DOI: 10.1002/ejoc.200900350

Syntheses and ^{15}N NMR Spectra of Iminodiaziridines – Ring-Expansions of 1-Aryl-3-iminodiaziridines to 1*H*- and 3a*H*-Benzimidazoles, 2*H*-Indazoles, and 5*H*-Dibenzo[*d*,*f*][1,3]diazepines

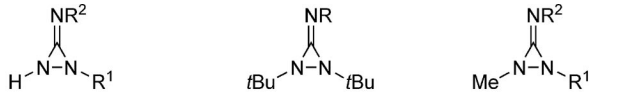
Helmut Quast,*[a][‡] Karl-Heinz Ross,[a] Gottfried Philipp,[a] Manfred Hagedorn,[b] Harald Hahn,[b] and Klaus Banert[b]

Keywords: Elimination / Diaziridines / Guanidines / Nitrogen heterocycles / Sigmatropic rearrangement

Iminodiaziridines are synthesized by (i) 1,3-dehydrochlorination with potassium *tert*-butoxide of *N*-chloroguanidines, generated in situ from *N*,*N*′,*N*′′-substituted guanidines with *tert*-butyl hypochlorite, and (ii) base-mediated 1,3-elimination of sulfuric acid from *N*,*N*′,*N*′′-substituted hydroxyguanidine *O*-sulfonic acids. At elevated temperatures, (alkylimino)diaziridines undergo valence isomerization by 1,3-shift, [2+1] cycloelimination to afford isocyanides and diazenes, and ring-opening elimination to yield alkylideneguanidines. *N*′-Aryl-*N*-hydroxyguanidine *O*-sulfonic acids furnish (*N*-arylimino)diaziridines, but no 1-aryl-3-iminodiaziridines, instead giving rearranged isomers. Precursors containing perdeuterated *tert*-butyl groups give rearranged products that show complete scrambling. This indicates that 1-aryl-3-iminodiaziridines are intermediates that undergo very rapid degenerate valence isomerization. Provided that the *ortho*-aryl positions are substituted, high yields of (arylimino)diaziridines are obtained, along with 2-imino-2,3-dihydro-3a*H*-benzimidazoles. Otherwise, 2-amino-1*H*-benzimidazoles and strongly fluorescent 3-amino-2*H*-indazoles, originating from rearrangements of the elusive 1-aryl-3-iminodiaziridines, predominate. *N*′,*N*′′-Diaryl-*N*-hydroxyguanidine *O*-sulfonic acids give only rearranged products: a 2-amino-1*H*-benzimidazole and a 6-amino-5*H*-dibenzo[*d*,*f*][1.3]diazepine if aryl = phenyl, or a 2-imino-2,3-dihydro-3a*H*-benzimidazole if aryl = mesityl. 3a*H*-Benzimidazoles slowly dimerize through Diels–Alder reactions. ^{15}N NMR signals were assigned to the *syn* and *anti* ring nitrogen atoms of iminodiaziridines with the help of a combination of homonuclear NOE and HN-HMBC or HN-gHMBC experiments.

Introduction

High reactivity toward various reagents may make three-membered heterocycles that contain exocyclic double bonds[1] attractive synthetic building blocks. Indeed, many of them react with rates, driving force, and selectivities that resemble those of "click reactions".[2] However, only a few of these promising systems are readily accessible with variable substitution patterns; examples include methylenaziridines,[3a] alkylideneoxiranes,[1c–1f,3b,3c] alkylidenethiiranes,[4] aziridinones,[1g] and iminoaziridines.[5] So far, iminodiaziridines do not belong to this group – although some of them have been employed in syntheses[6] – because only iminodiaziridines containing at least two *tert*-butyl groups, such as **2a**,[7a,7c] **2b**,[7b–7d] and **2d**,[7e] have been obtained in useful quantities. The parent iminodiaziridine (**1a**) and monoalkyl derivatives **1b** and **1c** are elusive intermediates,[8] whereas the methyl compounds **3** have been generated in small-scale experiments by photodenitrogenation of 5-iminodihydrotetrazoles.[9]



1a $R^1 = R^2 = H$
1b $R^1 = Me$, $R^2 = H$
1c $R^1 = H$, $R^2 = Bu$

2a R = Me
2b R = *t*Bu
2c R = *i*Pr
2d R = CN, Tos, $OP(OEt)_2$, $OP(OPh)_2$

3a $R^1 = R^2 = Me$
3b $R^1 = t$Bu, $R^2 = Me$
3c $R^1 = Me$, $R^2 = t$Bu

To develop synthetic applications of iminodiaziridines, we set out to explore the scope and limitations of the cyclization of guanidine derivatives, with a view to obtaining preparative amounts of iminodiaziridines *not* shielded by *tert*-butyl groups. An additional goal was regioselectivity of the 1,3-elimination to furnish single isomers rather than mixtures if different alkyl groups were present. (Arylimino)-diaziridines were synthesized. Their ring-arylated isomers immediately rearranged to 2*H*-indazoles, 1*H*-benzimidazoles, and stable 3a*H*-benzimidazoles. Precursors with two aryl groups afforded 1*H*- and 3a*H*-benzimidazoles and 5*H*-

[a] Institut für Organische Chemie der Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
[b] Institut für Chemie der Technischen Universität Chemnitz, Strasse der Nationen 62, 09111 Chemnitz, Germany
E-mail: klaus.banert@chemie.tu-chemnitz.de
[‡] Current address: Hoetgerstrasse 10, 49080 Osnabrück, Germany
Fax: +49-541-8141935
E-mail: hquast@uni-osnabrueck.de
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900350.

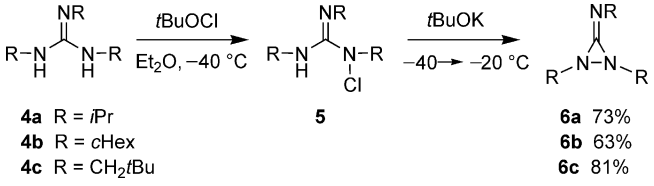
dibenzo[*d*,*f*][1,3]diazepines. Novel routes to these heterocycles and ^{15}N NMR spectra of iminodiaziridines are reported.

Results and Discussion

All guanidines in this study were synthesized by known routes (acid-catalyzed addition of primary amines[10,11] or *N*-alkylhydroxylamine *O*-sulfonic acids[12] to carbodiimides[10]), and these syntheses are detailed in the Supporting Information.

(Alkylimino)diaziridines

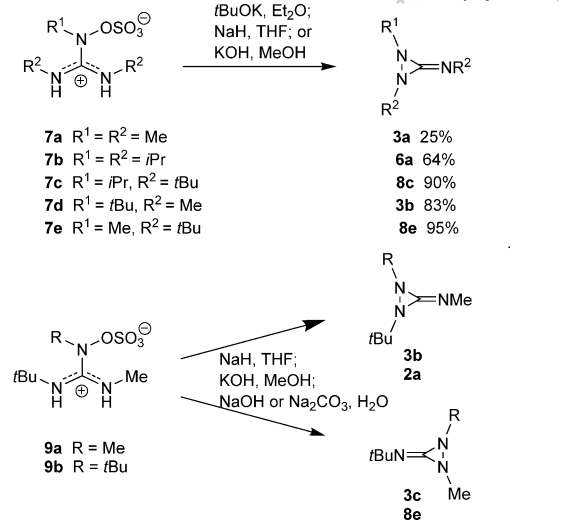
Chlorination of *N*,*N*′,*N*′′-trialkylguanidines **4**, containing only a single type of alkyl group, with *tert*-butyl hypochlorite at low temperature gave unstable *N*-chloroguanidines **5**. These were immediately dehydrochlorinated with potassium *tert*-butoxide to afford iminodiaziridines **6** in good yields (Scheme 1). In contrast with the synthesis of **2b**,[7b,7c] use of an excess of base had to be avoided because it led to substantial amounts of isocyanides. The isolation of multi-gram quantities of pure compounds **6** shows that shielding of the iminodiaziridine system by tertiary alkyl groups is not necessary for convenient preparation and handling.



Scheme 1. (Alkylimino)diaziridines **6** by cyclization of *N*,*N*′,*N*′′-trialkylguanidines **4**.

Chlorination of unsymmetrical *N*,*N*′,*N*′′-trialkylguanidines inevitably yields mixtures of isomeric *N*-chloroguanidines and iminodiaziridines, such as **2a** and **8e**.[7a,7c] Obviously, the selective synthesis of a pure iminodiaziridine isomer requires a guanidine derivative with a leaving group attached to a certain nitrogen atom. We obtained such guanidines – the hydroxyguanidine *O*-sulfonic acids **7** (Scheme 2) – by addition of *N*-alkylhydroxylamine *O*-sulfonic acids[12] to *symmetrical* carbodiimides.[8]

Treatment of **7** with strong bases, such as potassium *tert*-butoxide in diethyl ether, sodium hydride in THF, or concentrated solutions of potassium hydroxide in methanol or water, furnished iminodiaziridines in good yields (Scheme 2). The two methods using aprotic solvents were limited by the solubilities of compounds **7**, which are governed by the size of their alkyl groups. Compound **7d** did not react with sodium hydride in THF, for example. In other cases, however, sodium hydride was particularly convenient, because progress of the reaction could be monitored not only by IR spectroscopy but also by the evolution of hydrogen. To minimize solvolysis of iminodiaziridines, cyclizations of **7** in methanol or water were carried out in the presence of pentane, into which the products transferred immediately after formation. The low yield of **3a** is certainly due to loss of material during the attempt to separate **3a** from the solvent. Neat **3a** is quite unstable and decomposes violently.



Scheme 2. (Alkylimino)diaziridines by base-mediated 1,3-elimination of sulfuric acid from *N*-hydroxyguanidine *O*-sulfonic acids **7** and **9**.

Use of butyllithium in hexane as base failed to give satisfactory results; treatment of a suspension of **7e** in diethyl ether with 2 equiv. of butyllithium afforded about equal amounts of **8e** and bis(*tert*-butyl)carbodiimide (**18**), for example. The amount of the latter product was increased to 80% when THF was the solvent.

The formation of mixtures of isomeric iminodiaziridines from hydroxyguanidine *O*-sulfonic acids **9**, obtained from an *unsymmetrical* carbodiimide, presented the challenge of steering the regioselectivity of 1,3-elimination by means of the reaction conditions.

At room temperature, sodium hydride in THF slowly converted **9a** into a 97:3 mixture of **3b**/**3c** (69%), which corresponds to the thermal equilibrium between the two valence isomers. High concentrations of potassium hydroxide in methanol gave rise to the almost exclusive formation of the more stable isomer **3b** (75–80%, **3b**/**3c** ≥ 99:1), whereas aqueous 1 M sodium hydroxide or sodium carbonate yielded mixtures in which substantial proportions of the less stable isomer **3c** were present (82%; **3b**/**3c** 84:16 and 78:22, respectively).

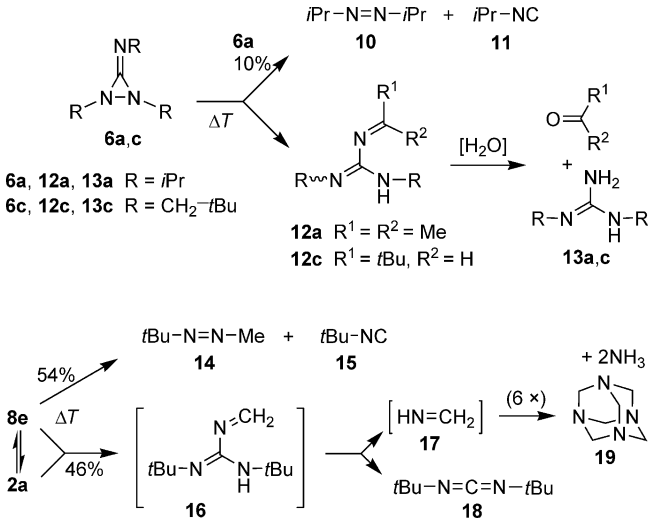
The direction of cyclization of **9b** depended more strongly on the base concentration than that of **9a**, but followed the same trend. In both cases high base concentrations favored ring-closure involving the *tert*-butyl-substituted nitrogen atom (**9a** → **3b**, **9b** → **2a**) over cyclization to afford **3c** and **8e**. Because the **2a**/**8e** thermal valence isomer-

ization proceeds only very slowly at room temperature,[7c] the product ratios reported below are the results of kinetic control. Use of concentrated solutions of potassium hydroxide in methanol thus converted **9b** mainly into the more stable isomer **2a** (**2a/8e** 85:15; 81%). The opposite result was obtained when dilute solutions of alkali hydroxide were employed (**2a/8e** 26:74; 88%). Use of sodium hydride in THF or potassium *tert*-butoxide in diethyl ether afforded ratios that ranged between these extremes. Neither the reaction temperature nor the nature of the cation influenced the ring-closure of **9b**.

(Alkylimino)diaziridines are colorless oils or low-melting solids (**6b** and **6c**), which could be stored at low temperatures and were characterized by NMR and IR spectroscopy. The latter method revealed very high C=N wavenumbers [1792 (**8c**) to 1816 cm^{-1} (**3b**, **6c**)]. These arise from high levels of kinetic coupling with the symmetric ring stretching mode, due to the large angle between the C=N bond and the ring C–N bonds.[13] The iminodiaziridines **3b**, **8c**, and **8e** would be expected to exist as mixtures of *E* and *Z* diastereomers. Assignment of the configurations of **3b** and **8c** was made with the help of asymmetric solvent-induced shifts in their ^1H NMR spectra[5,9,14] and resulted in *E*/*Z* ratios of 47.5:52.5 and 4:1, respectively. Only a single diastereomer was observed for **8e**, most probably (*E*)-**8e**.[7c]

We briefly investigated the thermal stabilities and decomposition products of (alkylimino)diaziridines (Scheme 3). The results are summarized here; details are reported in the Supporting Information. The long-known tri(*tert*-butyl) compound **2b** decomposed cleanly on heating at 150–180 °C, in a [2+1] cycloelimination into *tert*-butyl isocyanide and bis(*tert*-butyl)diazene.[7c] Surprisingly, this mode of thermal decomposition accounted for only 10% when a solution of **6a** in [D_{12}]cyclohexane was briefly heated at 180 °C. The major product then was *N*-isopropylideneguanidine **12a** (83%), the structure of which was established by hydrolysis to acetone and the known **13a**.[15] The same rearrangement was observed exclusively on heating of **6c** at 80 °C. It was noticeable after 1 h and complete after 3 h, affording two diastereomers of **12c** (7:3). Even at room temperature in the solid state, **6c** decomposed over two weeks to furnish **13c**, obviously by hydrolysis of intermediate **12c** due to traces of moisture. The isomerization **6** → **12**[16] may be interpreted in terms either of base-mediated eliminative ring fission[17a,17b] or of [1.5] sigmatropic H-shift.[17c]

At elevated temperatures, reversible valence isomerization of the iminodiaziridines **2a/8e**, **2c/8c**, and **3b/3c** is observed, involving exchange of one of the ring nitrogen atoms and the imino nitrogen atom in each case. Iminodiaziridines containing a (*tert*-butyl)imino group are less stable than their valence isomers with a primary or secondary alkyl group at the imino nitrogen atom [e.g., **2a/8e** 90.7:9.3 (60 °C)].[7c] After brief heating of solutions of **2a/8e** at 180 °C, only the [2+1] cycloelimination products **14** and **15** of the less stable isomer **8e** were detected (54%). Some surprising further products were bis(*tert*-butyl)carbodiimide (**18**, 46%), tetraazaadamantane (**19**, 46%), and ammonia. They may be explained if it is assumed that **2a** and/or **8e** rearranged to the *N*-methyleneguanidine **16**, which eliminated imine **17** to afford **18**. Finally, **17** condensed to **19**, concomitantly with loss of ammonia. However, the experimental results do not rule out a hypothetical [2+1] cycloelimination of **8e** into **18** and a nitrenoid fragment,[18] which rearranges to **17**.



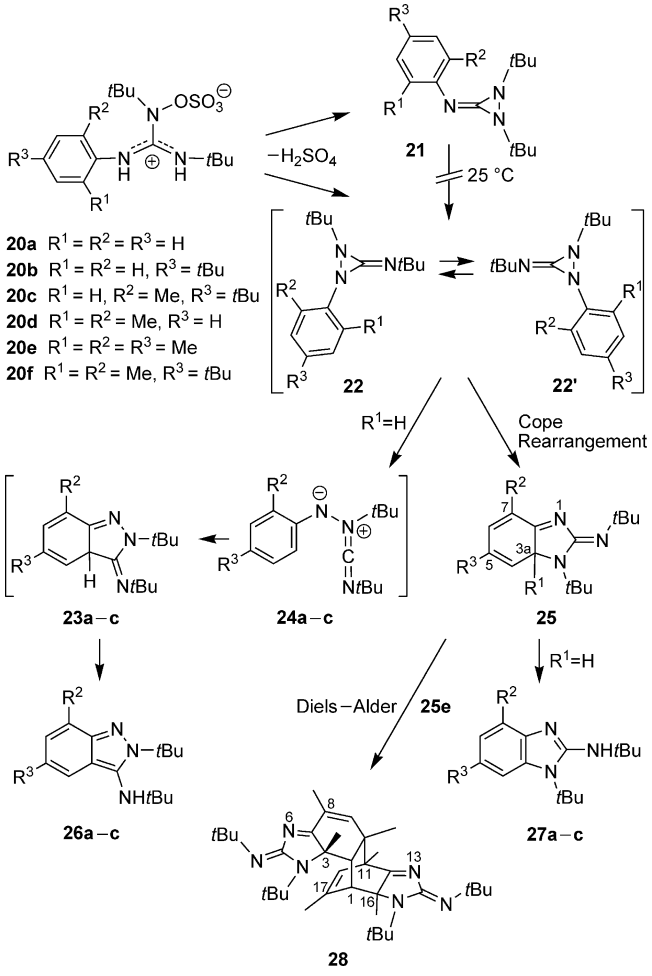
Scheme 3. Thermal decomposition of (alkylimino)diaziridines.

The iminodiaziridines **3b** and **3c** equilibrated more rapidly than **2a** and **8e**.[19] Neat mixtures of **3b** and **3c** solidified at room temperature over two weeks, probably through polymerization, but survived heating at 80 °C for 1 h. Onset of decomposition was observed at 100 °C. Solutions decomposed rapidly at 180 °C to afford the [2+1] cycloelimination products of **3b** (**14** and methyl isocyanide) and **3c** (dimethyldiazene and **15**), together with compounds analogous to those originating from the ring-opening rearrangements of **2a**, **6a**, **6c**, and **8e** described above.

(Arylimino)diaziridines

Phenyl-substituted three-membered heterocycles containing exocyclic double bonds are rare species.[1,5,16a,20a–20c] Some have been generated photochemically in solid argon;[20d,20e] others have only been invoked as intermediates en route to benzo-annellated five-membered heterocycles such as 2,3-dihydroindol-2-ones[16a,21] and benzimidazoles.[7d,20d,22] To develop a route to iminodiaziridines bearing aryl groups, we investigated base-induced cyclizations of the hydroxyguanidine *O*-sulfonic acids **20** and **32** in base/solvent combinations that were successful for the synthesis of (alkylimino)diaziridines. We obtained good to excellent yields of mixtures of isomers, which were easily separated by crystallization and chromatography (Scheme 4 and Scheme 7, Table 1).

The structures of the products were based on elemental analyses, spectroscopic evidence, X-ray diffraction analyses (**21e**,[23] **25f**[24]), comparison with authentic samples (**27a**, **37**, **38**,[7d] **41a**), and thermal (**25e**, **25f**, **35b**) or acid-mediated degradation (**26a**, **26b**). Prolonged heating of solutions of



Scheme 4. Base-mediated 1,3-elimination of sulfuric acid from *N*-hydroxyguanidine *O*-sulfonic acids **20** and sequential products. For bases, solvents, and reaction conditions, see Table 1.

Table 1. Products of the reactions of *N*-hydroxyguanidine *O*-sulfonic acids **20** and **32** with strong bases.

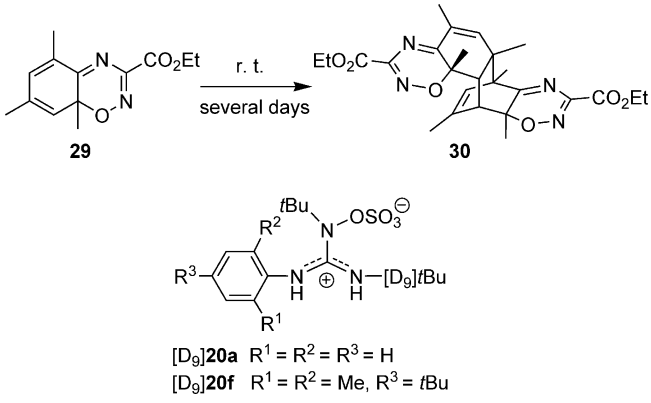
	[a]	Yield [%]	Products	Ratios
20a	A	80–89	**21a**, **26a**, **27a**	15:83:2 to 11:87:2
20b	A[b]	91	**21b**, **26b**, **27b**	4:71:25
20c	A[b]	86	**21c**, **26c**, **27c**	6:9:85
20d	A	72	**21d**	
	B	80	**21d**	
	C	64	**21d**	
20e	A	67	**21e**, **25e**	98:2
	D	67	**21e**, **25e**	72:28
20f	A[b]	75–78	**21f**, **25f**	98:2 to 86:14
32a	A	91	**37**, **38**	15:85
	E	98	**37**, **38**	75:25
32b	A	54	**35b**, **39**	96:4

[a] Base and solvent; A: KOH (40%) in methanol; B: KOH (50%) in water; C: NaH in THF; D: *t*BuOK in diethyl ether, –78 → 25 °C; E: aq. NaOH (2 M). [b] At 0 °C.

25f at 100 °C, for example, resulted in loss of the bridgehead methyl group and formation of **27c**. These experiments and compounds are detailed in the Supporting Information.

The structures of the (arylimino)diaziridines **21d–f** with two *ortho*-methyl groups were evident from the observation that their two *tert*-butyl groups could become equivalent on the ^1H NMR timescale: exchange-broadening of the two *N*-*tert*-butyl ^1H NMR signals at 400 MHz and their coalescence at ca. 35 °C in 60 MHz spectra indicated rapid inversion of the imino groups. The inversion occurred more slowly in the phenylimino compound **21a**, as shown by sharp *tert*-butyl signals at room temperature and their coalescence at 65 °C. Major products of **20a–c** were the isomeric 3-amino-2*H*-indazoles **26a–c** and 2-aminobenzimidazoles **27a–c** (Scheme 4, Table 1). The former set of compounds exhibit strong blue fluorescence, which allowed reliable distinction from the latter set. The analysis of mixtures of **26** and **27** was facilitated by the characteristic differences between the ^1H chemical shifts of the *tert*-butylamino groups (**26**: $\delta \approx 1.35$ ppm, **27**: $\delta \approx 1.5$ ppm in $CDCl_3$ solution).

Base-mediated elimination of sulfuric acid from **20** afforded mixtures that did contain (arylimino)diaziridines **21**, but no 1-aryl-3-iminodiaziridines **22** (Scheme 4). Although useful yields of the former compounds were obtained when the two *ortho* positions of their benzene rings were substituted as in **21d–f**, only small amounts of **21a–c** were formed in those cases in which this condition was not met. Surprisingly, **20a** and **20b** furnished the 3-amino-2*H*-indazoles **26a** and **26b**, respectively, as major products, whereas **20c** mainly yielded the 2-aminobenzimidazole **27c**. The yellow color of the crude iminodiaziridines **21e** and **21f** was indicative of the presence of byproducts, which eventually turned out to be the 2-imino-2,3-dihydro-3a*H*-benzimidazoles **25e** and **25f**, respectively.[25] At room temperature, **25e** slowly dimerized, but, as would be expected, the 5-(*tert*-butyl) compound **25f** did not. Structure **28**, a novel pentacyclic system, was assigned to the dimer on the basis of spectroscopic evidence and the mode of Diels–Alder cycloaddition observed in similar systems[26] (e.g., **29** → **30**; Scheme 5).[27] The high-field ^1H and ^{13}C NMR spectra recorded for **28** indicated restricted rotation of the two encumbered *tert*-butyl groups attached to the imidazole rings even at room temperature.[28]



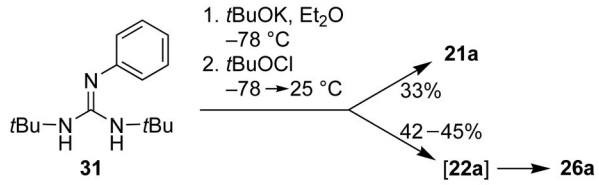
Scheme 5.

A number of routes that might lead to the benzimidazole (**25**, **27**) and indazole derivatives **26** shown in Scheme 4 are conceivable. The (arylimino)diaziridines **21** can be ruled out as intermediates, because **21a** and **21e** were stable and were completely recovered after having been subjected to the reaction conditions for extended periods of time. The N–N bonds in the aminoindazoles **26** suggest that they originate from the 1-aryl-3-iminodiaziridines **22**. Conclusive evidence as to the mode of formation of **25**–**27** was provided by the use of [D_9]**20a** and [D_9]**20f** (Scheme 5). Their labeled *tert*-butyl groups were completely scrambled in [D_9]**26a**, [D_9]-**27a**, and [D_9]**25f**.[29] This result rules out direct attack of the electrophilic nitrogen atoms of **20** at the benzene rings and pathways to **26** that bypass **22**. It can be explained by formation from **20** of intermediates containing two equivalent *tert*-butyl groups (triazatrimethylenemethane diradicals) that cyclize to yield **22**, or by 1,3-elimination of **20** to afford **22**, which undergo very rapid degenerate valence isomerizations (**22**/**22′**). Indeed, as may be inferred from the degenerate valence isomerization of 1-methylene-2,2-diphenylcyclopropane,[30] the [1.3] shifts in **22** and **22′** should be strongly accelerated by the presence of the aryl groups.

Although we have no direct evidence for the subtle mechanism of the scrambling, it seems plausible to invoke a very rapid **22**/**22′** equilibration as a crucial step. On the basis of this assumption, the multi-step routes to the final products are bifurcated at two stages: (i) the competing cyclizations of **20** to afford either the stable **21** or the elusive **22**, and (ii) the ring-expansions of **22** to furnish either the 2,3-dihydro-3a*H*-indazoles **23** or the 2,3-dihydro-3a*H*-benzimidazoles **25**. The regioselectivity of diaziridine ring-closure is mainly determined by the substitution pattern of the benzene rings of **20**: if at least one of the *ortho* positions is *not* occupied, as in **20a**–**c**, the aryl-substituted nitrogen atoms preferentially close the diaziridine ring. Otherwise, the *tert*-butyl-substituted nitrogen atoms predominantly participate in the 1,3-elimination. In addition, the outcome of the competition between the two different modes of cyclization did depend somewhat, but unpredictably, on the reaction conditions (Table 1), just as in the case of the alkyl compounds **9**.

Ring-expansion of compounds **22** to the 3-amino-2*H*-indazoles **26** was observed only if at least one of the *ortho* positions of the benzene rings was unsubstituted.[31] The initial step may be considered a formal [1.3] shift (**22** → **23**). Probably, azomethine imine 1,3-dipoles **24** are intermediates of this step,[32–34] favored by coplanarity of the benzene rings and the azomethine imine moieties. This prerequisite is precluded, though, by the presence of two *ortho* substituents. In contrast, conformations that are involved in the Cope rearrangements of **22** to the 2,3-dihydro-3a*H*-benzimidazoles **25** appear to be less influenced by *ortho* substituents, if at all. It is probably for these reasons that the competition between benzimidazole and indazole formation is determined by the *ortho* substituents: they hinder the Cope rearrangement much less than they disfavor ring-opening to the azomethine imines **24**. Accordingly, the isolated yield of **26c** dropped to 9%, compared with **26a** and **26b**, whereas the yield of **27c** reached 85% of the isolated material.

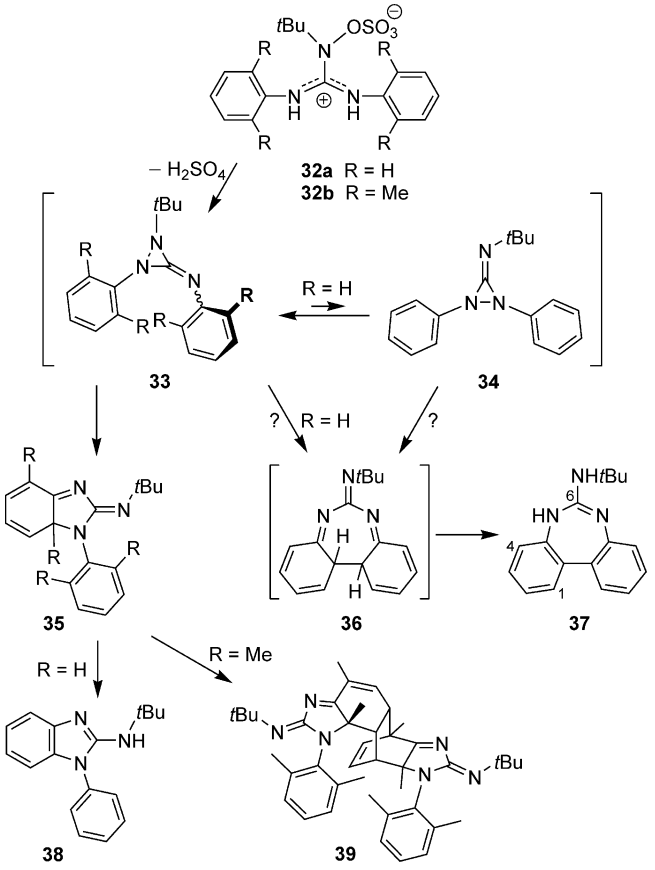
In view of the unsatisfactory yields of **21a**–**c**, we investigated cyclization of the guanidine derivative **31** in the presence of potassium *tert*-butoxide and *tert*-butyl hypochlorite. Gratifyingly, a reasonable yield of similar amounts of **21a** and **26a** was achieved (Scheme 6). Because separation can be conveniently achieved by chromatography, this alternative to the *N*-hydroxyguanidine *O*-sulfonic acid procedure appears to be the method of choice for (arylimino)diaziridines with unsubstituted *ortho* positions.



Scheme 6. Cyclization of guanidine **31** in the presence of potassium *tert*-butoxide and *tert*-butyl hypochlorite.

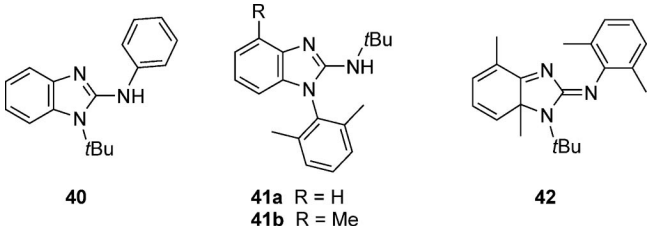
Considering the fleeting existence of the 1-aryl-3-iminodiaziridines **22**, we were not surprised that no **33**, let alone 1,2-diaryl-3-iminodiaziridines such as **34**, could be detected after treatment of **32** with strong bases, or that only products of their rearrangements were isolated (Scheme 7, Table 1). When the diphenyl compound **32a** was added to the strong base, a deep yellow color, probably indicative of intermediates such as **35a** and **36**, emerged for a short period of time. Workup yielded mixtures of the 6-amino-5*H*-dibenzo[*d*,*f*][1,3]diazepine **37** and the 2-aminobenzimidazole **38**. The former compound predominated when dilute aqueous sodium hydroxide was employed, whereas concentrated potassium hydroxide in methanol gave mainly the latter. The absence of the isomeric 2-aminobenzimidazole **40**, which we synthesized, ruled out direct attack of the electrophilic nitrogen atom of **32a** at a benzene ring. The unexpected formation of **37** can be explained most simply (i) by a base-induced oxidative coupling mechanism (**32a** → **36**), which bypasses **33a**,[35] (ii) by a [1.3] shift (**33a** → **34**), followed by a divinylcyclopropane/cycloheptadiene rearrangement (**34** → **36**),[36] or (iii) by a [3.5] sigmatropic shift (**33a** → **36**).[37] However, it is difficult to explain why the reaction conditions strongly influence the ratio of **37**/**38** if the formation of **37** and **38** commences with competing thermal rearrangements of **33**.[38]

If the *ortho* positions of both benzene rings were substituted, as in **32b**, deep yellow crystals were isolated. On heating in boiling heptane, this product lost CH_2 to furnish **41b**, which was identical with **41a**, synthesized independently, except for the methyl group at the benzene ring of **41b**. In addition, the characteristic chemical shifts of *tert*-butyl ^{1}H NMR signals permitted unequivocal confirmation of the structures of the 2-aminobenzimidazoles **38**, **40**, and **41**. The 2,3-dihydro-3a*H*-benzimidazole structure **35b** was therefore assigned to the yellow crystals, and not the hypothetical isomeric structure **42**, which might have resulted from direct attack of the electrophilic nitrogen atom of **32b** at a benzene ring. A small fraction of **35b** underwent di-



Scheme 7. Base-mediated elimination of sulfuric acid from *N*-hydroxyguanidine *O*-sulfonic acids **32** and sequential products. For bases and solvents, see Table 1.

merization to a pale yellow product to which the structure **39** was ascribed on the basis of spectral evidence and the analogy with **28**, **30**,[27] and a similar example.[26]



^{15}N NMR Spectra of Iminodiaziridines

So far, only ^{15}N NMR spectra of diaziridines,[39] and iminoaziridines[5] have been reported. The results of the first ^{15}N NMR study of iminodiaziridines are listed in Table 2.

Amino nitrogen atoms [$^{15}N(sp^3)$] resonate at higher field (by ca. 90 ppm) than double-bonded nitrogen atoms [$^{15}N(sp^2)$].[40] This well-established empirical relationship allows reliable assignment of signals to the exocyclic nitrogen atoms in iminodiaziridines. Their $^{15}N(sp^2)$ chemical shifts span a range of 50 ppm and resemble those of the imino nitrogen atoms in pentasubstituted guanidines.[41] In contrast, the ring nitrogen atoms resonate at significantly lower field than the sp^3 nitrogen atoms in guanidines. The signals of simple diaziridines[39b] are also found at higher field than those of iminodiaziridines, but the differences are smaller than in the case of guanidines. When the chemical shifts of **2a** and (*E*)-**8e** are compared with corresponding ^{15}N NMR spectroscopic data for iminoaziridines,[5] the first two species show ring nitrogen signals at lower field than the third ($\Delta\delta \approx 50$–60 ppm) but imino nitrogen signals at higher field ($\Delta\delta \approx 20$–30 ppm).

Table 2. Chemical shifts δ (ppm, relative to CH_3NO_2 as external standard) in 40.5 MHz ^{15}N NMR spectra recorded for solutions of iminodiaziridines in [D_6]benzene at a temperature of 22 °C.

	>N–*t*Bu$_{syn}$	>N–*t*Bu$_{anti}$	=N–R	R
2a[a]	–244.0	–253.8	–190.7	Me
2b[b]	–245.5[c] (N_B)	–264.7[c] (N_A)	–153.2	*t*Bu
21a[b]	–242.4	–255.6	–166.2	Ph
21b	–242.4	–256.3	–167.3	4-(*t*Bu)C_6H_4
21e	–238.9[c] (N_A)	–248.9[c] (N_B)	–169.5	2,4,6-$Me_3C_6H_2$
21f	–237.5[c]	–247.5[c]	–168.0	4-(*t*Bu)-2,6-$Me_2C_6H_2$
	>N–Me$_{syn}$			
(*E*)-**8e**[a]	–278.2	–250.5	–154.5	*t*Bu
	>N–*c*-Hex$_{syn}$	>N–*c*-Hex$_{anti}$		
6b[d]	–230.6[c]	–218.9[c]	–141.0	*c*-Hex

[a] HN-HMBC. [b] HN-gHMBC. [c] The chemical shifts may be exchanged. [d] 60.8 MHz spectrum with external aqueous NH_4Cl standard, recalculated to CH_3NO_2.

Resonance frequencies of ^{15}N NMR signals are shifted downfield by carbon atoms in β-positions. In ^{15}N NMR spectra of iminodiaziridines, these β-effects are particularly large for both types of nitrogen atoms if an *N*-methyl group is exchanged for an *N*-*tert*-butyl group. The signal of the exocyclic nitrogen atom of **2b**, for example, appeared at lower field ($\Delta\delta$ = 37.5 ppm) than that of **2a**. With the help of the β-effect, the *syn* and *anti* ring nitrogen signals of (*E*)-**8e** were assigned not only through $^{15}N,^1H$ correlation spectroscopy but also – and even more conveniently – by the difference in their chemical shifts [$\delta(^{15}N_{anti}) - \delta(^{15}N_{syn})$ = 27.7 ppm]. The assignment of these signals was more difficult for iminodiaziridines bearing two identical ring substituents. To this end, we performed HN-HMBC or HN-gHMBC and homonuclear NOE experiments, the last of these with a view to assigning the ^1H NMR signals. Whereas the $^{15}N,^1H$ correlation spectroscopy gave unequivocal results, the NOE experiments failed to do this in some cases. The distance between the signals of *syn* and *anti* ring nitrogen atoms amounted to $|\Delta\delta| \approx 10$–20 ppm. Similar values have been found for *N*′′-aryl-*N*,*N*,*N*′,*N*′-tetramethylguanidines and related compounds.[41]

Conclusions

(Alkylimino)- and (arylimino)diaziridines have been prepared by cyclization of *N*,*N*′,*N*′′-substituted guanidines in the presence of *tert*-butyl hypochlorite and potassium *tert*-butoxide, as well as by base-mediated 1,3-elimination of sulfuric acid from *N*-hydroxyguanidine *O*-sulfonic acids. The

scope and limitations of these iminodiaziridine syntheses are reported. At elevated temperatures, (alkylimino)diaziridines undergo valence isomerization by [1.3] shift, by [2+1] cycloelimination to isocyanides and azo compounds, and by ring-opening elimination to *N*-alkylidene guanidines. (Arylimino)diaziridines are persistent under the conditions of formation. Scrambling of perdeuterated *tert*-butyl groups in five-membered-ring products suggests that 1-aryl-3-iminodiaziridines are elusive intermediates. They rearrange to 3-amino-2*H*-indazoles, 2-amino-1*H*-benzimidazoles, and, if both *ortho* positions of the benzene rings are substituted, 2-imino-2,3-dihydro-3a*H*-benzimidazoles, which may slowly dimerize by Diels–Alder cycloaddition. Surprisingly, an *N*-hydroxy-*N*′,*N*′′-diphenylguanidine *O*-sulfonic acid afforded a 6-amino-5*H*-dibenzo[*d*,*f*][1,3]diazepine together with the expected 2-aminobenzimidazole, but no 3-amino-2*H*-indazole. Thermal reorganization of (arylimino)diaziridines in cascades of pericyclic reactions and oxidation of amino-2*H*-indazoles **26** to afford novel, very stable *N*-centered radicals will be reported separately.

Experimental Section

General: General experimental, syntheses of precursors and authentic compounds, thermolysis and degradation experiments, and NMR, UV/Vis, and IR spectra are reported in the Supporting Information. Reactions in aprotic solvents were performed in dry solvents in flame-dried glassware under N_2 or Ar . Solutions were freshly prepared. *t*BuOK was sublimed at 10^{-3} Torr. Petroleum ether had a boiling range of 30–50 °C. Iminodiaziridines were stored at –25 °C; liquid samples were kept in sealed vials. Ratios of isomers and diastereomers were determined by integration of appropriate ^{1}H NMR singlets.

(1,2-Di-*tert*-butyldiaziridin-3-ylidene)(methyl)amine (2a):[7a,7c] ^{1}H NMR (400 MHz, NOE): δ = 1.04 (s, 9 H, *t*Bu$_{syn}$), 1.08 (s, 9 H, *t*Bu$_{anti}$), 2.98 (s, 3 H, Me) ppm. ^{13}C NMR (100 MHz, HC-HMBC, C_6D_6): δ = 26.47 [$(CH_3)_3$, *t*Bu$_{anti}$], 27.62 [$(CH_3)_3$, *t*Bu$_{syn}$], 37.23 (CH_3), 57.37 (quat. C, *t*Bu$_{syn}$), 58.21 (quat. C, *t*Bu$_{anti}$), 148.38 (C=N) ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 26.2, 27.4 [$(CH_3)_3$], 37.2 (CH_3), 57.5, 58.2, 149.2 (quat. C) ppm. EI MS (14 eV): *m*/*z* (%) = 183 (15) $[M]^+$, 168 (3), 154 (2), 139 (2), 127 (20), 112 (16), 100 (4), 99 (2), 84 (3), 71 (2), 57 (100).

(*tert*-Butyl)(1,2-di-*tert*-butyldiaziridin-3-ylidene)amine (2b):[7b,7c] ^{1}H NMR (400 MHz, C_6D_6): δ = 1.08 (s, 9 H, *t*Bu$_A$), 1.10 (s, 9 H, *t*Bu$_B$), 1.24 (s, 9 H, =N*t*Bu) ppm. ^{13}C NMR (100 MHz, HC-gHMBC, C_6D_6): δ = 26.36 [$(CH_3)_3$, *t*Bu$_A$], 27.96 [$(CH_3)_3$, *t*Bu$_B$], 31.58 [$(CH_3)_3$, =N*t*Bu], 53.59 (quat. C, =N*t*Bu), 57.91 (quat. C, *t*Bu$_B$), 58.16 (quat. C, *t*Bu$_A$), 142.66 (C=N) ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 26.2, 27.7, 31.2 [$(CH_3)_3$], 53.6, 58.1, 58.3, 143.9 (quat. C) ppm.

General Procedure A. Alkyl-Substituted Iminodiaziridines 6 from Guanidines 4: *tert*-Butyl hypochlorite (7.06 g, 65 mmol) was added dropwise by syringe at –40 °C to stirred solutions of **4** (50 mmol) in diethyl ether (150 mL) kept in the dark. Stirring was continued at that temperature for 2 h, followed by the dropwise addition of solutions of *t*BuOK (64 mmol, as titrated with 0.1 M HCl) in dry diethyl ether over 1 h. The temperature of the mixtures was raised to –20 °C. The mixtures were stirred with cooling for 1 h and without cooling for 0.5 h. A solid (KCl) precipitated, and the suspensions turned brown. Workup is described separately for each compound.

General Procedure B. Products from *N*-Hydroxyguanidine *O*-Sulfonic Acids (7, 9, 20, 32) and Solutions of Alkali Hydroxides: *N*-Hydroxyguanidine *O*-sulfonic acids (50 mmol) were suspended in pentane (300 mL), petroleum ether (300 mL), or benzene. The suspensions were cooled in an ice/water bath. Ice-cold solutions of alkali hydroxide in methanol or water were slowly added to the vigorously stirred suspensions, followed by stirring without cooling for 1–2 h. Ice-cold water was added until the lower layers became clear. The lower layers were extracted with pentane or petroleum ether. The combined organic layers were dried by filtration through short columns packed with K_2CO_3. The solvent was distilled in vacuo. Alkyl-substituted iminodiaziridines were distilled at 20–30 °C bath temp./10^{-2}–10^{-3} Torr. Further workup of other products is described separately.

General Procedure C. Iminodiaziridines from *N*-Hydroxyguanidine *O*-Sulfonic Acids (7c, 9b, 20d) and Sodium Hydride: Suspensions of *N*-hydroxyguanidine *O*-sulfonic acids (20 mmol) and NaH (2.40 g, 100 mmol) in THF (100 mL) were stirred for 14–16 h, followed by removal of the solid material by filtration. Most of the solvent was distilled in vacuo. Pentane (150 mL) was added to the concentrated solutions. The mixtures were extracted with ice-cold water (2 × 50 mL), followed by filtration through short columns packed with K_2CO_3. The solvent was distilled in vacuo. Alkyl-substituted iminodiaziridines were distilled at 20–30 °C bath temp./10^{-2}–10^{-3} Torr.

General Procedure D. Iminodiaziridines from *N*-Hydroxyguanidine *O*-Sulfonic Acids (7e, 9b, 20e) and Potassium *tert*-Butoxide: *N*-Hydroxyguanidine *O*-sulfonic acids (50 mmol) were added to stirred solutions of *t*BuOK (11.2 g, 100 mmol) in diethyl ether (300 mL). Stirring was continued for 2–3 h, followed by addition of pentane (200 mL) and stirring for 1 h. The resulting suspensions were washed with ice-cold aq. Na_2CO_3 (0.5 M, 2 × 200 mL). The organic layers were filtered through short columns packed with K_2CO_3 and briefly dried with NaH. The solvent was distilled off in vacuo. Alkyl-substituted iminodiaziridines were distilled at 20–30 °C bath temp./10^{-2}–10^{-3} Torr.

(Alkylimino)diaziridines

(1,2-Dimethyldiaziridin-3-ylidene)(methyl)amine (3a): This compound was produced by Procedure B from **7a** (19.7 g, 0.10 mol), aq. KOH (50%, 50 mL), and pentane (150 mL) with use of an Ultra-Turrax® stirrer (IKA-Werke, 79219 Staufen, Germany). Stirring was continued with cooling in the ice/water bath for 1 h, followed by the usual workup. The solvent was distilled through a Vigreux column (1 m) at –10 °C bath temp./80–100 Torr until the volume of the residue was ca. 25 mL. Benzene (1.00 g) was added to the colorless solution. The yield (25%) was determined by integration of the ^{1}H NMR signals of benzene and the *N*-methylimino group. ***Caution: Complete removal of the solvent resulted in almost explosive decomposition and formation of a yellow smoke!*** ^{1}H NMR (90 MHz, pentane): δ = 2.62 (q, $^6J_{H,H}$ = 0.47 Hz, 3 H), 2.70 (q, $^6J_{H,H}$ = 0.47 Hz, 3 H), 3.05 (s, 3 H) ppm. IR (pentane): $\tilde{\nu}$ = 1855 (m), 1811 (s) cm^{-1}.

(1-*tert*-Butyl-2-methyldiaziridin-3-ylidene)(methyl)amine (3b): This compound was produced by Procedure B, from **7d** and KOH in methanol (40%, 100 mL). Colorless oil (6.20 g, 83%); (*E*)-**3b**/(*Z*)-**3b** = 47.5:52.5. ^{1}H NMR (60 MHz, C_6D_6): (*E*)-**3b**: δ = 1.13 (s, 9 H), 2.60 (s, 3 H), 3.04 (s, 3 H) ppm; (*Z*)-**3b**: δ = 1.08 (s, 9 H), 2.62 (s, 3 H), 3.06 (s, 3 H) ppm; the *tert*-butyl signals of (*E*)-**3b** and (*Z*)-**3b** coalesce at T_c = 109 °C ($\Delta\nu$ = 4.0 Hz, $\Delta G_c^{\ddagger}$ = 87 kJ mol^{-1}). ^{13}C

NMR (22.6 MHz, $CDCl_3$): δ = 26.1, 27.0 [$(CH_3)_3$], 36.1, 37.2, 45.6, 45.9 (CH_3), 58.4, 58.9, 151.7 (quat. C) ppm. IR (neat liquid): $\tilde{\nu}$ = 1816 (s) cm^{-1}. EI MS (14 eV): *m*/*z* (%) = 141 (12) $[M]^+$, 126 (12), 112 (3), 100 (6), 85 (21), 57 (100). $C_7H_{15}N_3$ (141.2): calcd. N 29.75; found N 29.81.

Base-Mediated Cyclizations of 9a To Afford 3b and (*tert*-Butyl)(1,2-dimethyldiaziridin-3-ylidene)amine (3c): 3c: ^1H NMR (60 MHz, CCl_4): δ = 1.24, (s, 9 H), 2.68 (s, 3 H), 2.80 (s, 3 H) ppm. (a) These compounds were produced by Procedure B, from **9a** and KOH in methanol (40%, 100 mL). Colorless oil (5.33 g, 75%); **3b/3c** = 99:1. A similar experiment with KOH in methanol (30%, 100 mL) and stirring at –20 °C for 4 h gave 3.56 g (50%); **3b/3c** = >99.5:0.5. (b) These compounds were produced by Procedure B, from **9a** and aq. NaOH [40 g, 1.0 mol, dissolved in water (240, 480, 950 mL, or 4.8 L)]. The mixtures were vigorously stirred for 2–3 h. Colorless oils (5.76–5.97 g, 81–84%); **3b/3c** (84 ± 1):(16 ± 1). (c) These compounds were produced by Procedure B from **9a** and aq. Na_2CO_3 (200 mL, 1.0 M). The mixture was vigorously stirred for 3 h. Colorless oil (5.83 g, 82%); **3b/3c** 78:22. (d) These compounds were produced by Procedure C from **9a** and NaH in THF. Colorless oil (1.95 g, 69%), **3b/3c** 97:3.

(1,2-Diisopropyldiaziridin-3-ylidene)(isopropyl)amine (6a): (a) This compound was produced by Procedure A, from **4a**, *tert*-butyl hypochlorite, and *t*BuOK (190 mL of 0.338 M solution). Part of the solvent was distilled in vacuo. The concentrated mixture was diluted with pentane (150 mL), washed with ice-cold water (3 × 100 mL), and briefly dried with K_2CO_3. The solvent was distilled in vacuo. Distillation of the residue at 20–30 °C bath temp./10^{-2} Torr yielded a colorless oil (6.69 g, 73%), which contained traces of isopropyl isocyanide (IR). Distillation through a 20 cm Spaltrohr column (bath temp. 20–35 °C/10^{-2} Torr, condenser at –30 °C, receiver at –78 °C) afforded pure **6a**. An experiment on tenfold scale gave the same yield. ^1H NMR (90 MHz, CCl_4): δ = 1.06–1.22 (m, 18 H), 2.50, 2.77, 3.58 (sept, $^3J_{H,H}$ = 6.4 Hz, 1 H) ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 20.3, 21.1, 21.3, 21.4, 24.7, 25.0 (CH_3), 51.5, 57.5, 59.2 (CH), 150.0 (C=N) ppm. IR (neat liquid): $\tilde{\nu}$ = 1857 (m), 1808 (s) cm^{-1}. EI MS (70 eV): *m*/*z* (%) = 183 (1) $[M]^+$, 168 (3), 126 (3), 114 (3), 111 (2), 99 (2), 85 (4) 84 (10), 83 (9), 70 (9), 69 (20) 43 (100). $C_{10}H_{21}N_3$ (183.3): calcd. C 65.53, H 11.55, N 22.93; found C 66.03, H 11.46, N 23.01. (b) This compound was produced by Procedure B, from **7b** and aq. KOH (40%, 100 mL). Workup as described under (a) yielded a colorless liquid (5.9 g, 64%).

(Cyclohexyl)(1,2-dicyclohexyldiaziridin-3-ylidene)amine (6b): This compound was produced by Procedure A from **4b**. Workup as described for **6a** and distillation of the solvent gave a very viscous, pale brown oil (14.3 g), which was dried at 10^{-5} Torr. Distillation in a sublimation apparatus at 80–90 °C bath temp./10^{-5} Torr yielded a very viscous, pale yellow oil (9.5 g, 63%). Repeated sublimation afforded colorless, waxy crystals, m.p. 37–39 °C. ^1H NMR (C_6D_6, 600 MHz): δ = 1.02–1.70 (m, 22 H), 1.74 (m, 2 H), 1.80 (br. d, $^2J_{H,H} \approx$ 13 Hz, 1 H), 1.89 (br. d, $^2J_{H,H} \approx$ 13 Hz, 1 H), 1.93 (br. d, $^2J_{H,H} \approx$ 12 Hz, 1 H), 1.99 (m, 2 H), 2.12 (br. d, $^2J_{H,H} \approx$ 13 Hz, 1 H), 2.48 (tt, $J_{H,H}$ = 10.0, 4.0 Hz, 1 H, CH_{anti}), 2.53 (tt, $J_{H,H}$ = 10.4, 3.9 Hz, 1 H, CH_{syn}), 3.57 (tt, $J_{H,H}$ = 9.8, 4.1 Hz, 1 H, =NCH) ppm. 1D-NOESY and 2D-TOCSY experiments show that the signals at δ = 1.93 and 2.12 ppm belong to the *syn* cyclohexyl group. The multiplet at δ = 1.99 ppm arises from 1 H of both the *syn* and the *anti* cyclohexyl group. ^{13}C NMR (100 MHz, C_6D_6): δ = 24.39 (CH_2), 24.53 (2 × CH_2), 24.83, 24.85, 24.88, 25.92, 25.98, 25.99, 30.98, 31.81, 32.02, 32.17, 35.31, 36.16 (CH_2), 59.38 (=NCH), 64.96 (CH_{syn}), 66.59 (CH_{anti}), 150.29 (C=N) ppm. IR (CCl_4): $\tilde{\nu}$ = 1807 (s) cm^{-1}. $C_{19}H_{33}N_3$ (303.5): calcd. N 13.85; found N 13.34.

[1,2-Bis(2,2-dimethylpropyl)diaziridin-3-ylidene](2,2-dimethylpropyl)-amine (6c): This compound was produced by Procedure A, from **4c**, *tert*-butyl hypochlorite, and *t*BuOK (97 mL of 0.663 M solution). The mixture was diluted with pentane (150 mL), and the colorless precipitate was removed by filtration. The solvent was distilled in vacuo. The residue was sublimed at 20–25 °C/10^{-5} Torr to afford colorless crystals (10.8 g, 81%), m.p. 50 °C (from acetonitrile at –20 °C). ^1H NMR (90 MHz, CCl_4): δ = 0.92, 0.99, 1.00 (s, 9 H), 2.36, 2.93 (AB, $^2J_{H,H}$ = 11.2 Hz, 2 H), 2.46, 2.89 (AB, $^2J_{H,H}$ = 13.8 Hz, 2 H), 3.06 (s, 2 H) ppm. ^1H NMR (CD_3CN): δ = 0.91 (s, 9 H), 0.98 (s, 18 H), 2.37, 3.00 (AB, $^2J_{H,H}$ = 11.5 Hz, 2 H), 2.44, 3.03 (AB, $^2J_{H,H}$ = 13.4 Hz, 2 H), 3.10, 3.15 (AB, $^2J_{H,H}$ = 12.0 Hz, 2 H) ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 27.6, 27.8, 28.0 [$(CH_3)_3$], 32.0, 32.1, 32.4 (quat. C), 61.2, 70.3, 71.2 (CH_2), 152.7 (C=N) ppm. IR (CCl_4): $\tilde{\nu}$ = 1816 (s) cm^{-1}. EI MS (70 eV): *m*/*z* (%) = 267 (4) $[M]^+$. $C_{16}H_{33}N_3$ (267.5): calcd. C 71.85, H 12.44, N 15.71; found C 71.35, H 12.25, N 15.68. Compound **6c** may be kept at –25 °C, but decomposed at room temperature in vacuo over silica gel during 14 d to afford a colorless powder (m.p. 155–175 °C). Repeated recrystallization from acetonitrile yielded colorless crystals, m.p. 175 °C, identical with authentic **13c**.

(*tert*-Butyl)(1-*tert*-butyl-2-isopropyldiaziridin-3-ylidene)amine (8c): (a) This compound was produced by Procedure B, from **7c** and KOH in methanol (40%, 100 mL). Colorless oil (8.14–8.75 g, 77–83%). (b) This compound was produced by Procedure C, from **7c** and NaH in THF. Colorless oil (3.72 g, 90%). The analytical sample was obtained by repeated recrystallization from pentane at –78 °C, followed by distillation. (*E*)-**8c**/(*Z*)-**8c** 4:1. ^1H NMR (90 MHz, neat liquid): δ = 0.97 [d, $^3J_{H,H}$ = 6 Hz, Me, (*E*)-**8c**], 1.07 [s, *t*Bu, (*E*)-**8c**], 1.17 [s, *t*Bu, (*Z*)-**8c**], 1.22 [s, *t*Bu, (*E*)-**8c**], 1.24 [s, *t*Bu, (*Z*)-**8c**], 2.41 [sept, $^3J_{H,H}$ = 6.4 Hz, CH, (*Z*)-**8c**], 3.23 [sept, $^3J_{H,H}$ = 6.3 Hz, CH, (*E*)-**8c**] ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): (*E*)-**8c**: δ = 18.3, 22.1 (CH_3), 26.1, 31.0 [$(CH_3)_3$], 54.1 (CH), 54.3, 57.7, 144.3 (quat. C); (*Z*)-**8c**: δ = 20.5, 21.3 (CH_3), 27.5, 31.0 [$(CH_3)_3$], 59.7 (CH), 53.2, 58.2, 145.5 (quat. C) ppm. IR (neat liquid): $\tilde{\nu}$ = 1850 (m), 1792 (s) cm^{-1}. EI MS (14 eV): *m*/*z* (%) = 211 (14) $[M]^+$, 196 (24), 186 (13), 155 (18), 140 (22), 128 (19), 113 (21), 99 (73), 84 (97), 57 (100). $C_{12}H_{25}N_3$ (211.4): calcd. C 68.20, H 11.92, N 19.88; found C 67.85, H 11.87, N 20.02.

(*tert*-Butyl)(1-*tert*-butyl-2-methyldiaziridin-3-ylidene)amine (8e): (a) This compound was produced by Procedure B, from **7e** and KOH in methanol (40%, 100 mL). Colorless oil (8.71 g, 95%); (*E*)-**8e**/(*Z*)-**8e** >50:1. EI MS (14 eV): *m*/*z* (%) = 183 (63) $[M]^+$, 168 (8), 154 (5), 139 (6), 127 (45), 120 (45), 112 (11), 100 (88), 84 (100). (***E***)**-8e:** ^1H NMR (400 MHz, C_6D_6): δ = 1.05 (s, 9 H, >N*t*Bu), 1.19 (s, 9 H, =N*t*Bu), 2.60 (s, 3 H, Me) ppm. ^{13}C NMR (100 MHz, HC-HMBC, C_6D_6): δ = 26.02 [$(CH_3)_3$, >N*t*Bu], 31.61 [$(CH_3)_3$, =N*t*Bu], 46.50 (CH_3), 54.63 (quat. C, =N*t*Bu), 58.50 (quat. C, >N*t*Bu), 145.94 (C=N) ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 25.9, 31.3 [$(CH_3)_3$], 46.5 (CH_3), 54.7, 58.6, 146.4 (quat. C) ppm. (b) This compound was produced by Procedure D, from **7e**. Colorless oil (7.33 g, 81%). An analytical sample was obtained by distillation through a 20 cm Spaltrohr column. $C_{10}H_{23}N_3$ (183.3): calcd. N 22.92; found N 22.88. (c) A stirred suspension of **7e** (844 mg, 3.0 mmol) in diethyl ether (30 mL) was cooled to –25 °C. A solution of butyllithium in hexane (2.8 mL, 2.185 M, 6.1 mmol) was added by syringe. The mixture was allowed to come to room temp. over 3 h, followed by stirring for 2 h. The colorless precipitate was removed by filtration. Distillation of the solvent in vacuo gave a colorless oil (509 mg, quant.), which consisted of **8e** and **18** (1:1, IR, ^1H NMR). Use of THF instead of diethyl ether afforded a colorless oil (85%), which consisted of **8e** and **18** (1:4).

Base-Mediated Cyclization of 9b To Afford 2a and 8e: (a) These compounds were produced by Procedure B, from **9b** (2.81 g, 10 mmol) and solutions of alkali hydroxides (250 mmol) in methanol (*a* g) and pentane (200 mL). The mixtures were stirred for *b* h to afford, after workup, *c*% of mixtures of **2a** and **8e**. KOH·H_2O: *a* = 28, *b* = 1.5, *c* = 81%; **2a/8e** 85:15. NaOH: *a* = 40, *b* = 3, *c* = 87%; **2a/8e** 56:44. NaOH, KOH·H_2O or CsOH: *a* = 50, *b* = 5, *c* = 77–81%; **2a/8e** 59:41. NaOH or KOH·H_2O: *a* = 550, *b* = 10, *c* = 83–88%; **2a/8e** 26:74. (b) These compounds were produced by Procedure B, from **9b** (2.81 g, 10 mmol), aq. NaOH (1 M, 200 mL), and pentane (200 mL). Colorless oil (1.08 g, 59%); **2a/8e** 40:60. (c) These compounds were produced by Procedure C, from **9b** and NaH in THF. Colorless oil (3.38 g, 92%); **2a/8e** 50:50. (d) These compounds were produced by General Procedure D, from **9b** (20 mmol) and *t*BuOK (4.48 g, 40 mmol) in diethyl ether (100 mL). Colorless oil (2.93 g, 80%); **2a/8e** 68:32. In a similar experiment, the solution of *t*BuOK in diethyl ether was cooled to –78 °C, followed by the addition of **9b**. The stirred mixture was allowed to come to room temp. over 26 h to afford 3.04 g (83%); **2a/8e** 68:32.

(Arylimino)diaziridines

(1,2-Di-*tert*-butyldiaziridin-3-ylidene)(phenyl)amine (21a), 2-*tert*-Butyl-3-(*tert*-butylamino)-2*H*-indazole (26a), and 1-*tert*-Butyl-2-(*tert*-butylamino)-1*H*-benzimidazole (27a): (a) These compounds were produced by Procedure B, but without external cooling, from **20a** (34.4 g, 0.10 mol), KOH in methanol (40%, 0.50 L), and petroleum ether (0.50 L). The mixture turned red. After separation of the organic layer, ice-cold water (1.5 L) was added to the aq. layer, followed by extraction with petroleum ether (3 × 0.2 L). The organic layers were filtered through a short column packed with K_2CO_3, and the solvent was distilled in vacuo until a substantial amount of crystals appeared. These were isolated by filtration and washed with cold (–70 °C) pentane. The mother liquor and washings were concentrated, and the resulting crystals were isolated as before. Repetition of this procedure yielded several fractions of **26a** as colorless needles (18.0 g, 74%, m.p. 97–98 °C). Distillation of the solvent from the mother liquor and washings then gave a pale red solid (3.86 g, 16%) consisting of **21a**, **26a**, and **27a** (63:25:12, ^{1}H NMR in C_6D_6). Sublimation at 35 °C/10^{-5} Torr gave crystals (2.34 g, **21a/26a/27a** 88:6:6). Recrystallization from pentane yielded crystals of **21a** and **26a** (96:4, 1.02 g, m.p. 52–53 °C). Sublimation raised the m.p. to 53.5–54.5 °C and the purity of **21a** to >99.5%. Yield of isolated products 89%, **21a/26a/27a** 11:87:2. A similar experiment with 15 mmol of **20a** yielded 80%, **21a/26a/27a** 15:83:2. (b) A stirred solution of **29** (990 mg, 4.0 mmol) in diethyl ether (30 mL) was cooled to –78 °C, followed by addition of a solution of freshly sublimed *t*BuOK (1.0 g, 8.9 mmol) in diethyl ether (25 mL). *tert*-Butyl hypochlorite (1.30 g, 12 mmol) was slowly added to the cooled (–78 °C) mixture, which was stirred at that temperature under exclusion of light for 12 h. The resulting red solution was allowed to come to room temp., transferred into a separatory funnel, and treated with a solution of $Na_2S_2O_4$ (1.0 g, 5.7 mmol) in water (20 mL). Methanol (2–3 drops) was added until the organic layer turned yellow. The organic layer was filtered through a short column packed with K_2CO_3, and the solvent was distilled in vacuo. The orange-colored residue was separated by prep. TLC on Al_2O_3 with cyclohexane/diethyl ether (97:3) or flash chromatography on Al_2O_3 with petroleum ether/diethyl ether to afford **21a** (blue first fraction, 0.32 g, 33%) and **26a** (blue fluorescent fraction, 0.41–0.49 g, 42–50%). Sublimation at 25 °C/10^{-5} Torr yielded **21a** as colorless crystals (m.p. 48–50 °C). **21a:** ^{1}H NMR (400 MHz, C_6D_6): δ = 0.94 (s, 9 H, *t*Bu$_{syn}$), 1.22 (s, 9 H, *t*Bu$_{anti}$), 6.94 [m, 1 H, *p*-H (Ph)], 7.14 [m, 2 H, *m*-H (Ph)], 7.27 [m, 2 H, *o*-H (Ph)] ppm; simulation yielded $^3J_{p,m}$ = 7.5, $^3J_{m,o}$ = 7.9, $^4J_{p,o}$ = 1.2, $^4J_{m,m}$ = 1.6, $^4J_{o,o}$ = 2.2, $^5J_{m,o}$ = 0.5 Hz. ^{1}H NMR (60 MHz, CCl_4): Coalescence of the *tert*-butyl signals at T_c = (65 ± 1) °C, $\Delta\nu$ = 18 Hz (25 °C), $\Delta G_c^{\ddagger}$ = 73 kJ mol^{-1}. ^{13}C NMR (100 MHz, C_6D_6): δ = 26.53 [$(CH_3)_3$, *t*Bu$_{anti}$], 27.43 [$(CH_3)_3$, *t*Bu$_{syn}$], 58.85 (quat. C, *t*Bu$_{syn}$), 59.24 (quat. C, *t*Bu$_{anti}$), 123.20 (CH, *o*-Ph), 124.58 (CH, *p*-Ph), 129.21 (CH, *m*-Ph), 148.21 (quat. C, *i*-Ph), 149.36 (C=N) ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 26.4, 27.2 [$(CH_3)_3$], 58.9, 59.3 (quat. C), 122.7, 124.4, 128.8 (CH), 147.0, 150.1 (quat. C) ppm. IR (neat): $\tilde{\nu}$ = 1799 (s), 1594 (m) cm^{-1}. EI MS (14 eV): *m*/*z* (%) = 245 (100) [M]$^+$, 231 (1), 220 (1), 189 (18), 174 (15), 133 (23), 105 (7), 104 (15), 85 (3), 57 (28). $C_{15}H_{23}N_3$ (245.4): calcd. C 73.43, H 9.45, N 17.13; found C 73.52, H 9.37, N 17.35. **26a:** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.351, 1.822 (s, 9 H), 2.855 (br. s, 1 H), 6.946 (ddd, $J_{H,H}$ = 8.5, 6.5, 0.9 Hz, 1 H), 7.177 (ddd, $J_{H,H}$ = 8.7, 6.5, 1.1 Hz, 1 H), 7.596 (td, $J_{H,H}$ = 8.7, 0.9 Hz, 1 H), 7.660 (td, $J_{H,H}$ = 8.5, 1.0 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 30.97, 31.41 [$(CH_3)_3$], 53.94, 61.68 (quat. C), 117.76, 119.92, 120.97, 125.12 (CH), 118.11, 137.30, 146.03 (quat. C) ppm. IR (Nujol): $\tilde{\nu}$ = 3320 (s), 1620 (m) cm^{-1}. UV (ethanol): λ_{max} (log ε) = 309 (3.749), 282 (3.585), 273 (3.532), 216 (4.55) nm. EI MS (70 eV): *m*/*z* (%) = 245 (24) [M]$^+$, 133 (100). $C_{15}H_{23}N_3$ (245.4): calcd. C 73.43, H 9.45, N 17.13, equiv. mass 245.4; found C 73.38, H 9.30, N 17.18, equiv. mass 245.2. **27a:** This compound was identical with the authentic compound described in the Supporting Information.

(4-*tert*-Butylphenyl)(1,2-di-*tert*-butyldiaziridin-3-ylidene)amine (21b), 2,5-Di-*tert*-butyl-3-(*tert*-butylamino)-2*H*-indazole (26b), and 1,6-Di-*tert*-butyl-2-(*tert*-butylamino)-1*H*-benzimidazole (27b): These compounds were produced by Procedure B, from **20b** (40.0 g, 0.10 mol), KOH in methanol (40%, 0.50 L), and petroleum ether (0.50 L). The mixture turned red. Workup as described for **21a** and **26a** under (a) yielded a solid mixture of **26b** and **27b** (25.4 g, 84%), which was recrystallized from acetonitrile to afford **26b** (colorless needles, 15.4 g, 51%, m.p. 219–220 °C). Concentration of the acetonitrile mother liquor gave a solid (10.0 g, 33%, **26b/27b** 38:62, ^{1}H NMR in C_6D_6). The solvent was distilled from the petroleum ether mother liquor and pentane washings. Flash chromatography of the residue on Al_2O_3 with pentane/diethyl ether gave **21b** (blue first fraction, 0.95 g, 3%) and a colorless mixture of **26b** and **27b** (blue fluorescent second fraction, 1.0 g, 3%, **26b/27b** 3:7). Yield of isolated products 91%, **21b/26b/27b** 3.5:71.5:25. **21b:** Sublimation at 35 °C/10^{-5} Torr afforded colorless crystals, m.p. 45–47 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.98 (s, 9 H, *t*Bu$_{syn}$), 1.22 (s, 9 H, C*t*Bu), 1.24 (s, 9 H, *t*Bu$_{anti}$), 7.24 (m, 2 H, HCCC), 7.28 (m, 2 H, HCCN); simulation yielded $^3J_{m,o}$ = 8.2, $^4J_{m,m}$ = 2.6, $^4J_{o,o}$ = 2.1, $^5J_{m,o}$ = 0.5 Hz (*o*, *m* rel. *N*-substituent) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 26.55 [$(CH_3)_3$, *t*Bu$_{anti}$], 27.51 [$(CH_3)_3$, *t*Bu$_{syn}$], 31.59 [$(CH_3)_3$, C*t*Bu], 34.38 (quat. C, C*t*Bu), 58.84 (quat. C, *t*Bu$_{syn}$), 59.17 (quat. C, *t*Bu$_{anti}$), 122.96 [CH, *C*CN (Ph)], 126.02 [CH, *C*CC (Ph)], 145.37 [quat. C, N*C*-*i* (Ph)], 147.23 [quat. C, C*C*-*i* (Ph)], 149.04 (C=N) ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 26.4, 27.2, 31.4 [$(CH_3)_3$], 34.3, 58.8, 59.2 (quat. C), 122.2, 125.5 (CH), 144.0, 147.1, 149.8 (quat. C) ppm. $C_{19}H_{31}N_3$ (301.5): calcd. C 75.70, H 10.36, N 13.94; found C 75.64, H 10.33, N 13.91. **26b:** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.351, 1.354, 1.806 (s, 9 H), 2.805 (br. s, 1 H), 7.307 (dd, $J_{H,H}$ = 9.1, 1.9 Hz, 1 H), 7.54–7.565 (m, 2 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 31.05, 31.32, 31.42 [$(CH_3)_3$], 34.74, 54.06, 61.58 (quat. C), 115.05, 117.25, 124.82 (CH), 117.90, 137.21, 142.37, 144.79 (quat. C) ppm. IR (KBr): $\tilde{\nu}$ = 3250 (s), 1632 (m) cm^{-1}. UV (propan-2-ol): λ_{max} (log ε) = 310 (3.87), 285 (3.62), 220 (4.41) nm. EI MS (70 eV): *m*/*z* (%) = 301 (17) [M]$^+$. $C_{19}H_{31}N_3$ (301.5): calcd. C 75.70, H 10.36, N 13.94; found C 75.60, H 10.62, N 14.10. **27b:** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.355, 1.516, 1.827 (s, 9 H), 4.367 (s, 1 H), 7.130 (dd, $J_{H,H}$ = 8.3, 1.8 Hz, 1 H), 7.395

(d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.475 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 29.24, 30.66, 32.03 [$(CH_3)_3$], 34.69, 52.43, 57.21 (quat. C), 109.16, 115.85, 117.94 (CH), 133.35, 140.94, 141.56, 153.09 (quat. C) ppm.

(4-*tert*-Butyl-2-methylphenyl)(1,2-di-*tert*-butyldiaziridin-3-ylidene)-amine (21c), 2,5-Di-*tert*-butyl-3-(*tert*-butylamino)-7-methyl-2*H*-indazole (26c), and 1,6-Di-*tert*-butyl-2-(*tert*-butylamino)-4-methyl-1*H*-benzimidazole (27c): These compounds were produced by Procedure B, from **20c** (20.7 g, 50 mmol), KOH in methanol (40%, 250 mL), and petroleum ether (300 mL). The mixture turned red. Workup as described for **21a** and **26a** under (a) afforded several crystallized fractions. Recrystallization of the combined fractions from benzene gave **27c** as colorless plates (8.01 g, 51%, m.p. 114 °C). The solvent was distilled in vacuo from the mother liquors and washings, and the residue was separated by flash chromatography on Al_2O_3 with pentane/diethyl ether. The blue first fraction afforded **21c** (0.83 g, 5%), the blue fluorescent second fraction **26c** (colorless needles, 0.87 g, 6%, m.p. 125–126 °C, from benzene), and a blue third fraction yielded a colorless product (3.80 g) consisting of **26c** and **27c** (8:92, ^1H NMR). Yield of isolated products 86%, **21c/26c/27c** 6:9:85. **21c:** Sublimation at 35 °C/10^{-5} Torr gave colorless crystals. ^1H NMR (60 MHz, C_6H_6): δ = 0.94, 1.22 (s, 9 H), 1.25 (s, 9 H), 2.40 (s, 3 H) ppm. $C_{20}H_{33}N_3$ (315.5): calcd. C 76.14, H 10.54, N 13.32; found C 76.01, H 10.64, N 13.11. **26c:** ^1H NMR (600 MHz, $CDCl_3$): δ = 1.338 (s, 18 H), 1.801 (s, 9 H), 2.564 (s, 3 H), 2.748 (br. s, 1 H), 7.041 (br. s, 1 H), 7.384 (s, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.77 (CH_3), 31.04 (br.), 31.35, 31.41 [$(CH_3)_3$], 34.67, 54.03, 61.55 (quat. C), 112.52, 123.54 (CH), 117.74, 127.03, 137.10, 142.54, 144.86 (quat. C) ppm. IR (KBr): $\tilde{\nu}$ = 3300 (s), 1627 (m) cm^{-1}. **27c:** This compound was identical with the product that was obtained from **25f** on prolonged heating in boiling heptane (see Supporting Information). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.345, 1.519, 1.804 (s, 9 H), 2.523 (unresolved m, 3 H), 4.253 (br. s, 1 H), 6.947 (m, 1 H), 7.298 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.71 (CH_3), 29.49, 30.60, 32.08 [$(CH_3)_3$], 34.61, 52.62, 56.95 (quat. C), 106.81, 118.64 (CH), 125.32, 132.82, 139.91, 141.30, 152.40 (quat. C) ppm. IR (Nujol): $\tilde{\nu}$ = 3475, 1616 cm^{-1}. UV (ethanol): λ_{max} (log ε) = 294 (3.93), 261 (4.03) 222 (4.60) nm. EI MS (70 eV): *m*/*z* (%) = 315 (18), 259 (8), 244 (11), 228 (4), 203 (71), 188 (100), 172 (10), 160 (9). $C_{20}H_{33}N_3$ (315.5): calcd. C 76.14, H 10.54, N 13.32; found C 75.91, H 10.80, N 13.25.

(1,2-Di-*tert*-butyldiaziridin-3-ylidene)(2,6-dimethylphenyl)amine (21d): (a) This compound was produced by Procedure B, but without external cooling, from **20d** (3.72 g, 10 mmol), KOH in methanol (40%, 40 mL), and pentane (100 mL). Yellow viscous oil [1.96 g, 72%, >98% **21d** (UV/Vis)]. Recrystallization from pentane at –78 °C gave pale yellow crystals (1.37 g, 50%, m.p. 26–27.5 °C). (b) This compound was produced by Procedure B, but without external cooling, from **20d** (3.72 g, 10 mmol), KOH in water (50%, 40 mL), and pentane (100 mL). Stirring was continued for 2 d. Orange-colored, viscous oil (2.23 g, 80%). Recrystallization from pentane at –78 °C gave pale yellow crystals (1.45 g, 53%, m.p. 26–27.5 °C). (c) This compound was produced by Procedure C from **20d** and NaH in THF. Orange-colored, viscous oil (3.53 g, 64%). Repeated crystallization from pentane at –78 °C yielded pale yellow crystals (2.19 g, 40%, m.p. 26–27.5 °C). Recrystallization from pentane gave colorless crystals, m.p. 26.5–28.5 °C. ^1H NMR (60 MHz, $CFCl_3$, –26 °C): δ = 0.88, 1.30 (s, 9 H), 2.22 (s, 6 H), 6.89 (s, 3 H) ppm. ^1H NMR (60 MHz, CCl_4): Coalescence of the *tert*-butyl signals at T_c = (33 ± 1) °C, $\Delta\nu$ = 25.5 Hz (–26 °C), $\Delta G_c^{\ddagger}$ = 65 kJ mol^{-1}. IR (neat): $\tilde{\nu}$ = 1798 (s) cm^{-1}. UV (hexane): λ_{max} (log ε) = 280 (sh, 3.24), 252 (3.756) nm. EI MS (14 eV): *m*/*z* (%) = 273 (100) $[M]^+$, 259 (19), 243 (6), 217 (8), 202 (11), 190 (3), 188 (5), 161 (6), 133 (19), 132 (19), 121 (3), 105 (8). $C_{17}H_{27}N_3$ (273.4): calcd. C 74.68, H 9.95, N 15.37; found C 74.92, H 9.97, N 15.57.

(1,2-Di-*tert*-butyldiaziridin-3-ylidene)(2,4,6-trimethylphenyl)amine (21e) and 3-*tert*-Butyl-2-(*tert*-butylimino)-3a,5,7-trimethyl-2,3-dihydro-3a*H*-benzimidazole (25e): (a) These compounds were produced by Procedure B, but without external cooling, from **20e** (38.6 g, 0.10 mol), KOH in methanol (40%, 0.67 L), and petroleum ether (1.0 L). Pale yellow crystals of **21e** (19.3 g, 67%, m.p. 82–92 °C, **21e/25e** 98:2, UV/Vis). The solvent was distilled in vacuo from the mother liquor. A solution of the residue in CH_2Cl_2 was placed on top of a column packed with silica gel (200 g, 0.2–0.5 mm). Exhaustive elution with CH_2Cl_2 gave a crystallized mixture (4.58 g), which was separated into **21e** (3.76 g, 13%, soluble in pentane/diethyl ether) and *N*-(*tert*-butyl)-*N*′-(2,4,6-trimethylphenyl)urea (0.78 g, 3%, insoluble in pentane). The yellow zone was eluted with CH_2Cl_2/Et_3N (20:1), and the resulting yellow oil was chromatographed on basic Al_2O_3 with petroleum ether/diethyl ether (20:1), followed by distillation in a sublimation apparatus at 60–67 °C bath temp./10^{-3} Torr to afford **25e** as a yellow oil (0.23 g, 0.8%). (b) These compounds were produced by Procedure D, from **20e** (7.71 g, 20 mmol) and *t*BuOK (2.25 g, 20 mmol) in diethyl ether (250 mL), cooled to –78 °C. The colorless suspension was warmed slowly to room temp. The yellow color of **25e** began to appear at –27 °C. Workup yielded a yellow mixture (3.90 g, 67%, **21e/25e** 72:28, ^1H NMR, UV/Vis). Separation of the components by chromatography as described under (a) afforded **25e** as a yellow oil (0.89 g, 15%). **21e:** Recrystallization from pentane (100 mL) gave colorless needles (13.7 g, 48%, m.p. 94.5–95.5 °C). ^1H NMR (400 MHz, C_6D_6, 20 °C): δ = 0.87 (br. s, 9 H, $t\mathrm{Bu}_A$), 1.24 (br. s, 9 H, $t\mathrm{Bu}_B$), 2.15 (s, 3 H, Ar-CH_3), 2.32 (s, 6 H, Ar-CH_3), 6.78 (s, 2 H, Ar-H) ppm. ^1H NMR (60 MHz, CCl_4): Coalescence of the *tert*-butyl signals at T_c = (38 ± 1) °C, $\Delta\nu$ = 25 Hz (–22 °C), $\Delta G_c^{\ddagger}$ = 66 kJ mol^{-1}. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = 19.58 (br, Ar-CH_3), 20.91 (Ar-CH_3), 27.07, 27.28 [$(CH_3)_3$, *t*Bu], 58.47, 58.57 (quat. C, *t*Bu), 129.36 (CH, Ar-CH), 132.68 (quat. C, Ar-C-Me), 143.31 (quat. C, Ar-C-N), 145.89 (quat. C) ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 19.1 (2 CH_3), 20.7 (CH_3), 27.1 [$(CH_3)_3$], 58.5, 128.9 (quat. C), 129.5 (Ar-CH), 132.6, 142.6, 146.1 (quat. C). IR (neat): $\tilde{\nu}$ = 1798 (s) cm^{-1}. UV (hexane): λ_{max} (log ε) = 286 (sh, 3.228), 255 (3.750), 220 (sh, 4.22), 205 (4.66) nm. EI MS (14 eV): *m*/*z* (%) = 287 (100) $[M]^+$, 273 (14), 231 (7), 216 (4), 202 (11), 146 (33), 85 (5), 57 (44). $C_{18}H_{29}N_3$ (287.5): calcd. C 75.21, H 10.17, N 14.62; found C 75.55, H 10.07, N 14.51. **25e:** ^1H NMR (90 MHz, CCl_4): δ = 1.28 (s, 9 H), 1.40 (s, 3 H, 3a-CH_3), 1.51 (s, 9 H), 1.77 (d, $^4J_{H,H} \approx$ 1.5 Hz, 3 H, 5-CH_3), 2.07 (br. d, $^4J_{H,H} \approx$ 1.5 Hz, 3 H, 7-CH_3), 5.98 (sept, $J_{H,H} \approx$ 1.5 Hz, 1 H), 6.24 (br., 1 H) ppm. IR (neat): $\tilde{\nu}$ = 1662 (s), 1599 (s) cm^{-1}. UV/Vis (hexane): λ_{max} (log ε) = 400 (sh, 3.217), 334 (3.575), 240 (sh, 3.75), 209 (4.21) nm. EI MS (70 eV): *m*/*z* (%) = 287 (55) $[M]^+$, 231 (27). $C_{18}H_{29}N_3$ (287.5): calcd. N 14.62; found N 14.64.

Dimer 28 by Diels–Alder Reaction of 25e: Freshly distilled **25e** (575 mg, 2.0 mmol) was kept at 25 °C in the absence of light and air for 3 weeks, followed by recrystallization of the product from hexane to afford pale yellow crystals (440 mg, 76%, m.p. 135.5–136.5 °C). ^1H NMR (600 MHz, HH-COSY, HC-HSQC, HC-HMBC, $CDCl_3$): δ = 1.121 (s, 3 H, 10-CH_3), 1.311 (s, 3 H, 16-CH_3), 1.331, 1.335 (s, 9 H), 1.355 (s, 3 H, 11-CH_3), 1.416 (s, 3 H, 3-CH_3), 1.554 (br. s, 18 H), 1.599 (d, $^4J_{H,H}$ = 1.7 Hz, 3 H, 17-CH_3), 1.894 (d, $^4J_{H,H}$ = 1.4 Hz, 3 H, 8-CH_3), 2.030 (unresolved m, 1 H, 2-H), 3.082 (unresolved m, 1 H, 1-H), 5.189 (m, 1 H, 18-H), 5.677 (unresolved m, 1 H, 9-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 13.09 (11-CH_3), 17.17 (8-CH_3), 21.74 (10-CH_3), 21.84 (16-CH_3), 22.37 (17-CH_3), 29.87 (3-CH_3), 26–26.5, 29.5–31, 31.77, 31.95

[$(CH_3)_3$], 49.38 (quat. C, C-11), 50.56 (CH, C-2), 51.36 (CH, C-1), 53.55, 53.59, 54.96, 55.17 [quat C, N-*C*$(CH_3)_3$], 53.70 (quat. C, C-10), 69.72 (quat. C, C-3), 74.05 (quat. C, C-16), 128.87 (CH, C-18), 130.00 (quat. C, C-8), 138.96, (CH, C-9), 140.68 (quat. C, C-17), 157.83 (quat. C, C-5), 158.68 (quat. C, C-14), 180.87 (quat. C, C-7), 193.71 (quat. C, C-12) ppm. IR (Nujol): $\tilde{\nu}$ = 1669 (m), 1650 (m), 1613 (s) cm^{-1}. UV (hexane): λ_{max} (log ε) = 325 (3.69), 260 (4.20) nm. EI MS (70 eV): *m*/*z* (%) = 575 (38). $C_{36}H_{58}N_6$ (574.9): calcd. C 75.21, H 10.17, N 14.62, mol. mass 574.9; found C 75.35, H, 9.99, N 14.46, mol. mass 582 (osmometric in $CHCl_3$).

(4-*tert*-Butyl-2,6-dimethylphenyl)(1,2-di-*tert*-butyldiaziridin-3-ylidene)amine (21f) and 3,5-Di-*tert*-butyl-2-(*tert*-butylimino)-3a,7-dimethyl-2,3-dihydro-3a*H*-benzimidazole (25f): (a) These compounds were produced by Procedure B, from **20f** (8.55 g, 20 mmol), KOH in methanol (40%, 140 mL), and petroleum ether (200 mL). Pale yellow crystals (**21f**, 4.66 g, 71%, m.p. 75–77 °C). The solvent was distilled in vacuo from the mother liquor. Chromatography of the residue on silica gel with CH_2Cl_2, as described for **21e** and **25e**, gave a pale yellow oil. Crystallization from pentane at –78 °C yielded **21f** as colorless crystals (0.18 g, 3%, m.p. 78–79 °C). Continued elution with CH_2Cl_2/Et_3N (20:1) and subsequent chromatography on basic Al_2O_3 with petroleum ether/diethyl ether afforded a yellow oil, which crystallized from pentane at –78 °C to furnish yellow cubes (**25f**, 0.11 g, 2%, m.p. 84 °C). Yield of isolated products 75%, **21f**/**25f** 98:2. (b) In a variation of Procedure B, **20f** (8.55 g, 20 mmol) was stirred in a solution of KOH in methanol (40%, 70 mL) for 5 min, followed by addition of petroleum ether (200 mL), stirring for 1 h, and workup as described under (a). Colorless crystals of **21f** (4.44 g, 67%, m.p. 78–79 °C) and yellow cubes of **25f** (0.74 g, 11%, m.p. 84 °C). **21f**/**25f** 86:14. **21f:** Colorless needles from pentane, m.p. 78–79 °C. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 0.87, 1.25 (br. s, 9 H, N*t*Bu), 1.28 (s, 9 H, C*t*Bu), 2.39 (s, 6 H, Ar-CH_3), 7.11 (s, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = 19.98 (br., CH_3, Ar-CH_3), 27.05, 27.30 [$(CH_3)_3$, N*t*Bu], 31.79 [$(CH_3)_3$, C*t*Bu], 34.21 (quat. C, C*t*Bu), 58.47, 58.56 (quat. C, N*t*Bu), 125.47 (CH, Ar-CH), 129.5 (br., quat. C, Ar-C-Me), 143.38 (quat. C, Ar-C), 145.88, 146.24 (quat. C) ppm. ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 19.4 (CH_3), 27.0 [2 $(CH_3)_3$], 31.5 [$(CH_3)_3$], 33.9, 58.4 (quat. C), 124.9 (CH), 128.8, 142.4, 146.1 (quat. C) ppm. IR (Nujol): $\tilde{\nu}$ = 1802 (s) cm^{-1}. UV (heptane): λ_{max} (log ε) = 254 (3.78) nm. EI MS (70 eV): *m*/*z* (%) = 329 (13) $[M]^+$, 315 (6), 314 (9), 273 (11), 258 (39), 217 (24), 202 (100), 188 (37), 161 (60). $C_{21}H_{35}N_3$ (329.5): calcd. C 76.54, H 10.71, N 12.75; found C 76.30, H 10.52, N 12.62. **25f:** Yellow cubes from pentane, m.p. 84 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.061, 1.349, 1.573 (s, 9 H), 1.417 (s, 3 H), 2.092 (dd, $J_{H,H} \approx 1.2$, ≈ 0.6 Hz, 3 H), 6.316 (dq, $^4J_{H,H} \approx 1.6$ Hz, 1 H), 6.349 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.47, 28.25 (CH_3), 28.69, 28.83, 31.97 [$(CH_3)_3$], 34.14, 53.76, 54.99, 71.19 (quat. C), 128.46, 131.51 (CH), 130.03, 142.23, 156.10, 186.50 (quat. C) ppm. IR (Nujol): $\tilde{\nu}$ = 1651 (s), 1598 (s) cm^{-1}. UV/Vis (hexane): λ_{max} (log ε) = 390 (sh, 3.27), 331 (3.63), 235 (sh, 3.85), 207 (4.27) nm. EI MS (70 eV): *m*/*z* (%) = 329 (3), 258 (9), 216 (7), 203 (10), 202 (24), 188 (16), 187 (25), 162 (22), 161 (15), 57 (100). $C_{21}H_{35}N_3$ (329.5): calcd. C 76.54, H 10.71, N 12.75; found C 76.77, H 10.76, N 12.69.

6-(*tert*-Butylamino)-5*H*-dibenzo[*d*,*f*][1,3]diazepine (37) and 2-(*tert*-Butylamino)-1-phenyl-1*H*-benzimidazole (38): (a) These compounds were produced by Procedure B, but without external cooling, from **32a** (3.64 g, 10 mmol), KOH in methanol (40%, 80 mL), and benzene (180 mL). The lower layers were extracted with benzene. Almost colorless crystals (2.42 g, 91%, m.p. 133–135 °C, **37**/**38** 15:85, ^{1}H NMR). Flash chromatography on Al_2O_3 with benzene/ethyl acetate (1:1) yielded **38** as colorless crystals (first fraction, 2.04 g, 77%, m.p. 140–142 °C). Elution with pure ethyl acetate afforded **37** as colorless crystals (0.36 g, 14%, m.p. 224–225 °C). Compounds **37** and **38** were identical with authentic compounds described in the Supporting Information. (b) An experiment performed as described under (a), but at the temperature of boiling benzene, gave a crude product (85%) consisting of **37**/**38** 12:88 (^{1}H NMR). (c) Compound **32a** (3.64 g, 10 mmol) was added to a stirred solution of KOH in methanol (40%, 80 mL). Stirring was continued for 10 min, followed by the addition of benzene (180 mL) and workup as described under (a). The crude product (90%) consisted of **37**/**38** 40:60 (^{1}H NMR). (d) A mixture of **32a** (3.64 g, 10 mmol) and aq. NaOH (2 M, 50 mL) was vigorously shaken in a 200 mL Erlenmeyer flask for 5 min. At the onset, an intense yellow color appeared and faded rapidly, followed by the precipitation of a voluminous solid material. A second portion of aq. NaOH (2 M, 50 mL) was added, and the mixture was kept at room temp. for 1 h. The solid was isolated by filtration, washed with water, and dried in vacuo to afford a colorless product (2.60 g, 98%, m.p. 202–204 °C, **37**/**38** 75:25, ^{1}H NMR). Separation as described under (a) and recrystallization from $CHCl_3$ yielded **37** as colorless crystals (1.41 g, 53%, m.p. 225–226.5 °C).

2-(*tert*-Butylimino)-3a,7-dimethyl-3-(2,6-dimethylphenyl)-2,3-dihydro-3a*H*-benzimidazole (35b) and Dimer 39: These compounds were produced by Procedure B, but without external cooling, from **32b** (10.5 g, 25 mmol), KOH in methanol (40%, 100 mL), and petroleum ether (300 mL). Usual workup and distillation of the solvent in vacuo gave a yellow residue, which was triturated with petroleum ether (10 mL) to afford yellow crystals. Recrystallization from petroleum ether yielded **35b** as large, deep yellow crystals (4.12 g, 52%, m.p. 132–133.5 °C). The solvent was distilled from the first mother liquor, and the residue was subjected to flash chromatography on Al_2O_3 with benzene, followed by flash chromatography of the first fraction on Al_2O_3 with ethyl acetate to furnish **39** as pale yellow crystals (0.15 g, 2%, m.p. 180–181 °C). **35b:** ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.30 (s, 9 H), 1.38 (s, 3 H, 3a-CH_3), 2.03, 2.27 (s, 3 H, Ar-CH_3), 2.19 (d, $^4J_{H,H}$ = 2 Hz, 3 H, 7-CH_3), 5.73–6.27 (m, 3 H), 7.07 (s, 3 H) ppm. IR (Nujol): $\tilde{\nu}$ = 1662 (s), 1626 (m), 1580 (s) cm^{-1}. UV (hexane): λ_{max} (log ε) = 388 (3.345), 323 (3.603), 240 (sh, 3.83), 210 (sh, 4.45) nm. EI MS (70 eV): *m*/*z* (%) = 321 (40) $[M]^+$, 306 (100). $C_{21}H_{27}N_3$ (321.5): calcd. C 78.46, H 8.47, N 13.07, equiv. mass 321.5; found C 78.40, H 8.32, N 13.32, equiv. mass 322. **39:** ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.433, 1.450 (9 H), 1.74 (s, 12 H), 1.81 (s, 9 H), 1.94–2.20 (m, 12 H), 2.68 (br. s, 2 H, 2-H, 10-H), 3.43 (d, $^3J_{H,H}$ = 7 Hz, 1 H, 1-H), 5.57 (d, $^3J_{H,H}$ = 8 Hz, 1 H, 18-H), 5.83–6.17 (m, 2 H, 9-H, 17-H), 6.67–7.10 (m, 6 H) ppm. IR (Nujol): $\tilde{\nu}$ = 1670 (s), 1651 (m), 1613 (s) cm^{-1}. UV (hexane): λ_{max} (log ε) = 316 (3.76), 263 (4.36), 232 (4.43), 203 (4.93) nm. $C_{42}H_{54}N_6$ (642.9): calcd. C 78.46, H 8.47, N 13.07, mol. mass 642.9; found C 78.78, H 8.54, N 12.96, mol. mass 647 (osmometric in $CHCl_3$).

Supporting Information (see footnote on the first page of this article): General experimental (1 page), syntheses of precursors (9 pages) and authentic compounds (4 pages), thermolysis and degradation experiments (4 pages), NMR spectra (30 pages), UV/Vis spectra (2 pages), IR spectra (3 pages).

Acknowledgments

We are grateful to the late Dr. Palle E. Iversen, University of Aarhus, Denmark, for generous gifts of *N*-alkylhydroxylamine hydrochlorides and to the late Dr. Viktor Formáček, Bruker, Karlsruhe, for recording ^{13}C NMR spectra during the early stage

of this work. We express our gratitude to Mrs. Elfriede Ruckdeschel and Dr. Matthias Grüne, University of Würzburg, for taking high-field NMR spectra of products of iminodiaziridines. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, Frankfurt am Main, for financial support.

[1] Reviews: a) G. L'abbé, *Angew. Chem.* **1980**, *92*, 277–290; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 276–289; b) G. L'abbé, in *Lectures in Heterocyclic Chemistry*, vol. 9 (Eds.: R. N. Castle, R. Neidlein), *J. Heterocycl. Chem.* **1987**, *24* (Suppl.), pp. S-51–S-58; c) T. H. Chan, B. S. Ong, *Tetrahedron* **1980**, *36*, 2269–2289; d) J. A. Deyrup, in *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues* (Ed.: S. Patai), Wiley, Chichester, UK, **1980**, part 1, pp. 177–214; e) P. J. Stang, in *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues* (Ed.: S. Patai), Wiley, Chichester, UK, **1980**, part 2, pp. 859–879; f) H. W. Heine, in *The Chemistry of Heterocyclic Compounds*, vol. 42 (Small Ring Heterocycles) (Ed.: A. Hassner), Wiley, Chichester, UK, **1983**, part 2, pp. 616–628; g) R. V. Hoffman, V. Cesare, in *Science of Synthesis*, vol. 21 (Ed.: S. M. Weinreb), Thieme, Stuttgart, **2005**, pp. 591–608.

[2] a) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056–2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021; b) V. D. Bock, H. Hiemstra, J. H. van Maarseveen, *Eur. J. Org. Chem.* **2006**, 51–68; c) M. V. Gil, M. J. Arévalo, Ó. López, *Synthesis* **2007**, 1589–1620; d) H. Nandivada, X. Jiang, J. Lahann, *Adv. Mater.* **2007**, *19*, 2197–2208; e) W. H. Binder, C. Kluger, *Curr. Org. Chem.* **2006**, *10*, 1791–1815.

[3] a) M. Shipman, *Synlett* **2006**, 3205–3217; b) E. J. Corey, K. Ritter, M. Yus, C. Najera, *Tetrahedron Lett.* **1987**, *28*, 3547–3550; c) J. K. Crandall, E. Rambo, *Tetrahedron* **2002**, *58*, 7027–7036.

[4] S. K. Richardson, A. R. Howell, *Synthesis* **2007**, 2755–2778.

[5] H. Quast, S. Aldenkortt, B. Freudenreich, P. Schäfer, M. Hagedorn, J. Lehmann, K. Banert, *J. Org. Chem.* **2007**, *72*, 1659–1666.

[6] a) H. Quast, E. Spiegel, *Angew. Chem.* **1977**, *89*, 112–113; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 109–110; b) H. Quast, K.-H. Ross, E. Spiegel, K. Peters, H. G. von Schnering, *Angew. Chem.* **1977**, *89*, 202–203; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 177–178; c) B. Zhao, H. Du, Y. Shi, *Org. Lett.* **2008**, *10*, 1087–1090.

[7] a) H. Quast, E. Schmitt, *Angew. Chem.* **1969**, *81*, 429–430; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 449–450; b) H. Quast, E. Schmitt, *Angew. Chem.* **1969**, *81*, 428; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 448; c) H. Quast, E. Schmitt, *Chem. Ber.* **1970**, *103*, 1234–1249; d) C. J. Wilkerson, F. D. Greene, *J. Org. Chem.* **1975**, *40*, 3112–3118; e) G. L'abbé, A. Verbruggen, T. Minami, S. Toppet, *J. Org. Chem.* **1981**, *46*, 4478–4481.

[8] a) R. Ohme, H. Preuschhof, *Justus Liebigs Ann. Chem.* **1969**, *721*, 25–33; b) A. Heesing, G. Imsieke, G. Maleck, R. Peppmöller, H. Schulze, *Chem. Ber.* **1970**, *103*, 539–552.

[9] H. Quast, L. W. Bieber, *J. Org. Chem.* **2008**, *73*, 3738–3744.

[10] a) F. Kurzer, K. Douraghi-Zadeh, *Chem. Rev.* **1967**, *67*, 107–152; b) H. Ulrich, *Chemistry and Technology of Carbodiimides*, 1st ed., Wiley-VCH, Weinheim, **2007**.

[11] a) P. Molina, E. Aller, A. Lorenzo, *Synlett* **2003**, 714–716; b) W.-X. Zhang, Z. Hou, *Org. Biomol. Chem.* **2008**, *6*, 1720–1730.

[12] a) O. Westphal, W. de Burlet, *Angew. Chem.* **1945**, *58*, 77; b) P. A. S. Smith, H. R. Alul, R. L. Baumgarten, *J. Am. Chem. Soc.* **1964**, *86*, 1139–1145; c) E. Schmitz, R. Ohme, D. Murawski, *Chem. Ber.* **1965**, *98*, 2516–2524.

[13] a) P. von Ragué Schleyer, R. D. Nicholas, *J. Am. Chem. Soc.* **1961**, *83*, 182–187; b) J. E. Bertie, M. G. Norton, *Can. J. Chem.* **1970**, *48*, 3889–3902; c) R. W. Mitchell, J. A. Merritt, *Spectrochim. Acta A* **1971**, *27*, 1609–1618.

[14] a) G. J. Karabatsos, S. S. Lande, *Tetrahedron* **1968**, *24*, 3907–3922; b) G. J. Karabatsos, R. A. Taller, *Tetrahedron* **1968**, *24*, 3923–3927; c) F. H. A. Rummens, R. H. Krystynak, *J. Am. Chem. Soc.* **1972**, *94*, 6914–6921.

[15] a) S. I. Burmistrov, Yu. V. Sukhoruchkin, *Zh. Obshch. Khim.* **1963**, *33*, 1227–1233; b) I. A. Larionova, A. V. Golounin, V. A. Sokolenko, *Russ. J. Org. Chem.* **2006**, *42*, 766–767.

[16] Ring-opening isomerizations of three-membered rings with exocyclic double bonds have been observed; a) aziridinones: I. Lengyel, J. C. Sheehan, *Angew. Chem.* **1968**, *80*, 27–37; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 25–36; b) iminoaziridines: H. Quast, P. Schäfer, *Tetrahedron Lett.* **1977**, *18*, 1057–1060; c) protonated iminoaziridines: H. Quast, S. Aldenkortt, B. Freudenreich, P. Schäfer, E.-M. Peters, K. Peters, H. G. von Schnering, E.-U. Würthwein, *Liebigs Ann.* **1996**, 87–98.

[17] a) C. J. M. Stirling, *Chem. Rev.* **1978**, *78*, 517–567; b) S. Hughes, G. Griffiths, C. J. M. Stirling, *J. Chem. Soc. Perkin Trans. 2* **1987**, 1253–1264; c) C. W. Spangler, *Chem. Rev.* **1976**, *76*, 187–217.

[18] For the thermolysis of diaziridinones via a nitrenoid fragment, see: P. E. McGann, J. T. Groves, F. D. Greene, G. M. Stack, R. J. Majeste, L. M. Trefonas, *J. Org. Chem.* **1978**, *43*, 922–925.

[19] $k_{\mathbf{3b\rightarrow3c}} + 2k_{\mathbf{3c\rightarrow3b}} = (5.9 \pm 0.1) \times 10^{-5}\ s^{-1}$, **3b/3c** 96.8:3.2 at 35.5 °C. In contrast, at a temperature of 40 °C, the valence isomerization **2a/8e** required ca. 3 months to reach the equilibrium; $2k_{\mathbf{2a\rightarrow8e}} + k_{\mathbf{8e\rightarrow2a}} = (1.335 \pm 0.005) \times 10^{-5}\ s^{-1}$, **2a/8e** 90.7:9.3 at 60.0 °C; ref.[7c]

[20] a) U. Schuchardt, L. A. Ortellado, G. Zelada, *J. Chem. Res. (S)* **1983**, 270–271; b) H. Quast, T. Hergenröther, *Chem. Ber.* **1992**, *125*, 2095–2101; c) R. V. Hoffman, Z. Zhao, A. Costales, D. Clarke, *J. Org. Chem.* **2002**, *67*, 5284–5294; d) A. Gómez-Zavaglia, I. D. Reva, L. Frija, M. L. Cristiano, R. Fausto, *J. Photochem. Photobiol. A: Chem.* **2006**, *179*, 243–255; e) L. M. T. Frija, I. D. Reva, A. Gómez-Zavaglia, M. L. S. Cristiano, R. Fausto, *Photochem. Photobiol. Sci.* **2007**, *6*, 1170–1176.

[21] a) R. F. Meyer, *J. Org. Chem.* **1965**, *30*, 3451–3454; b) S. Sarel, J. T. Klug, A. Taube, *J. Org. Chem.* **1970**, *35*, 1850–1857; c) K. Ramakrishnan, J. B. Fulton, J. Warkentin, *Tetrahedron* **1976**, *32*, 2685–2688; d) P. Legrel, M. Baudy-Floc'h, A. Robert, *Tetrahedron Lett.* **1986**, *27*, 5609–5610; e) J. B. Fulton, J. Warkentin, *Can. J. Chem.* **1987**, *65*, 1177–1184; f) H. Quast, T. Hergenröther, *Chem. Ber.* **1992**, *125*, 2625–2627.

[22] a) H. G. Aurich, H.-G. Scharpenberg, *Chem. Ber.* **1973**, *106*, 1881–1896; b) T. Sasaki, S. Eguchi, T. Ogawa, *Heterocycles* **1975**, *3*, 193–196.

[23] K. Peters, H. G. von Schnering, *Chem. Ber.* **1976**, *109*, 1384–1388.

[24] K. Peters, E.-M. Peters, G. Philipp, H. Quast, *Z. Kristallogr. NCS* **2000**, *215*, 305–306.

[25] 3a*H*-Benzimidazoles have previously been postulated as elusive intermediates: a) C. W. Rees, *Pure Appl. Chem.* **1979**, *51*, 1243–1253; b) C. A. Ramsden, H. L. Rose, *J. Chem. Soc. Perkin Trans. 1* **1995**, 615–617.

[26] R. Trave, L. Garanti, G. Zecchi, *J. Chem. Soc. Perkin Trans. 1* **1987**, 1533–1536.

[27] T. L. Gilchrist, M. E. Peek, C. W. Rees, *J. Chem. Soc., Chem. Commun.* **1975**, 914–915.

[28] Restricted rotation of *tert*-butyl groups at *low* temperatures has often been documented: S. Sternhell, "Rotation About Single Bonds in Organic Molecules", in *Dynamic Nuclear Magnetic Resonance Spectroscopy* (Eds.: L. M. Jackman, F. A. Cotton), 1st ed., Academic Press, New York, **1975**, chapter 6, pp. 163–201.

[29] These results are in accord with scrambling of labeled substituents in the photodenitrogenation products of phenyl-substituted 5-imino-4,5-dihydro-1*H*-tetrazoles: H. Quast, A. Fuß, U. Nahr, *Chem. Ber.* **1985**, *118*, 2164–2185.

[30] J. C. Gilbert, J. R. Butler, *J. Am. Chem. Soc.* **1970**, *92*, 2168–2169.

[31] For the similar ring-expansion of 2,2-diphenyl-*N*-tosyliminothiirane, see ref.[1b]

[32] Related azomethine imines are invoked as intermediates of the formation of indazoles by addition of unsaturated carbenes at aromatic azo compounds: a) P. J. Stang, M. G. Mangum, *J. Am. Chem. Soc.* **1977**, *99*, 2597–2601; b) P. J. Stang, *Pure Appl. Chem.* **1983**, *55*, 369–374.
[33] For a recent review on azomethine imines, see: J. G. Schantl, *Science of Synthesis*, vol. 27 (Ed.: A. Padwa), Thieme, Stuttgart, **2004**, pp. 731–824.
[34] Similar 1,3-dipoles – that is, carbodiimide *N*-oxides – have been invoked as intermediates in studies of diaziridinones.[7d]
[35] A similar mechanism has been proposed for the oxidation of *N*,*N*′-diphenylsulfamide with sodium hypochlorite/sodium carbonate to afford 5*H*-dibenzo[*c*,*e*][1,2,7]thiadiazepine 6,6-dioxide, see: D. L. Forster, T. L. Gilchrist, C. W. Rees, *J. Chem. Soc. C* **1971**, 993–999.
[36] a) T. Hudlický, R. Fau, J. W. Reed, K. G. Gadamasetti, *Org. React.* **1992**, *41*, 1–133; b) J. D. Eckelbarger, J. T. Wilmot, D. Y. Gin, *J. Am. Chem. Soc.* **2006**, *128*, 10370–10371; c) Divinylcyclopropane/cycloheptadiene and heteroanalogous rearrangements that involve one vinyl group confined in an aromatic ring are known.[36a,36b] However, we are unaware of examples in which this applies to *both* vinyl groups.
[37] For thermal [3.5] sigmatropic shifts, see: a) K. Dimroth, O. Schaffer, G. Weiershäuser, *Chem. Ber.* **1981**, *114*, 1752–1766; b) P. J. Battye, D. W. Jones, *J. Chem. Soc., Chem. Commun.* **1986**, 1807–1808; c) P. J. Battye, D. W. Jones, H. P. Tucker, *J. Chem. Soc., Chem. Commun.* **1988**, 495–496; d) Y. Endo, T. Uchida, S. Hizatate, K. Shudo, *Synthesis* **1994**, 1096–1105; e) S. Kohmoto, N. Nakayama, J.-i. Takami, K. Kishikawa, M. Yamamoto, K. Yamada, *Tetrahedron Lett.* **1996**, *37*, 7761–7764; f) F. Risitano, G. Grassi, F. Foti, F. Filocamo, *Tetrahedron* **1997**, *53*, 1089–1098; g) D. M. Birney, X. Xu, S. Ham, *Angew. Chem.* **1999**, *111*, 147–150; *Angew. Chem. Int. Ed.* **1999**, *38*, 189–193; h) S. Quideau, M. A. Looney, L. Pouysegu, S. Ham, D. M. Birney, *Tetrahedron Lett.* **1999**, *40*, 615–618.
[38] Cf. the competing thermal ring-expansions of 1-allylidene-2-vinylcyclopropane, which may be considered an archetype of **33**: W. E. Billups, W. Y. Chow, K. H. Leavell, E. S. Lewis, *J. Org. Chem.* **1974**, *39*, 274–275.
[39] a) G. J. Martin, M. L. Martin, J.-P. Gouesnard, *^{15}N NMR Spectroscopy*, 1st ed., Springer, Berlin–Heidelberg–New York, **1981**; b) H. Hilpert, R. Hollenstein, *Helv. Chim. Acta* **1986**, *69*, 136–140.
[40] M. Witanowski, L. Stefaniak, G. A. Webb, in *Annual Reports on NMR Spectroscopy* (Ed.: G. A. Webb), Academic Press, London, **1993**, vol. 25, pp. 1–480.
[41] a) M. Witanowski, L. Stefaniak, G. A. Webb, in *Annual Reports on NMR Spectroscopy* (Ed.: G. A. Webb), Academic Press, London, **1981**, vol. 11B, pp. 50–51; b) M. Witanowski, L. Stefaniak, G. A. Webb, in *Annual Reports on NMR Spectroscopy* (Ed.: G. A. Webb), Academic Press, London, **1986**, vol. 18, p. 322.

Received: April 1, 2009
Published Online: July 6, 2009

