Ring Expansion of 2-Alkylidenedihydroquinazolines to Iminodihydro-1,4-benzodiazepines by Methanesulfonyl and Trifluoromethanesulfonyl Azide

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Dedicated to Dr. Leo H. Sternbach on the occasion of his 92nd birthday

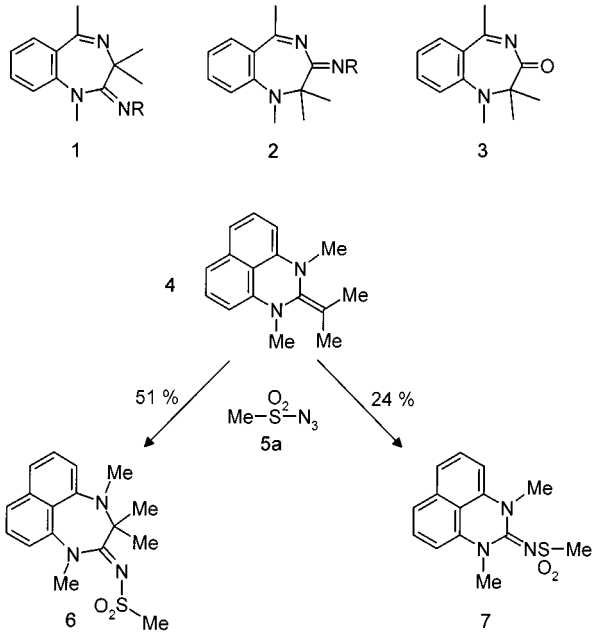
Keywords: Azides / Cleavage reactions / Cycloadditions / Nitrogen heterocycles / Polycycles / Ring expansion / Synthetic methods

2-Alkyl-1-methylquinazolinium hexafluorophosphates **9** are deprotonated by sodium or potassium hydride to afford solutions of 2-alkylidenedihydroquinazolines **10**, which were investigated by NMR spectroscopy. Trapping with methanesulfonyl azide (**5a**) of **10** in situ or subsequent treatment with trifluoromethanesulfonyl azide (**5b**) gives mixtures of colourless (**15**) and intensely yellow *N*-sulfonylimino-1,4-benzodiazepines **16** along with products due to cleavage of the exocyclic double bond of **10**, viz. **11** and **13**. The ethylidene compound **10b** yields the bicyclic products **18** and **19**, apparently by complex sequences of reactions that are triggered by removal of the acidic proton at C-2 of **16b** and **16f**. The structures of the products are based on spectroscopic evidence and X-ray diffraction analyses performed on **15b**, **16d**, **16e**, and **19**.

Introduction

Sternbach's seminal discovery of physiologically active benzo[*e*][1,4]diazepines some 40 years ago[2] triggered an enormous, and still ongoing, research effort in this field,[3–5] which has led to the synthesis of a host of benzo[*e*][1,4]diazepine derivatives. More recently, benzo[*e*][1,4]diazepines have become the target of combinatorial syntheses.[6] Nevertheless, certain structural variations have been neglected by the mainstream synthetic efforts, apparently due to the lack of convenient access. For example, only a few imines of type **1** have been described and these are mainly in the patent literature.[7] 3-Iminobenzodiazepines of general formula **2** are unknown as yet[4] and even the corresponding benzo-1,4-diazepin-3-ones **3** are very rare species.[8]

Since Sternbach's pioneering studies on the ring expansion of quinazoline derivatives to afford benzo-1,4-diazepines,[2,9] a number of additional methods have been developed for this conversion.[10] Recently, we have investigated the scope and limitations of Sato's[11] ring expansion with electrophilic organic azides of 2-alkylquinolinium salts via 2-alkylidenedihydroquinolines.[12] The analogous sequence of reactions has previously led to the imino-1,4-*naphtho*diazepine **6**[13] and a variety of six-membered heterocyclic imines.[13,14] These results encouraged us to extend this ring expansion method to quinazolinium salts **9** with a view to finding a route to novel imino-1,4-*benzo*diazepines related to Sternbach's 1,4-benzodiazepinones. The results of this study are reported here.



Results and Discussion

We restricted the present study to 2-alkyl-*4-phenyl*quinazolines **8** because the anticipated imino-5-phenyl-1,4-benzodiazepines resemble physiologically active benzodiazepinones. The unknown 2-alkyl-4-phenylquinolines **8d** and **8e** were prepared according to the procedure reported for **8a–c**.[15] 1-Methylquinazolinium salts **9** were required as starting materials for the projected ring expansion sequence.

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Methylation with dimethyl sulfate (**8a**, **8b**, and **8d**) or methyl triflate (**8c** and **8e**) yielded viscous oils, which were converted into the nicely crystalline hexafluorophosphates **9**. Proton spectra of the crude products indicated the regioselective formation of a single quaternary salt in every case. Unequivocal proof for the structures **9b**, **9d**, and **9e** was provided by X-ray crystallography of the products from methanesulfonyl azide (Figures 3–5). Deprotonation of the alkylquinazolinium salts **9** with potassium hydride in deuterated solvents[12] gave persistent, yellow to violet solutions of 2-alkylidenedihydroquinazolines **10**, which could be stored under argon at low temperatures.

The 2-alkylidenedihydroquinazolines **10b**, **10c**, and **10e** may exist in the (*E*) and (*Z*) configuration. Only one diastereomer, however, could be observed by proton- and carbon-13 NMR spectroscopy in each case. We assign these diastereomers the (*E*) configuration because the (*Z*) configuration is destabilised by unfavourable steric interactions. This assignment is confirmed for **10b** and **10c** by the carbon-13 shifts of the *N*-methyl groups (δ = 33–34, Table 2), which absorb at the same resonance frequency as that of the 2-methylene compound **10a** (δ = 33). By contrast, the *N*-methyl group of **10d**, which may be taken as a model for (*Z*)-**10b** and (*Z*)-**10c**, absorbs at much lower field (δ = 41).

We have previously drawn attention to the useful correlation between the high-field shifts of the exocyclic carbon atoms of 2-alkylidene-*N*-heterocycles and their reactivity towards electrophiles.[12,16] A graphical representation of the carbon-13 shifts for the 2-methylene compounds (Figure 1) reveals that 2-alkylidenedihydroquinazolines should be less nucleophilic than 2-alkylidenedihydroquinolines, which to date have marked the lower end of the reactivity scale. Therefore, only highly electrophilic azides such as the sulfonyl azides **5** appeared as promising reagents for the ring expansion.

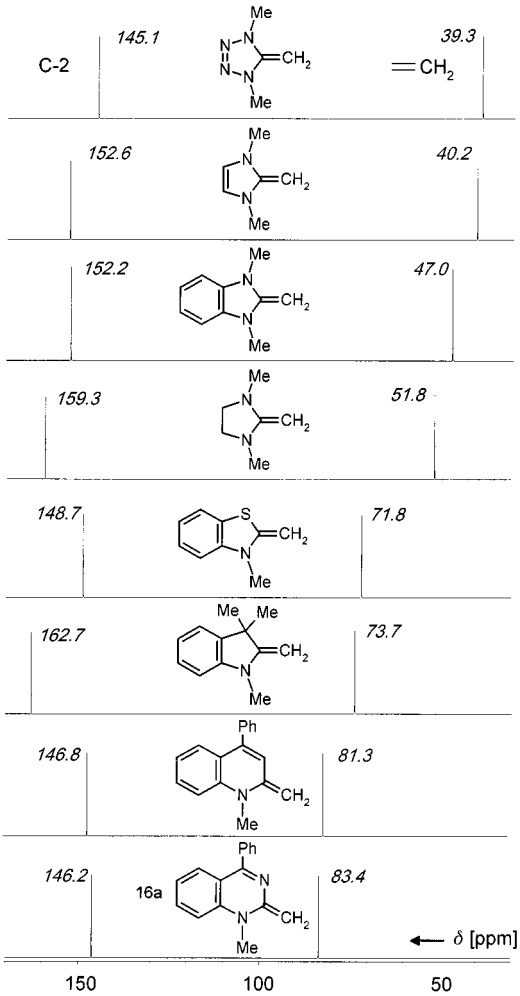
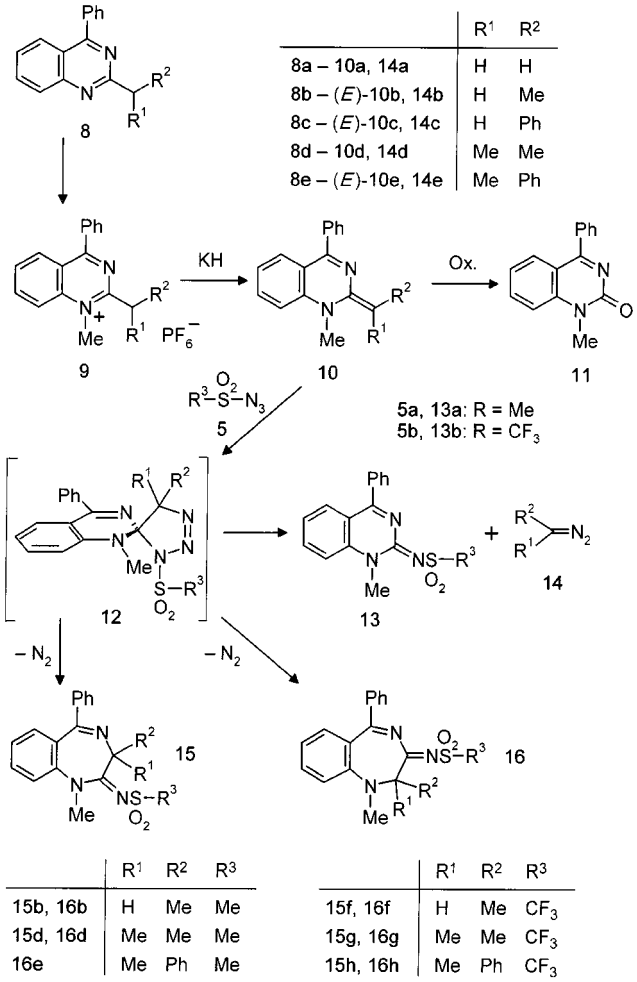


Figure 1. Chemical shifts (δ values) of the methylene groups and the neighbouring ring carbon atoms in carbon-13 spectra of various 2-methylene heterocycles



	R1	R2
8a – 10a, 14a	H	H
8b – (*E*)-10b, 14b	H	Me
8c – (*E*)-10c, 14c	H	Ph
8d – 10d, 14d	Me	Me
8e – (*E*)-10e, 14e	Me	Ph

	R1	R2	R3
15b, 16b	H	Me	Me
15d, 16d	Me	Me	Me
16e	Me	Ph	Me

	R1	R2	R3
15f, 16f	H	Me	CF_3
15g, 16g	Me	Me	CF_3
15h, 16h	Me	Ph	CF_3

In the experiments with *methane*sulfonyl azide (**5a**), the 2-alkylidenedihydroquinazolines **10** were generated in tetrahydrofuran solution by deprotonation of **9** with sodium hydride and *trapped* in situ by an excess of **5a**. Work up of the solid material present in the reaction mixtures afforded the major portion of the almost insoluble *N*-sulfonylimine **13a**. The dark, semi-solid crude products obtained from the solution were complex mixtures according to their proton spectra. Separation by flash chromatography and medium-pressure liquid chromatography[17] yielded crystalline products along with small amounts of **13a** (Table 1). Whereas

the methylene (**10a**) and benzylidene (**10c**) compounds exclusively gave **13a** by cleavage of the exocyclic double bond, the other 2-alkylidenedihydroquinazolines investigated (**10b**, **10d**, and **10e**) yielded, besides **13a**, colourless and yellow products whose molecular formulae correspond to the isomeric ring-expansion products **15** and **16**. A single, colourless product of this type was obtained from **10b** (**15b**), and a single, yellow compound from **10e** (**16e**), while **10d** gave both the colourless and the yellow product (**15d** and **16d**).

For the ring expansion with *trifluoromethane*sulfonyl azide (**5b**), solutions of **10** were prepared by deprotonation with potassium hydride and subsequently treated with a solution of **5b** in dichloromethane. Again, the methylene compound **10a** gave exclusively the cleavage product **13b**. In all other cases (**10b**, **10d**, and **10e**) both the colourless and the yellow ring expansion products could be isolated, in low yields, along with **13b**. In the experiments involving the isopropylidenedihydroquinazoline **10d**, small amounts of the known quinazolone **11**[18] were isolated. This compound could also be detected by scrutiny of the proton spectra of all other product mixtures that were obtained from **5b**. It is likely that **11** arises by autoxidation of **10** by molecular oxygen that is still dissolved in the incompletely degassed dichloromethane solutions of **5b** employed.[12]

Table 1. Products, yields obtained in preparative experiments, melting points taken after recrystallisation from the solvent listed, and IR data

Starting materials	Products	Yield [%]	M. p. [°C] (Solvent)	IR [cm^{-1}] (KBr) C=N, C=C	NH (br)
methanesulphonyl azide (**5a**)					
9a	**13a**	53	297 – 300 (EtOH/$CHCl_3$, 4 : 1)	1591, 1542, 1508	
9b	**13a**	37			
	15b	15	193 – 196 (EtOH)	1618, 1575, 1542	
	18a	5	198 – 200 (dec.) ($CHCl_3$/PE, 1 : 1)	1633	3265
	19	20	157 – 159 (dec.)	1631	3235
9c	**13a**	78			
9d	**13a**	4			
	15d	3	134 – 136 (EtOH)		
	16d	59	146 – 148 (EtOH)	1618, 1603, 1591	
9e	**13a**	75			
	16e	17	191 – 193 (EtOH)	1620, 1590	
trifluoromethanesulphonyl azide (**5b**)					
9a	**13b**	40	254 – 256 (EtOH)	1549, 1517	
9b	**13b**	5			
	15f	6	131 – 134 (EtOH)	1620, 1581, 1570, 1539	
	16f	12	169 – 172 (EtOH)	1568, 1521	
	18b	5	165 – 167 (dec.) (EtOH)	1616	3309
9d	**11**	12	145 – 147 (EtOH)	1647[a], 1607, 1596, 1540	
	13b	2			
	15g	19	194 – 197 (EtOH)	1617, 1578, 1537	
	16g	23	137 – 140 (EtOH)	1622, 1610, 1561	
9e	**13b**	45			
	15h	15	253 – 256 (EtOH/H_2O)	1587, 1573, 1552	
	16h	13	230 – 234 (EtOH/H_2O)	1582, 1524, 1511	

[a] C=O.

The structures of the *N*-sulfonylimino-1,4-benzodiazepines were based on UV/Vis (Figure 2), proton and carbon-13 NMR spectra, and ^1H,^{13}C-COSY experiments (Tables 3 and 4). Two types of compounds could be immediately distinguished by virtue of the colour of the crystals; one is colourless while the second forms intensely yellow crystals, some of which exhibit yellow fluorescence. UV/Vis spectra indicated the presence of an extended conjugated system in the latter, which were therefore assigned the 3-(*N*-sulfonylimino)-1,4-benzodiazepine structures **16**. The most characteristic difference between the NMR spectra of the colourless and the yellow products are the chemical shifts of the *N*-methyl groups. Those of the former resonate at lower field (δ^H = 3.5–3.9; δ^C = 40–45) than those of the latter (δ^H = 2.8–3.4; δ^C = 34–40). These results left little room for doubt about the structures of cyclic *N*-sulfonylamidines **15** for the colourless ring-expanded products and of 3-(*N*-sulfonylimino)-1,4-benzodiazepines **16** for the yellow compounds.

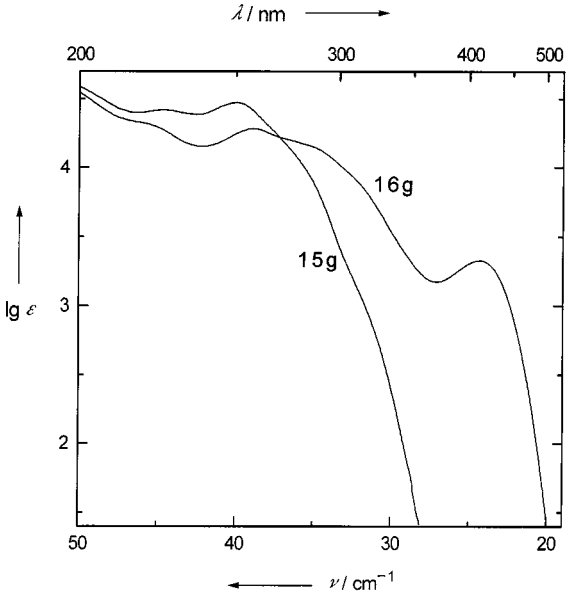


Figure 2. UV/Vis spectra of the *N*-(trifluoromethanesulfonyl)imino-1,4-benzodiazepines **15g** and **16g** recorded for solutions in acetonitrile at 20 °C

The structures and configurations of (*E*)-**15b** (Figure 3), (*Z*)-**16d** (Figure 4), and (*Z*)-**16e** (Figure 5) were established by X-ray diffraction analyses. In the solid state, (*E*)-**15b** adopts a half-chair conformation where six atoms define the plane from which only C-3 is twisted. The methyl group at C-3 occupies the axial position in which steric interactions are minimised. The crystal and molecular structures of (*Z*)-**16d** and (*Z*)-**16e** are similar. The asymmetric unit of (*Z*)-**16e** contains one disordered molecule of ethanol, which is not shown in Figure 5. In all refinements, the observed position parameters of the non-hydrogen atoms were fixed; the hydrogen atoms were neglected.

Whereas in the solid state only a single diastereomer is present, viz. (*ax*,*E*)-**15b**, two diastereomers of **15b**, and of **15f** also, appear in solution. The NMR spectra of the predominant diastereomer of **15b** and the minor diastereomer

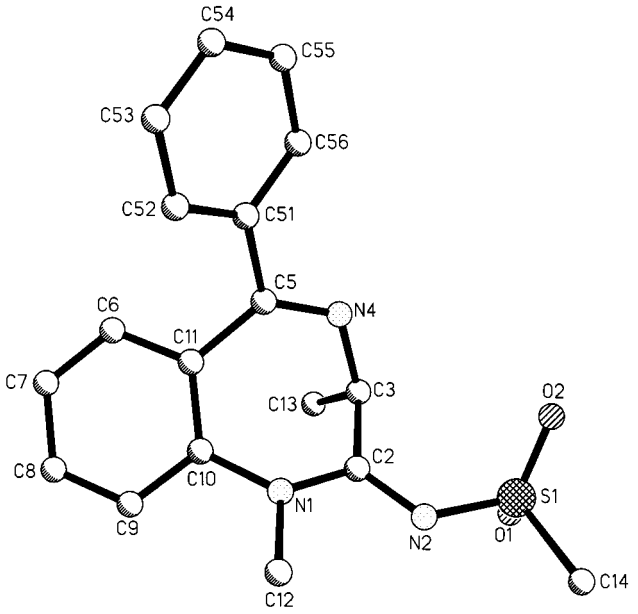


Figure 3. Perspective drawing of the 2-iminodihydrobenzazepine (*ax*,*E*)-**15b** showing the numbering of the atomss

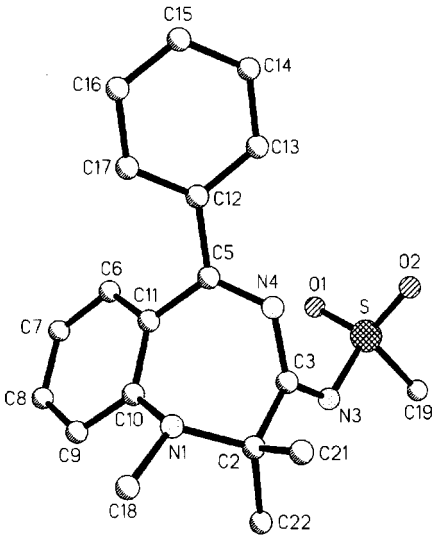


Figure 4. Perspective drawing of the 3-iminodihydrobenzazepine **16d** showing the numbering of the atoms

of **15f** are characterised by high-field resonances of the 3-methyl group (δ^H = 1; δ^C = 12) and an unusual low-field shift of the quadruplet for the proton at C-3 (δ = 6.3–6.5). The opposite is true for the corresponding signals of the other diastereomers (3-methyl: δ^H = 1.8–1.9; δ^C = 18–19; 3-H: δ = 3.8–3.9) (Tables 3 and 4). These results are interpreted in terms of (*E*) diastereomers with a quasi-axial 3-methyl group [(*ax*,*E*)-**15b** and (*ax*,*E*)-**15f**] and (*Z*) diastereomers with a quasi-equatorial 3-methyl group [(*eq*,*Z*)-**15b** and (*eq*,*Z*)-**15f**].

While the geminal methyl groups of the 3-(*N*-sulfonylimino)benzodiazepines **16d** and **16g** are shift-equivalent in the NMR spectra due to rapid exchange, those of the 2-(*N*-sulfonylimino)benzodiazepine **15g** do *not* undergo rapid exchange relative to both NMR time scales. Exchange broadening at room temperature is observed only for the

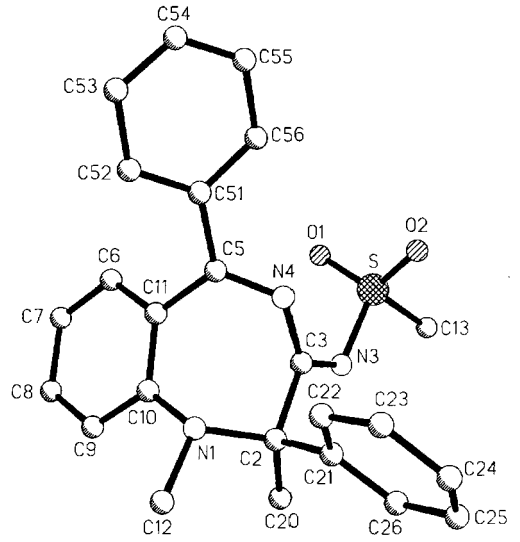
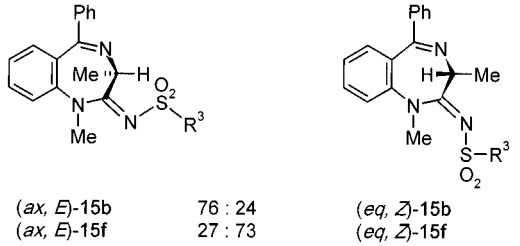


Figure 5. Perspective drawing of the 3-iminodihydrobenzazepine **16e**·C_2H_5OH showing the numbering of the atoms; the disordered ethanol molecule is not shown

methyl groups of **15d**. Cooling leads to further broadening of the proton signal and splitting at a coalescence temperature of 284 K. From the frequency difference of the two methyl signals in the limit of slow exchange (Δν = 181.3 Hz at 219 K and 200.13 Hz) the rate constant for the ring inversion at the coalescence temperature is calculated as k_c = 403 s^{-1} and the free enthalpy of activation at $\Delta G_c^{\ddagger}$ = 54 $kJmol^{-1}$.[19]



The 2-ethylidenedihydroquinazoline **10b** reacted with the sulfonyl azides **5** to afford unexpected products along with the products of ring expansion (**16f**, **15b**, and **15f**) and cleavage of the exocyclic double bond (**13**). All three isolated compounds form colourless, high-melting crystals and have remarkable molecular formulae corresponding to (**16b** or **16f** + O) = **18** and (**16b** + NSO_2CH_3) = **19**. The combined IR (Table 1) and NMR-spectroscopic evidence (Tables 3 and 4) indicated the presence of bicyclic systems and led us to propose the benzo-8-oxa-2,6-diazabicyclo[3.2.1]oct-3-ene (**18**) and benzo-2,6,8-triazabicyclo[3.2.1]oct-3-ene structures **19** or **21**, respectively. The structure of the benzo-8-oxa-2,6-diazabicyclo[3.2.1]octenone **20**, which closely resembles **18**, has been elucidated by Sternbach et al. with the help of single-crystal X-ray diffraction analysis.[20] A search of the Beilstein Data Base failed to uncover derivatives of the apparently novel 2,6,8-triazabicyclo[3.2.1]octane system.[21]

An X-ray diffraction analysis unequivocally proved structure **19** for the major bicyclic product obtained from **16b**. The compound crystallises with one molecule of dichloro-

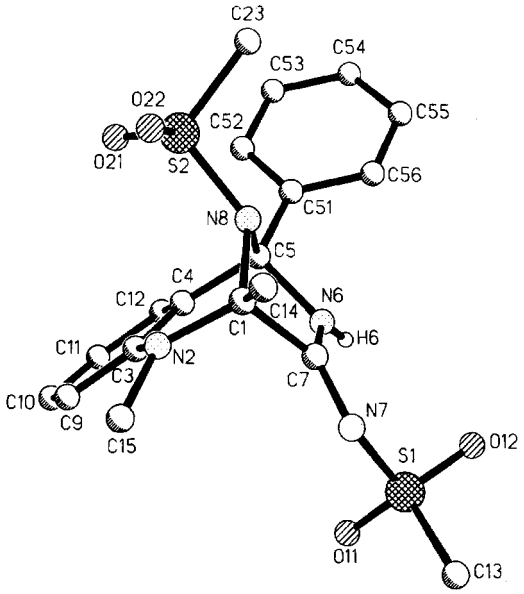
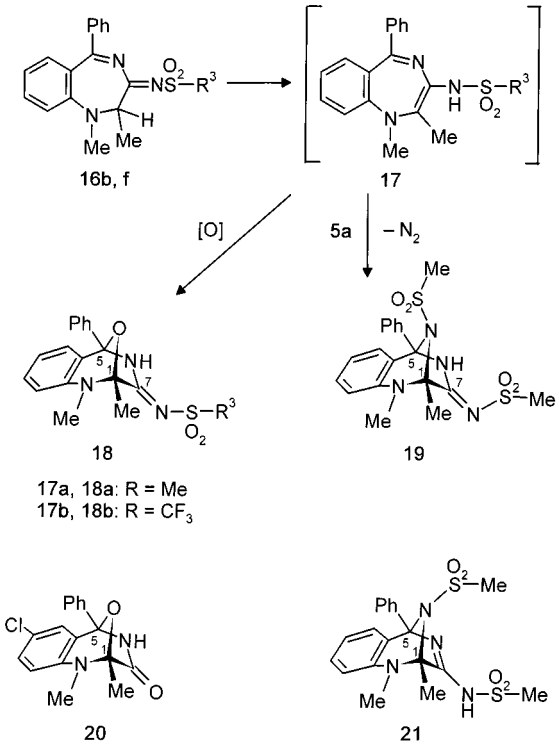


Figure 6. Perspective drawing of the benzo-2,6,8-triazabicyclo[3.2.1]octene **19**·CH_2Cl_2 showing the numbering of the atoms; the disordered molecule of dichloromethane is not shown

methane (not shown in Figure 6), which was included in the anisotropic refinements except for its hydrogen atoms. The confirmation of structure **19** lent credence to the proposed structures **18** for the minor bicyclic products because it provided the opportunity to compare their NMR data with those of **19**.



In the absence of mechanistic investigations, only tentative explanations can be offered for the formation of the unusual products **18** and **19**. Certainly, the proton at C-2 of **16b** and **16f** is involved. Tautomerisation or deprotonation in the basic medium may yield the tautomers **17** or the corresponding anions, which are cyclic 8π systems. Autoxidation with molecular oxygen that is still present in incompletely degassed reaction mixtures may give rise to the formation of **18**. [3 + 2] Cycloaddition of **5a** to **17**, or the anion derived thereof, followed by extrusion of molecular nitrogen and cyclisation across the seven-membered ring by nucleophilic addition at C-4 may afford **19**.

Conclusion

The ring enlargement of 1-methyl-2-alkylquinazolinium salts **9** by sulfonyl azides yields two types of novel *N*-sulfonylimino-1,4-benzodiazepines **15** and **16**, which arise by 1,2-shift of N-3 and N-1, respectively. In addition, cleavage products (**11** and **13**) of the exocyclic double bond of **10** are formed. While the quinazolinone **11** apparently results from autoxidation of **10**, all other products may be interpreted by invoking labile spirocyclic [3+2] cycloadducts **12** as crucial intermediates which decompose in three different ways. If C-2 of the 3-(*N*-sulfonylimino)-1,4-benzodiazepine bears a proton as in **16b** and **16f**, subsequent reactions occur that eventually furnish the heterobicycles **18** and **19**. These reactions and, perhaps, others that involve the electrophilic group C=N–C=NSO_2R in **16** result in low yields of *N*-sulfonylimino-1,4-benzodiazepines, but may be suppressed by optimisation of the reaction conditions. Finally, we note that the substitution patterns that favour ring expansion are the same as have been found with 2-alkylidenedihydroquinolines[12] and five-membered 2-alkylidene-N-heterocycles.[13,14] Usually, 2-methylene and 2-benzylidene compounds undergo cleavage of the exocyclic double bond, whereas alkyl groups at the exocyclic carbon atom promote ring enlargement.

Experimental Section

General Remarks: Yields and melting points: Table 1. – ^{1}H NMR: Table 2 and Table 3. – ^{13}C NMR: Table 2 and Table 4. – Molecular formulae and masses, and elemental analyses: Table 5. – Melting points: Apparatus from Reichert, Vienna. – ^{1}H and ^{13}C NMR: Bruker AC 200, AC 250 and DMX 600 (**10a–e**, **15b**, and **15f**). The assignments of the signals of **15b**, **15d**, **15f**, **16d**, **16e**, **16h**, **18a**, **18b**, and **19** were based on ^{13}C,^{1}H COSY experiments. – IR: Perkin-Elmer 1420. – UV/Vis: Perkin-Elmer 330. – Flash chromatography: (40 × 4) cm and (30 × 2.5) cm glass columns with silica gel 32–63 μm (ICN Biomedicals), UV detector Knauer 87.00 (λ = 254 nm), 1.8 bar N_2. – MPLC: (70 × 7)cm glass column packed with silica gel LiChroprep Si60, 15–20 μm (Merck), UV detector Knauer 87.00 (λ = 254 nm), differential refractometer Bischoff 8110. – MS, 70 eV or chemical ionisation with isobutane, 0.3 mbar (**15b**, **15f**, **16f**, **18a**, **18b**, **19**): Finnigan MAT 8200.

Tetrahydrofuran and benzene were dried with powdered KOH and distilled from NaH. Petroleum ether (PE), boiling range 50–70°C, ethyl acetate (EA), and 1,2-dichloroethane were distilled from P_2O_5. – [D_3]Acetonitrile and [D_6]dimethyl sulfoxide were dried with

CaH_2. [D_6]Benzene was dried with NaH. – NaH and KH, suspended in paraffin oil, were washed three times with pentane and dried in the stream of Ar. Experiments involving NaH, KH, and **10** were carried out in dry solvents under Ar (99.998%). – 2-Aminobenzonitrile was purchased from Acrôs Organics. – The following compounds were prepared as described: **5a**,[13] solutions of **5b** in dichloromethane,[22] **8a**–**c**.[15]

2-Alkyl-4-phenylquinazolines (8d and 8e). – General Procedure: A solution of 2-aminobenzonitrile (11.8 g, 100 mmol) in tetrahydrofuran (100 mL) was added dropwise to a stirred solution of phenylmagnesium bromide in tetrahydrofuran (300 mL) prepared from bromobenzene (40.8 g, 260 mmol) and magnesium (5.4 g, 220 mmol). The mixture was heated under reflux for 2 h. Subsequently, 2-methylpropionyl chloride (for **8d**, 15.9 g, 150 mmol) or 2-phenylpropionyl chloride (for **8e**, 25.2 g, 150 mmol) was added dropwise to the stirred mixture, which was cooled with ice, followed by heating under reflux for 2 h. The mixture was allowed to cool. A saturated aq. solution of NH_4Cl (200 mL) was added and sufficient water to dissolve the inorganic precipitate. The aqueous layer was extracted with ether (4 × 50 mL). The combined organic layers were dried with $MgSO_4$. Distillation of the solvent in vacuo gave brown oily residues.

2-(1-Methylethyl)-4-phenylquinazoline (8d): The residue was extracted with aq. HCl (2 M, 200 mL). The aq. solution was made alkaline by dropwise addition of aq. NaOH (20%) under cooling with ice. The precipitate was collected by filtration, washed with water, and dried. Yellow powder (17.3 g, 70%). Recrystallisation from ethanol/water (1:1) gave a white powder (12.7 g, 51%, m.p. 59–60 °C).

2-(1-Phenylethyl)-4-phenylquinazoline (8e): Repeated recrystallisation from ethanol afforded a colourless powder (8.0 g, 26%, m.p. 107–108 °C).

2-Alkyl-1-methyl-4-phenylquinazolinium Hexafluorophosphates 9a, 9b, and 9d. – General Procedure: A mixture of **8a**, **8b**, or **8d** (25 mmol) and dimethyl sulfate (4.73 g, 37.5 mmol) was stirred at 110–120 °C for 1 h. After cooling to 70 °C, ethanol (10 mL) was added and the mixture was stirred to give a clear solution. A solution of NH_4PF_6 (4.08 g, 25 mmol) in water (10 mL) was added dropwise. A pale yellow oil formed and solidified slowly (1–24 h). The solid material was collected by filtration, washed with water, and recrystallised.

1,2-Dimethyl-4-phenylquinazolinium Hexafluorophosphate (9a): Brown powder (6.46 g, 68%). Recrystallisation from ethanol gave pale yellow needles (3.23 g, 34%, m.p. 235–238 °C, dec.).

2-Ethyl-1-methyl-4-phenylquinazolinium Hexafluorophosphate (9b): Pale brown powder (7.48 g, 76%). Recrystallisation from ethanol gave pale yellow needles (5.52 g, 56%, m.p. 226–232 °C, dec.).

Table 2: Chemical shifts (δ values) and coupling constants ([Hz], *in italics*) in proton (top) and carbon-13 spectra (bottom) of 2-alkylidene-1-methyldihydroquinazolines **10**

Cpd.	R^1			R^2	*J* [Hz]	NMe	Aryl			[a]
10a	H	3.77	4.17	H		3.09	6.6 – 7.6			F
10b	H	4.20 (q)	1.90 (d)	Me	*6.8, 3J*	3.00	6.6 – 7.7			F
10c	H	5.27		Ph		3.30	6.7 – 8.0			F
10d	Me	1.65	2.31	Me	*0.6, 4J*	2.77	6.3 – 7.8			B
10e	Me	2.43		Ph		2.67	6.7 – 7.8			F
					C=N		CH		quat.C	
10a	H		83.4	H	162.1	33.1	112.2 128.68 129.77 134.1	119.1 128.73 129.82	118.0 138.8 146.2	F
10b	H		93.8 11.6	Me	160.7	32.9	112.0 128.49 129.78 133.9	118.56 128.73 129.86	118.23 139.1 146.3 147.4	F
10c	H		100.6	Ph	162.3	34.1	113.1 124.1 128.63 130.18 134.4	119.6 128.27 128.97 130.20	118.3 138.8 139.6 146.46 146.94	F
10d	Me	19.67	107.8 19.85	Me	157.7	41.0	113.4 127.6 129.07 132.1	118.4 128.3 129.82	120.4 138.8 142.7 149.4	B
10e	Me	19.2	110.7	Ph	159.3	40.7	113.4 125.9 128.78 129.11 130.22	119.5 127.9 128.79 129.93 133.4	120.2 138.8 144.10 144.30 148.8	F

[a] Solvents: B = [D_6]benzene, F = [D_8]tetrahydrofuran.

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

Cpd.	Me—CH_n		*3J*	NMe	SO_2Me	NH	Ring protons	[a]
8d	1.49	3.44 (sept)	*6.9*				7.4 – 8.1	T
8e	1.88	4.64 (q)	*7.2*				7.1 – 8.1	T
9a	3.19			4.37			7.6 – 8.5	A
9b	1.55	3.45 (q)	*7.3*	4.37			7.6 – 8.5	A
9c		4.84[b]		4.40			7.3 – 8.5	A
9d	1.54	3.86 (sept)	*6.6*	4.42			7.6 – 8.5	A
9e	1.89	5.03 (q)	*6.7*	4.34			7.2 – 8.5	A
11				3.79			7.2 – 7.9	T
13a				3.94	3.29		7.3 – 8.1	T
13b				3.97			7.4 – 8.2	T
(*E*)-**15b**	0.99	6.53 (q)	*7.3*	3.50	3.13			
(*Z*)-**15b**	1.82	3.84 (q)	*6.5*	3.73	3.15			
15d[c]	0.91 1.81			3.92	3.22		7.2 – 7.7	T
[d]	1.34			3.86	3.13		7.2 – 7.7	T
(*E*)-**15f**	1.01	6.27 (q)	*7.3*	3.59				
(*Z*)-**15f**	1.92	3.90 (q)	*6.6*	3.67				
15g	0.92 1.93			3.83			7.3 – 7.7	T
15h	2.10			3.89			6.7 – 7.8	T
16d	1.49			2.85	3.03		7.0 – 7.8	T
16e	1.89			2.91	3.04		6.9 – 7.6	T
16f	1.40	3.44 (q)	*6.7*	3.43			6.9 – 7.9	T
16g	1.49			2.92			7.0 – 7.8	T
16h	2.12			3.42			6.9 – 7.8	T
18a	1.89			3.07	2.97	8.86	6.5 – 7.6	T
18b	1.95			3.10		9.07	6.5 – 7.6	T
19	2.01			2.95	2.15 2.86	10.63	6.7 – 8.0	D

[a] Solvents: A = [D_3]acetonitrile, D = [D_6]dimethyl sulfoxide, T = [D]trichloromethane. – [b] CH_2Ph. – [c] Spectrum in the slow-exchange limit (–54 °C). At room temperature, a broad signal (δ = 0.8–1.8) is observed for the geminal methyl groups. – [d] Spectrum in the limit of fast exchange (58 °C).

Table 4. Chemical shifts (δ values) and $^{19}F,^{13}C$ coupling constants ([Hz] *in italics*) in carbon-13 spectra; similar chemical shifts of carbon atoms that bear the same number of protons are printed *in italics* and may be exchanged

Cpd.	CH_n—Me		NMe	SO_2Me	CF_3	C=N	Other ring-C CH						quat. C			[a]
8d	38.0	21.9				168.3 171.1	126.53 133.2	126.90	128.52	128.55	129.73	130.02	121.4	137.7	151.5	T
8e	49.3	20.9				168.27 168.48	126.34 128.74	126.77 129.79	126.84 130.13	128.02 133.3	128.25	128.47	121.4 151.5	137.6	144.5	T
9a		25.7	40.0			164.4 175.7	119.1 140.5	130.2	131.46	131.57	132.4	134.0	122.9	135.9	143.6	A
9b	31.0	11.1	39.2			167.3 175.5	119.1	130.2	131.5	132.6	134.0	140.4	122.7	136.0	143.7	A
9c	42.1		38.5			164.7 174.1	119.3 131.81	128.8 132.7	130.04 134.2	130.23 140.6	130.61	131.57	123.0 144.0	134.7	138.8	A
9d	34.7	21.1	39.1			170.4 175.5	119.4 140.3	130.2	131.34	131.49	132.7	134.1	122.7	136.1	143.8	A
9e	45.8	22.1	39.3			166.8 175.2	119.3 131.75	128.94 132.9	129.16 134.3	130.25 140.53	130.29	131.45	122.8 144.1	136.0	140.94	A
11			31.5			156.2 175.0[b]	114.5 135.7	122.6	128.8	130.12	130.37	131.00	116.3	136.8	144.5	T
13a			33.4	41.4		154.3 171.8	115.1 136.5	123.9	127.8	130.21	130.53	131.6	116.7	135.7	143.0	T
13b			34.0		[c]	155.2 172.1	115.4 136.8	124.9	128.8	130.53	130.99	132.0	117.4	135.0	142.8	T
(*E*)-**15b**[d]	56.3	12.1	40.1	43.3		163.08	122.6	123.2	125.0	125.75	128.17	128.29	130.04	137.8	138.74	T
(*Z*)-**15b**[d]	60.2	18.9	41.8	44.8		168.0 169.26 169.60	129.73 131.50	129.77 131.80	129.80	130.04	130.62	130.77	138.80	143.8	144.9	
(*E*)-**15f**[d]	58.8	11.7	40.96		119.18 *J = 317*	166.4 168.39	122.7 129.84	123.02 130.04	123.03 130.30	128.24 130.77	128.38 130.98	129.59 131.86	129.99 138.8	130.57 142.5	137.4 143.4	T
(*Z*)-**15f**[d]	59.7	18.5	41.42		119.50 *J = 316*	168.72 171.3	131.89									
15h	71.3	35.3	44.5		119.5 *J = 316*	168.8 170.1	123.3 129.38	124.4 129.70	126.26 131.16	126.78 131.38	128.21	128.48	131.79 141.5	138.2	141.4	T
16f	64.5	12.4	40.2		119.4 *J = 319*	149.4 170.6	119.26 135.90	119.64	128.6	130.6	131.3	135.59	118.5	138.9	147.8	T
16h	75.0	24.4	39.1		119.3 *J = 321*	156.0 170.4	120.5 130.15	121.7 131.2	127.32 133.8	127.53 134.8	128.09	128.28	123.6 149.8	137.6	138.9	T
	C	Me_2														
15d	63.8	[e]	*45.05*	*45.17*		166.3 167.6	123.6 131.6	125.8	128.2	129.35	129.56	130.42	130.65	139.2	144.9	T
[f]	63.7	20.6 34.0	*45.11*	*45.26*		166.7 169.3	123.5 131.9	126.0	128.4	129.40	129.71	130.6	134.6	139.0	144.7	T
15g	63.4	20.1 33.3	44.8		119.4 *J = 316*	166.4 171.1	123.3 132.0	126.8	128.3	129.49	129.90	130.79	130.34	138.6	143.6	T
16d	76.8	22.1	33.7	42.1		168.1 182.9	122.59 131.94	122.87	128.4	130.50	130.77	131.62	133.1	136.3	151.2	T
16e	80.0	19.0	36.1	41.1		168.5 171.5	121.9 130.3	122.4 131.39	127.47 131.81	127.75 132.7	128.23	128.32	129.6 149.9	137.3	140.1	T
16g	75.3	22.1	34.9		118.9 *J = 318*	169.1 182.9	122.79 132.72	123.15	128.6	131.04	131.34	132.57	131.10	136.0	151.1	T
	C-1, C-5	Me														
18a	93.9 95.5	18.7	32.5	42.1		158.8	112.7 130.4	117.5	124.6	126.4	128.7	129.9	124.27	134.0	142.2	T
18b	94.6 96.7	18.4	32.2		121.9 *J = 320*	161.6	112.7 131.0	117.9	124.8	126.2	129.0	130.37	122.6	132.8	141.4	T
19	80.99 81.08	19.5	32.6	41.2 44.1		155.0	113.8 130.4	116.6	125.3	127.8	129.0	129.8	123.4	131.0	143.1	D

[a] Solvents: See Table 3. – [b] C=O. – [c] The quadruplet of the CF_3 group could not be detected. – [d] Signals with δ > 100 could not be assigned to the individual diastereomers. – [e] Due to exchange broadening, the signals of the geminal methyl groups disappeared in the noise. – [f] Spectrum recorded in the limit of slow exchange (–54 °C).

1-Methyl-2-(1-methylethyl)-4-phenylquinazolinium Hexafluorophosphate (9d): Colourless powder (8.40 g, 82%). Recrystallisation from ethanol/water (10:1) gave colourless needles (4.76 g, 45%, m.p. 198–200 °C).

2-Benzyl-1-methyl-4-phenylquinazolinium Hexafluorophosphate (9c): Methyl trifluoromethanesulfonate (0.55 g, 3.4 mmol) was added dropwise by syringe under Ar to a stirred solution of **8c** (1.0 g, 3.4 mmol) in 1,2-dichloroethane (5 mL). The mixture was heated under reflux for 4 h. The solvent was distilled in vacuo. The oily residue was dissolved in ethanol (5 mL). A solution of NH_4PF_6 (0.55 g, 3.4 mmol) in water (10 mL) was added dropwise. A colourless oil formed and solidified slowly (5 d). The solid material was collected by filtration. Colourless powder (1.51 g, 98%). Recrystallisation from ethanol afforded colourless crystals (0.89 g, 59%, m.p. 172–174 °C).

1-Methyl-4-phenyl-2-(1-phenylethyl)quinazolinium Hexafluorophosphate (9e): This compound was prepared from **8e** (2.74 g, 8.8 mmol) according to the procedure described for **9c**. Colourless powder (3.68 g, 90%). Recrystallisation from ethanol afforded colourless crystals (1.68 g, 41%, m.p. 199–201 °C).

2-Alkylidene-1,2-dihydro-1-methylquinazolines 10a–e. – General Procedure: Suspensions of powdered **9a**–**e** (0.2 mmol) and KH (0.08 g, 2 mmol) in [D_8]tetrahydrofuran (1 mL, **9a**–**c** and **9e**) or [D_6]benzene (1 mL, **9d**) were stirred in 10-mL centrifuge tubes, equipped with a septum, for 1 or 24 h, respectively. The solid material was separated with the help of the centrifuge. The solutions were transferred by syringe into NMR sample tubes and degassed by standard freeze-thaw techniques. The NMR sample tubes were evacuated (10^{-2} Torr) and sealed with a torch.

Experiments with Methanesulfonyl Azide (5a). – General Procedure: Suspensions of powdered **9a**–**e** (3 mmol), NaH (0.22 g, 9 mmol), and **5a** (0.91 g, 7.5 mmol) in tetrahydrofuran (30 mL) were stirred under Ar in 80-mL centrifuge tubes, equipped with a septum, until the gas evolution had ceased (1 d). The solid material was separated with the help of the centrifuge, washed with tetrahydrofuran (2 × 5 mL), and suspended in tetrahydrofuran (5 mL). The excess of NaH was destroyed by dropwise addition of ethanol until the gas evolution ceased. Dilution of the mixture with water (50 mL) yielded a precipitate, which was collected by filtration, washed with water and tetrahydrofuran, and dried to give **13a**. After separation of the solid material from the reaction mixtures, the solvent was distilled under vacuum from the combined organic solutions and washings to give an oily residue, which was separated by flash chromatography.

1,2-Dihydro-1-methyl-2-[*N*-(methylsulfonyl)imino]-4-phenylquinazoline (13a). – (a) From 9a: Green needles (0.48 g, 50%, m.p. 296–299 °C) were obtained from the solid material. Flash chromatography of the oily residue with EA gave a second crop, brown needles (30 mg, 3%, m.p. 295–298 °C). Recrystallisation from ethanol/$CHCl_3$ (4:1) afforded almost colourless needles (m.p. 297–300 °C). – MS, *m*/*z* (%): 313 (10) [M^+], 298 (12) [M^+ – Me], 235 (21), 234 (100) [M^+ – SO_2Me], 205 (16), 194 (6). – **(b) From 9c:** Brown needles (0.72 g, 76%, m.p. 296–298 °C) were obtained from the solid material. Flash chromatography with EA of the oily residue gave a second crop (18 mg, 2%).

Trapping of the Ethylidenedihydroquinazoline 10b with 5a. – From 9b: Compound **13a** was obtained from the solid material (0.20 g, 21%). Flash chromatography of the oily residue with PE/EA (1:1) gave a brown oil (**18a**) and colourless crystals (**19**, 0.26 g, 20%, m.p. 156–157 °C, dec.). Continued flash chromatography with EA yielded a brown solid (**15b**, 0.56 g) and a second crop of **13a** (0.15 g, 16%). – Compound **18a** was purified by flash chromatography with PE/EA (1:1) to give a colourless powder (50 mg, 5%, m.p. 190–195 °C, dec.). Recrystallisation from $CHCl_3$/PE (1:1) afforded a colourless powder; MS, *m*/*z* (%): 358 (100) [M^+ + H]. – Compound **19** was purified by flash chromatography with PE/EA (3:2) to give colourless crystals; MS, *m*/*z* (%): 435 (0.6) [M^+ + H], 247 (9), 193 (9), 191 (91), 176 (51), 153 (8), 152 (100), 113 (16). – Compound **15b** was purified by flash chromatography with PE/EA (1:1) and recrystallised from ethanol to give colourless crystals (0.15 g, 15%, m.p. 187–193 °C); MS, *m*/*z* (%): 342 (100) [M^+ + H].

2,3-Dihydro-1,3,3-trimethyl-2-[*N*-(methylsulfonyl)imino]-5-phenyl-1*H*-benzo[*e*][1,4]diazepine (15d), and 2,3-Dihydro-1,2,2-trimethyl-3-[*N*-(methylsulfonyl)imino]-5-phenyl-1*H*-benzo[*e*][1,4]diazepine (16d). – From 9d: Compound **13a** was obtained from the solid material (32 mg, 3%). Flash chromatography of the oily residue with PE/EA (1:1) gave a yellow solid (**16d**, 0.70 g) as the first fraction and a colourless solid (**15d**, 0.09 g). Continued flash chromato-

Table 5. Molecular formulae and masses, and elemental analyses

Cpd.		Molecular Mass		Elemental analysis C	H	N	S
8d	$C_{17}H_{16}N_2$	248.3	Calcd.	82.23	6.49	11.28	
			Found	82.20	6.43	11.26	
8e	$C_{22}H_{18}N_2$	310.4	Calcd.	85.13	5.84	9.03	
			Found	84.77	5.86	8.68	
9a	$C_{16}H_{15}F_6N_2P$	380.3	Calcd.	50.53	3.98	7.37	
			Found	50.79	4.03	7.21	
9b	$C_{17}H_{17}F_6N_2P$	394.3	Calcd.	51.78	4.35	7.11	
			Found	51.54	4.18	6.99	
9c	$C_{18}H_{19}F_6N_2P$	408.3	Calcd.	52.95	4.96	6.86	
			Found	52.70	4.95	6.80	
9d	$C_{22}H_{19}F_6N_2P$	456.4	Calcd.	57.89	4.20	6.14	
			Found	57.55	4.22	6.06	
9e	$C_{23}H_{21}F_6N_2P$	470.4	Calcd.	58.73	4.50	5.96	
			Found	58.27	4.38	5.93	
13a	$C_{16}H_{15}N_3O_2S$	313.4	Calcd.	61.33	4.82	13.41	10.23
			Found	60.82	4.96	13.55	10.19
13b	$C_{16}H_{12}F_3N_3O_2S$	367.3	Calcd.	52.31	3.29	11.44	8.73
			Found	52.01	3.51	11.28	8.74
15b	$C_{18}H_{19}N_3O_2S$	341.4	Calcd.	63.32	5.61	12.31	9.39
			Found	62.52	5.87	12.41	9.34
15d	$C_{19}H_{21}N_3O_2S$	355.5	Calcd.	64.20	5.95	11.82	9.02
			Found	63.74	5.59	11.52	9.03
16d			Found	64.17	6.12	11.76	9.12
15f	$C_{18}H_{16}F_3N_3O_2S$	395.4	Calcd.	54.68	4.08	10.63	8.11
			Found	54.99	4.04	10.68	8.07
16f			Found	54.96	4.17	10.64	8.17
15g	$C_{19}H_{18}F_3N_3O_2S$	409.4	Calcd.	55.74	4.43	10.26	7.83
			Found	55.87	4.45	10.23	7.62
16g			Found	55.67	4.60	10.28	7.84
15h	$C_{24}H_{20}F_3N_3O_2S$	471.5	Calcd.	61.14	4.28	8.91	6.80
			Found	60.95	4.27	8.85	6.70
16h			Found	61.23	4.40	8.89	7.47
16e	$C_{24}H_{23}N_3O_2S$	417.5	Calcd.	69.04	5.55	10.06	7.68
			Found	68.84	5.50	9.77	7.70
18a	$C_{18}H_{19}N_3O_3S$	375.4	Calcd.	60.49	5.36	11.76	8.97
			Found	60.07	5.36	11.78	9.04
18b	$C_{18}H_{16}F_3N_3O_3S$	411.4	Calcd.	52.55	3.92	10.71	7.79
			Found	52.46	4.01	10.47	7.90
19	$C_{19}H_{22}N_4O_4S_2$	434.5	Calcd.	52.52	5.10	12.89	14.76
			Found	52.40	5.23	12.49	15.08

graphy with EA yielded a yellow oil (second crop of **13a**, 7 mg). Recrystallisation of the different fractions from ethanol afforded **13a** (1 mg, 1%), **15d** (colourless crystals), and **16d** (yellow needles). – Compound **15d**: MS, *m/z* (%): 355 (8), [M^+], 299 (9), 277 (23), 276 (100) [$M^+ - SO_2Me$], 236 (27), 235 (31), 220 (28), 219 (11). – Compound **16d**: MS, *m/z* (%): 355 (0.5) [M^+], 277 (14), 276 (61) [$M^+ - SO_2Me$], 235 (29), 234 (100), 220 (17), 219 (9).

2,3-Dihydro-1,2-dimethyl-3-[*N*-(methylsulfonyl)imino]-2,5-diphenyl-1*H*-benzo[*e*][1,4]diazepine (15e). – From 9e: Compound **13a** was obtained from the solid material (0.65 g, 70%). Flash chromatography of the oily residue with PE/EA (1:1) gave an orange-coloured oil (**16e**, 0.49 g). Continued flash chromatography with EA yielded a second crop of **13a** (47 mg, 5%). Recrystallisation of **16e** from ethanol afforded yellow needles (0.21 g, 17%, m.p. 191–193 °C). – MS, *m/z* (%): 417 (2) [M^+], 339 (26), 338 (100) [$M^+ - SO_2Me$], 297 (31), 296 (83), 280 (6), 237 (5), 236 (31), 235 (8), 221 (7), 220 (34), 204 (6).

Experiments with Trifluoromethanesulfonyl Azide (5b). – General Procedure: Suspensions of powdered **9a**, **9b**, **9d**, or **9e** (2 mmol) and KH (0.40 g, 10 mmol) in tetrahydrofuran (**9a**, **9b**, **9e**, 25 mL) or benzene (**9d**, 25 mL) were stirred for 1 or 24 h, respectively, in a centrifuge tube equipped with a septum and connected to a supply of Ar. Solid material was removed with the help of a centrifuge. The supernatant solution was transferred by syringe into a 100-mL flask, and the solid material was washed twice with the solvent employed (5 mL). A solution of **5b** (1.05 g, 6 mmol) in dichloromethane (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and room temperature. The solvent was distilled under vacuum.

1,2-Dihydro-1-methyl-2-[*N*-(trifluoromethylsulfonyl)imino]-4-phenylquinazoline (13b). – From 9a: The brown oily residue was dissolved in EA (20 mL). The resulting precipitate was removed by filtration. Pale brown powder (0.23 g, 32%, m.p. 251–256 °C). Flash chromatography of the mother liquor with PE/EA (1:1) gave a second crop as a mixture of brown oil and crystals, which was recrystallised from ethanol to afford a brown powder (60 mg, 8%, m.p. 249–256 °C). Repeated recrystallisation from ethanol yielded an almost colourless powder, m.p. 254–256 °C. – MS, *m/z* (%): 367 (7) [M^+], 300 (6), 299 (16), 298 (100) [$M^+ - CF_3$], 234 (19) [$M^+ - SO_2CF_3$], 219 (6), 205 (9).

2,3-Dihydro-1,3-dimethyl-2-[*N*-(trifluoromethylsulfonyl)imino]-5-phenyl-1*H*-benzo[*e*][1,4]diazepine (15f), 2,3-Dihydro-1,2-dimethyl-3-[*N*-(trifluoromethylsulfonyl)imino]-5-phenyl-1*H*-benzo[*e*][1,4]diazepine (16f) and 18b. – From 9b: Flash chromatography of the residue with EA gave a brown oil (mixture of **15f**, **16f**, and **18b**) and a brown powder (**13b**, 38 mg, 5%, m.p. 254–256 °C). MPLC of the oil with PE/EA (4:1) yielded colourless crystals (**18b**, 36 mg, 5%, m.p. 162–167 °C, dec.), a yellow oil (**15f**, 100 mg), and yellow crystals (**16f**, 94 mg, 12%, m.p. 160–165 °C). – Recrystallisation from ethanol afforded colourless crystals of **18b** {m.p. 165–167 °C (dec.); MS, *m/z* (%): 412 (100) [$M^+ + H$]}, and **15f** {48 mg, m.p. 131–134 °C; MS, *m/z* (%): 396 (100) [$M^+ + H$]}, and yellow, yellow

Table 6. Experimental details and results of the X-ray diffraction analyses of (*ax*,*E*)-**15b**, **16d**, **16e**·C_2H_5OH and **19**·CH_2Cl_2

Compound	(*ax*,*E*)-**15b**	**16d**	**16e**·C_2H_5OH	**19**·CH_2Cl_2
Molecular formula	$C_{18}H_{19}N_3O_2S$	$C_{19}H_{21}N_3O_2S$	$C_{24}H_{23}N_3O_2S$•C_2H_5OH	$C_{19}H_{22}N_4O_4S_2$•CH_2Cl_2
Molecular mass	341.43	355.45	463.6	519.47
Crystal system	triclinic	orthorhombic	orthorhombic	triclinic
Space group	*P*1bar	*Pbca*	*Pbcn*	$P\bar{1}$
a [pm]	764.8(1)	1725.3(4)	3035.9(3)	920.99(6)
b [pm]	1034.6(1)	2336.9(8)	891.9(1)	1006.10(7)
c [pm]	1118.3(1)	907.7(3)	1720.1(2)	1453.78(8)
α [deg]	96.836(6)			75.740(5)
β [deg]	94.686(6)			73.587(5)
γ [deg]	102.458(7)			75.740(5)
V [nm^3]	0.8526(1)	3.6679(2)	4.6575(2)	1.1533(2)
Z	2	8	8	2
d (calcd.) [g cm^{-3}]	1.330	1.287	1.322	1.496
Size of the crystal [mm]	0.3 x 0.35 x 0.2	0.3 x 0.6 x 0.08	0.25 x 0.45 x 0.02	0.5 x 0.65 x 0.2
Range *h*	–1 → 9	0 → 11	–32 → 0	–11 → 18
k	–13 → 13	0 → 22	0 → 9	–12 → 12
l	–14 → 14	–1 → 30	0 → 18	–18 → 18
No. of measured reflections	4679	4960	5906	6227
Symmetry-independent reflections	3798	4211	5275	5241
Observed reflections $F>3\sigma(F)$	3130	1904	2059	1589
Linear absorpt. coeff. [mm^{-1}]	0.21	0.19	0.17	0.50
Absorption correction	ψ-scan	ψ-scan	ψ-scan	ψ-scan
Ratio F_{obs}/parameters	14.42	8.39	7.20	15.30
R	0.049	0.083	0.129	0.045
R_w	0.053	0.073	0.100	0.048
Diff. Four. $\Delta\rho_{max}$[a] [eÅ^{-3}]	0.25	0.33	0.91	0.61
$\Delta\rho_{min}$[b]	0.26	0.37	0.52	0.54

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

fluorescing crystals of **16f** {m.p. 169–172 °C; MS, *m*/*z* (%): 396 (100) [M^+ + H]}.

2,3-Dihydro-1,3,3-trimethyl-2-[*N*-(trifluoromethylsulfonyl)imino]-5-phenyl-1*H*-benzo[*e*][1,4]diazepine (15g), 2,3-Dihydro-1,2,2-trimethyl-3-[*N*-(trifluoromethylsulfonyl)imino]-5-phenyl-1*H*-benzo[*e*][1,4]diazepine (16g), and 1-Methyl-4-phenyl-1,2-dihydroquinazol-2-one (11). – From 9d: Flash chromatography of the residue with EA gave a yellow oil (mixture of **15g** and **16g**), pale yellow crystals (**13b**, 14 mg, 2%, m.p. 252–255 °C), and pale yellow needles (**11**, 50 mg, 12%, m.p. 145–147 °C). MPLC of the oil with PE/EA (7:3) yielded **15g** and **16g** as yellow solids. Recrystallisation from ethanol afforded pale yellow needles of **11** {m.p. 145–147 °C (ref.[18] pale yellow prisms, m.p. 142–143 °C); MS, *m*/*z* (%): 236 (70) [M^+], 235 (100), 221 (37), 220 (18), 194 (41)}, colourless crystals of **15g** (155 mg, 19%, m.p. 194–197 °C), and yellow needles of **16g** (189 mg, 23%, m.p. 137–140 °C). – **15g:** UV/Vis, λ_{max} [nm] (log ε) (Figure 2): 224 (4.418), 250 (4.473.). – MS, *m*/*z* (%): 409 (2) [M^+], 277 (14), 276 (62) [$M^+ - SO_2CF_3$], 235 (26), 234 (100), 220 (19), 219 (9). – **16g:** UV/Vis, λ_{max} [nm] (log ε) (Figure 2): 220 (4.311) (sh), 257 (4.283), 288 (4.135) (sh), 410 (3.327). – MS, *m*/*z* (%): 409 (15) [M^+], 353 (10), 277 (31), 276 (100) [$M^+ - SO_2CF_3$], 236 (29), 220 (31), 219 (14).

2,3-Dihydro-1,3-dimethyl-2-[*N*-(trifluoromethylsulfonyl)imino]-3,5-phenyl-1*H*-benzo[*e*][1,4]diazepine (15h), and 2,3-Dihydro-1,2-dimethyl-3-[*N*-(trifluoromethylsulfonyl)imino]-2,5-diphenyl-1*H*-benzo[*e*][1,4]diazepine (16h). – From 9e: The yellow oily residue was dissolved in EA (20 mL). The resulting precipitate was removed by filtration to afford a colourless powder (**13b**, 0.31 g, 42%, m.p. 250–252 °C). Flash chromatography of the mother liquor with PE/EA (1:1) gave a yellow oil (mixture of **15h** and **16h**), and colourless crystals (**13b**, 21 mg, 3%, m.p. 250–252 °C). The yellow oil was dissolved in EA (10 mL). Yellow crystals formed overnight and were removed with the help of a centrifuge (**16h**, 0.12 g, 13%, m.p. 230–234 °C). Colourless crystals precipitated from the mother liquor and were removed by filtration (**15h**, 76 mg, 8%, m.p. 253–256 °C). MPLC of the mother liquor with PE/EA (7:3) yielded second crops of **15h** (yellow oil) and **16h** (orange-coloured oil). Recrystallisation of the fractions from aq. ethanol afforded colourless crystals of **15h** {42 mg, 5%, 253–256 °C; MS, *m*/*z* (%): 471 (1) [M^+], 339 (18), 338 (61) [$M^+ - SO_2CF_3$], 284 (23), 283 (95), 237 (16), 236 (100), 235 (20), 220 (36), 219 (11), 205 (10)}, and yellow, yellow fluorescing crystals of **16h** {16 mg, 2%, m.p. 227–232 °C; MS, *m*/*z* (%): 471 (1) [M^+], 339 (239), 338 (80) [$M^+ - SO_2CF_3$], 297 (35), 296 (100), 236 (11), 220 (32)}.

X-ray Diffraction Analyses: Analysis was performed on transparent, colourless [(*ax*,*E*)-**15b**, **19**·CH_2Cl_2] and yellow (**16d**, **16e**·C_2H_5OH) crystals. 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 Siemens P4 system. The programme SHELXTL PLUS[23] was employed. The structures were solved by direct methods and refined anisotropically by the least-squares method. The weighting scheme for R_w is $1/\sigma^2$. The positions of hydrogen atoms were calculated and included in the refinements with isotropic description.[24]

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[24] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-127358 (**16d**), -127359 (**15b**), -127360 (**19**·CH_2Cl_2), and -127361 (**16e**·C_2H_5OH). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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