122. The Quest for Bridgehead Bridgehead Dications with Bicyclo[2.2.2]octyl Skeletons

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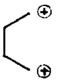
It is predicted by MINDO/3 calculations that the 1,5-trishomobarrelenediyl dication **4** would be as much stabilized over the bicyclo[2.2.2]octanediyl dication **3** as the monocation **7**-H is energetically favored over the hypothetical 1-bicyclo[2.2.2]octyl **10**-H. In spite of this, the bridgehead cations generated from the 1,5-dihalotrishomobarrelenes **6**-F, **6**-Cl, **6**-Br, and **6**-I and from the 1,5-diol **6**-OH under long-lived ion conditions were only the 5-substituted monocations **7**-F, **7**-Cl, **7**-Br, **7**-I, and **7**-OH, respectively, unequivocally identified by their ^{1}H- and ^{13}C-NMR spectra as well as quenching products. Although there is efficient charge delocalization in **7**-X, as revealed by the ^{13}C-chemical shifts, the lack of formation of the bridgehead bridgehead dication **4** is not due to an unforeseen destabilization by the three α-annellated cyclopropyl groups. Even the 1,5-dichlorotetracyclo[3.3.2.0^{2,4}.0^{6,8}]decanes **17**-Cl_2 and **19**-Cl_2 and 1,5-dichlorotricyclo[3.2.2.0^{2,4}]nonane **12**-Cl_2 with only two and one α-cyclopropyl groups, respectively, gave the bridgehead monocations **18**-Cl, **20**-Cl, and **13**-Cl, respectively.

1. Introduction. – It is well-documented that a cyclopropyl group stabilizes a neighboring carbenium ion in a unique way [1–3]. One would, therefore, conceive the possibility of equally well stabilizing a 1,4-diyl dication **1** [4] by the formal insertion of a cyclopropyl group between the two positively charged centers as in **2**.



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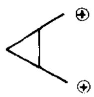

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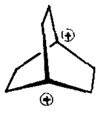

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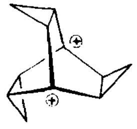

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With regard to the reported remarkable stability of the bicyclo[2.2.2]octane-1,4-diyl dication (**3**) [5] [6] we have, therefore, attempted to generate, from suitable dihalide precursors, the bridgehead dication **4** and similar dications with bicyclo[2.2.2]octyl skeletons having two or one cyclopropyl groups annellated to the bridges. Taking into account that the bridgehead monocation of trishomobarrelene[2]) experiences about 30% of the maximum stabilizing power of three adjacent cyclopropyl groups [7] [8], **4** was expected to be a particularly interesting test case.

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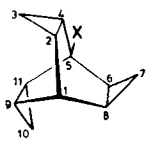
[1]) Case Western Reserve University, Cleveland, Ohio, USA.

[2]) Systematic name: pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane (**5**-H).



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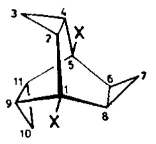

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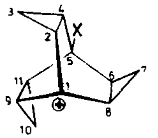

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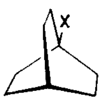

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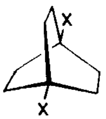

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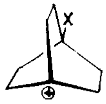

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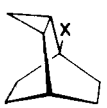
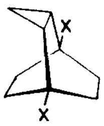
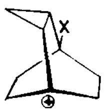


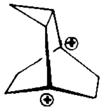
11 X = H, Cl



12 X = Cl



13 X = H, Cl



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2. Semiempirical Calculations. – To probe for the possible influence of the α-annelated cyclopropyl groups on the geometries and stabilities of such dications, we have performed a series of MINDO/3 calculations [9]. The geometries of **5**-H, **5**-Cl, **6**-Cl, **7**-H, **7**-Cl and **4** and for comparison of **8**-H, **8**-Cl, **9**-Cl, **10**-H, **10**-Cl, and **3** [5] were fully optimized under the assumption of C_3 symmetry. The calculated structural parameters for the hydrocarbon trishomobarrelene (**5**-H) and its monochloride **5**-Cl are in reasonable agreement with the experimental ones [8] [10]. On going from the precursors **5**-Cl, or **6**-Cl to the cations **7**-H or **7**-Cl, respectively, and to the dication **4**, only a slight bond shortening adjacent to the carbenium centers and a small lengthening of the C(2)–C(4) bridges is predicted, but the bridgehead·bridgehead distance C(1)–C(5) decreases considerably by 0.2 and 0.64 Å, respectively. This is, of course, due to the flattening of the cationic bridgehead C-atoms, which is counteracted by increasing ring strain. Therefore, the flattening of C(1) in **7**-H and **7**-Cl (see angle C(2), C(1), C(8) in *Table 1*) is slightly less

Table 1. *MINDO/3-Calculated Structural Parameters and Enthalpies of Formation* (ΔH_f) *of* **5**-*H*, **5**-*Cl*, **6**-*Cl*, **7**-*H*, **7**-*Cl and* **4**

Parameter	5-H		5-Cl		6-Cl	7-H	7-Cl	4
	Calc.	Exper. [8]	Calc.	Exper. [10]				
C(1)–C(2) [Å]	1.55	1.54	1.55	1.515	1.55	1.49	1.49	1.51
C(2)–C(4) [Å]	1.56	1.516	1.56	1.52	1.57	1.60	1.60	1.61
C(2)–C(3) [Å]	1.50	1.515	1.50	1.496	1.50	1.51	1.51	1.51
C(3)–C(4) [Å]	1.50	1.515	1.50	1.49	1.50	1.51	1.51	1.51
C(4)–C(5) [Å]	1.55	1.54	1.55	1.515	1.55	1.55	1.55	1.51
C(1)–C(5) [Å]	2.65		2.63		2.62	2.43	2.42	1.97
Angle C(2), C(1), C(8) [°]	108.4	108.9	108.4	108.4	109.2	116.6	116.6	118.6
Angle C(4), C(5), C(6) [°]	108.4	108.9	109.2	109.4	109.2	108.4	108.6	118.6
Angle C(1), C(2), C(4), C(5) [°]	0	0	0.1	0.3	0	0.5	0.44	0
ΔH_f [kcal/mol]	103.2		96.3		90.1	288.3	287.6	593.7

pronounced than in the corresponding bicyclo[2.2.2]octyl cations **10**-H and **10**-Cl [5]. Surprisingly, however, the bridgeheads C(1) and C(5) in the dication **4** are predicted to be more flattened than C(1) and C(4) in **3** [5], in spite of a more efficient delocalization of the positive charges in **4**.

The slight twist (0.5 and 0.44°) of the bridges (dihedral angle C(1), C(2), C(4), C(5) and corresponding ones) calculated for the monocations **7**-H and **7**-Cl confirms the conclusions drawn from experimental solvolysis rates of the complete series of cyclopropane-annellated bicyclo[2.2.2]octyl chlorides [7]. These bridgehead cations gain better overlap of their empty p-orbitals with the *Walsh* orbitals of the α-cyclopropyl groups through twisting, whereas the dication remains untwisted because the two ends counteract each other.

The dissociation energies of the trishomobarrelenyl bridgehead monocations **7**-H and **7**-Cl as obtained from the calculated heats of formation according to *Eqn. 1* are 15.3 and 14.9 kcal/mol, respectively, lower than those of the corresponding bicyclo[2.2.2]octyl monocations **10**-H and **10**-Cl (see *Table 2*). These stabilization energies for the free cations in the gas phase are in remarkably good agreement with the experimental value of $\Delta\Delta G^{\neq}_{298}$ = 11.5 kcal/mol from the solvolysis-rate ratio of the bridgehead chlorides **5**-Cl and **8**-Cl [7]. The stabilization of the cation by one annellated cyclopropane ring as in **13**-H and **13**-Cl is found to be intermediate between three and none annellated cyclopropane ring, both experimentally [7] and theoretically *(Table 2)*.

Table 2. *Dissociation Enthalphies [$\Delta H(R^+) = -\Delta H_f(RCl) + \Delta H_f(R^+) + \Delta H_f(Cl^-)$ in kcal/mol] of Bicyclo[2.2.2]octyl, Tricyclo[3.2.2.0^{2,4}]nonyl and Trishomobarrelenyl Chlorides from MINDO/3-Calculated Enthalpies of Formation*

Compd.	**7**-X			**10**-X[a]			**13**-X[b]		
X	ΔH_f	$\Delta H(R^+)$	$\Delta\Delta H$	ΔH_f	$\Delta H(R^+)$	$\Delta\Delta H$	ΔH_f	$\Delta H(R^+)$	$\Delta\Delta H$
H	288.3	159.1	5.6	191.2	174.4	5.2	221.8	167.9	5.2
Cl	287.6	164.7	108.5	191.2	179.6	107.6	221.6	173.1	108.1
⊕	593.7	273.2		511.2	287.2		535.6	281.2	

[a] ΔH_f(**8**-H) = −10.1; ΔH_f(**8**-Cl) = −16.1; ΔH_f(**9**-Cl) = −21.3.

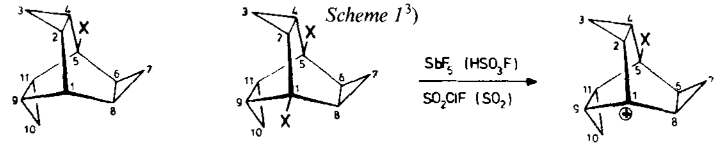
[b] ΔH_f(**11**-H) = 27.3; ΔH_f(**11**-Cl) = 21.1; ΔH_f(**12**-Cl_2) = 15.6; ΔH_f(Cl^-) = −32.85.

$$\Delta H(R^+) = \Delta H_f(R^+) + \Delta H_f(Cl^-) - \Delta H_f(RCl) \qquad (1)$$

As one would expect intuitively, the calculations predict about the same degree of stabilization (14.0 kcal/mol) for the trishomobarrelene-1,5-diyl dication **4** over the bicyclo[2.2.2]octyl system **3**, with the tricyclononanediyl dication **14** falling in between. Although the transmission of electronic effects from substituents on one bridgehead to the other is more efficient in the trishomobarrelene skeleton as determined experimentally [11] [12] and expressed by the calculated $\Delta\Delta H$ values for **7**-H/**7**-Cl, **10**-H/**10**-Cl and **7**-Cl/**4**, **10**-Cl/**3** (see *Table 2*), the trishomobarrelenediyl dication **4** is by no means destabilized in such a way that it should not possibly be formed similarly to the purported bicyclo[2.2.2]octanediyl dication **3** [5].

3. Bridgehead Cations from 1,5-Dihalotrishomobarrelenes 6-F, 6-Cl and 6-Br. – With regard to the remarkable stabilization of the trishomobarrelenyl bridgehead cation **7**-H [7] and the fact that it could easily be observed under long-lived ion conditions [13], we tried to generate the predictedly stable dication **4** by treating the 1,5-dihalotrishomobarrelenes **6**-F, **6**-Cl and **6**-Br *(Scheme 1)* [7] [14] with SbF_5 in SO_2ClF, SO_2, or HSO_3F, respectively, at −78 or −100 °C. The ^1H- and ^{13}C-NMR spectra of the resulting clear solutions were recorded between −100 and 0 °C. While the ^1H-NMR spectra (SO_2ClF/HSO_3F) of the cation solution from the dichloride **6**-Cl and the dibromide **6**-Br showed only 3 signals *(Table 3)* as expected for a dication **4**, the difluoride **6**-F yielded a cation with 4 signals (intensities 3:3:3:3) in the ^1H-NMR spectrum, which is compatible only with a less symmetric species such as the monofluoro monocation **7**-F. This was confirmed by the ^{13}C-NMR spectra registered with the same cation solutions *(Table 4)*.

Scheme 1[3])



5
X = H, F, Cl, Br, I, OH

6
X = F, Cl, Br, I, OH, $OH_2^{\oplus}$, $CO^{\oplus}$

7
X = H, F, Cl, Br, I, $I^{\oplus}$, OH, $OHSbF_5$, $OH_2^{\oplus}$

Table 3. *^1H-NMR Parameters[a]) of the Bridgehead Cations Generated from Precursors* **6**-*F*, **6**-*Cl*, **6**-*Br*, **6**-*I and* **6**-*OH*

Cation	H–C(2,8,9)	H_{anti}–C(3,7,10)[b])	H_{syn}–C(3,7,10)[b])	H–C(4,6,11)	H–C(5)	Thermally stable up to
7-H[c])	3.47	2.34	3.14	3.72	3.14	−10°
7-F[c])	3.63	2.59	3.52	3.77		0°
7-Cl[c])	3.82	2.63	3.50	3.82		0°
7-Br[c])	3.88	2.65	3.47	3.88		−80°
7-I^+[c])	4.23	2.99	3.65	4.23		−80°
7-OH...SbF_5[c])[d])	3.65	2.35	3.20	3.75		0°
7-OH_2^+[e])	4.02	2.79	3.66	4.02		−40°
6-CO^+[d])	1.64	0.88	1.32	1.64		0°

[a]) δ in ppm from external TMS (capillary).
[b]) *syn* and *anti* indicate the position of a proton towards the 'interior' and the 'exterior' of the parent skeleton, respectively.
[c]) In SO_2ClF.
[d]) In SO_2.
[e]) In SO_2ClF/HSO_3F.

All these ^{13}C-NMR spectra showed at least 5 signals in close similarity to that of the authentic monocation **7**-H. On the basis of the signal multiplicities in the off-resonance decoupled spectra, all the methine, methylene and quaternary C-atoms could be unequivocally assigned. In addition, the systematic chemical-shift variations, especially those of C(5) (ranging from 82.6 to 46.2 ppm), clearly proved the equivalent structures of the monohalo monocations **7**-F, **7**-Cl, and **7**-Br (see *Table 4*). Additional proof is obtained

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[3]) The numbering in formula **5** was chosen to correspond to that in **6** and **7**, differing from the systematic numbering, in order to facilitate the comparative discussion of the NMR data.

Table 4. *^{13}C-NMR Parameters of 1-Halotrishomobarrelenes* **5**, *1,5-Dihalotrishomobarrelenes* **6** *and 5-Substituted Trishomobarrelen-1-yl Cations* **7**

X	δ(**5**)[a][3] [ppm]					δ(**6**)[a] [ppm]			
	C(1)	C(2,8,9)	C(3,7,10)	C(4,6,11)	C(5)	C(1,5)	C(2,4,6,8,9,11)	C(3,7,10)	X
H						22.2(*s*)	9.5(*d*)	0.7(*t*)	
F[b]	22.1(*dd*) [3.7]	12.6(*dd*) [3.8]	1.1(*t*)	14.7(*dd*) [33.1]	95.2(*d*) [189.4]	93.3(*AA'XX'*) [198.1]	16.7(*d*)	1.5(*t*)	
Cl	21.7(*d*)	13.6(*d*)	1.3(*t*)	19.0(*d*)	69.8(*s*)	65.0(*s*)	22.3(*d*)	2.0(*t*)	
Br	21.5(*d*)	14.9(*d*)	1.9(*t*)	20.5(*d*)	65.5(*s*)	58.5(*s*)	24.8(*d*)	2.9(*t*)	
I	20.7(*d*)	15.8(*d*)	2.3(*t*)	23.3(*d*)	45.1(*s*)	36.3(*s*)	28.6(*d*)	3.6(*t*)	
I^+									
OH	22.2(*d*)	11.9(*d*)	0.9(*t*)	16.6(*d*)	71.5(*s*)	67.9(*s*)	18.1(*d*)	0.8(*t*)	
OH...SbF_5									
OH_2						94.8(*s*)	17.6(*d*)	2.8(*t*)[c]	
CO^+						37.2(*s*)	15.2(*d*)	3.5(*t*)	150.0(*s*)[c]

X	δ(**7**)[d] [ppm]					$\Delta\delta = \delta(\mathbf{7}) - \delta(\mathbf{5})$ [ppm]				
	C(1)	C(2,8,9)	C(3,7,10)	C(4,6,11)	C(5)	C(1)	C(2,8,9)	C(3,7,10)	C(4,6,11)	C(5)
H	287.7(*s*)	45.7(*d*)	14.7(*t*)	80.5(*d*)	35.8(*s*)	265.5	36.2	14.0	71.0	13.6
F[b]	298.3(*s*)	40.8(*d*)	13.6(*t*)	65.8(*dd*) [−37.9]	82.6(*dd*) [203.5]	276.1	28.2	12.5	51.1	−12.6
Cl	294.1(*s*)	44.8(*d*)	14.3(*t*)	75.5(*d*)	56.1(*s*)	272.4	30.9	13.0	56.5	−13.7
Br	290.3(*s*)	46.5(*d*)	14.8(*t*)	78.8(*d*)	46.2(*s*)	268.8	31.6	12.9	58.3	−19.3
I	–	49.5(*d*)	15.6(*t*)	83.4(*d*)	31.7(*s*)	?	33.7	13.1	60.1	−13.4
I^+	290.3(*s*)	48.1(*d*)	16.2(*t*)	77.9(*d*)	54.4(*s*)	269.6	32.3	13.9	54.6	9.3
OH	299.9(*s*)	44.2(*d*)	14.6(*t*)	73.0(*d*)	61.7(*s*)[c]	277.7	32.3	13.7	56.4	−9.8
OH...SbF_5	299.4	42.1	14.1	66.8	76.0[c][d]	277.2	30.2	13.2	50.2	4.5
OH_2^+	289.5(*s*)	42.1(*d*)	14.2(*t*)	66.8(*d*)	78.9(*s*)[e]	267.3	30.2	13.3	50.2	7.4

[a] In $CDCl_3$; **5**-F in CCl_4/C_6D_6, **6**-OH in (D_6)-DMSO; internal standard: 0.5% TMS.

[b] ^{13}C,F-Coupling constant [Hz] in brackets.

[c] In SO_2.

[d] In SO_2ClF, external (capillary) standard: CS_2 (193.7 ppm from TMS) [14b].

[e] In $HSO_3F/SbF_5/SO_2ClF$.

from the observed C,F-couplings of C(5) and C(4,6,11) in **7**-F giving rise to *d*'s at 82.6 and 65.8 with ^1J(C,F) = 203.0 and ^2J(C,F) = −37.9 Hz [15] [16].

It is consistent with published ^{13}C-NMR data for other cyclopropyl carbinyl cations [17] [18] that the C(β)-atoms C(4,6,11) in **7**-F, **7**-Cl, and **7**-Br are more strongly deshielded than the C(α)-atoms C(2,8,9). On the premises that a correlation of ^{13}C-chemical shifts and charge densities can be made [19–22], the excessive application of which was critically evaluated [3], one can say that C(4,6,11) must carry a higher positive charge than C(2,8,9). This is also expressed in the ^{1}H-NMR data of **7**-Cl and **7**-Br.

For reasonable correlations between ^{13}C-chemical shifts and charge densities, differences in hybridization and substitution have to be taken into account [19] [20] [23]. Therefore, it is better to compare Δδ values of the kind δ(**7**-X) − δ(**5**-X) (see *Table 4*). By this criterion, the positive charge is best delocalized in the monocation **7**-H, in which $\Delta\delta$ for C(1) is 265.5 ppm, the smallest value within the series, and $\Delta\delta$ for C(4,6,11) is 71.0 ppm, the largest value in this column. The least delocalization occurs in the fluoro cation **7**-F with $\Delta\delta$(C(1)) = 276.1 ppm and $\Delta\delta$(C(4,6,11)) = 51.1 ppm. Cations **7**-Cl and **7**-Br are intermediate between the two extremes. The smaller variations of $\Delta\delta$ for C(2,8,9) follow the same trend.

The largest variations of $\Delta\delta$ values were observed for C(5). In contrast to the monocation **7**-H with $\Delta\delta$ = +13.6 ppm, it is −12.6, −13.7, and −19.3 ppm for the halocations **7**-F, **7**-Cl, and **7**-Br, respectively. The negative sign means that C(5) is more shielded in the cationic than in the uncharged system. The positively charged center apparently forces the halogen atom at the opposite bridgehead to donate electrons back to its adjacent C-atom [24]; this is either induced by through-space or rather by trough-bond interaction [25]. Since the C-halogen bond is strengthened by this back-donation, the abstraction of the second halide from a monocation should be retarded. Although the transmitting power of a cyclopropyl group for substituent resonance effects is rather small [1], its ability to transmit inductive efffects of substituents is substantially larger than that of a normal C−C σ-bond *(vide supra)* [11] [12].

4. Cationic Species from 1,5-Disubstituted Trishomobarrelenes 6-I and 6-OH. – In contrast to the behaviour of the dihalides **6**-F, **6**-Cl, and **6**-Br towards SbF_5, the results with the diol **6**-OH and the diiodide **6**-I were more complex.

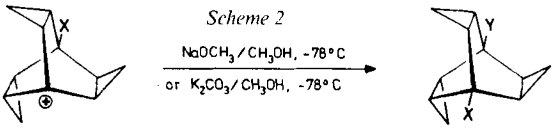
Different types of cations were obtained from **6**-OH, depending on the solvents and superacids used. With 'magic' acid (HSO_3F/SbF_5) in SO_2ClF, the ^{13}C-NMR spectrum of the resulting cation **7**-OH_2^+ consisted of 5 signals (see *Table 4*), fitting very well into the scheme of data for **7**-H, **7**-F, **7**-Cl, and **7**-Br, except for the signal of C(5) (78.9 ppm) which was shifted downfield relative to that of the monoalcohol **5**-OH. Therefore, its $\Delta\delta$ value is positive (+7.4 ppm) indicating the absence of any back-donation by the remaining C(5) substituent. When **6**-OH in SO_2 was reacted with SbF_5 only, two cationic species, apparently **7**-OH and **7**-OH...SbF_5 were observed. The minor product **7**-OH (~35%) showed a signal for C(5) at 61.7 ppm, corresponding to a negative $\Delta\delta$ value of −9.8 ppm, which is consistent with the assignment of the plain hydroxy monocation **7**-OH, whereas **7**-OH_2^+ had to possess a protonated OH group. The ^{13}C-NMR spectrum of the major cation **7**-OH...SbF_5 looked very much like that of **7**-OH_2^+, except for the chemical shifts of C(1) and C(5). Since the ^{1}H-NMR spectra of **7**-OH_2^+ and **7**-OH...SbF_5 (*Table 3*; pure **7**-OH...SbF_5 was obtained from **6**-OH and SbF_5 in SO_2ClF) also showed substantially different chemical shifts, **7**-OH...SbF_5 most likely was a donor-acceptor complex of **7**-OH with SbF_5.

The diiodide **6**-I with SbF_5 in SO_2ClF led to yet a new carbocation, most probably **7**-I^+ on the basis of its ^{13}C-NMR spectrum. The signal of C(5) was shifted downfield with respect to the corresponding one in **5**-I with a positive value of +9.3 ppm, which is even larger than that for C(5) in **7**-OH_2^+. Apparently, the C(5) iodo substituent in **7**-I^+ carried a second positive charge [26] due to acceptor complexation of SbF_5 with **7**-I.

When **6**-I was treated with silver hexafluoroantimonate in SO_2, the resulting solution gave a ^{13}C-NMR spectrum showing 4 signals consistent with the cation **7**-I (see *Table 4*), except for the undetected signal of C(1). However, the spectrum showed 3 signals at 94.9 (C–X), 17.6 (≡CH), and 2.8 ppm (>CH_2) which could not be assigned to any of the known cationic species. These same signals showed up in the spectra of **7**-Cl and **7**-Br, when they were generated from **6**-Cl and **6**-Br with $AgSbF_6$. Upon addition of small amounts of H_2O to these mixtures, the signals of the monocations **7**-I, **7**-Cl, or **7**-Br disappeared completely, the remaining signals, therefore, had to belong to a hydrolysis product, most probably the diprotonated diol **6**-OH_2^+. Treatment of the solution of **6**-OH_2^+ with excess SbF_5 led to a monocation with a ^{13}C-NMR spectrum identical to that of **7**-OH...SbF_5.

5. Chemical Quenching of Cation Solutions from 6-F, 6-Cl and 6-OH. – The cation solutions obtained from 1,5-disubstituted trishomobarrelenes were quenched under two types of conditions (see *Scheme 2*). With NaOMe in MeOH at –78 °C, **7**-Cl gave predominantly 1,5-dimethoxytrishomobarrelene (**15**-$(OMe)_2$; 24% yield), along with a smaller amount of 1-chloro-5-methoxytrishomobarrelene (**15**-Cl/OMe; 10%). However, treating **7**-Cl with a suspension of K_2CO_3 in MeOH at –78 °C led to isolated yields of 12% of **15**-$(OMe)_2$ and 23% of **15**-Cl/OMe. Under the same conditions, **7**-F gave 31% of 1-fluoro-5-methoxytrishomobarrelene (**15**-F/OMe) and only 4% of diether **15**-$(OMe)_2$.

Scheme 2



7 X = F, Cl, OH

15 X, Y = OMe
Y = OMe, X = F
Y = OMe, X = Cl
Y = OMe, X = OH

Quenching of the cation solns. from **6**-OH with K_2CO_3 in MeOH gave nearly the same amount of diether **15**$(OMe)_2$ (6% isolated yield) and 1-hydroxy-5-methoxytrishomobarrelene (**15**-OH/OMe; 7%). In addition, a mixture of alcohols of low volatility was isolated (22%), the ^{1}H-NMR spectrum of which proved the presence of the intact trishomobarrelene skeleton. The average molecular weight of 490 as determined osmometrically indicated a mixture of oligomeric hydroxy ethers which contained an average of three trishomobarrelene units linked by ether bridges. Quenching the solution of **6**-OH_2^+ (obtained from **6**-Cl, **6**-Br, or **6**-I by $AgSbF_6$, and H_2O treatment) with K_2CO_3 in MeOH at –78 °C gave mixtures of oligomeric diols with ^{1}H-NMR spectra similar to those of the high-molecular-weight products from **7**-OH and **7**-OH...SbF_5.

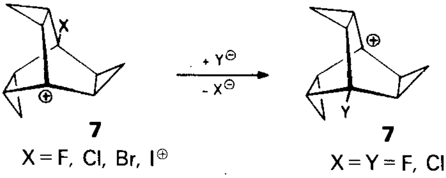
Although significant amounts of diether **15**-(OMe)$_2$ were obtained in most of these quenching experiments, the isolation of **15**-F/OMe, **15**-Cl/OMe, and **15**-OH/OMe strongly corroborates the structure assignments for the monohalo monocations made from their NMR spectra. Diether **15**-(OMe)$_2$ apparently arose from SbF$_5$-assisted solvolysis during the quenching or normal solvolysis during the workup as it was formed to a larger extent in the reaction of **7**-Cl with chloride being the better leaving group. The bromo cation **7**-Br was not quenched because of its thermal lability. In none of the quenching experiments could any product be detected arising from a skeletal rearrangement of the starting materials.

6. Halide Exchange and Carbonylation Reactions of Halomonocations 7-F, 7-Cl, 7-I$^+$, and 7-Br. – The thermal stabilities of the individual cations **7** differred substantially. The temperature at which decomposition or polymerization occurred was determined by variable-temperature ^{1}H-NMR spectroscopy *(Table 3)*. It was not possible to assign structures to any of the products formed upon decomposition.

However, when a solution of **7**-I$^+$ in SO$_2$ClF, which had been kept at –80 °C for about 2 h, was reexamined, it showed the ^{13}C-NMR spectrum of the chloro cation **7**-Cl. The solution of the bromocation **7**-Br behaved similarly, showing signals of **7**-Cl, the fluoro cation **7**-F, and the original **7**-Br after 1 h at –80 °C. Further investigations of these halide-exchange reactions were complicated by sidereactions of the abstracted bromide and iodide ions with SbF$_5$ [27].

While neither **7**-F nor **7**-Cl showed signs of halide exchange in their ^{1}H-NMR spectra from –70 to 0 °C, small amounts of **7**-Cl and **7**-F, respectively, were detected in their ^{13}C-NMR spectra after the solutions had been warmed to +10 °C (boiling point of SO$_2$ClF) for about 5 min (see *Scheme 3*).

Scheme 3

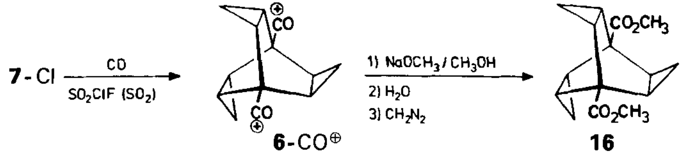


When the difluoride **6**-F or the dichloride **6**-Cl was added to SbF$_5$ in SO$_2$ClF much faster than normally and at –78 °C instead of –100 °C, mixtures of the cations **7**-F and **7**-Cl resulted from both halides. The ratio of **7**-F to **7**-Cl, as estimated from their ^{13}C-NMR intensities, was approximately 3:1 with **6**-Cl as the precursor. Apparently, halide exchange occurs to a significant extent, when the precursor is added to the SbF$_5$ solution too rapidly because this may cause local overheating even above +10 °C.

To make sure that this was not due to a surface reaction of the precursors which were added as powdered solids to the SbF$_5$/SO$_2$ClF mixture, a small amount of CH$_2$Cl$_2$ was added to a solution of the pure monofluoro cation **7**-F at –78 °C. After 5 min, the ^{13}C-NMR spectrum showed the line pattern of the pure chloro cation **7**-Cl besides the signals of CH$_2$Cl$_2$ (54.2 ppm, *s*) and CH$_2$F$_2$ (109.3 ppm, *t*, ^1J(C,F) = 243.7 Hz).

When the solution of the chloro cation **7**-Cl was treated with CO at –78 °C, the dicarbonylium ion **6**-CO$^+$ was formed quantitatively [13] (see *Scheme 4*). In SO$_2$ClF, the

Scheme 4



salt precipitated; it could be redissolved completely by adding SO_2. The ^{13}C-NMR spectrum showed no evidence for the presence of a monocarbonylium monocation 7-CO$^+$. The cation **6**-CO$^+$ was the sole product, even when SO_2 was used as the only solvent.

Upon quenching with NaOMe/MeOH and subsequently with H_2O, the suspension of **6**-CO$^+$ in SO_2ClF or the solution in SO_2 gave 74% of 1,5-trishomobarrelenedicarboxylic acid, which was characterized after reaction with CH_2N_2 as its dimethyl ester **16**. No other quenching product could be isolated or detected.

7. Cations from Other Bridgehead Halides and Dihalides with a Bicyclo[2.2.2]octyl Skeleton. – In order to exclude the possibility that for some unforeseeable reason the dication **4** might be destabilized by the three adjacent cyclopropyl groups, we have generated bridgehead cations from chlorides and dichlorides of the two stereoisomeric tetracyclo[3.3.2.0^{2,4}.0^{6,8}]decyl (bishomodihydrobarrelenyl) and of the tricyclo[3.2.2.0^{2,4}]-nonyl systems. Towards this end, the bridgehead monochlorides **17**-H/Cl, **19**-H/Cl, and **11**-H/Cl and dichlorides **17**-Cl_2, **19**-Cl_2, and **12**-Cl_2 were reacted with SbF_5 under the same conditions as described above (see *Scheme 5*).

Scheme 5

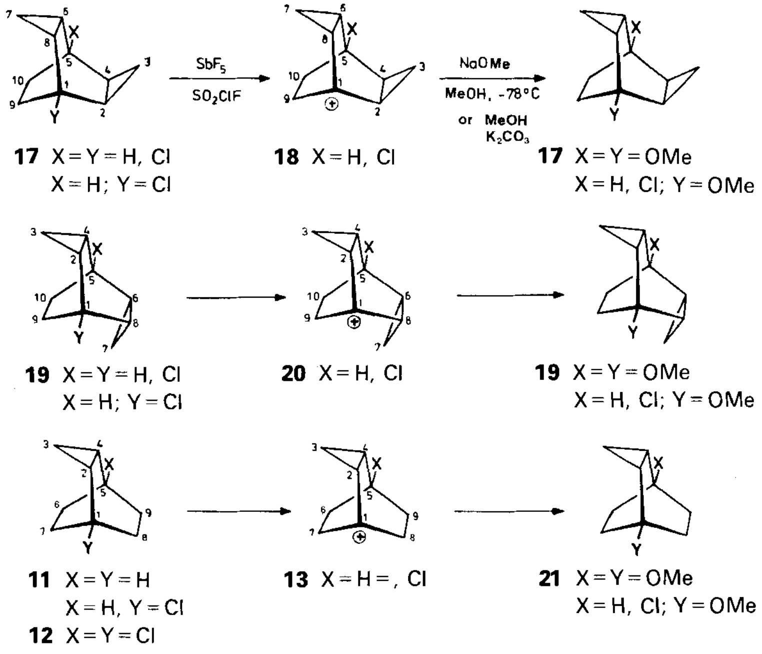


Table 5. *^{13}C-NMR Parameters [ppm] of the Monocations* **18**-*H*, **18**-*Cl*, **20**-*H*, **20**-*Cl*, **13**-*H*, *and* **13**-*Cl* *and of their Precursors* **17**-*H/Cl*, **17**-*Cl_2*, **19**-*H/Cl*, **19**-*Cl_2*, **11**-*H/Cl*, *and* **12**-*Cl_2*

C-Atom	δ(**17**)[a]		δ(**18**)[b]		$\Delta\delta$ = δ(**18**-Cl) – δ(**17**-H/Cl)	δ(**19**)[a]		δ(**20**)[b]		$\Delta\delta$ = δ(**20**-Cl) – δ(**19**-H/Cl)	δ(**11**)[a]		δ(**13**)[b]		$\Delta\delta$ = δ(**13**-Cl) – δ(**11**-H/Cl)
	X = H Y = Cl	X = Cl Y = Cl	X = H	X = Cl		X = H Y = Cl	X = Cl Y = Cl	X = H	X = Cl		X = H Y = Cl	X = Cl Y = Cl	X = H	X = Cl	
C(1)	23.5	65.7	300.7	305.9	282.4	24.6	65.2	306.1	306.9	282.3	23.7	65.2	306.6	306.8	283.1
C(2)	17.8	21.6	48.2	56.2	38.4	23.9	31.5	55.6	56.2	32.2	17.7	24.9	67.4	67.8	50.1
C(3)	1.2	3.6	17.0	16.5	15.3	8.8	9.4	26.0	25.6	16.8	3.6	4.4	26.9	26.0	22.4
C(4)	20.7	21.6	108.0	101.0	80.3	26.6	31.5	115.6	108.9	82.3	21.6	24.9	101.6	90.6	69.0
C(5)	70.1	65.7	37.1	57.5	–12.6	69.1	65.2	37.1	58.3	–10.8	69.4	65.2	36.1	57.7	–11.7
C(6)	19.9	25.7	71.8	64.2	44.3	26.6	31.5	115.6	108.9	82.3	34.8	35.0	40.9	38.4	3.6
C(7)	3.0	2.0	21.6	20.5	17.5	8.8	9.4	26.0	25.6	16.8	25.1	35.0	49.7	50.2	25.1
C(8)	13.6	25.7	56.3	46.4	32.8	23.9	31.5	55.6	56.2	32.3	30.4	40.7	87.8	86.9	56.5
C(9)	27.2	37.8	67.5	68.6	41.4	21.7	32.2	39.4	40.5	18.8	37.0	40.7	51.3	49.4	12.4
C(10)	35.8	37.8	45.3	43.4	7.6	33.2	32.2	38.7	36.5	3.3					

[a] In $CDCl_3$, δ in ppm from internal TMS.

[b] In SO_2ClF, δ in ppm from TMS (external (capillary) standard: CS_2).

The ^{13}C-NMR spectra (*Table 5*) proved unequivocally that in no case a dication had been formed. The ions resulting from **17**-Cl_2 and **19**-Cl_2 as well as from **12**-Cl_2 were just the monochlorocations **18**-Cl, **20**-Cl and **13**-Cl, respectively. In general, these ions were thermally more stable than the monocations **18**-H, **20**-H, and **13**-H, respectively. A comparison of $\Delta\delta$ values (calculated as for **7**; see *Table 5*), especially the ones for C(5), demonstrates that the back-donation effect is operative in all ions.

The remarkable difference in $\Delta\delta$ values for C(4) (44.3 ppm) and C(6) (80.3 ppm) in **18**-Cl can best be explained with a geometry change in going from **17**-Cl_2 to **18**-Cl, *i.e.* the carbon skeleton of **18**-Cl in contrast to that of the precursor **17**-Cl_2, is most probably twisted in such a way that the overlap of the empty p-orbital at C(1) and the cyclopropyl orbitals increase. This twist at the same time changes the anisotropy effect of the cyclopropyl groups on adjacent nuclei.

The low $\Delta\delta$ for C(5) in **20**-Cl ($\Delta\delta$(C(5)) = −10.8 ppm), therefore, indicates less transmission of positive charge in comparison with **18**-Cl ($\Delta\delta$(C(5)) = −12.6 ppm). While **18**-Cl may gain delocalisation energy by a twist of the skeleton, **20**-Cl should not be twisted because the increased overlap of the empty orbital with one cyclopropyl group would be compensated by a decreased overlap with the other cyclopropyl group. This interpretation is consistent with the detailed analysis of solvolysis rates in the series **17**-H/Cl, **19**-H/Cl, and **11**-H/Cl [7].

In contrast to the ^{13}C-, the ^{1}H-NMR spectra of cations **18**-H, **20**-H, **13**-H, **18**-Cl, **20**-Cl, and **13**-Cl were so complicated that almost no signals could be assigned. For example, the ^{1}H-NMR spectrum of **18**-Cl consisted of at least 10 *m* spread over a region of 2.40 ppm. The higher symmetry of **20**-H and **20**-Cl allowed a partial assignment of their spectra (see *Table 6*).

The quenching products of all these cations strongly support the structural assignments on the basis of their ^{13}C-NMR spectra. The monocations **18**-H, **20**-H, and **13**-H gave only the bridgehead methyl ethers **17**-H/OMe, **19**-H/OMe, and **21**-H/OMe, respectively [7] (25 to 50%), and the chloro cations **18**-Cl, **20**-Cl, and **13**-Cl each yielded a mixture of the chloromethoxy derivative and the dimethoxy compound **17**-Cl/OMe

Table 6. *^{1}H-NMR Parameters of* 'exo,exo'-*Bishomodihydrobarrelenyl and 5-Chloro-*'exo-exo'-*bishomodihydrobarrelen-1-yl Cations*4) **20**-*H and* **20**-*Cl in SO_2ClF (δ in ppm from capillary TMS)*

	Compound	
Position	**20**-H	**20**-Cl
H–C(2,8)	4.88 (*m*)	5.08 (*m*)
H_{anti}–C(3,7)a)	3.53 (*q*, *J* = 8 Hz)	3.78 (*q*, *J* = 8 Hz)
H_{syn}–C(3,7)a)	2.63 (*m*)	2.67 (*dd*, *J* = 8 and 6)
H–C(4,6)	6.34 (*m*)	6.18 (*m*)
H–C(5)	3.88	
H–C(9)	3.88	3.96 (*AA'BB'* system)
H–C(10)	3.20	3.44 (*AA'BB'* system)

a) See *Footnote b* in *Table 3*.

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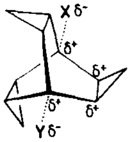
4) The terms *'exo'* and *'endo'* indicate that the cyclopropane moieties are located on the same and opposite side, respectively, with respect to the main bridge C(9), C(10) (or C(8), C(9)) of the mean plane defined by C(1), C(2), C(4), C(5), C(6), and C(8) (or C(7)). The term *'exo'* or *'endo'* first mentioned in a name refers to the C(2), C(3), C(4) moiety.

(93%)/**17**-$(OMe)_2$ (7%), **19**-Cl/OMe (31%)/**19**-$(OMe)_2$ (69%), and **21**-Cl/OMe (44%)/**21**-$(OMe)_2$ (56%), respectively. The fact that **17**-$(OMe)_2$ was detected in trace amounts only, is most likely due to accidentally different conditions during quenching and workup.

8. Final Conclusions. – In spite of the possible stabilization of the trishomobarrelenediyl dication **4** with respect to the parent bicyclo[2.2.2]octanediyl dication **3**, predicted by MINDO/3 calculations, it was not possible to generate **4** from any of the 1,5-disubstituted trishomobarrelene derivatives **6** under any type of conditions well established for other bicyclic dications [4]. Even in highly dilute solutions (1 mg of **6**-Cl in 0.4 ml of SbF_5/SO_2ClF 1:5), no trace of **4** could be detected with highly sensitive ^{13}C-NMR instrumentation *(Bruker WH 400)*. Instead, 5-substituted monocations **7**-X were formed reproducibly. Acceptor complexes of SbF_5 with **7**-I and **7**-OH were the only species with more than one unit positive charge distributed over the skeleton. The halide-exchange reactions observed (see *Scheme 3*), might indicate the transient occurrence of the energetically unfavorable dication **4**. This exchange, however, could also take place with a transition state of type **22**, resembling that of a S_N2 reaction on a saturated C-atom.



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The discrepancy of this result with that reported earlier on the bicyclo[2.2.2]octanediyl dication **3** [5] cannot be due to a yet unknown kind of destabilization by the three annellated cyclopropyl groups, since the bridgehead dichlorides **17**-Cl_2, **19**-Cl_2, and **12**-Cl_2 with only two or one annellated cyclopropyl groups also gave only chloro monocations **18**-Cl, **20**-Cl, and **13**-Cl, respectively. In fact, even under high-dilution conditions, the parent 1,4-dichlorobicyclo[2.2.2]octane (**9**-Cl_2) could not be transformed to the dication **3**, but rather to the 4-chloro-substituted monocation. This result has recently been established independently in our and in *Olah*'s laboratory [28].

We are indebted to Prof. *T.S. Sorensen*, University of Calgary, Calgary, Alberta (Canada) for rerunning the spectrum of the 4-chlorobicyclo[2.2.2]octyl cation. We thank Drs. *C. Weitemeyer, W. Spielmann*, and *B. Schrader* for samples of the halides **17**-Cl_2, **19**-Cl_2, and **12**-Cl_2 and Drs. *W. Weber* and *D. Bruchmann*, who have reconfirmed essential parts of our spectroscopic results during a number of years. Financial support by the *Deutsche Forschungsgemeinschaft* (Projects Me 405/3/8), the *Fonds der Chemischen Industrie*, and the *Deutsche Shell Chemie GmbH, Frankfurt* is gratefully acknowledged.

Experimental Part

1. *General.* All trishomobarrelene bridgehead derivatives **5** and **6** used in this study were prepared as described elsewhere [7] [14]. The preparation of the chlorides **17**-H/Cl, **19**-H/Cl, and **11**-H/Cl has also been reported [7]. Anal. GLC work was done on a *Siemens* gaschromatograph *L 402* with columns of ⅛" diameter; a *Varian Associates* model *Aerograph 90 P* with columns of ⅜" diameter was used for prep. separations. All m.p. and b.p. are uncorrected. ^{1}H-NMR spectra were recorded on *Varian-HA-100* and *Bruker-WH-270* spectrometers. A capillary

filled with TMS was used as an external standard for the spectra of the cations. All other spectra were recorded with TMS as internal standard. ^{13}C-NMR spectra were recorded on *Varian-XL-100-15* and *Bruker-WH-400* spectrometers. The δ_c's of the cations were measured relative to CS_2 in a capillary. In all other spectra, TMS was used as an internal standard. Elemental analyses were performed by the analytical laboratory of the Organisch-Chemisches Institut der University Göttingen, West-Germany.

2. *1,5-Dichloro-*'endo,exo'*-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]decane*(**17**-*Cl_2*). A soln. of 850 mg (6.35 mmol) of **17**-H_2 [29] and 3.5 g (32.2 mmol) of *tert*-butyl hypochlorite in 120 ml of CCl_3F was irradiated with a 150-Watt medium-pressure UV lamp (*Pyrex* filter) at –30° for 2 h. The solvent was distilled off at r.t. and the residue submitted to prep. GLC (1-m column, 15% *DOW 710* on *Chromosorb W-AW-DMCS*, 60/80 mesh, column temp. 120°). Of the 6 peaks, the first 3 were collected separately. The 1st (t_R (rel. retention time) 1.0) corresponded to **17**-H_2 (1% isolated yield), the 2nd (t_R 2.1) to **17**-H/Cl [7] (3%), and the 3rd (t_R 3.9) to **17**-Cl_2 (355 mg, 28%). White crystals, m.p. 129°. ^{1}H-NMR (CCl_4): 1.98–1.70 (*AA'BB'*, H_{syn}–C(9,10), H_{anti}–C(9,10)); 1.42 (*m*, H–C(2,4), H_{syn}–C(3)); 1.18 (*dd*, $J(6(8), 7_{syn}) = 4.0$, $J(6(8), 7_{anti}) = 7.5$, H–C(6,8)); 0.82 (*td*, $J(7_{syn}, 6(8)) = 4.0$, $^2J = 7.5$, H_{syn}–C(7)); 0.52 (*m*, H_{anti}–C(3,7)). Anal. calc. for $C_{10}H_{12}Cl_2$: C 59.14, H 5.96, Cl 34.91; found: C 59.12, H 5.55, Cl 35.12.

3. *1,5-Dichloro-*'exo,exo'*-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]decane*[4]) (**19**-*Cl_2*). A soln. of 960 mg (7.16 mmol) of **19**-H_2 [29] and 1.9 g (17.7 mmol) of *tert*-butyl hypochlorite was irradiated as described above for **17**-H_2. GLC separation as used for **17**-Cl_2 gave 5 products: **19**-H_2 (t_R 1.0; 2% isolated yield), **19**-H/Cl [7] (t_R 2.19; 306 mg, 25%), **19**-Cl_2 (t_R 3.94; 481 mg, 33%), and 2 unidentified components with t_R 4.05 and 4.76. **19**-Cl_2: white crystals, m.p. 76°. ^{1}H-NMR (CCl_4): 1.84 (*dd*, $J(2(4,6,8), 3(7)_{syn}) = 4.0$, $J(2(4,6,8), 3(7)_{anti}) = 7.5$, H–C(2,4,6,8)); 1.56 (*s*, H–C(9,10)); 1.26 (*td*, $J(3(7)_{syn}, 2(4,6,8)) = 4.0$, $J(3(7)_{syn}, 3(7)_{anti}) = 7.5$, H_{syn}–C(3,7)); 0.76 (4 lines, *dt*, $J(3(7)_{anti}, 2(4,6,8)) = 7.5$, H_{anti}–C(3,7)). Anal. calc. for $C_{10}H_{12}Cl_2$: C 59.14, H 5.96, Cl 34.91; found: C 58.64, H 5.91, Cl 35.65.

4. *1,5-Dichlorotricyclo[3.2.2.0^{2,4}]nonane* (**12**-*Cl_2*). Monochloride **11**-H/Cl [7] (1.1 g, 7.0 mmol) and 1.5 g (13.8 mmol) of *tert*-butyl hypochlorite were irradiated as described above. GLC separation as for **17**-Cl_2 showed at least 6 components. The 1st (t_R 1.0) was **11**-H/Cl (4% isolated yield), the 2nd (t_R 1.9) **12**-Cl_2 (190 mg, 14%), and the remaining 5 with longer t_R were not characterized. **12**-Cl_2: white crystals, m.p. 171–173°. ^{1}H-NMR (CCl_4): 2.28–1.70 (*AA'BB'*, 2H–C(8), 2H–C(9)); 1.84 (*s*, 2H–C(6), 2H–C(7)); 1.54 (*dd*, $J(2(4), 3_{syn}) = 4.0$, $J(2(4), 3_{anti}) = 7.5$, H–C(2,4)); 0.98 (*td*, $J(3_{syn}, 2(4)) = 4.0$, $J(3_{syn}, 3_{anti}) = 7.5$, H_{syn}–C(3)); 0.65 (4 lines, *td*, $J(3_{anti}, 3_{syn}) = 7.5$, $J(3_{anti}, 2(4)) = 7.5$, H_{anti}–C(3)). Anal. calc. for $C_9H_{12}Cl_2$: C 56.56, H 6.33, Cl 37.10; found: C 56.62, H 6.30, Cl 37.08.

5. Generation of the Carbenium Ions. 5.1. In a NMR tube (12 mm diameter), 9–10 mmol of freshly distilled SbF_5 (*Merck-Schuchardt*, Darmstadt) was dissolved in 3 ml of freshly distilled SO_2ClF[5]) (or SO_2). The soln. was cooled to –100° in an EtOH/liq. N_2 bath. To this soln. 0.9–1.0 mmol of the powdered bridgehead halide or alcohol was added in 10-mg portions. After the addition of each portion, the mixture was well shaken with removal of the tube from the cooling bath for 5–10 s, placing it in the bath again for *ca.* 5–10 min, and repeating this procedure until all of the solid material had dissolved. Then a new 10-mg portion of solid was added. All the solns. prepared from the fluorides, chlorides, and alcohols were light to deep yellow. A brownish colour appeared in some cases indicating partial polymerization and/or decomposition. The bromides and the iodides gave deep brown solns.

Each of these solns. (0.5 ml) was transferred to a 5-mm NMR tube which was equipped with a capillary filled with TMS and used to record the ^{1}H-NMR spectrum. A capillary filled with CS_2 was inserted into the 12-mm tube, which was immediately subjected to ^{13}C-NMR measurements.

5.2. $AgSbF_6$ (2.8–2.9 mmol) was dissolved in 3.0–3.5 ml of SO_2. The soln. was cooled to –70° in a MeOH dry-ice bath. The dihalide **6**-Cl, **6**-Br, or **6**-I (0.9–1.0 mmol) was added in 10-mg portions producing a precipitate of silver halide. The clear soln. was removed from the precipitate with a precooled pipette and transferred to a precooled NMR tube. After recording the spectra, the soln. was transferred into another precooled NMR tube containing a mixture of 10 mmol of SbF_5 and 0.5 ml of SO_2, and the spectra were recorded again.

6. *Pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane-1,5-dicarbonylium (**6**-CO$^+$).* Dry CO was bubbled through a SO_2ClF soln. of **7**-Cl (prepared as described above) in a 12-mm NMR tube at –78° for 1 h. The soln. turned from yellow to dark brown. After a few min, a solid started to precipitate. The supernatant soln. was removed with a pipette, the solid residue dissolved in SO_2, and the NMR of the soln. recorded.

7. Quenching Experiments. 7.1. *With NaOMe in MeOH.* After the ^{13}C-NMR measurements, the cold solns. of the cations were added dropwise to a soln. of NaOMe in MeOH (5 g of Na in 150 ml of MeOH) at –78°. After complete addition, the mixture was stirred for 1–3 h. Then 200 ml of H_2O were added at –78°, and the resulting, almost clear soln. was immediately extracted 8 times with CH_2Cl_2 (15 ml each). The combined org. layers were

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[5]) Obtained from *Aldrich* or made by reacting SO_2Cl_2 with dry NaF in anh. MeCN and distilled over dry KF.

washed with H_2O extensively and then dried over Na_2SO_4. The solvent was distilled off through a 30-cm column packed with glass helices and the residue subjected to GLC separation.

7.1.1. *5-Chloropentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undec-1-ylium* (**7**-*Cl*). The ion was generated from 200 mg (0.93 mmol) of **6**-Cl. After quenching, **15**-$(OMe)_2$ and **15**-Cl/OMe were isolated by GLC (1.5-m column, ⅜", 15% *FFAP* on *Chromosorb P*, 150°). *1,5-Dimethoxypentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane* (**15**-$(OMe)_2$): t_R 1, 46 mg (24%), colourless liquid. ^{1}H-NMR (CCl_4): 3.24 (*s*, 2 CH_3O); 0.96 (*m*, H_{syn}–C(3,7,10)); 0.66 (*m*, H–C(2,4,6,8,9,11)); 0.17 (*m*, H_{anti}–C(3,7,10)). Anal. calc. for $C_{13}H_{18}O_2$: C 75.69, H 8.80; found: C 75.61, H 8.81.

1-Chloro-5-methoxypentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane (**15**-Cl/OMe): t_R 1.08, 20 mg (10%), white crystals, m.p. 67°. ^{1}H-NMR (CCl_4): 3.26 (*s*, CH_3O); 1.20 (*m*, H_{syn}–C(3,7,10)); 1.08 (*m*, H–C(4,6,11)); 0.80 (*m*, H–C(2,8,9)); 0.38 (*m*, H_{anti}–C(3,7,10)). Anal. calc. for $C_{12}H_{15}ClO$: C 68.40, H 7.18, Cl 16.83; found: C 68.47, H 7.09, Cl 16.93.

7.1.2. *5-Chloro-*'endo,exo'*-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-1-ylium*[4]) (**18**-*Cl*). The ion was generated from 120 mg (0.59 mmol) of **17**-Cl_2. A mixture (25 mg, 21%) of *1,5-dimethoxy-* (**17**-$(OMe)_2$; 7%) and *1-chloro-5-methoxy-*'endo,exo'*-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]decane*[4]) (**17**-Cl/OMe; 93%) could be isolated. ^{1}H-NMR (CCl_4): 3.24 (*s*, CH_3O of **17**-$(OMe)_2$); 3.19 (*s*, CH_3O of **17**-Cl/OMe); 2.08–0.26 (*mm*, 14H). MS: 194 (M^+, $C_{12}H_{18}O_2$, **17**-$(OMe)_2$), 198 and 200 (3:1, $C_{11}H_{15}ClO$ **17**-Cl/OMe). MS (HR): 194.1310 ($C_{12}H_{18}O_2$, calc. 194.1307), 198.0818 ($C_{11}H_{15}ClO$, calc. 198.0811).

7.1.3. *5-Chloro-*'exo,exo'*-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-1-ylium*[4]) (**20**-*Cl*). The ion was generated from 110 mg (0.54 mmol) of **19**-Cl_2. A mixture (15 mg, 13%) of *1,5-dimethoxy-*(**19**-$(OMe)_2$; 69%) and *1-chloro-5-methoxy-*'exo,exo'*-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]decane*[4]) (**19**-Cl/OMe; 31%) could be isolated. ^{1}H-NMR (CCl_4): 3.19 (*s*, CH_3O of **19**-$(OMe)_2$); 3.16 (*s*, CH_3O of **19**-Cl/OMe); 1.98–0.58 (*mm*, 14H). MS: 194 (M^+, $C_{12}H_{18}O_2$, **19**-$(OMe)_2$), 198 and 200 (3:1, $C_{11}H_{15}ClO$, **19**-Cl/OMe). MS (HR): 194.1308 ($C_{12}H_{18}O_2$, calc. 194.1307), 198.0812 ($C_{11}H_{15}ClO$, calc. 198.0811).

7.1.4. *5-Chlorotricyclo[3.2.2.0^{2,4}]non-1-ylium*[4]) (**13**-*Cl*). The ion was generated from 120 mg (0.63 mmol) of **12**-Cl_2. A mixture (20 mg, 17%) of *1,5-dimethoxy-*(**21**-$(OMe)_2$; 56%) and *1-chloro-5-methoxytricyclo[3.2.2.0^{2,4}]nonane* (**21**-Cl/OMe; 44%) could be isolated. ^{1}H-NMR (CCl_4): 3.17 (*s*, CH_3O of **21**-$(OMe)_2$); 3.13 (*s*, CH_3O of **21**-Cl/(OMe); 2.33–0.37 (*mm*, 14H). MS: 182 (M^+, $C_{11}H_{18}O_2$, **21**-$(OMe)_2$), 186 and 188 (3:1, $C_{10}H_{15}ClO$, **21**-Cl/OMe). MS (HR): 182.1305 ($C_{11}H_{18}O_2$, calc. 182.1307), 186.0808 ($C_{10}H_{15}ClO$, calc. 186.0811).

7.1.5. *Dication* **6**-*CO*$^+$. A suspension of **6**-CO^+ (prepared from 200 mg (0.93 mmol) of **6**-Cl) was added dropwise to the NaOMe soln. After the addition of H_2O, the mixture was refluxed for 1 h. The inorg. precipitate was removed by filtration and the clear soln. extracted with pentane (4 × 15 ml). The MeOH was evaporated from the aq. soln. under vacuum and *pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane-1,5-dicarboxylic acid* precipitated by acidification with HCl. It was filtered off and dried under vacuum to give 159 mg (73%) of white crystals, m.p. 230° (dec.). ^{1}H-NMR ((D_6)-DMSO): 0.49 (*m*, 9H). MS: 234 (M^+, $C_{13}H_{12}O_4$).

The diacid was treated with CH_2N_2/Et_2O to give a quantitative yield of *dimethyl pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane-1,5-dicarboxylate* (**16**), white crystals, m.p. 90°. ^{1}H-NMR (CCl_4): 3.67 (*s*, 2 CH_3O); 0.98 (*m*, H_{syn}–C(3,7,10)); 0.89 (*m*, H–C(2,4,6,8,9,11)); 0.25 (*m*, H_{anti}–C(3,7,10)). Anal. calc. for $C_{15}H_{18}O_4$: C 68.69, H 6.92; found: C 68.52, H 6.88.

7.2. *With K_2CO_3 and MeOH.* The cold soln. of a cation was added dropwise to a vigorously stirred suspension of 10 g of powdered K_2CO_3 in 150 ml of dry MeOH at –78°. After complete addition, the mixture was stirred for 1–3 h and then worked up as in *7.1*.

7.2.1. *5-Chloropentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undec-1-ylium* (**7**-*Cl*). Quenching of the ion **7**-Cl generated from 200 mg (0.93 mmol) of **6**-Cl gave 23 mg (12%) of *1,5-dimethoxy-* (**15**-$(OMe)_2$) and 45 mg (23%) of *1-chloro-5-methoxypentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane* (**15**-Cl/Me) after GLC separation.

7.2.2. *5-Fluoropentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undec-1-ylium* (**7**-*F*). The ion **7**-F was generated from 150 mg (0.82 mmol) of **6**-F and quenched as described above. After the usual workup, **15**-F/OMe and **15**-$(OMe)_2$ were collected by GLC. *1-Fluoro-5-methoxypentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane* (**15**-F/OMe): t_R 0.57, 50 mg (31%), colourless liquid. ^{1}H-NMR (CCl_4): 3.26 (*s*, CH_3O); 1.10 (*m*, H_{syn}–C(7, 10)); 0.85 (*m*, H–C(2,4,6,8,9,11)); 0.33 (*m*, H_{anti}–C(3,7,10)). Anal. calc. for $C_{12}H_{15}FO$: C 74.20, H 7.78, F 9.78; found: C 74.16, H 7.71, F 9.98.

*1,5-Dimethoxypentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane (**15**-(OMe)$_2$):* t_R 1.0, 5 mg (5%); identified by comparison with an authentic sample.

7.2.3. *Pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane-1,5-diolium* (**6**-*OH*$_2^+$). A soln. of **6**-OH_2^+ prepared from 300 mg (0.76 mmol) of **6**-I, 780 mg (2.17 mmol) $AgSbF_6$ and 30 mg (1.64 mmol) of H_2O was quenched with 6 g of K_2CO_3 in 150 ml of MeOH after the ^{1}H-NMR spectra had been recorded. The usual workup gave 70 mg of a light yellow solid, melting interval 120–140°. ^{1}H-NMR (CDCl$_3$): 1.11 (*m*, 1 OH); 0.72 (*m*, 3.5H); 0.30 (*m*, 4.2H). MS: 338 ($C_{22}H_{26}O_3$), 498 ($C_{33}H_{38}O_4$). Average molecular weight: 481 (osmometrically).

7.2.4. *5-Hydroxypentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,10}]undec-1-ylium* (*7-OH*). The ion was generated from 200 mg (1.12 mmol) **6**-OH and SbF$_5$ in SO$_2$. After the usual workup, the volatile part of the crude product mixture was removed by sublimation (120°/0.01 Torr) and submitted to GLC. 1st fraction (t_R 1.0, 28 mg (12%)): *Dimethoxypentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane* (**15**-(OMe)$_2$), identified by comparison with an authentic sample. 2nd fraction (t_R 2.8, 30 mg (14%)) *5-Methoxypentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecan-1-ol* (**15**-OH/OMe), white crystals, m.p. 84°. ^{1}H-NMR (CCl$_4$): 3.27 (*s*, CH$_3$O): 1.72 (*s*, 1OH); 1.04 (*m*, H$_{syn}$–C(3,7,10)); 0.69 (*m*, H–C(2,4,6,8,9,11)); 0.24 (*m*, H$_{anti}$–C(3,7,10)). Anal. calc. for $C_{12}H_{16}O_2$: C 74.97, H 8.39; found: C 74.61, H 8.13. The light-yellow solid residue of the sublimation (20 mg) gave a ^{1}H-NMR which was almost identical with that of the quenching product obtained from the *pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane-1,5-diolium* (**6**-OH$_2^+$).

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