Formation of a 1,3-Azulenediacylium Ion in SbF_5–FSO_3H–SO_2

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Summary The stepwise production of 6-bromoazulene-1,3-diacylium ion is observed from the diconjugate acid of 6-bromoazulene-1,3-dicarboxylic acid or diester *via* the monoacylium ion–monocarboxy-conjugate acid in SbF_5–FSO_3H–SO_2.

OXYGEN and ring carbon protonation have been reported from azulene-1-carboxylic acid[2] and a number of azulen-1-yl alkyl ketones and azulene-1-carboxaldehydes.[2,3] Protonated azulene-1-carboxylic acid is dehydrated slowly in sulphuric acid to yield the stabilized azulen-1-ylacylium ion,[2c] the rate undoubtedly dependent on O *vs.* ring C(3) protonation.

While seeking an extension of the Nozoe azulene synthesis,[4] we found that 6-bromoazulene-1,3-dicarboxylic acid (**1**) could be produced from its diester in 95% yield by dissolving the diester in conc. sulphuric acid followed by quenching in water. Thermal decarboxylation of (**1**) gives 6-bromoazulene (35—45%).

Although intermediate acylium ions were not observed (n.m.r.) in conc. sulphuric acid, the use of 'super acid,' SbF_5–FSO_3H, in SO_2 allows the observation of the stepwise transformations from diconjugate acids, (**3**) and (**4**), to monoacylium ions, (**5**) and (**6**), to diacylium ion, (**7**),† derived from diacid (**1**) and its dimethyl ester, (**2**), respectively. The dimethyl ester was chosen to eliminate the possibility of alkyl ester cleavage which has been reported for ethyl esters in this medium,[7] and the methyl group simplifies the n.m.r. spectra. The n.m.r. spectra for these species are summarized in the Table.

In the conversion of (**4**) into (**6**), protonated methanol

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† The formation of acylium ions by dehydration of carboxylic acids has been reported for a number of carboxylic acids in acid media of various strengths.[5] Acyclic diacylium ions have been generated from acid fluorides[6] and by the dehydration of diacids[7] previously, but little attention has been given to the formation of homonuclear aromatic diacylium ions generated by this procedure.[6]

N.m.r. spectral absorptions for the various species[a]

Cmpd.	Solvent	C(2)H (s)	C(4), C(5), C(7), and C(8) protons[b]	Ester OCH$_3$
(**1**)	(CD$_3$)$_2$SO	8·66	A$_2$B$_2$, 8.15 and 9·45 (*J* 11 Hz)	5·72(OH)
(**2**)	CDCl$_3$	8·82	A$_2$B$_2$, 8·02 and 9·45 (*J* 11 Hz)	3·95
(**3**)	H$_2$SO$_4$	9·43	A$_2$B$_2$, 8·78 and 9·43 (*J* 11 Hz)	
(**3**)	FSO$_3$H–SbF$_5$–SO$_2$[c]	9·30	A$_2$B$_2$, 8·79 and 9·41 (*J* 11 Hz)	
(**4**)	FSO$_3$H–SbF$_5$–SO$_2$[c]	9·30	A$_2$B$_2$, 8·94 and 9·52 (*J* 11 Hz)	4·87
(**5**)	FSO$_3$H–SbF$_5$–SO$_2$[d]	9·87	multiplet, 8·99—9·74	
(**6**)	FSO$_3$H–SbF$_5$–SO$_2$[d]	9·84	multiplet, 9·06—9·66	5·24
(**7**)	FSO$_3$H–SbF$_5$–SO$_2$[e]	10·36	A$_2$B$_2$, 9·34 and 9·68 (*J* 11 Hz)	

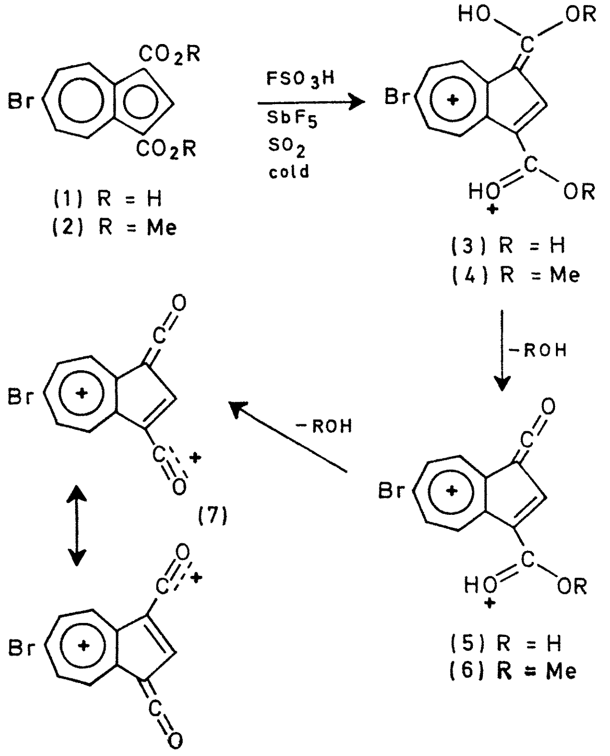
[a] All values given in acid media are in δ p.p.m. relative to external Me$_4$Si. Spectra were determined on a Varian A-60 n.m.r. spectrometer.

[b] For the A$_2$B$_2$ patterns, the values given are the centres.

[c] The spectra of (**3**) and (**4**) were at −78° and −60°, respectively.

[d] The temperatures and time used for conversion of (**3**) into (**5**) were 0° and 30 min, and for (**4**) into (**6**) were 30° and 1 h.

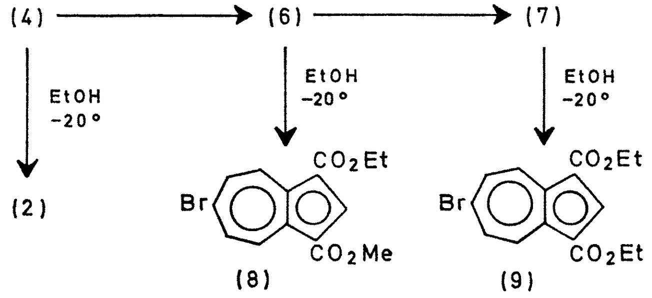
[e] The temperature and time used for conversion of (**5**) into (**7**) were 30° and 1 h, and for (**6**) into (**7**) were 40° and 30 h.



SCHEME 1

(1 mol. equiv.) (δ 4·70 and 9·68 p.p.m. for CH$_3$ and $\overset{+}{\mathrm{O}}\mathrm{H}_2$, respectively)[8] is formed; at the higher temperature required for the conversion of (**6**) into (**7**) a singlet absorption at δ 4·80 p.p.m. is observed which may correspond to methyl fluorosulphonate.

The results of quenching experiments are summarized in Scheme 2. In each case the diester products (**2**), (**8**), and



SCHEME 2

(**9**) were isolated in *ca.* 90% yield. Similar results were obtained from quenching the three species derived from diacid (**1**). These results give clear evidence that the structures of the intermediates from (**1**) and (**2**) in SbF$_5$–FSO$_3$H–SO$_2$ are those given.

Ring-carbon protonation of diacid (**1**) or diester (**2**) was not observed at low temperature in the "super acid" medium. Dehydration of (**3**) to the acylium ion (**5**) appears to occur more readily than that described for azulene-1-carboxylic acid (**10**)[2c] which is probably a result of the lack of ring carbon protonation.[2,9] The further dehydration of (**5**) to (**7**) would be expected to be even slower since the azulenium ion stabilization is already apparent in (**5**). However, the resulting product (**7**) has the structure of a α-ketenylvinylacylium ion and is expected to be resonance stabilized. A similar hybrid also is involved in (**3**) and (**4**) which contributes to the lack of ring protonation found for (**1**) compared with (**10**). Likewise, decarboxylation of (**1**) was not observed under the present strong acid conditions nor could it be effected at certain lower acid concentrations as described for (**10**)[9] or the dealkoxycarbonylation of dialkyl 2- and 6-hydroxyazulene-1,3-dicarboxylates.[10]

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