Ring Expansion of 2-Alkylidenedihydroquinolines to 2-Iminodihydro-1-benzazepines by Phenyl, Methanesulphonyl, and Trifluoromethanesulphonyl Azide[1]

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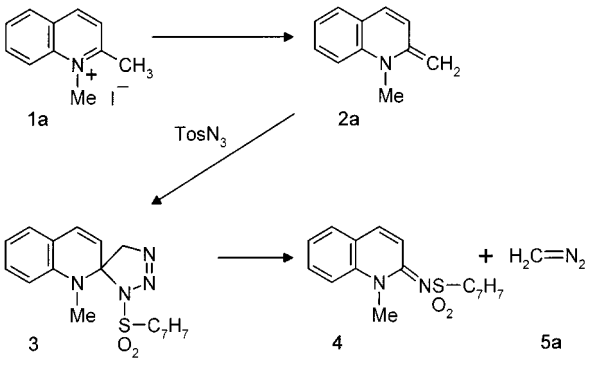
2-Alkyl-1-methylquinolinium hexafluorophosphates **1** are deprotonated by sodium or potassium hydride to afford solutions of 2-alkylidenedihydroquinolines **2**, which are investigated by NMR spectroscopy. 1,3-Dipolar cycloaddition of phenyl azide to **2** yields the spirocyclic products **10**. While, at 80−110 °C, the [3 + 2] cycloaddition that afforded (*u*)-**10f** is reversible and accompanied by epimerisation to give (*l*)-**10f**, thermolysis of the dimethyl compounds **10b** and **d** affords the ring-expanded products **14b** and **d**, respectively, in good yields along with molecular nitrogen. Irradiation of **10d** with light of $\lambda > 320$ nm results in the formation of similar amounts of **14d** and [3 + 2] cycloreversion products, viz. 2-diazopropane (**5b**) and the *N*-phenylimine **15d**. − Trapping of **2** by methanesulphonyl azide (**18a**) gives mixtures of the products of ring expansion (**21b**, **d**−**f**, 10−50 %) and [3 + 2] cycloreversion (**22a**, **d**, 10−80 %) of the apparently very labile intermediate spirocyclic cycloadducts **19**. The ratio of **21** vs. **22** is significantly improved when **18a** is replaced by trifluoromethanesulphonyl azide (**18b**), which affords the iminodihydrobenzazepines **21i**−**k** in 50−75 % yield. The structures of the products are based on NMR evidence and X-ray diffraction analyses performed with **21b**, **d**, and (*ax,E*)-**21e**.

Introduction

Deprotonation of 1,2-dialkylquinolinium ions, e.g. **1a**, with alkali hydroxides yields 1-alkyl-2-alkylidenedihydroquinolines, e.g. **2a**, which form pale yellow, low-melting crystals.[2] They tend to polymerisation and autoxidation, which, in some cases, leads to cleavage of the exocyclic double bond and formation of 1-methyl-2-quinolones.[3] Almost 30 years ago, Regitz and Himbert observed cleavage of that double bond of **2a** by tosyl azide to afford *N*-sulphonylimine **4** and diazomethane in low yields. This result was interpreted in terms of a [3 + 2] cycloaddition reaction furnishing the unstable spirocyclic adduct **3** followed by its [3 + 2] cycloreversion to the final products.[4]



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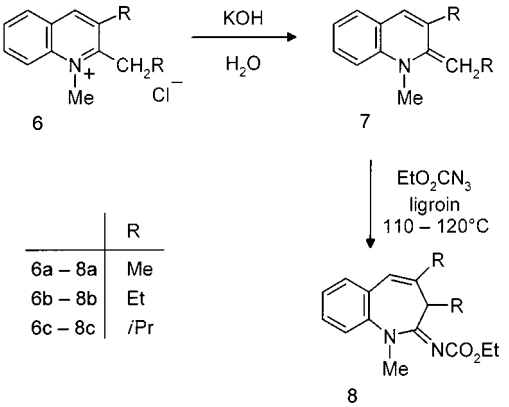
Years later, analogous [3 + 2] cycloadducts of similar precursors were reported to decompose in a completely different way: Sato et al. obtained 2-iminodihydro-1-benzazepines **8** on treatment of 1,3-dialkyl-2-alkylidenedihydroquinolines **7** with ethyl azidoformate in refluxing ligroin.[5] Subsequently, phenyl and benzoyl azide were found to convert **7a** into the analogous imines under the same conditions.[6] If the 3-alkyl group of **7** was lacking, ethyl azidoformate did *not* give ring expansion, however, but formed 2-(*N*-ethoxycarbonyl)imino-1-methyldihydroquinoline.[5] Taken together with the observation by Regitz and Himbert, this result appeared to indicate that the presence of an alkyl group at the 3-position of the alkylidenedihydroquinoline might be a prerequisite for the ring expansion reaction. Scope and further limitations of this intriguing sequence remained unexplored.



Previous studies of five-membered 2-alkylidene-*N*-heterocycles (cyclic ketene-*N,X*-acetals) have shown that strongly

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electrophilic azides give rise to analogous ring enlargement reactions already at low temperatures, thus opening a convenient access to a number of uncommon, interesting heterocyclic systems.[7] With the view of defining the parameters that determine the course of the reactions between alkylidenedihydroquinolines **2** and azides, and optimising the conditions for iminodihydro-1-benzazepine formation, we investigated the reactions of phenyl (**9**), methanesulphonyl (**18a**), and trifluoromethanesulphonyl azide (**18b**) with 2-alkylidenedihydroquinolines whose substitution pattern differ from those employed by Sato et al.[5] The electron-deficient azides allowed us to trap **2**, which were generated from *N*-methylquinolinium salts **1** by deprotonation with sodium or potassium hydride. Last but not least, these experiments were stimulated by the prospect of an efficient synthesis of 5-*aryl*-2-iminodihydro-1-benzazepines,[8] which are related to Sternbach's 5-aryl-1,4-benzodiazepines, whose pharmacological importance cannot be overestimated.[9] The results are reported here.

Results and Discussion

Substituted *N*-Methylquinolinium Hexafluorophosphates

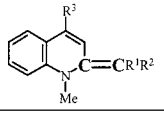
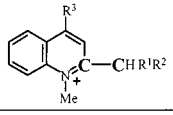
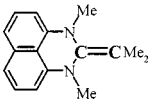
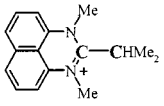
Substituted 4-phenylquinolines employed as starting materials were prepared by Friedländer synthesis from 2-aminobenzophenone.[10] Wolff–Kishner reduction of 2-benzoyl-4-phenylquinoline (**30**) via the semicarbazone[11] afforded 2-benzyl-4-phenylquinoline (**31**).[10b] Quaternisation of the quinolines was performed with dimethyl sulphate or methyl triflate followed by conversion of the quinolinium salts into the nicely crystalline, nonhygroscopic hexafluorophosphates **1c**–**g**. The 2-isopropylquinolinium hexafluorophosphate **1b** was obtained from 1,2-dimethylquinolinium methosulphate by repeated deprotonation of the α-carbon atom with sodium hydride and methylation of the intermediates with methyl iodide.[12]

Carbon-13 Spectra of 2-Alkylidenedihydroquinolines

Cyclic ketene *N,X*-acetals (2-alkylidene-*N*-heterocycles) that do not possess electron-withdrawing groups at the exocyclic α-carbon atom exhibit very high nucleophilic reactivity which is reflected by extreme high-field resonances of the α-^{13}C atoms.[13] These properties support the formal description of the compounds with a betaine structure.[14] The reactivity of 2-alkylidene-*N*-heterocycles in 1,3-dipolar cycloaddition reactions with organic azides may be estimated on the basis of ^{13}C chemical shifts.[13] With this view, we have recorded the NMR spectra of a number of 2-alkylidenedihydroquinolines **2**. Only carbon-13 data of **2a**[3a] and 1,3-dimethyl-2-ethylidene-1,2-dihydroquinoline have so far been reported.[3b]

Solutions of 2-alkylidenedihydroquinolines **2** in deuterated solvents were obtained by deprotonation of *N*-methylquinolinium hexafluorophosphates **1** with potassium hydride. The resonances of the carbon atoms that form the exocyclic double bond and those of the corresponding ^{13}C atoms of the quinolinium ions **1** are compiled in Table 1. Relevant data of two perimidine derivatives are included for comparison.[13]

Table 1. Carbon-13 chemical shifts (δ values) of the alkylidene groups of 2-alkylidene-1-methyldihydroquinolines **2** and the corresponding carbon atoms of 2-alkyl-1-methylquinolinium ions **1**; the data for the perimidine derivatives are included for comparison[13]

R^1	R^2	R^3	Cpd.			[a]	Cpd.			[a]
H	H	H	**2a**	146.0 146.1	81.0 79.7	B F	**1a**	162.1	23.8	A
Me	Me	H	**2b**	147.2	106.9	B	**1b**	169.7	33.4	A
H	H	Ph	**2c**	146.2 146.8	81.5 81.3	B F	**1c**	159.5 161.1	23.7 23.4	A T
Me	Me	Ph	**2d**	147.4	107.6	B	**1d**	167.0	32.5	T
H	Me	Ph	(*E*)-**2e**	144.2 144.7	90.8 90.8	B F	**1e**	164.8	29.9	A
H	*t*Bu	Ph	(*E*)-**2f**	145.1 145.1	109.8 110.0	B F	**1f**	161.9	47.8	A
H	Ph	Ph	(*E*)-**2g**	144.2	99.7	F	**1g**	161.3	41.8	A
										
				144.6	110.7	B		167.3	31.0	D

[a] Solvents: A = [D_3]acetonitrile, B = [D_6]benzene, D = [D_6]dimethyl sulphoxide, F = [D_8]tetrahydrofuran, T = [D]trichloromethane.

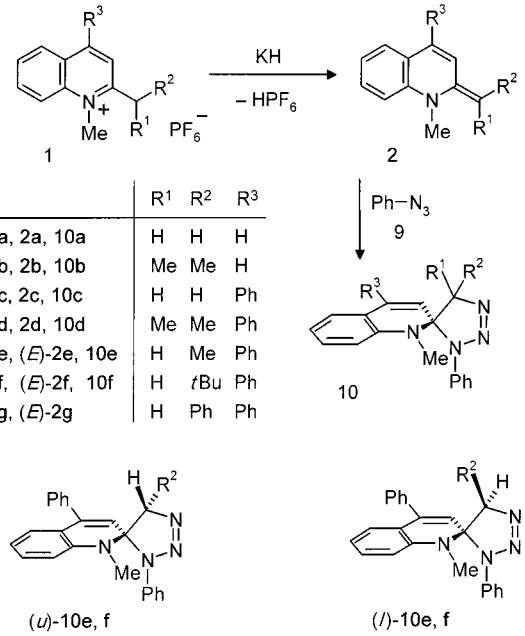
The 2-alkylidenedihydroquinolines **2e**–**g** may exist in the (*E*) and (*Z*) configuration. Only one diastereomer, however, could be observed by proton and ^{13}C spectroscopy in each case. We assign these diastereomers the (*E*) configuration because the (*Z*) configuration is destabilised by unfavourable steric interaction [$A^{(1,3)}$ strain][15] between the *N*-methyl group and the substituent at the α-carbon atom. The assignment is corroborated by the ^{13}C shifts of the *N*-methyl groups, which absorb at δ = 33–35, i. e. in the same range as those of the 2-methylene compounds **2a** and **c** (δ = 32–33). In contrast, the *N*-methyl groups of the strained 2-isopropylidene compounds **2b** and **d**, which may be considered as models for the hypothetical diastereomers (*Z*)-**2e**–**g**, resonate at much lower field (δ = 44–45).

The high-field shifts of the signals observed for the α-^{13}C atoms of **2** are much less pronounced than those of 2-alkylidene derivatives of five-membered heterocycles. Even the least reactive of this type studied so far, which are derived from benzothiazole and 3,3-dimethyldihydroindole, exhibit these resonances at higher field. The greatest similarity is observed between **2b**, **d** and the perimidine derivative as shown in Table 1.[13] Therefore, we conjecture, that none of the 2-alkylidenedihydroquinolines **2** will form an

observable − let alone isolable − zwitterion in the reaction with an electrophilic azide. Zwitterions are only obtained from electrophilic azides and extremely nucleophilic 2-alkylidene compounds that are derived from dihydrotetrazole, dihydroimidazole, and dihydrobenzimidazole.[16] The preparative experiments with organic azides were hence aided by the idea of neglecting any elusive intermediates and optimising the ring expansion. Furthermore, the positions of the α-^{13}C resonances of **2** are useful for the choice of the organic azides. Neither *N*-methyl-2-isopropylidenedihydrobenzothiazole nor the corresponding perimidine derivative shown in Table 1 react with alkyl azides at all. With phenyl azide, they react sluggishly.[17] This is also to be expected for **2** and indeed born out by the experiment. Therefore, we used phenyl azide and the more electrophilic sulphonyl azides **18** in the present work.

1,3-Dipolar Cycloaddition Reactions of 2-Alkylidenedihydroquinolines and Phenyl Azide

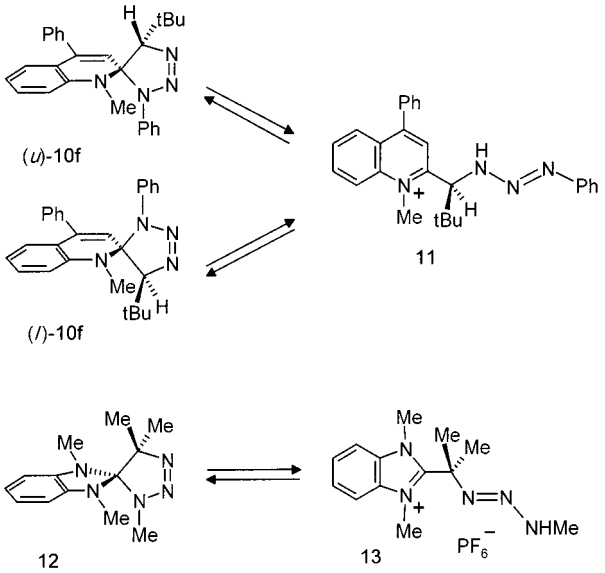
Solutions of **2a**−**f** were prepared as described above. Addition of phenylazide (**9**) slowly gave rise to the formation of the spirocyclic [3 + 2] cycloadducts **10a**−**f**, of which only two (**10d** and **f**) were isolated as pale yellow, crystalline compounds. All the other were characterised by their proton spectra (Table 3). The rates of the [3 + 2] cycloadditions, as estimated by monitoring the conversion by proton spectroscopy, depended on the substituents at the α-carbon atoms. Whereas the reactions of the methylene compounds **2a** and **c**, and the ethylidene compound (*E*)-**2e** ran to completion within one day, the isopropylidene compounds **2b** and **d**, and the neopentylidene compound (*E*)-**2f** required 6−10 days at room temperature.



	R1	R2	R3
1a, 2a, 10a	H	H	H
1b, 2b, 10b	Me	Me	H
1c, 2c, 10c	H	H	Ph
1d, 2d, 10d	Me	Me	Ph
1e, (*E*)-2e, 10e	H	Me	Ph
1f, (*E*)-2f, 10f	H	*t*Bu	Ph
1g, (*E*)-2g	H	Ph	Ph

The spirocyclic compounds **10e** and **f** may exist as (*u*)- and (*l*)-diastereomers, the former arising from (*E*)-**2e**, **f** the latter from (*Z*)-**2e**, **f**, provided the [3 + 2] cycloaddition is *cis* stereospecific.

The ethylidene compound (*E*)-**2e** yielded, surprisingly, *two* isomeric products **10e** in the ratio 13:7. By contrast, the 2-neopentylidenedihydroquinoline (*E*)-**2f** afforded a single product which was isolated as high-melting crystals and assigned the configuration (*u*)-**10f** by invoking the well-known *cis* stereospecificity of [3 + 2] cycloaddition reactions. Attempted flash chromatography of crude (*u*)-**10f** on silica gel with petroleum ether/ethyl acetate as eluent led to partial diastereomerisation yielding a mixture of (*l*)- and (*u*)-**10f** (13:7). This epimerisation is most readily interpreted in terms of a proton-catalysed ring opening−cyclisation sequence involving the triazene intermediate **11**. Precedence exists for this sequence in the tetrazole and benzimidazole series, e.g. **12** ⇋ **13**, where the triazene **13** could be isolated almost quantitatively and characterised by X-ray crystallography.[17]



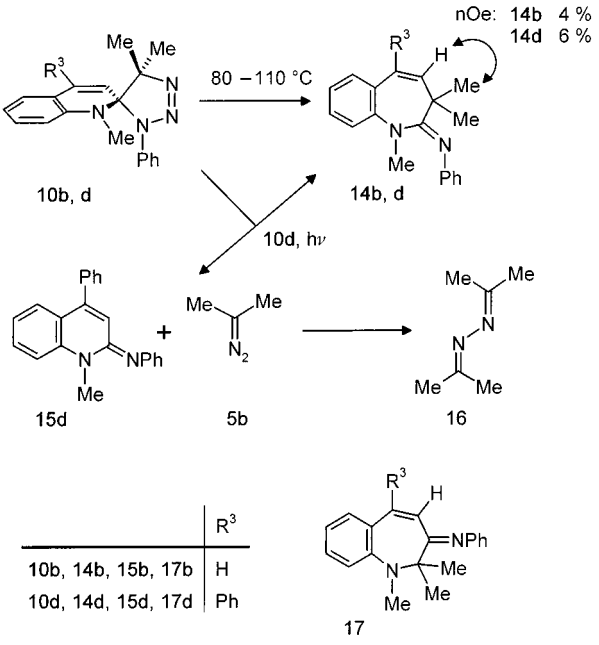
Surprisingly, no loss of molecular nitrogen with concomitant ring expansion but the same diastereomerisation was observed, when a degassed solution of (*u*)-**10f** in [D_8]toluene was heated in a flame-sealed NMR sample tube at 110°C. Besides the two diastereomers (*l*)- and (*u*)-**10f**, significant amounts of the [3 + 2] cycloreversion products (*E*)-**2f** and phenyl azide made their appearance (5:1:2). When the sample was subsequently kept at room temperature, (*u*)-**10f** slowly formed again but not (*l*)-**10f**. Because extremely acid-sensitive (*E*)-**2f** is present, acid catalysis of the epimerisation at higher temperatures is highly unlikely. The results do not, however, permit a distincion between other conceivable mechanistic scenarios.

The configurations of the two cycloadducts **10e**, obtained from **2e** immediately, could eventually be assigned by comparison of their proton spectra with those of (*l*)- and (*u*)-**10f**. The triazoline proton of the major diastereomer [(*l*)-**10e**] absorbs near the corresponding signal of (*l*)-**10f**, while the signals of the minor diastereomer [(*u*)-**10e**] and of (*u*)-**10f** are even closer (Table 3). The triazoline protons that

point to the nitrogen atom, as in (*u*)-**10e** and **f**, are more deshielded as expected.

None of the spirocyclic [3 + 2] cycloadducts, that had a proton at the triazoline ring (**10a**, **c**, **e**, **f**) gave iminodihydro-1-benzazepines. Heating at 80°C of solutions, obtained by [3 +2] cycloaddition of phenyl azide to **2a**, **c**, **e**, **f**, resulted in slow, undefined decomposition. Neither signals of ring-expanded nor those of [3 + 2] cycloreversion products, viz. the known iminodihydroquinolines **15b**,[18] **d**,[19] and diazo compounds **5a**, **e**, **f** could be detected in the proton spectra. In contrast, heating at 80−110°C of the two cycloadducts **10b** and **d** that have geminal methyl groups at the triazoline ring resulted in loss of molecular nitrogen and the rise of a single ring-expanded product in each case, which could be isolated in good yields (Table 2). The thermolysis of **10d** was particularly clean in a degassed [D_8]toluene solution at 110°C and complete within 2.5 hours.

The NMR spectra of the products indicated the presence of only one diastereomer. Obviously, the CN double bonds prefer a certain configuration. The diastereotopic geminal methyl groups gave single signals in the proton and ^{13}C spectra recorded at room temperature. Exchange by ring inversion apparently is fast on both NMR time scales. Of the two conceivable iminobenzazepine structures **14** and **17** for the products, the former arises from migration of the ring carbon atom C-3, the latter from a 1,2-shift of the nitrogen atom of the quinoline ring. The decision in favour of the structures **14b** and **d** was based on nuclear Overhauser experiments. Irradiation with the resonance frequency of the ring proton 4-H enhanced the signal of the geminal methyl groups thus excluding the structures **17b** and **d**.



The photolysis of **10d** was briefly investigated. Irradiation of a degassed solution of **10d** in [D_6]benzene with light of $\lambda \geq 320$ nm afforded the products of ring expansion (**14d**) and [3 + 2] cycloreversion (**5b** and **15d**) in the ratio 11:9 (Figure 1) besides small amount of acetone azine (**16**). The diazo compound **5b** quantitatively formed acetone azine, when the solution was kept at room temperature for one day. Clearly, thermolysis is the preferred method for the synthesis of 2-(*N*-phenylimino)benzazepines by ring enlargement of 2-isopropylidenedihydroquinolines.

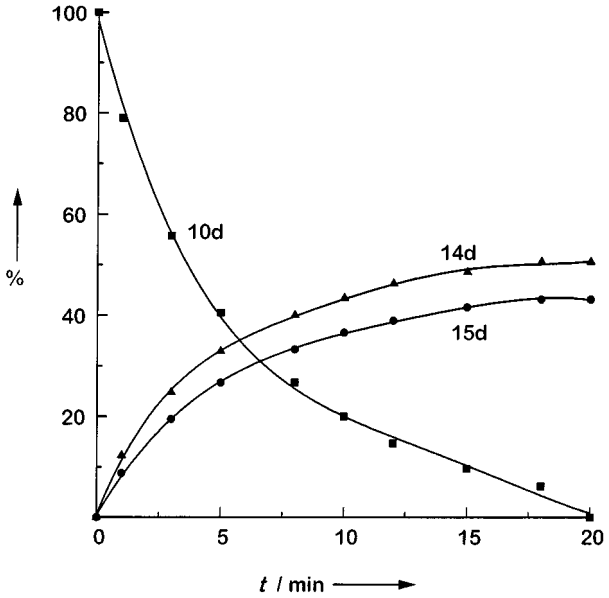


Figure 1. Conversion vs. time diagram for the photolysis of **10d** in [D_6]benzene solution ($\lambda \geq 320$ nm, 25°C)

Ring Expansion of 2-Alkylidenedihydroquinolines by Sulphonyl Azides

Methanesulphonyl azide is the favoured reagent for the ring expansion of 2-alkylidene compounds that are derived from five-membered ring heterocycles.[7,16b,20] Reaction with methanesulphonyl azide of the 2-alkylidenedihydroquinolines **2a**−**g**, prepared in situ with sodium hydride, afforded solid product mixtures. Separation by flash chromatography gave, unfortunately, no iminodihydrobenzazepines at all (**2a**, **c**, **g**) or only low to moderate yields (**2b**, **d**−**f**) along with the products of diazoalkane cleavage, viz. the *N*-(methylsulphonyl)imines **22a** (from **2a**, **b**) and **d** (from **2c**−**g**) (Table 2). The ratio of ring expansion (route **A**) vs. diazoalkane cleavage ([3 + 2] cycloreversion, route **B**), as determined from the proton spectra of the crude mixtures, was largest (3:2) in the case of the 2-isopropylidene compounds **2b** and **d**, but still unsatisfactory.

The structures of the 2-(*N*-methylsulphonyl)iminodihydrobenzazepines **21b**, **d**−**f** were based on proton and ^{13}C spectra, and ^{13}C,^{1}H COSY experiments. The configurations and conformations of **21b**, **d**, and **e** were established by X-ray crystallography (Figures 2−4). The dihydroazepine rings of **21b**, **d**, and **e** adopt a half-chair conformation where six atoms define an almost perfect plane from which only C3 is twisted. Geminal methyl groups at that atom, as in **21b** and **d**, force the imino group to take the (*Z*) configuration, whereas the (*E*) configuration is preferred provided that only a single methyl group, which occupies the axial

Table 2. Results of preparative experiments, yields (based on **1**) of isolated products, melting points taken after recrystallisation from the solvent given, IR data, and ratios of ring expansion (route **A**) vs. diazoalkane cleavage (route **B**)

Starting materials	Products	Yield [%]	M. p. [°C] (Solvent)	IR [cm^{-1}] (KBr) C=C, C=N	**21** : **22**[a]
1d + **9**	**10d**	70	144 – 147 (dec.) (THF/pentane, 1 : 3)		
1f + **9**	(*u*)-**10f**	66	205 – 207 (THF/pentane, 1 : 3)		
1b + **9**	**14b**[b]	62	[oil]		
1d + **9**	**14d**[b]	81	89 – 91 (EtOH)		
1a + **18a**	**22a**	11	156 – 159 (EtOAc)	1630 (s) 1573 (w) 1524	
1b + **18a**	**21b**	10	144 – 146 (PE/EtOH, 10 : 1)	1573 1530 (vs)	3 : 2
	22a	11			
1c + **18a**	**22d**	37	202 – 204 (EtOH)	1619 (vs) 1560	
1d + **18a**	**21d**	51	190 – 192 (EtOH)	1567 1544 (vs)	3 : 2
	22d	20			
1e + **18a**	**21e**	15	206 – 207 (EtOH)	1570 1534 (vs)	1 : 4
	22d	59			
1f + **18a**	**21f**[c]	8	178 – 188 (EtOH)	1540 (vs)	1 : 10
	22d	77			
1g + **18a**	**22d**	74			
1c + **18b**	**22h**	7	190 – 192 (EtOH)	1737 (s) 1626 (w) 1584	
	26[d]	6	143 – 145 (EtOH)		
1d + **18b**	**21i**	59	155 – 157 (EtOH)	1560 (w) 1526 (vs)	9 : 1
	22h	6			
	26[d]	14			
1e + **18b**	**21j**	74	210 – 212 (EtOH)	1573 1531 (s)	9 : 1
	22h	8			
	26[d]	10			
1f + **18b**	**21k**	51	204 – 205 (EtOH)	1573 1532 (s)	3 : 1
	22h	17			
	26[d]	2			
1g + **18b**	**21l**	13	199 – 200 (EtOH)	1572 (w) 1516 (vs)	1 : 5
	22h	82			

[a] Calculated from integrations of methyl signals in proton spectra recorded from solutions of the crude products in [D]trichloromethane. – [b] After thermolysis of the intermediate spirocyclic [3 + 2] cycloadduct. – [c] Mixture of (*E*) and (*Z*) diastereomers. – [d] M. p. 141 – 142 °C.[24a]

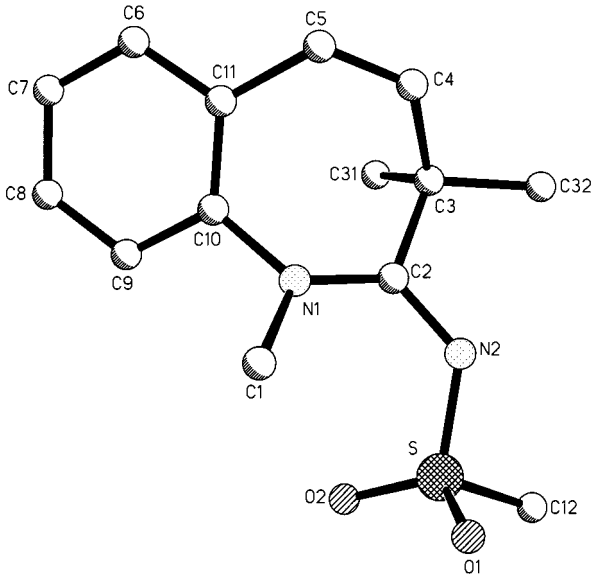


Figure 2. Perspective drawing of the 2-iminodihydrobenzazepine **21b** showing the numbering of the atoms

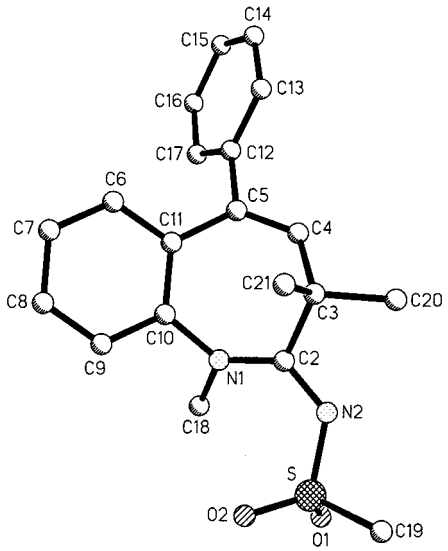


Figure 3. Perspective drawing of the 2-iminodihydrobenzazepine **21d** showing the numbering of the atoms

position, is present as in (*ax,E*)-**21e** (Figure 4). The planes of the phenyl rings at C4 of **21d** and (*ax,E*)-**21e** are twisted from the dihydroazepine ring plane by 43.5 and 48.1°, respectively.

The results of the X-ray diffraction analyses served as starting point for the interpretation of the NMR spectra. The 3-methyl compound **21e** exists as a single diastereomer in solution, most probably (*ax,E*)-**21e** as in the crystal. This structure results in pronounced low- and high-field chemical shifts for the signals of the equatorial proton 3-H (δ = 4.89) and the *N*-methyl group (δ = 3.52), respectively (Table 5). By contrast, the 3-*tert*-butyl compound **21f** forms *two* diastereomers (74:26). Comparison of their proton spectra with that of (*ax,E*)-**21e** suggests that the major diastereomer (3-H: δ = 4.88, *N*-methyl: δ = 3.58) adopts the configuration (*ax,E*)-**21f** where the *tert*-butyl group (δ = 0.76) occupies the axial position. Consequently, the minor stereoisomer (3-H: δ = 2.41, *N*-methyl: δ = 3.85) is assigned the configuration (*eq,Z*)-**21f**, where the *tert*-butyl protons (δ = 1.56) are strongly deshielded due to the equatorial position of the *tert*-butyl group.

While, relative to both NMR time scales, ring inversion rapidly exchanges the diastereotopic methyl groups of the iminodihydrobenzazepines **14b**, **d** and **21b**, the rate of this process could be measured for **21d** by dynamic proton spectroscopy. On cooling, the broad singlet for the methyl protons broadened further and was split at a coalescence temperature of 276 K. From the frequency difference of the two methyl signals in the limit of slow exchange ($\Delta\nu$ = 146.4 Hz at 219 K and 200.13 MHz), the rate constant at the coalescence temperature and the free enthalpy of activation were

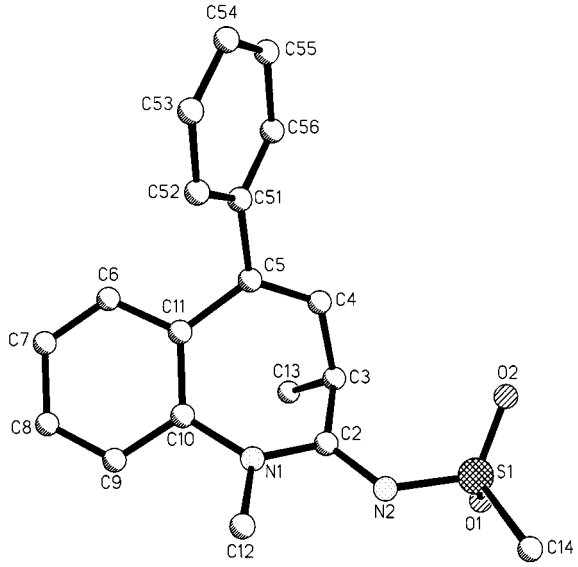
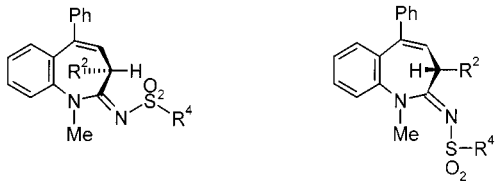


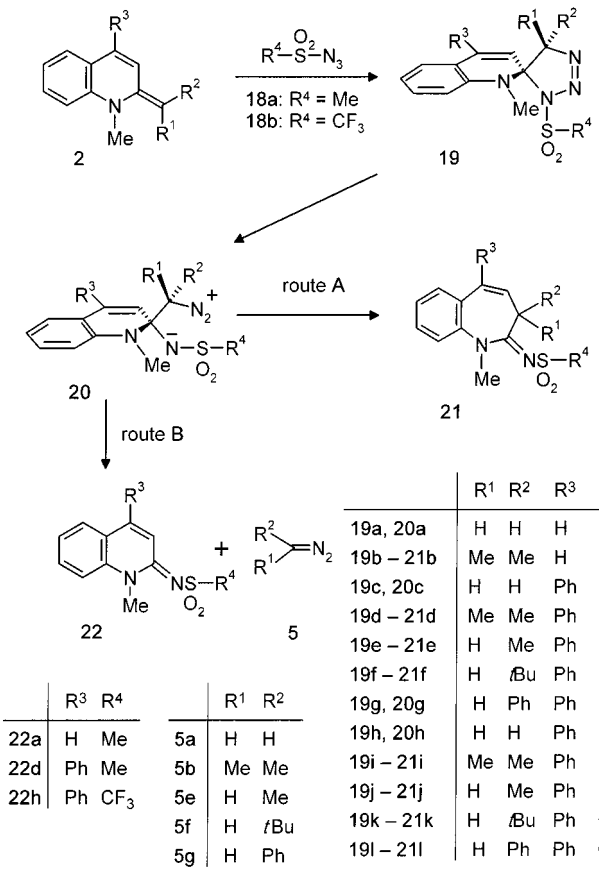
Figure 4. Perspective drawing of the 2-iminodihydrobenzazepine (*ax,E*)-**21e** showing the numbering of the atoms



(*ax, E*)-**21f**	74 : 26	(*eq, Z*)-**21f**
(*ax, E*)-**21j**	63 : 35	(*eq, Z*)-**21j**
(*ax, E*)-**21k**	64 : 36	(*eq, Z*)-**21k**

calculated at $k_c = 325\ s^{-1}$ and $\Delta G^{\neq}_c = 54\ kJmol^{-1}$, respectively.[21]

Our search for an improvement of the unsatisfactory ratio of ring expansion vs. diazoalkane cleavage was based on the assumption[7,20b] that the hypothetical intermediate zwitterions **20** are the point of branching of the reaction pathways, route **A** and **B**. An analogue of the former is the second step of the well-known ring expansion reaction of cyclic ketones **23** with diazoalkanes **5**, i.e. **24** → **25**.[22] Likewise, the undesired latter resembles the hypothetical reversion of the formation of the zwitterions **24** from **5** and **23**. Consequently, any factors that favour this reaction should disfavour the diazoalkane cleavage of **20**. Because one such factor is a high carbonyl reactivity of **23**[22a,b] we resorted to trifluoromethanesulphonyl azide (**18b**) as reagent which should lead to a particularly reactive imine (**22h**).[23] Comparison of the results obtained from **18b** with those from methanesulphonyl azide (**18a**) (Table 2) demonstrates that **18b** is indeed a superior reagent for ring expansion: Except for the methylene compound **2c**, which failed to give any ring-expanded product, all the other alkylidenedihydroquinolines **2d** −**f** afforded iminodihydro-1-benzazepines in much better yields. The ratios **21** (route **A**) vs. **22** (route **B**) were greatly increased (**1d**) or reverted (**1e**, **f**). Even benzylidenedihydroquinoline **2g**, which was cleaved by **18a** exclusively into imine **22d** and phenyldiazomethane, gave a small

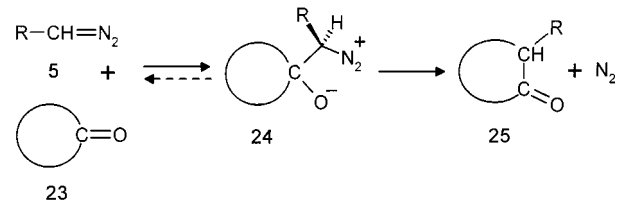


	R^3	R^4
22a	H	Me
22d	Ph	Me
22h	Ph	CF_3

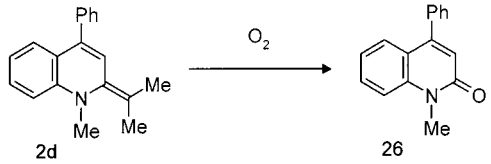
	R^1	R^2
5a	H	H
5b	Me	Me
5e	H	Me
5f	H	*t*Bu
5g	H	Ph

	R^1	R^2	R^3	R^4
19a, 20a	H	H	H	Me
19b – 21b	Me	Me	H	Me
19c, 20c	H	H	Ph	Me
19d – 21d	Me	Me	Ph	Me
19e – 21e	H	Me	Ph	Me
19f – 21f	H	*t*Bu	Ph	Me
19g, 20g	H	Ph	Ph	Me
19h, 20h	H	H	Ph	CF_3
19i – 21i	Me	Me	Ph	CF_3
19j – 21j	H	Me	Ph	CF_3
19k – 21k	H	*t*Bu	Ph	CF_3
19l – 21l	H	Ph	Ph	CF_3

amount of the ring-expanded product **21l**. These results lend credence to the rationale behind the choice of the azide.

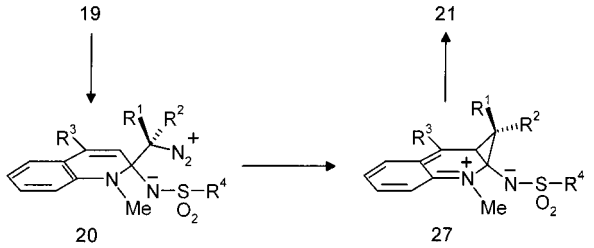


Just like **21e** and **f**, the trifluoromethylsulphonylimines **21j**−**l** may exist, in principle, as the two different diastereomers denoted (*ax,E*) and (*eq,Z*). Only one is, however, observed in the case of the 3-phenyl compound **21l**, while both configurations are adopted by **21j** and **k**. Their assignment is based on NMR evidence (Tables 5 and 6) resembling that which supported the configurations (*ax,E*)- and (*eq,Z*)-**21f**.



In the experiments performed with solutions of trifluoromethanesulphonyl azide (**18b**), small amounts of the quinolone **26**[24] were isolated by flash chromatography of the

product mixture (Table 2). Probably, **26** arose by autoxidation of the alkylidenedihydroquinolines **2c**−**f** by molecular oxygen that was still dissolved in the incompletely degassed dichloromethane solutions of **18b** employed. This source of **26** was suggested by a control experiment which afforded **26** in 60% yield by deliberate treatment of a solution of **2d** with oxygen.



Conclusion

The present study explores and extends the limits of the ring expansion reaction of 2-alkylidenedihydroquinolines **2** by electrophilic azides.[4−6] Alkyl groups at the terminal carbon atom of the exocyclic double bond are a prerequisite for ring expansion. Formation of the [3 + 2] cycloadduct **10f** of phenyl azide to the neopentylidene compound (*E*)-**2f** is reversible at higher temperatures. The [3 + 2] cycloadducts **19** that lack alkyl groups at the ring carbon prefer [3 + 2] cycloreversion into imino and diazo compounds, either in a concerted process or in two steps via the zwitterions **20**. The substitution pattern favouring ring expansion might suggest the development of a positive partial charge at that atom in the product-determining transition state. The poor yields of ring-expanded products obtained with the 2-benzylidene compound (*E*)-**2g**, however, indicate that stabilisation of a positive partial charge cannot be an important factor.

We recall that neighbouring-group participation by phenyl rings or CC double bonds in the β position relative to a good leaving group is a common phenomenon,[25] leading, for example, to intermediate phenonium ions. We suggest that the present ring expansion may take a similar course: Departure of molecular nitrogen from the zwitterions **20** is facilitated through nucleophilic backside attack by the π electrons of the C3-C4 double bond resulting in the stabilised zwitterions **27**, which undergo opening of the three-membered ring to afford the ring-enlarged products **21**.

In the absence of mechanistic investigations, it is difficult to rationalise the subtle interplay of steric and electronic substituent effects on the various conceivable intermediates in the complex mechanistic scenario which eventually furnishes the isolated products. The empirical rules, however, concerning the favourable substitution pattern and the choice of the azide that can be derived from the present and previous work[5−7,16,20] render the expeditious one-pot ring expansion of 2-alkyl-*N*-heterocycles by electrophilic azides a useful contribution to the synthetic methods of heterocyclic chemistry.

Experimental Section

General Remarks: Yields, melting points, ratios of products and IR: Table 2. − ^{1}H NMR: Tables 3 and 5. − ^{13}C NMR: Tables 1, 4, and 6. − Molecular formulae and masses, and elemental analyses: Table 7. − Melting points: Kofler apparatus from Reichert, Vienna. − ^{1}H and ^{13}C NMR: Bruker AC 200, AC 250 and DMX 600 (**2a**−**g**, **10f**, **14d**, and **21f**). The assignment of the signals was based on ^{1}H, ^{1}H COSY (**2a**, **f**) and ^{13}C, ^{1}H COSY experiments (**2f**, **21d**−**f**, and **22d**). Samples for nOe experiments (**14b**, **d**) were degassed; the NMR sample tubes were evacuated (10^{-2} Torr) and sealed with a torch. − IR: Perkin-Elmer 1420. − Flash chromatography: (40 × 4) cm and (30 × 2.5) cm glass columns packed 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 stainless steel column packed with silica gel LiChrosorb Si60, 5 μm (Knauer), 1.5 mL/min petroleum ether (50−70°C) (PE)/ethyl acetate (EA) (1:1). − 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): Finnigan MAT 8200. The exact masses of **14b** and **d** were determined by means of a Finnigan MAT 90 high-resolution mass spectrometer and perfluorokerosene calibration.

Irradiation was performed with a 500-W high-pressure mercury lamp (Osram HBO 500 W/2) which was focussed by quartz optics. The light passed a 10-cm water filter and subsequently a 5-mm cut-off filter, type WG 320 from Schott & Gen., Mainz.

Tetrahydrofuran was dried with powdered KOH and distilled from NaH. Benzene and toluene were distilled from NaH and CaH_2, respectively. 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 sulphoxide were dried with CaH_2, [D_6]benzene and [D_8]toluene were dried with NaH. − NaH and KH, suspended in paraffin oil, were washed three times with pentane and dried in a stream of Ar. Experiments involving NaH, KH, and **2** were carried out in dry solvents under Ar (99.998 %). − **9**,[26] **18a**,[20c] solutions of **18b** in dichloromethane,[27] 2-methyl-4-phenylquinoline,[10a] 2-ethyl-4-phenylquinoline,[10a] and 2-benzoyl-4-phenylquinoline (**30**)[10b] were prepared as described.

Quinolines

2-(1-Methylethyl)-4-phenylquinoline (28): A solution of 2-aminobenzophenone (19.7 g, 0.1 mol), 3-methyl-2-butanone (68.8 g, 0.8 mol) and 67% aq. KOH (47 mL) in ethanol (160 mL) was heated under reflux for 10 h. After cooling, the org. layer was separated and acidified with a mixture of conc. sulphuric acid and water (1:1). Inorganic material was removed by filtration. Ethanol was distilled in vacuo. The residue was diluted with water to give a clear solution, and extracted with ether (200 mL). The aq. layer was made alkaline by addition of aq. NaOH (20%) and extracted with ether (2 × 100 mL). Both org. layers were dried with $MgSO_4$. After distillation of the solvent i. vac., the first extract gave a brown oil and the second pale yellow crystals (17.1 g, 69%, m.p. 50−55°C). The brown oil was extracted with aq. HCl (2 M, 3 × 10 mL). The aq. layer was made alkaline with aq. NaOH (20%) and extracted with ether (2 × 20 mL). The combined org. layers were dried with $MgSO_4$. The solvent was distilled i. vac. to give a pale yellow solid (5.7 g, 23%, m.p. 53−56°C). Recrystallisation of the combined fractions from ethanol/water (3:2) gave pale yellow needles (18.0 g, 73%, m.p. 58−59°C).

2-(2,2-Dimethylpropyl)-4-phenylquinoline (29) was prepared from 4,4-dimethyl-2-pentanone according to the procedure described

above for **28**. Yellow crystals (16.5 g, 60%, m.p. 70−75°C). Recrystallisation from ethanol afforded colourless crystals (11.5 g, 42%, m.p. 76−78°C).

Semicarbazone of 2-Benzoyl-4-phenylquinoline: Semicarbazide hydrochloride (2.9 g, 25.8 mmol) and sodium acetate trihydrate (3.54 g, 25.8 mmol) were dissolved in water (20 mL). Ethanol (300 mL) was added, and the solution was heated and filtered. **30** (4.0 g, 12.9 mmol) was added to the hot filtrate, and the mixture was heated under reflux for 1 d. The solvent was distilled in vacuo until the final volume was about 50 mL. The precipitate, formed on cooling, was collected by filtration and washed with ethanol (10 mL) to yield a pale yellow powder (3.88 g, 82%, m.p. 202−208°C). Recrystallisation from ethanol yielded colourless crystals, m.p. 212−214°C. − ^{1}H NMR ([D$_6$]dimethyl sulphoxide): δ = 6.7−7.1 (br. s, NH$_2$), 7.3−7.8 (m, ar H), 8.52 (NH). − IR (KBr): $\tilde{\nu}$ = 3340, 3370 (NH), 1705 cm^{-1} (C=O).

2-Benzyl-4-phenylquinoline (31): Because direct Wolff−Kishner reduction of **30** with hydrazine hydrate gave only poor results in our hands,[10b] the procedure via the semicarbazone was adopted.[11] The semicarbazone of **30** (1.0 g, 2.7 mmol) was added under Ar in small portions to a stirred solution of KOH (0.5 g, 8.2 mmol) in hot diethylene glycol (5 mL, 130°C). The mixture was heated at 150°C for 0.5 h, and at 180−210°C for 2 h. The mixture was allowed to cool to room temp., diluted with water (50 mL) and extracted with cyclohexane (2 × 30 mL). The combined org. layers were washed with water (30 mL) and dried with MgSO$_4$. Distillation of the solvent i. vac. yielded orange-coloured crystals (0.63 g, 78%, m.p. 76−78°C). Flash chromatography with PE/EA = 1:1 gave colourless crystals, m.p. 77−78, ref.[10b] 77−78.5°C.

1,2-Dimethylquinolinium Hexafluorophosphate (1a): A solution of NH$_4$PF$_6$ (6.06 g, 37.2 mmol) in water (20 mL) was added to a stirred solution of 1,2-dimethylquinolinium methosulphate[28] (10.0 g, 37.2 mmol) in water (100 mL). The precipitate was collected by filtration. Colourless powder (11.0 g, 98%). Recrystallisation from ethanol gave colourless needles (8.9 g, 79%, m.p. 165°C).

1-Methyl-2-(1-methylethyl)quinolinium Hexafluorophosphate (1b): A suspension of 1,2-dimethylquinolinium methosulphate[28] (12.3 g, 45.5 mmol), NaH (4.37 g, 182 mmol), and methyl iodide (25.8 g, 182 mmol) in tetrahydrofuran (100 mL) was stirred for 1 d, until the gas evolution had ceased. Acetic acid (21.8 g, 0.36 mol) was added dropwise, and the suspension was stirred for 0.5 h. The precipitate was collected by filtration, washed with tetrahydrofuran (30 mL), and dissolved in water (100 mL). A solution of NH$_4$PF$_6$ (7.41 g, 45.5 mmol) in water (30 mL) was added. The precipitate was collected by filtration and washed with water. Red powder (10.6 g, 66%). Repeated recrystallisation from ethanol gave colourless needles (4.97 g, 31%, m.p. 164−166°C).

2-Alkyl-1-methyl-4-phenylquinolinium Hexafluorophosphates (1c−f). − General Procedure: A stirred mixture of a 2-alkyl-4-phenylquinoline (25 mmol) and dimethyl sulphate (4.73 g, 37.5 mmol) was heated 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. The solution was diluted with water (40 mL). A solution of NH$_4$PF$_6$ (4.08 g, 25 mmol) in water (10 mL) was added dropwise. The resulting pale yellow oils solidified slowly (1−24 h). The solid material was collected by filtration, washed with water, and recrystallised. The yields of crude products were almost quantitative.

1,2-Dimethyl-4-phenylquinolinium Hexafluorophosphate (1c): Pale brown powder. Recrystallisation from ethanol/water (4:1) gave pale yellow needles (5.91 g, 63%, m.p. 187−188°C).

2-Ethyl-1-methyl-4-phenylquinolinium Hexafluorophosphate (1d): Colourless powder. Recrystallisation from ethanol/water (7:1) gave colourless scales (7.27 g, 74%, m.p. 169−171°C).

1-Methyl-2-(1-methylethyl)-4-phenylquinolinium Hexafluorophosphate (1e): Pale brown powder. Recrystallisation from ethanol/water (2:1) gave pale yellow needles (8.55 g, 84%, m.p. 121−123°C).

1-Methyl-2-(2,2-dimethylpropyl)-4-phenylquinolinium Hexafluorophosphate (1f): Colourless powder. Recrystallisation from ethanol/water (10:1) gave colourless needles (8.71 g, 80%, m.p. 203−205°C).

2-Benzyl-1-methyl-4-phenylquinolinium Hexafluorophosphate (1g): Methyl trifluoromethanesulphonate (0.28 g, 1.7 mmol) was added via syringe under Ar to a stirred solution of **31** (0.5 g, 1.7 mmol) in 1,2-dichloroethane (5 mL). The mixture was heated under reflux for 4 h. The solvent was distilled i. vac. The oily residue was dissolved in ethanol (5 mL). A solution of NH$_4$PF$_6$ (0.28 g, 1.7 mmol) in water (10 mL) was added dropwise. The precipitate was collected by filtration. Colourless powder (0.75 g, 96%). Recrystallisation

Table 3. Chemical shifts (δ values) and coupling constants ([Hz], *in italics*) in proton spectra of 2-alkylidene-1-methyldihydroquinolines **2** and their [3 + 2] cycloadducts **10** with phenyl azide. Single figures refer to singlets if not stated otherwise

Cpd.	R^1			R^2	NMe	3-H	4-H	Aryl-H	[a]
2a[b]	H	3.63 (m)	3.70(d) *^2J = 0.6*	H	3.06	6.30 (d) *^3J = 9.6*	6.43 (dm)	6.6 – 7.2	F
		3.46	3.87		2.53	6.16 (d) *^3J = 9.5*	6.19 (d)	6.2 – 7.0	B
2b	Me	1.57	1.64	Me	2.85	6.22 (d) *^3J = 10.0*	6.50 (d)	6.4 – 7.1	B
2c	H	3.72	3.77	H	3.13	6.28		6.5 – 7.5	F
		3.73	3.91		2.61	6.23		6.4 – 7.3	B
2d	Me	1.79	1.81	Me	3.28	6.24		6.2 – 7.4	F
		1.64	1.66		2.95	6.54		6.5 – 7.4	B
(*E*)-**2e**	H	4.25 (q) *^3J = 7.1*	1.70 (d)	Me	3.07	6.49		6.5 – 7.5	F
		4.11 (qm) *^3J = 7.1*	1.66 (d)		2.62	6.63		6.4 – 7.4	B
(*E*)-**2f**	H	4.34	1.23	*t*Bu	3.08	6.74		6.6 – 7.6	F
		4.29 (m)	1.26		2.65	6.95		6.4 – 7.4	B
(*E*)-**2g**	H	5.43		Ph	3.28	7.01		6.6 – 7.5	F
10a	H	3.64 (d) *^2J = 18.5*	4.14 (d)	H	2.04	4.89 (d) *^3J = 9.8*	6.22 (d)	6.0 – 7.5	B
10b	Me	0.91	1.09	Me	2.16	5.07 (d) *^3J = 10.0*	6.39 (d)	6.1 – 7.7	B
10c	H	3.69 (d) *^2J = 18.5*	4.21 (d)	H	2.12	5.01		6.1 – 7.6	B
10d	Me	0.96	1.14	Me	2.26	5.27		6.2 – 7.8	B
		1.24	1.31		2.54	5.43		6.6 – 7.6	T
(*l*)-**10e**	H	3.63 (q) *^3J = 7.4*	1.26 (d)	Me	2.14	5.11		6.2 – 7.7	B
(*u*)-**10e**		4.20 (q) *^3J = 7.5*	0.96 (d)		2.20	5.06		6.2 – 7.7	B
(*l*)-**10f**	H	3.24	1.15	*t*Bu	2.19	5.17		6.3 – 7.3	B
		3.53	1.21		2.43	5.37		6.5 – 7.6	T
(*u*)-**10f**		4.10	1.10		2.33	5.40		6.3 – 7.3	B
		4.13	1.15		2.73	5.37		6.5 – 7.6	T

[a] Solvents: see Table 1. − [b] Proton spectrum of **2a** recorded for a solution in [D$_8$]toluene: ref.[3a]

Table 4. Chemical shifts (δ values) in ^{13}C spectra recorded for solutions of 2-alkylidene-1-methyldihydroquinolines **2** and some [3 + 2] cycloadducts **10** with phenyl azide

Cpd.	R¹		C		R²	NMe	C-2	Other ring carbons: CH						quat. C			[a]
2a[b]	H		79.7		H	32.0	146.1	110.7	118.6	125.6	126.43	126.84	128.9	122.4	142.4		F
			81.0			33.1	146.4	111.2	119.2	126.3	127.04	127.49	129.35	122.9	142.8		B
2b	Me	19.8	106.9	21.7	Me	44.2	147.2	114.0	119.2	123.2	123.7	126.3	128.4	124.9	138.3		B
2c	H		81.3		H	33.2	146.8	112.2 129.67	119.3 129.99	126.6	127.2	128.3	129.1	123.2 143.6	138.3	139.8	F
			81.5			32.7	146.2	111.7 129.30	119.0 129.43	126.4	127.0	127.7	128.6	122.9 143.0	137.9	139.3	B
2d	Me	19.8	107.6	21.8	Me	44.3	147.4	114.5 129.5	119.0	123.6	125.5	127.5	128.6	125.0 140.4	135.3	138.0	B
(E)-**2e**	H		90.8	11.8	Me	33.5	144.7	112.1 129.75	118.6 130.02	121.7	126.5	128.2	129.1	123.1 140.75	138.1	140.45	F
			90.8	11.8		33.1	144.2	111.7 129.43	118.5 129.61	121.6	126.5	127.7	128.7	122.9 140.26	137.8	140.04	B
(E)-**2f**	H		110.0	32.5 31.8 (quat.)	*t*Bu	34.6	145.1	112.7 129.66	118.7 130.00	122.99	126.5	128.3	129.20	122.90 140.51	137.6	140.21	F
			109.8	32.4		34.2	145.1	112.7 129.72	118.7 130.05	123.01	126.6	128.4	129.27	129.93 140.51	137.6	140.24	B
(E)-**2g**	H		99.7		Ph	34.3	144.2	113.1 128.81	119.6 128.90	122.5 129.17	125.0 129.62	126.6 130.32	128.38	123.6 139.99	139.69 141.9	139.93	F
							Spiro-C										
10d	Me	20.2	88.1	23.0	Me	32.8	84.3	111.4 128.23	116.6 128.65	117.4 129.08	119.1 129.29	123.3 130.17	127.0	120.0 141.7	130.1 143.8	139.0	T
(*l*)-**10f**	H		97.1	28.6 32.4 (quat.)	*t*Bu	34.4	84.0	110.7 128.5	115.7 129.2	123.1 130.3	123.7	126.8	127.9	118.9 140.54	138.4 142.4	140.48	T
(*u*)-**10f**			92.8	27.9 34.1 (quat.)		30.7	84.9	111.5 127.8	117.13 128.31	117.51 128.43	119.88 128.93	123.4 130.0	126.7	119.98 140.29	138.4 142.1	139.78	T

[a] Solvents: see Table 1. – [b] Carbon-13 spectrum of **2a** recorded for a solution in [D_8]toluene: ref.[3a]

from ethanol afforded colourless crystals (0.53 g, 68%, m.p. 181–184°C).

2-Alkylidene-1-methyldihydroquinolines 2a–g. – General Procedure: Suspensions of powdered **1a–g** (0.2 mmol) and KH (0.08 g, 2 mmol) in [D_8]tetrahydrofuran or [D_6]benzene (1 mL) were stirred for 1 or 24 h, respectively, in centrifuge tubes which were equipped with a septum and connected to a supply of Ar. After separation of the solid material with the help of a centrifuge, the supernatant solutions were transferred via syringe into NMR sample tubes, which were degassed by standard freeze-thaw techniques, evacuated (10^{-2} Torr), and sealed with a torch.

Experiments with Phenyl Azide (9)

Spirocycles 10a–f. – General Procedure: Phenyl azide (**9**) (24 mg, 0.2 mmol) was added to solutions of **2a–f** (0.2 mmol) in [D_6]benzene which were kept in NMR sample tubes at room temp. in the dark. The conversion was monitored by ^{1}H-NMR spectroscopy, until **2a–f** had disappeared (1 d for **2a**, **c**, and **e**, 6 d for **2f**, 7 d for **2b**, and 10 d for **2d**). Thereupon the proton spectra indicated the presence of **10a–d**, (*l*)- and (*u*)-**10e** (13:7), and (*u*)-**10f**, besides small amounts of unidentified products.

Thermolysis of the Spirocycles 10a–f: a) Solutions of **10a–f** in [D_6]benzene, prepared as described above, were heated at 80°C in NMR sample tubes. The conversion was monitored by ^{1}H-NMR spectroscopy, until **10a–f** had disappeared (4 h for **10a** and **c**, 10 h for **10e**, 2 d for **10b** and **d**, and 6 d for **10f**). **10b** and **d** gave **14b** and **d**, respectively, besides small amounts of unidentified products. **10a**, **c**, **e**, and **f** afforded solutions that showed only signals of aromatic protons.

b) A degassed solution of **10d** or (*u*)-**10f** (0.2 mmol) in [D_8]toluene (0.7 mL) was heated at 110°C in an evacuated, flame-sealed NMR sample tube for 2.5–3 h. The conversion was monitored by ^{1}H NMR spectroscopy. **10d** gave **14d**. (*u*)-**10f** afforded a mixture of **2f**, (*l*)- and (*u*)-**10f** (2:5:1).

1,5′,5′-Trimethyl-3,4′-diphenylspiro[1*H*-quinoline-2,4′-(3′,5′-dihydro[1,2,3]triazole)] (10d): A suspension of powdered **1d** (0.82 g, 2 mmol) and KH (0.40 g, 10 mmol) in benzene (5 mL) was stirred for 1 d in a centrifuge tube which was equipped with a septum and connected to a supply of Ar. Solid, inorganic material was removed with the help of a centrifuge. The supernatant solution was transferred via syringe into a 25-mL flask, and the remaining solid material was washed twice with benzene (5 mL). **9** (2.38 g, 20 mmol) was added and the mixture was kept at room temp. in the dark for 7 d. The mixture was diluted with pentane (100 mL) and cooled at –30°C for 2 d to afford brown crystals (0.47 g, 61%, m.p. 145–147°C, dec.). The solvent was distilled i. vac. from the mother liquor. The brown, oily residue was recrystallised from tetrahydrofuran/pentane (1:3, 50 mL) to afford a second crop (brown powder, 0.07 g, 9%, m.p. 144–147°C, dec.). Recrystallisation from tetrahydrofuran/pentane (1:3) afforded pale yellow prisms, m.p. 144–147°C (dec.).

5′-(1,1-Dimethylbutyl)-1-methyl-3,4′-diphenylspiro[1*H*-quinoline-2,4′-(3′,5′-dihydro[1,2,3]triazole)] [(*u*)-10f]: A suspension of pow-

dered **1f** (0.87 g, 2 mmol) and KH (0.40 g, 10 mmol) in tetrahydrofuran (5 mL) was stirred for 1 h in a centrifuge tube which was equipped with a septum and connected to a supply of Ar. Solid, inorganic material was removed with the help of a centrifuge. The supernatant solution was transferred via syringe into a 25-mL flask, and the remaining solid material was washed twice with tetrahydrofuran (5 mL). **9** (2.38 g, 20 mmol) was added and the mixture was kept at room temp. in the dark for 5 d. The mixure was diluted with pentane (100 mL) and cooled at −30°C for 2d to afford pale yellow crystals (0.45 g, 55%), m.p. 200−207°C. The solvent was distilled i. vac. from the mother liquor. The brown, oily residue was treated with pentane (3 × 15 mL) to give a second crop (yellow powder, 0.09 g, 11%, m.p. 200−205°C). Recrystallisation from tetrahydrofuran/pentane (1:3) afforded colourless crystals, m.p. 205−207°C.

Photolysis of 10d: A degassed solution of **10d** (38 mg, 0.1 mmol) in [D_6]benzene (0.7 mL) contained in an evacuated, flame-sealed NMR sample tube was irradiated at 25°C. The conversion was monitored by ^{1}H-NMR spectroscopy (Figure 1). The proton spectrum, recorded 1 d after termination of the irradiation, indicated the presence of **14d** and **15d** (11:9), besides **16**[29] and small amounts of unidentified products. Flash chromatography with PE/EE (7:3) of the solution yielded **14d** (colourless oil, 14 mg, 40%) and **15d** (yellow crystals, 10 mg, 32%, m.p. 165, ref.[19] 165°C)

2,3-Dihydro-1,3,3-trimethyl-2-(*N*-phenylimino)-1*H*-benz[*b*]azepine (14b): A suspension of powdered **1b** (0.66 g, 2 mmol), KH (0.4 g, 10 mmol), and 18-crown-6 · KCN (32 mg, 0.1 mmol) in toluene (10 mL) was stirred at 60°C for 3 h in a centrifuge tube which was equipped with a septum and connected to a supply of Ar. Solid, inorganic material was removed with the help of a centrifuge. The supernatant solution was transferred via syringe into a 25-mL flask, and the remaining solid material was washed twice with toluene (5 mL). **9** (0.48 g, 4 mmol) was added and the mixture was heated under reflux for 3 h. Flash chromatography of the resulting solution with PE/EA (9:1) yielded a pale yellow oil (0.34 g, 62%).

2,3-Dihydro-1,3,3-trimethyl-2-(*N*-phenylimino)-5-phenyl-1*H*-benz[*b*]azepine (14d) was prepared from **1d** according to the procedure described for **14b**. Flash chromatography yielded a pale yellow viscous oil, which crystallised on trituration with ethanol. Recrystallisation from ethanol afforded colourless crystals (0.57 g, 81%, m.p. 89−91°C).

Experiments with Methanesulphonyl Azide (18a)

In Situ Trapping of the Alkylidene Compounds 2a−g with Methanesulphonyl Azide (18a). − General Procedure: Suspensions of powdered **1a−g** (5 mmol), NaH (15 mmol), and **18a** (12.5 mmol) in tetrahydrofuran (30 mL) were stirred in centrifuge tubes, which were equipped with a septum and connected to a supply of Ar, until the gas evolution had ceased (1 d). Solid, inorganic material was removed with the help of a centrifuge and washed with tetrahydrofuran (2 × 5 mL). The solvent was distilled i. vac. to afford solid residues.

1,2-Dihydro-1-methyl-2-[*N*-(methylsulphonyl)imino]quinoline (22a): From **1a**. Flash chromatography of the solid residue with EA gave a black solid. Repeated flash chromatography with PE/EA (1:1) yielded colourless crystals (0.13 g, 11%), m.p. 150−155°C. Recrystallisation from EA under Ar afforded colourless scales, m.p. 156−159°C. − MS, *m/z* (%): 236 (14) [M^+], 158 (12), 157 (100) [$M^+ - SO_2Me$], 142 (10), 130 (8), 128 (55).

2,3-Dihydro-1,3,3-trimethyl-2-[*N*-(methylsulphonyl)imino]-1*H*-benz[*b*]azepine (21b) and 22a: From **1b**. Flash chromatography of the solid residue with PE/EA (1:1) gave a yellow oil as first fraction (**21b**, 0.18 g) and brown crystals (**22a**, 0.18 g, m. range 145−155°C). Recrystallisation from PE/ethanol (10:1) afforded colourless crystals (**21b**, 0.15 g, 11%, m.p. 144−146°C; **22a**, 0.12 g, 10%, m.p. 149−150°C). − **21b**, MS, *m/z* (%): 278 (26) [M^+], 205 (32), 199 (29) [$M^+ - SO_2Me$], 184 (15), 183 (14), 158 (21), 157 (10), 130 (27).

1,2-Dihydro-1-methyl-2-[*N*-(methylsulphonyl)imino]-4-phenylquinoline (22d): − a) From **1c**. Flash chromatography of the solid residue with EA gave a black solid. Repeated flash chromatography with PE/EA (1:1) yielded pale brown crystals (0.57 g, 37%, m.p. 195−200°C). Recrystallisation from ethanol afforded colourless crystals, m.p. 200−202°C. − MS, *m/z* (%): 312 (21) [M^+], 234 (17), 233 (100) [$M^+ - SO_2Me$], 218 (6), 205 (6), 204 (28), 176 (5).

Table 5. Chemical shifts (δ values) and ^{1}H,^{1}H coupling constants ([Hz], *in italics*) in proton spectra of starting materials (**1**, **28**, **29**), 2-iminodihydro-1-benzazepines (**14**, **21**), and 2-iminodihydroquinolines (**15**, **22**)

Cpd.	Me——CH_n		^3J [Hz]	NMe (s)	SO_2Me (s)	4-H (d)	^3J [Hz]	5-H (d)	Aryl-H (m)	[a]
1a[b]	3.03			4.38					7.8 – 8.9	A
1b	1.49	3.85 (sept)	*6.7*	4.47					7.9 – 9.0	A
1c	3.06			4.43					7.5 – 8.5	A
	3.29			4.70					7.7 – 8.7	T
1d	1.53	3.89 (sept)	*6.8*	4.55					7.5 – 8.5	T
1e	1.49	3.38 (q)	*7.5*	4.46					7.6 – 8.5	A
1g		4.77[c]		4.42					7.2 – 8.5	A
15d				3.81					6.5 – 7.6	T
				3.46					6.6 – 7.4	B
21e	0.83	4.89 (dq)	*7.3*	3.52	3.08	6.45	*9.2*		7.1 – 7.5	T
(*E*)-**21j**	0.84	4.70 (dq)	*7.3*	3.62		6.41	*9.2*		7.1 – 7.5	T
(*Z*)-**21j**	1.78	2.89 (quint)	*7.0*	3.60		6.11	*7.0*		7.1 – 7.5	T
28	1.42	3.30 (sept)	*7.0*						7.2 – 8.2	T
	CMe_2									
14b		1.34		2.86		5.81	*10.7*	6.60	6.6 – 7.3	T
		1.36		2.62		5.70	*10.7*	6.46	6.5 – 7.1	B
14d		1.20		3.03		6.08 (s)			6.7 – 7.4	T
		1.29		2.91		6.08 (s)			6.7 – 7.3	B
21b		1.15		3.81	3.14	5.83	*10.4*	6.64	7.2 – 7.4	T
21d[d]	0.80	1.54		3.91	3.24	6.01 (s)			7.1 – 7.5	T
[e]		1.17		3.85	3.12	5.98 (s)			7.0 – 7.5	T
21i	0.82	1.71		3.83		5.98 (s)			7.1 – 7.5	T
	*t*Bu——CH_n (d)									
1f	1.14	3.40 (s)		4.53					7.6 – 8.5	A
(*E*)-**21f**	0.76	4.88	*9.8*	3.58	3.07	6.28			7.0 – 7.5	T
(*Z*)-**21f**	1.56	2.41	*7.3*	3.85	3.12	6.23			7.0 – 7.5	T
(*E*)-**21k**	0.78	4.62	*9.6*	3.67		6.22			7.1 – 7.6	T
(*Z*)-**21k**	1.14	2.43	*7.3*	3.90		6.24			7.1 – 7.6	T
21l		6.09 [f]	*9.0*	3.63		6.68			7.0 – 7.5	T
22a				3.89	3.14				7.2 – 7.9	T
22d				3.95	3.16				7.2 – 7.8	T
22h				4.14					7.4 – 7.9	T
29	1.05	2.92							7.2 – 8.2	T

[a] Solvents: see Table 1. − [b] Proton spectrum of **1a**·I recorded for a solution in deuterium oxide: ref.[30a] − [c] CH_2Ph. − [d] Spectrum for the slow-exchange limit (−54°C). A broad signal (δ = 0.9−1.4) is observed for the geminal methyl groups at room temperature. − [e] Spectrum for the limit of fast exchange (58°C). − [f] C*H*Ph.

Table 6. Chemical shifts (δ values) and $^{19}F,^{13}C$ coupling constants ([Hz], *in italics*) in carbon-13 spectra of starting materials (**1**, **28**, **29**), 2-iminodihydro-1-benzazepines (**14**, **21**), and 2-iminodihydroquinolines (**15**, **22**)

Cpd.	Me—CH_n		NMe	SO_2Me	CF_3	C=N	Other ring-C CH						quat. C			[a]
1a[b]	23.8		40.6			162.1	119.6	126.1	130.3	131.6	136.5	147.0	129.3	140.8		A
1b	21.7	33.4	39.9			169.7	120.1	121.7	130.5	131.5	136.5	147.5	129.2	141.1		A
1c	23.7		40.4			159.5	118.6 130.3	125.0 134.63	128.36	128.86	128.94	129.4	126.3 157.2	134.69	140.0	A
	23.4		40.3			161.1	120.0 131.4	126.3 135.89	129.35	130.05	130.15	130.61	127.5 158.2	135.96	141.3	T
1d	21.6	32.5	38.7			167.0	119.3 130.7	120.2 135.61	128.7	129.26	129.42	129.61	126.7 158.7	135.10	140.3	T
1e	12.8	29.9	40.1			164.8	120.1 131.6	125.0 136.08	129.71	130.22	130.37	130.86	127.7 159.0	136.13	141.5	A
1g		41.8	40.7			161.3	120.2 130.69	126.1 130.81	128.9 131.8	129.87 141.8	130.23	130.40	128.0 136.4	135.3 159.3	136.0	A
15d			31.1			151.3	113.6 128.27	115.3 128.41	120.4 128.90	121.89 129.38	122.18 130.5	127.3	120.62 146.5	137.8 150.7	141.6	T
			30.6			151.7	113.8 128.29	115.6 128.68	120.27 129.06	122.21 129.8	122.44 130.5	127.5	120.89 146.8	138.3 150.9	142.2	B
21e	11.4	36.6	41.4	43.6		169.9	123.4 130.03	125.2 130.06	127.99	128.34	128.56	128.73	133.2 142.9	140.6	141.7	T
(*E*)-**21j**[c]	11.5	38.4	42.84		119.32 *J* = 327	167.7 171.3	123.44 128.53	123.70 128.59	126.37 128.63	126.73 128.82	128.40 129.16	128.47 129.20	133.1 140.1	134.1 141.0	138.9 141.86	T
(*Z*)-**21j**[c]	15.9	39.2	42.27		119.60 *J* = 316		129.25	130.08	130.13	130.28			142.15	142.19		T
21l		47.5	42.0		120.2 *J* = 254	169.2	123.5 128.74	125.89 129.4	126.05	126.22	128.05	128.64	132.7 141.5	134.1 144.3	139.5	T
26			29.5			161.9[d]	114.5 128.91	121.24 130.7	121.90	127.70	128.56	128.67	120.5 150.9	137.1	140.3	T
28	22.6	37.4				167.2	119.4 129.39	125.59 129.56	125.70	128.25	128.51	129.13	125.5 148.73	138.6	148.23	T
	*t*Bu—CH_n															
1f	30.0 36.4	47.8	41.9			161.9	120.7 131.6	127.81 135.93	129.70	130.23	130.57	130.82	128.00 157.6	136.01	141.8	A
(*E*)-**21f**[c]	29.7 36.7	51.8	42.8	44.11		162.3 168.2	124.1 128.36	124.7 128.51	125.5 128.52	126.2 128.59	127.95 128.65	128.12 128.76	134.14 140.5	134.19 141.2	139.7 143.32	T
(*Z*)-**21f**[c]	28.0 32.4	53.8	44.44	44.63		120.05	129.30	129.55	130.6				143.36	144.8		
(*E*)-**21k**[c]	29.9 38.8	54.43	44.24		119.4 *J* = 317	164.7 171.1	123.7 128.47	124.6 128.53	126.64 128.66	127.04 128.68	128.31 128.96	28.39 129.16	133.86 140.72	133.98 141.30	139.1 142.4	T
(*Z*)-**21k**[c]	28.1 32.6	54.69	44.64				130.70						143.37	143.68		
29	29.8 32.5	52.7				160.4	123.5 129.51	125.53 129.57	125.71	128.24	128.52	129.02	125.1 148.3	138.4	147.5	T
	Me_2	C														
14b	26.0	45.0	41.0			160.0	114.8 129.30	119.7 131.9	120.8 137.5	122.4	128.53	128.97	125.0	142.7	150.0	T
14d	27.3		43.0			163.1	120.43 128.53	120.82 128.62	121.9 128.65	123.3 130.0	127.5 138.9	128.22	133.2 145.8	140.0 150.6	142.2	T
	27.6	43.41	43.01			162.6	120.74 128.75	121.09 128.93	122.2 129.03	123.5 130.3	127.7 139.1	128.52	133.6 151.2	140.5	142.7	B
21b	25.7	43.4	46.6	45.1		168.2	123.8	125.9	128.40	128.44	128.50	140.4	131.2	143.2		T
21d[a]	20.3 31.0	42.8	46.3	45.1		168.7	123.9 129.4	126.0 137.1	127.87	128.29	128.35	128.84	132.5 143.9	139.5	140.1	T
[e]	25.9	42.2	46.2	45.1		169.5	124.2 129.6	126.0 137.7	127.97	128.40	128.55	128.88	133.3 144.4	140.32	140.64	T
21i	20.0 30.3	43.0	45.9		119.6 *J* = 254	171.7	123.7 129.90	126.8 136.8	128.38	128.55	128.64	129.31	132.7 142.9	139.95	140.56	T
22a			32.7	43.3		156.0	115.4	117.6	123.9	129.3	132.0	139.00	121.7	139.22		T
22d			32.7	43.2		155.4	115.4 129.18	117.1 131.9	123.6	128.2	128.6	129.16	121.4 151.3	136.4	139.5	T
22h			34.0		120.1 *J* = 256	156.3	116.65 129.74	116.98 132.9	125.3	128.45	128.91	129.16	122.7 153.7	135.8	139.5	T
[f]						149.1 154.1 156.0[g]	118.7 129.40	125.6 129.52	127.2 129.73	128.49 130.46	128.64	128.90	126.4 148.10	130.90 148.58	138.2	T

[a] Solvents: see Table 1. – [b] Carbon-13 spectrum of **1a**·**I** recorded for a solution in [D_6]dimethyl sulphoxide: ref.[30b]). – [c] Signals with δ > 100 could not be assigned to one of the different diastereomers. – [d] Spectrum in the slow-exchange limit (−54°C). Due to exchange-broadening, the signals for the geminal methyl groups could not be observed at room temperature. – [e] Spectrum in the limit of fast exchange (58°C). – [f] Semicarbazone of **30**. – [g] C=O.

b) From **1g**. Flash chromatography of the solid residue with EA gave colourless crystals (0.95 g, 74%), m.p. 198−202°C.

2,3-Dihydro-1,3,3-trimethyl-2-[*N*-(methylsulphonyl)imino]-5-phenyl-1*H*-benz[*b*]azepine (21d) and 22d: From **1d**. Flash chromatography of the residue with PE/EA (1:1) gave yellow crystals as first fraction (**21d**, 0.83 g, 51%, m.p. 188−192°C), and brown crystals (**22d**, 0.64 g, m. range. 142−147°C). Recrystallisation from ethanol afforded colourless crystals (**21d**, m.p. 190−192°C; **22d**, 0.32 g, 20%, m.p. 202−204°C). − **21d**, MS, *m/z* (%): 354 (2) [M^+], 281 (8), 275 (12) [$M^+ - SO_2Me$], 295 (5), 234 (7), 208 (14), 207 (100), 129 (5).

2,3-Dihydro-1,3-dimethyl-2-[*N*-(methylsulphonyl)imino]-5-phenyl-1*H*-benz[*b*]azepine (21e) and 22d: From **1e**. Flash chromatography of the residue with EA gave yellow crystals as first fraction (**21e**, 0.60 g, m. range 170−200°C), and pale brown crystals (**22d**, 1.80 g, m. range 150−175°C). Recrystallisation from ethanol afforded colourless crystals (**21e**, 0.25 g, 15%, m.p. 206−207°C; **22d**, 0.92 g, 59%, m.p. 198−201°C). − **21e**, MS, *m/z* (%): 340 (8) [M^+], 281 (15), 262 (11), 261 (55) [$M^+ - SO_2Me$], 246 (10), 231 (7), 208 (15), 207 (100), 165 (8).

2,3-Dihydro-3-(2,2-dimethylpropyl)-2-[*N*-(methylsulphonyl)imino]-5-phenyl-1*H*-benz[*b*]azepine (21f) and 22d: From **1f**. Recrystallisation from ethanol afforded colourlesss crystals (**22d**, 0.92 g, 59%, m.p. 198−201°C). Flash chromatography of the residue from the mother liquor with PE/EA (1:1) gave an orange-coloured oil (**21f**, 0.25 g) and a second crop of **22d** (0.28 g, 18%, colourless crystals, m.p. 194−198°C). MPLC of the orange-coloured oil with PE/EA (1:1) gave yellow crystals (0.22 g, m. range 130−170°C). Recrystallisation from ethanol yielded yellow needles. − MS, *m/z* (%): 382 (4) [M^+], 326 (16), 304 (9), 303 (40) [$M^+ - SO_2Me$], 248 (21), 247(100), 221 (16), 220 (66), 218 (10), 208 (14), 207 (70), 206 (26), 205 (7), 204 (22), 169 (17), 165 (14).

Experiments with Trifluoromethanesulphonyl Azide (18b)

General Procedure: Suspensions of powdered **1c−g** (3 mmol) and KH (0.60 g, 15 mmol) in tetrahydrofuran (25 mL) or benzene (**1d**, 25 mL) were stirred for 1 or 24 h, respectively, in centrifuge tubes which were equipped with a septum and connected to a supply of Ar. Solid, inorganic material was removed with the help of a centrifuge. The supernatant solutions were transferred via syringe into 100-mL flasks, and the solid material was washed twice with the solvent employed (5 mL). A solution of **18b** (1.58 g, 9 mmol) in dichloromethane (15 mL) was added dropwise at 0°C. The mixture was stirred at 0°C for 1 h and at room temp. for 1 h. The solvent was distilled i. vac. to afford solid residues.

1,2-Dihydro-1-methyl-2-[*N*-(trifluoromethylsulphonyl)imino]-quinoline (22h) and 1,2-Dihydro-1-methyl-4-phenyl-2-quinolinone (26): From **1c**. Flash chromatography of the solid residue with PE/EA (1:1) gave brown crystals (**22h**, 0.20 g, m. range 175−180°C) and a dark solid (**26**, 0.09 g, m. range 80−90°C). Recrystallisation from ethanol afforded colourless crystals (**22h**), and colourless needles (**26**, 42 mg, 6%, m.p. 143−145, ref.[24a] 141−142°C). − **22h**, MS, *m/z* (%): 366 (21) [M^+], 298 (18), 297 (100) [$M^+ - CF_3$], 234 (15), 233 (81) [$M^+ - SO_2CF_3$], 218 (42), 205 (11), 204 (42), 203 (12).

2,3-Dihydro-1,3,3-trimethyl-2-[*N*-(trifluoromethylsulphonyl)imino]-5-phenyl-1*H*-benz[*b*]azepine (21i), 22h, and 26: From **1d**. Flash chromatography of the solid residue with PE/EA (1:1) gave an orange-coloured oil (**21i**, 0.85 g) and colourless crystals (**22h**, 0.08 g, m. range 178−188°C; **26**, 0.10 g, 14%, m.p. 143−145°C). Recrystallisation from ethanol afforded **21i** and **22h** as colourless crystals. − **21i**, MS, *m/z* (%): 408 (7) [M^+], 281 (37), 276 (13), 275 (74) [$M^+ - SO_2CF_3$], 259 (14), 234 (17), 208 (16), 207 (100).

Table 7. Molecular formulae and masses, and elemental analyses

Cpd.		Molecular Mass		Elemental analysis C	H	N	S
1a	$C_{11}H_{12}F_6NP$	303.2	Calcd.	43.58	3.99	4.62	
			Found	43.39	3.96	4.68	
1b	$C_{13}H_{16}F_6NP$	331.2	Calcd.	47.14	4.87	4.23	
			Found	47.13	4.91	4.29	
1c	$C_{17}H_{16}F_6NP$	379.3	Calcd.	53.83	4.25	3.69	
			Found	53.62	4.14	3.72	
1d	$C_{19}H_{20}F_6NP$	407.3	Calcd.	56.02	4.95	3.44	
			Found	55.84	4.98	3.55	
1e	$C_{18}H_{18}F_6NP$	393.3	Calcd.	54.97	4.61	3.56	
			Found	54.61	4.59	3.51	
1f	$C_{21}H_{24}F_6NP$	435.4	Calcd.	57.93	5.56	3.22	
			Found	57.74	5.59	3.17	
1g	$C_{23}H_{20}F_6NP$	455.4	Calcd.	60.66	4.43	3.08	
			Found	60.21	4.44	3.01	
10d	$C_{25}H_{24}N_4$	380.5	Calcd.	78.92	6.36	14.72	
			Found	78.77	6.48	14.24	
10f	$C_{27}H_{28}N_4$	408.5	Calcd.	79.38	6.91	13.71	
			Found	79.79	6.93	13.36	
14b	$C_{19}H_{20}N_2$	276.4	Calcd.	82.57	7.29	10.14	
			Found	81.55	7.30	10.15	
14d	$C_{25}H_{24}N_2$	352.5	Calcd.	85.19	6.86	7.95	
			Found	84.17	7.05	7.75	
21b	$C_{14}H_{18}N_2O_2S$	278.4	Calcd.	60.40	6.53	10.06	11.52
			Found	60.22	6.63	9.97	11.39
21d	$C_{20}H_{22}N_2O_2S$	354.5	Calcd.	67.77	6.26	7.90	9.04
			Found	67.49	6.34	8.19	9.34
21e	$C_{19}H_{20}N_2O_2S$	340.4	Calcd.	67.03	5.92	8.23	9.42
			Found	66.88	6.03	8.15	9.43
21f	$C_{22}H_{26}N_2O_2S$	382.5	Calcd.	69.08	6.85	7.32	8.38
			Found	68.98	6.94	7.21	8.61
21i	$C_{20}H_{19}F_3N_2O_2S$	408.4	Calcd.	58.81	4.69	6.86	7.85
			Found	57.89	4.90	6.72	7.92
21j	$C_{19}H_{17}F_3N_2O_2S$	394.4	Calcd.	57.86	4.34	7.10	8.13
			Found	57.96	4.53	7.19	8.15
21k	$C_{22}H_{23}F_3N_2O_2S$	436.5	Calcd.	60.54	5.31	6.42	7.34
			Found	60.58	5.64	6.37	7.50
21l	$C_{24}H_{19}F_3N_2O_2S$	456.5	Calcd.	63.15	4.20	6.14	7.02
			Found	63.00	3.18	5.89	6.67
22a	$C_{11}H_{12}N_2O_2S$	236.3	Calcd.	55.92	5.12	11.86	13.57
			Found	55.69	5.12	11.57	13.42
22d	$C_{17}H_{16}N_2O_2S$	312.4	Calcd.	65.36	5.16	8.97	10.26
			Found	65.23	5.16	9.22	10.56
22h	$C_{17}H_{13}F_3N_2O_2S$	366.4	Calcd.	55.73	3.58	7.65	8.75
			Found	55.89	3.76	7.79	8.59
28	$C_{18}H_{17}N$	247.3	Calcd.	87.41	6.93	5.66	
			Found	87.23	6.73	5.84	
29	$C_{20}H_{21}N$	275.4	Calcd.	87.23	7.69	5.09	
			Found	87.06	7.95	5.05	
[a]	$C_{23}H_{18}N_4O$	366.4	Calcd.	75.39	4.95	15.29	
			Found	74.72	4.91	15.23	
				Exact mass			
14b			Calcd.	276.1626			
			Found	276.1621			
14d			Calcd.	352.1939			
			Found	352.1930			

[a] Semicarbazone of **30**.

2,3-Dihydro-1,3-dimethyl-2-[*N*-(trifluoromethylsulphonyl)imino]-5-phenyl-1*H*-benz[*b*]azepine (21j), 22h, and 26: From **1e**. Recrystallisation of the solid residue from EA yielded colourless crystals (**21j**, 0.68 g, 57%, m.p. 208−210°C). Flash chromatography with PE/EA (1:1) of the residue obtained from the mother liquor gave a second

Table 8. Experimental details and results of the X-ray diffraction analyses of **21b**, **d**, and (*ax,E*)-**21e**

Compound		**21b**	**21d**	(*ax,E*)-**21e**
Molecular formula		$C_{14}H_{18}N_2O_2S$	$C_{20}H_{22}N_2O_2S$	$C_{19}H_{20}N_2O_2S$
Molecular mass		278.40	354.47	340.44
Crystal system		monoclinic	triclinic	monoclinic
Space group		$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [pm]		893.53(5)	798.4(1)	1045.41(7)
b [pm]		1433.85 (9)	1048.2(1)	792.42(6)
c [pm]		1139.68(7)	1166.9(1)	2193.6(2)
α [deg]			103.670(8)	
β[deg]		99.258(7)	100.112(8)	98.796(6)
γ [deg]			92.485(8)	
V [nm^3]		1.4411(1)	0.9304(2)	1.7958(2)
Z		4	2	4
d (calcd.) [g cm^{-3}]		1.283	1.265	1.259
Size of the crystal [mm]		0.15 x 0.3 x 0.4	0.45 x 0.85 x 0.15	0.5 x 0.5 x 0.4
Range	*h*	0 → 11	–1 → 10	0 → 13
	k	0 → 18	–13 → 13	0 → 10
	l	–14 → 14	–15 → 15	–28 → 28
No. of measured reflections		3667	5168	4625
Symmetry-independent reflections		3316	4248	4093
Observed reflections $F>3\sigma(F)$		2497	3430	3197
Linear absorpt. coeff. [mm^{-1}]		0.22	0.19	0.19
Absorption correction		ψ-scan	ψ-scan	ψ-scan
Ratio F_{obs}/parameters		14.43	15.18	14.73
R		0.058	0.060	0.068
R_w		0.058	0.062	0.065
Diff. Four.	$\Delta\rho_{max}$[a] [eÅ^{-3}]	0.34	0.41	0.37
	$\Delta\rho_{min}$[b]	0.23	0.24	0.48

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

crop of **21j** (0.20 g, 17%, m.p. 203−208 C) and colourless crystals (**22h**, 90 mg, 8%, m.p. 189−192°C; **26**, 40 mg, 6%, m. range 138−147°C). Recrystallisation from ethanol afforded colourless crystals (**21j** and **22h**), and colourless needles (**26**, 22 mg, 3%). − **21j**, MS, *m/z* (%): 394 (16) [M$^+$], 281 (31), 262 (16), 261 (75) [M$^+$ − SO_2CF_3], 246 (14), 245 (14), 231 (11), 208 (16), 207 (100), 206 (17), 204 (13).

2,3-Dihydro-3-(2,2-dimethylpropyl)-2-[*N*-(trifluoromethylsulphonyl)imino]-5-phenyl-1*H*-benz[*b*]azepine (21k), 22h, and 26: From **1f**. Recrystallisation of the solid residue from ethanol yielded colourles crystals (**21k**, 0.35 g, 26%, m.p. 202−204°C). Flash chromatography with PE/EA (1:1) of the residue obtained from the mother liquor gave a second crop of **21k** (yellow oil, 0.42 g) and colourless crystals (**22h**, 0.24 g, m. range 175−185°C; **26**, 15 mg, 2%, m.p. 145−147°C). Recrystallisation from ethanol afforded colourless crystals (**21k** and **22h**). − **21k**, MS, *m/z* (%): 436 (4) [M$^+$], 381 (10), 380 (43) [M$^+$ − *t*Bu], 303 (9) [M$^+$ − SO_2CF_3], 248 (20), 247 (100), 221 (12), 220 (62), 207 (29), 206 (14), 204 (11).

2,3-Dihydro-2-[*N*-(trifluoromethylsulphonyl)imino]-3,5-diphenyl-1*H*-benz[*b*]azepine (21l) and 22h: From **1g**. Flash chromatography of the solid residue with PE/EA (1:1) gave a yellow oil (**21l**, 0.21 g) and colourless crystals (**22h**, 0.84 g, 82%, m.p. 186−189°C). Crystallisation of the yellow oil from ethanol afforded colourless needles. − MS, *m/z* (%): 456 (11) [M$^+$], 324 (20), 323 (100) [M$^+$ − SO_2CF_3], 307 (15), 245 (14), 207 (30), 206 (16).

1,2-Dihydro-1-methyl-4-phenyl-2-quinolinone (26) by Oxidation of 2d with Molecular Oxygen: A suspension of powdered **1d** (3 mmol) and KH (0.60 g, 15 mmol) in benzene (**1d**, 20 mL) was stirred for 1 d in a centrifuge tube which was equipped with a septum and connected to a supply of Ar. Solid, inorganic material was removed with the help of a centrifuge. The supernatant solution was transferred via syringe into a 100-mL flask, and the solid material was washed with benzene (5 mL). Oxygen was introduced into the solution for 2 h. The solvent was distilled i. vac. Flash chromatography of the residue with PE/EA (1:1) gave colourless crystals (0.14 g, 60%, m.p. 138−140°C). Recrystallisation from ethanol afforded colourless crystals (0.11 g, m.p. 141−143, ref.[24a] 141−142°C). − ^{1}H NMR: ref.[24b]

X-ray Diffraction Analyses were performed from transparent colourless crystals of **21b**, **d**, and (*ax,E*)-**21e**. The cell parameters were determined on the basis of 22 reflections. The numbers of reflections reported in Table 8 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. Computations were performed with a computer Micro-VAX II. The programme SHELXTL PLUS[31] 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.[32]

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