Considering the magnitude of the missing group, the remaining atoms are quite well behaved if the remaining nitro group at C-9 is located in a pseudoaxial syn configuration. All calculations were made by using Molecular Structure Corporations TEXRAY 230 modification of the SDS-PLUS series of programs.

**Acknowledgment.** We thank J. C. Huffman and J. D. Korp for the X-ray crystallographic determination of the photoadducts and the National Science Foundation and the Robert A. Welch Foundation for financial support.

**Supplementary Material Available:** Tables of the crystallographic data for the photoadducts including the fractional coordinates, thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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# Reinvestigation of the Bicyclo[2.2.2]octane-1,4-diyl Dication[1]

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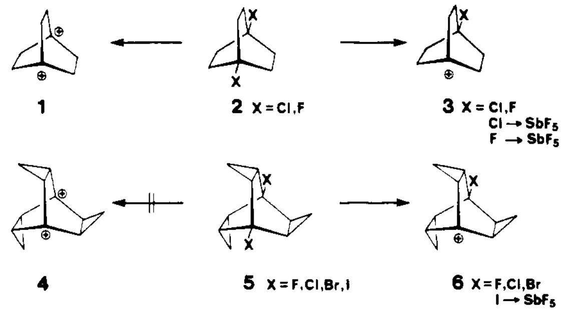
The reaction of 1,4-dihalobicyclo[2.2.2]octanes **2**-Cl and -F with $SbF_5/SO_2ClF$ was reinvestigated and found by $^{13}C$ NMR spectroscopy and quenching experiments to yield only the 4-halo-1-bicyclo[2.2.2]octyl monocation mono-donor–acceptor complexes **3**-X–$SbF_5$ under any of the tested conditions. In $SO_2$-containing solutions disulfoxonium ion **7** formed, indicating that if dication **1** were intermediately formed it alkylates $SO_2$. **7** may, however, also be formed by stepwise alkylation. The previously reported stable 1,4-bicyclo[2.2.2]octanediyl dication **1** could not be detected. The results are consistent with the observation that the structurally similar 1,5-trishomobarrelenediyl dication **4**, which is expected to be more stable than **1**, could not be observed.

Previously Olah et al. reported[2a] that treatment of 1,4-dichlorobicyclo[2.2.2]octane (**2**-Cl) with $SbF_5$ in $SO_2ClF$ gave the elusive 1,4-bicyclo[2.2.2]octanediyl dication **1** characterized by its $^1H$ and $^{13}C$ NMR spectra as well as its methanol quench product 1,4-dimethoxybicyclo[2.2.2]octane (**10**). The $^{13}C$ chemical shift additivity criterion was consistent with a carbodication.[3] The existence of **1** with two positive charges 1,4-disposed and separated by only two carbons in a bicyclo[2.2.2]octyl skeleton was rationalized with positive charge delocalization into a pseudo 2π aromatic like skeletal system on the basis of MINDO/3 theory.[2b] In contrast the related 1,5-trishomobarrelenyl dication **4** could not be observed by de Meijere et al., when 1,5-dihalotrishomobarrelenes **5** were treated with $SbF_5/SO_2ClF$.[4] Instead, halo monocations **6** were formed,[4,5] although MINDO/3 calculations predicted the same degree of stabilization. This was unexpected since cyclopropylcarbinyl cations in anellated bicyclooctyl systems are known to be stabilized.[6,7] Indeed, MINDO/3 calculations predicted a large degree of extra stabilization (14 kcal/mol) for the dication **4** over the parent **1** due to the three anellated cyclopropyl groups.[5,8] Experimentally, the 1-trishomobarrelenyl monocation is more stable than the 1-bicyclo[2.2.2]octyl bridgehead monocation.[9] The behavior of bridgehead dihalides similar to **5** with only one or two anellated cyclopropanes is analogous.[5,8] Hence, a thorough reinvestigation of the reaction of 1,4-dihalobicyclo[2.2.2]octanes **2** (X = Cl, F) with $SbF_5$–$SO_2ClF$ was initiated. This has now been carried out independently in two of our laboratories and elsewhere.[10]



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[1] Considered Carbocations. 265. At University of Southern California.

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[6] Cf.: Rhodes, Y. E.; Di Fate, V. G. *J. Am. Chem. Soc.* **1972**, *94*, 7582.

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[8] Chandrasekhar, J., unpublished MINDO/3 calculations at Erlangen on mono-, di-, and tricyclopropyl anellated bicyclo[2.2.2]octanes with one and two bridgehead carbenium ions.

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[10] We thank Prof. T. S. Sorensen, Calgary, and Dr. D. Bruchmann, Hamburg, for their reconfirmation of our results on **1** and **4**.

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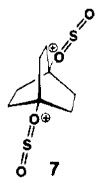
## Results

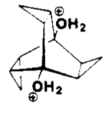
Reaction of **2**-Cl with $SbF_5$ in pure $SO_2ClF$ at −90 or −78 °C under various conditions (different excesses of $SbF_5$, different concentrations of **2**-Cl) always gave a solution, which showed a single broad absorption in the $^1H$ NMR spectrum at $\delta$ 3.28 and four signals in the $^{13}C$ NMR at $\delta$ 348.7 (s), 128.8 (s), 68.3 (t), and 52.2 (t). This is consistent only with the 4-chloro-1-bicyclo[2.2.2]octyl monocation **3**-Cl or its donor–acceptor complex **3**-Cl–$SbF_5$, as the cationic center is strongly deshielded.[11]

In order to favor the formation of dication **1** over the monocation mono-donor–acceptor complex **3**-Cl–$SbF_5$, one cation solution was prepared with extremely low concentration of **2**-Cl (1 mg in 500 mg $SbF_5$–$SO_2ClF$) with a >20-fold excess of $SbF_5$, yet only the monocation complex **3**-Cl–$SbF_5$ was the only observable species. In another attempt to force the second ionization the solution of **3**-Cl was warmed to −60 °C, which, however, resulted in rapid decomposition without **1** being formed.

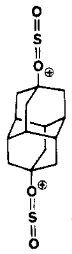
Ionization of **2**-Cl in $SbF_5/SO_2$, on the other hand, resulted in alkylation of $SO_2$ giving symmetrical onium dication **7** which showed two $^{13}C$ NMR absorptions: $\delta$ 128.4 (s) and 32.9 (t). The $^{13}C$ absorptions are, however, rather shielded compared to those reported[2a] for the dication **1** at $\delta$ 308.7 (s) and 45.3 (t). This clearly indicates that there is very little dipositive character on the strained bridgehead carbons in **7**, similar to that in the hydrolysis product of the dication **4**, the 1,5-dionium dication **8** with $\delta_{^{13}C\text{-}1(5)}$ 94.8.[5] $SO_2$ complexes such as **7** but with more dipositive character have been previously observed; e.g., the diamantane-4,9-diyl dication in $SO_2$ gave the complex **9**, wherein the 4,9-cationic centers were observed at $\delta_{^{13}C}$ 230.9.[12]



**7**



**8**

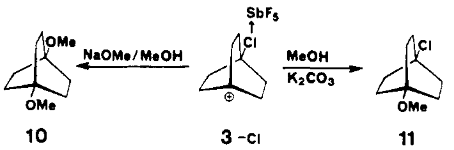


**9**

Attempts to generate **1** from the corresponding difluoro derivate **2**-F in $SbF_5$–$SO_2ClF$ at −78 °C also resulted only in the monocation mono-donor–acceptor complex **3**-F–$SbF_5$. The ion **3**-F–$SbF_5$ showed four absorptions characteristic of its symmetry; $\delta_{^{13}C}$ 348.9 (s), 80.1 ($J_{C\text{-}F}$ = 201.1 Hz), 58.5 ($J_{C\text{-}CF}$ = 26.8 Hz), and 48.5 ($J_{C\text{-}C\text{-}F}$ = 6.1 Hz). The interesting difference between **3**-Cl and **3**-F is the relative shielding of the methylene carbons in the latter. The disulfoxonium ion **7** was again obtained when **2**-F was ionized in $SO_2/SbF_5$.

Upon quenching with sodium methoxide in methanol, solutions of **3**-Cl–$SbF_5$ gave predominantly the dimethoxy derivate **10** as observed previously[2a] and, in addition, a trace of the 1-chloro-4-bicyclo[2.2.2]octyl methyl ether (**11**). With potassium carbonate in methanol the chloro monoether **11** was the only main product (30% isolated yield) fully characterized by $^1H$ and $^{13}C$ NMR and elemental analysis.

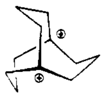
From all these observations it is apparent that in pure $SO_2ClF$ only a monocation mono-donor–acceptor complex **3**-X–$SbF_5$ is obtained. In $SO_2$, on the other hand, the disulfoxonium ion **7** is formed. This indicates that dication **1** which may be formed as an intermediate immediately alkylates the solvent $SO_2$. Alternatively, it is also possible that alkylation of $SO_2$ to **7** occurs in a stepwise fashion without the involvement of **1**. Consequently we attempted to ionize **2**-X in $SbF_5/SO_2ClF$ with small amounts of added $SO_2$ as it is now realized that commercial $SO_2ClF$, if not carefully purified, always contains varying amounts of $SO_2$, and this could have been the reason for the generation and observation of **1** in the previously reported study.[2a] However, even with different amounts of added $SO_2$ the $SO_2$-complexed dipositive onium ion **7** was the only observable species. We also tried to generate **1** by carrying out ionization in $AsF_5/SO_2ClF$ at −90 °C from the difluoro precursor **2**-F. An exchanging system with very broad $^{13}C$ lines was observed and hence no structural details could be ascertained.



**10** **3**-Cl **11**

## Conclusions

The reported[2a] preparation of dication **1** could not be reproduced.[10] Similar to the trishomobarrelene dication **4** [tris(cyclopropyl) anellated bicyclo[2.2.2]octanediyl dication], the parent species **1** remains elusive. Attempts to generate **4** have resulted only in either monocation mono-donor–acceptor complex **6** or a rapidly exchanging system which reacts with CO and sodium methylate to give trishomobarrelene-1,5-dicarboxylic acid and 1,5-dimethoxytrishomobarrelene, respectively.[4,5,7,13] On the other hand, the related but less strained bicyclo[3.3.3]undecyl dication **12** has been observed under nonexchanging conditions.[14]



**12**

Recently the halomonocation complex **3** has been found[5] to undergo halide exchange (with external halides) similar to that observed in complex **6**, indicating the intermediacy of the dication **1** (nucleophilic $S_N2$ halide exchange seems improbable). We are continuing our efforts to observe the elusive dications **1** and **4** under conditions of very high dilution or via two-electron $\sigma$-oxidation of related propellanes.

## Experimental Section

In Hamburg 1,4-dichlorobicyclo[2.2.2]octane (**2**-Cl) was prepared from 1,4-bicyclo[2.2.2]octanedicarboxylic acid by adopting the general procedure of C. A. Grob et al.[15] (see below). Another sample of **2**-Cl as well as **2**-F was donated to us.[16]

**1,4-Dichlorobicyclo[2.2.2]octane (2-Cl).** To a degassed solution of 27.0 g (0.2 mol) of *N*-chlorosuccinimide and 3.5 g (17.7 mmol) of 1,4-bicyclo[2.2.2]octanedicarboxylic acid,[17] obtained by

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(11) Cf.: Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem.* **1983**, *95*, 356; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390 and references cited therein.

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(13) See also: de Meijere, A. *Angew. Chem.* **1979**, *91*, 867; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809.

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saponification of its diethyl ester,[18] in 120 mL dimethylformamide/acetic acid (5:1) was added under nitrogen 15.1 g (34 mmol) of lead tetraacetate and the solution degassed again. The mixture was stirred and slowly warmed to 100 °C. Carbon dioxide started to evolve at 75 °C, and a white precipitate appeared after 15 min at 100 °C. After 1.5 h, when the reaction mixture had turned into a brownish yellow solution, it was cooled to room temperature, poured into 250 mL of water, and extracted with methylene chloride (5 × 50 mL). The combined organic phases were washed with sodium bicarbonate solution (3 × 5 mL) and 50 mL of saturated sodium bisulfite solution and then dried over magnesium sulfate. The solvent was removed on a rotatory evaporator and the residue purified by sublimation [50 °C (0.1 torr)] to give 960 mg (35%) of **2**-Cl: $^1H$ NMR (100 MHz, $CDCl_3$) $\delta$ 2.17 (s, 12 H); $^{13}C$ NMR (25.4 MHz, $CDCl_3$) $\delta$ 63.8 (s), 37.9 (t).

**Preparation of Carbocations.** To freshly distilled $SbF_5$ dissolved in a twofold excess of $SO_2ClF$ or $SO_2$ was added at −80 to −90 °C with vigorous stirring a cooled slurry or solution of the appropriate precursor in $SO_2ClF$ or $SO_2$ resulting in an approximately 10–15% solution of the cation. In one laboratory (Hamburg), the solid **2**-Cl was added to the precooled (−80 to −100 °C) $SbF_5/SO_2ClF$ in small portions with occasional vigorous shaking on a VORTEX vibrator. In one case, only 1 mg of **2**-Cl was added to 0.5 mL $SbF_5/SO_2ClF$ and the cation $^{13}C$ NMR spectrum recorded on a Bruker WH 400 spectrometer. Ionizations in $AsF_5$ were carried out in a well-ventilated hood at −90 °C. $AsF_5$ should be handled very carefully as it is volatile (bp −53 °C) and highly toxic.

$^{13}C$ NMR spectra were obtained on Varian Models FT-80, XL-100, XL-200 as well as Bruker WH-270 and WH-400 spectrometers equipped with low-temperature broad band probes. The $^{13}C$ chemical shifts are referenced from external capillary tetramethylsilane.

**Quenching Experiment.** A cation solution was prepared from 100 mg (0.56 mmol) of dichloride **2**-Cl and 1.2 g of $SbF_5$ in 3 mL of $SO_2ClF$ at −110 to −90 °C and checked by $^{13}C$ NMR spectroscopy to contain the species **3**-Cl. The solution was transferred with a precooled pipet into a vigorously stirred suspension of 7 g of $K_2CO_3$ in 100 mL of methanol kept at −78 °C and the mixture stirred at this temperature for 4 h. After warming to room temperature it was worked up in the usual way (addition of $H_2O$, extraction with ether, removal of solvent from dried solution). The product was isolated by preparative gas chromatography (1.5 m 10% FFAP on Chromosorb W 60-80), yielding 30 mg (30%) of 4-chloro-1-bicyclo[2.2.2]octyl methyl ether (**11**): mp 45 °C; $^1H$ NMR (100 MHz, $CDCl_3$) $\delta$ 3.02 (s, 3 H, $OCH_3$), 2.07 (m, 6 H), 1.72 (m, 6 H); $^{13}C$ NMR (25.4 MHz, $CDCl_3$) $\delta$ 71.1 (s), 65.1 (s), 49.2 (q), 36.8 (t), 31.0 (t). Anal. Calcd for $C_9H_{15}ClO$: C, 61.89; H, 8.66; Cl, 20.30; O, 9.16. Found: C, 61.99; H, 8.74; Cl, 20.30.

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**Registry No.** **2** (X = Cl), 1123-39-3; **2** (X = F), 20277-40-1; **3** (X = Cl$\rightarrow$SbFs), 98922-12-4; **3** (X = F$\rightarrow$SbFs), 98922-13-5; **7**, 98922-10-2; **11**, 98922-14-6; *N*-chlorosuccinimide, 128-09-6; 1,4-bicyclo[2.2.2]octanedicarboxylic acid, 711-02-4.

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# A Two-Step Preparation of $\alpha$-Alkylidene $\gamma$-Lactones from $\gamma$-Lactones: A Synthesis of (±)-Ancepsenolide[1]

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$\gamma$-Butyrolactone, $\gamma$-valerolactone, and the cis lactone of 2-hydroxycyclohexaneacetic acid have been C-silylated via their respective lithium enolates with diphenylmethylchlorosilane. The resulting $\alpha$-silylated $\gamma$-lactones can be deprotonated and condensed with aldehydes and ketones to give $\alpha$-alkylidene $\gamma$-lactones in moderate to excellent yield. The enolate of the $\alpha$-diphenylmethylsilyl cis lactone of 2-hydroxycyclohexaneacetic acid condensed with 1-butanal but not with benzaldehyde or acetaldehyde.

Although $\alpha$-silyl acetates and their derivatives have been used in the preparation of $\alpha,\beta$-unsaturated esters,[3] $\alpha$-silyl lactones have been reported as precursors to $\alpha$-alkylidene lactones in only two instances.[4] We have reported that the lithium enolates of esters and $\gamma$-lactones can be cleanly C-silylated with diphenylmethylchlorosilane as opposed to the more common O-silylation observed with trialkylchlorosilanes.[5] Due to their ease of preparation and potential differences in the reactivity of the $\alpha$-diphenylmethylsilyl $\gamma$-lactones from that of the $\alpha$-trimethylsilyl lactones we were interested to see if the $\alpha$-diphenylmethylsilyl $\gamma$-lactones were viable precursors to $\alpha$-alkyl-

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[1] The Chemistry of $\alpha$-Silyl Carbonyl Compounds. 10.

[2] Graduate student supported by the NIH-MBRS program (RR-8102-10).

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