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Thermal Rearrangements of (Arylimino)diaziridines by Simultaneous Cascades of Pericyclic Reactions

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Dedicated to Professor Frank Seela on the occasion of his 70th birthday

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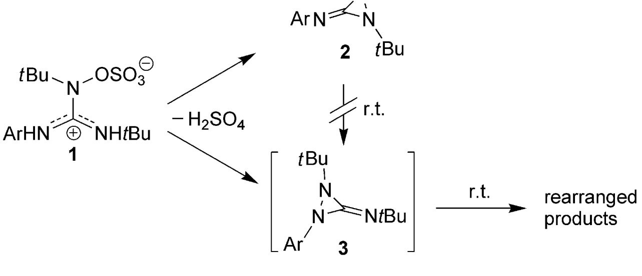
(Arylimino)diaziridines rearrange in several cascade reactions at temperatures 60–100 °C. Those that possess unoccupied *ortho* positions yield fluorescent 3-amino-2*H*-indazoles and 2-amino-1*H*-benzimidazoles. If both *ortho* positions are blocked by methyl groups, indazoles are not formed and deeply yellow 2-imino-2,3-dihydro-3a*H*-benzimidazoles are formed, which partly dimerize through Diels–Alder reaction or regenerate the aromatic system by formal loss of CH_2. In addition, one of the methyl groups of 2,6-dimethylphenyl rings is involved in a [1,7] H shift affording orthoquinonoid intermediates which undergo 1,6-electrocyclization to furnish 2-amino-3,4-dihydroquinazolines. The formation of five-membered ring heterocycles is interpreted in terms of valence isomerization by [1,3] N shift to yield elusive 1-aryl-3-iminodiaziridines as first step. These immediately experience triaza-Cope rearrangement to benzimidazole derivatives or electrocyclic opening of the N–C bond to generate conjugated azomethine imines (1,5-dipoles), followed by their 1,5-electrocyclization to indazoles. First-order rate constants of the decay of (arylimino)diaziridines refer to the [1,3] N shifts as rate-determining steps. They are larger than the corresponding rate constants for alkylsubstituted iminodiaziridines.

Introduction

Since more than a decade, cascades of pericyclic reactions emerge as powerful strategies for organic syntheses.[1,2] Here we report on thermal rearrangements by *simultaneous* pericyclic cascade reactions, which have the origin in common, but take different directions. Bifurcations of this type are rare in chemistry as well as in geography. A famous example for the latter is Isa Lake at Craig Pass, the Continental Divide in the Yellowstone National Park, Wyoming. In the present study, the sources of the cascades are (arylimino)diaziridines **2**, which we have described recently.[3]

Weakness of their NN ring bonds renders iminodiaziridines more prone to thermal reorganization than alkylidenecyclopropanes and alkylideneaziridines. Therefore, valence isomerizations of *alkyl*-substituted iminodiaziridines that exchange the nitrogen atoms of the imino groups and the ring nitrogen atoms by [1,3] shift[4] must surmount considerably lower enthalpy barriers than analogous rearrangements of alkylidenecyclopropanes[5] and alkylideneaziridines.[6] Furthermore, alkyl-substituted iminodiaziridines may rearrange by [1,5] H shift to afford alkylideneguanidines.[3] *Aryl*-substituted iminodiaziridines are expected by analogy with aryl-substituted alkylidenecyclopropanes[7] to experience additional thermal rearrangements involving the aryl groups. Indeed, putative ring-arylated iminodiaziridines (**3**), which arose from **1** by 1,3-elimination besides stable (arylimino)diaziridines **2**, were so labile at room temperature that only rearranged, ring-expanded products could be detected (Scheme 1).[3] We now studied (arylimino)diaziridines **2** with the views to tracing their thermal



Scheme 1. Aryl-substituted iminodiaziridines by base-mediated 1,3-elimination of sulfuric acid from hydroxyguanidine *O*-sulfonic acids **1**.

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stability and uncovering the course of thermolysis. A number of those ring-expanded products of **3** also emerged in the present study. The results are reported here.

Results and Discussion

We chose 1,2-di-*tert*-butyl compounds **4** and **11** for the present study to avoid ring cleavage that affords alkylideneguanidines by [1,5] H shifts involving secondary or primary alkyl substituents.[3]

Solutions of **4** and **11** in inert solvents were heated at a temperature between 60 and 100 °C, while the conversion was monitored by ^{1}H NMR spectroscopy. The decay of **4** and **11** followed the first-order rate law during several half-lifes. This was confirmed by IR spectra in the range $\tilde{\nu}$ = 1500–2000 cm^{-1} recorded for 0.05 M (path 0.1 mm) and 0.005 M (path 1 mm) solutions of **11c** in heptane. The IR spectra were superimposable after partial thermal decomposition of **11c**. As shown by constant ratios, the products were persistent under the reaction conditions, except for the 2-imino-2,3-dihydro-3a*H*-benzimidazoles **14** (see below). Workup involving separation by chromatography and crystallization afforded pure products (Table 1, entries 1, 10, 14, 16, 17). These were identified by comparison with known compounds (**9**, **10**, **14b**, **14c**, **16**, **18b**, **18c**, **19c**)[3] and authentic samples synthesized independently (**15**, **17c**), or elucidated by analytical and spectroscopic methods (**17b**, **19a**). The results are compiled in Table 1.

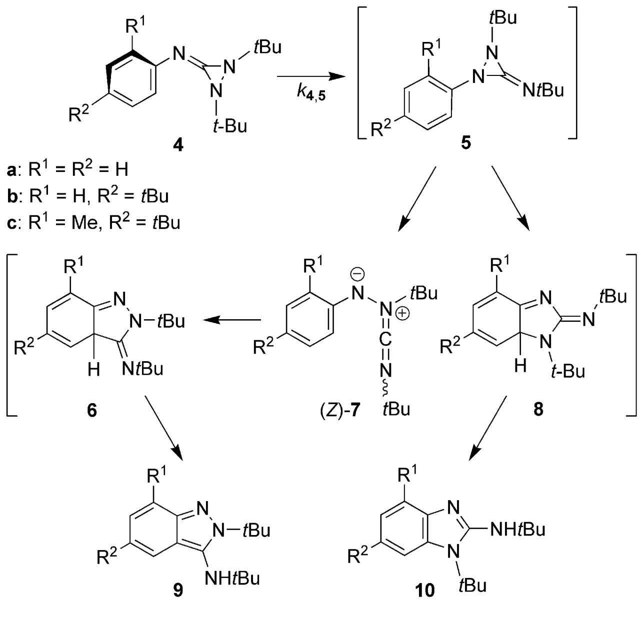
Inspection of Table 1 reveals a principal difference between (arylimino)diaziridines **4** that possess at least one unoccupied *ortho* position and their homologs **11** whose *ortho* positions are both blocked by methyl groups. Both types furnished benzimidazole derivatives **10** and **14**, **18**, **19**, respectively, but the former gave strongly fluorescent 3-amino-2*H*-indazoles **9** (Scheme 2) while the latter produced colorless 2-amino-3,4-dihydroquinazolines **17** besides minor amounts of azo compounds **15** and *tert*-butyl isocyanide (**16**) (Scheme 3). This difference warrants separate consideration of **4** and **11**. Since there is no evidence for the subtle nature of individual steps, e.g., an involvement of triazatrimethylenemethane diradicals, we disregard conceivable diradical intermediates and discuss each stage of the cascades in Scheme 2 and Scheme 3 in terms of a pericyclic reaction,[8] except for the hydrogen migrations **6**→**9** and **8**→**10** (Scheme 2) and the formal loss of CH_2 from **14** (Scheme 3).

Thermolyses of the (arylimino)diaziridines **4** afforded two aminoheterocycles **9** and **10** that previously had been obtained, along with **4**, on 1,3-elimination of sulfuric acid from **1** (cf. Scheme 1). Because the arylimino compounds **4** were stable under the conditions of the elimination, both **9** and **10** were explained by rearrangements of elusive 1-aryl-3-iminodiaziridines **5**.[9] Indeed, the substitution pattern of the NN bond in the aminoindazoles **9** proved that they stemmed from **5**: Conrotatory opening of an N–C bond of **5** yields conjugated azomethine imines (*E*)- and (*Z*)-**7**, 1,5-dipoles of which the latter are suitable to 1,5-electrocyclization to furnish **6** while the former are not.[10] Similar conjugated azomethine imines result from the addition of unsaturated carbenes at azo compounds and undergo 1,5-electrocyclization to indazoles.[11] The mechanism depicted in Scheme 2 explains why the two *ortho* methyl groups in **11** completely inhibit formation of indazole derivatives: The required *Z* configuration of hypothetical 1,5-dipoles of type **7** cannot be adopted due to excessive strain. Even the single *ortho* methyl group in **4c** disfavors the indazole route (cf. entries 1–7/8, 9, Table 1).

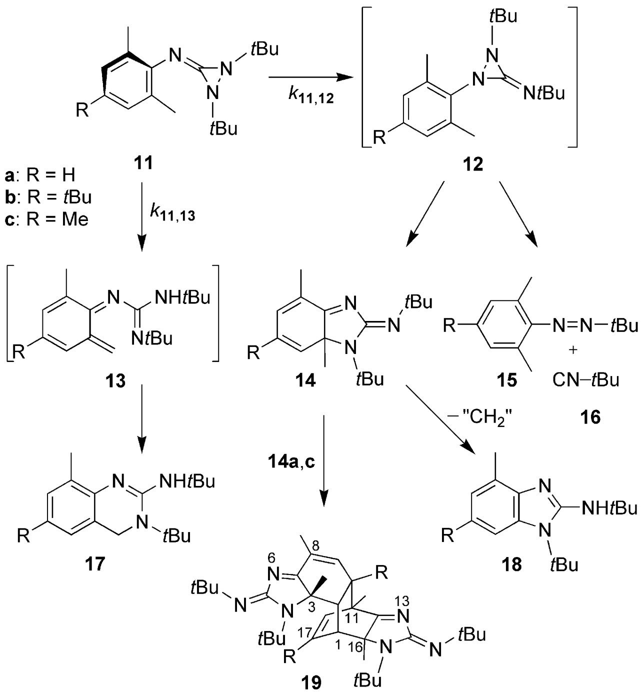
Table 1. Reaction conditions and results of the thermal rearrangements of (arylimino)diaziridines **4** and **11**. Rate constants $k_{\mathbf{26,27}}$ of the valence isomerization **26**→**27** are given for comparison.[4]

Entry	Cpd.	Solvent	Conc. [mol/L]	Temp. [°C][a]	Duration [h]	$10^5 \times k$ [s^{-1}][b]	Products[c]	Ratios
1	**4a**	C_6H_6		60.0	40	3.9	**9a** (62), **10a**	94:6
2		C_6H_6	0.7	60.0		4.10 ± 0.01	**9a**, **10a**	93:7
3		C_6H_6	0.7	70.0		13.50 ± 0.03	**9a**, **10a**	92:8
4		C_6H_6	0.6	80.0		40.6 ± 0.1	**9a**, **10a**	93:7
5		CD_3CN	0.6	60.0		3.68 ± 0.01	**9a**, **10a**	93:7
6	**4b**	C_6H_6	0.6	80.0		99.5 ± 0.3	**9b**, **10b**	77:23
7		CD_3CN	0.6	60.0		11.00 ± 0.05	**9b**, **10b**	69:31
8	**4c**	C_6H_6	0.7	80.0		164.9 ± 0.5	**9c**, **10c**	25:75
9		CD_3CN	0.8	60.0		19.20 ± 0.15	**9c**, **10c**	21:79
10	**11a**	hexane	2	reflux temp.	90		**15a** (10), **19a** (33)[d]	
11	**11b**	C_6H_6	0.6	80.0		4.43 ± 0.01[e]	**14b**, **15b**, **17b**, **18b** (= **10c**)	66:5:26:3
12		C_6H_6	0.5	98	7.5		**14b**, **15b**, **17b**, **18b**	56:8:23:13
13		CD_3CN	0.6	60.0		0.59 ± 0.001[f]	**14b**, **17b**	73:27
14		heptane	0.025	reflux temp.	8		**14b** (38), **15b** (2), **17b** (8), **18b** (7)	
15	**11c**	decalin	0.037	80.0		4.1[g]		
16		heptane	0.020	reflux temp.	6		**14c** (17), **15c** (2), **17c** (10), **18c** (8)	65:3:22:10
17		hexane	1	reflux temp.	51		**14c** (36), **19c** (13)[d]	
	26	–		60.0		0.12 ($k_{\mathbf{26,27}}$)	**27**	
	26	–		80.0		1.92 ($k_{\mathbf{26,27}}$)	**27**	

[a] ± 0.2 °C. [b] First-order rate constants of the decay of **4** and **11**. [c] Isolated yields [%] are given in brackets. [d] Isolation of further products was not attempted. [e] $k_{\mathbf{11,12}}/k_{\mathbf{11,13}}$ = (**14b** + **15b** + **18b**):**17b**, $k_{\mathbf{11,12}} = 3.28 \times 10^{-5}$ s^{-1}, $k_{\mathbf{11,13}} = 1.15 \times 10^{-5}$ s^{-1}. [f] $k_{\mathbf{11,12}}/k_{\mathbf{11,13}}$ = **14b**:**17b**, $k_{\mathbf{11,12}} = 0.43 \times 10^{-5}$ s^{-1}, $k_{\mathbf{11,13}} = 0.16 \times 10^{-5}$ s^{-1}. [g] Determined by means of a calibration curve from the decay of the IR absorption of **11c** at 1798 cm^{-1}.



Scheme 2. Thermal rearrangements at 60–80 °C of (arylimino)diaziridines **4**; for reaction conditions, see Table 1.



Scheme 3. Thermal rearrangements at 60–100 °C of (arylimino)diaziridines **11**; for reaction conditions, see Table 1.

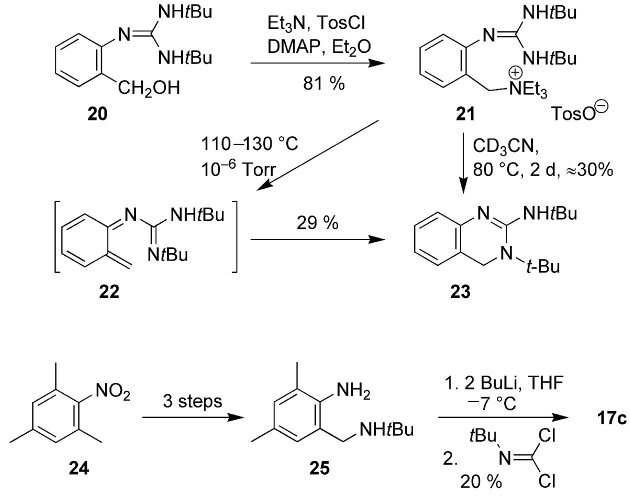
The ratios **9**/**10** found on thermolysis of **4** resemble those that were obtained from **1** in elimination experiments at room temperature or below and attributed to rearrangements of intermediates **5** (**9a**/**10a** 97:3 to 98:2, **9c**/**10c** 10:90).[3] Therefore, it is highly probable that the aminobenzimidazoles **10**, thermally generated from **4**, also arise by triaza-Cope rearrangement of the intermediate valence isomers **5** en route **4**→**5**→**8**→**10**.[12] However, we cannot exclude that a small fraction of **10** is formed by a mechanism beginning with a [1,5] N shift **4**→**8**.

The polarity of the solvent did not affect the ratios **9**/**10** (cf. entries 2/5, 6/7, and 8/9, Table 1). This indicates that both, the electrocyclic ring-opening of **5** to afford the putative 1,5-dipoles (*Z*)-**7** and the triaza-Cope rearrangement of **5**, show a very similar solvent dependence, as expected for pericyclic reactions.[13]

Thermolysis of *ortho*-disubstituted (arylimino)diaziridines **11** furnished mixtures of several products (Scheme 3), not only of two as in case of **4**. Small amounts of azo compounds **15** and *tert*-butyl isocyanide (**16**) arose by [2+1]-cycloelimination of 1-aryl-3-iminodiaziridines **12**,[9] which were formed from **11** by valence isomerization. Deeply yellow isomers of **11** made the appearance as major components of the mixtures. They were identical with dihydro-3a*H*-benzimidazole derivatives **14**, which previously had been isolated on elimination of sulfuric acid from **1** and rationalized by triaza-Cope rearrangement of intermediates **12**.[3] Most probably, the yellow compounds **14** were generated in this way via **12** also in the present study, but a fraction might have been formed by a [1,5] N shift **11**→**14** involving one of the ring nitrogen atoms of **11**.

When the thermolyses were monitored by recording UV/Vis spectra, formation of **14** was observed, but no isosbestic points were detected. Their absence indicated that the yellow compounds **14** were not persistent under the reaction conditions. Thus, prolonged heating of concentrated solutions of **11a** and **11c** afforded Diels–Alder dimers **19a** and **19c**, respectively, of the yellow compounds **14a** and **14c** (Table 1, entries 10/17). On heating of more dilute solutions of **11b** and **11c** for shorter periods of time (entries 11/12/14/16), formation of aromatic benzimidazoles **18b** and **18c**, respectively, was observed. Obviously, **14b** and **14c** slowly lost formally CH_2, probably in a radical sequence.[14] The dimerization **14c**→**19c** and the thermal degradation in boiling heptane of **14b** and **14c** have already been described.[3] Separation of the mixtures by chromatography uncovered the presence of a second type of major products, which turned out to be colorless isomers of **11**. As these were missing, when the unstable 1-aryl-3-iminodiaziridines **12** were generated from **1** by elimination at room temperature,[3] an involvement of **12** in the formation could be excluded. Consequently, the colorless isomers were attributed to a rearrangement of **11**. Spectroscopic evidence indicated that one of the *ortho* methyl groups of **11** participated in the isomerization.

The 2-amino-3,4-dihydroquinazoline structures **17** of the colorless isomers of **11** were established by independent synthesis of **17c** (Scheme 4; for details, see Supporting Information). Toward this end, we initially explored a synthetic route to the parent compound **23**, which started with the addition of the hydrochloride of 2-aminobenzyl alcohol at bis(*tert*-butyl)carbodiimide to yield guanidine **20**. Attempts at tosylation of **20** under a variety of conditions gave intractable mixtures, except in the presence of triethylamine, which afforded the stable quaternary ammonium salt **21**. Dry thermolysis of **21** under high vacuum or prolonged heating of its solution in acetonitrile gave **23**. However, low yield of the last step and expectation of further obstacles to the synthesis of homolog **17c** on this route let us resort to the cyclization of *o*-aminobenzylamine **25**.[15] NBS bromination of **24** gave a 1:1 mixture of the *o*- and *p*-nitrobenzyl bromides which reacted with *tert*-butylamine to afford a 1:2 mixture of the *o*- and *p*-nitrobenzyl-*N*-*tert*-butylamines. Separation by crystallization of the hydrochlorides followed by hydrogenation of the *o*-isomer furnished **25**. Lithiated **25** reacted with *tert*-butyl isocyanide dichloride to yield a mixture of products from which chromatography separated **17c**, which was identical with the colorless thermolysis product of **11c**.



Scheme 4. Syntheses of 2-amino-3,4-dihydroquinazolines.

The formation of **17** can be explained if an antarafacial [1,7] H shift in **11** is assumed as first step.[16,17] Conformations of **11** in solution that resemble the conformation of **11c** adopted in the solid state (Figure 1)[18] are perfectly suited to this process. The resulting orthoquinonoide intermediates[19] **13** undergo 1,6-electrocyclization to afford the 2-amino-3,4-dihydroquinazolines **17**.

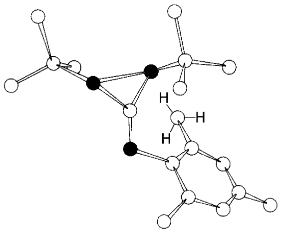
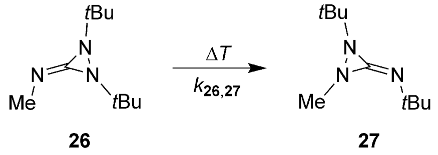


Figure 1. Conformation of (arylimino)diaziridine **11c** apt to yield **13c** by antarafacial [1,7] H shift (adopted from ref. 18).

Kinetic Experiments

The first-order rate constants k measured for the decay of **4** and **11** indicate that the thermal stabilities of (arylimino)diaziridines are quite limited and almost unaffected by the polarity of the solvents (Table 1, entries 2/4). As no intermediates were observed during the course of the thermolysis experiments, the rearrangements of **4** and **11** are the slow steps of the reaction cascades. Provided that they begin as depicted in Scheme 2 and Scheme 3, the experimental rate constants k can be assigned to the valence isomerizations **4**→**5**, **11**→**12** and the [1,7] H shift **11**→**13**, viz., $k = k_{\mathbf{4,5}}$ (entries 1–9) and $k = k_{\mathbf{11,12}} + k_{\mathbf{11,13}}$ (entries 11/13). As both ring nitrogen atoms, N_{syn} and N_{anti}, of **4**, **11**, and **26** can participate in the valence isomerizations, their rate constants are sums of the rate constants for N_{syn} and N_{anti}.

Alkyl substituents of the aryl rings of **4** accelerate the [1,3] N shift **4**→**5**, as long as there is one unoccupied *ortho* position (cf. entries 4/6/8 and 5/7/9). Blocking of the free *ortho* position of **4c** by a methyl group to furnish **11b** retards the valence isomerization by more than an order of magnitude (cf. entries 8/11 and 9/13). The reason can be detected in Figure 1: A 2,6-dimethylphenyl ring cannot adopt a conformation that is coplanar with the diaziridine ring and hence optimal for conjugation with the 1,3-diazaallyl moiety in the transition structure of the [1,3] N shift. Nevertheless, all aryl rings of **4** and **11** accelerate the [1,3] N shifts compared with the methyl group of **26**.[4] For example, formal exchange of the methyl group of **26** for a phenyl ring to afford **4a** lowers the enthalpy barrier by 14 kJ mol⁻¹ from $\Delta H^{\ddagger}_{\mathbf{26,27}} = 123\ \text{kJ mol}^{-1}$ (Scheme 5) to $\Delta H^{\ddagger}_{\mathbf{4,5}} = 109\ \text{kJ mol}^{-1}$ while the entropy of activation remains close to zero.



Scheme 5.

Conclusions

(Arylimino)diaziridines **4** and **11** are labile systems and isomerize at temperatures above 60 °C in two simultaneous cascades of pericyclic reactions, depending on the substitution pattern of the aromatic rings. If an *ortho* position is unoccupied as in **4**, both cascades commence with the valence isomerization to unstable 1-aryl-3-iminodiaziridines **5** and continue by ring expansions of **5** to five-membered ring heterocycles, viz., 3-amino-2*H*-indazoles **9** and 2-amino-1*H*-benzimidazoles **10**. In contrast, two *ortho* methyl groups as in **11** still permit valence isomerization to **12** and subsequent triaza-Cope rearrangement of **12** to 3a*H*-benzimidazoles **14**, but prohibit ring expansion of **12** to indazoles. Instead, a novel cascade originates from **11** by [1,7] H shift which involves one of the *ortho* methyl groups and eventually leads to aminodihydroquinazolines **17**. The only fleeting existence of 1-aryl-3-iminodiaziridines and the rate constants of the decay of (arylimino)diaziridines show that aryl groups do *not* increase thermal stability compared to alkylsubstituted iminodiaziridines. Instead, aryl rings accelerate the valence isomerization by [1,3] N shift and give rise to additional pericyclic rearrangements.

Experimental Section

General: Synthetic procedures for **15**, **17c**, and **23**; NMR, IR, and UV/Vis spectra; and conversion-vs.-time diagrams are reported in the Supporting Information. Petroleum ether had a boiling range of 50–70 °C.

Thermolysis of 4a: A solution of **4a** (49 mg, 0.20 mmol) in dry benzene (ca. 1 mL), contained in a sealed, degassed NMR sample tube, was heated at (60.0 ± 0.2) °C for 40 h, while the ratios of **4a** and the thermolysis products **9a** and **10a** were monitored by ^{1}H NMR spectroscopy (**9a**/**10a** = 94:6). Evaporation of the solvent in a stream of N_2 and recrystallization of the residue from hexane afforded colorless needles of **9a** (30.5 mg, 62%, m.p. 97–98 °C).

Thermolysis of 11a: A solution of **11a** (2.73 g, 10 mmol) in hexane (5 mL) was heated under reflux for 90 h. Crystals of **19a** precipitated from the cooled solution, which were isolated by filtration and dried in vacuo: Yellow crystals (0.89 g, 33%, m.p. 164–164.5 °C). ^{1}H NMR (600 MHz, HH-COSY, HC-HSQC, HC-HMBC, C_6D_6): δ = 0.917 (s, 3 H, 3-CH_3), 1.089 (s, 3 H, 16-CH_3), 1.349 (s, 3 H, 11-CH_3), 1.6–1.8 (br., 18 H), 1.712, 1.744 (s, 9 H), 1.804 [dd, ^4J(H,H) = $^5J_{H,H}$ = 1.5 Hz, 3 H, 8-CH_3], 2.499 (m, $^3J_{H,H}$ = 7.3 Hz, 1 H, 10-H), 2.546 (part of AB spectrum, $^3J_{H,H}$ = 7.3 Hz, 1 H, 2-H), 3.301 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, 1-H), 5.265 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 18-H), 5.497 (dq, $^3J_{H,H}$ = 3.6, $^4J_{H,H}$ = 1.5 Hz, 1 H, 9-H), 5.899 (dd, $^3J_{H,H}$ = 8.0, 7.0 Hz, 1 H, 17-H) ppm. ^{13}C NMR (151 MHz, C_6D_6): δ = 16.40 (11-CH_3), 17.30 (8-CH_3), 21.61 (16-CH_3), 27.70 (3-CH_3), 32.30, 32.47 [$(CH_3)_3$], 44.78 (HC-2), 46.73 (C-11), 47.51 (HC-1), 54.15, 54.26, 55.19, 55.46 (quat. C), 56.79 (HC-10), 69.96 (C-3), 74.39 (C-16), 132.20 (C-8), 132.23 (HC-17), 133.64 (HC-9), 134.25 (HC-18), 158.56 (C-5), 159.79 (C-14), 181.90 (C-7), 197.94 (C-12) ppm. IR (Nujol): $\tilde{\nu}$ = 1670 (m), 1649 (m), 1612 (s) cm^{-1}. UV (hexane): λ_{max} [nm] ($\log\varepsilon$) = 328 (3.65), 260 (4.19). EI MS (70 eV): *m*/*z* = 546 [M^+]. $C_{34}H_{54}N_6$ (546.8): calcd. C 74.68, H 9.95, N 15.37, mol. mass 546.8; found: C 74.70, H, 9.81, N 15.36, mol. mass 545 (osmometric in $CHCl_3$). Chromatography of the mother liquor on silica gel with CH_2Cl_2 gave a yellow oil (1st fraction, 0.55 g), half of which consisted of **15a** (^{1}H NMR). The oil was dissolved in pentane (20 mL). The solution was extracted with aq. HCl (2 M, 4 × 20 mL). Drying of the organic layer with K_2CO_3 and distillation of the solvent in vacuo yielded **15a** as yellow oil (0.20 g, 10%).

Thermolysis of 11b: A solution of **11b** (3.30 g, 10 mmol) in heptane (400 mL) was heated under reflux for 8 h, followed by distillation of the solvent in vacuo into a receiver cooled to –78 °C. The distillate contained **16** (GC, comparison with an authentic sample). The residue was chromatographed with CH_2Cl_2 on a water-cooled column, packed with silica gel, to afford **15b** as yellow oil (51 mg, 2%, UV/Vis). Repeated distillation at room temp./2×10^{-5} Torr in a sublimation apparatus yielded a yellow oil, which crystallized to give orange-yellow crystals of **15b** (46 mg, 2%, m.p. 94 °C). Elution with CH_2Cl_2/triethylamine (20:1) gave yellow, greasy crystals (2.20 g), whose components were separated by chromatography on a water-cooled column, packed with basic Al_2O_3. Elution with benzene/chloroform (4:1) furnished yellow cubes of **14b** (1st fraction, 1.25 g, 38%, m.p. 84 °C, from petroleum ether at low temp.) and colorless crystals of **18b** (2nd fraction, 0.23 g, 7%, m.p. 114 °C, from petroleum ether at low temp.). Elution with diethyl ether gave colorless crystals of **17b** (0.26 g, 8%, m.p. 87 °C, from petroleum ether at low temp.). ^{1}H NMR (60 MHz, CCl_4): δ = 1.10, 1.25, 1.48 (s, 9 H), 2.28 (s, 3 H), 3.73 (br. s, 1 H), 3.87 (s, 2 H), 6.68, 6.89 (m, 1 H) ppm. ^{1}H NMR (60 MHz, C_6D_6): δ = 1.00, 1.35, 1.47 (s, 9 H), 2.57 (s, 3 H), 3.67 (br. s, 1 H), 3.87 (s, 2 H), 6.85, 7.14 (m, 1 H) ppm. UV (ethanol) λ_{max} [nm] ($\log\varepsilon$) = 281 (4.81), 217 (4.33). IR (Nujol): $\tilde{\nu}$ = 3465, 1620 cm^{-1}. EI MS (70 eV): *m*/*z* = 329 [M^+]. $C_{21}H_{35}N_3$ (329.5): calcd. C 76.74, H 10.71, N 12.75; found C 76.31, H 10.59, N 12.63.

Thermolysis of 11c: (a) A solution of **11c** (2.87 g, 10 mmol) in heptane (500 mL) was heated under reflux for 6 h, followed by distillation of the solvent in vacuo and drying of the residue at 10^{-3} Torr to afford a viscous, yellow oil consisting of **14c**, **15c**, **17c**, and **18c** (65:3:22:10, ^{1}H NMR). Chromatography on basic Al_2O_3 with pentane/diethyl ether (8:1) yielded a yellow oil (1.27 g) which was separated by chromatography on silica gel with CH_2Cl_2 into **15c** (2.3% by UV/Vis, yellow oil) and, by elution with CH_2Cl_2/triethylamine (20:1), crude **14c**. This was chromatographed again on basic Al_2O_3 with pentane/diethyl ether (20:1) and distilled in a molecular distillation apparatus at 60–65 °C bath temp./10^{-3} Torr to furnish **14c** as yellow oil (0.48 g, 17%). The 1st chromatography on basic Al_2O_3 was continued by elution with pentane/diethyl ether (4:1) to yield crystals (0.33 g), which were recrystallized from petroleum ether to yield colorless crystals of **18c** (0.22 g, 8%, m.p. 120.5–121.5 °C). The 1st chromatography on basic Al_2O_3 was further continued by elution with diethyl ether to yield an oil (0.53 g), which crystallized from pentane at –20 °C to afford colorless crystals of **17c** (0.29 g, 10%, m.p. 83–85.5 °C). Repeated recrystallization from petroleum ether raised the m.p. to 87.5–88.5 °C. (b) A solution of **11c** (2.87 g, 10 mmol) in hexane (10 mL) was heated under reflux for 51 h, followed by chromatography on basic Al_2O_3 with pentane. The 1st fraction (yellow oil, 1.51 g) was distilled in a molecular distillation apparatus at 60–65 °C bath temp./10^{-3} Torr to furnish **14c** as yellow oil (1.04 g, 36%). The nonvolatile residue (0.38 g, 13%) was recrystallized from petroleum ether to give pale yellow crystals of **19c** (m.p. 133–134.5 °C).

Kinetic Experiments: NMR sample tubes were carefully freed from traces of acids, dried at 150 °C, attached to a vacuum line (10^{-5} Torr), and charged with an iminodiaziridine (ca. 0.3 mmol). Solvents were kept over a drying agent ($LiAlH_4$ for benzene; CaH_2 for acetonitrile), degassed, and transferred in vacuo into the sample tubes, which were degassed by means freeze-pump-thaw cycles and sealed with a torch. The NMR sample tubes were completely immersed in a thermostat (±0.2 °C). Progress of the thermolyses was monitored by ^{1}H NMR spectra (90 MHz, relative TMS as internal standard). Ratios of starting materials and products were determined by 6–8 integrations of *tert*-butyl signals in ^{1}H NMR spectra, recorded at expanded scale (3 Hz/cm). Peak heights were used in rare cases, when signal separation was not sufficient for satisfactory integration. The errors, given in Table 1 for the first-order rate constants *k*, are statistical errors of non-linear least-squares fits.

Supporting Information (see also the footnote on the first page of this article): General experimental and syntheses of authentic compounds (6 pages), NMR spectra (10 pages), UV/Vis spectra (1 page), IR spectra (1 page), conversion-vs.-time diagrams (2 pages).

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