Intramolecular [4 + 2] Cycloaddition Reaction of Six- and Seven-Membered Cyclic *N*-Allyl-*C*-arylethynyl Iminium Salts

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Received January 26, 2001

N-Allyl-2-(het)arylethynyl-3,4,5,6-tetrahydropyridinium triflates **1c**,**d**,**e** and *N*-allyl-2-(het)aryl-4,5,6,7-tetrahydro-3*H*-azepinium triflates **1g**,**h** undergo a thermal isomerization reaction leading to derivatives of [*a*,*f*]-annulated isoindolium salts **2** in good yields. Similarly, *N*-allyl-2-phenylethynyl-pyridinium triflate **4** is transformed into the condensed pyridinium salt **5**. An intramolecular [4 + 2] cycloaddition reaction, in which the (het)arylethynyl moiety acts as the 4π component, is considered as the key step of this transformation. In contrast, the related *N*-allyl-4,5-dihydro-3*H*-pyrrolium salts **1a**,**b** and *N*-homoallyl-3,4,5,6-tetrahydropyridinium salt **1f** undergo unspecific decomposition under thermal impact.

Introduction

Propyne iminium salts, in which a carbon−carbon triple bond is activated by conjugation with an iminium function, have recently emerged as useful building blocks in organic synthesis. They undergo conjugate addition with a variety of soft heteronucleophiles[1] and of organocuprates[2] to form aminoallenes or eventually the tautomeric amino-1,3-dienes. Nucleophilic attack at the iminium carbon atom leads to highly substituted propargylamines.[2a] The electrophilic alkyne function can also serve as a dienophile in Diels−Alder reactions[3,4] and as a 2π component in polar [2 + 2] cycloaddition reactions with enaminones[3] and imines.[5] In this paper, we describe a novel reaction mode of certain propyne iminium salts, namely, the intramolecular [4 + 2] cycloaddition between a (het)arylethyne and an olefin unit tethered by a cyclic iminium function. It should be remembered that the intramolecular Diels−Alder reaction involving a butadiene and an alkene function is a valuable method for the construction of often complex carbocyclic or heterocyclic molecules.[6,7] However, arylethynyl moieties are not common 4π components in intramolecular Diels−Alder reactions, although their long known intramolecular [4 + 2] cycloaddition reactions with a nonconjugated C≡C bond have recently found renewed interest mainly for mechanistic reasons.[8,9]

Results and Discussion

The synthesis of semicyclic propyne iminium salts **1a**−**f**, in which the iminium function is incorporated in a five-, six-, or seven-membered ring, has been reported.[10] When solutions of these salts in acetonitrile were heated in a thick-walled Schlenk tube, the results summarized in Scheme 1 were obtained. In the case of *N*-allyl-3,4,5,6-tetrahydropyridinium salts **1c**,**d**,**e** and of *N*-allyl-4,5,6,7-tetrahydro-3*H*-azepinium salts **1g**,**h**, a thermal isomerization reaction started to occur at about 120 °C. At 190 °C, this transformation was complete within 1−2.5 h, and the novel tetracyclic isoindolium derivatives **2c**,**d**,**e**,**g**,**h** were isolated in good yields (Table 1). In contrast, *N*-allyl-4,5-dihydro-3*H*-pyrrolium salts **1a**,**b** and *N*-homoallyl-3,4,5,6-tetrahydropyridinium salt **1f** underwent unspecific decomposition under the same conditions, and no product could be isolated.

The constitution of the tetracyclic skeleton of products **2** was established by one- and two-dimensional NMR spectra (^{1}H, ^{13}C, COSY-45, C−H correlation, gradient-selected HMBC). An additional proof was furnished by a single-crystal X-ray diffraction analysis of salt **2e** (Figure 1). According to this structural investigation, the angular proton at the B/C ring junction occupies the axial position and has HCCH torsion angles of 51° and 169° with the CH_2 protons in the six-membered ring, and of 19° and 140° with those of the five-membered ring. For the CH_2 group in the six-membered ring of this and the other salts **2**, the proton signal at higher field is therefore attributed to the axial proton on the basis of the larger ^3J coupling constant (ca. 17 vs 8 Hz); δ values are found in the range 2.52−2.76 as compared to 3.1−3.4 for the equatorial proton). For the CH_2 protons in the five-

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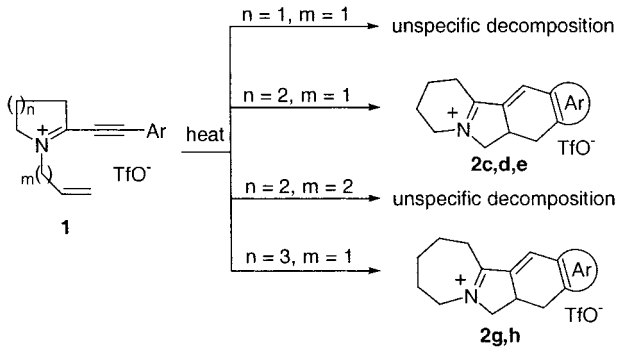
10.1021/jo015546y CCC: $20.00
Published on Web 04/11/2001

Scheme 1. Cycloisomerization of Propyne Iminium Triflates 1; See Also Table 1



1,2	m	n	Ar
a	1	1	2-thienyl
b	1	1	C_6H_4-4-Cl
c	1	2	2-thienyl
d	1	2	3-thienyl
e	1	2	C_6H_4-4-Cl
f	2	2	C_6H_4-4-Cl
g	1	3	2-thienyl
h	1	3	C_6H_4-4-Cl

membered ring, assignments of chemical shifts are not immediately obvious since the torsion angles mentioned above suggest similar ^3J coupling constants for both protons.

The tetrahydropyridinium ring of salts **1c**−**e** was replaced with a pyridinium ring by alkylation of pyridine **3**[11] with allyl triflate (Scheme 2). The resulting *N*-allylpyridinium salt **4** underwent the same thermal cycloisomerization reaction as salts **1c**−**e**, leading to 6,6a-dihydro-7*H*-benzo[*f*]pyrido[2,1-*a*]isoindolium salt **5**, but a considerably longer reaction time was required (50 h at 190 °C). The structural identification of **5** was based mainly on the close similarity of the ^{1}H and ^{13}C chemical shifts and the proton coupling patterns of the CH_2CHCH_2 moiety.

The cycloisomerization of iminium salts **2** and **4** includes an intramolecular [4 + 2] cycloaddition reaction involving, quite unusually, a (het)arylethyne unit acting as the 4π component and the olefinic C=C bond. As is shown exemplarily for **1e** in Scheme 3, this cycloaddition generates the bis-annulated 1,2-cyclohexadiene **6**, which undergoes rearomatization through a formal 1,3-hydrogen shift, thus generating the final product **2e**. Monocyclic 1,2-cyclohexadiene is a highly strained and short-lived cycloallene that has been characterized so far by IR spectroscopy in cryogenic matrices,[12,13] a He(I) UV photoelectron spectrum,[14] and by chemical trapping experiments.[15] While 1,2-cyclohexadienes are typically generated by elimination reactions[15] or by rearrangement of bicyclo[3.1.0]hex-6-ylidenes (i.e., bicyclic carbenes),[15,16]

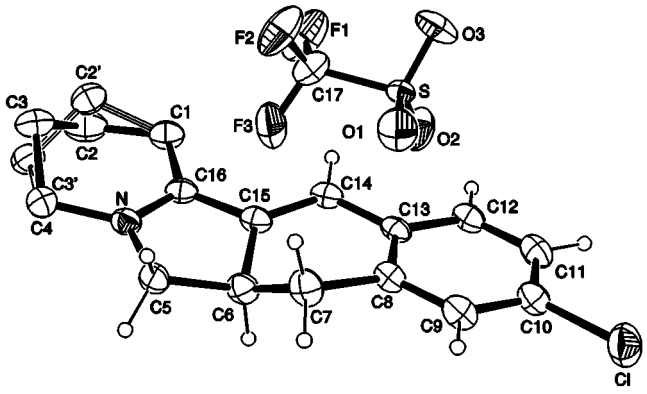


Figure 1. Structure of salt **2e** in the solid state. Ellipsoids of thermal vibration are shown at the 20% probability level. Two conformations of the tetrahydropyridinium ring involving the C1−C2−C3−C4 moiety are found. Bond lengths: C16−N 1.292(5) Å; C14−C15 1.332(6) Å.

the so-called "dehydro Diels−Alder reaction" involving a vinylacetylene and an alkene was recognized long ago[17] as a potential route to six-membered cycloallenes, and the reaction of 2,5-dimethylhexa-1,5-dien-3-yne with maleic anhydride, leading to 1:2 cycloaddition product, seems to be a case in point.[18] Thus, the intramolecular cycloaddition of **1** leading to **6** would represent a novel example of the dehydro Diels−Alder reaction, in which a phenylacetylene rather than a vinylacetylene unit plays the part of the 4π component.

The mechanism of the formation of cycloallene **6** from **1e** (Scheme 3) is of some interest. An alternative to the Diels−Alder-type concerted [4 + 2] cycloaddition process focuses on the allenyl cation resonance structure **1e′** of the propyne iminium salt. Intramolecular [4 + 2] cycloaddition of **1e′** would generate the bent vinyl cation **7** rather than the angle-strained cycloallene **6**, and a formal hydride shift would transform **7** into the final product **2e′** ↔ **2e**. It should be noted that **6** and **7** are not related as resonance structures. However, **7** may be considered as a resonance structure of a zwitterionic allyl-type system (not shown). A planar zwitterion or triplet diradical corresponds to the transition state of the racemization of 1,2-cyclohexadiene which itself has a chiral, slightly distorted C_2 symmetry.[16,19,20]

The step **1e′** → **7** is reminescent of the thermal isomerization of allyl-(3-phenylprop-2-ynyl)ammonium salts under base catalysis (e.g., **8** → **9**, Scheme 4).[21] In these cases, as well as for related amines and ethers,[22] it is assumed that a base-catalyzed propyne-to-allene

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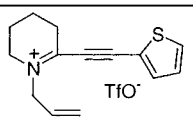
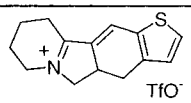
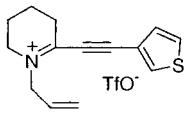
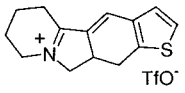
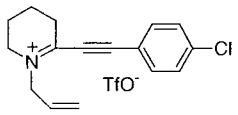
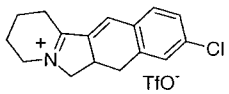
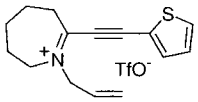
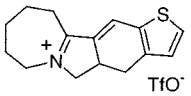
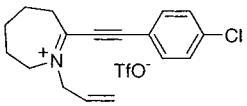
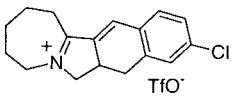
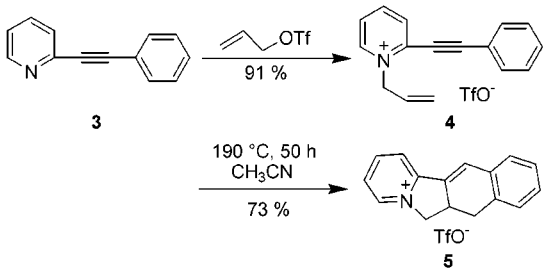
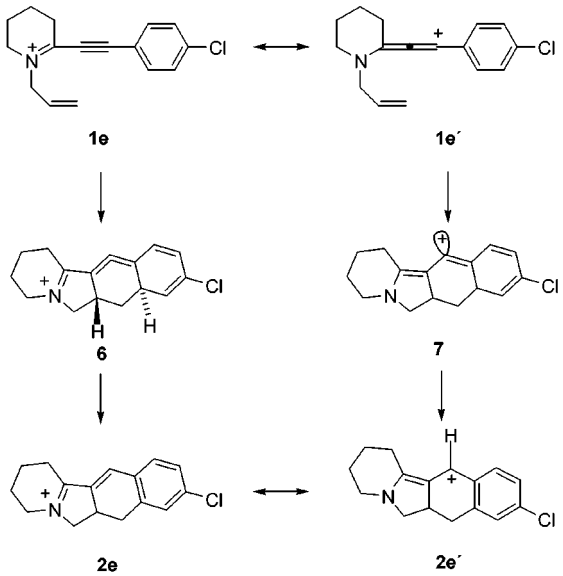
Table 1. Thermal Cycloisomerization of Propyne Iminium Salts 1c–e,g,h at 190 °C

Propyne Iminium Salt	Time, h	Product	Yield, %
	1		76
1c 	1	**2c** 	75
1d 	2.5	**2d** 	83
1e 	1	**2e** 	86
1g 	1.5	**2g** 	79
1h		**2h**	

Scheme 2. Synthesis and Thermal Reaction of Salt 4



Scheme 3



isomerization is the initial step, so that a phenylethenyl rather than a phenylethynyl moiety constitutes the 4π component in the cycloaddition step. Despite this analogy, we consider involvement of cation **1e′** in the cycloaddition step as less likely, because the allenyl cation structure does not contribute much to the bond state of propyne iminium ions according to calculations[1] and experimentally determined bond lengths.[23]

The formation of a 1,2-cyclohexadiene intermediate **6** is also reminescent of the thermal isomerization of 1-[2-(phenylethynyl)phenyl]-3-phenylprop-2-yn-1-ol and related 3-ene-1,6-diynes into benzo[*b*]fluorene derivatives.[8,9] For some of these cases,[9] there is experimental and

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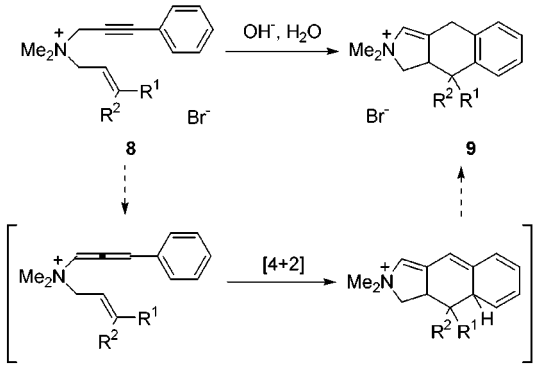
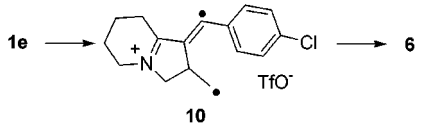
Scheme 4. Base-Assisted Thermal Isomerization of Ammonium Salts 8

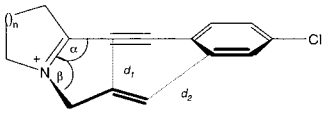


Scheme 5



computational evidence for a two-step biradical [4 + 2] cycloaddition involving a C≡C bond and an arylethynyl unit yielding a 1,2,4-cyclohexatriene intermediate that rearomatizes by an intermolecular hydrogen transposition. For iminium salts **1**, an analogous pathway would include 1,4-biradical **10** (Scheme 5), which then affords cycloallene **6** by intramolecular radical coupling. Not unexpectedly, no trapping product of biradical **10** (which contains an unstabilized alkyl radical center) was found when the thermal isomerization of **1e** was conducted in excess 1,4-cyclohexadiene, and therefore there is currently no experimental argument for or against a biradical pathway.

As mentioned above, the propyne iminium salts **1a**,**b**, in which the iminium function is part of a five-membered ring, did not cycloisomerize to isoindolium salts **2a**,**b**. We reasoned that this failure might be a consequence of larger exocyclic bond angles at the five-membered iminium ring of **1a**,**b** as compared to those of the six- and seven-membered ring systems. Geometry optimization of cations **1b** and **1e** (see Supporting Information) showed that this is indeed the case (Figure 2), and as a consequence, the termini of the 4π and 2π fragments undergoing the [4 + 2]-cycloaddition are farther apart in the reactive conformation of **1b** (0.16 kcal mol^{-1} above the minimum energy conformation) as compared to **1e**. As the cycloaddition proceeds, angles α and β are compressed considerably as a result of formation of the five-membered ring in the isoindolium system [see bond angles in the crystalline state (Figure 1): N−C16−C15, 109.8(3)°; C5−N−C16, 113.6(3)°]. The angle strain caused by this deformation of valence angles around the sp^2-hybridized atoms of the iminium function is accommodated better with a 6,5- or 7,5- than with a 5,5-annulation at this function. The distinctly longer reaction time of pyridinium system **4** may be attributed in part to electronic effects and in part to the unability of the pyridinium ring to accommodate some of the developing angle strain around the iminium function (i.e., internal bond angles becoming larger than 120°) by adopting a nonplanar conformation as for example in the case of the tetrahydropyridinium systems **2c**,**d**,**e**. In the case of **1f**, the flexibility and conformational preference of the chain



	n	α (°)	β (°)	d_1 (Å)	d_2 (Å)	ΔE^a
1b (MMFF)	1	121.7	128.1	3.54	4.60	0.00
1b (PM3)	1	124.5	126.9	3.75	4.80	0.16
1e (MMFF)	2	119.0	123.4	3.40	4.37	0.00
1e (PM3)	2	119.6	122.1	3.45	3.80	0.00

Figure 2. Calculated geometries [Merck Force Field (MMFF) and PM3] of the reactive conformations of **1b** and **1e**. ΔE = energy difference between reactive conformer and conformer of lowest energy (kcal mol^{-1})

is likely to prevent a proper alignment of the π systems on the way to the TS of the cycloaddition reaction.

Conclusion

In conclusion, we have reported a versatile route to derivatives of [*a*,*f*]-annulated isoindolium salts that is based on an intramolecular [4 + 2] cycloaddition reaction involving as the 4π component a (het)arylethynyl moiety of semicyclic propyne iminium salts. This cycloisomerization reaction works when the iminium function is part of a saturated six- or seven-membered ring or of a pyridinium ring but not when it belongs to a saturated five-membered ring. On the basis of geometrical considerations, this structural dependence is traced back to the distance of the reacting centers in the reactive conformation and to angle strain building up during the cycloaddition. The cycloaddition is likely to generate a bis-annulated 1,2-cyclohexadiene as an intermediate. The chemistry of these novel isoindolium derivatives will be the subject of a forthcoming paper.

Experimental Section

General Methods. The NMR spectra were taken on a Bruker AMX 500 (^{1}H, 500.14 MHz; ^{13}C, 125.77 MHz) instrument. For the ^{1}H NMR spectra, tetramethylsilane was used as the internal standard, whereas the solvent signal was used as standard in the ^{13}C NMR spectra [δ (CD_3CN = 1.3 ppm]; pt = pseudotriplet. IR spectra were recorded on a Perkin-Elmer IR 883 spectrometer. Microanalyses were carried out at the Analytical Laboratories of the University of Ulm with analyzer systems Elementar Vario E1 and Heraeus CHN rapid. Melting points were determined in an apparatus after Dr. Tottoli (Buechi) and are not calibrated. All reactions were carried out in rigorously dried glassware. Solvents were dried according to standard methods and stored under an argon atmosphere. The propyne iminium salts **1a**−**h** were prepared as published.[10]

1-Allyl-(2-phenyl-1-ethynyl)pyridinium Trifluoromethanesulfonate (4). To a magnetically stirred solution of allyl triflate[24] (1.65 g, 8.7 mmol) in diethyl ether (10 mL), cooled at 0 °C, was slowly added a solution of 2-(2-phenylethynyl)-pyridine[11] (**3**) (1.40 g, 7.8 mmol) in diethyl ether (10 mL). A pale yellow precipitate was formed immediately. The reaction mixture was then stirred at room temperature for 30 min. The supernatant solution was decanted, and the solid residue was washed with diethyl ether (3 × 20 mL). Recrystallization from CH_3CN/diethyl ether furnished **4** (2.63 g, 91%) as light yellow

(24) Vedejs, E.; Engler, D. A.; Mullins, M. J. *J. Org. Chem.* **1977**, *42*, 3109−3113.

crystals: mp 113 °C; IR (KBr) ν 3073 m, 2221 vs, 2185 m, 1282/1277/1261 vs, 1172 vs, 1030 vs cm^{-1}; ^{1}H NMR (CD_3CN) δ 5.40−5.54 (m, 4 H, NCH_2CH=CH_2), 6.18 (m_c, 1 H, CH=CH$_2$), 7.53 (pt, 2 H), 7.61 (pt, 1 H), 7.76 (d, 2 H), 8.00 (pt, 1 H), 8.23 (d, 1 H), 8.51 (pt, 1 H), 8.80 (d, 1 H); ^{13}C NMR (CD_3CN) δ 62.9 (NCH_2), 80.7 (C≡), 107.5 (C≡), 120.2, 122.2 (q, $J_{C,F}$ = 321.0 Hz, TfO$^-$), 122.9 (CH=*C*H$_2$), 128.2, 130.2, 130.9 (*C*H=CH$_2$), 132.9, 133.5, 133.6 (2 C), 138.7, 146.5, 147.0. Anal. Calcd for $C_{17}H_{14}F_3NO_3S$ (369.36): C, 55.28; H, 3.82; N, 3.79. Found: C, 55.16; H, 3.60; N, 3.67.

4a,5,7,8,9,10-Hexahydro-4*H*-pyrido[2,1-*a*]thieno[3,2-*f*]-isoindol-6-ium Trifluoromethanesulfonate (2c). A solution of **1c** (3.80 g, 10.0 mmol) in CH_3CN (15 mL) was placed in a thick-walled Schlenk tube. The tube was closed, immersed in an oil bath, and heated at 190 °C for 1 h. After concentration of the solution to half of its volume and cooling at −30 °C, the product was precipitated by addition of diethyl ether. The supernatant solution was decanted, and the solid residue was washed with diethyl ether (3 × 50 mL) and recrystallized from CH_3CN/diethyl ether to afford **2c** (2.89 g, 76%) as yellow crystals: mp 152 °C; IR (KBr) ν 3101 m, 3059 m, 2961 m, 2877 m, 1633 m, 1611 s, 1272 vs, 1150 vs, 1029 vs cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.77−2.07 (m, 4 H, 8-H, 9-H), 2.52 (pt, 1 H, 4-H^{ax}), 2.82−3.01 (m, 2 H, 10-H), 3.08−3.20 (m, 1 H, 4a−H), 3.31 (dd, ^2J = 16.1 Hz, ^3J = 8.3 Hz, 1 H, 4-H^{eq}), 3.65−3.80 (m, 3 H, 5-H^A, 7-H), 4.27 (dd, ^2J = 13.4 Hz, ^3J = 9.2 Hz, 1 H, 5-H), 7.11 (d, ^3J = 5.0 Hz, 1 H, 3-H), 7.65 (d, ^4J = 3.1 Hz, 1 H, 11-H), 7.68 (d, ^3J = 5.0 Hz, 1 H, 2-H); ^{13}C NMR (CD_3CN) δ 17.3 (C-9), 21.6 (C-8), 24.1 (C-10), 28.7 (C-4), 34.3 (C-4a), 49.2 (C-7), 63.7 (C-5), 122.2 (q, $J_{C,F}$ = 321.0 Hz, TfO$^-$), 129.2 (C-3, C-11), 132.7 (C-2), 134.5 (C-3a), 135.0 (C-10b), 142.3 (C-11a), 176.9 (C-10a). Anal. Calcd for $C_{15}H_{16}F_3NO_3S_2$ (379.41): C, 47.49; H, 4.25; N, 3.69. Found: C, 47.42; H, 4.30; N, 3.65.

6,7,8,10,10a,11-Hexahydro-5*H*-pyrido[2,1-*a*]thieno[2,3-*f*]isoindol-9-ium Trifluoromethanesulfonate (2d). Thermal treatment of **1d** (3.80 g, 10.0 mmol) and workup as described above for **2c** gave yellow crystals of **2d** (2.84 g, 75%): mp 157 °C; IR (KBr) ν 3085 m, 3070 m, 2967 m, 1640 m, 1616 s, 1272 vs, 1151 vs, 1027 vs cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.76−2.06 (m, 4 H, 6-H, 7-H), 2.67 (pt, 1 H, 11-H^{ax}, ^2J = ^3J = 16.3 Hz), 2.83−3.03 (m, 2 H, 5-H), 3.15−3.24 (m, 1 H, 10a−H), 3.39 (dd, ^2J = 16.3 Hz, ^3J = 8.2 Hz, 1 H, 11-H^{eq}), 3.64−3.80 (m, 3 H, 8-H, 10-H^A), 4.28 (dd, ^2J = 13.2 Hz, ^3J = 8.8 Hz, 1 H, 10-H^B), 7.17 (d, ^3J = 5.2 Hz, 1 H, 3-H), 7.34 (d, ^3J = 5.2 Hz, 1 H, 2-H), 7.58 (d, ^4J = 3.0 Hz, 1 H, 4-H); ^{13}C NMR (CD_3CN) δ 17.2 (C-6), 21.5 (C-7), 24.1 (C-5), 28.1 (C-11), 34.4 (C-10a), 49.2 (C-8), 63.4 (C-10), 122.2 (q, $J_{C,F}$ = 320.5 Hz, TfO$^-$), 126.1 (C-2), 127.5 (C-3), 130.4 (C-4), 135.4 (C-3a), 135.7 (C-4a), 143.5 (C-11a), 177.6 (C-4b). Anal. Calcd for $C_{15}H_{16}F_3NO_3S_2$ (379.41): C, 47.49; H, 4.25; N, 3.69. Found: C, 47.48; H, 4.47; N, 3.71.

9-Chloro-1,2,3,4,6,6a-hexahydro-7*H*-benzo[*f*]pyrido[2,1-*a*]isoindolium Trifluoromethanesulfonate (2e). Thermal treatment of **1e** (8.16 g, 20.0 mmol) at 190 °C for 2.5 h and workup were done as described above for **2c**. Colorless crystals of **2e** (6.72 g, 83%) were obtained: mp 186 °C; IR (KBr) ν 3052 w, 2962 w, 1629 s, 1274 vs, 1152 vs, 1034 vs cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.79−2.07 (m, 4 H, 2-H, 3-H), 2.71 (pt, ^2J = ^3J = 14.8 Hz, 1 H, 7-H^{ax}), 2.85−3.05 (m, 2 H, 1-H), 3.06−3.21 (m, 2 H, 6a−H, 7-H^{eq}), 3.66−3.86 (m, 3 H, 4-H, 6-H), 4.26−4.36 (m, 1 H, 6-H^B), 7.31−7.37 (m, 2 H, 8-H, 10-H), 7.41 (d, ^3J = 8.0 Hz, 1 H, 11-H), 7.54 (d, ^4J = 2.3 Hz, 1 H, 12-H); ^{13}C NMR (CD_3CN) δ 17.1 (C-2), 21.4 (C-3), 24.3 (C-1), 32.1 (C-7), 33.0 (C-6a), 49.4 (C-4), 64.4 (C-6), 128.7 (C-10), 129.8 (C-8), 131.7 (C-11a), 132.3 (C-11), 133.7 (C-12), 137.0 (C-9), 139.3 (C-7a), 139.6 (C-12a), 178.3 (C-12b), triflate-C not observed. Anal. Calcd for $C_{17}H_{17}ClF_3NO_3S$ (407.84): C, 50.07; H, 4.20; N, 3.43. Found: C, 50.03; H, 4.27; N, 3.33.

4,4a,5,7,8,9,10,11-Octahydroazepino[2,1-*a*]thieno[3,2-*f*]-isoindol-6-ium Trifluoromethanesulfonate (2g). Thermal treatment of **1g** (3.94 g, 10.0 mmol) and workup were done as described above for **2c**. Yellow crystals of **2g** (3.40 g, 86%) were obtained: mp 179 °C; IR (KBr) ν = 3078 m, 3043 m, 2946 m, 2869 m, 1596 vs, 1413 s, 1264 vs, 1142, vs, 1032 vs cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.65−1.88 (m, 4 H, 8-H, 10-H), 1.89−1.98 (m, 2 H, 9-H), 2.58 (pt, ^2J = ^3J = 16.1 Hz, 1 H, 4-H^{ax}), 2.99−3.02 (m, 2 H, 11-H), 3.13−3.26 (m, 1 H, 4a−H), 3.33 (dd, ^2J = 16.1 Hz, ^3J = 8.4 Hz, 1 H, 4-H^{eq}), 3.85−4.02 (m, 3 H, 5-H^A, 7-H), 4.38 (dd, ^2J = 13.8 Hz, ^3J = 8.8 Hz, 1 H, 5-H^B), 7.14 (d, ^3J = 4.9 Hz, 1 H, 3-H), 7.74 (d, ^3J = 4.9 Hz, 1 H, 2-H), 7.76 (d, ^4J = 3.0 Hz, 1 H, 12-H); ^{13}C NMR (CD_3CN) δ 23.1 (C-10), 25.4 (C-8), 27.0 (C-11), 28.6 (C-4), 30.2 (C-9), 35.0 (C-4a), 53.6 (C-7), 65.2 (C-5), 121.8 (q, $J_{C,F}$ = 320.7 Hz, TfO$^-$), 129.2 (C-3), 131.0 (C-12), 133.6 (C-2), 134.8 (C-3a), 136.0 (C-11b), 143.0 (C-12a), 181.8 (C-11a). Anal. Calcd for $C_{16}H_{18}F_3NO_3S_2$ (393.44): C, 48.85; H, 4.61; N, 3.56. Found: C, 48.81; H, 4.65; N, 3.59.

10-Chloro-(2,3,4,5,7a,8-hexahydro-1*H*,7*H*)-azepino[2,1-*a*]benzo[*f*]isoindolium Trifluoromethanesulfonate (2h). Thermal treatment of **1h** (4.22 g, 10.0 mmol) at 190 °C for 1.5 h and workup were done as described above for **2c**. Colorless crystals of **2h** (3.32 g, 79%) were obtained: mp 183 °C; IR (KBr) ν 2936 m, 2857 w, 1623 m, 1260 vs, 1150 vs, 1032 vs cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.63−1.88 (m, 6 H, 2-H, 3-H, 4-H), 2.76 (pt, ^2J = ^3J = 15.3 Hz, 1 H, 8-H^{ax}), 2.97−3.09 (m, 2 H, 1-H), 3.11−3.23 (m, 2 H, 7a−H, 8-H^{eq}), 3.86−4.04 (m, 3 H, 5-H, 7-H^A), 4.40 (dd, ^2J = 14.0 Hz, ^3J = 8.3 Hz, 1 H, 7-H^B), 7.31−7.38 (m, 2 H, 9-H, 11-H), 7.44 (d, ^3J = 8.1 Hz, 1 H, 12-H), 7.64 (d, ^4J = 2.5 Hz, 1 H, 13-H); ^{13}C NMR (CD_3CN) δ 22.8 (C-2), 25.1 (C-4), 27.2 (C-1), 30.1 (C-3), 32.0 (C-8), 33.7 (C-7a), 53.9 (C-5), 66.1 (C-7), 122.2 (q, $J_{C,F}$ = 320.6 Hz, TfO$^-$), 128.8 (C-11), 129.8 (C-9), 131.8 (C-12a), 132.7 (C-12), 135.5 (C-13), 137.4 (C-10), 139.5 (C-8a), 140.6 (C-13a), 183.2 (C-13b). Anal. Calcd for $C_{18}H_{19}ClF_3NO_3S$ (421.86): C, 51.25; H, 4.54; N, 3.32. Found: C, 51.12; H, 4.52; N, 3.22.

6,6a-Dihydro-7*H*-benzo[*f*]pyrido[2,1-*a*]isoindolium Trifluoromethanesulfonate (5). Thermal treatment of **4** (1.00 g, 2.7 mmol) at 190 °C for 50 h and workup were done as described for **2c**. Pale-yellow crystals of **5** (0.73 g, 73%) were obtained: mp 186 °C; IR (KBr) ν 3081 m, 3043 m, 1656 s, 1469 m, 1278 vs, 1267 vs, 1155, vs, 1028 vs cm^{-1}; ^{1}H NMR (CD_3CN) δ 2.82 (pt, ^2J = ^3J = 15.3 Hz, 1 H, 7-H^{ax}), 3.28 (dd, ^2J = 15.3 Hz, ^3J = 6.8 Hz, 1 H, 7-H^{eq}), 3.36−3.46 (m, 1 H, 6a−H), 4.49 (dd, ^2J = 13.1 Hz, ^3J = 9.1 Hz, 1 H, 6-H^A), 5.16 (dd, ^2J = 13.1 Hz, ^3J = 9.1 Hz, 1 H, 6-H^B), 7.29−7.38 (m, 3 H, 8-H, 9-H, 10-H), 7.42 (d, 1 H, 11-H), 7.72 (d, ^4J = 3.1 Hz, 1 H, 12-H), 7.81 (pt, 1 H, 3-H), 8.26 (d, 1 H, 1-H), 8.42 (pt, 1 H, 2-H), 8.71 (d, 1 H, 4-H); ^{13}C NMR (CD_3CN) δ 32.4 (C-7), 35.0 (C-6a), 63.4 (C-6), 122.1 (C-1), 122.2 (q, $J_{C,F}$ = 321.0 Hz, TfO$^-$), 126.6 (C-3), 128.7 (C-10), 129.7 (C-8), 130.2 (C-11), 130.6 (C-12), 131.3 (C-9), 133.4 (C-11a), 134.9 (C-12a), 136.3 (C-7a), 142.5 (C-4), 146.2 (C-2), 152.9 (C-12b). Anal. Calcd for $C_{17}H_{14}F_3NO_3S$ (369.4): C, 55.28; H, 3.38; N, 3.79. Found: C, 54.96; H, 3.60; N, 3.72.

X-ray Crystal Structure Determination of 2e.[25] Crystal data: $C_{17}H_{17}ClF_3NO_3S$; triclinic space group $P\bar{1}$, a = 7.663(1), b = 9.899(1), c = 12.463(2) Å, α = 82.50(1)°, β = 78.94(1)°, γ = 77.37(1)°; V = 901.4(2) Å^3; Z = 2; d_{calcd} = 1.503 Mg/m^3, μ(Mo Kα) = 0.37 mm^{-1}. Data collection: T = 223 K, crystal size 0.46 × 0.23 × 0.15 mm^3, diffractometer Stoe-IPDS, radiation Mo Kα; Θ range 1.67−24.11°; 6302 reflections collected, 2664 independent reflections (R_{int} = 0.0426). Structure solution and refinement: structure solution by direct methods (program SHELXS-97), full-matrix least-squares refinement on F^2 (program SHELXL-97) with 2664 reflections and 254 variables (6 restraints). Hydrogen atoms are in calculated positions and were refined as riding atoms. R = 0.0737, $wR2$ = 0.1477 for all reflections; R = 0.0524, $wR2$ = 0.1365 for 1922 reflections with $I > 2\sigma(I)$); residual electron density ≤ 0.49 e Å^{-3}. The tetrahydropyridinium ring is

(25) The authors have deposited atomic coordinates, bond lengths, and bond angles for the structure of **2e** with the Cambridge Crystallographic Data Centre (CCDC 155760). The data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

disordered, and two conformations for the moiety C1−C2−C3−C4 in this ring were refined (occupancy factors of 0.65 and 0.35, respectively).

Acknowledgment. This work was supported financially by the Deutsche Forschungsgemeinschaft. A graduate fellowship to H.-G.H. by the State of Baden-Württemberg is gratefully acknowledged.

Supporting Information Available: Geometry optimization of iminium ions **1b** and **1e** (PM3 and MMFF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO015546Y