Ring Expansion of Heterocyclic Ketene *N,X*-Acetals and 2-Alkylidenedihydroindoles with Methanesulphonyl Azide by [3 + 2] Cycloaddition and Subsequent Extrusion of Molecular Nitrogen[1]

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Methanesulphonyl azide (**2**) reacts readily with isolated cyclic ketene *N,X*-acetals of type **1**, viz. **10a**, **d**, **15b**, **d**, and **22a–c**, or those that are generated in situ by deprotonation of the corresponding 2-alkylbenzazolium tetrafluoroborates, i.e. **14a** → **15a**, **14b** → **15b**, and **18** → **19**. Ring-expanded products are formed by extrusion of molecular nitrogen from intermediate labile [3 + 2] cycloadducts **3** with concomitant 1,2-shift of N (route **A1** → **12**, **24**) or X (route **A2** → **16**, **20**, **21**). In addition, **3** may undergo [3 + 2] cycloreversion into *N*-sulphonylimine **5** and diazoalkane **6** (route **B** → **13**, **17**, **25**). The configurations of the cyclic *N*-sulphonylamidines **16b** and **21b**, the *N*-sulphonylimine **24** and the *N*-sulphonylamine **27** are elucidated by means of X-ray diffraction analyses. The ratio of the (useful) ring-expansion reactions vs. the unwanted formation of **5** + **6** is hardly influenced by the solvent employed and temperature of the experiment but strongly by the nature of the potential migrating atom and the substituents at the α-carbon atom.

2-Alkylidenedihydroindoles **1** (X = CR_2) and, in particular, heterocyclic ketene *N,X*-acetals **1** (X = NR, O, S) that lack electron-withdrawing groups at the α-carbon atom are strong bases and nucleophiles whose reactivity may be estimated on the basis of the chemical shift of the α-carbon atom[2,3]. Compounds of type **1** add electrophilic azides, e.g. sulphonyl azides, to yield unstable spirocyclic [3 + 2] cycloadducts **3**, either in a concerted reaction or in two steps via isolable zwitterions[4,5]. The [3 + 2] cycloadducts **3** may undergo [3 + 2] cycloreversion into *N*-sulphonylimines **5** and diazo compounds **6** (route **B**) or extrude molecular nitrogen with concomitant 1,2-shift to afford ring-expanded products **7** or **8** (routes **A**)[6,7]. The latter reactions open an expeditious access to heterocyclic systems that are otherwise less readily available. The present study was undertaken with the intent of (i) uncovering the structural features and reaction conditions that favour ring expansion, (ii) delineating the scope and limitations of the ring-expansion reactions, and (iii) deriving a rationalisation of the mechanistic dichotomy from an enlarged body of experimental observations.

Except 2-ethylidenedihydrobenzimidazole **10b**, all other isolated heterocyclic ketene *N,X*-acetals employed in this study, viz. **10a**[2,8], **d**[2], **15b**[9], **d**[2], and the 2-alkylidenedihydroindoles **22a**[10], **b**[11], and **d**[12], have already been described. We prepared the ketene *N,X*-acetals by deprotonation of the corresponding *N*-methylbenzazolium tetrafluoroborates with sodium hydride, employing the technique reported in one of the foregoing papers[2]. Three types of experiments were performed. First, the heterocyclic ketene *N,X*-acetals **10a**, **b**, **15b** and the 2-alkylidenedihydroindole **22b**, which exists as a 10:1 mixture of the *E* and *Z* diastereomer[11], were allowed to react with methanesulphonyl azide (**2**) in toluene solution at 0–25 °C. The course of these preparative experiments was monitored by HPLC, and the products were separated by crystallisation and chromatography. Their structures are based on analytical and spectroscopic evidence, in particula proton (Table 3) and carbon-13 spectra (Table 4). For several products, the configuration was determined with the help of X-ray diffraction analyses (Table 6).

In the second set of experiments, the methylenedihydrobenzimidazole **10a**, the ethylidenedihydrobenzothiazole **15b** and the methylene compounds that are notorious for their instability (**15a**[13] and **19**[14]), were generated in situ by deprotonation of the corresponding tetrafluoroborates and trapped with methanesulphonyl azide. Products, yields and some data are listed in Table 1. Finally, the course of the reaction of the ketene *N,X*-acetals **10**, **15**, and alkylidenedihydroindoles **22** with methanesulphonyl azide in various deuterated solvents was monitored by proton spectroscopy.

Results

The methylenedihydrobenzimidazole **10a** reacted with methanesulphonyl azide to afford molecular nitrogen and a black solid, which was insoluble in ethyl acetate and consisted of several unknown products as shown by the proton spectrum recorded for a solution in [D_3]acetonitrile. In

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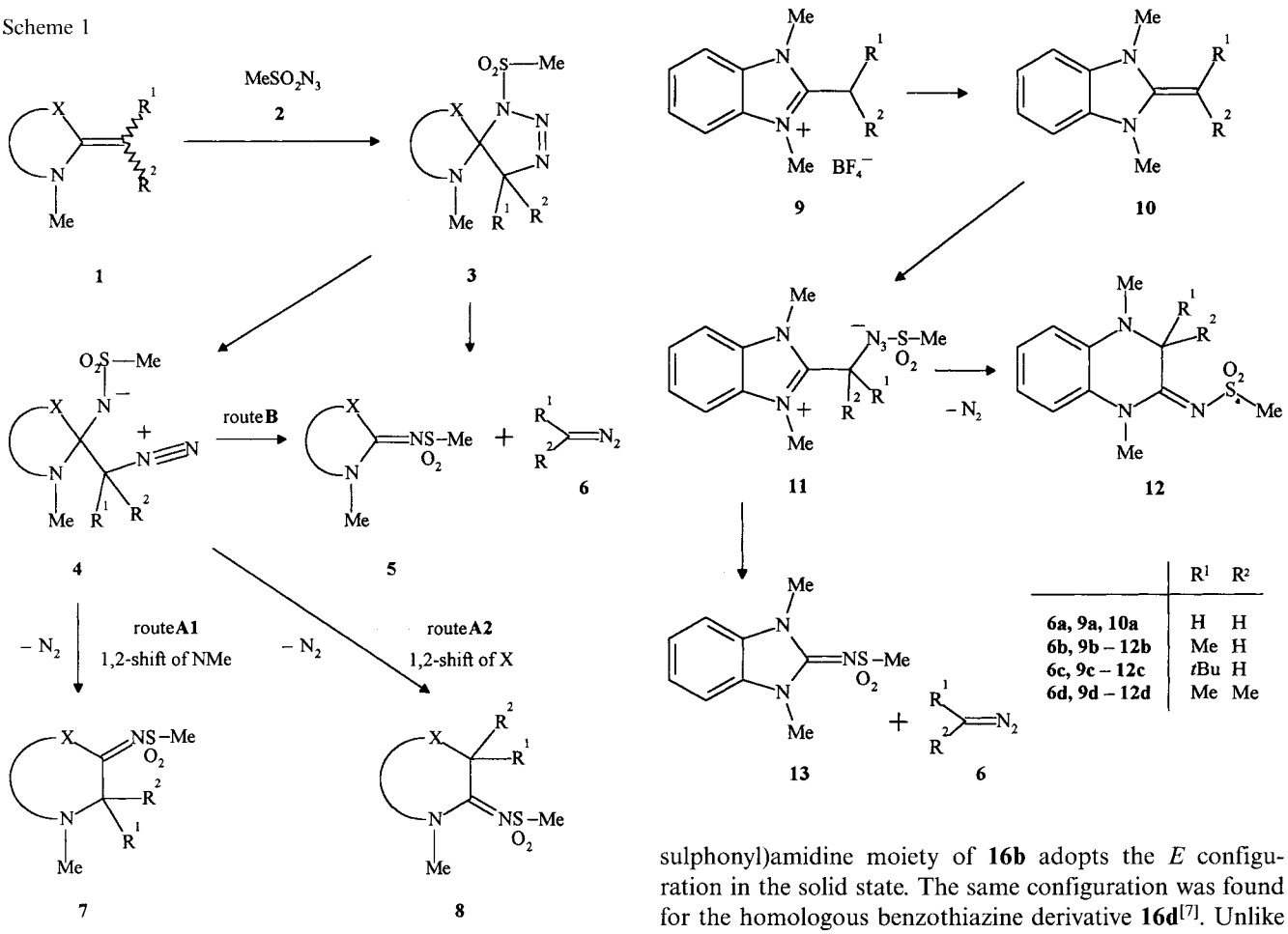
Scheme 1

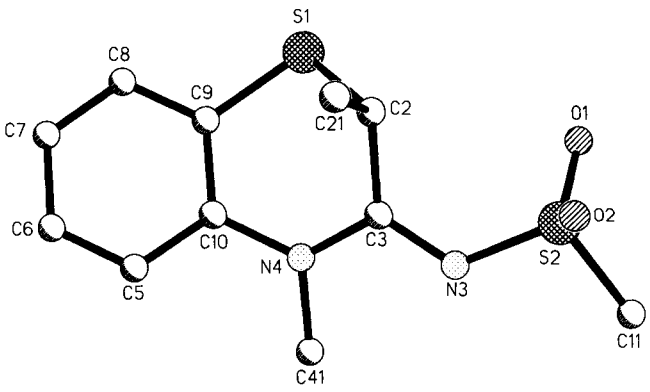


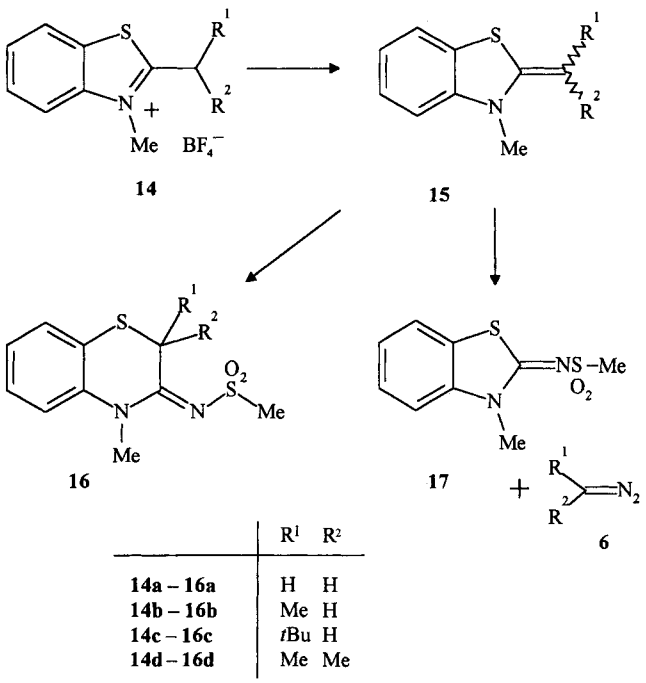
small-scale experiments carried out in NMR sample tubes, small amounts of the *N*-(methylsulphonyl)imine **13** could be detected in the mixture of products. The same compound was isolated in low yield (18%) when **10a** was generated by deprotonation of the tetrafluoroborate **9a** with sodium hydride in the presence of methanesulphonyl azide. In addition, a similar amount of 1,3-dihydro-1,3-dimethyl-2*H*-benzimidazol-2-one was formed.

Unlike the isopropylidene compound **10d**, which reacted with methanesulphonyl azide to yield the *unstable* zwitterion **11d** (decomposition above −20 °C)[5], the ethylidene compound **10b** and the neopentylidene compound **10c** afforded the surprisingly *stable* zwitterions **11b** and **c**, respectively, which precipitated from the reaction mixtures. Heating in boiling acetonitrile was required for the decomposition of **11b** and **c** which furnished the ring-expanded products **12b** and **c** in moderate yields besides the *N*-(methylsulphonyl)imine **13**. The zwitterions **11** and their thermolysis are described in detail in the following paper[5].

While the zwitterions **11b** and **c** yielded molecular nitrogen only on heating, immediate gas evolution was observed already at 0 °C in the reaction of the 2-ethylidenedihydrobenzothiazole **15b** with methanesulphonyl azide. Only two products were formed, viz. predominantly the ring-expanded imine **16b** besides small amounts of **17**. As shown by an X-ray diffraction analysis (Figure 1), the *N*-(methylsulphonyl)amidine moiety of **16b** adopts the *E* configuration in the solid state. The same configuration was found for the homologous benzothiazine derivative **16d**[7]. Unlike the methylenedihydrobenzimidazole **10a**, which can be isolated and handled without difficulty[8], the analogous methylenedihydrobenzothiazole **15a**[13] and methylenedihydrobenzoselenazole **19**[14] are notorious for their instability and readily form dimers[9,15]. Therefore, we generated both methylene compounds by deprotonation of the corresponding 2-methylbenzazolium tetrafluoroborates **14a** and **18**, respectively, with sodium hydride in the presence of methanesulphonyl azide as trapping reagent. As in the case of the other alkylidenedihydrobenzothiazoles **15b** and **15c**, **d**[7], ring expansion was accompanied by [3 + 2] cycloreversion to furnish the *N*-sulphonylimine **17**.

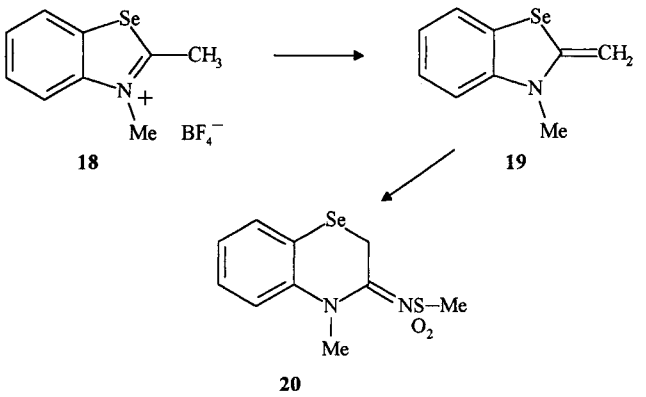
Figure 1. Perspective drawing of the 3-iminobenzothiazine **16b** showing the numbering of the atoms





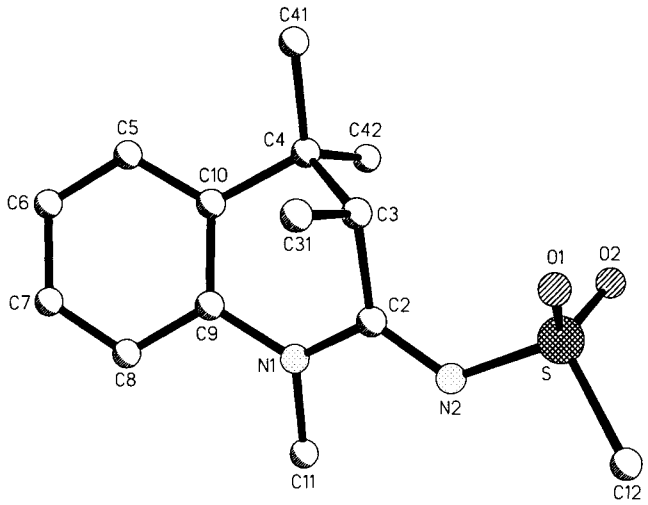
	R^1	R^2
14a – 16a	H	H
14b – 16b	Me	H
14c – 16c	*t*Bu	H
14d – 16d	Me	Me

A [3 + 2] cycloreversion corresponding to route **B** in Scheme 1 was *not* observed in the benzoselenazole series. Only the ring expanded 3-(sulphonylimino)benzoselenazine **20** was obtained in the reaction of the methylenedihydrobenzoselenazole **19**, generated in situ, and methanesulphonyl azide.



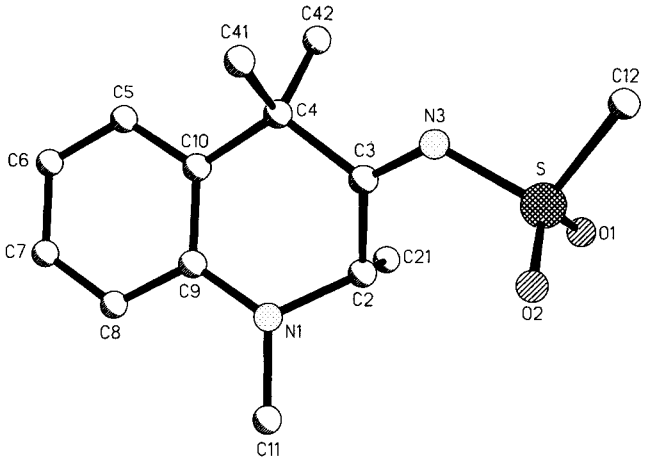
The ethylidenedihydroindoles *E*- and *Z*-**22b** showed a similar reactivity toward methanesulphonyl azide as the ethylidenedihydrobenzothiazole **15b** but furnished a complex mixture of products. The major component was the known *N*-sulfonylimine **25**[7] as result of a [3 + 2] cycloreversion of the intermediate spirocyclic adduct **23b** (see below). Surprisingly, only 2% of the 2-iminotetrahydroquinoline **21b** could be isolated. This *N*-(methylsulphonyl)imine was the expected second product on the grounds that the isopropylidene compound **22c** gave exclusively the homologue **21c**[7,12]. Like the analogous benzothiazine derivatives **16b** and **d**, the *N*-(methylsulphonyl)imine **21b** exists in the *E* configuration as shown by an X-ray diffraction analysis (Figure 2).

Figure 2. Perspective drawing of the 2-iminotetrahydroquinoline **21b** showing the numbering of the atoms



Careful chromatography furnished two further products of **22b**, viz. an isomer of **21b**, which exhibited a C=N signal at very low field in the carbon-13 spectrum (δ = 196.2)[16], and small amounts of an *N*-(methylsulfonyl)*amine*, whose molecular formula corresponded to that of (**21b** + ethylene). On the basis of the combined analytical and spectroscopic evidence (Tables 1, 3, and 4) the 3-iminotetrahydroquinoline structure **24** was assigned to the former, the 3-(sulfonylamino)-3-vinyltetrahydroquinoline structure **27** to the latter. The configurations of both products were elucidated by X-ray diffraction analyses (Figures 3 and 4). Accordingly, **24** prefers the *Z* configuration in the solid state, and **27** is the *like* diastereomer with a diaxial arrangement

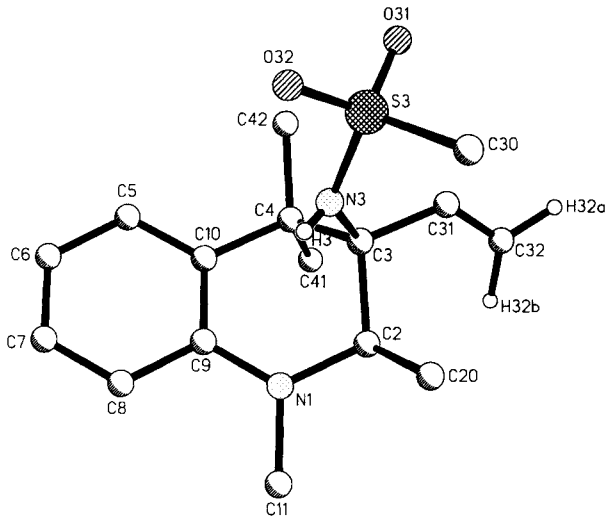
Figure 3. Perspective drawing of the 3-iminotetrahydroquinoline **24** showing the numbering of the atoms



of the *N*-(methylsulfonyl)amino group and the proton 2-H.

While the formation of both *N*-(methylsulfonyl)imines **21b** and **24** from the 2-ethylidenedihydroindole **22b** is readily interpreted according to Scheme 1, namely by loss of molecular nitrogen from a zwitterion of type **4** with concomitant 1,2-shift of CMe_2 (→**21b**, route **A2**) or NMe

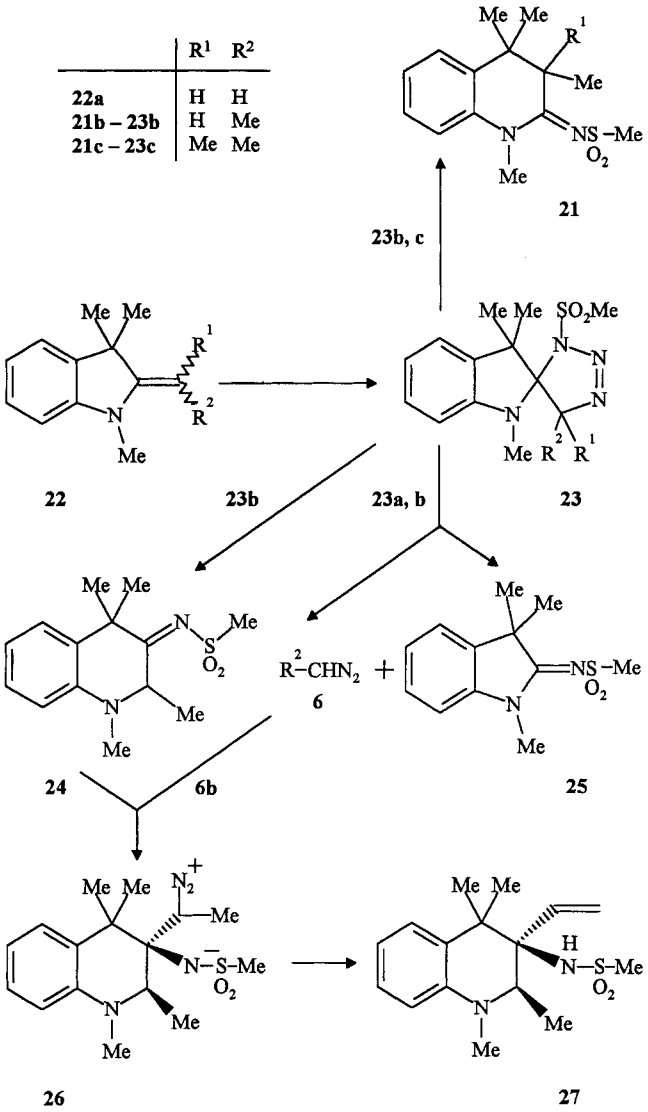
Figure 4. Perspective drawing of the 3-aminotetrahydroquinoline **27** showing the numbering of the atoms



(→**24**, route **A1**), the origin of the 3-(sulfonylamino)-3-vinyltetrahydroquinoline **27** justifies a comment. Obviously, **27** arises by nucleophilic addition of an ethylene equivalent to the highly reactive *N*-sulfonylimine moiety of **24**. Since the major pathway in the decomposition of the [3 + 2] cycloadduct **23b** affords *N*-sulphonylimine **25** and diazoethane (**6b**), it is very likely that the latter plays the role of the nucleophilic ethylene equivalent. Thus, diastereoface-differentiating *unlike* addition of **6b** to **24**, that is from the *trans* direction relative to the methyl group at C-2, produces the zwitterion **26**. Loss of nitrogen from **26** and a proton shift to the anionic sulfonamide moiety eventually yield the isolated product **27**.

After the structures of the products had been elucidated, a number of small-scale experiments were performed with the intent of determining the relative importance of the routes of Scheme 1 in solvents of different polarity. Towards this end, 2-alkylidene heterocycles of the present (**15b**, **22b**) and foregoing study (**10d**, **15d**, **22a** and **c**)[7] were allowed to react with methanesulfonyl azide under different conditions, and the course of the conversions was monitored by proton spectroscopy. The results are listed in Table 2, which includes previous results[7] and those from the thermolysis of the zwitterions **11b** and **c**[5].

Eventually, we studied the reactions at low temperatures with the view of detecting unstable intermediates. Only the final products could be observed by proton spectroscopy, when **15b** and **c**[7], and **22c** were allowed to react with methanesulfonyl azide in the temperature range of −60 to −40°C. In contrast, the unstable [3+2] cycloadduct **23b** arose slowly above −60°C and survived on warming up to −20°C. At higher temperatures, it decomposed into the products that had been isolated in the preparative experiment. The same sequence of reactions has been observed in the reaction of the Fischer base (**22a**) with methane sulphonyl azide[7].



Discussion

The product ratios of Table 2 resemble more or less those of the preparative experiments (Table 1 and ref.[7]). Differences are probably due to losses in the process of separation and purification. Inspection of Table 2 reveals little, if any, influence of the solvent polarity upon the ratio of ring expansion (routes **A**) and cleavage into *N*-(methylsulphonyl)-imine **5** and diazoalkane **6** (route **B** in Scheme 1). This result is not compatible with the hypothesis that the former procedes via zwitterion **4** and the latter by a concerted mechanism **3** → **5** + **6**. Therefore, we favour zwitterion **4** as common intermediate. Similar zwitterions have been invoked as intermediates in the decomposition of unstable [3 + 2] cycloadducts of azides to enamines. These zwitterions also either lose molecular nitrogen with simultaneous 1,2-shift of a carbon atom or undergo cleavage into an imine and a diazo compound[17]. We note in passing that the postulated zwitterion **26** results from the reversal of the latter process.

The fate of the zwitterion **4** is determined in a subtle way by structural features, viz. the nature of R^1 and R^2 and, in

Table 1. Products, yields obtained in preparative experiments (after flash chromatography), melting points (after recrystallisation from ethanol), and IR data. Melting points reported in the literature are given in brackets

Cpd.	Product(s)	Yield	m. p.	IR [cm^{-1}] (KBr)	
		[%]	[° C]	C=N, C=C	SO_2
9a	**13**	18	205 – 207	1565, 1552	1255
			(206 – 208)[7]		1119
14a	**16a**	32	173 – 175	1590, 1550	1265
				1535	1120
	17	18			
14b	**16b**	64			
	17	15			
15b[a]	**16b**	85	155 – 157	1550	1270
					1133
	17	8	166 – 168	1520	1290
			(164 – 165 [7])		1118
18	**20**	71	148 – 150	1550	1200
22b[b]	**21b**	2	144 – 145	1550	1285
					1137
	24	13.5	117 – 119	1635, 1600	1295
				1500	1150
	25	56	150 – 155	1600	1270
			(151 – 152 [7])		1120
	27	0.5	165 – 167	1600, 1500	1300
					1160

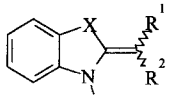
[a] Single diastereomer, probably *Z* configuration. – [b] Mixture of the *E* and *Z* diastereomer (10:1)[11].

particular, that of the potential migrating atom, N or X in Scheme 1. Only ring expansion is observed with 2-alkylidenedihydrobenzoxazoles (route **A1**)[7] and with the methylenedihydrobenzoselenazole **19** (route **A2**). In the alkylidenedihydrobenzothiazole series **15**, the groups R^1 and R^2 hardly influence the competition of route **A2** and route **B**. The 1,2-shift of the (soft) sulphur atom predominates always. The contrary is true for the 2-alkylidenedihydroindole series **22**, where methyl groups at the carbon carbon double bond favour ring-expansion. In fact, **22b** is the only compound which gave products of both possible ring-expansion reactions (routes **A1** and **A2** of Scheme 1).

The results of the present and the foregoing papers[6,7] demonstrate that, with few exceptions, 2-alkylidene *N*-heterocycles, derived from indole, perimidine, imidazole, oxazole, tetrazole, benzothiazole, and benzoselenazole can be ring-expanded with the help of electrophilic azides. It is particularly advantageous that sensitive or unstable 2-alkylidene *N*-heterocycles do not need to be isolated but can be generated by deprotonation and trapped in situ by the electrophilic azide present. These conversions are wellcome additions to the arsenal of useful ring-expansion reactions of *N*-heterocyclic compounds[12,18]. The results of studies directed toward the extension of this ring expansion to other, in particular six-membered, *N*-heterocycles will be reported in due course.

We are indebted to Professor *C. Reichardt* for a gift of the 2-ethylidenedihydroindole **22b**. We thank Mrs. *E. Ruckdeschel* and Dr. *D. Scheutzow* for recording NMR spectra and Dr. *G. Lange* and Mr. *F. Dadrich* for measuring the mass spectra. Financial support by the *Fonds der Chemischen Industrie*, Frankfurt am Main, is gratefully acknowledged. S. I. thanks particularly the *Deutsche Akademische Austauschdienst (DAAD)*, for a generous stipend.

Table 2. Ratios of products obtained in the reactions of 2-alkylidene *N*-heterocycles and methanesulfonyl azide (**2**). The ratios were calculated from integrations of methyl signals in proton spectra recorded from solutions of the crude products. The routes **A1**, **A2**, and **B** refer to Scheme 1



Cpd.	X	R^1	R^2	[a]	Temp. [°C]	Products	Routes A	Routes B	Ref.
10d	NMe	Me	Me	C	0	**12d, 13**	81	19	[b]
				THF	0		73	27	[b]
				D	0		78	22	[7]
				A	0		80	20	[b]
11b	NMe	Me	H	A	80	**12b, 13**	52	48	[5]
11c	NMe	*t*Bu	H	A	80	**12c, 13**	27	73	[5]
							A1 A2	**B**	
15a[c]	S	H	H	THF	25	**16a, 17**	64	36	[b]
15b	S	Me	H	T	0	**16b, 17**	95	5	[b]
				D	– 60		96	4	[b]
				A	0		97	3	[b]
15b[c]				THF	25		87	13	[b]
15c	S	*t*Bu	H	T	0	**16c, 17**	79	21	[7]
15d	S	Me	Me	D	0	**16d, 17**	94	6	[7]
				A	0		97	3	[b]
19[c]	Se	H	H	THF	25	**20**	> 99	1	[b]
22a	CMe_2	H	H	T	0	**25**	> 99		[b]
				D	0		> 99		[7]
				A	0		> 99		[b]
22b	CMe_2	Me	H	T	0	**24, 21b, 25**	8 : 17	75	[b]
				D	– 20 → 0	**21b, 25**	[d] 24	76	[b]
				A	0		[d] 40	60	[b]
22c	CMe_2	Me	Me	D	– 20 → 0	**21c**	> 99		[7]
				A	0		> 99		[b]

[a] Solvents: A = [D_3]acetonitrile, C = [D_{12}]cyclohexane, D = [D_2]dichloromethane, THF = [D_8]tetrahydrofuran, T = [D_8]toluene. – [b] This work. – [c] The ketene *N,X*-acetal was generated from the *N*-methylbenzazolium tetrafluoroborate with sodium hydride and trapped in situ by **2**. – [d] Traces of **24** were detected by HPLC.

Experimental

Yields, melting points and IR data: Table 1. – ^{1}H NMR: Table 3. – ^{13}C NMR: Table 4. – Molecular formulae, masses and elemental analyses: Table 5. – Melting points: apparatus from C. Reichert, Vienna, or Büchi, Flawil, Switzerland. – ^{1}H and ^{13}C NMR: Bruker AC 200 and AC 250. – TLC: Aluminium sheets with silica gel 60 F_{254} equipped with a concentrating zone (Merck). – Flash chromatography: (40 × 4)cm glass column with silica gel 32–63 μm (ICN Biomedicals), UV detector Knauer 87.00 (λ = 254 nm), 1.8 bar N_2. – HPLC: Waters M-6000A equipped with UV detector 440 (λ = 254 nm) and differential refractometer R401, (250 × 4.6)mm steel column with silica gel LiChrosorb Si60, 5 μm (Knauer), 1.5 ml/min, petroleum ether (50–70 °C) (PE)/ethyl acetate (EA) (80:20). – MPLC: (70 × 7)cm glass column with silica gel LiChroprep Si60, 15–20 μm (Merck), UV detector Knauer 87.00 (λ = 254 nm), differential refractometer Bischoff 8110. – MS (70 eV): Finnigan MAT 8200.

Tetrahydrofuran was dried with powdered potassium hydroxide and distilled from sodium hydride. Toluene and acetonitrile were distilled from calcium hydride. [D_2]Dichloromethane, [D_3]acetonitrile, and [D_8]toluene were dried with calcium hydride, [D_6]benzene with sodium hydride. – Sodium hydride, suspended in paraffin oil, was washed three times with pentane and dried in a stream of argon. – Experiments with ketene *N,X*-acetals and 2-alkylidenedihydroindoles were carried out in dry solvents under argon

Table 3. Chemical shifts (δ values) and coupling constants [Hz] in proton spectra

Cpd.	CMe_2	Me—CH_n	^3J	NMe	SO_2Me	Ring proton	[a]
14b	1.54	3.41	7.3	4.15		7.7 – 8.3	A
15b	1.72	4.13	6.4	2.41		6.0 – 6.9	B
16a		4.05		3.53	3.14	7.0 – 7.4	C
16b	1.33	4.99	7.1	3.54	3.14	7.1 – 7.4	C
20		3.94		3.52	3.14	7.0 – 7.5	C
21b	1.22 1.35	3.70	7.1	3.49	3.12	7.0 – 7.3	C
23b[b]	1.21 1.39	4.23	7.4	2.53	3.23	6.4 – 7.2	D
24	1.42 1.65	4.97	6.8	3.18	2.68	6.7 – 7.3	C
27	1.03 1.44	3.88	6.0	*3.007*[c]	*2.997*[c]	6.6 – 7.2 [d]	C

[a] Solvents: A = [D_3]acetonitrile, B = [D_6]benzene, C = [D]trichloromethane, D = [D_2]dichloromethane. – [b] The spectrum was recorded at −40 °C. – [c] May be exchanged. – [d] Further signals: δ = 4.05 (s, NH), 5.20 (δ_A), 5.56 (δ_M), 6.40 (δ_X), $^2J_{AM}$ = 0, $^3J_{AX}$ = 11.6, $^3J_{MX}$ = 17.9 Hz (AMX spectrum, −CH=CH_2).

(99.998%). – The following compounds were prepared as described: **2**[7], **10d**, **15d**[2], **22c**[12]. – 2-Methylbenzoselenazole (Aldrich), 2-methylbenzothiazole (Aldrich), and **22a** (Merck) were distilled in vacuo. – **22b** was donated by Professor C. Reichardt[11].

2-Ethylbenzothiazole: A suspension of 2-aminothiophenol (100 g, 0.8 mol) and zinc powder (2.4 g, 32 mmol) in trichloromethane (130 ml) was heated under reflux for 0.5 h. Propanoic anhydride (104 g, 0.8 mol) was added dropwise in 1 h, while the mixture was cooled with ice. The mixture was heated under reflux for 1 h, cooled, and poured into ice-cold water (250 ml). The organic layer was washed with an aq. solution of Na_2CO_3 (10%) and water (3 × 150 ml), until the washings were neutral, and dried with Na_2SO_4. The solvent was distilled at normal pressure and the residue in vacuo to afford a colourless oil (114.3 g, 88%), b.p. 60–70 °C/0.2 Torr (b.p. 115 °C/7 Torr[19]).

1,2,3-Trimethylbenzimidazolium Tetrafluoroborate (**9a**): Dimethyl sulphate (72.1 g, 0.57 mol) was added dropwise to a stirred suspension of $NaHCO_3$ (57.7 g, 0.69 mol) and 2-methyl-1*H*-benzimidazole[20] (30.2 g, 0.23 mol) in water (150 ml)[21]. The mixture was stirred for 14 h and the solid removed by filtration. A sat. aq. solution of $NaBF_4$ (100 ml), acidified with 3 drops of aq. HBF_4 (50%), was added dropwise to the filtrate to afford colourless crystals, 47.7 g (84%). Recrystallisation of crude product from ethanol/water (10:1) furnished colourless plates (41.3 g, 73%), m.p. 207–209 °C (m.p. 202 °C[8]).

2,3-Dimethylbenzothiazolium Tetrafluoroborate (**14a**): Dimethyl sulphate (12.5 g, 0.10 mol) was added dropwise with stirring to 2-methylbenzothiazole (11.8 g, 80 mmol) under cooling with ice. The mixture was heated at 110 °C for 1.5 h, cooled to 60 °C, and diluted with ethanol (20 ml). After cooling to room temp., a sat. aq. solution of $NaBF_4$ (50 ml) was added dropwise. The precipitate which had formed after 3 d was collected by filtration, washed with water and dried to afford colourless crystals (17.2 g, 86%). Recrystallisation of the crude product from ethanol gave colourless needles, m.p. 120–122 °C (m.p. 120 °C[14]).

2-Ethyl-3-methylbenzothiazolium Tetrafluoroborate (**14b**) was prepared from 2-ethylbenzothiazole as described above for **14a** and recrystallised from ethanol. Colourless needles, m.p. 110–112 °C.

2,3-Dimethylbenzoselenazolium Tetrafluoroborate (**18**) was prepared from 2-methylbenzoselenazole as described above for **14a** and recrystallised from ethanol. Colourless needles, m.p. 141–142 °C (m.p. 142.5 °C[14]).

Ketene N,X-Acetals **10a** *and* **15b**. – *General Procedure*[2]: A suspension of powdered 2-alkyl-*N*-methylbenzazolium tetrafluoroborate (20 mmol) and sodium hydride (30 mmol) in tetrahydrofuran (25 ml) was stirred under argon in an 80-ml centrifuge tube, equipped with septum, until the gas evolution had ceased. The solid material was removed under argon with the help of a centrifuge. The solvent and the crude product were distilled in vacuo to afford colourless low-melting solids.

Tab. 4. Chemical shifts (δ values) in carbon-13 spectra

Cpd.	CH_n—Me				NMe	SO_2Me	C=N	Other ring-C		[a]
								CH	quat. C	
14b	25.7	12.3			37.2		180.4	119.0 125.1 129.6 130.9	143.4 168.7	A
15b	81.9	14.7			30.0		145.2 [b]	106.6 119.2 121.4 125.8	124.6 143.6	B
16a	28.1				35.8	43.3	160.7	119.1 124.6 127.5 128.4	125.7 139.0	C
16b	34.0	16.6			36.0	43.5	162.9	118.4 124.9 127.4 129.7	121.7 138.2	C
20	19.9				37.4	43.4	161.6	120.7 124.9 128.0 130.9	123.3 140.4	C
	C	Me_2	CH—Me							
21b	35.0	23.1 28.3	44.3	12.4	32.9	43.8	169.2	116.7 124.9 125.3 127.4	133.9 137.5	C
24	44.0	20.9 30.8	59.3	12.9	43.0	36.2	196.2	113.5 119.7 125.0 127.7	131.0 143.8	C
27	42.6	21.5 25.3	55.9	16.8	44.4	36.4	[c]	112.2 118.3 125.5 128.0	127.3 143.9	C

[a] Solvents: A = [D_3]acetonitrile, B = [D_6]benzene, C = [D]trichloromethane. – [b] C-2. – [c] Further signals: δ = 68.2 (quat. C, C-3), 118.3, 133.1 (CH_2=CH–).

Tab. 5. Molecular formulae and masses, and elemental analyses

Cpd.	Formula	Mol. mass	Elemental analysis	C	H	N	S
14b	$C_{10}H_{12}BF_4NS$	265.1	Calcd.	45.31	4.56	5.28	
			Found	45.53	5.11	5.22	
16a	$C_{10}H_{12}N_2O_2S_2$	256.3	Calcd.	46.86	4.72	10.93	25.01
			Found.	46.92	4.63	11.01	25.17
16b	$C_{11}H_{14}N_2O_2S_2$	270.4	Calcd.	48.87	5.22	10.36	23.72
			Found	49.04	5.20	10.19	23.97
20	$C_{10}H_{12}N_2O_2SSe$	302.3	Calcd.	39.60	4.00	9.24	10.57
			Found	39.66	3.76	9.18	10.86
21b	$C_{14}H_{20}N_2O_2S$	280.4	Calcd.	59.07	7.19	9.99	11.43
			Found	59.77	7.18	9.80	11.29
24			Found	60.17	6.91	9.85	11.38
27	$C_{16}H_{24}N_2O_2S$	308.4	Calcd.	62.31	7.84	9.08	
			Found	62.32	7.02	9.00	

2,3-Dihydro-1,3-dimethyl-2-methylene-1H-benzimidazole (**10a**): Yield 88%, m.p. 50–52°C, b.p. 97–110°C/0.15 Torr (m.p. 49–50°C[8]).

2-Ethylidene-2,3-dihydro-3-methylbenzothiazole (**15b**): Yield 84%, m.p. 30–31°C, b.p. 73–74°C/0.15 Torr (b.p. 155–156°C/9 Torr[9]).

3,4-Dihydro-2,4-dimethyl-3-[(methylsulphonyl)imino]-2H-benzothiazine (**16b**) *and 2,3-Dihydro-3-methyl-2-[(methylsulphonyl)-imino]benzothiazole* (**17**). – a) A solution of **2** (1.33 g, 11.0 mmol) in toluene (5 ml) was added dropwise under argon to a stirred solution of **15b** (1.91 g, 10.8 mmol) in toluene (5 ml) at 0–5°C. The mixture was stirred for 1 h at 0°C and 1 h without cooling. The solvent was distilled in vacuo. TLC (PE/EA, 1:1) of the solid residue showed two spots. Recrystallisation from EA afforded **16b** (2.01 g, 69%) as colourless crystals, m.p. 152–156°C. Flash chromatography (PE/EA, 1:1) of the residue, which was obtained from the mother liquor after distillation of the solvent in vacuo, gave a second crop of **16b** (0.48 g, 16%) as colourless crystals, m.p. 152–156°C, and **17** (0.16 g, 8%) as colourless crystals, m.p. 166–168°C. The crude products were recrystallised from ethanol. – **16b**, MS, *m/z* (%): 270 (27) [M^+], 192 (13), 191 (100) [$M^+ - SO_2Me$], 164 (28), 158 (11), 137 (50), 136 (42), 109 (11), 40 (15).
b) A suspension of powdered **14b** (2.65 g, 10 mmol), sodium hydride (0.36 g, 15 mmol), and **2** (1.23 g, 10.2 mmol) in tetrahydrofuran (30 ml) was stirred under argon in an 80-ml centrifuge tube, equipped with a septum, until the gas evolution had ceased (20 h). The solid material was removed under argon with the help of a centrifuge and washed with tetrahydrofuran (5 ml). The solvent was distilled in vacuo. Flash chromatography (PE/EA, 1:1) of the solid residue gave **16b** (1.74 g, 64%, yellow crystals, m.p. 150–157°C), and **17** (0.35 g, 15%, colourless crystals, m.p. 160–164°C). The crude products were recrystallised from ethanol to afford colourless crystals.

In situ-Trapping of the Methylene Compounds **10a**, **15a**, *and* **19** *with Methanesulphonyl Azide* (**2**). – *General Procedure:* A suspension of powdered 2,*N*-dimethylbenzazolium tetrafluoroborate (**9a**, **14a**, or **18**, 10 mmol), sodium hydride (15 mmol), and **2** (11 mmol) in tetrahydrofuran (30 ml) was stirred under argon in an 80-ml centrifuge tube, equipped with a septum, until the gas evolution had ceased (20–24 h). The solid material was removed under argon with the help of a centrifuge and washed with tetrahydrofuran (5 ml). The solvent was distilled in vacuo.

2,3-Dihydro-1,3-dimethyl-2-[(methylsulphonyl)imino]-1H-benzimidazol (**13**) *and 1,3-Dihydro-1,3-dimethyl-2H-benzimidazol-2-one:* Flash chromatography (EA) of the residue obtained from **10a** gave 1,3-dihydro-1,3-dimethyl-2*H*-benzimidazol-2-one (0.28 g, 16%, yellow solid) and **13** (0.44 g, 18%, yellow crystals, m.p. 200–205°C). 1,3-Dihydro-1,3-dimethyl-2*H*-benzimidazol-2-one was recrystallised from PE to afford yellow crystals, m.p. 100–102°C (m.p. 102°C[22]). – ^{1}H NMR ($CDCl_3$): δ = 3.42 (s, 2 NMe), 6.9–7.2 (4 Ar-H) (ref.[22]). – ^{13}C NMR ($CDCl_3$): δ = 27.1 (NMe), 107.4, 121.2 (ring CH), 130.0 (quat. C), 154.6 (C=O) (ref.[23]). – **13** was recrystallised from ethanol to afford colourless needles.

3,4-Dihydro-4-methyl-3-[(methylsulphonyl)imino]-2H-benzothiazine (**16a**) *and 2,3-Dihydro-3-methyl-2-[(methylsulphonyl)imino]benzothiazole* (**17**): Flash chromatography (PE/EA, 1:1) of the solid residue obtained from **15a** gave **16a** as first fraction (0.64 g, 24%, brown needles, m.p. 165–170°C). MPLC of the residue (PE/EA, 1:1), which was obtained after evaporation of the solvent from the combined later fractions, gave a second crop of **16a** (0.19 g, 7%, yellow needles, m.p. 170–175°C) and **17** (0.44 g, 18%, orange-coloured powder, m.p. 165–168°C). The crude products were recrystallised from ethanol to afford pale yellow scales (**16a**), m.p. 173–175°C, and orange-coloured needles (**17**), m.p. 167–168°C.
16a, MS, *m/z* (%): 256 (48) [M^+], 178 (10), 177 (89) [$M^+ - SO_2Me$], 150 (100), 137 (44), 136 (71).

3,4-Dihydro-4-methyl-3-[(methylsulphonyl)imino]-2 H-benzoselenazine (**20**): Flash chromatography (PE/EA, 1:1) of the solid residue obtained from **19** gave **20** (2.04 g, 71%) as brown needles, m.p. 140–149°C. Recrystallisation from ethanol afforded pale yellow scales, m.p. 148–150°C. – MS, *m/z* (%): 304 (77), 302 (40) [M^+], 225 (71), 223 (47) [$M^+ - SO_2Me$], 198 (100), 185 (58), 184 (84), 183 (30), 182 (52), 181 (24), 157 (23), 145 (57), 118 (70).

Reaction of 2-Ethylidene-2,3-dihydro-1,3,3-trimethyl-1H-indole (**22b**) *with Methanesulphonyl Azide* (**2**): A solution of **2** (2.71 g, 22.4 mmol) in toluene (5 ml) was added dropwise under argon to a stirred solution of **22b** (3.80 g, 22 mmol) in toluene (5 ml) at 0–5°C. The mixture was stirred for 1 h at 0°C and 1 h without cooling. The solvent was distilled in vacuo. Recrystallisation of the solid residue from ethanol (25 ml) afforded **25** (2.75 g, 50%) as colourless crystals, m.p. 150–155°C. Flash chromatography (PE/EA, 7:3) of the yellow, syrupy residue, which was obtained from the mother liquor after distillation of the solvent in vacuo, gave **24** as first fraction (0.8 g, 13%, colourless crystals, m.p. 117–119°C). MPLC (PE/EA, 7:3) of the residue, which was obtained after evaporation of the solvent from the combined later fractions, gave **21b** (0.13 g, 2%), **24** (0.023 g, 0.4%), **25** (0.35 g, 6%) as yellow crystals, and **27** (0.031 g, 0.5%) as violet crystals. The crude products were recrystallised from ethanol to afford colourless crystals.
21b, MS, *m/z* (%): 280 (33) [M^+], 265 (44) [M^+ – Me], 202 (14), 201 (100) [$M^+ - SO_2Me$], 187 (11), 186 (80), 184 (10), 132 (16), 131 (19).
24, MS, *m/z* (%): 280 (33) [M^+], 265 (44) [M^+ – Me], 202 (15), 186 (46), 171 (36), 160 (11), 159 (26), 158 (16), 156 (11), 144 (17), 132 (18).
27, MS, *m/z* (%): 308 (6) [M^+], 229 (8) [$M^+ - SO_2Me$], 187 (17), 186 (100), 171 (21), 145 (6), 144 (8), 132 (7).

Reaction of the Ketene N,X-Acetals (X = N, S) **10a**, **d**, **15b**, **d** *and 2-Alkylidenedihydroindoles* **22a–c** *with Methanesulphonyl Azide* (**2**) *in Deuterated Solvents. – General Procedure:* **2** (0.5 mmol) was added at 0°C under argon to a solution of the ketene *N,X*-acetal or 2-alkylidenedihydroindole (0.5 mmol) in a deuterated solvent (0.6 ml) contained in an NMR sample tube. The mixture was briefly shaken and kept at 0°C for 1 h and without cooling until the evolution of gas had subsided. The proton spectra were recorded at room temp. When products precipitated, the solvent was evaporated under reduced pressure, and the proton spectrum was recorded from a solution of the residue in $CDCl_3$. Results: Table 2.

Reaction of the Ketene N,X-Acetals (X = N, S) **10a**, **15b** *and 2-Alkylidenedihydroindole* **22b** *with Methanesulphonyl Azide* (**2**) *at Low Temperatures. – General Procedure*[7]: A solution of the ketene *N,X*-acetal or **22b** (0.5 mmol) in CD_2Cl_2 (0.3 ml), contained in an NMR sample tube under argon, was frozen by cooling with liquid nitrogen. Special care was taken to avoid condensation of argon. A small amount of CD_2Cl_2 (0.1 ml) was placed on top of the solid. A solution of **2** (0.5 mmol) in CD_2Cl_2 (0.2 ml) was added. The NMR sample tube was cooled with liquid nitrogen, evacuated, and flame-sealed. The mixture was brought to –78°C in a methanol/dry ice bath and briefly shaken. Proton spectra were recorded at –60, –50, –40, –30, –20, –10, and 0°C. In the case of **15b**, gas evolved already at –78°C, and the proton spectrum indicated only the presence of **16b** and **17** (Table 2).

1,3,3',5'-Tetrahydro-1,1,3,5'-tetramethyl-3'-(methylsulfonyl)-spiro[2H-indole-2,4'-1,2,3-triazole] (**23b**): The solution prepared

Table 6. Experimental details and results of the X-ray diffraction analyses of **16b**, **21b**, **24**, and **27**

Compound	**16b**	**21b**	**24**	**27**
Molecular formula	$C_{11}H_{14}N_2O_2S_2$	$C_{14}H_{20}N_2O_2S$	$C_{14}H_{20}N_2O_2S$	$C_{16}H_{24}N_2O_2S$
Molecular mass	270.36	280.38	280.38	308.44
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [pm]	1024.9(1)	889.6(1)	909.7(1)	844.1(1)
b [pm]	718.9(1)	909.8(1)	1102.0(1)	940.2(1)
c [pm]	1750.4(1)	1112.4(1)	1457.6(1)	1205.9(1)
α [deg]		66.882(7)		70.120(6)
β [deg]	105.287(7)	85.698(7)	93.804(6)	71.159(7)
γ [deg]		61.426(6)		68.394(7)
V [nm^3]	1.2441(1)	0.7200(1)	1.4580(2)	0.8153(2)
Z	4	2	4	2
d (calcd.) [g cm^{-3}]	1.443	1.239	1.277	1.256
Size of the crystal [mm]	0.2 × 0.4 × 0.6	0.3 × 0.3 × 0.2	0.3 × 0.25 × 0.1	0.15 × 0.4 × 0.45
Range h	0 → 13	−1 → 11	0 → 11	−1 → 10
k	0 → 9	−9 → 10	0 → 14	−11 → 11
l	−22 → 21	−14 → 14	−18 → 18	−15 → 15
No. of measured reflections	4113	3808	3744	4455
Symmetry-independent reflections	2852	3186	3351	3699
Observed reflections $F>3\sigma(F)$	2541	2591	2677	2562
Linear absorpt. coeff. [mm^{-1}]	0.42	0.22	0.22	0.20
Absorption correction	ψ-scan	ψ-scan	ψ-scan	ψ-scan
Ratio F_{obs}/parameters	16.39	14.98	15.47	12.81
R	0.044	0.052	0.048	0.064
R_w	0.046	0.053	0.049	0.059
Diff. Four. $\Delta\rho_{max}$[*] [eÅ^{-3}]	0.45	0.42	0.35	0.37
$\Delta\rho$[**]	−0.26	−0.32	−0.23	−0.27

[*] Maximum and [**] minimum of the remaining electron density in the final differential Fourier synthesis.

from **22b** and **2** in CD_2Cl_2 according to the General Procedure contained both **22b** and **23b** at −60°C, only **23b** between −40 and −20°C.

X-Ray Diffraction Analyses of transparent colourless crystals of **16b**, **21b**, **24**, and **27** were performed. The cell parameters were determined on the basis of 22 reflections. The numbers of reflections reported in Table 6 were obtained with Mo-K_α radiation and $2\Theta_{max} = 55°$ (graphite monochromator, Wyckoff scan). Measurements were carried out with a system Siemens P4. The programme SHELXTL PLUS[24] was employed. The structures were solved by direct methods and refined anisotropically by the least-squares method. The weighting scheme for R_w is $1/\sigma^2(F)$. The positions of hydrogen atoms were calculated and included in the refinements with isotropic description[25].

[1] The results are taken from the projected dissertation by S. Ivanova, University of Würzburg.

[2] H. Quast, M. Ach, M. K. Kindermann, P. Rademacher, M. Schindler, *Chem. Ber.* **1993**, *126*, 503−516.

[3] For less reactive ketene *N,X*-acetals, which possess electron-withdrawing groups at the α-carbon atom, see R. W. Saalfrank, M. Fischer, U. Wirth, H. Zimmermann, *Angew. Chem.* **1987**, *99*, 1218−1219; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1160−1161; R. W. Saalfrank, U. Wirth, *Chem. Ber.* **1989**, *122*, 969−973; R. W. Saalfrank, C.-J. Lurz, U. Wirth, H. G. von Schnering, K. Peters, *J. Heterocycl. Chem.* **1991**, *28*, 1863−1868; M.-X. Wang, Z.-T. Huang, *J. Org. Chem.* **1995**, *60*, 2807−2811, and references cited therein.

[4] H. Quast, D. Regnat, E.-M. Peters, K. Peters, H. G. von Schnering, *Angew. Chem.* **1990**, *102*, 724−726; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 695−697.

[5] H. Quast, M. Ach, S. Ivanova, E.-M. Peters, K. Peters, H. G. von Schnering, *Liebigs Ann.* **1996**, 1551−1553, following paper in this issue.

[6] H. Quast, D. Regnat, J. Balthasar, K. Banert, E.-M. Peters, K. Peters, H. G. von Schnering, *Liebigs Ann. Chem.* **1991**, 409−416.

[7] H. Quast, M. Ach, E.-M. Peters, K. Peters, H. G. von Schnering, *Liebigs Ann. Chem.* **1992**, 1259−1269.

[8] C. Reichardt, N. Kaufmann, *Chem. Ber.* **1985**, 118, 3424−3427.

[9] J. Metzger, H. Larivé, É.-J. Vincent, R. Dennilauler, *J. Chim. Phys.* **1963**, *60*, 944−949.

[10] E. Fischer, A. Steche, *Liebigs Ann. Chem.* **1887**, *242*, 348−366.

[11] C. Reichardt, H. D. Engel, *Chem. Ber.* **1988**, *121*, 1009−1011.

[12] A. S. Bailey, R. Scattergood, W. A. Warr, *J. Chem. Soc. (C)* **1971**, 3769−3778.

[13] J. R. Owen, *Tetrahedron Lett.* **1969**, 2709−2712; *Org. Chem. Bull.* (Eastman Kodak) **1971**, *43*, 3−7 [*Chem. Abstr.* **1972**, *76*, 114815u].

[14] C. Reichardt, W. Mormann, *Chem. Ber.* **1972**, *105*, 1815−1839.

[15] W. König, W. Meier, *J. Prakt. Chem.* **1925**, *109*, 324−344; O. Mumm, H. Hinz, J. Diederichsen, *Ber. Dtsch. Chem. Ges.* **1939**, *72*, 2107−2120.

[16] G. I. Georg, G. C. B. Harriman, S. A. Peterson, *J. Org. Chem.* **1995**, *60*, 7366−7368.

[17] R. Huisgen, R. Grashey, J. Sauer in *The Chemistry of Alkenes* (Ed.: S. Patai), Wiley, New York, **1964**, p. 835−844; W. Lwowski in *1,3-Dipolar Cycloaddition Chemistry* (Ed.: A. Padwa), 1st ed., vol. 1, Ch. 5, Wiley, New York, **1984**; P. K. Kadaba, B. Stanovnik, M. Tišler, *Adv. Heterocycl. Chem.* **1984**, *37*, 217−349; M. Regitz, G. Maas, *Diazo Compounds*, 1st ed., Academic Press, New York, **1986**, p. 384−389.

[18] H. C. van der Plas, *Ring Transformation of Heterocycles*, 1st. ed., Academic Press, New York, **1973**; A. R. Katritzky, *Handbook of Heterocyclic Chemistry*, 1st. ed., Pergamon Press, Oxford, **1985**, p. 388, 396; M. Hesse, *Ring Enlargement in Organic Chemistry*, 1st ed., VCH, Weinheim, **1991**; D. C. Liotta, M. Volmer, *Organic Syntheses, Reaction Guide*, 1st. ed., Wiley, New York, **1991**, p. 112−116; J. K. Crandall, L. C. Crawley, J. B. Komin, *J. Org. Chem.* **1975**, *40*, 2045−2047; C. M. Shafer, T. F. Molinski, *ibid.* **1996**, *61*, 2044−2050.

[19] J. Metzger, H. Plank, *Bull. Soc. Chim. Fr.* **1956**, 1692−1696.

[20] N. Suzuki, T. Yamabayashi, Y. Izawa, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 353–354.
[21] H. Quast, E. Schmitt, *Chem. Ber.* **1968**, *101*, 4012–4014.
[22] G. Vernin, H. Domlog, C. Siv, J. Metzger, A. K. El-Shafei, *J. Heterocycl. Chem.* **1981**, *18*, 85–89.
[23] H.-O. Kalinowski, H. Kessler, *Org. Magn. Res.* **1974**, *6*, 305–307.
[24] G. M. Sheldrick, University of Göttingen, unpublished results.
[25] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-404783 (**16b**), –404784 (**21b**), –404785 (**24**), and –404782 (**27**), the names of the authors and the journal citation.

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