liquid: bp 130 °C (30 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 4.47 (s, 2 H), 6.75–7.10 (m, 3 H), 7.10–7.36 (m, 2 H); MS, *m/e* (rel intens) 150 (M^+), 107 (70), 77 (100), 43 (77); IR (liquid film) 1740, 1610, 1525, 1240, 1190, 770, 700 cm^{-1}. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.75; H, 6.92.

Tetraethylene Glycol Decyl Acetonyl Ether (4d). With the general procedure described above, **4d** was obtained in yield of 83% as a colorless liquid: bp 160 °C (0.05 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 0.75–1.05 (t, 3 H), 1.20–1.60 (m, 16 H), 2.20 (s, 3 H), 3.40 (t, 2 H), 3.60–3.85 (m, 16 H), 4.20 (s, 2 H); MS, *m/e* (rel intens) 390 (M^+), 101 (70), 57 (100), 45 (60); IR (liquid film) 2900, 1720, 1470, 1350, 1120 cm^{-1}. Anal. Calcd for $C_{21}H_{42}O_6$: C, 64.58; H, 10.84. Found: C, 64.17; H, 10.98.

Triethylene Glycol Acetonyl Ether (4e). With the general procedure described above, **4e** was obtained in yield of 67% as a colorless liquid: bp 115 °C (0.05 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 2.85 (s, 1 H), 3.32–3.90 (m, 12 H), 4.25 (s, 2 H); MS, *m/e* (rel intens) 206 (M^+), 101 (25), 57 (30), 45 (100); IR (liquid film) 3500, 2900, 1720, 1140 cm^{-1}. Anal. Calcd for $C_9H_{18}O_5$: C, 52.47; H, 8.80. Found: C, 52.07; H, 8.84.

***tert*-Butyl Acetonyl Ether (4g).**[8] After metallic potassium (11.7 g, 0.3 mol) was dissolved in *tert*-butyl alcohol (200 mL), **1** (17.3 g, 0.1 mol) was added and the mixture was stirred at 80 °C for 6 h. Water (100 mL) was added at room temperature, and the organic phase was extracted with diethyl ether. The solvent was removed by distillation at reduced pressure, 10 mL of 1% aqueous sulfuric acid was added into the residue, and then the mixture was stirred at 60 °C for 30 min. The product was extracted with dichloromethane, and **4g** was isolated by Kugelrolr distillation at reduced pressure in yield of 42% (5.4 g) as a colorless liquid: bp 54 °C (25 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 9 H), 2.15 (s, 3 H), 3.92 (s, 2 H); MS, *m/e* (rel intens) 130 (M^+), 57 (100), 41 (37), 29 (26); IR (liquid film) 2970, 1720, 1380, 1200, 1110 cm^{-1}.

Diacetonyl Ether (4h). The mixture of **1** (8.7 g, 0.05 mol), 30% aqueous potassium hydroxide solution (28 g, 0.15 mol), and tetrabutylammonium bisulfate (0.85 g) was stirred at 60 °C for 50 h. After neutralization with diluted sulfuric acid and extraction with diethyl ether, the hydrolysis was carried out at room temperature for 1 h. Diacetonyl ether (**4h**) was obtained as a colorless liquid in yield of 58% (1.9 g): bp 85 °C (7 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 6 H), 4.20 (s, 4 H); MS, *m/e* (rel intns) 130 (M^+), 87 (37), 57 (67), 43 (100); IR (liquid film) 2900, 1740, 1425, 1360, 1130 cm^{-1}. Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.68; H, 8.04.

Registry No. 1, 70905-45-2; **2**, 105104-40-3; **3a**, 105104-41-4; **3b**, 105104-42-5; **3c**, 105104-43-6; **3d**, 105104-44-7; **3e**, 105104-45-8; **3f**, 105104-46-9; **3g**, 105104-47-0; **4a**, 40657-11-2; **4b**, 83171-86-2; **4c**, 621-87-4; **4d**, 105104-48-1; **4e**, 105104-49-2; **4f**, 105121-45-7; **4g**, 28047-99-6; **4h**, 76089-31-1; $C_{10}H_{21}OH$, 112-30-1; C_6H_5OH, 108-95-2; $C_{10}H_{21}OCH_2(CH_2OCH_2)_3CH_2OH$, 5703-94-6; $HOCH_2(CH_2OCH_2)_2CH_2OC_5H_9O$, 60221-37-6; $HOCH_2(CH_2OCH_2)_2CH_2OH$, 112-27-6; $(CH_3)_3COH$, 75-65-0; cyclohexanol, 108-93-0.

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Ionization of Fluorobullvalene. Proton Rearrangements in Protonated Naphthalene

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Bullvalene[1] is a fascinating compound that undergoes a rapid, degenerate rearrangement, interchanging all atoms with an activation energy of 11.8 ± 1 kcal/mol.[2] After the first synthesis by Schröder, rearrangement was demonstrated by NMR[3] and by preparing substituted bullvalenes. For example, halogenation of bullvalene[4] produces a thermodynamic mixture of isomers. The carbocation formed from the ionization of halobullvalenes would be of great interest. If the positive charge were on the carbon along the threefold axis, it would be a bridgehead cation, which would formally be triply allylic and in homoconjugation with three cyclopropylcarbinyl centers. However, this conjugation would be *inhibited* by the lack of overlap between the p orbital and the π orbitals of the double bonds.

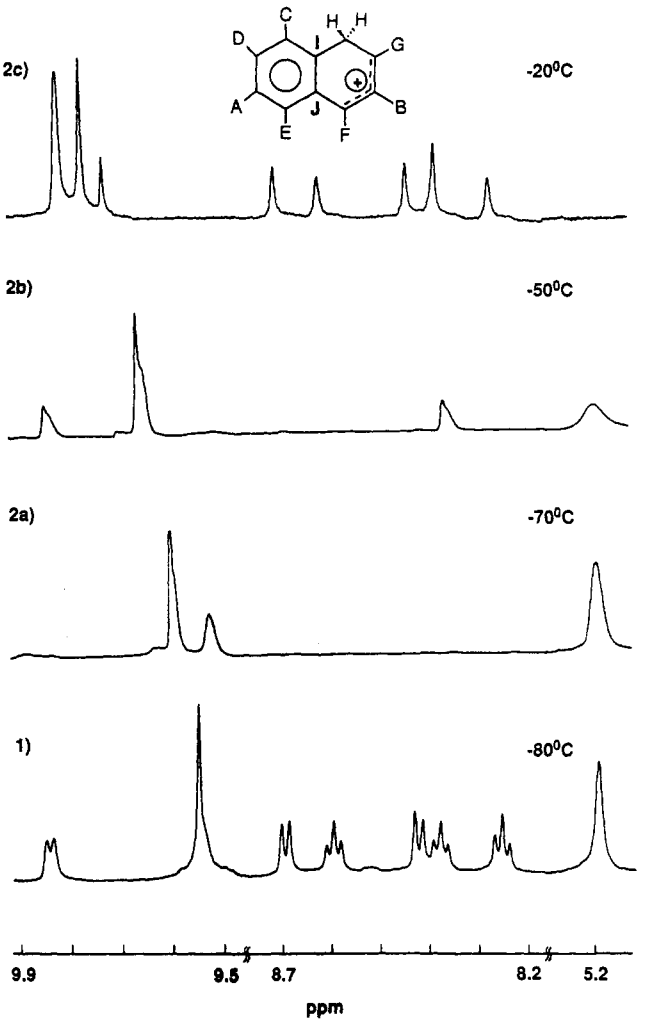

Figure 1. ^{1}H NMR at 500 MHz. (1) Cation solution resulting from addition of fluorobullvalene, at −110 °C, to SbF_5 in SO_2ClF. The sharp singlet at 9.55 ppm presumably results from HF. (2a–c) Cation solution resulting from addition of perdeuteriated naphthalene with FSO_3H and SbF_5 in SO_2ClF at indicated temperatures. Additional downfield peaks appearing at elevated temperatures presumably result from irreversible cation decomposition to unidentifiable products.

Professor Schröder generously supplied us with fluorobullvalene (fluorine is predominately along the threefold axis) and suggested that we attempt the ionization. Employing our usual procedure,[5] we codeposited it with antimony pentafluoride, under vacuum at liquid nitrogen temperatures. Addition of SO_2ClF at −110 °C resulted in a blood red solution. The solution was kept cold and transferred to an NMR tube that was placed in a precooled

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Table I. NMR Spectral Assignments for α-Protonated Naphthalene

	^{1}H NMR			^{13}C NMR	
posn	chem[a,b] shift, δ	mult[c]	rel intens	chem[a,d] shift, δ	$J_{^{13}C-^1H}$, Hz
A	8.26	t	1.0	130.4	167.2
B	8.38	t	1.0	133.2	175.9
C	8.43	d	1.0	132.0	171.2
D	8.58	t	0.9	144.9	165.1
E	8.71	d	0.9	140.4	165.8
F	9.84	d	1.0	181.0	171.7
G	9.54	d	1[e]	185.5	166.0
H	5.28	s	2.1	45.3	125.4
I				157.8	
J				134.7	

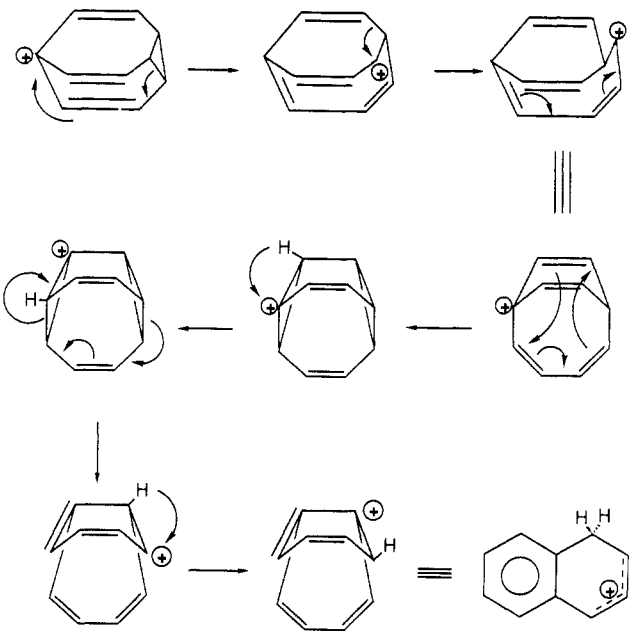
[a] In ppm, relative to Me_4Si. [b] Calibrated by setting the central peak of the methyl triplet of anhydrous ethanol to 1.11 ppm at 500 MHz and −110 °C. [c] $J_{^1H-^1H}$ are all approximately 7.5 Hz. [d] Calibrated by setting the methyl peak of anhydrous ethanol to 17.2 ppm at 125.7 MHz and −110 °C. [e] Chemical shift of impurity peak (HF) nearly coincides with proton G, interfering with integral measurement.

NMR probe. ^{1}H NMR spectra of the unwarmed cation solution did not display the expected symmetry associated with the cation formed by direct ionization of the starting material.

Over a wide range of concentrations of starting material, cation solutions were obtained with identical ^{1}H NMR spectra at 500 MHz and −110 °C (see Figure 1), containing eight carbocation-associated resolvable resonances. As seen in the figure and listed in Table I there are four doublets (each with relative intensity 1), three triplets (each with relative intensity 1), and one singlet (of intensity 2) in the ^{1}H NMR spectrum. Systematic decoupling shows that proton A is coupled to protons D and E, proton B is coupled to protons F and G, and proton C is coupled to proton D; the two protons of type H are not detectably coupled to any other protons. As the NMR probe and cation solution temperature is increased, the signals corresponding to protons G and H in the ^{1}H NMR spectrum (taken at 500 MHz) broaden into the base line (by −40 °C) and coallesce to a single observable signal (by 20 °C) at a position that is one-third of the way between the original signals, closer to the initially upfield peak. Recooling to −110 °C restores the ^{1}H NMR spectrum to its original appearance. This information, along with the ^{13}C NMR spectrum taken of a relatively dilute solution (see Table I) identified the chemical species as *α-protonated naphthalene*. It is interesting to note that when bullvalene itself is subjected to temperatures of 400 °C, H_2 is liberated and naphthalene is produced.[6]

The identity of the carbocation produced was verified by comparison of NMR spectra obtained from such cation preparations with spectra obtained from authentic protonated naphthalene. Published spectra (at much lower fields)[7,8] of protonated naphthalene agree well with those presented here. The spectra reported here are essentially identical with those obtained from carbocation solutions prepared by subliming naphthalene with codistillation of fluorosulfonic acid and subsequent addition of antimony pentafluoride and SO_2ClF. thus, even at low temperature, fluorobullvalene is converted to protonated naphthalene upon ionization with antimony pentafluoride! A possible pathway for the conversion of bullvalenyl cation to protonated naphthalene is presented in Scheme I. A suggestion, from a reviewer, that the rearrangement results from initial protonation of fluorobullvalene by adventitious acid must also be considered. This would have to be due to trace proton acid impurity, since none is produced in the overall process. However, once fluorobullvalene ionizes through fluoride abstraction, protonation is no longer likely and only rearrangements such as those in Scheme I are viable as routes to the product ion.

Scheme I



With ^{1}H NMR spectra obtained at substantially higher frequency than previously reported, along with the new coupling information (obtained from decoupling experiments), ^{1}H NMR spectral assignments for each proton in protonated naphthalene can be made with confidence. ^{13}C NMR spectral assignments were based on chemical shifts, multiplicities in proton-coupled spectra, and information obtained by a 2D ^{1}H–^{13}C chemical shift correlation (COSY) NMR experiment,[9,10] at −90 °C. Extending the early work of Olah,[7] the five tightly clustered ^{1}H NMR signals (8.26–8.71 ppm) can now be assigned to protons of the cation (see the table and figure). Our 2D NMR results support the ^{13}C NMR assignments made by Olah,[8] with one variation: positions 8 and 10, with his notation (corresponding to our notation of A and C, respectively), are interchanged.

In agreement with earlier findings,[7,8] the temperature-dependent changes in the ^{1}H NMR spectrum result from a 1,2 hydride shift, reversibly converting the α-protonated naphthalene to β-protonated naphthalene. The furthest downfield peak and the most upfield peak in the ^{13}C NMR are also seen to broaden with temperature. Magnetization transfer experiments performed from −110 to +40 °C had only clearly identified the occurence of this 1,2 shift. At temperatures between −110 and −50 °C, saturation of the signal corresponding to protons H resulted in a substantial decrease in signal intensity of proton G, and vice versa. No other detectable changes resulted when either proton G or protons H were irradiated, nor were any changes in

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(9) Bruker-supplied XHCORR.AU (of DISNMRP) was used to generate the 2D NMR spectrum, where ^{1}H decoupler 90° pulse length was determined with DEC90.AU.
(10) In addition to each cross peak, which correlates proton/carbon positions, there are peaks that imply extended coupling for protons C and D to carbons D and C, respectively.

the ^1H NMR spectrum detected when any other signals were saturated.

Further rearrangement processes were observed by examination of the ^1H NMR spectrum of the cation formed by mixing perdeuteriated naphthalene and FSO_3H. Despite the presence of some extraneous peaks in the ^1H NMR spectrum (resulting from excess FSO_3H and from cation decomposition), no regions containing signals for any protons in the carbocation are obscured until higher temperatures are achieved (see the figure). The proton is initially delivered to position H (as expected from literature precedent[7]), and at −100 °C, the protons corresponding to types H and G are the only major signals (tiny singlets for protons of types A–F are detectable and undoubtedly arise from the residual protons in the 98% perdeuteriated naphthalene used as precursor in the cation preparation). The appearance of G is consistent with the known fast process that intercoverts α- and β-protonated naphthalene. The relative intensity ratio of protons type H to type G is about 2:1. With increasing temperature, the signals broaden, as seen in the nondeuteriated cation.

At −50 °C, there is a definite and simultaneous increase in the intensity of proton type B and F. At −30 °C, the signals originally corresponding to protons G and H are gone from view and the intensities of proton types B and F has greatly increased with relative intensities of about 1:1. This indicates the presence of a, previously unreported, second 1,2 shift occurring in the carbocation. This shift interconverts the β- and β'-protonated naphthalene and also results in the production of α'-protonated naphthalene (all of ring A). All the protons of ring A are thus able to interconvert by −40 °C. At −20 °C, signals corresponding to proton types A, C, D, and E simultaneously increase in intensity at the expense of proton types B and F. When allowed to come to equilibrium at −20 °C, proton types A–F are represented by singlets of essentially equal intensity in the ^1H NMR spectrum. This suggests that there is also a process taking place at elevated temperatures that allows for shifts *between the rings* of the protonated naphthalene, presumably by two successive 1,2 shifts via the quarternary carbon. This allows for the production of α-, β-, and β'-protonated naphthalene (all of ring B). Rings A and B have changed identities, and thus protons of ring A and ring B are able to interconvert at −20 °C. This cation solution appears to be less stable than that prepared from fluorobullvalene and antimony pentafluoride; because of the presence of FSO_3H, the cation rapidly and irreversibly decomposes to unidentifiable products at 0 °C.

Thus, attempted preparations of the bullvalenyl cation from fluorobullvalene and SbF_5 in SO_2ClF with the molecular beam method at low temperatures did not produce a detectably stable solution of this cation. If it is formed as such, the bullvalenyl cation quickly rearranges to α-protonated naphthalene at temperatures below −100 °C. High-field NMR and the 2D heteronuclear COSY pulse sequence allows for unambiguous ^1H NMR and ^{13}C NMR spectral assignments of the cation. A series of 1,2 hydride shifts are detected (at elevated temperatures) in the ^1H NMR spectrum of a sample prepared by mixing perdeuteriated naphthalene with FSO_3H/SbF_5 in SO_2ClF. These processes result in *complete* proton scrambling in protonated naphthalene, below 0 °C (the temperature where the sample irreversibly decomposes to unidentifiable products).

Acknowledgment. This work was supported by a grant from the National Science Foundation, R.M.J. acknowledges support by a fellowship administered by the American Chemical Society Division of Organic Chemistry and sponsored by the Proctor and Gamble Co.

Registry No. Fluorobullvalene, 27576-97-2; α-protonated naphthalene, 41636-41-3.

Stereoselective Synthesis of *cis*-3-(2,2-Dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic Acid[1]

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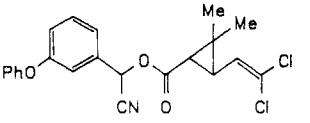
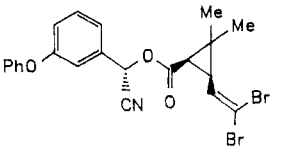
The synthetic pyrethroid insecticides play an important role in modern methods of insect control in agriculture.[2] Among the more important members of this class are cypermethrin (1) and deltamethrin (2).[2] A key structural element of these materials is the 2,2-dimethyl-3-(2,2-dihalovinyl)cyclopropanecarboxylic acid (3). The relative



1



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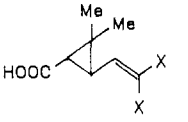

3a: X=Cl
3b: X=Br

and absolute stereochemistry about the cyclopropane ring influences both the spectrum and level of insecticidal activity exhibited by these compounds.[2,3] Consequently, methods for the stereoselective synthesis of **3** are highly desirable.

Numerous imaginative approaches to compounds of general structure **3** have been described.[4] Conceptually, one of the simplest approaches involves the formation of the cyclopropane ring by an intramolecular alkylation of an enolate anion derived from an appropriate carbonyl compound as the key step (Scheme I). Significant levels of stereochemical control have been achieved with this approach.[4] Stereoselection has been observed in the cyclization of methyl ketone **4** (R = Me, X = Cl) and ester **4** (R = OEt, X = Br).[5,6] The solvent effect in the reaction of ester **4** (R = OEt, X = Br) suggests that stereoselection in enolate formation influences the stereochemical outcome of the ring closure.[7]

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