Carbodications. 5.[1] Ring opening of the cyclopropanecarbonyl cation in superacid

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The cyclopropanecarbonyl cation (**11**) was prepared from cyclopropanecarbonyl chloride in 1:1 HF–SbF_5, 1:1 FSO_3H–SbF_5, and 4:1 FSO_3H–SbF_5. Ring opening occurred in the strongest superacids 1:1 HF–SbF_5 and (much slower) 1:1 FSO_3H–SbF_5, but not in 4:1 FSO_3H–SbF_5. The crotyl (**2**) and methacryloyl (**14**) cations were formed in 1:1 FSO_3H–SbF_5, but very little or no **14** accompanied **2** in 1:1 HF–SbF_5. Thus, **2** is formed by acid catalysis only, whereas formation of **14** involves base catalysis supplementing the acid catalysis in superacids. Dehydrochlorination of the 4-chlorobutanoyl cation in HF–SbF_5 and H/D exchange at C3 of **2** (involving attack by the acid at C3 of 3-butenoyl cation) in 1:1 DF–SbF_5, both reported before, cannot involve intramolecular assistance with the formation of ring-hydronated **11** as intermediate. Instead, a 1,4 acyl alkyl dication in a tight ion pair is indicated by the results. Reaction in 1:1 FSO_3H–SbF_5 under CO pressure followed by methanol quenching gave the methyl esters of glutaric (major) and methylsuccinic acid (minor); at least the latter should be formed by an S_N2-like attack by CO. The reaction of **11** in deuterated superacids 1:1 DF–SbF_5 and 1:1 FSO_3D–SbF_5 was much slower than the reaction in the corresponding protio-acids. At the same time, H/D exchange in the ring of unreacted **11** was observed. The extent of exchange could be assessed for the reaction in 1:1 FSO_3H–SbF_5, where conversion to **2** was small. The deuteration of the ring in this medium is similar in rate to the ring cleavage. Together with the observed rate reduction in the deuterated acids, this result suggests that H/D exchange in **11** and its ring opening do not occur on the same reaction pathway.

Introduction

As part of our studies of reactions which have rates dependent upon acidity and are potentially useful for acidity calibration in the superacid range,[3] we reported earlier on the dehydrochlorination of 4-chlorobutanoyl cation (**1**) to the but-2-enoyl cation (**2**) in composite superacids based on antimony pentafluoride [eqn. (1)].[3a] A study of the reaction over a broad

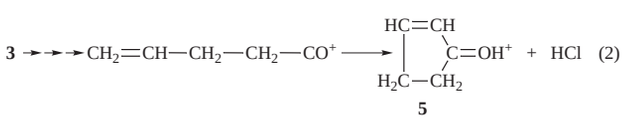
$$\text{Cl-CH}_2\text{-CHR-CH}_2\text{-CO}^+ \longrightarrow \text{Me-CR=CH-CO}^+ + \text{HCl} \quad (1)$$

1, R = H **2**, R = H

3, R = Me **4**, R = Me

range of superacidic strength (from 16:1 CF_3SO_3H–TaF_5 to 1:1 HF–SbF_5)[4] proved that it is acid-catalyzed. An inverse dependence of the rate upon acidity was found, however, upon comparing rates in 1:1 and 4:1 FSO_3H–SbF_5 solutions, indicating that in the weaker superacids the acid-catalyzed carbon–chlorine bond cleavage is assisted by a nucleophile or by a base which removes a hydron[5] from C3.[3a]

For the conversion of the branched-chain homologue, 4-chloro-3-methylbutanoyl cation (**3**), the rates varied monotonically with the superacid strength, 1:1 HF–SbF_5 > 1:1 FSO_3H–SbF_5 > 4:1 FSO_3H–SbF_5. The reaction of **3** proceeds along two competitive pathways: the first involves a hydrogen shift and gives the 3-methylbut-2-enoyl cation [**4**, eqn. (1)], the second involves a methyl shift and leads ultimately to hydronated cyclopentenone [**5**, eqn. (2)].[3b]



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Whereas the **4/5** ratio varied somewhat with acidity and temperature, the two products were formed in similar quantities, showing that ionization of chloride was not concerted with (assisted by) the methyl and hydrogen shift. Work in 1:1 FSO_3D–SbF_5 showed that in the straight-chain dications resulting from **1** (ionization) and **3** [ionization followed by methyl migration, eqn. (2)] elimination-rehydronation is favored over 1,2 hydrogen shift.[3]

In a separate study, it was shown that heating a solution of ion **2** over a long period of time (174 h at 60 °C) in 1:1 DF–SbF_5 led to significant deuterium incorporation, indicating reversible deuteronation of the alkenoyl cation [eqn. (3)].[1] Computer

$$\underset{\textbf{9}}{\text{MeCHD-CH}^+\text{-CO}^+} \leftrightarrows \underset{\textbf{2}\text{-}\alpha\text{-}d}{\text{MeCH=CH-CO}^+} \rightleftharpoons$$

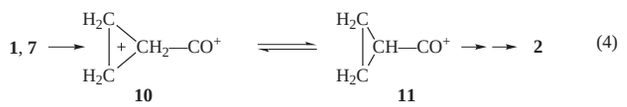
$$\underset{\textbf{6}\text{-}\alpha\text{-}d}{\text{MeCH}^+\text{-CHD-CO}^+} \rightleftharpoons \underset{\textbf{7}\text{-}\alpha\text{-}d}{\text{CH}_2\text{=CHCHD-CO}^+} \rightleftharpoons$$

$$\underset{\textbf{8}\text{-}\alpha,\beta\text{-}d_2}{{}^+\text{CH}_2\text{-CHD-CHD-CO}^+} \quad (3)$$

† For current address, see ref. 2.

modeling of the kinetics for this exchange to fit the observed isotope distribution (38.2% **2**-d_0, 4.5% **2**-d_1, 7.4% **2**-d_2, 16.7% **2**-d_3, 22.8% **2**-d_4, and 10.5% **2**-d_5) allowed the evaluation of the relative rate constants and isotope effects for the formation of the carbodications and elimination to regenerate the alkenoyl cations [eqn. (3)]. Thus, elimination from **6** favors **7** over **2** by a factor of 6–7 and **6** is formed from **7** 30–40 times faster than **8**. The latter ratio reflects the balance between charge repulsion and primary *vs.* secondary carbocation stabilities. The dication **9**, with charges at adjacent positions, does not intervene (the rate constant for its formation is calculated to be zero). Other features of the process are a very low primary isotope effect for elimination from **6** and **7** (*ca.* 1.5) and a uniquely high β secondary isotope effect for the formation of **6** from **2** or **7** (almost 2).[1]

An alternative mechanism, base-catalyzed conversion of **2** to vinylketene followed by deuteron addition, was not compatible with the isotope distribution pattern.[1] It was possible, however, that dication **8** does not intervene in the ionization of **1** and hydronation of **7**, but cyclization occurs instead, to form the hydronated cyclopropylmethanoyl cation **10** [hydronated cyclopropanecarbonyl cation, eqn. (4)]. To check this possibility, we investigated the reaction of the parent ion, cyclopropanecarbonyl cation (**11**) in superacid and we report our findings here.



(4)

Experimental

General

Cyclopropanecarbonyl chloride (**12**), crotyl chloride, methacryloyl chloride, methyl cyclopropanecarboxylate, dimethyl glutarate, and methylsuccinic acid (all from Aldrich), the superacids 1 : 1 HF–SbF_5, 1 : 1 FSO_3H–SbF_5, 4 : 1 FSO_3H–SbF_5, and 1 : 1 FSO_3D–SbF_5 (from Columbia Organics), and all other reagents and solvents were used as purchased. A 0.95 : 1 DF–SbF_5 solution was available from the previous study.[1] It will be referred to as 1 : 1 DF–SbF_5 throughout this paper. The packed-column GLC and GC–MS analyses were conducted as described previously.[6] Separation of the methyl esters of crotonic and cyclopropanecarboxylic acids was conducted on a 50 m × 0.32 mm capillary column coated with dimethyl silicone. An IBM NR 250 NMR instrument[3a,b] was used in preliminary experiments. The rest of the NMR spectra were recorded on a Bruker instrument at 300.13 MHz for ^1H and 75.468 for ^{13}C. The ^{13}C chemical shifts are based on external $CDCl_3$, taken as δ 77.0 ppm.[7]

Conversion of 11

The acyl cation was prepared and reacted as described in our previous papers.[1,3a,b] For conversion to esters by MeOH quenching of the mixture of acyl cations formed by thermal reaction, **11** was prepared from 0.5 ml of **12** and 10 ml of 1 : 1 FSO_3H–SbF_5.

Reaction with carbon monoxide[8]

A solution of **11** was prepared from cyclopropanecarbonyl chloride (0.4 ml, 4.4 mmol) and 1 : 1 FSO_3H–SbF_5 (8 ml) in a 40 ml Teflon-lined Hastelloy C autoclave. The vessel was pressurized with 4 MPa CO, sealed, and heated at 71 °C in an oil bath for a total of 168 h, being refilled once with CO during that time. The solution was magnetically stirred throughout. The methanol quenching, extraction, and washing steps were conducted as described.[8] The solution of esters was used as such for the GC and GC–MS analyses.

Dimethyl methylsuccinate[9]

A mixture of methylsuccinic acid (2.5 g, 18.9 mmol), methanol (2 g, 78 mmol), benzene (10 ml) and 96% H_2SO_4 (0.3 g) was boiled under reflux for 20 h, with azeotropic removal of water. The solution was washed with water, 10% $NaHCO_3$, and again with water, dried (Na_2SO_4) and evaporated to leave the crude ester as an oil. The GLC and GC–MS analyses were conducted on the crude ester.

Results and discussion

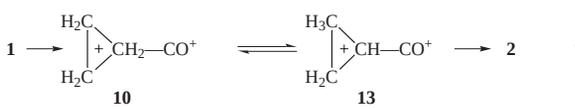
Cyclopropanecarbonyl chloride (**12**) was fully converted to **11** in the weakest superacid used, 4 : 1 FSO_3H–SbF_5, as shown clearly by ^{13}C NMR. The changes in chemical shifts from those for **12** (δ 12.27, CH_2; 23.71, CH; 175.02, CO) to those for **11** (δ 21.40, CH_2; −8.34, CH; 151.24, CO), with the signals for the carbonyl carbon and C-α moving upfield by 23.78 and 32.05 ppm, respectively, are normal for the conversion of an acid chloride to an acyl cation.[8,10] It is noteworthy that in **11** the alpha carbon resonates at higher field than TMS.[11]

Cyclopropane ring opening by acids occurs easily in the simple molecules.[12] The reaction is hindered, however, by electron-withdrawing substituents. Thus, cyclopropanecarboxylic acid requires 96% sulfuric acid at 100 °C to be converted to acyclic products.[13] Based on this precedent, one would predict the three-membered ring of **11** to be rather unreactive. Nevertheless, strong non-oxidizing superacids, such as dilute HF–SbF_5[14] and HF–TaF_5,[15] cleave even nonstrained carbon-carbon bonds in cyclic and acylic hydrocarbons. Oxidizing strong superacids also break nonactivated carbon-carbon single bonds,[16] but the simple acid cleavage reaction mechanism in those media has been contested by other authors.[17]

Cation **11** was not changed after 24 hours in 4 : 1 FSO_3H–SbF_5 at 40 °C, conditions under which **1** had been converted more than 75% to **2**. No reaction of **11** was seen in this acid even at 57 °C. This observation eliminated **11** from contention as an intermediate in eqn. (1). The cyclopropane ring of **11** was cleaved only in the very strong superacids 1 : 1 HF–SbF_5 and 1 : 1 FSO_3H–SbF_5. The reaction in 1 : 1 HF–SbF_5 showed reasonable first-order kinetics: $k_1 = 2.21 \times 10^{-5}$ s^{-1} (half-life 8.7 h) at 57.5 °C, 1.57×10^{-6} s^{-1} at 45.5 °C, and 1.12×10^{-6} s^{-1} at 40.2 °C ($\Delta H^{\ddagger} = 36.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = 30.6$ e.u.). Because of the narrow temperature range, the activation parameters are tentative. The reaction in 1 : 1 FSO_3H–SbF_5 was significantly slower and had to be run at higher temperature, making rates less reliable. Half-lives of the order of 42 h at 70 °C and 95 h at 60 °C were observed. For comparison, HCl loss from **1** had $k_1 = 8.96 \times 10^{-4}$ s^{-1} at 50 °C in 1 : 1 HF–SbF_5.

The rate dependence upon acidity argues for a mechanism involving a hydron transfer from the acid to the substrate, rather than a thermal or nucleophile-catalyzed rearrangement of **11** similar to the isomerization of cyclopropylcarbinyl to allyl cations.[18] On the other hand, the difference in rate between 1 : 1 HF–SbF_5 and 1 : 1 FSO_3H–SbF_5 was smaller than for other reactions in which a hydron was transferred in the rate-determining step.[19]

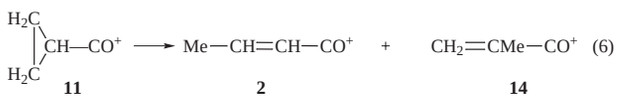
It was still possible, however, that dehydrochlorination of **1**[3] and the deuterium incorporation at C3 in **2**[1] occur with cyclization to the dication **10**, if the hydron loss from Cα of the latter to form **11** was much slower than the hydron loss from Cβ with ring opening to the non-conjugated but-3-enoyl cation, **7**. The hydron shift from Cα to Cβ to form the isomeric hydronated cyclopropane structure, **13**, followed by ring opening concerted with hydron loss from the other Cβ to give directly **2** [eqn. (5)]



(5)

can be discounted. This is because deuterium incorporation was observed in **2** formed from **1** in 1:1 DF–SbF_5,[3] whereas H–D exchange of **2** was significantly slower than conversion of **1** to **2**.[1]

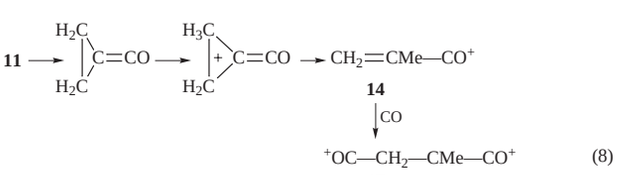
Another difference from the reaction of **1** was that a mixture of two products, **2** and the 2-methylpropenoyl (methacryloyl) cation (**14**), formed in similar quantities, was obtained from **11** in 1:1 FSO_3H–SbF_5. The two isomers were easily identified by their ^{13}C NMR spectra, exhibiting signals at 202.2 (C-3), 149.6 (C-1), 84.3 (C-2), and 24.9 (C-4) for **2** and 171.2 (C-3), 147.9 (C-1), 103.8 (C-2) and 14.3 ppm (Me) for **14**, checked with spectra of ions prepared from their acid chlorides and in agreement with the literature values.[20] Thus, both the Cα–Cβ bonds (forming **2**) and the Cβ–Cβ′ bond (forming **14**) were cleaved [eqn. (6)]. Cα–Cβ (minor) and Cβ–Cβ′ (major) bond



cleavage had also been observed in the reaction of cyclopropanecarboxylic acid in sulfuric acid.[13] By contrast, the reaction of **11** in 1:1 HF–SbF_5 consistently gave ratios **2**/**14** greater than 10. In some runs, no **14** could be detected by NMR in the reaction mixture. It appears, therefore, that **14** was formed on the account of basic impurities introduced during the preparation of some of the samples in 1:1 HF–SbF_5, whereas formation of **2** does not require base catalysis. Formation of **14** from **11** provides further evidence against the pathway of eqn. (5) for the reaction of **1**, because no **14** was formed from the latter in 1:1 HF–SbF_5, 1:1 FSO_3H–SbF_5, or 4:1 FSO_3H–SbF_5.[3a]

The nature of the basic catalyst can be ascertained from the observation that HCl elimination from **1** in 1:1 and 4:1 FSO_3H–SbF_5 is autocatalytic. After an induction period it exhibits second-order kinetics, first order in reactant **1** and first order in product **2**.[3a] This result suggests that the base catalyst is the anion, $FSO_3SbF_5^-$, which forms tight ion pairs with **1**, but solvent-separated ion pairs or even free ions in solution in the case of the much more stable cation **2**.[21]

The reaction of **11** with 1:1 FSO_3H–SbF_5 was also run under CO pressure and quenched with methanol in pentane at −80 °C.[8] This reaction sequence has been used to trap unstable carbocations.[22] The GC–MS analysis of the solution of esters resulting from **11**, illustrated in Fig. 1, shows that the dimethyl esters of both glutaric acid (**15**, Cα–Cβ cleavage) and methylsuccinic acid (**16**, Cβ–Cβ′ cleavage) were formed [eqn. (7)], the latter in very small amount.



Because the kinetic study indicated that cleavage of the Cβ–Cβ′ requires assistance from a nucleophile or a base, ring opening of the hydronated ring of **13** to a 1,3-acyl-primary alkyl dication followed by CO trapping can be eliminated as the possible mechanism for the formation of the methylsuccinyl dication (**17**). As an alternative, cation **11** could be converted to a ketene which reacts further as in eqn. (8). That mechanism is

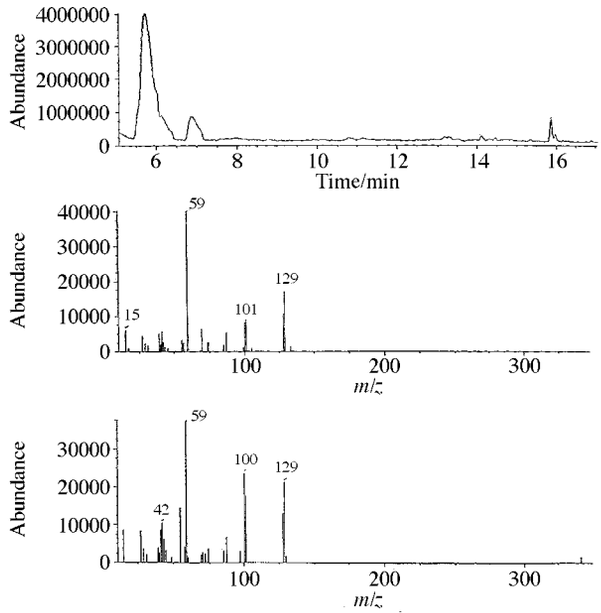


Fig. 1 GC–MS of the methyl esters from reaction of **11** in 1:1 FSO_3H–SbF_5 under CO, followed by methanol quenching. Upper MS, t = 14.131 min, MeOCO-CHMe-CH_2-COOMe (**16**); Lower MS, t = 15.832 min, MeOCO-$(CH_2)_3$-COOMe (**15**).

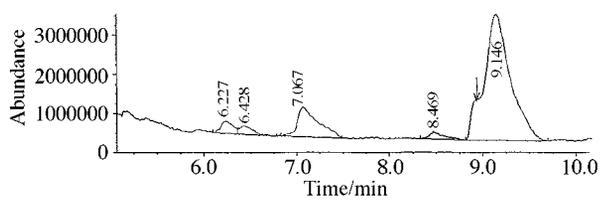
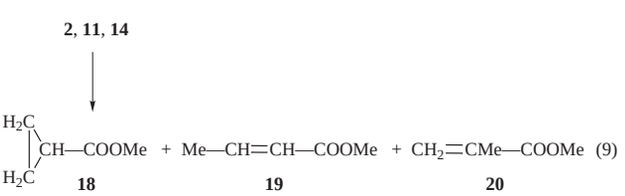


Fig. 2 GC trace of the GC–MS analysis of the methyl esters from the reaction of **11** in 1:1 FSO_3D–SbF_5. t = 7.067 min, CH_2=CMe-COOMe (**19**); t = 8.469 min, *cis*-Me-CH=CH-COOMe; t = 8.925 min, *trans*-MeCH=CH-COOMe (**18**); t = 9.146 min, cyclo-C_3H_5-COOMe (**17**).

also unlikely, because formation of the ketene should be easier in the weaker acid 4:1 FSO_3H–SbF_5 and the ketene should ring-open in that acid just as cyclopropanecarboxylic acid ring-opens in sulfuric acid.[13] As stated above, however, the ring of **11** does not open in 4:1 FSO_3H–SbF_5, that is the base-catalyzed mechanism which forms **14** applies to a dication. We have, therefore to consider that at least for the formation of the methylsuccinyl dication the CO attack can be concerted with the ring opening (S_N2 attack by carbon monoxide).

The reaction of **11** in 1:1 FSO_3D–SbF_5 was so slow that no estimate of the reaction rate could be made. ^2H NMR spectra indicated, however, that deuterium was incorporated into the cyclopropyl moiety of **11**, pointing to the interconversion of **11** and dication **10** [eqn. (4)]. A sample held for 400 h at 71 °C was then reacted with methanol as shown above, to convert the acyl cations to the corresponding methyl esters,[1] methyl cyclopropanecarboxylate (**18**), methyl crotonate (**19**), and methyl methacrylate (**20**) [eqn. (9)], which were then analyzed by



GC–MS. As shown in Fig. 2, all peaks are broadened and the peaks for **18** and **19** are severely overlapped because of isotope fractionation on the GLC column. For each compound, the first part of the peak contains only polydeuterated isotopomers and the last part of the peak contains only unlabelled material

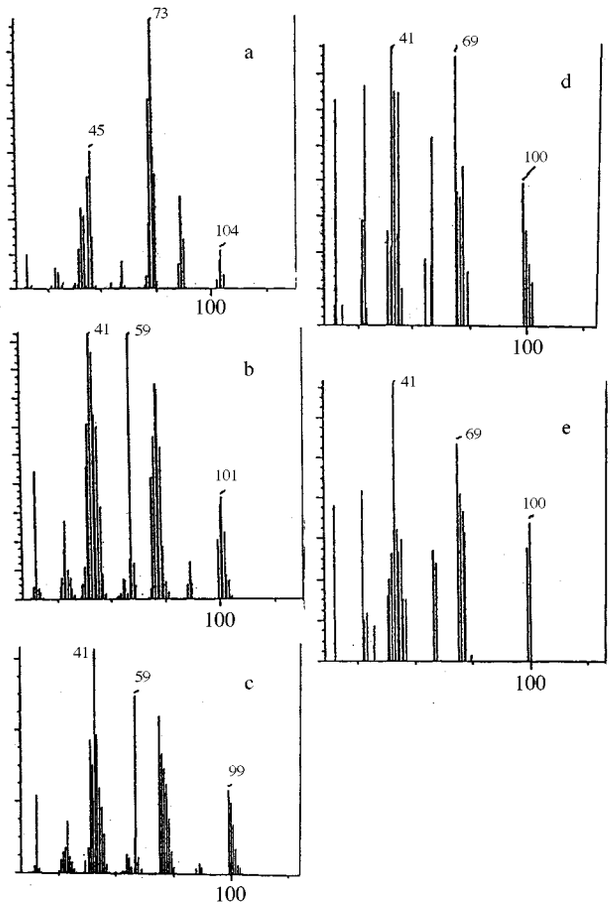


Fig. 3 Mass spectra of the sample from Fig. 2, at various elution times. **a**, $t = 8.925$ min; **b**, $t = 9.084$ min; **c**, $t = 9.136$ min; **d**, $t = 9.219$ min; **e**, $t = 9.307$ min.

(d_0).[1] Nonetheless, because the peak of **19**, which elutes first, is much smaller than that of **18**, a rough estimate of the extent of deuteration in the latter is possible.

Some representative mass spectra of the (**19** + **18**) peak are shown in Fig. 3. The distinctive features, obtained from the spectra of the individual components, are the $(M\text{-}Me)^+$ fragment of *m*/*z* 85 (in the non-deuterated material) which is strong in the spectrum of **19** (intensity 1.8 times that of the parent, *m*/*z* 100) but is insignificant in the spectrum of **18** and the $(M\text{-}H)^+$ fragment, observed for **18** (7 times the intensity of the parent ion) but not for **19**. Then, the spectrum recorded for the reaction mixture at 8.925 min (Fig. 3a) is that of pure **19** and the spectra collected at 9.219 min (Fig. 3d) and 9.307 min (Fig. 3e) can be considered to represent pure **18**. An estimate of the contribution of **19** to the parent ion cluster (*m*/*z* 100–105) from the intensities at *m*/*z* 85–87 can be made for the spectra at 9.084 min (Fig. 3b) and 9.136 min (Fig. 3c). The remaining intensities of the *m*/*z* 99–105 ions are then used to evaluate the isotopomer distribution of **18** at those positions in the GLC peak. It is thus found that at 9.084 min, **18** was 21.5% d_0, 30.5% d_1, 32.0% d_2, and 15.5% d_3, and had undergone 140 exchange events ($30.5 + 2 \times 32.0 + 3 \times 15.5$) per 100 molecules. Likewise, we obtain 44.0% d_0, 31.0% d_1, 21.5% d_2, 3.5% d_3, and 83 exchange events per 100 molecules at 9.136 min; 59.0% d_0, 21.0% d_1, 14.5% d_2, 5.0% d_3, and 65 exchange events per 100 molecules at 9.242 min (not shown in Fig. 3);[23] 48% d_0, 52% d_1, and 52 exchange events per 100 molecules at 9.307 min. In these calculations, every approximation which was made was made so as to reduce the calculated extent of exchange in **18**. It can be seen that the exchange rate is at least comparable to the rate of ring opening. Therefore, if the pathways of eqns. (4) and (5) played any role in the reactions of **1** and **7**, ion **11** would have been seen in the mixture during the reaction.

Cation **11** was also reacted in 1 : 1 DF–SbF_5 in the manner described previously,[1] for 85 h at 51 °C and 86 h at 57 °C, the latter representing about ten half-lives for the ring opening in the protio-acid (1 : 1 HF–SbF_5). The ester product contained similar quantities of **18** and **19**, perhaps somewhat more of the latter. Deuteration in the starting material **18** was indicated, but no reliable estimate of the number of exchange events in it was possible. The ester **20**, formed in small amounts in this experiment, was extensively deuterated. Likewise, ester **20** formed in similar quantity with **19** in 1 : 1 FSO_3D–SbF_5 was extensively deuterated.

The hydrogen/deuterium exchange observed in ion **11** indicates that ring opening occurs in a step subsequent to reversible hydron addition to a methine or methylene group of the cyclopropane ring. At the same time, the large rate reduction observed in the deuterated acids indicates a hydron transfer in the rate-determining step for ring opening. We thought at first that rate retardation in 1 : 1 FSO_3D–SbF_5 might reflect the existence of some basic impurities in the commercial acid, but the extent of the base-assisted Cβ–Cβ′ cleavage was not increased over that observed in nonlabelled superacid. The latter observation was also made for the experiment in 1 : 1 DF–SbF_5. A possible rationalization of the concomitant rate-retardation and H/D exchange in the deuterated superacids is that cleavage of the cyclopropane ring involves, at least in some cases, direct hydron attack at a C–C bond, rather than addition at a methine or methylene group followed by or concerted with ring opening. Stereospecific ring opening of three-membered rings with electrophiles other than hydron was reported,[24] but it was considered that the attack occurs at the C–C bond and the edge-hydronated cyclopropane rearranges to a non-symmetrical corner hydronated isomer, rather than opens directly.[24b] For hydron as the electrophile, however, the "top" (bridging) methyl group should undergo rotation with little if any energy barrier.[25] *Ab initio* calculations, conducted on various dication structures derived from **11**, preferably ion-paired,[26] might offer some insight into the mechanism.

It appears that in 1 : 1 HF–SbF_5, ring opening of **11**, HCl loss from **1**, and H/D exchange at C3 in **2**, all involve a primary alkyl cation structure in the alkyl acyl dication intermediate (**8**). This ion should intervene only in tight ion pairs.[26,27] Primary carbocations have been implicated from the product slates as intermediates in thermolyses,[28a] and in solvolyses in phenol and acetic acid,[28b] of *N*-(*n*-alkyl)-5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium cations. Compelling evidence for primary carbocation intermediates in solvolyses of such *N*-(primary alkyl)acridinium cations in deuterated methanol and deuterated acetic acid arises from lack of deuterium uptake in the normal and rearranged products, and the simultaneous lack of rate-enhancing anchimeric assistance.[29]

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