Ring Expansion vs. Cleavage of the Exocyclic Double Bond of 2-Cycloalkylidenedihydrobenzothiazoles and -benzimidazoles by Methanesulfonyl Azide

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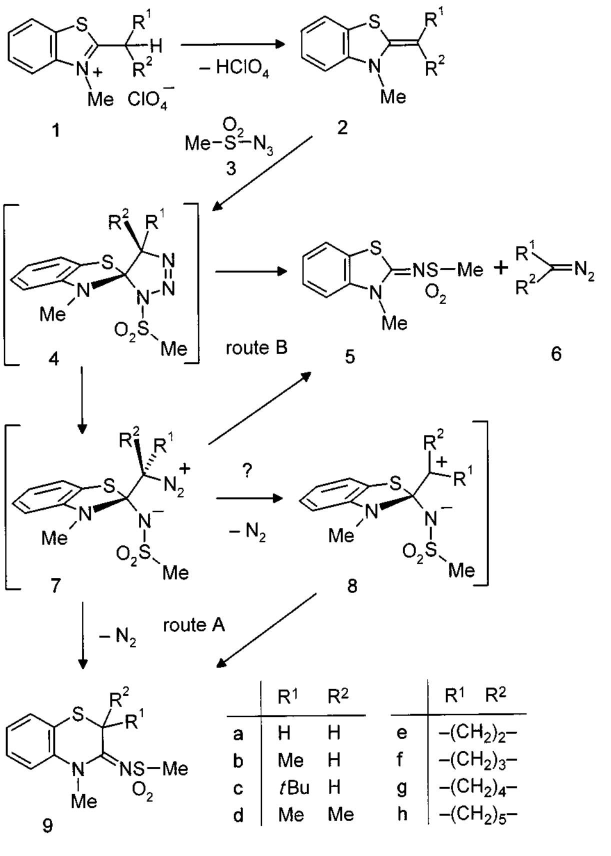
Deprotonation of the 2-cycloalkylbenzothiazolium perchlorates **1f–h** with sodium hydride in the presence of methanesulfonyl azide (**3**) affords the spirocyclic dihydro-1,4-benzothiazines **9f–h** together with small amounts of the 2-iminobenzothiazole **5**. The 2-cycloalkylidenedihydrobenzimidazoles **11e–h** are generated by deprotonation with potassium hydride from the corresponding 2-cycloalkylbenzimidazolium salts **10e–h**, and trapped with **3** to yield the zwitterions **12e–h**. Whereas **12h** is thermally unstable, **12e–g** are isolated and thermolysed at 20–80 °C. The cyclopropyl zwitterion **12e** decomposes in an ill-defined way, only at temperatures above 80 °C. In contrast, **12f,g**, and, in particular, **12h**, decompose more readily to furnish the products of ring expansion (**13f–h**) and those of a [3 + 2] cycloreversion (**6** and **14**) of intermediate spirocyclic triazolines. Products that might be indicative of the intervention of hypothetical zwitterions of type **8** cannot be detected.

Introduction

A number of heterocyclic ketene *N,X*-acetals, e.g. of type **2a–d** and **11b–d**, readily add electrophilic azides such as methanesulfonyl azide (**3**, Schemes 1 and 2). While 2-alkylidenedihydrobenzimidazoles **11b–d** yield zwitterions **12** (Scheme 2), which can be isolated in most cases,[2] the adducts of the benzothiazole derivatives **2a–d** (and other heterocycles) with **3** immediately loose molecular nitrogen and undergo ring expansion, or are cleaved into *N*-sulfonylimine **5** and a diazo compound **6**. The zwitterions **12b–d** behave likewise, but in general only at higher temperatures. Previous studies have uncovered structural features that favour the useful ring expansion reaction over the undesired diazoalkane cleavage:[3,4] Soft heteroatoms like sulfur and selenium, whose tendency to form bridged cations is well-known,[5] and one alkyl group or, better, two methyl groups at the exocyclic carbon atom of the heterocyclic *N,X*-acetals as in **2b–d** and **11b–d** favour ring expansion. We have now used two representative 2-alkylidene heterocycles, whose exocyclic carbon atom is a member of a cycloalkane ring, to study the effect of the size of that ring. The cyclopropylidene compounds **2e** and **11e** were particularly intriguing because of the notorious reluctance of the cyclopropane ring to undergo nucleophilic substitution reactions,[6] and the possibility of detecting products that would be indicative of ring opening of hypothetical cyclopropyl cations,[7] e.g. **8e**.



	R¹	R²		R¹ R²
a	H	H	e	$-(CH_2)_2-$
b	Me	H	f	$-(CH_2)_3-$
c	*t*Bu	H	g	$-(CH_2)_4-$
d	Me	Me	h	$-(CH_2)_5-$

Scheme 1

Cycloalkylidenedihydrobenzothiazoles **2e–h** were generated by deprotonation of the benzothiazolium perchlorates **1e–h** with sodium hydride, and trapped in situ by methanesulfonyl azide. Products were separated and purified by flash chromatography. The structures of new compounds are based on elemental analyses (Table 4) and spectroscopic evidence (Table 2 and Table 3). Except for the cyclopropylidene compound **2e**, satisfactory material balances were obtained in all cases. Again with exception of **2e**, the spirocyclic dihydrobenzothiazines **9f–h** were the major products. Only about 10% of the *N*-sulfonyliminodihydrobenzothia-

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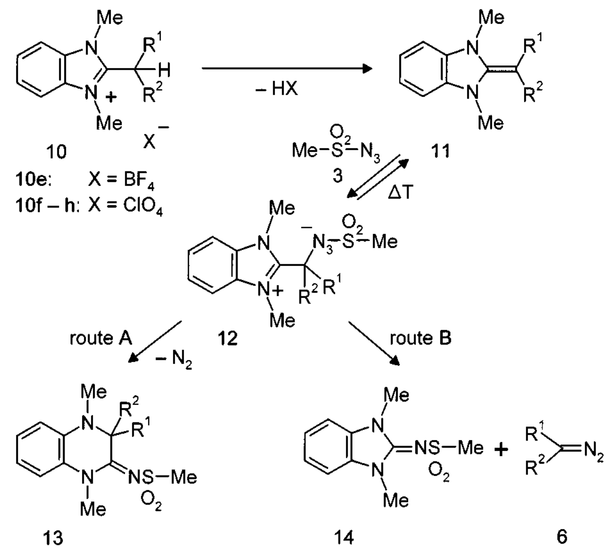

Scheme 2

zole **5** was formed by cleavage of the carbon–carbon double bond in **2f–h.** In contrast, no trace of a ring expansion product was obtained from the cyclopropylidene compound **2e**. Instead, only a moderate yield of **5** was obtained. The results are summarised in Table 1.

Solutions of the cycloalkylidenedihydrobenzimidazoles **11e–h** in tetrahydrofuran were prepared by deprotonation of the benzimidazolium salts **10e–h** with potassium hydride, which were subsequently treated with methanesulfonyl azide. Like the isopropylidene compound **11d**,[3] the cyclohexylidene derivative **11h** formed a highly unstable zwitterion **12h**, which could be characterised only at low temperatures (Table 2 and Table 3) because of rapid decomposition at temperatures above 0 °C. The other zwitterions **12e–g** were prepared at room temperature and isolated as almost colourless solids in good yields (Table 1). These compounds could be kept at 0 °C or even at room temperature (**12e**, **f**) without decomposition.

The thermal stability of the isolated zwitterions **12e–g** increased with decreasing size of the cycloalkyl ring. While thermal decomposition of the cyclopropyl compound **12e** required heating in boiling acetonitrile for several hours, the cyclobutyl zwitterion **12f** decomposed at 60 °C, and a solution of the cyclopentyl zwitterion **12g** began to evolve nitrogen already at temperatures as low as 0 °C.

Except for the cyclopropyl zwitterion **12e**, which yielded, besides numerous unidentified compounds, small amounts of the cleavage products **10e** and **14** (1:1, ^{1}H NMR), thermal decomposition of **12f–h** resulted in a reasonable material balance. Ring expansion to the spirocyclic tetrahydroquinoxalines **13f–h** occurred to the same or greater extent as cleavage to the *N*-methylsulfonylimine **14**, rendering this sequence as a useful ring expansion method (Table 1). The occurrence of benzimidazolium ions, which would indicate reversibility of the zwitterion formation,[2] was not observed when the thermolysis of **12f–h** was monitored by proton spectroscopy. This is a further difference between these zwitterions and the cyclopropyl zwitterion **12e**.

Table 1. Products, yields obtained in preparative experiments, melting points after recrystallisation from ethanol, and ratios of products (route **A**:route **B**) as calculated from integration of the methyl signals in proton spectra recorded for solutions of the crude products; ranges of decomposition for the crude zwitterions are given in brackets

Precursor	[a]	Base	Temp. [°C]	Products	Yield [%]	M. p. [°C]	Route **A** : Route **B**
1e	THF	NaH	25	**5**	57	166 – 168 [b]	
1f	THF	NaH	25	**5** **9f**	9 74	 144 – 146	9 : 1
1g	THF	NaH	25	**5** **9g**	8 82	 139 – 141	9 : 1
1h	THF	NaH	25	**5** **9h**	10 80	 135 – 136	9 : 1
10e	THF	KH	25	**12e**	63	(112 – 120)	
10f	THF	KH	25	**12f**	95	(126 – 128)	
10g	THF	KH	25	**12g**	72	(85 – 95)	
12e	AN		82	**14**[c]	7	205 – 206 [d]	
12f	T		61	**13f** **14**	49 44	124 – 126	1 : 1
	T		60	**13f, 14**	[e]		1 : 1
	T		25		[e]		1 : 1
	AN		60		[e]		7 : 3
12g	T		61	**13g** **14**	56 25	158 – 160	7 : 3
	T		25	**13g, 14**	[e]		7 : 3
10h	THF	KH	25	**13h** **14**	37 27	127 – 129	6 : 4
12h	T		25	**13h, 14**	[e]		7 : 3

[a] Solvents: AN = acetonitrile or [D$_3$]acetonitrile, T = trichloromethane or [D]trichloromethane, THF = tetrahydrofuran. – [b] Ref.:[3] m.p. 164–165 °C. – [c] Equal amounts of the cation **10e** and the imine **14** were observed besides unidentified products (^{1}H NMR). – [d] Ref.:[3] m.p. 206–208 °C. – [e] Small-scale experiment, carried out in an NMR sample tube.

The present results extend the range of structural parameters that allow ring expansion of heterocyclic *N,X*-acetals with electrophilic azides. With the exception of the first members of the series, viz. the 2-cyclopropylidene heterocycles **2e** and **11e**, the larger cycloalkylidene compounds **2f–h** and **11f–h** afford reasonable to good yields of spirocyclic products that are otherwise difficult to come by. Due to the complexity of the various conceivable mechanistic schemes, all of which involve several intermediates and elementary steps, a rationalisation of the influence of substituents disclosed in the present and the foregoing studies[2–44] must remain speculative. We note that a 1,2 shift to a cyclopropyl carbon atom bearing a very good leaving group is disfavoured, as are S$_N$2 reactions at the cyclopropane ring.[6] These features may be invoked to rationalise the chemical behaviour of the cyclopropyl compounds **2e** and **12e**. The relatively stable zwitterions **12b**, **c**, and **12e** prefer the two modes of decomposition over ring expansion, viz. reversion of their formation, thus affording eventually benzimidazolium ions, and cyclisation to the spirocyclic intermediates

Table 2. Chemical shifts (δ values) in ^{1}H NMR spectra

Cpd.	$(CH_2)_n$	CH (mc)	NMe	SO_2Me	Ar H	[a]
1e	1.4 – 1.9	3.08	4.54		7.8 – 8.4	A
1f	2.0 – 2.9	4.67	4.35		7.8 – 8.5	A
1g	1.8 – 2.7	4.22	4.46		7.8 – 8.3	A
1h	1.3 – 2.5	3.88	4.50		7.8 – 8.5	A
9f	1.6 – 3.1		3.61	3.16	7.0 – 7.4	T
9g	1.6 – 2.4		3.83	3.15	7.0 – 7.4	T
9h	1.2 – 2.0		3.82	3.15	7.0 – 7.4	T
10e	1.1 – 1.5	2.13	4.02		7.65 7.77[b]	AN
10f	1.9 – 2.1	4.22	3.93		7.62 7.75[b]	AN
10g	1.8 – 2.4	3.84	3.98		7.64 7.78[b]	AN
10h	1.4 – 2.1	3.45	4.04		7.64 7.78[b]	AN
12e	1.39 1.78[c]		4.10	2.80	7.55	T
12f	1.8 – 3.0		4.05	2.84	7.51	T
12g[d]	0.8 – 2.4		4.11	2.77	7.60	T
12h[d]	1.2 –2.4		4.03	2.75	7.4 – 7.7	T
13f	1.7 – 2.6		2.56 3.76	3.18	6.9 – 7.2	T
13g	1.6 – 2.3		2.81 3.82	3.13	6.8 – 7.3	T
13h	1.2 – 1.9		2.76 3.77	3.14	7.0 – 7.2	T

[a] Solvents: A = [D$_6$]acetone, AN = [D$_3$]acetonitrile, T = [D]trichloromethane. – [b] AA′BB′ spin system. – [c] AA′XX′ spin system. – [d] The spectrum was recorded at a temperature of –50 °C.

Table 3. Chemical shifts (δ values) in ^{13}C NMR spectra

Cpd.	$(CH_2)_n$	CH	NMe	SO_2Me	C=N	Ring-C			[a]
						CH		quat. C	
1e	14.2	13.6	37.0		184.2	117.3 129.2	125.1 130.5	128.6 143.5	A
1f	19.2 29.4	36.2	36.9		185.9	117.6 129.2	125.2 130.7	129.6 143.8	A
1g	27.4 35.6	43.2	38.5		187.9	118.8 130.42	126.2 131.7	130.37 144.8	A
1h	26.52 26.87 34.0	41.6	38.0		187.4	118.6 130.03	125.9 131.4	130.34 144.1	A
10e	7.1	5.2	31.6		153.3	113.6	127.5	132.6	AN
10f	20.2 31.1	32.1	33.3		155.4	113.4	127.3	131.1	AN
10g	27.6 31.1	35.4	32.0		156.8	113.5	127.4	133.2	AN
10h	25.9 26.7 28.7	36.8	33.6		156.1	113.6	127.5	133.1	AN
		quat. C							
9f	15.9 31.4	48.8	38.8	44.8	161.2	119.3 127.2	124.4 129.2	126.2 139.9	T
9g	24.6 36.6	56.6	42.7	45.4	162.1	119.3 127.7	125.23 129.1	125.48 140.9	T
9h	24.5 25.6 31.5	49.2	41.8	44.8	171.2	117.7 127.2	124.7 128.7	121.7 139.6	T
12e	14.8	37.0	33.0	38.7	156.2	112.0	126.5	131.5	T
12f	18.3 34.02	63.0	33.75	38.9	156.0	111.8	126.3	131.9	T
12g[b]	25.1 36.6	69.8	34.8	38.8	158.1	111.8	126.0	131.9	T
12h[b]	22.3 25.5 33.5	63.5	35.2	38.5	158.9	11.9	126.0	132.1	T
13f	14.1 28.3	64.8	34.1 38.4	44.9	159.4	116.6 121.3	117.3 125.3	132.1 138.4	T
13g	25.0 33.99	72.1	34.34 39.6	45.0	162.0	116.44 120.7	116.72 125.5	132.1 139.3	T
13h	21.5 25.6 30.6	60.2	37.2 38.3	45.0	159.4	115.4 123.0	122.3 125.1	133.7 137.8	T

[a] Solvents: see Table 2. – [b] The spectrum was recorded at a temperature of –50 °C.

followed by their cleavage into *N*-methylsulfonylimine **14** and diazo compounds **6**.

Experimental Section

General: Yields, melting points, and ratios of products: Table 1. – ^{1}H NMR: Table 2. – ^{13}C NMR: Table 3. – Molecular formulae and masses, and elemental analyses: Table 4. – Melting points: Kofler apparatus from Reichert, Vienna. – ^{1}H and ^{13}C NMR: Bruker AC 200 and AC 250. – Flash chromatography: (40 × 3)cm glass column packed with silica gel 32–63 µm (ICN Biomedicals), UV detector Knauer 87.00 (λ = 254 nm), 1.5 bar N_2. – MS (70 eV): Finnigan MAT 8200.
Tetrahydrofuran was dried with powdered KOH and distilled from NaH. Petroleum ether (PE), boiling range 50–70 °C, and ethyl acetate (EA) were distilled from P_2O_5. Acetonitrile was distilled from CaH_2. [D$_3$]Acetonitrile was dried with CaH_2. – NaH and KH, suspended in paraffin oil, were washed three times with pentane and dried in a stream of Ar. – Experiments involving ketene *N,X*-acetals were carried out in dry solvents under Ar (99.998%). – The following compounds were available from previous work: **1e–h** (X = ClO_4),[8] **3**,[3] **10f–h** (X = ClO_4).[8]

2-Cyclopropyl-1*H*-benzimidazole: A mixture of *o*-phenylenediamine (15.7 g, 0.145 mol), cyclopropane carboxylic acid (25.0 g, 0.29 mol) and 3 drops of conc. sulfuric acid was heated for 8 h. The temperature of the mixture was gradually raised from 120 °C to 220 °C, and water was allowed to distil. After cooling, the solid product was washed with a sat. aq. solution of $KHCO_3$ and water until the washings were neutral. Recrystallisation from ethanol/water (1:1) gave colourless needles (12.0 g, 52%), m.p. 232–234 °C (m.p. 234–236 °C[9]).

2-Cyclohexyl-1*H*-benzimidazole: Prepared from cyclohexane carboxylic acid, as described in the preceding experiment for 2-cyclopropyl-1*H*-benzimidazole, and recrystallised from ethanol/water (2:1). Colourless needles (23.5 g, 81%), m.p. 281–282 °C (m.p. 281–282 °C[10]).

2-Cyclopropyl-1,3-dimethylbenzimidazolium Tetrafluoroborate (10e, X = BF_4): Dimethyl sulfate (12.3 g, 96 mmol) was added dropwise to a stirred suspension of $NaHCO_3$ (9.7 g, 116 mmol) and 2-cyclopropyl-1*H*-benzimidazole (6.1 g, 39 mmol) in water (40 mL).[11] The mixture was stirred for 14 h, and the solid removed by filtra-

Table 4. Molecular formulae, masses, and elemental analyses

Cpd.	Formula	Molecular mass		Elemental analysis			
				C	H	N	S
9f	$C_{13}H_{16}N_2O_2S_2$	296.4	Calc.	52.67	5.45	9.45	21.63
			Found	52.35	5.61	9.35	21.18
9g	$C_{14}H_{18}N_2O_2S_2$	310.5	Calc.	54.16	5.86	9.08	20.65
			Found	54.22	6.00	9.00	20.10
9h	$C_{15}H_{20}N_2O_2S_2$	324.5	Calc.	55.52	6.23	8.64	
			Found	55.48	6.80	8.53	
10eBF$_4$	$C_{12}H_{15}BF_4N_2$	274.7	Calc.	52.59	5.22	10.22	
			Found	52.08	5.52	10.09	
13f	$C_{14}H_{19}N_3O_2S$	293.4	Calc.	57.32	6.53	14.32	10.93
			Found	57.56	6.61	14.23	10.85
13g	$C_{15}H_{21}N_3O_2S$	307.4	Calc.	58.61	6.89	13.67	10.43
			Found	58.11	6.96	13.59	10.90
13h	$C_{16}H_{23}N_3O_2S$	321.4	Calc.	59.79	7.21	13.07	9.97
			Found	59.62	7.34	12.83	9.66

tion. A sat. aq. solution of $NaBF_4$ (20 mL), acidified with 3 drops of aq. HBF_4 (50%), was added dropwise to the filtrate to afford colourless crystals, 9.8 g (93%). Recrystallisation from ethanol/water (10:1) furnished colourless needles (6.0 g, 57%), m.p. 188–190 °C.

In situ Trapping of the Ketene *N,S*-Acetals 2e–h with Methanesulfonyl Azide (3). – General Procedure: A suspension of powdered **1** (X = ClO_4, 3.3 mmol), NaH (0.12 g, 5 mmol), and **3** (0.42 g, 3.5 mmol) in tetrahydrofuran (30 mL) was stirred in an 80-mL centrifuge tube, equipped with a septum, until the gas evolution had ceased (1 d). The solid material was removed with the help of a centrifuge and washed with tetrahydrofuran (5 mL). The solvent was distilled in vacuo to afford a solid residue which was purified and/or separated by flash chromatography (PE/EA, 1:1). The crude products obtained from the different fractions by distillation of the solvent in vacuo were recrystallised from ethanol to yield colourless crystals.

2,3-Dihydro-3-methyl-2-[*N*-(methylsulfonyl)imino]benzothiazole (5): From **1e**. Flash chromatography gave colourless crystals (0.46 g, 57%), m.p. 158–165 °C.

3,4-Dihydro-4-methyl-3-[*N*-(methylsulfonyl)imino]-2*H*-1,4-benzothiazine-2-spiro-1′-cyclobutane (9f) and 5: From **1f**. Flash chromatography gave a colourless solid (**9f**, 0.74 g, 76%, m. range 90–130 °C). The second fraction yielded colourless crystals (**5**, 80 mg, 10%, m. range 100–140 °C). – **9f:** MS; *m/z* (%): 296 (84) [M$^+$], 268 (51), 253 (72), 237 (27), 217 (86) [M$^+$ – SO$_2$Me], 216 (27), 202 (18), 200 (36), 189 (100), 162 (21), 155 (22), 149 (34), 137 (39), 136 (85).

3,4-Dihydro-4-methyl-3-[*N*-(methylsulfonyl)imino]-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopentane (9g) and 5: From **1g**. Flash chromatography gave colourless prisms (**9g**, 0.80 g, 82%, m.p. 130–139 °C). The second fraction yielded colourless crystals (**5**, 70 mg, 9%, m. range 130–160 °C). – **9g:** MS; *m/z* (%): 310 (26) [M$^+$], 231 (21) [M$^+$ – SO$_2$Me], 217 (16), 216 (100), 138 (19), 137 (20), 136 (29).

3,4-Dihydro-4-methyl-3-[*N*-(methylsulfonyl)imino]-2*H*-1,4-benzothiazine-2-spiro-1′-cyclohexane (9h) and 5: From **1h**. Flash chromatography gave a colourless solid (**9h**, 0.78 g, 80%, m.p. 130–133 °C). The second fraction yielded colourless crystals (**5**, 80 mg, 10%, m.p. 164–166 °C). – **9h:** MS; *m/z* (%): 324 (42) [M$^+$], 246(18), 245 (100) [M$^+$ – SO$_2$Me], 230 (48), 204 (16), 150 (10), 138 (18), 137 (17), 136 (32).

Synthesis of the Zwitterions 12. – General Procedures: a) Preparative Experiments: A suspension of a powdered 2-cycloalkyl-1,3-dimethylbenzimidazolium salt (**10e–g,** 3 mmol) and KH (0.24 g, 6 mmol) in tetrahydrofuran (30 mL) was stirred in an 80-mL centrifuge tube, equipped with a septum, until the gas evolution had ceased (1–2 days). The solid material was removed with the help of a centrifuge and washed with tetrahydrofuran (5 mL). The combined solutions were transferred via syringe into a 100-mL flask, and a solution of **3** (0.40 g, 3.3 mmol) in tetrahydrofuran (2 mL) was added dropwise with stirring. After stirring at room temperature for 1 h, the precipitate was collected by filtration. Yields and temperature ranges of decomposition are listed in Table 1.

b) Small-Scale Experiments at Low Temperatures: A suspension of a powdered 2-cycloalkyl-1,3-dimethylbenzimidazolium salt (**10g**, **h**, 0.2 mmol) and KH (40 mg, 1 mmol) in [D$_8$]tetrahydrofuran (0.7 mL) was stirred for 1 day in a 10-mL centrifuge tube, equipped with a septum. The solid material was removed with the help of a centrifuge. The solution was transferred into an NMR sample tube and frozen by cooling in liquid nitrogen. Careful attention was paid to avoid condensation of Ar. Azide **3** (24 mg, 0.2 mmol) was placed on top of the frozen solution. The mixture was placed into a bath of –40 °C, briefly shaken and kept therein for 3 h. The pale brown precipitate was collected with the help of a centrifuge at –30 °C and dissolved in cold [D]trichloromethane (0.7 mL, –50 °C).

1-[1-(1,3-Dimethylbenzimidazol-2-ylio)cyclopropyl]-3-methylsulfonyltriazenide (12e): a) Pale brown powder (0.58 g) from **10e**.

1-[1-(1,3-Dimethylbenzimidazol-2-ylio)cyclobutyl]-3-methylsulfonyltriazenide (12f): a) Pale yellow powder (0.93 g) from **10f**.

1-[1-(1,3-Dimethylbenzimidazol-2-ylio)cyclopentyl]-3-methylsulfonyltriazenide (12g): a) Pale yellow powder (0.72 g) from **10g**.

b) Proton and ^{13}C NMR spectra were recorded at –50 °C. Gas evolved at room temperature. Subsequently, the proton spectrum indicated the presence of **13g** and **14** (7:3). The solvent was evaporated in a stream of N_2, and the solid residue was dissolved in [D$_3$]acetonitrile. The proton spectrum showed no signals of **10g**.

1-[1-(1,3-Dimethylbenzimidazol-2-ylio)cyclohexyl]-3-methylsulfonyltriazenide (12h): b) Proton and ^{13}C NMR spectra were recorded at –50 °C. Gas evolved at room temperature. Subsequently, the proton spectrum indicated the presence of **13h** and **14** (7:3). The solvent was evaporated in a stream of N_2, and the solid residue was dissolved in [D$_3$]acetonitrile. The proton spectrum showed no signals of **10h**.

Thermolysis of the Zwitterions 12. – General Procedures: a) Preparative Experiments: A suspension of **12e–g** (2.5 mmol) in acetonitrile or trichloromethane was heated under reflux until the evolution of gas had subsided. The solution was immediately placed on top of a silica gel column followed by flash chromatography with ethyl acetate. Distillation of the solvent in vacuo from the various fractions and recrystallisation of the residues from ethanol yielded colourless crystals. Yields and melting points are listed in Table 1.

b) Small-Scale Experiments. Solutions of **12e–g** (0.1 mmol) in [D$_3$]acetonitrile or [D]trichloromethane (0.7 mL) contained in NMR sample tubes were heated while the conversion was monitored by proton spectroscopy until **12** had disappeared. The ratios of **13**:**14** (route **A**:route **B**) were calculated from integration of the methyl signals. Temperatures and results are listed in Table 1.

Thermolysis of 12e: a) Acetonitrile (5 mL), 5 h. Flash chromatography gave colourless crystals (**14**, 42 mg, 7%, m.p. 200–204 °C).

b) [D$_3$]Acetonitrile, 5 h, 80 °C. The proton spectrum indicated the presence of **14** and the cation **10e** (1:1) as well as several unidentified compounds.

Thermolysis of 12f: a) Trichloromethane (25 mL), 2 h. Flash chromatography gave yellow crystals (**13f**, 0.36 g, 49%, m.p. 124–126 °C), and colourless crystals as second fraction (**14**, 0.26 g, 44%, m.p. 205–206 °C). – **13f:** MS; *m*/*z* (%): 293 (2) [M$^+$], 265 (20), 250 (10), 215 (129), 214 (81) [M$^+$ – SO$_2$Me], 187 (15), 186 (100), 146 (16), 154 (13).

b) [D$_3$]Acetonitrile, 60 °C, 2 h. The proton spectrum indicated the presence of **13f** and **14** (7:3) as well as a small amount of **10f**. – [D]Trichloromethane, 60 °C, 1.5 h. The proton spectrum indicated the presence of **13f** and **14** (1:1). The solvent was evaporated in a stream of N$_2$. The proton spectrum of the solid residue, dissolved in [D$_3$]acetonitrile, showed the presence of **13f** and **14** (1:1), but no signals of **10f**. The same result was obtained when the solution of **12f** in [D]trichloromethane was kept for 2 weeks at room temperature.

Thermolysis of 12g: a) Trichloromethane (20 mL), 2 h. Flash chromatography gave colourless crystals (**13g**, 0.42 g, 56%, m.p. 150–157 °C), and colourless crystals as second fraction (**14**, 0.15 g, 25%, m.p. 200–204 °C). – **13g:** MS; *m*/*z* (%): 307 (12) [M$^+$], 229 (16), 228 (100) [M$^+$ – SO$_2$Me], 187 (15), 160 (9), 159 (19).

1,2,3,4-Tetrahydro-1,4-dimethyl-2-[*N*-(methylsulfonyl)imino]-quinoxalin-3-spiro-1′-cyclohexane (13h): A suspension of powdered **10h** (X = BF$_4$, 0.95 g, 3 mmol), KH (0.24 g, 6 mmol) in tetrahydrofuran (30 mL) was stirred in an 80 mL centrifuge tube, equipped with a septum, until the gas evolution had ceased (1 day). The solid material was removed with the help of a centrifuge and washed with tetrahydrofuran (5 mL). The combined solutions were transferred via syringe into a 100 mL flask, and a solution of **3** (0.40 g, 3.3 mmol) in tetrahydrofuran (2 mL) was added dropwise with stirring. The mixture was stirred at room temperature for 1 h. Flash chromatography of the resulting solution with EA gave, as first fraction, a yellow oil (**13h**, 0.61 g), and colourless crystals as second fraction (**14**, 0.19 g, m.p. 203–205 °C). Recrystallisation from ethanol afforded colourless crystals (**13h**, 0.36 g). – **13h:** MS; *m*/*z* (%): 321 (11) [M$^+$], 234 (18), 242 (100) [M$^+$ – SO$_2$Me], 184 (6), 160 (12), 159 (12).

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