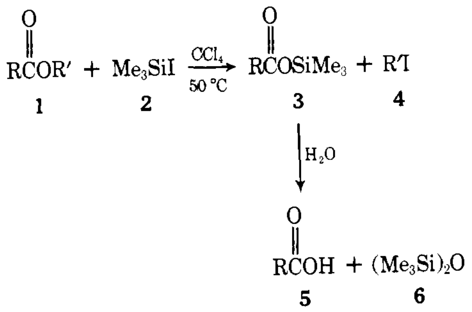
Quantitative Dealkylation of Alkyl Esters via Treatment with Trimethylsilyl Iodide. A New Method for Ester Hydrolysis

Sir:

The hydrolysis of alkyl carboxylic esters is usually carried out under acidic or basic conditions. Recently, several procedures have been developed which allow for hydrolysis under neutral conditions.[1] However, these procedures usually require the use of strong nucleophiles and high temperatures to effect dealkylation. We wish to report a very mild and extremely efficient alternative to the above methods, which proceeds in essentially quantitative yield under neutral conditions. It involves the treatment of alkyl carboxylic esters with trimethylsilyl iodide[2-4] followed by aqueous hydrolysis.

When a carboxylic ester **1** is mixed with trimethylsilyl iodide **2** in an aprotic solvent, e.g., carbon tetrachloride or deuteriochloroform, and the solution is warmed to 50 °C, a clean and efficient dealkylation occurs resulting in the formation of the trimethylsilyl carboxylate **3** and the alkyl iodide **4**. Aqueous hydrolysis of the silyl ester affords the acid **5** in essentially quantitative yield and presumably hexamethyldisiloxane **6**. For example, when a series of methyl esters **7a–l** is treated with trimethylsilyl iodide **2** in CCl_4 at 50 °C, the corresponding silyl esters **8a–l** and methyl iodide **9** are produced in quantitative yields.



$$\underset{\mathbf{1}}{\overset{\displaystyle O}{\overset{\|}{\mathrm{RCOR'}}}} + \underset{\mathbf{2}}{\mathrm{Me_3SiI}} \xrightarrow[50\,^{\circ}\mathrm{C}]{\mathrm{CCl_4}} \underset{\mathbf{3}}{\overset{\displaystyle O}{\overset{\|}{\mathrm{RCOSiMe_3}}}} + \underset{\mathbf{4}}{\mathrm{R'I}}$$

$$\xrightarrow{\mathrm{H_2O}} \underset{\mathbf{5}}{\overset{\displaystyle O}{\overset{\|}{\mathrm{RCOH}}}} + \underset{\mathbf{6}}{\mathrm{(Me_3Si)_2O}}$$

$$\underset{\mathbf{7a\text{–}l}}{\mathrm{RCO_2Me}} + \underset{\mathbf{2}}{\mathrm{Me_3SiI}} \xrightarrow[50\,^{\circ}\mathrm{C}]{\mathrm{CCl_4}} \underset{\mathbf{8a\text{–}l}}{\mathrm{RCO_2SiMe_3}} + \underset{\mathbf{9}}{\mathrm{MeI}}$$

The time required for the conversion varies depending on the ester and ranges from 4 h for methyl cinnamate **7e** to 35 h for methyl benzoate **7b**. A variety of other alkyl esters (ethyl, isopropyl, *tert*-butyl, benzyl, etc.) **7m–y** can also be dealkylated in quantitative yield by this process. The results for a series of esters are listed in Table I.

We have investigated the effect of this dealkylation-hydrolysis technique upon other functionality in various ester substrates and have found it stable to a wide range of functional groups. For example, molecules containing isolated double bonds (e.g., methyl oleate **7f** and methyl linoleate **7g**), ketones (**7i**), aromatic ethers (**7j**), thioethers (**7k**), amines (**7l** and **7r**), and amides (**7s**) can all be converted into the corresponding acids in high yield without significant destruction of the additional functionality. However, Me_3SiI rapidly converts dialkyl ethers into alkyl silyl ethers (and thus by hydrolysis into alcohols),[5] transforms alcohols into iodides,[6] and hydrolyzes some ketals to the corresponding ketones[7] in high yields so that these functionalities are not compatible with this ester hydrolysis technique. Further studies with more functionalized molecules are currently underway to determine the effect of Me_3SiI on other functionality.

The possibility that the reactions we observe could be due entirely to small amounts of HI present in the Me_3SiI cannot be totally discounted. However, in the presence of 10–15 mole % pyridine, ester dealkylation does occur, although at a somewhat slower rate. This leads us to believe that Me_3SiI itself is causing dealkylation.

The possibility of selectivity between various alkyl esters toward this dealkylative hydrolysis procedure prompted us to investigate the reaction of a series of alkyl acetates and alkyl benzoates with differing alkyl groups (**7a, b, m, n, t–y**) under our conditions. From the data in Table I, it is obvious that *tert*-butyl esters and benzyl esters are rapidly dealkylated at 25 °C while with methyl, ethyl, and isopropyl esters dealkylation is very slow at 25 °C but proceeds at a moderate rate at 50 °C.[8] This would imply that *tert*-butyl and benzyl esters could be hydrolyzed selectively by this technique in the presence of the other alkyl esters, but that there would be essentially no selectivity between methyl, ethyl, and isopropyl esters at 50 °C.

We suggest a rather straightforward mechanism for this process: the ester **1** reacts with trimethylsilyl iodide **2** in a fast and reversible step to produce the silylated ester iodide salt **10** which can then go on to products (**3** and **4**) in a slow, irreversible process by either an S_N2 mechanism (R′ = Me, Et) or an S_N1 (S_Ni) mechanism (R′ = *t*-Bu, CH_2Ph). Further mechanistic discussion will await the full paper.

We have also made the interesting observation that when