Synthesis and Thermolysis of a Chiral, Non-Racemic Iminoaziridine[1]

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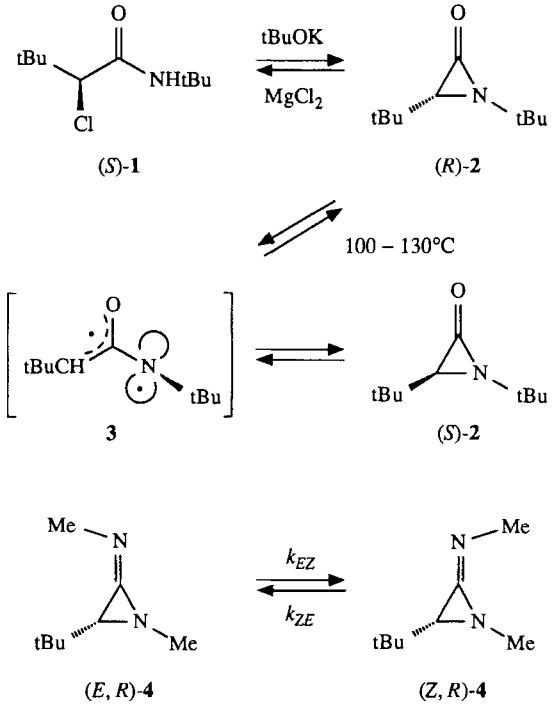
Received March 9, 1994

Key Words: Aziridines, 2-imino-, chiral, non-racemic / Imidoyl halides, 2-halo / Imidates, 2-chloro / 1,3,2-Thiazaphospholidines / Amidines, 2-halo / 1,3-Elimination, inversion of configuration in / *E/Z* Diastereomerization / [2 + 1] Cycloreversion, kinetics of thermal

The 2-halo imidoyl chlorides **7** are obtained from the amide **5** and the 2-halo amides **6** by the action of phosphorus pentachloride and thionyl chloride, respectively. Non-racemic (*S*)-**6a** is converted into **7a** which is racemic, however. The reaction of Lawesson's reagent with **6a** furnishes the diastereomeric 1,3,2-thiazaphospholidine derivatives **15**. Treatment of (*S*)-**6a** (98% ee) with methyl triflate affords 2-chloro imidate **8** (95% ee) which reacts with methanamine in the presence of methanammonium chloride to yield the 2-chloro amidine (*S*)-**9a** (90% ee). The 2-halo imidoyl halides **7a** and **b** react with methanamine to produce the 2-halo amidines **9a** and **b**. – Strong bases, e.g. potassium *tert*-butoxide or sodium hydride in the presence of catalytic amounts of *tert*-butyl alcohol, eliminate hydrogen chloride or bromide from the 2-halo amidines **9a** and **b** and (*S*)-**9a** to yield mixtures of the 2-iminoaziridines (*E*)- and (*Z*)-**4**, and (*E,R*)- and (*Z,R*)-**4** (83% ee), respectively. The 1,3-elimination of hydrogen bromide from **9b** is diastereoselective at −30 to −40°C [(*E*)-**4**:(*Z*)-**4** = <10:>90]. The diastereomers equilibrate at 36°C with $(k_{EZ} + k_{ZE}) = (5.92 \pm 0.08) \cdot 10^{-5}\ s^{-1}$ ($K = k_{EZ}/k_{ZE} = 0.428 \pm 0.013$). – The thermolysis of (*E*)- and (*Z*)-**4** in [D_6]benzene solution yields the imine **16** and methyl isocyanide (**17**). The decomposition follows the first-order rate law. The following Arrhenius and Eyring parameters are calculated from five rate constants obtained in the temperature range of 70–110°C: $E_a = (115.2 \pm 0.4)$ kJmol^{-1}, lg$A = (12.06 \pm 0.28)$, $\Delta H^{\neq} = (112.1 \pm 0.4)$ kJmol^{-1}, $\Delta S^{\neq} = (-23.9 \pm 0.7)$ JK^{-1} mol^{-1}, $\Delta G^{\neq}_{373K} = 121$ kJmol^{-1}. The enantiomeric excess of the surviving fraction of (*E,R*)- and (*Z,R*)-**4** is unchanged after two half-lives at 80°C.

Recently, we demonstrated that the formation of the chiral non-racemic aziridinone (*R*)-**2** from the α-chloro amide (*S*)-**1** by base-promoted dehydrochlorination[2] as well as the nucleophilic cleavage of the N–C(3) bond of (*R*)-**2**[3,4] occur with inversion of configuration, thus excluding the intervention of achiral (acyclic) intermediates. In the temperature range of 100–170°C, however, slow racemization accompanies the thermolysis of (*R*)-**2** and indicates the existence of an achiral or a racemic transient, e.g. (*M*)-**3** + (*P*)-**3**. Indeed, high-level quantum-chemical calculations reveal that an activation energy of (170 ± 25) kJmol^{-1} is required for the unimolecular ring opening of the parent aziridinone which affords a species of high diradical character[4]. Subsequently, the unstable *N*-phenylaziridinone invoked in the decomposition of the (*S*)-2-bromopropananilide anion was shown to react with *tert*-butylamine or dimethylformamide with inversion of configuration at C(3)[5]. Thus, the stereochemical evidence *in the series of 3-alkylaziridinones* excludes achiral (acyclic) aziridinone isomers as intermediates *at low temperatures*[6]. Similar stereochemical studies are still missing in the related series of iminoaziridines. Therefore, we report on the synthesis and thermolysis of the diastereomeric chiral racemic (*E*)- and (*Z*)-(**4**)[7] and non-racemic iminoaziridines (*E,R*)- and (*Z,R*)-**4**.



Racemic Iminoaziridines (*E*)- and (*Z*)-4

Though a photochemical route to the iminoaziridines (*E*)- and (*Z*)-**4** has been devised more recently, i.e. the photoextrusion of molecular nitrogen from the 5-alkylidenedihydrotetrazole **10**[8], the base-induced dehydrohalogenation of the α-chloro (**9a**) or α-bromo amidine **9b**[7] remains the

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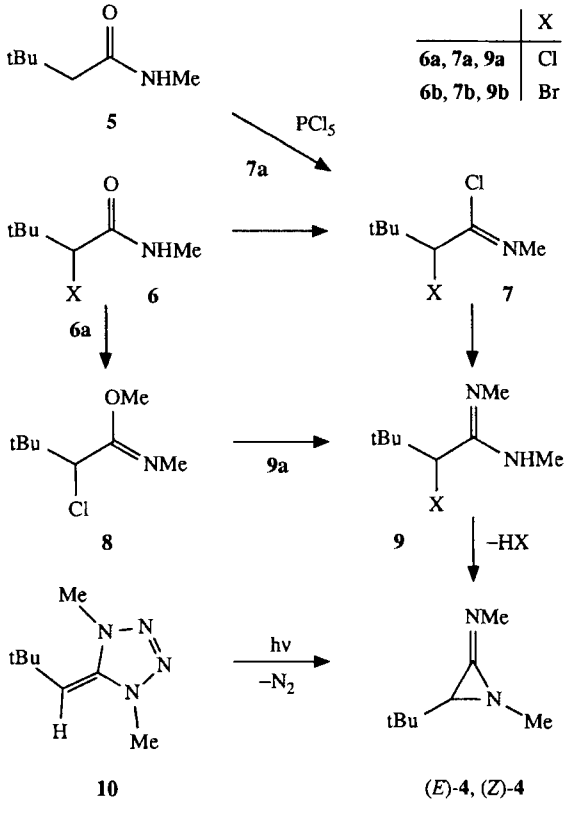
method of choice if substantial amounts of product are required. Even more important, (*S*)-2-chloro-3,3-dimethylbutanoic acid of high enantiomeric excess (≥ 97%) has become conveniently available[2], and several established routes starting from this α-chloro acid promised to lead to the non-racemic (*S*)-2-chloro amidine (*S*)-**9**. For these reasons, the synthesis of the racemic iminoaziridines (*E*)- and (*Z*)-**4**, required for preliminary studies, started from the *N*-methyl amides of 3,3-dimethylbutanoic acid (**5**), 2-chloro-3,3-dimethylbutanoic acid (**6a**), or 2-bromo-3,3-dimethylbutanoic acid (**6b**) which were converted into the α-halo imidoyl chlorides **7a** and **b**, respectively, by the action of phosphorus pentachloride (**5** → **7a**) or thionyl chloride (**6a** → **7a**, **6b** → **7b**[9]). Treatment of the α-halo imidoyl chlorides **7** with an excess of methanamine at low temperature afforded the α-halo amidines **9** in high yields as colourless oils distillable in vacuo (Table 1). Sealed in glass tubes and kept at −25°C, they can be stored for long periods of time. Alternatively, they may be converted into the crystalline perchlorates **9**·$HClO_4$ which are shelf-stable. As expected[10], both amidinium perchlorates **9**·$HClO_4$ exist in the *E,Z* configuration as shown by the proton (Table 2) and carbon-13 NMR spectra (Table 3) which exhibit signals originating from two different *N*-methyl groups.

The 1,3-dehydrohalogenation of the α-halo amidines **9a** and **b** is induced by strong bases in diethyl ether or tetrahydrofuran, e.g. potassium *tert*-butoxide or sodium hydride in the presence of catalytic amounts of *tert*-butyl alcohol, to yield mixtures of the diastereomeric iminoaziridines (*E*)- und (*Z*)-**4** as colourless, volatile, typically smelling oils (Table 1), which are stable for long times in sealed tubes at low temperatures.

The formation of the iminoaziridines (*E*)- und (*Z*)-**4** from the α-halo amidines **9a** and **b** can be conveniently monitored by IR spectroscopy because the IR spectra of the former are characterized by a strong absorption at 1805 cm^{-1}, while the latter absorb in the usual range of amidine C=N frequencies[10]. By analogy with the interpretation of the IR spectrum of methylenecyclopropane[11], the very high wavenumber of the C=N absorption of iminoaziridines has to be ascribed to a strong coupling of the C=N vibration with a vibration of the aziridine ring[12]. The assignment of configuration for (*E*)- und (*Z*)-**4** is based on the extent of the long-range coupling between the ring proton and the methyl protons of the $C{=}NCH_3$[8] moiety and an asymmetric solvent-induced shift (tetrachloromethane or [D]trichloromethane vs. [D_6]benzene). This high-field shift, which is caused by the asymmetric solvation of the $C{=}NCH_3$ moiety by [D_6]benzene molecules, is larger for protons *cis* to the imino methyl group than for *trans* protons[8,13].

The ratio of the diastereomers (*E*)- und (*Z*)-**4** in the mixture produced and isolated at or slightly below room temperature is 57:43. When the dehydrobromination of **9b** is carried out at −40°C followed by workup at low temperatures, the *Z* diastereomer (*Z*)-**4** is preferred [(*E*)-**4**:(*Z*)-**4** = < 10:> 90]. The *E/Z* equilibration can be monitored conveniently by proton spectroscopy leading to $(k_{EZ} + k_{ZE})$ = (5.92 ± 0.08)·$10^{-5}s^{-1}$ and $K = k_{EZ}/k_{ZE}$ = (*Z*)-**4**/(*E*)-**4** = (0.428 ± 0.013) at 36°C in the absence of solvent, $\Delta G^{\neq}$ = 97.5 $kJmol^{-1}$. In contrast to the dehydrobromination of **9b**, photoextrusion of molecular nitrogen from the neopentylidenedihydrotetrazole **10** at low temperatures produces predominantly the *E* diastereomer [(*E*)-**4**:(*Z*)-**4** = 95:5 at −60°C][8]. By analogy with the formation of aziridinones from α-bromo amide anions[5], anions of the α-halo amidines **9a** and **b** are probably involved in the base-induced dehydrohalogenation which decompose into the halide ion and the iminoaziridine (*Z*)-**4**. Thus, the high *Z* diastereoselectivity may be traced back to the relative stability of diastereomeric α-bromo amidine anions. Apparently, the anion with the *Z,Z* configuration, which leads to (*Z*)-**4**, is more stable because repulsion of the nitrogen lone pairs is minimized in this particular configuration.



Non-Racemic Iminoaziridines (*E,R*)- and (*Z,R*)-4

Since the non-racemic α-chloro amide (*S*)-**6a** (98% ee) is readily available from (*S*)-*tert*-leucin[2], the synthesis of the non-racemic iminoaziridines (*E,R*)- and (*Z,R*)-**4** appeared to be straightforward on the route via the α-chloro imidoyl chloride followed in the preparation of racemic (*E*)- and (*Z*)-**4**. Treatment of (*S*)-**6a** with thionyl chloride yielded the α-chloro imidoyl chloride **7a** which was racemic, however, as shown by the proton spectrum obtained in the presence of Pirkle's alcohol **11** as chiral shift reagent[14] which was employed throughout this work. Presumably, deprotonation/reprotonation at the α-carbon atom had occurred in a step of the sequence. In order to shed some light on this process, we treated in separate experiments racemic **6a** and [D]**6a**, the amide proton of which had been replaced

Table 1. Precursors, reagents, solvents, reaction conditions, yields, ratios of *E*/*Z* diastereomers, boiling points, and spectroscopic data (recorded from solutions in tetrachloromethane) of some 3,3-dimethylbutanoic acid derivatives and the iminoaziridines (*E*)-**4** and (*Z*)-**4**

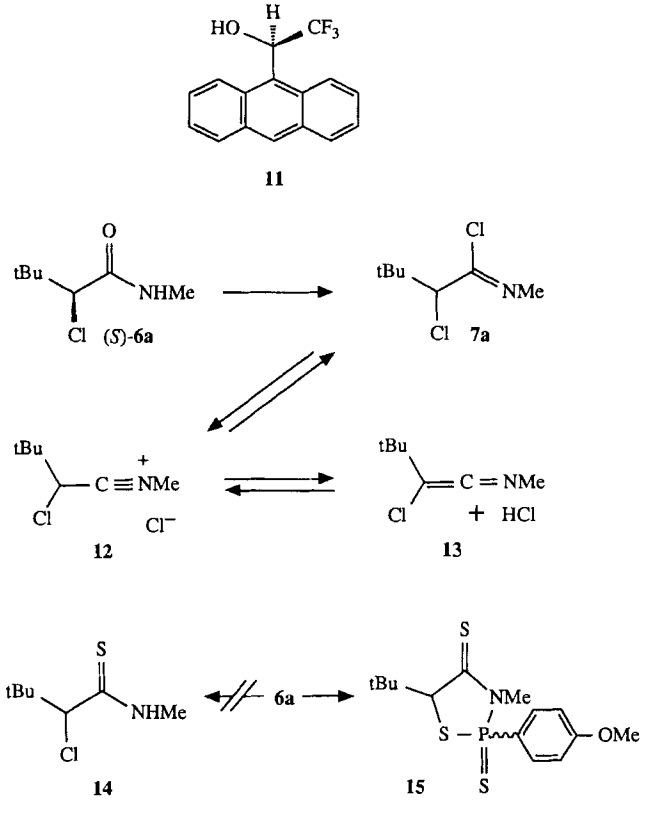
Cpd.	Pre-cursor	Reagent, Solvent	Condition [°C/h]	Yield [%]	(*E*)-**4** : (*Z*)-**4**	b. p. [°C/Torr]	IR [cm^{-1}] C=N	(CCl_4) NH
7a	**5**	PCl_5, cyclohexane	85/7	72		85 – 87/23	1680, 1710	
	6a	$SOCl_2$, trichloromethane	65/1.5	65		83 – 84/16		
8	**6a**	1. F_3CSO_3Me 2. $KHCO_3$, H_2O	20–25/240	83		33 – 34/10^{-2}	1683	
15	**6a**	$[(4\text{-}MeOC_6H_4PS_2)]_2$ toluene	95/2	55		85 – 86[a]	1580, 1565 (C=C)	
9a	**7a**	$MeNH_2$, pentane	–20/1	68		48 – 50/10^{-2}	1642	3450
	8	$MeNH_2$, $MeNH_3^+Cl^-$ MeOH	65/5	88		30 – 31/10^{-3}		
9b	**7b**	$MeNH_2$, petroleum ether	–20 → 25/20	84		30 – 31/5·10^{-4}	1642(s)	3445 (m) 3380 (br)[b]
(*E*)-**4**, (*Z*)-**4**	**9a**	*t*BuOK, Et_2O	0/10	49	57 : 43	20 – 25/10^{-2}	1805	
		NaH (*t*BuOH), THF	20–25/40	71	57 : 43			
	9b	NaH, THF	20–25/70	65				
		*t*BuOK, Et_2O	–40 → –30/3	23	<10 : >90			

[a] Melting point. – [b] Recorded in the absence of solvent.

by deuterium, in sealed NMR sample tubes at 65°C with a mixture of thionyl chloride and [D]trichloromethane (3:1) and monitored the course of the reaction by proton spectroscopy. The amide **6a** reacted somewhat faster than its isotopomer [D]**6a** (82% vs. 62% conversion after three hours). The α-proton of the α-chloro imidoyl chloride obtained from [D]**6a** had been replaced by deuterium to a considerable extent (> 50%). A probable mechanism of this exchange involves equilibration of **7a** with the nitrilium chloride **12** and the ketene imine **13** plus hydrogen chloride[15] followed by the addition to **13** of deuterium chloride which was formed from [D]**6a** and thionyl chloride.

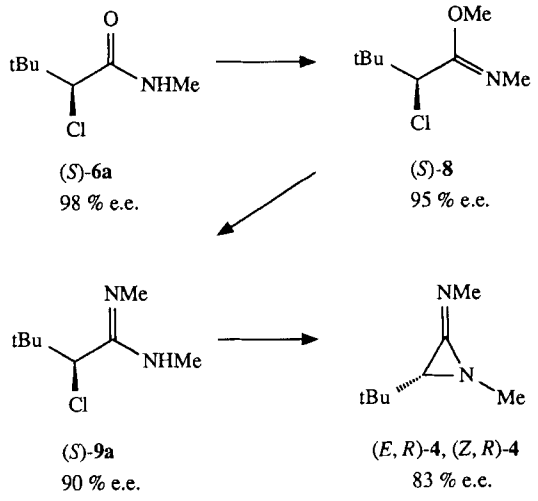
A second attempt to convert the α-chloro amide (*S*)-**6a** into a reactive non-racemic derivative suitable for the reaction with methanamine failed likewise. Treatment of **6a** at 95°C in toluene as solvent with Lawesson's reagent did not yield the expected α-chloro thioamide **14** but a chlorine-free, phosphorus-containing product as a mixture of two diastereomers (6:1, proton NMR analysis). The 1,3,2-thiazaphospholidine structure was assigned to the components of this mixture on the basis of analytical and spectroscopic evidence. The relative configurations were not determined, however.

Eventually, the long-known imidate route to amidines[16] was followed. Because the chlorine atom in the α-position reduces the reactivity of **6a** toward methylating agents, even methyl triflate in the absence of solvent reacted only slowly with **6a**. Nevertheless, after several days at ambient temperature and workup with aqueous potassium hydrogen carbonate, a high yield of the imidate **8** was realized which was obtained as a colourless oil distillable in vacuo. It was



even more gratifying that, when the reaction started from non-racemic (*S*)-**6a** (98% ee), the enantiomeric excess of the product (*S*)-**8** was still as high as 95%.

While the imidate **8** was very reluctant toward methanamine in the absence of acid catalysis[17], an excess of methanamine in boiling methanol in the presence of one mol of methanammonium chloride smoothly converted (*S*)-**8** into the amidinium chloride (*S*)-**9a**·HCl from which the free base (*S*)-**9a** was obtained in 88% yield with only little racemization (90% ee).

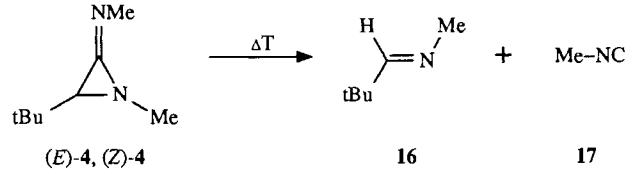


The 1,3-dehydrochlorination of the non-racemic α-chloro amidine (*S*)-**9a** was carried out as before by means of the preferred base-solvent combination, i.e. sodium hydride in tetrahydrofuran in the presence of a catalytic amount of *tert*-butyl alcohol. The mixture of diastereomeric iminoaziridines (*E,R*)- and (*Z,R*)-**4** was isolated in 71% yield. Both diastereomers possessed an enantiomeric excess of 83%. Rigorous proof of the absolute configuration of the diastereomers was not attempted. Because it is reasonable to assume that the steric course of aziridine ring formation is the same, i.e. inversion, in both the 3-alkylaziridin-2-one and the 3-alkyl-2-iminoaziridine series, we assign the *R* configuration to the iminoaziridines obtained from (*S*)-**9a**. Thus, a consistent mechanistic picture describes the sequence of events: Deprotonation by a strong base affords the α-bromo amide and the α-chloro amidine anion, respectively, which decompose on a semi-W path[18] into the aziridine derivative and a halide ion.

Thermolysis of the Iminoaziridines (*E*)- and (*Z*)-4

Iminoaziridines decompose thermally into imines and isocyanides at temperatures that depend on the nature of the alkyl groups attached to the ring nitrogen atom and the imino group[7]. This thermolysis poses an upper limit on the temperature range suitable for a study of reagent-induced ring opening reactions. The question whether the decomposition is a truly unimolecular process has not been answered as yet, neither is any quantitative information available concerning rate constants and the activation barrier. Furthermore, monitoring the enantiomeric excess of (*R*)-**4** at higher temperatures would perhaps uncover a thermal generation of achiral or racemic transients as has been the case in the thermolysis of the aziridinone (*R*)-**2**[4].

Therefore, we embarked on a kinetic study of the thermolysis of racemic **4** and non-racemic (*R*)-**4**. To this end, carefully degassed solutions in [D_6]benzene were heated in evacuated, sealed NMR sample tubes to temperatures between 70 and 110°C. In a very clean process, the imine **16** and methyl isocyanide (**17**) emerged as the sole products within the limits of detection (1%). Integration of the proton signals of the *tert*-butyl groups during 2–3 half-lives demonstrated a perfect first-order behaviour for the decomposition (Figure 1) and yielded the rate constants summarized in Table 4 which were calculated by the non-linear least-squares method[19].



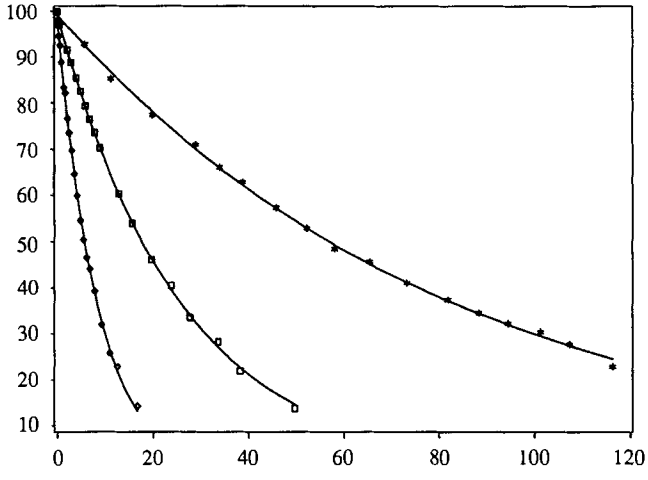


Figure 1. Conversion [%] vs. time [h] in the thermal decomposition of (*E*)- and (*Z*)-**4** in [D_6]benzene solution at 343.16 (*), 353.16 (□), and 363.16 K (◇)

From the temperature dependence of the rate constants according to the Arrhenius equation, $\ln k = \ln A - E_a/RT$ (Figure 2), and the Eyring equation, $\ln k/T = \ln k_B/h + \Delta S^{\neq}/R - \Delta H^{\neq}/RT$, the following parameters of activation are obtained: E_a = (115.2 ± 0.4) kJmol^{-1}, lg A = (12.06 ± 0.28), and $\Delta H^{\neq}$ = (112.1 ± 0.4) kJmol^{-1}, $\Delta S^{\neq}$ = (−23.9 ± 0.7) JK^{-1}mol^{-1}, $\Delta G^{\neq}_{373K}$ = 121 kJmol^{-1}.

The iminoaziridines (*E*)- and (*Z*)-**4** are thermally rather labile. The free enthalpy of activation for the decomposition, extrapolated to 36°C ($\Delta G^{\neq}_{309K}$ = 119.5 kJmol^{-1}), is higher than that of the *E/Z* isomerization by only 22 kJmol^{-1}. A few kinetic studies[4,20] of thermal [2+1] cycloeliminations have been carried out, but accurate parameters of activation are scarce. We note that the entropy of activation for the thermolysis of (*E*)- and (*Z*)-**4** is different from what is to be expected for normal unimolecular thermal reactions ($\Delta S^{\neq} \approx 0$[21]), i.e. it is relatively large and negative. This is indicative of a constrained transition state

From 1995:
The new "Chemische Berichte" and "Liebigs Annalen" will be published exclusively in English!

Dear Reader,

You may already have heard about the decisions made by the Board of the German Chemical Society regarding the future of some of our core journals. As Managing Editor of "Chemische Berichte" and "Liebigs Annalen der Chemie", I would like to inform readers and authors, especially those from outside Germany, about the planned alterations.

- The division of "Chemische Berichte" into Parts A (Inorganic Chemistry) and B (Organic Chemistry) will be discontinued. In future, the important fields of inorganic chemistry and organic chemistry will each be allocated a separate journal. Part B of "Chemische Berichte" together with "Liebigs Annalen der Chemie" will form the new "Liebigs Annalen". Part A of the former "Chemische Berichte" will remain an independent journal, covering the entire spectrum of inorganic chemistry including solid-state inorganic chemistry, organometallic chemistry and bioinorganic chemistry.
- "Chemische Berichte", "Liebigs Annalen" and "Bunsen Berichte" (physical chemistry) will appear with new cover designs and will be available to libraries as a journals package together with "Angewandte Chemie" and "Nachrichten aus Chemie, Technik und Laboratorium".
- From 1995, English will be the official language of publication for "Chemische Berichte", "Liebigs Annalen" and "Bunsen Berichte".

In any case, the well known features of "Chemische Berichte" and "Liebigs Annalen der Chemie" will be upheld:

- The sections "Full Papers" and "Notes" will publish contributions with experimental details from inorganic chemistry, organometallic chemistry, bioinorganic chemistry, solid-state chemistry, organic chemistry (synthetic methods and reaction mechanisms), organometallic chemistry, physical organic chemistry, bioorganic chemistry and natural products chemistry.
- Members of the Editoral Board *and* peer reviewers from around the world guarantee high quality papers. There will be little change to the Editorial Bord.
- The editorial team here in Weinheim will be expanded to include English native speakers, and will continue providing as efficient a service as possible.

None of the changes described above have been decisions that the German Chemical Society has taken lightly. In order to understand the reasons for these decisions, you should know the following:

1) Not only in industry has competition become more fierce and more international.
2) National journals published in a national language will have reduced chances of survival in the future. Their Impact Factors (a measure of citation frequency) are below those of international journals published in English. Of course, acceptance, status and distribution of a journal are not solely dependent upon the language of publication, but with the introduction of English these factors can only be improved upon! If "Chemische Berichte" and "Liebigs Annalen" are to be renowned world-wide and provide serious competition for other juornals, then a change must occur *now*.
3) It is not true that the number of articles voluntarily submitted in English over the last few years has increased, nor that any turning point is forseeable.
4) It is also not true that there is a large number of non-German scientists with sufficient knowledge of the German language. My experiences with non-German speaking, potential reviewers supports this.

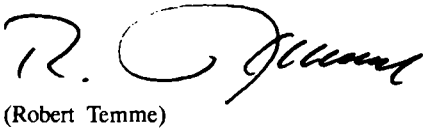
Im am pleased to be able to present you with a range of improvements for 1995:

- You will no longer have difficulties allocating your manuscripts from the different areas of chemistry to one of the two journals – the division ist clear.
- Cross-references in both journals will keep you informed about the contents of the other.
- The peer review system will now be extended to all manuscripts. This will ensure an even better "quality control".
- Our competitive publication times will be improved. At the moment our t_{50} values (where t_{50} is the time after which 50 % of manuscripts accepted have been published) are 4.8 months ("Liebigs Annalen") and 5.4 months ("Chemische Berichte").
- An issue will appear at the end of the previous month, so that you should have it on your desk at the beginning of the relevant month.
- Current subscribers to "Chemische Berichte" need not miss out. For an initial period, these subscibers will continue to receive the organic papers of Part B in form of the new "Liebigs Annalen", in addition to the new-style "Chemische Berichte"; all at the 1994 subscription rate for "Chemische Berichte".
- If you are a member of the German Chemical Society, you can take out a personal subscription at a reduced rate.
- If you preferred publishing in German in the past, you can now take advantage of our language polishing service. In certain cases, the publisher will offer a translation service for an initial period.

Since the number of pages of any one volume is limited, it will not be possible to print all German-language articles before the end of the year. Hence issues 1 and 2 of 1995 will still have a few German-language papers.

I hope that you will continue sending your best papers to "Chemische Berichte" and "Liebigs Annalen" and look forward to your cooperation in making the future for both journals a bright one.

Yours sincerely,



(Robert Temme)

Die neuen „Berichte“ und „Annalen“ – ab 1995 ganz in Englisch!

Liebe Leserinnen, liebe Leser,

viele von Ihnen haben bereits von den im Frühjahr 1994 getroffenen wichtigen Beschlüssen des GDCh-Vorstandes zu einigen unserer chemischen Fachzeitschriften gehört. Mir als Chefredakteur ist es sehr wichtig, Sie alle noch einmal über die Neuerungen in Kenntnis zu setzen (vgl. auch *Nachr. Chem. Tech. Lab.* **1994**, *42*, 685):

- Die Unterteilung der „Berichte“ in Teil A (Anorganische Chemie) und Teil B (Organische Chemie) wird aufgehoben. Künftig wird den großen Wissenschaftsgebieten Anorganische Chemie und Organische Chemie jeweils ein Journal zugeordnet sein. Aus Teil B der „Chemischen Berichte“ und „Liebigs Annalen der Chemie“ entstehen die neuen „Liebigs Annalen“. Der Teil A der alten „Chemischen Berichte“ wird zu einem eigenständigen Journal, das die Entwicklung der gesamten Anorganischen Chemie einschließlich Festkörper-Chemie, Metallorganischer Chemie und Bioanorganischer Chemie reflektieren soll.
- Diese zwei Zeitschriften und die „Bunsen-Berichte“ (Physikalische Chemie) mit je einer Leitfarbe und ähnlichem Layout bilden mit der „Angewandten Chemie“ und „Nachrichten aus Chemie, Technik und Laboratorium“ ein „Paket“ von fünf Journalen.
- Englisch soll bei den neuen „Chemischen Berichten“, „Liebigs Annalen“ und „Bunsen-Berichten“ ab 1995 einzige Publikationssprache sein.

Die bewährten Merkmale der beiden großen chemischen Primär-Journale bleiben auf jeden Fall unangetastet:

- In den Rubriken „Full Papers“ und „Notes“ werden Beiträge mit ausführlichen experimentellen Teilen aus den Bereichen Anorganische Chemie, Metallorganische Chemie, Bioanorganische Chemie, Festkörper-Chemie sowie Organische Chemie (Synthese und Reaktionsmechanismen), Metallorganische Chemie, Physikalisch-Organische Chemie, Bioorganische Chemie und Naturstoff-Chemie abgedruckt.
- Peer-Reviewer aus dem In- und Ausland *und* die Herausgeber wachen gemeinsam über die Qualität der Beiträge. Bei den Hauptherausgebern wird es keine Veränderungen geben.
- Eine engagierte Redaktion, die mit englischen Muttersprachlern ergänzt werden wird, ist nach wie vor um möglichst optimale Abwicklung der einzelnen Bearbeitungsschritte bemüht.

Um diese Neuerungen, die weder der GDCh-Vorstand noch alle anderen für die Zeitschriften Verantwortlichen leichtfertig beschlossen haben und denen 1993 eine Autorenbefragung vorausging, richtig verstehen zu können, müssen Sie folgendes wissen:

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Ich freue mich, Ihnen für 1995 eine Reihe von Verbesserungen in Aussicht stellen zu können:

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- Es werden Querverweise abgedruckt, die Sie über den Inhalt des jeweiligen anderen Journals informieren.
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- Die attraktiven Publikationsfristen werden nach Möglichkeit noch verbessert. Derzeit liegen die t_{50}-Werte (t_{50} ist die Zeit, nach der 50 % der angenommenen Manuskripte erschienen sind) bei 4.8 Monaten („Annalen“) und 5.4 Monaten („Berichte“).
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- Wer bisher nur „Chemische Berichte“ bezogen hat, bekommt von uns für eine Übergangszeit die neuen „Chemischen Berichte“ sowie den organischen Teil in Form der neuen „Liebigs Annalen“ zum gleichen Preis wie die „Chemischen Berichte“ 1994.
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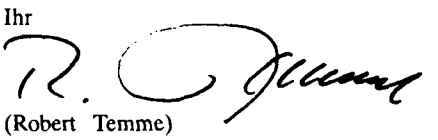
Ich weiß, daß besonders die Einführung der obligatorischen Publikationssprache Englisch bei einigen deutschen Autoren auf Unwillen stößt. Ich habe volles Verständnis für manche der Einwände. Es würde den Rahmen sprengen, dieses Thema hier auszudiskutieren. Aber vielleicht tröstet es die Skeptiker ein wenig und zeigt umso mehr, wie sehr den Verantwortlichen die Sorge um die Zukunft der Zeitschriften am Herzen liegt: auch Redaktion und Herausgeber werden durch die Sprachumstellung erheblich zusätzlich belastet.

Da der jährliche Druckseitenumfang der Zeitschriften begrenzt ist, wird es nicht möglich sein, alle in Deutsch abgefaßten Beiträge noch in diesem Jahrgang abzudrucken. In den Heften 1 und 2 des neuen Jahrgangs werden Sie daher noch einige Arbeiten in Deutsch finden.

Ich bitte Sie nun, den neuen „Berichten“ und „Annalen“ auch weiterhin Ihre besten Beiträge anzuvertrauen. Die Zukunft dieser Zeitschriften wird wesentlich davon abhängen, wie sich auch die deutschen Autoren mit ihnen identifizieren und ihre internationalen Kollegen zur Publikation einladen. Das in manchen Bereichen der deutschen Chemical Scientific Community zu beobachtende Verhalten „Wenn schon in Englisch – dann im Ausland publizieren“ ist bedauerlich und birgt eine Gefahr für die Zukunft der Journale. *Sie* haben es mit in der Hand, was aus den „Berichten“ und „Annalen“ wird.

Ihr



(Robert Temme)

which may be explained in terms of the mode of decomposition following the non-linear cheletropic reaction path as predicted by Woodward and Hoffmann[22].

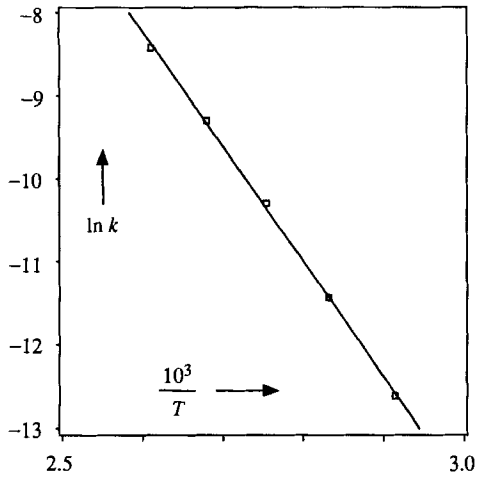


Figure 2. Temperature dependence of the rate constants according to the Arrhenius equation for the thermolysis of the iminoaziridines (*E*)- and (*Z*)-**4**

Attempts to detect a thermal racemization of (*E*,*R*)- and (*Z*,*R*)-**4** were frustrated by their lability at higher temperatures. After carefully degassed samples of a [D_6]benzene solution had been kept at 80°C for up to 2 half-lives, the enantiomeric excess of the surviving fractions of the iminoaziridines (*E*,*R*)- and (*Z*,*R*)-**4** had not been diminished. Therefore, the search for achiral or racemic (acyclic) transients in the iminoaziridine series has to await the advent of non-racemic examples of higher thermal stability.

Nucleophilic ring-opening reactions of racemic and non-racemic (*E*)- and (*Z*)-**4** will be the subject of a separate report.

We are indepted to the *DEGUSSA AG*, Hanau, for generous gifts of valuable chemicals. We thank Mrs. *E. Ruckdeschel* and Dr. *D. Scheutzow* for recording high-field proton and carbon-13 NMR spectra, Mrs. *M. Schäfer* for taking phosphorus-31 NMR spectra, and Dr. *G. Lange* and Mr. *F. Dadrich* for running the mass spectra. Financial support by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*, Frankfurt am Main, is gratefully acknowledged.

Experimental

Starting materials, reagents, solvents, reaction conditions, yields, physical and IR data: Table 1. – ^{1}H-NMR data: Table 2. – ^{13}C-NMR data: Table 3. – Details of the kinetic investigation and results: Table 4. – Molecular formulae and masses, and elemental analyses: Table 5. – Melting points: Sealed capillary tubes, apparatus from Büchi, Flawil, Switzerland. – IR: Beckman IR 10 and Perkin-Elmer 1420. – ^{1}H NMR: Bruker AC 250 (0.305 Hz/pt.), Varian A60, Enantiomeric excesses (ee) were calculated from 5 integrations of 250-MHz ^{1}H-NMR spectra recorded in the presence of 2 equivalents of **11**[14]. – ^{13}C NMR: Bruker AC 200 and AC 250. The assignments are based on DEPT spectra or ^{13}C,^{1}H COSY spectra [**9a**, (*E*)- and (*Z*)-**4**]. – ^{31}P NMR: Jeol FX 90Q, (external standard: 85% phosphoric acid). – MS (70 eV): Finnigan MAT 8200.

Ether and tetrahydrofuran were distilled under Ar from sodium-potassium alloy. Under N_2, pentane, petroleum ether, and toluene were distilled from sodium hydride, dichloromethane and trichloromethane from diphosphorus pentoxide. – Sodium hydride was freed from paraffin oil by repeated washings with pentane and dried in a stream of N_2. Gaseous methanamine was dried with potassium hydroxide pellets. Thionyl chloride was distilled under N_2 before use. Potassium *tert*-butoxide was sublimed three times at 200°C/5 · 10^{-2} Torr and kept under Ar. (*S*)-2-Chloro-3,3-dimethylbutanoyl chloride[2], **5**[23], **7b**[9], and methyl triflate[24] were prepared according to literature procedures.

(S)-2-Chloro-N,3,3-trimethylbutanamide [(*S*)-**6a**]: A solution of (*S*)-2-chloro-3,3-dimethylbutanoyl chloride (13.3 g, 79 mmol) in dichloromethane (240 ml) and a solution (250 ml) of methanamine (0.72 M, 0.18 mol) in the same solvent were added simultaneously dropwise during 2 h to stirred dichloromethane (400 ml) cooled to −10°C. Stirring was continued for 0.5 h without cooling. The reaction mixture was extracted with hydrochloric acid (2 M, 200 ml) followed by an aqueous solution of potassium carbonate (2 M, 200 ml) and dried with magnesium sulfate. Distillation of the solvent in vacuo afforded colourless crystals (12.4 g, m.p. 112–113°C). Recrystallization from cyclohexane (70 ml) yielded colourless needles (10.3 g, 80%, m.p. 118–119°C, ref.[2] 118–119°C, ee 98%).

Racemic 2-Chloro-N,3,3-trimethylbutanamide (**6a**) was obtained as described in the preceding experiment from 2-chloro-3,3-dimethylbutanoyl chloride and methanamine in 80% yield as colourless needles (m.p. 106–108°C) after recrystallization from cyclohexane.

2-Chloro-N-deuterio-N,3,3-trimethylbutanamide ([D]**6a**): Repeated recrystallizations from a 1:1 mixture of deuterium oxide and [D_4]methanol of 5.0 g **6a** with strict exclusion of moisture yielded colourless crystals (3.7 g, m.p. 106°C) which were dried at 10^{-2} Torr over diphosphorus pentoxide. – IR (CCl_4): 2570 cm^{-1} (ND).

2-Chloro-N,3,3-trimethylbutanimidoyl Chloride (**7a**)

a) According to the method by von Braun et al.[25], phosphorus pentachloride (16.6 g, 80 mmol) was added under N_2 in several portions to a stirred solution of **5** (5.2 g, 40 mmol) in cyclohexane (15 ml), and the resulting mixture was heated under reflux for 7 h while the conversion was monitored by ^{1}H-NMR spectroscopy. Petroleum ether (30–50°C, 50 ml) was added to the cooled reaction mixture, and the solution was decanted from inorganic material. The solvent was distilled in vacuo at a bath temp. below 50°C. Distillation of the residue afforded a colourless oil (5.0 g, 72%, b.p. 85–87°C/23 Torr).

b) Thionyl chloride (65 g, 0.55 mol) was added under N_2 to a stirred solution of **6a** (9.00 g, 55 mmol) in trichloromethane (20 ml). The mixture was heated to 65°C for 1.5 h while the conversion was monitored by ^{1}H-NMR spectroscopy. The solvent and excess thionyl chloride were distilled in vacuo. Distillation of the remaining pale brown oil yielded a colourless oil (6.50 g, 65%, b.p. 83–84°C/16 Torr).

c) A solution of (*S*)-**6a** (1.0 g, 6.1 mmol) and thionyl chloride (4.4 ml, 60 mmol) in trichloromethane (4 ml) was heated to 65°C for 2 h. Workup as described under b) yielded a colourless oil (0.98 g, 88%) which afforded completely racemized **9a** after treatment with methanamine.

Methyl 2-Chloro-N,3,3-trimethylbutanimidate (**8**): A stirred suspension of **6a** (40.8 g, 0.25 mol) in methyl triflate (49.1 g, 0.30 mol) was heated to 45°C for 1.5 h and subsequently kept at 20–25°C for 10 d. A saturated aqueous solution of potassium hydrogen carbonate (200 ml) was added to the reaction mixture followed by

extraction with ether (2 × 200 ml). The combined organic layers were washed with water (200 ml) and dried with potassium carbonate. Distillation of the solvent in vacuo afforded a pale yellow oil (47.1 g, quant.) which was distilled to yield a colourless oil (36.6 g, 83%, b.p. 30–31°C/10^{-2} Torr).

Methyl (S)-2-Chloro-N,3,3-trimethylbutanimidate [(*S*)-**8**] was obtained as described for **8** from (*S*)-**6a** (7.71 g, 47 mmol) and methyl triflate (9.21 g, 56 mmol) as a colourless oil (6.88 g, 83%, b.p. 30–31°C/10^{-2} Torr, ee 95%).

5-tert-Butyl-2-(4-methoxyphenyl)-3-methyl-1,3,2-thiazaphospholidine-4-thione 2-Sulfide (**15**, 6:1 Mixture of Diastereomers): Lawesson's reagent[26] (4.19 g, 10.4 mmol) was added to a stirred solution of **6a** (2.26 g, 13.8 mmol) in toluene (30 ml). The mixture was heated to 95°C for 2 h. Water (20 ml) was added to the cooled, clear solution followed by stirring of the mixture for 0.5 h. The phases were separated, and the aqueous layer was extracted with ether (5 × 20 ml). The combined organic layers were dried with magnesium sulphate. Distillation of the solvent in vacuo followed by flash chromatography of the residue [50 × 5 cm glass column packed with silica gel 32–63 µm (ICN Biomedicals), petroleum ether (30–75°C)/ethyl acetate (9 : 1), 1.8 bar N_2] and recrystallization from ether/pentane (1:1) yielded yellow crystals (2.63 g, 55%, m.p. 85–86°C). – MS; *m/z* (%): 345 (18) [M^+], 289 (100), 87 (62), 86 (34), 63 (38), 57 (30), 43 (30), 42 (79), 41 (44). – *Major diastereomer:* ^{1}H NMR ($CDCl_3$): δ = 1.29 (*t*Bu), 2.99 ($^3J_{PH}$ = 8.3 Hz, NMe), 3.89 (OMe), 4.73 ($^3J_{PH}$ = 12.2 Hz, CH), 6.99 ($H_AH'_A$, $^4J_{PH}$ = 8.9 Hz), 7.28 ($H_BH'_B$, $^3J_{PH}$ = 15.3 Hz, AA'BB'X spectrum). – ^{13}C NMR ($CDCl_3$): δ = 28.6, 38.1 (*t*Bu), 33.4 ($^2J_{PC}$ = 8.2 Hz, NMe), 55.6 (OMe), 74.2 ($^2J_{PC}$ = 2.0 Hz, CH), 114.2 ($^2J_{PC}$ = 16.3 Hz, *o*-C), 124.3 ($^1J_{PC}$ = 108.1 Hz, P–C=), 134.2 ($^3J_{PC}$ = 15.0 Hz, *m*-C), 163.5 ($^4J_{PC}$ = 3.3 Hz, C–OMe), 202.3 ($^2J_{PC}$ = 12.1 Hz, C=S). – ^{31}P NMR ($CDCl_3$): δ = 89.9. – *Minor diastereomer:* ^{1}H NMR ($CDCl_3$): δ = 1.31 (*t*Bu), 3.10 ($^3J_{PH}$ = 8.9 Hz, NMe), 3.90 (OMe). – ^{31}P NMR ($CDCl_3$): δ = 85.8.

2-Chloro-N,N',3,3-tetramethylbutanamidine (**9a**)

a) A solution of methanamine (4.4 ml, 100 mmol) in pentane (20 ml) was added dropwise during 1 h to a stirred solution of **7a** (9.1 g, 50 mmol) in pentane (30 ml) cooled to −20°C. The suspension was allowed to attain 20°C. The precipitated methanammonium chloride was filtered and washed with pentane. Distillation of the solvent from the combined filtrates and subsequently of the pale yellow residue in vacuo yielded a colourless oil (6.0 g, 68%, b.p. 48–50°C/10^{-2} Torr).

b) According to ref.[27], gaseous methanamine was introduced during 4 h into a boiling solution of **8** (7.00 g, 39.5 mmol) and methanammonium chloride (2.70 g, 39.5 mmol) in methanol (50 ml). After the conversion was virtually complete (^{1}H NMR), the solvent was distilled in vacuo. A cold aqueous solution of sodium hydroxide (2 M, 50 ml) was added to the residue, and the mixture was quickly extracted with petroleum ether (30–50°C, 100 ml). Small amounts of unchanged **8** were removed by extraction with a mixture (100 ml) of a saturated aqueous solution of potassium dihydrogen phosphate and water (1:3) immediately followed by the addition to the aqueous layer of a cold aqueous solution of sodium hydroxide (2 M, 50 ml). By rapid extraction with petroleum ether (30–50°C, 100 ml), **9a** was recovered. The organic layer was dried with potassium carbonate. The solvent and the colourless residue were distilled in vacuo to afford a colourless oil (6.20 g, 88%, b.p. 48–50°C/10^{-2} Torr).

(S)-2-Chloro-N,N',3,3-tetramethylbutanamidine [(*S*)-**9a**]: According to procedure b) given for **9a**, a colourless oil (3.54 g, 87%, ee 90%) was obtained from (*S*)-**8** (4.32 g, 24.3 mmol).

2-Chloro-N,N',3,3-tetramethylbutanamidinium Perchlorate (**9a** · $HClO_4$): An aqueous solution of perchloric acid (85%, 0.40 g, 3.54 mmol) was added to a stirred solution of **9a** (0.50 g, 2.83 mmol) in ethanol (3 ml) cooled to 0°C. After the addition of ether (10 ml) the mixture was stirred for 10 min, and the solid was filtered to yield colourless crystals (0.76 g, 96%, m.p. 198–199°C). Recrystallization from ethanol afforded colourless crystals (0.71 g, 90%, m.p. 199–200°C).

(S)-2-Chloro-N,N',3,3-tetramethylbutanamidinium Perchlorate [(*S*)-**9a** · $HClO_4$] was obtained as described for **9a** · $HClO_4$ from (*S*)-**9a** (0.50 g, 2.83 mmol) as colourless crystals (0.71 g, 90%, m.p. 201–202°C).

2-Bromo-N,N',3,3-tetramethylbutanamidine (**9b**): An excess of gaseous methanamine was introduced under N_2 into a stirred solution of **7b** (41.0 g, 181 mmol) in petroleum ether (30–50°C, 400 ml) cooled to −20°C. The mixture was allowed to attain room temp. overnight. The white precipitate (methanammonium chloride, 11.8 g, 96%) was filtered under N_2 and washed with petroleum ether. Distillation of the solvent from the combined filtrates and subsequently of the pale yellow residue in vacuo yielded a colourless oil (33.5 g, 84%, b.p. 30–31°C/5 · 10^{-4} Torr).

2-Bromo-N,N',3,3-tetramethylbutanamidinium Perchlorate (**9b** · $HClO_4$): An aqueous solution of perchloric acid (70%, 1.5 ml, 17.4 mmol) was added dropwise to a stirred solution of **9b** (2.21 g, 10 mmol) in ethanol (3 ml) cooled to 0°C. After the addition of ether (20 ml) the mixture was stirred at 0°C for 10 min to afford colourless crystals (3.19 g, 99%, m.p. 208–210°C). Recrystallization from ethanol raised the m.p. to 210–210.5°C.

N-(3-tert-Butyl-1-methyl-2-aziridinylidene)methanamine, Mixture of Diastereomers [(*E*)- and (*Z*)-**4**]

a) Potassium *tert*-butoxide (13.8 g, 123 mmol) was added under Ar to a stirred solution of **9a** (10.9 g, 61.7 mmol) in ether (400 ml) cooled to 0°C. Stirring at 0°C was continued for 10 h followed by the addition of pentane (100 ml). The mixture was quickly extracted with iced water (3 × 50 ml) and dried with potassium carbonate. Distillation of the solvent and the remaining pale yellow oil in vacuo yielded a colourless oil (4.02 g, 49%, b.p. 20–25°C/10^{-2} Torr) consisting of (*E*)- and (*Z*)-**4** (57:43, ^{1}H NMR).

b) Sodium hydride (6.09 g, 250 mmol) and *tert*-butyl alcohol (0.3 ml, 4.4 mmol) were added under Ar to a stirred solution of **9a** (5.32 g, 30.1 mmol) in tetrahydrofuran (100 ml). Stirring was continued at 20–25°C for 40 h while the conversion was monitored by IR spectroscopy. After the addition of pentane (100 ml), the white precipitate was filtered and washed with pentane. The filtrate and the washing were combined, quickly extracted with iced water (3 × 50 ml), and dried with potassium carbonate. Distillation of the solvent and the remaining pale yellow oil in vacuo yielded a colourless oil (2.99 g, 71%) consisting of (*E*)- and (*Z*)-**4** (57:43, ^{1}H NMR).

c) Sodium hydride (3.80 g, 158 mmol) was added under N_2 to a solution of **9b** (5.51 g, 25 mmol) in tetrahydrofuran (50 ml). The mixture was stirred at 20–25°C for 70 h. Workup as described under b) and distillation in vacuo yielded a colourless oil (2.26 g, 65%).

d) Potassium *tert*-butoxide (18.4 g, 164 mmol) was dissolved in ether (260 ml) with stirring for 1 h, and the solution was filtered under Ar and cooled to −40°C. **9b** (8.84 g, 40 mmol) was added followed by stirring at −40°C for 3 h. Most of the solvent was distilled at −30 to −35°C (bath temp.)/14 → 10^{-1} Torr. Hexane (100 ml, cooled to −50°C) was added, and the mixture was stirred at −30°C for 5 min followed by evaporation of the solvent at −30 to −35°C/10^{-1} Torr. After the addition of pentane (80 ml, cooled

Table 2. Chemical shifts (δ values) in ^{1}H-NMR spectra of some 3,3-dimethylbutanoic acid derivatives. The ^{1}H-NMR spectra of solutions of **6a**, **8**, **9a**, and the iminoaziridines (*E*)- and (*Z*)-**4** were also recorded in the presence of 2 equivalents of (*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol (**11**); the average of the chemical shifts of the enantiomers [δ(*R*) + δ(*S*)]/2 and (in *italics*) the differences of resonance frequencies ν(*R*) − ν(*S*) [Hz] are listed

Cpd.	*t*Bu	CH	=NMe	Me—N—H[a]	^3J	[b]
5	1.03	2.07 (CH_2)		2.79	6.1	*4.8*	$CDCl_3$
6b	1.15	4.18		2.84	6.6	*4.8*	$CDCl_3$
(*E*)-**4**	0.80 *4.4*	1.66 *7.6*	2.89	2.36 *−27.6*			B
(*Z*)-**4**	0.66 *3.5*	1.39 *9.2*	2.54	2.47 *−20.2*			B
7a	0.99	4.38	2.91				$CDCl_3$
	0.93 |*1.1*|	4.43 |*5.8*|	2.81 |*1.0*|				B
8[c]	0.99	4.43	2.85				C_6D_6
	0.97 *−4.6*	4.33 *4.4*	2.84 *−5.8*				C
9a	0.97	4.43	2.98[d]	2.61[d]	4.1		C_6D_6
	0.89 *−5.2*	4.53	2.55[d]	2.55[d]	4.1		B
9a · $HClO_4$	1.13	4.97		2.95 3.14	7.4 7.6	*5.3* *5.3*	CD_3CN
9b	1.13	4.82	3.02[d]	2.70[d]	4.1		CCl_4
	1.13	4.88		2.80[d]	5.4		$[CD_3]_2SO$
9b · $HClO_4$	1.17	4.95[d]		2.96 3.13[d]	7.5		CD_3CN

[a] Broad signal. − [b] Solvent: B = [D_6]benzene/tetrachloromethane (1 : 3); C = [D_{12}]cyclohexane/tetrachloromethane (1:12). − [c] OMe: δ = 3.49; 3.45, *2.0*. − [d] Broadened singlet.

Table 3. Chemical shifts (δ values) in ^{13}C-NMR spectra of some 3,3-dimethylbutanoic acid derivatives

Cpd.	Me_3C		CH	C=O	=NMe	NHMe	Solvent
5	29.7	30.7	50.3 (CH_2)	172.5		26.0	$CDCl_3$
6b	27.4	34.9	63.4	168.8		26.6	$CDCl_3$
				C=N			
7a	26.8	36.4	74.5	143.1	39.9		$CDCl_3$
8[a]	26.9	35.3	52.2	159.7	35.3		C_6D_6
9a	27.0	36.3	61.9	155.3	36.0[b]	28.2[b]	C_6D_6
9a · $HClO_4$	26.0	38.0	61.3	164.8		29.0 31.6	CD_3CN
9b[c]	27.6	35.8	55.6	155.7	35.8[b]	28.7[b]	C_6D_6
9b · $HClO_4$	26.7	37.2	51.6	165.3		29.1 31.5	CD_3CN

[a] OMe: δ = 59.2. − [b] Broad signal. − [c] 100.6-MHz spectrum (1.526 Hz/pt.).

Table 4. Experimental details and results of the kinetic investigation of the thermolysis of (*E*)- and (*Z*)-**4** in [D_6]benzene solution

Temp. [K] (±0.2)	No. of points	conversion [%]	[h]	$10^5 \cdot k$ [s^{-1}]	$t_{\frac{1}{2}}$ [min]
343.16	18	77	116	0.334 ± 0.003	3500
353.16	22	86	50	1.08 ± 0.01	1070
363.16	19	75	11	3.38 ± 0.03	342
373.16	21	81	5	9.18 ± 0.09	126
383.16	18	75	1.5	22.0 ± 0.5	53

to −50°C) to the residue and stirring for 10 min, the suspension was filtered at −30°C under N_2 into a precooled flask (−50°C), and the filtrate was concentrated at −50 to 0°C/12 → 10^{-2} Torr. The remaining oil was distilled at 0−20°C/10^{-3} Torr to afford a colourless oil (1.31 g, 23%) consisting of (*E*)- and (*Z*)-**4** (<10:>90, ^{1}H NMR) which was kept at dry-ice temperature.

(E,R)- and (Z,R)-**4**: According to the preceding procedure b), (*S*)-**9a** (3.10 g, 17.5 mmol) was allowed to react with sodium hydride (3.67 g, 153 mmol) and *tert*-butyl alcohol (0.3 ml, 4.4 mmol) in tetrahydrofuran (100 ml) to afford a colourless oil (1.75 g, 71%, ee 83%).

Equilibration (*E*)-**4** ⇌ (*Z*)-**4**: A mixture of neat (*E*)- and (*Z*)-**4** (1:9) and tetramethylsilane was sealed in a degassed, evacuated NMR sample tube and kept at 36°C in the insert of a Varian A60 NMR spectrometer. The equilibrium constant $K = k_{EZ}/k_{ZE}$ was determined after 22 h. From 15 integrations during the first 7 h, the sum ($k_{EZ} + k_{ZE}$) was calculated by the least-squares method according to the (non-linear) equation[28] $[m_E K - m_Z] = [(m_E)_0 K - (m_Z)_0]\exp - (k_{EZ} + k_{ZE})t$; m_E, m_Z = mole fractions of (*E*)- and (*Z*)-**4**, respectively; $(m_E)_0$, $(m_Z)_0$ = mole fractions at the beginning.

Thermolysis of (E)- and (Z)-**4**: The mixture of (*E*)- and (*Z*)-**4** (samples of 40 mg, 0.29 mmol) was placed into NMR sample tubes which had been dried at 200−300°C/10^{-1} Torr and flushed with Ar while being attached to a high-vacuum line. [D_6]Benzene (0.5 ml) was dried with $LiAlH_4$, repeatedly degassed at 10^{-5} Torr, and condensed into the NMR sample tubes which were flame-sealed at 10^{-5} Torr. The sample tubes were completely immersed in a Lauda Ultrathermostate NS-S15/22/SP, the temperature of which was measured with calibrated thermometers. The identity of the products **16** and **17** was confirmed by ^{1}H- and ^{13}C-NMR spectra. The conversion was monitored by 200-MHz ^{1}H-NMR spectra and calculated from integrations of the *tert*-butyl signals at 10 Hz/cm scale expansion. The rate constants were calculated by the non-linear least-squares method[19] according to $I = I_0\exp(-kt)$; I = sum of the integrations of (*E*)- and (*Z*)-**4**; I_0 = sum of the integrations of (*E*)- and (*Z*)-**4** and **16**. Details and results are listed in Table 4.

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[1] Iminoaziridines, part 4. − For part 3 see ref.[12]. − The results are taken from the Dissertations by S. Aldenkortt (**1995**) and P. Schäfer (**1977**), and the Diploma Thesis by E. Heller (**1991**), University of Würzburg.

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Table 5. Molecular formulae, masses, and elemental analyses for some 3,3-dimethylbutanoic acid derivatives, the iminoaziridines (*E*)- and (*Z*)-**4** and the diastereomeric 1,3,2-thiazaphospholidines **15**

Cpd.		Molecular Mass		Elemental Analysis C	H	N
(*E*)-**4**, (*Z*)-**4**	$C_8H_{16}N_2$	140.2	Calcd.	68.52	11.50	19.98
			Found	68.36	11.77	19.87
7a	$C_7H_{13}Cl_2N$	182.1	Calcd.	46.17	7.20	7.69
			Found	46.58	7.77	8.09
8	$C_8H_{16}ClNO$	177.7	Calcd.	54.08	9.08	7.88
			Found	54.27	9.30	7.98
9a	$C_8H_{17}ClN_2$	176.7	Calcd.	54.38	9.70	15.87
			Found	54.38	10.02	16.05
(*S*)-**9a** · $HClO_4$	$C_8H_{18}Cl_2N_2O_4$	277.2	Calcd.	34.67	6.55	10.11
			Found	34.70	6.33	9.99
15	$C_{14}H_{20}NOPS_3$	345.5	Calcd.	48.67	5.83	4.05
			Found	48.38	5.76	4.14
				Br		
9b	$C_8H_{17}BrN_2$	221.1	Calcd.	36.14		12.67
			Found	36.28		12.77
				Br + Cl		
9b · $HClO_4$	$C_8H_{18}BrClN_2O_4$	321.6	Calcd.	35.87		8.71
			Found	36.27		8.73

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