Carbon-13 and Proton Nuclear Magnetic Resonance Spectroscopic Study of Protonated Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one, a Model 1,3-Bishomocubyl Cation. Attempted Preparation of the Parent and Alkyl- (Aryl-) Substituted Ions and Their Opening to 3-Substituted *endo*-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dienyl Cations[1]

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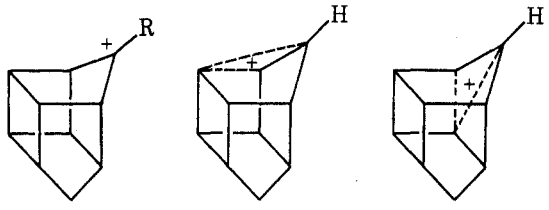
Protonation of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one in FSO_3H/SO_2ClF at −78 °C gave the 6-hydroxypentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl cation. 6-Methyl- and 6-phenylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-ol (syn and anti) in FSO_3H/SO_2ClF at −78 °C gave ring-opened allylic 3-methyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-yl cation and 8- or 9-fluorosulfonated allylic 3-phenyl-*endo*-tricyclo[5.2.1.0^{2,6}]dec-4-en-3-yl cations. The structure of these ions was proved by ^{13}C and ^1H NMR spectroscopy and by the ionization of 3-methyl- and 3-phenyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ols in FSO_3H/SO_2ClF at −90 °C. Ionization of 6-phenylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-dec-6-ol and 3-phenyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ols in HF/SO_2ClF at −78 °C gave the same allylic 3-phenyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-yl cation. All attempts to prepare the parent secondary or tertiary 1,3-bishomocubyl cations as well as the parent secondary *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dienyl cation were unsuccessful.

Dilling and co-workers[2a] have carried out extensive investigations to determine the nature of 1,3-bishomocubyl cations in solvolytic and related reactions. In their solvolytic studies it was indicated that stereochemical and kinetic data seemed most consistent in secondary systems with the bridged ions **4** and **5**, but the classical ion **1** was not completely ruled out.



1, R = H
2, R = Ph
3, R = CH_3

4 **5**

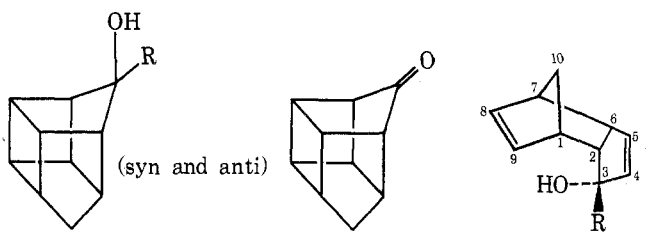
They also pointed out, however, that formation of bridged ions in the tertiary systems is ambiguous.[2a,e] In a subsequent paper[3] they reported their attempts to observe the secondary and tertiary 1,3-bishomocubyl cations **1** and **3** in superacidic media by ^1H NMR spectroscopy and also carried out some related reactions to reveal the nature of these ionic species. They were not successful either in observing the 1,3-bishomocubyl cations nor in confirming the structure of ions obtained, based on ^1H NMR spectroscopic studies.

In our continued studies on carbocations, we now would like to report our studies relating to 1,3-bishomocubyl cations.

Results

We have investigated carbocations formed under stable ion conditions from both pentacyclic and tricyclic precursors **6–13** which were synthesized starting from dicyclopentadiene by reported methods.[2a,b,c,e] Alcohol **14** was prepared by the reaction of phenyllithium on **12** in ether.

Treatment of pentacyclic ketone **9** in FSO_3H/SO_2ClF at −78 °C gave a yellow-colored solution whose ^{13}C and ^1H NMR spectra were consistent with the protonated ketone **15**. **15** can be considered a model for a 1,3-bishomocubyl cation. **12** under similar conditions gave a species whose spectral data were in accordance with 8- or 9-fluorosulfonated protonated ketonic species **18**. However, in HF/SO_2ClF solution protonated ketone **19** was obtained.

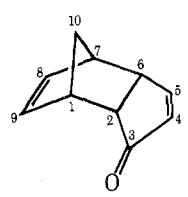


(syn and anti)

6, R = H
7, R = CH_3
8, R = Ph

9

10, R = CH_3
11, R = H
14, R = Ph



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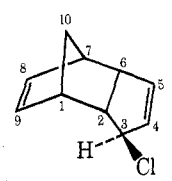


13

A mixture of syn and anti alcohols **7** with FSO_3H/SO_2ClF at −78 °C gave a clean, yellowish brown solution, whose ^1H NMR spectrum was identical with that reported by Dilling.[3] The solution was stable up to −30 °C. Ionization of **7** even at −120 °C gave the same ion. The tricyclic alcohol **10** under similar conditions at −90 °C gave a similar solution whose ^1H NMR spectrum was identical with that of the former ion generated from **7**. The ^{13}C NMR spectra for both solutions were also identical, indicating that both pentacyclic and tricyclic precursors **7** and **10** gave the same ion under these conditions. The ^1H and ^{13}C NMR spectra of the ion are shown in Figure 1.

Ionization of pentacyclic and tricyclic precursors **8** and **14**, respectively, in $FSO_3H–SO_2ClF$ at −78 °C gave rise to solutions which showed similar but more complicated ^1H NMR spectra indicating formation of a mixture of ions. ^{13}C NMR spectra of the ions showed them to be a mixture of two species. However, ionization of the same precursors in HF/SO_2ClF at −78 °C gave rise to solutions whose ^1H and ^{13}C NMR spectra indicated the formation of the same single ion. The spectra are shown in Figure 2.

Dissolution of the pentacyclic secondary alcohol **6** in FSO_3H/SO_2ClF at −78 °C gave a light yellow colored solution whose ^1H NMR spectrum was identical with that of the pre-

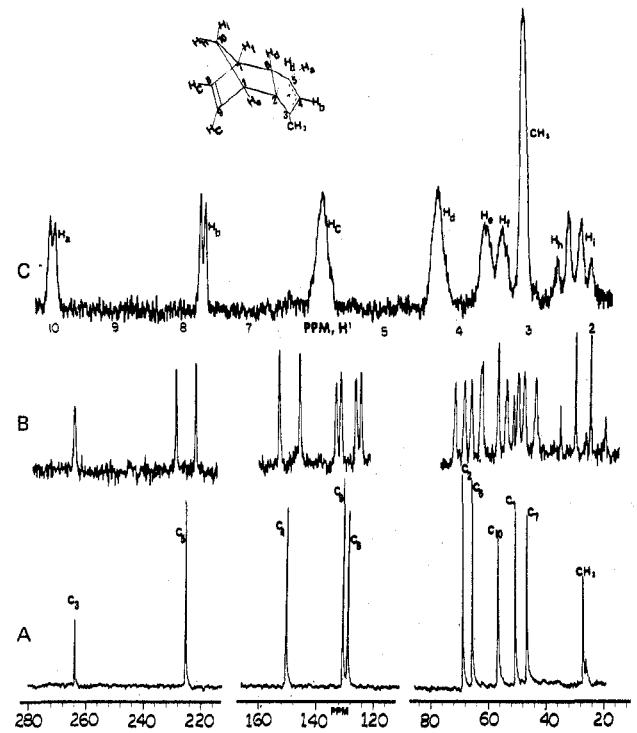


Figure 1. ^{1}H (C) and ^{13}C (A, B) NMR spectra of 3-methyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-yl cation in FSO_3H/SO_2ClF solution at −70 °C: A, proton noise decoupled; B, proton noise coupled.

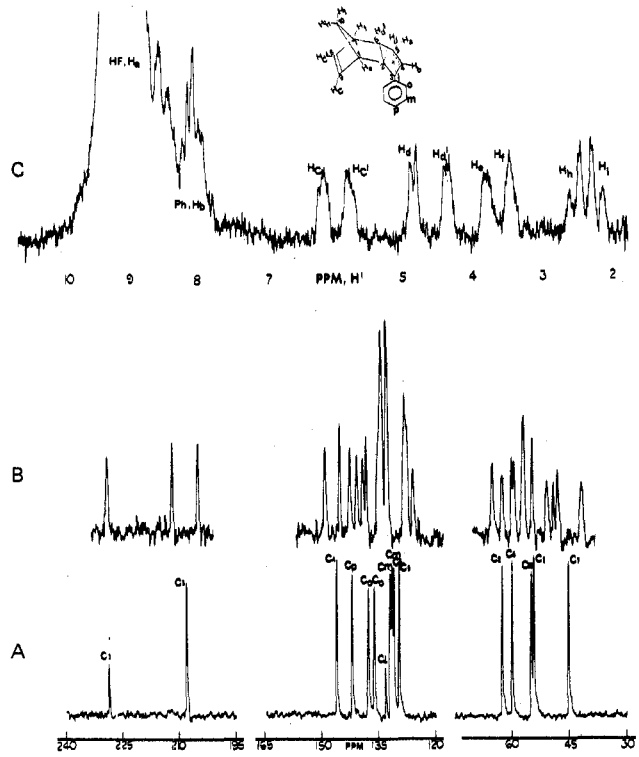


Figure 2. ^{1}H (C) and ^{13}C (A, B) NMR spectra of 3-phenyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-yl cation in HF/SO_2ClF solution at −70 °C: A, proton noise decoupled; B, proton noise coupled.

cursor **6** in $CDCl_3$, except for 1.1-ppm deshielding of the proton shift for carbinol carbon. The ^{13}C NMR spectrum of this solution at −70 °C showed the species to be a protonated alcohol. The solution was stable up to −10 °C.

All attempts at preparing the secondary pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl cation **1** or the tertiary analogues **2** and **3** from precursors **6**, **7**, and **8** either in $FSO_3H/SbF_5/SO_2ClF$ or SbF_5/SO_2ClF solutions at low temperatures were unsuccessful. It was also not possible to prepare the secondary *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dienyl cation from tricyclic precursors **11** and **13**.

The ^{1}H and ^{13}C NMR data of the studied ions are summarized in Tables I and II. ^{13}C NMR data for some of the precursors are given in Table III.

Table I. ^{1}H NMR Parameters of Ions[a]

22	8.4–9.4 broad (HF, H_a), 7.65–8.4 broad (aromatic protons, H_b), 6.1 broad (1 H, H_c), 5.7 broad (1 H, H'_c), 4.7 (d, 1 H, H_d, J_{HH} = 5 Hz), 4.2 (d, 1 H, H'_d, J_{HH} = 3.5 Hz), 3.7 (b, 1 H, H_e), 3.3 (b, 1 H, H_f), 2.5 (t, 1 H, H_h, J_{HH} = 9 Hz), 2.1 (2, 1 H, J_{HH} = 9 Hz) Fluorosulfonated ion ^{19}F shift −38.1
20	9.7 (d, 1 H, H_a), 7.6 (d, 1 H, H_b), 5.88 (2 H, H_c), 4.23 (2 H, H_d), 3.55 (1 H, H_e), 3.22 (1 H, H_f), 3.02 (3 H, CH_3), 2.40 (d, 1 H, H_h), 2.03 (d, 1 H, H_i)
23	5.4 (s, 1 H, $CHOH_2^+$), 2.9–3.0 (m, 8 H, cage protons), 1.8 and 1.4 unsymmetrical doublets (CH_2) (1 H each, J = 11 Hz)
19	8.8 (d, 1 H, H_a), 6.7 (d, 1 H, H_b), 5.8 (broad singlet, 2 H, H_c), 3.9 (b, 2 H, H_d), 3.0–3.4 (broad doublet, H_e, H_f), 1.9 (s, 2 H, H_h, H_i) Fluorosulfonated ion ^{19}F shift −37.8
15	3.0–3.9 (broad peak, 8 H, cage protons), 2.1 (broad singlet, 2 H, CH_2)

[a] Proton shifts in parts per million from external capillary Me_4Si; ^{19}F shifts in parts per million from external capillary CCl_3F.

Table II. ^{13}C NMR Parameters of Ions[a]

20	C_3 263.1, C_5 224.7, C_4 150.9, C_9 131.3 (J_{CH} = 169.3 Hz), C_8 129.6 (J_{CH} = 174.1 Hz), C_2 69.2, C_6 66.0, C_{10} 57.1, C_1 51.1, C_7 47.1, CH_3 27.7
22	C_3 228.7, C_5 208.1, C_4 146.4, C_p 142.3, C_o 138.0, 136.4, C_i 133.5, C_m 132.2, 131.8, C_9 131.2 (J_{CH} = 163.1 Hz), C_8 129.8 (J_{CH} = 164.2 Hz), C_2 62.6, C_6 60.0, C_{10} 55.0, C_1 54.3, C_7 45.3
21	C_3 227.2, C_5 202.6, C_4 148.5, C_p 143.0, C_o 139.7, 138.5, C_i 133.5, C_m 132.3, 131.7, C_8 or C_9 93.0, C_2 57.7, C_6 56.8, C_1 45.2, C_{10} 37.8, C_8 or C_9 27.6
18	C_3 227.8, C_5 197.8, C_4 134.8, C_8 or C_9 91.9, C_2 54.0, C_6 50.5, C_1 41.7, C_7 38.7, C_{10} 36.9, C_8 or C_9 27.5
19	C_3 228.6, C_5 197.6, C_4 134.7, C_9 132.8, C_8 130.2, C_2 54.8, C_6 54.1, C_1 53.2, C_{10} 47.4, C_7 44.2
15	$C{=}OH^+$ 254.4, 51.1, 48.3, 44.7, 44.4, 43.4, 43.2, 41.7, CH_2 40.2, 31.4
23	$CHOH_2^+$ 95.5, 49.9, 43.9, 41.5, 41.2, 40.5, 40.1, 39.5, 38.9, 36.4

[a] Shifts in parts per million from external capillary Me_4Si.

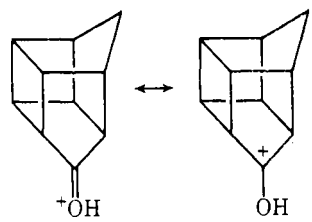
Table III. ^{13}C NMR Parameters of Precursors[a]

10	C_4 140.8, C_5 136.4, C_8, C_9 134.2 (J_{CH} = 162.1 Hz), C_3 82.1, C_1 55.2, C_7 54.7, C_{10} 53.6, C_6 47.9, C_2 45.3, CH_3 32.0
14	C_i 150.2, C_p 139.8, C_o 136.1, 135.9, C_4 134.9, C_8, C_9 129.3 (J_{CH} = 159.5 Hz), C_5 127.6, C_m 125.9, C_3 85.9, C_1 58.1, C_7 55.3, C_{10} 53.7, C_6 47.8, C_2 46.6
9	$C{=}O$ 220.2, 50.2, 44.3, 43.5, 42.7, 42.1, 41.1, CH_2 40.4, 39.0, 32.4
6	CHOH 81.1, 53.6, 45.4, 44.8, 42.8, 42.1, 41.1, 40.8, 40.0, CH_2 38.4
12	C_3 221.4, C_4 166.9, C_5 137.9, C_8 133.5, C_1 53.9, C_7 51.3, C_{10} 49.4, C_2 46.2, C_6 45.4

[a] Shifts are in parts per million from external capillary Me_4Si in $CDCl_3$ at 37 °C.

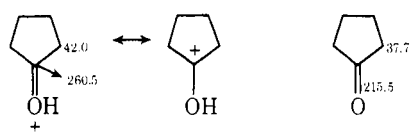
Discussion

Protonated pentacyclodecanone obtained from ketone **9** in FSO_3H/SO_2ClF at −78 °C can be considered as a model 6-hydroxypentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl (1,3-bishomocubyl) cation **15a**. Comparing its ^{13}C shifts to the shifts of the precursor, the protonated carbonyl carbon is deshielded by 34 ppm, but at the same time there is little deshielding of the cage carbon atoms; the shifts indicate that the contribution from the structure **15** is predominant. Comparing ^{13}C



15 **15a**

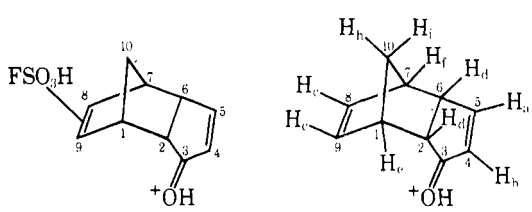
shift differences of **15** and **9** to the differences in ^{13}C shifts of protonated cyclopentanone **16** and cyclopentanone **17**,[4] the former is less by about 11 ppm than the latter indicating the rigidity of the cage system. Contribution from the structure **16a** seems to be more significant in protonated cyclopenta-



16 **16a** **17**

none as the α-carbon shifts are more deshielded than those of other protonated higher alicyclic homologues.[4a] The contribution of structure **15a** is thus more limited, as the cage ring carbons show no significant deshielding. This conclusion may be, however, somewhat ambiguous as the rigid cage structure may not allow sufficient predictions to be made from ^{13}C NMR shifts as to the carbocationic nature of **15a**.

8- or 9-fluorosulfonated protonated ketone **18** was obtained from ketone **12** in FSO_3H/SO_2ClF solution at −78 °C. However, protonated ketone **19** was formed in HF/SO_2ClF solution at −78 °C. It is indicated from the ^{13}C shifts that significant

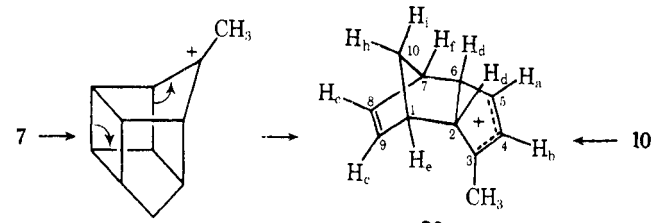


18 **19**

charge has been delocalized into the C_4 and C_5 centers. The ^{13}C data are summarized in Table II.

The ^1H NMR spectrum of the ion generated from the alcohol **7** (both the syn and anti isomers) was tentatively assigned the structure **20** by Dilling and co-workers,[3] as their ^1H NMR data were consistent with this ion. We have now confirmed the structure of the ion by ionizing tricyclic alcohol **10** in FSO_3H/SO_2ClF at −90 °C which gave the same allylic ion. The ^{13}C NMR spectra also clearly indicate the formation of the allylic ion **20**.[4b] The formation of ion **20** from **7** can be visualized to take place through the intermediacy of the 1,3-bishomocubyl cation **3** as shown in Scheme I. ^{13}C NMR chemical shifts are in good agreement with those of reported substituted cyclopentenyl cations.[5] The assignments were made by the customary methods discussed previously.[6] The ^{13}C shifts and their assignments are summarized in Table II. We were unable to observe the parent ion **3** even when the

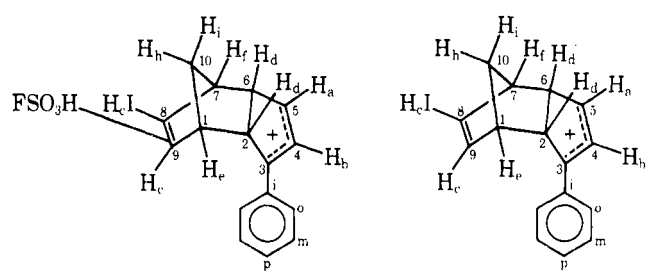
Scheme I



20

ionization was carried out at −120 °C. Ionization in even stronger superacids leads to unidentifiable species. Our studies thus confirm the tentative assignment made by Dilling and co-workers[3] for the ion generated from the alcohol **7**.

A phenyl group adjacent to a carbocationic center is known to delocalize positive charge very efficiently.[7] Hence, we felt that the tertiary phenyl substituted precursor **8** would give rise to the corresponding phenyl substituted 1,3-bishomocubyl cation **2**. Ionization of alcohol **8** in FSO_3H/SO_2ClF at −78 °C gave a species which displayed a complicated ^1H NMR spectrum. The low field signals were attributable to an allylic cation. The ^{13}C NMR spectrum revealed the presence of a mixture of closely related allylic ions, with one ion predominating. Ionization of alcohol **14** under similar conditions gave rise to the same mixture of ions whose ^1H and ^{13}C NMR spectra were identical. The ^{13}C signal at $\delta_{C^{13}}$ 93 (doublet) clearly indicated the fluorosulfonation at C_8 or C_9 site of the isolated double bond of **22**. The ion was assigned the structure **21**. Further evidence for fluorosulfonation came from the ^{19}F



21 **22**

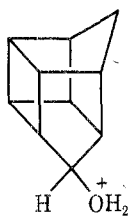
NMR spectrum (Table I). It was, however, not possible to decide whether the fluorosulfonation site is C_8 or C_9. ^{13}C NMR shifts of the major fluorosulfonated species are given in Table II. Ionization of **8** in HF/SO_2ClF solution at −90 °C resulted in ring-opened 3-phenyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-yl cation **22** whose ^1H and ^{13}C NMR spectra are shown in Figure 2. The ion **22** was also obtained by the ionization of **14** under similar conditions. The parent ion **2** was never observed from **8** either in $FSO_3H/SbF_5/SO_2ClF$ or SbF_5/SO_2ClF solutions even at very low temperatures.

Our failure to obtain 1,3-bishomocubyl ions **2** and **3** can be attributed to the instability of these species under long life superacidic conditions. Indeed there is evidence for these ions in solvolytic reactions[3,4c] where the lifetimes are shorter. The obvious driving force for the ring opening is the relief of strain of the pentacyclic ring systems (roughly 16.4 kcal/mol) as indicated by Cookson and co-workers.[8] Thus, this explains the reason for the limited contribution from **15a** to ion **15**.

It is interesting to note that alcohols **7** and **10** gave allylic cation **20** in FSO_3H/SO_2ClF solution, whereas alcohols **8** and **14** lead to a mixture of fluorosulfonated allylic ions **21**. This may be due to differences in the solvation of the ionic species and also to the different degree of participation of the isolated C_8=C_9 double bond with the allylic center. In the ion **22** (in HF/SO_2ClF) most of the charge is delocalized into the phenyl ring whereas no such participating group exists in ion **20** as indicated by ^{13}C chemical shifts and also by the C–H coupling is at C_8 and C_9 positions of ions **20** and **22** as compared to their

precursors (Tables II and III). Ion **20** shows increased coupling (δ_{C_8-H} 7.2 Hz, δ_{C_9-H} 12 Hz) as compared to the ion **22** (δ_{C_8-H} 3.6 Hz, δ_{C_9-H} 4.7 Hz). This is probably due to the greater degree of participation of the isolated double bond with the allylic center in ion **20** as compared to the ion **22.** Hence, ready fluorosulfonation occurring on the isolated double bond of the incipient ion **22** is indicated during the ionization of precursors **8** and **14** in FSO_3H/SO_2ClF solutions. However, we were able to obtain ion **22** in HF solutions because under the experimental conditions at low temprature it does not easily attack isolated double bonds.

The secondary alcohol **6** when dissolved in FSO_3H/SO_2ClF at −78 °C gave only protonated alcohol **23** which was stable up to −10 °C. The carbinol carbon showed ^{13}C NMR deshielding of 14 ppm (Tables II and III). Dilling[3] observed ^{1}H NMR deshielding of 1.1 ppm of the carbinyl methine proton.



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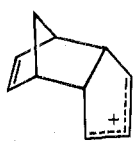


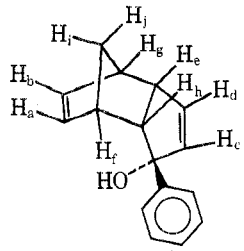
24

The stability of protonated alcohol **23** up to −10 °C demonstrates the instability of the parent ion **1.** The lack of any rearrangement of **23** into **24** is further attributable to the relative instability of ion **24.** Alcohol **6** in stronger superacids such as FSO_3H/SbF_5 or SbF_5 solutions gave only polymeric material. We were also unable to obtain the secondary allylic tricyclic ion **24** either from precursors **11** or **13** using superacids under varied conditions.

Experimental Section

Materials. Precursors **6–13** were prepared by known methods[2a,b,c,e,3] starting from dicyclopentadiene.

3-Phenyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol. To freshly prepared phenyllithium (prepared from 0.35 g of lithium metal in dry ether under nitrogen with 8.25 g of bromobenzene in ether) was slowly added 7.3 g of dienone **12** in 25 ml of dry ether over a period of 15 min. The resulting mixture was refluxed for 3 h. Then the reaction mixture was worked up in the usual manner. The product obtained was recrystallized from hexane twice to obtain 8.2 g of **13** (65%): mp 67–68 °C (lit.[9] mp 65–66 °C); ^{1}H NMR δ 7.64 (s, 5 H, aromatic), an unsymmetrical doublet of doublets centered at 6.64 (1 H, H_a or H_b, J_{ab} = 4, J_{af} or J_{bj} = 2 Hz), 6.24 (1 H, J_{ab} = 4, J_{af} or J_{bj} = 2.6 Hz, H_a or H_b), 5.94 (m, 2 H, H_c and H_d), unresolved multiplet around 3.8 and 3.3 (4 H, H_h, H_e, H_f, and H_g), singlet at 2.3 (1 H, OH), overlapping two unsymmetrical doublets of triplets centered at 1.9 (H_i or H_j, J_{ij} = 7, J_{fj} = 2 Hz) and 1.7 (J_{fi} = 3 Hz).



Preparation of Ions. Twice distilled FSO_3H was dissolved in a twofold amount of SO_2ClF at dry ice/acetone temperature (ca. −78 °C). To this solution was slowly added with vigorous stirring a cold solution of appropriate precursor dissolved in SO_2ClF, to give approximately 15–20% solution of the ion. Solutions of ions in HF/SO_2ClF were similarly prepared using quartz equipment. An ethanol/liquid N_2 bath was used to obtain temperatures below −78 °C.

^{19}F and ^{1}H NMR spectra were obtained on a Varian Model A56/60A spectrometer equipped with variable temperature probes and external Me_4Si and CCl_3F capillaries were used as references.

^{13}C NMR spectra were obtained using a Varian Model XL-100 NMR spectrometer equipped with FT accessory with variable temperature probe as previously described.[10]

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Registry No.—**6,** 15443-36-4; **9,** 15584-52-8; **10,** 52916-88-8; **12,** 5530-96-1; **13,** 51965-70-9; **14,** 59231-05-9; **15,** 59231-06-0; **18,** 59230-92-1; **19,** 59231-07-1; **20,** 59230-93-2; **21,** 59230-95-4; **22,** 59230-94-3; **23,** 59231-08-2.

References and Notes

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