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Experimental and Theoretical Characterization of the Aromatization, Epimerization, and Fragmentation Reactions of Bi-2*H*-azirin-2-yls Prepared from 1,4-Diazidobuta-1,3-dienes**

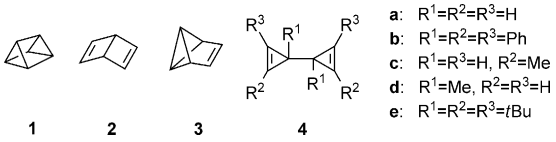
Klaus Banert,*[a] Frank Köhler,[a] Antje Melzer,[a] Ingolf Scharf,[a] Gerd Rheinwald,[b] Tobias Rüffer,[b] Heinrich Lang,[b] Rainer Herges,*[c] Kirsten Heß,[c] Nugzar Ghavtadze,[d] and Ernst-Ulrich Würthwein*[d]

Abstract: 1,4-Diazidobuta-1,3-dienes (*Z*,*Z*)-**10**, **17**, and **21** were photolyzed and thermolyzed to yield the pyridazines **13**, **20**, and **23**, respectively. To explain these aromatic final products, the generation of highly strained bi-2*H*-azirin-2-yls **12**, **19**, and **22** and their valence isomerization were postulated. In the case of *meso*- and *rac*-**22**, nearly quantitative formation from diazide **21**, isolation as stable solids, and complete characterization were possible. On the thermolysis of **22**, aromatization to **23** was only a side reaction, whereas equilibration of *meso*- and *rac*-**22** and fragmentation, which led to alkyne **24** and acetonitrile, dominated. Prolonged irradiation of **22** gave mainly the pyrimidine **25**. The change of the configuration at C-2 of the 2*H*-azirine unit was observed not only in the case of bi-2*H*-azirin-2-yls **22** but also for simple spirocyclic 2*H*-azirines **29** at a relatively low temperature (75 °C). The fragmentation of *rac*-**22** to give alkyne **24** and two molecules of acetonitrile was also studied by high-level quantum chemical calculations. For a related model system **30** (methyl instead of phenyl groups), two transition states TS-**30**–**31** of comparable energy with multiconfigurational electronic states could be localized on the energy hypersurface for this one-step conversion. The symmetrical transition state complies with the definition of a coarctate mechanism.

Keywords: azides · density functional calculations · nitrogen heterocycles · reactive intermediates · small-ring systems

Introduction

The valence isomers of benzene, prismane (**1**), Dewar benzene (**2**), benzvalene (**3**), and bicycloprop-2-enyl (**4a**), stimulated the fantasy of chemists for nearly one and a half centuries.[1] When Breslow et al. synthesized the first derivative of this latter $(CH)_6$ species, the highly substituted compound **4b**, they discovered also the aromatization of this product to give hexaphenylbenzene on heating, for example, in refluxing xylene.[2] Less substituted starting materials, for instance,



meso-**4c**, *rac*-**4c**, and **4d**, isomerize at 160–200 °C in the gas phase each to give mixtures of *o*-, *m*-, and *p*-xylenes.[3] Several mechanisms were proposed to explain these aromatization reactions,[3b,4] which are accompanied by Cope rearrangements, such as the isomerization **4d**→**4c**.[3c]

Some attempts were made to generate the diaza analogues of bicycloprop-2-enyls **4**, namely, the bi-2*H*-azirin-2-yls of type **7** (Scheme 1). However, neither the Neber reaction of hydrazonium salts or similar starting materials nor the coupling reaction of 2-chloro-2*H*-azirines with various reagents led to the heterocycles **7**.[5] Moreover, efforts to prepare 1,4-diazidobuta-1,3-dienes of type **6** as potential precursors of the target compounds **7** failed.[5a,6,7] But recently, diazides **6** were synthesized by electrocyclic conrotatory ring opening of the diazidocyclobutenes **5b** available by nucleophilic substitution of the corresponding dihalides **5a**.[8] The products **6** proved to be ideal starting compounds to generate bi-2*H*-azirin-2-yls **7** in excellent yields by photolysis or thermal reaction below ambient temperature. The highly strained heterocycles **7** could not be isolated because they isomerized nearly quantitatively to give pyridazines **8**

[a] Prof. Dr. K. Banert, Dr. F. Köhler, Dr. A. Melzer, Dr. I. Scharf
Organic Chemistry, Chemnitz University of Technology
Strasse der Nationen 62, 09111 Chemnitz (Germany)
Fax: (+49) 371-531-21229
E-mail: klaus.banert@chemie.tu-chemnitz.de

[b] Dr. G. Rheinwald, Dr. T. Rüffer, Prof. Dr. H. Lang
Inorganic Chemistry, Chemnitz University of Technology
Strasse der Nationen 62, 09111 Chemnitz (Germany)

[c] Prof. Dr. R. Herges, K. Heß
Institute of Organic Chemistry, University of Kiel
Otto-Hahn-Platz 4, 24098 Kiel (Germany)

[d] Dr. N. Ghavtadze, Prof. Dr. E.-U. Würthwein
Institute of Organic Chemistry, University of Münster
Corrensstrasse 40, 48149 Münster (Germany)

[**] Reactions of Unsaturated Azides, Part 28. For Part 27, see reference [11].

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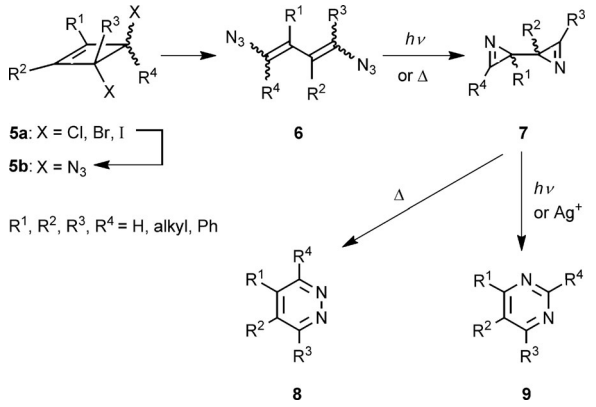


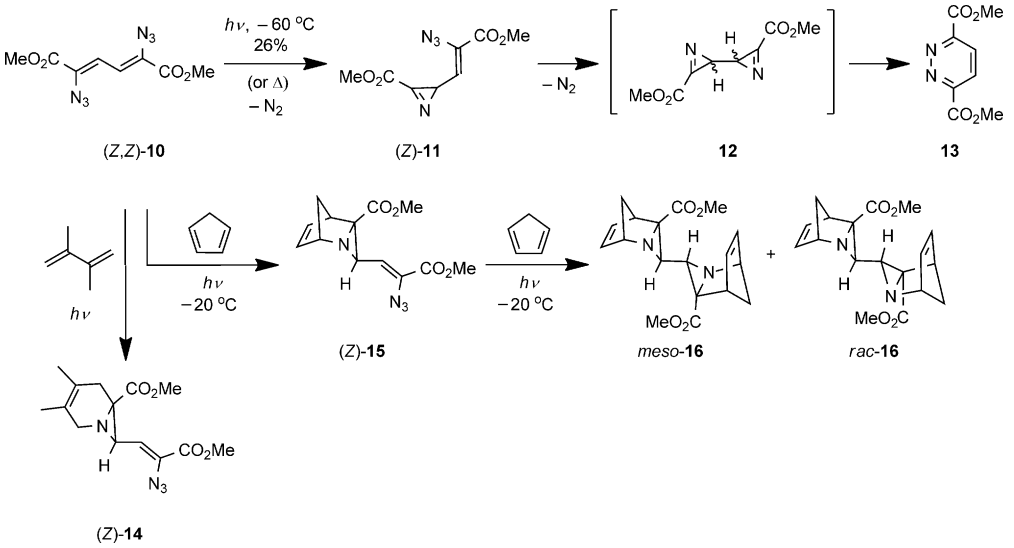
Scheme 1. Synthesis and aromatization of known bi-2*H*-azirin-2-yls **7**.

even at low temperatures, whereas also pyrimidines **9** were formed by prolonged irradiation or in the presence of silver salts. Thus, the reported[8] aromatizations of **7** indicate that valence isomerizations to prepare pyridazines **8** are possible although rearrangements to produce other diazabenzenes were postulated in the literature.[5,6] The thermal transformation **7**→**8** showed some remarkable singularities.[8] Compared to thermal reactions of simple 2*H*-azirines,[9] the low temperature (−25 to +10 °C) at which the aromatization of **7** could be performed was surprising, especially when compared to the temperatures that were necessary for analogous valence isomerizations of bicycloprop-2-enyls **4**.[3,4] The very different reactivities of stereoisomeric *meso*- and *rac*-**7** or *unlike*- and *like*-**7**, respectively, are also noteworthy. Furthermore, the exclusive thermal transformation of **7** to yield pyridazines **8** is in contrast to bicycloprop-2-enyls, such as **4c** or **4d**, which led to mixtures of *o*-, *m*-, and *p*-xylenes.[3] The formation of pyridazines from two molecules of simple 2*H*-azirines was observed only in rare cases and in a very low yield.[10] On the other hand, similar dimerizations to produce pyrazine derivatives were reported several times.[9]

Unfortunately, the substitution pattern of **5** is limited to R^1, R^2, R^3, R^4 = H and small alkyl or phenyl groups, and the synthesis **5a**→**5b**→**6**→**7** cannot be performed on a large scale. Moreover, the high reactivity of **7** did not allow isolation of these substances and prevented experimental assignment of the stereoisomers of **7**. Very recently, however, large-scale synthesis of novel 1,4-diazidobuta-1,3-dienes was presented.[11] We describe here the complete characterization of isolable stereoisomeric bi-2*H*-azirin-2-yls prepared from such diazides. Thus, it was possible to investigate not only aromatization but also epimerization and fragmentation processes of such heterocycles. Furthermore, we studied these reactions by quantum chemical calculations.

Results and Discussion

When a solution of diazide (*Z*,*Z*)-**10**[11] was irradiated by a high-pressure mercury lamp at low temperature, only the mono-azirine (*Z*)-**11** (yield: 26%) but not the corresponding biazirinyls **12** could be detected (Scheme 2). Prolonged photolysis gave only traces of the known[12] pyridazine **13**, whereas heating of (*Z*,*Z*)-**10** in dichloromethane or chloroform resulted in the formation of **13** in 27% yield besides small amounts of (*Z*)-**11** (up to 2%). We assumed that (*Z*,*Z*)-**10** was transformed into **13** via the intermediates (*Z*)-**11** and the highly unstable biazirinyl **12**. Thus, we irradiated (*Z*,*Z*)-**10** in the presence of cyclopentadiene to give the trapping products *meso*-**16** and *rac*-**16** with excellent yield. The assignment of the stereoisomers was confirmed by X-ray single-crystal structure analysis of *meso*-**16** (Figure 1). In the case of incomplete photolysis, the aziridine (*Z*)-**15** was also isolated. If less reactive 2,3-dimethylbuta-1,3-diene was used



Scheme 2. Photolysis and thermolysis of diazide (*Z*,*Z*)-**10**.

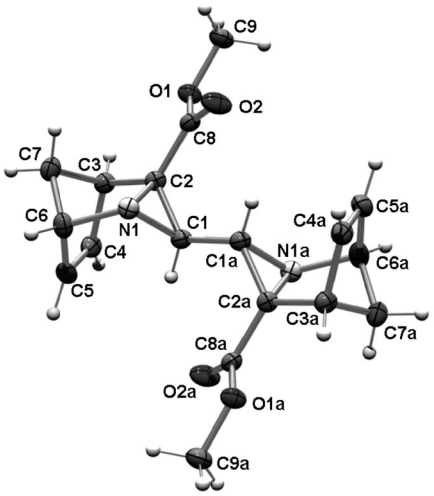
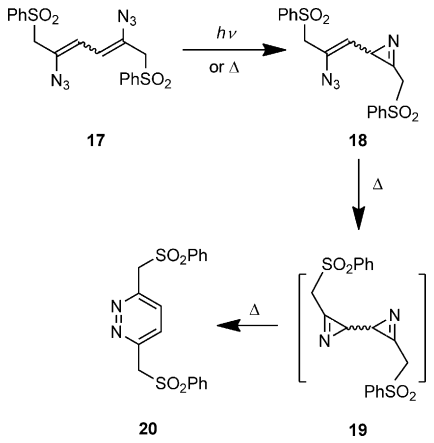


Figure 1. Molecular structure of *meso*-**16** determined by single-crystal X-ray diffraction analysis.

for such interception of azirines by [4+2]-cycloaddition, only the product (*Z*)-**14** could be characterized.

It is well-known from the work of Gilchrist et al.[13] and others[14] that 2*H*-azirines with an electron-withdrawing group in the 3-position are unstable but good dienophiles in stereoselective Diels–Alder reactions. In the case of (*Z*,*Z*)-**10**, the ester groups made it possible to prepare the diazide by simple nucleophilic substitution of the corresponding dichloride,[11] but these electron-withdrawing groups increase the electron deficiency at the C=N carbon atoms of the heterocycles **12**, which are strongly destabilized. Thus, we looked for other types of 1,4-diazidobuta-1,3-dienes to generate bi-2*H*-azirin-2-yls.

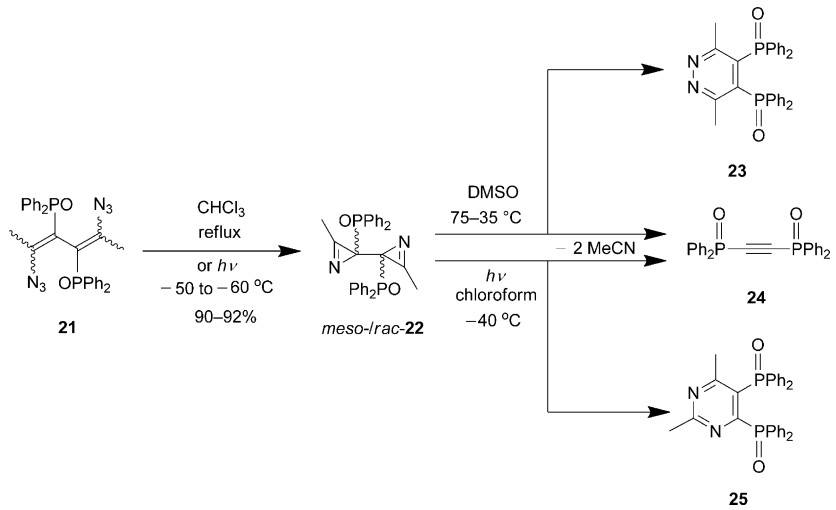
When we photolyzed a solution of the diazide (*E*,*Z*)-**17**,[11] a mixture of two diastereomeric, highly unstable 2*H*-azirines **18**, formed with 60 and 26% yield, was detected by ^{1}H NMR spectroscopy, whereas the analogous treatment of a symmetrical isomer of **17**[11] gave only a single stereoisomer of **18** in 67% yield (Scheme 3). Even irradiation at −85 °C did not bring about signals of the desired biazirinyls **19**. However, we assume that these elusive intermediates are involved in the thermolysis of **17** (DMSO, 82 °C), which led to pyridazine **20** in low yields (16–37% based on ^{1}H NMR spectroscopy). The surprising and disappointing instability of **18** and **19** is most probably also caused by acceptor properties of the substituents at C-3 of the heterocyclic rings although the CH_2SO_2Ph unit is a weak electron-withdrawing group.[15]



Scheme 3. Photolysis and thermolysis of diazides **17**.

In refluxing chloroform, the starting material (*E*,*E*)-**21** or the diastereomeric 1,4-diazidobuta-1,3-dienes of type **21** were transformed into a 1:2 mixture of *meso*- and *rac*-**22** with 92% yield (Scheme 4). The same products were formed in a 1:1 ratio on irradiation of **21** in 90% yield. The bi-2*H*-azirin-2-yls **22** are stable solids, which were separated easily by simple recrystallization. Since **21** is conveniently available on a large scale,[11] multigram amounts of *meso*- and *rac*-**22** could be prepared without effort. Structure assignment was performed with the help of single-crystal X-ray diffraction analyses (Figure 2). The relatively high thermal stability of **22** is based upon steric shielding due to the bulky substituents. In the case of **22**, electron-withdrawing substituents are bonded at C-2 but not at C-3 of the heterocycles. Thus, significant electronic destabilization of the azirine units, as is plausible for **12** and **19**, is avoided in **22**.

On heating the pure biazirinyls *meso*- or *rac*-**22** in DMSO at 75–135 °C, pyridazine **23** was generated only in a side reaction with 3–10% yield. However, a fragmentation affording two molecules of acetonitrile and the known[16] alkyne **24** (yield: 92%) was mainly observed. These thermal re-



Scheme 4. Synthesis, thermolysis, and photolysis of biazirinyls **22**.

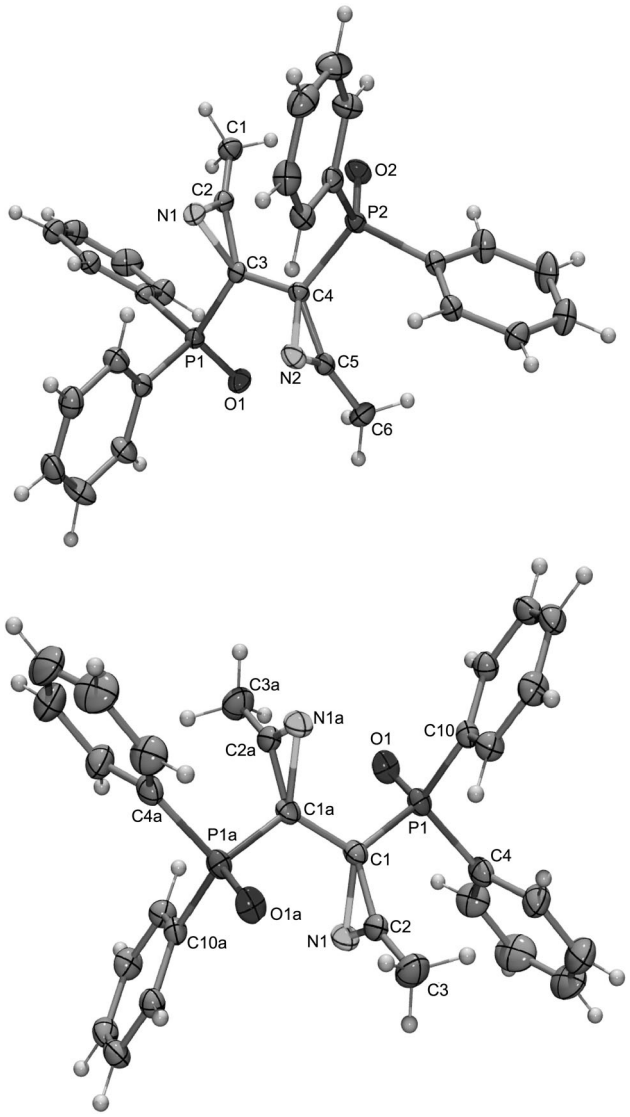


Figure 2. Molecular structures of *rac*- (top) and *meso*-**22** (bottom) determined by single-crystal X-ray diffraction analysis. In the case of *rac*-**22**, an oxygen-bonded water molecule was omitted for reasons of clarity. Analogously, an enclosed solvent molecule of benzene is not shown in the case of *meso*-**22**.

actions were accompanied by an equilibration of *meso*- and *rac*-**22**. A more detailed investigation supported by ^{1}H NMR spectroscopic monitoring of the thermolyses showed that formation of **23** and **24** started exclusively from *rac*-**22**. Thus, *meso*-**22** had to be epimerized into *rac*-**22** before **23** and **24** could be produced (Figure 3). This outcome is compatible with recent quantum chemical calculations, which analyzed the valence isomerization of biazirinyls of type **7** to give pyridazines **8** and postulated a significantly higher reactivity of *rac*-**7** than that of diastereomeric *meso*-**7**.[8b] When the corresponding rate constants for the balance of *rac*- and *meso*-**22**, and the irreversible generation of **23** and **24** from *rac*-**22** and possibly from *meso*-**22** were estimated from ^{1}H NMR spectroscopic analysis of the processes and with the help of GEPASI fitting,[17] two results were indicat-

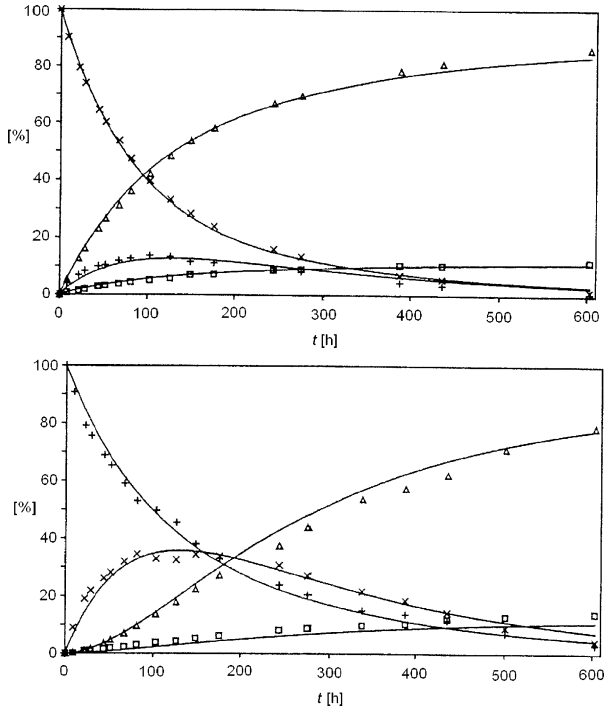
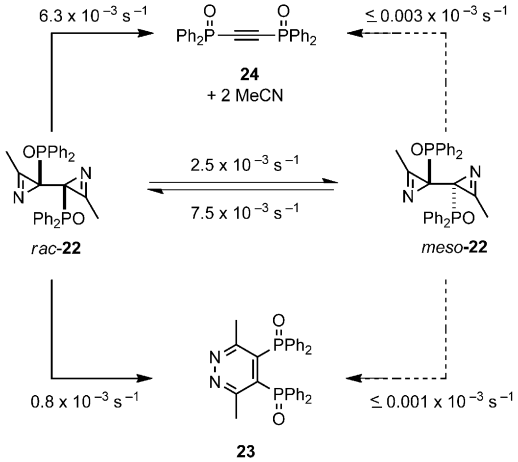


Figure 3. Thermolyses of *rac*- and *meso*-**22** in [D$_6$]DMSO at 75 °C monitored by ^{1}H NMR spectroscopy. x = *rac*-**22**; + = *meso*-**22**; □ = **23**; △ = **24**.

ed: The equilibration alone should lead to a ratio of *rac*-**22**/*meso*-**22** 3:1, and nearly no products **23** and **24** are formed directly from *meso*-**22** (Scheme 5). An analogous balance was previously found in the case of bicycloprop-2-enyls *rac*- and *meso*-**4c**, which gave very similar distributions of *o*-, *m*-, and *p*-xylene on gas-phase pyrolysis at 160–200 °C.[3a] On the other hand, fragmentation related to *rac*-**22**→**24**+2 MeCN was observed as a side reaction in the thermolysis (>200 °C) or in the photolysis of hydrocarbon **4e** furnishing di-*tert*-bu-



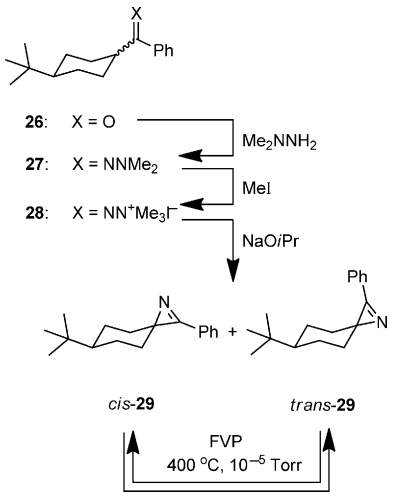
Scheme 5. Rate constants for fragmentation, epimerization, and aromatization of *rac*- and *meso*-**22** based on ^{1}H NMR spectroscopic data (Figure 3) and first-order kinetics for each of the reactions. The thermolyses were performed in [D$_6$]DMSO at 75 °C, and the rate constants were calculated by using GEPASI fitting.

tylacetylene without any products of aromatization or valence isomerization processes.[18]

When anhydrous solutions of the single stereoisomers *meso*-**22** and *rac*-**22** were irradiated in a prolonged way, neither epimerization of the biazirinyls nor formation of pyridazine **23** could be detected. The photolyses of both substrates proceeded similarly and led mainly to pyrimidine **25** besides small amounts (ca. 3% yield) of the fragmentation products **24** and acetonitrile. However, the yields of **25** were limited to approximately 22% because this aromatic compound was not photostable.

The thermal epimerization of *meso*- and *rac*-**22**, observed already at 75°C, raises the question whether the change of configuration at such a low temperature is limited to biazirinyls or can be found also in the case of simple 2*H*-azirines. Optically active derivatives of the latter heterocycles with a stereogenic center at C-2 were used repeatedly as building blocks in organic synthesis.[19] Moreover, some examples of naturally occurring 2*H*-azirines are known.[20] These antibiotic compounds are all optically active 2*H*-azirines bearing a center of chirality at C-2. However, an unwanted racemization on heating seems to be possible.

To clarify the configuration stability of simple 2*H*-azirines, we prepared a mixture of *cis*- and *trans*-**29** by a Neber reaction of the hydrazonium iodide **28**, which was accessible from ketone **26**[21] via hydrazone **27** (Scheme 6). After separation of *cis*- and *trans*-**29** by simple chromatography, assignment of the diastereomers was performed with the help of NMR spectroscopy, especially NOE experiments, and confirmed by single-crystal X-ray diffraction analysis (Figure 4). Flash vacuum pyrolysis (FVP) of both spirocyclic compounds led nearly quantitatively (93–95%) to 1:1 mixtures of the stereoisomeric heterocycles. Equilibration was also observed on heating *cis*- or *trans*-**29** in toluene at 75°C. But in these cases, the reactions were accompanied by decomposition. On irradiation of *cis*- or *trans*-**29** in chloroform at −40°C, no equilibration could be detected. Thus, the thermal load of optically active 2*H*-azirnes, for example, during distillation, should be avoided to exclude undesirable racemization, which occurs most probably via vinyl nitrenes as short-lived intermediates.[22]



Scheme 6. Synthesis and equilibration of azirines **29**.

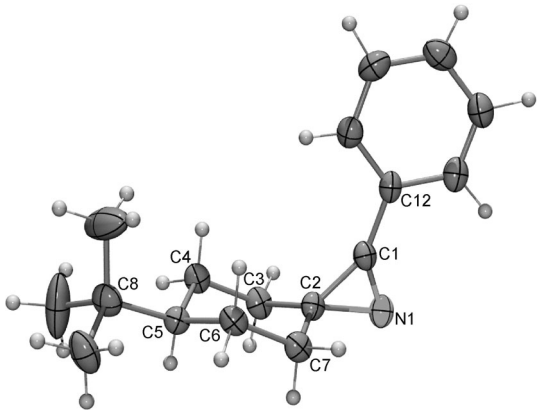
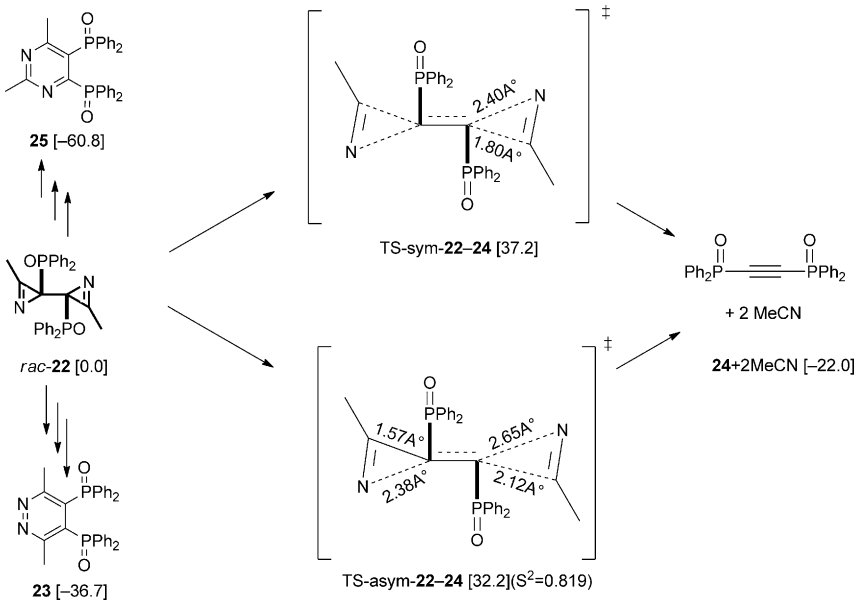
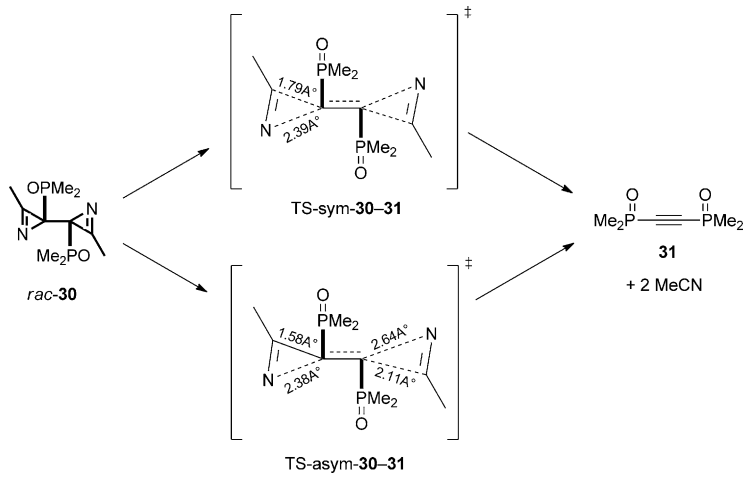


Figure 4. Molecular structure of *trans*-**29** determined by single-crystal X-ray diffraction analysis. Only one of two crystallographically nonequivalent molecules of *trans*-**29** is shown (see the Supporting Information).

Quantum chemical calculations: To investigate the mechanism of the twofold elimination reaction, by starting from biazirinyl *rac*-**22** and leading to the alkyne **24** and two molecules of acetonitrile, quantum chemical calculations were performed. At first, DFT-calculations by using the (U)B3LYP/6-31+G(d) method as implemented in the GAUSSIAN 09 program package[23] were performed to localize the appropriate structures on the energy hypersurface. All stationary points were checked by frequency analyses, and zero-point corrections at this level are included in all relative energies. By utilizing the restricted DFT method, we localized a symmetrical transition state TS-sym-**22**–**24** (C2-symmetry), which perfectly fulfils all geometrical requirements of a coarctate reaction mechanism (Scheme 7).[24] The calculated barrier (37.2 kcal mol^{-1}) fits reasonably well to the reaction conditions (thermolysis in DMSO at 75–135°C), and the reaction is predicted to be exothermic by −22.0 kcal mol^{-1}. By using UB3LYP, we were able to localize another transition with asymmetrical structure and significant diradical character TS-asym-**22**–**24** (S^2 expectation value of 0.819) with a slightly lower relative energy of 32.2 kcal mol^{-1}. The pyridazine **23**, which is obtained in a small yield as a byproduct, is calculated to be lower in energy by −36.7 kcal mol^{-1} relative to *rac*-**22**, the pyrimidine **25**, obtained by irradiation, is lower by −60.8 kcal mol^{-1}. The formation of the pyridazine may be explained by multistep diradical pathways, which were calculationally investigated in one of our earlier studies.[8b] Due to the size of the system studied, high-level calculations to appropriately treat both open-shell and closed-shell species were not possible. Therefore, we continued our studies by using the simpler model system **30**, in which the phenyl groups of the experimentally studied system were replaced by methyl groups (Scheme 8 and Figure 5). Here, the



Scheme 7. Calculated reaction pathways for the conversion of *rac*-**22** into **24** involving two possible transition states TS-sym-**22**–**24** and TS-asym-**22**–**24**. The pyridazine **23** and pyrimidine **25** are also included. Relative energies at the (U)B3LYP/6-31+G(d) level [kcal mol^{-1}].



Scheme 8. Calculated reaction pathways for the conversion of model compound *rac*-**30** into **31** involving two possible transition states TS-sym-**30**–**31** and TS-asym-**30**–**31**. Geometries at the (U)B3LYP/6-31+G(d) level of theory, for relative energies at various levels see text.

B3LYP-activation barriers were calculated 34.5 (TS-sym-**30**–**31**, closed shell) and 30.1 kcal mol^{-1} (TS-asym-**30**–**31**, open shell with $S^2=0.783$) with an exothermicity to form **31** and two molecules of acetonitrile of -20.7 kcal mol^{-1}. These data indicate that the phenyl groups have only a minor influence on the reaction mechanism and its thermodynamic data. Both transition states interconnect the starting material with the products without any other intermediates as demonstrated by IRC calculations.

However, it seems as if the electronic states of these transition structures are very complicated and not even two-configurational but truly multiconfigurational, which is in agreement with the large S^2 values (>1 in the case of a Hartree–Fock (HF) determinant, see HF values reported below). Thus, to approximately treat both open-shell and closed-shell species CCSD(T) on an equal footing, single-point calculations on these two transition-state geometries by using the restricted (CCSD(T)) and the unrestricted UCCSD(T)-method were performed. The corresponding results are expected to have larger errors than typical for CCSD(T) because of the partial multireference (MR) character involved in the electronic structures. Again, the unrestricted method gives a lower barrier of 36.8 kcal mol^{-1} in favor of the unsymmetrical open-shell transition structure TS-asym-**30**–**31** with significant open-shell/MR character ($S^2=1.616$), whereas for the symmetrical transition state TS-sym-**30**–**31**, which also has significant open-shell/MR character ($S^2=1.399$), a slightly higher barrier of 39.3 kcal mol^{-1} is calculated. Note, that a perfectly localized diradical would yield an S^2 value of unity with Hartree–Fock. The formation of the final products **31** plus two molecules of acetonitrile is exothermic by -9.3 kcal mol^{-1}. The computed barriers are in reasonable agreement with those from the corresponding B3LYP treatments.

In summary, both (U)CCSD(T) and (U)B3LYP methods predict two possible competing transition states with symmetrical (coarctate) and asymmetrical geometry, both showing significant open-shell/MR character. From the computational point of view, we have reached here the present limit of the theoretical methods applicable, considering the size of the system studied. Reasonable CASSCF or MRCI calculations, for example, are not feasible for such a system. The coarctate transition presented here offers a theoretically interesting alternative to the asymmetrical transition state.

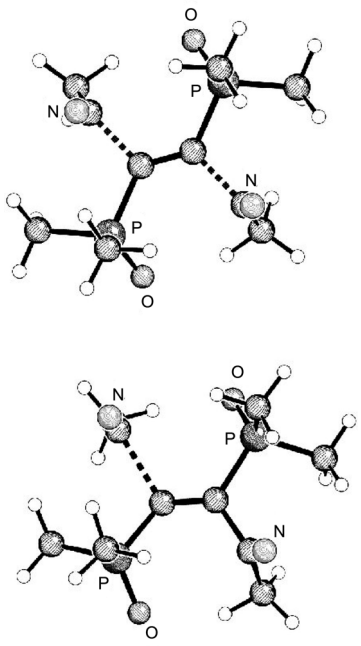


Figure 5. Calculated structures of the two transition states TS-sym-**30**–**31** (top) and TS-asym-**30**–**31** (bottom; (U)B3LYP/6-31+G(d)).

Conclusion

Clearly, the substitution pattern plays a dominant role when 1,4-diazidobuta-1,3-dienes lose dinitrogen to generate the corresponding 2*H*-azirines. The nearly quantitative formation of bi-2*H*-azirin-2-yls **22** from diazides **21** is a felicitous case, which allows us to study aromatization, epimerization, and fragmentation reactions in detail. The reaction mechanisms postulated for these transformations are based on quantum chemical calculations and include diradical intermediates[8b] and one-step processes with competing transition states with open-shell/multireference (MR) character possessing symmetrical (coarctate) and asymmetrical geometry.

Experimental Section

Caution! Care must be taken in handling azides, which are explosive. Especially, neat azides can lead to large explosions on friction, impact, or heating.

Instrumentation and measurement: Melting points were determined with a Pentakon Dresden Boetius apparatus. FTIR spectra were recorded with a Bruker IFS 28 FTIR spectrophotometer. IR measurements were made on solutions in KBr cuvettes. UV/Vis spectra were acquired with Specord UV VIS from Carl Zeiss Jena. ^{1}H NMR spectra were recorded with Varian Gemini 2000 or Unity Inova 400 spectrometers operating at 300 and 400 MHz, respectively. By using the same spectrometers, ^{13}C NMR spectroscopic data were recorded at 75 and 100 MHz. NMR signals were referenced to TMS ($\delta=0$) or solvent signals and recalculated relative to TMS. The multiplicities of ^{13}C NMR spectroscopic signals were determined with the aid of DEPT135 experiments. ^{31}P NMR spectroscopic data were recorded at 121.5 MHz by using 85% H_3PO_4 as an external standard with ($\delta=0$), whereas ^{15}N NMR spectra were measured at 30.4 MHz by utilizing $MeNO_2$ as an external standard with ($\delta=0$). MS and HRMS (ESI) spectra were recorded with an Applied Biosystems Mariner 5229 mass spectrometer or Bruker micrOTOF-QII spectrometer. Elemental analyses were performed with a Vario EL elemental analyzer from Elementar Analysensysteme GmbH Hanau or with a Vario Micro Cube from Elementar. Elemental analyses of explosive azides and highly unstable azirines could not be performed. TLC was performed with Macherey–Nagel Polygram SIL G/UV$_{254}$ polyester sheets. Flash column chromatography was performed with 32–63 μm silica gel. HPLC pump 64 (Knauer) and a UV/VIS photometer ($\lambda=254$ nm, Knauer) were utilized for isolation of compounds by HPLC.

General procedure for photolysis: Irradiation was conducted by using a high-pressure mercury lamp (TQ150, Heraeus GmbH) supplied with glass equipment and an ethanol cryostat (−50 to −80 °C). Most of these photolyses were monitored by NMR spectroscopic analysis by utilizing anhydrous $CDCl_3$ (−20 °C to −60 °C) or CD_2Cl_2 (−85 °C). A solution of the appropriate starting material (typical concentration: 0.1 to 0.01 mol L^{-1}) was irradiated in an NMR tube. To exclude oxygen, the solution was flushed with argon in an ultrasonic bath prior to irradiation. Dioxane or DMSO were used as standard to determine yields based on ^{1}H NMR spectroscopic data.

Single-crystal X-ray diffraction analysis: The data collection for *meso*-**16**, *trans*-**29**, and *rac*-**22** were performed at 173 K on a Bruker Smart CCD 1k diffractometer and for *meso*-**22** at 293 K on an Oxford Gemini S diffractometer. All calculations, including structural solutions and refinement by full-matrix least-squares on F^2, were performed by using the SHELXTL program.[25] CCDC-810980 (*trans*-**29**), 810981 (*rac*-**22**), 810982 (*meso*-**16**), and 810983 (*meso*-**22**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Methyl 2-[(*Z*)-2-azido-2-(methoxycarbonyl)ethenyl]-2*H*-azirine-3-carboxylate [(*Z*)-11]: Photolysis of (*Z,Z*)-**10**[11] in $CDCl_3$ was performed at −60 °C to give a maximum yield of (*Z*)-**11** of 26% (^{1}H NMR spectroscopy). ^{1}H NMR ($CDCl_3$): $\delta=3.29$ (d, $^3J=8.7$ Hz, 1H; 2-H), 3.82 (s, 3H; OMe), 4.02 (s, 3H; OMe), 5.58 ppm (d, $^3J=8.7$ Hz, 1H; 1′-H); ^{13}C NMR ($CDCl_3$): $\delta=34.35$ (d; C-2), 53.19 (q; OMe), 54.27 (q; OMe), 126.13 (d; C-1′), 130.37 (s; C-2′), 157.30 (s), 162.24 (s), 165.89 ppm (s).

Thermolysis of (*Z,Z*)-**10** in $CDCl_3$ at 60 °C led to a maximum proportion of (*Z*)-**11** of 2%, whereas the pyridazine **13** was formed in 27% yield. The latter compound was prepared through a known[12] procedure for comparison.

Photolysis of (*Z,Z*)-10 in the presence of cyclopentadiene or 2,3-dimethylbuta-1,3-diene: A solution of (*Z,Z*)-**10** in a 4:1 mixture of $CDCl_3$ and cyclopentadiene was irradiated in an NMR tube at −20 °C until liberation of nitrogen was complete. The products *meso*-**16** and *rac*-**16** were formed quantitatively in a ratio 4:5. When a solution of (*Z,Z*)-**10** (500 mg, 2.0 mmol) in a mixture of $CHCl_3$ and cyclopentadiene was treated similarly but without photolyzing to completeness, a mixture of (*Z*)-**15**, *meso*-**16**, and *rac*-**16** was generated. Separation was achieved by chromatography using silica gel and Et_2O (for (*Z*)-**15**), Et_2O/acetone 3:1 (for *rac*-**16**), and then acetone (for *meso*-**16**). If 2,3-dimethylbuta-1,3-diene was utilized instead of cyclopentadiene in the analogous photolysis of (*E,E*)-**10**, compound (*Z*)-**14** was isolated with 35% yield as the only product, which could be detected.

Methyl 7-[(*Z*)-2-azido-2-(methoxycarbonyl)ethenyl]-3,4-dimethyl-1-azabicyclo[4.1.0]hept-3-ene-6-carboxylate ((*Z*)-14): Yellow liquid; ^{1}H NMR ($CDCl_3$): $\delta=1.52$ (s, 3H; Me), 1.66 (s, 3H; Me), 2.53 (d, $^2J=18.2$ Hz, 1H; H-5), 2.69 (d, $^2J=18.2$ Hz, 1H; H-5), 3.00 (d, $^3J=8.6$ Hz, 1H; H-7), 3.27 (d, $^2J=17.5$ Hz, 1H; H-2), 3.64 (d, $^2J=17.5$ Hz, 1H; H-2), 3.71 (s, 3H; OMe), 3.77 (s, 3H; OMe), 6.06 ppm (d, $^3J=8.6$ Hz, 1H; H-1′); ^{13}C NMR ($CDCl_3$): $\delta=16.27$ ppm (q; Me), 18.66 (q; Me), 28.42 (t; C-5), 39.33 (d; C-7), 47.35 (s; C-6), 52.36 (t; C-2), 52.39 (q; OMe), 52.69 (q; OMe), 119.23 (s), 120.34 (s), 126.38 (d; C-1′), 129.94 (s; C-2′), 162.44 (s; C-3′), 170.99 ppm (s; C=O).

Methyl 3-[(*Z*)-2-azido-2-(methoxycarbonyl)ethenyl]-2-azatricyclo[3.2.1.0^{2,4}]oct-6-ene-4-carboxylate ((*Z*)-15): Orange liquid; IR (CCl_4): $\tilde{\nu}=2128$ cm^{-1} (N_3), 1725 (C=O); ^{1}H NMR ($CDCl_3$): $\delta=1.65$ (br d, $^2J=$

8.1 Hz, 1H; 8-H), 1.96 (dt, ^2J=8.1, J=1.7 Hz, 1H; 8-H), 2.48 (d, ^3J=8.4 Hz, 1H; 3-H), 3.55 (m, 1H; 5-H), 3.69 (s, 3H; OMe), 3.72 (s, 3H; OMe), 4.15 (m, 1H; 1-H), 5.71 (ddd, ^3J=5.4, J=2.5, J=1.0 Hz, 1H; 7-H), 6.11 (d, ^3J=8.4 Hz, 1H; 1′-H), 6.20 ppm (ddd, ^3J=5.4, J=3.3, J=1.6 Hz, 1H; 6-H); ^{13}C NMR $CDCl_3$): δ=46.96, 49.26, 50.35 (s; C-4), 52.42, 52.60, 59.30 (t; C-8), 67.08 (d; C-1), 124.56 (d; C-1′), 128.46 (d; C-7), 129.00 (s; C-2′), 132.93 (d; C-6), 162.53 (s; C-3′), 171.05 ppm (s; C-1″).

***meso*-4,4′-Bis(methoxycarbonyl)bi-2-azatricyclo[3.2.1.0^{2,4}]oct-6-en-3-yl (*meso*-16)**: Yellow solid; m.p. 150 °C (Et_2O); IR (CCl_4): $\tilde{\nu}$=1742 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ=1.59 (br d, ^2J=8.1 Hz, 2H; 8-H), 1.87 (dt, ^2J=8.1, J=1.9 Hz, 2H; 8-H), 1.97 (s, 2H; 3-H), 3.47 (m, 2H; 5-H), 3.67 (s, 6H; OMe), 3.99 (m, 2H; 1-H), 5.57 (ddd, ^3J=5.4, J=2.6, J=1.1 Hz, 2H; 7-H), 6.06 ppm (ddd, ^3J=5.4, J=3.4, J=1.7 Hz, 2H; 6-H); ^{13}C NMR ($CDCl_3$): δ=46.67, 47.64 (s; C-4), 51.22, 52.21, 58.98 (t; C-8), 66.59 (d; C-1), 128.39 (d; C-7), 132.75 (d; C-6), 171.80 ppm (s; C=O); elemental analysis calcd (%) for $C_{18}H_{20}N_2O_4$ (328.37): C 65.84, H 6.14, N 8.53; found: C 65.33, H 6.13, N 8.58.

***rac*-4,4′-Bis(methoxycarbonyl)bi-2-azatricyclo[3.2.1.0^{2,4}]oct-6-en-3-yl (*rac*-16)**: Yellow liquid; IR (CCl_4): $\tilde{\nu}$=1727 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ=1.59 (br d, ^2J=8.1 Hz, 2H; 8-H), 1.87 (dt, ^2J=8.1, J=1.9 Hz, 2H; 8-H), 1.97 (s, 2H; 3-H), 3.47 (m, 2H; 5-H), 3.67 (s, 6H; OMe), 3.99 (m, 2H; 1-H), 5.57 (ddd, ^3J=5.4, J=2.6, J=1.1 Hz, 2H; 7-H), 6.06 ppm (ddd, ^3J=5.4, J=3.4, J=1.7 Hz, 2H; 6-H); ^{13}C NMR ($CDCl_3$): δ=46.45, 47.18 (s; C-4), 52.19, 52.61, 59.03 (t; C-8), 66.78 (d; C-1), 128.78 (d; C-7), 132.51 (d; C-6), 171.61 ppm (s; C=O); elemental analysis calcd (%) for $C_{18}H_{20}N_2O_4$ (328.37): C 65.84, H 6.14, N 8.53; found: C 65.49, H 5.64, N 8.44.

Photolysis of diazides 17: A solution of **17** (symmetrical major isomer,[11] 11 mg, 0.025 mmol) in $CDCl_3$ (0.75 mL) was irradiated at −50 °C for 13 min to give the corresponding highly unstable 2-[2-azido-3-(phenylsulfonyl)prop-1-enyl]-3-[(phenylsulfonyl)methyl]-2*H*-azirine (**18**) in 67% yield (^{1}H NMR spectroscopy). IR ($CDCl_3$): $\tilde{\nu}$=2126 (N_3), 1324 (SO_2), 1154 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$/−50 °C): δ=2.62 (d, ^3J=8.4 Hz, 1H; C*H*−N), 3.81 (d, ^2J=14.3 Hz, 1H; CH_2), 4.06 (d, ^2J=14.3 Hz, 1H; CH_2), 4.64 (s, 2H; CH_2), 4.76 (d, ^3J=8.4 Hz, 1H; C*H*=), 7.56–7.76 (m, 6H; Ph), 7.88–8.00 ppm (m, 4H; Ph); the same product was formed in 26% yield when (*E,Z*)-**17**[11] was photolyzed similarly. In this case, the other diastereomer of **18** was generated with 60% yield. ^{1}H NMR ($CDCl_3$): δ=2.65 (d, ^3J=8.1 Hz, 1H; C*H*−N), 3.90 (s, 2H; CH_2), 4.22 (d, ^3J=8.1 Hz, 1H; C*H*=), 4.55 (s, 2H; CH_2), 7.56–7.76 (m, 6H; Ph), 7.88–8.00 ppm (m, 4H; Ph).

3,6-Bis[(phenylsulfonyl)methyl]pyridazine (20): A solution of (*E,Z*)-**17** (2.0 mg, 0.0045 mmol) in [D$_6$]DMSO (0.78 g) was heated at 81.5 °C for 2.5 h to achieve the formation of **20** in a maximum yield of 37% (^{1}H NMR spectroscopy). When **17** (symmetrical major isomer) was treated similarly, the product **20** was generated in a maximum yield of 16% after 30 min. After heating **17** (mixture of diastereomers)[11] in boiling CH_2Cl_2 for 5 h, the product **20** could be isolated as a white solid. M.p. 232–235 °C (CH_2Cl_2, decomp.); IR ($CDCl_3$): $\tilde{\nu}$=1323 (SO_2), 1155 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$): δ=4.72 (s, 4H; CH_2), 7.43–7.50 (m, 4H; Ph), 7.58–7.65 (m, 6H; Ph), 7.82 ppm (s, 2H; C*H*); ^{1}H NMR ([D$_6$]DMSO): δ=5.08 (s, 4H; CH_2), 7.55–7.77 ppm (m, 12H; Ar, C*H*); ^{13}C NMR ([D$_6$]DMSO): δ=60.46 (t), 127.91 (d), 129.24 (d), 129.27 (d), 134.13 (d), 138.05 (s, *i*-Ph), 152.29 ppm (s); HRMS (ESI): *m/z:* calcd for $C_{18}H_{17}N_2O_4S_2$: 389.0635 [*M*+H]$^+$; found: 389.0624.

2,2′-Bis(diphenylphosphinoyl)-3,3′-dimethylbi-2*H*-azirin-2-yl (22): A solution of (*E,E*)-**21**[11] (0.50 g, 0.89 mmol) in $CHCl_3$ (20 mL) was heated to reflux (bath temperature: 80 °C) for 16 h. After removal of the solvent, the residue was recrystallized from MeOH/H_2O and dried over P_2O_5 to give *rac*-**22** (278 mg, 62%). The mother liquor was extracted with $CHCl_3$, and the organic layer was dried with $MgSO_4$. After removal of the solvent, nearly pure *meso*-**22** (137 mg, 30%) was isolated as a viscous orange oil, which crystallized after addition of Et_2O. Thermolysis of (*E,E*)-**21** or a mixture of diastereomers **21**[11] could be performed on a 10 g scale, and workup was possible also by recrystallization from benzene first to obtain *meso*-**22** followed by concentration of the mother liquor and purification of *rac*-**22** by recrystallization from CH_2Cl_2/hexane. Very slow formation of the corresponding mono-azirine and *meso*- and *rac*-**22** was detected when a light-protected solution of (*E,E*)-**21** was stored some weeks at ambient temperature. After irradiation of a solution of (*E,E*)-**21** (10 mg, 0.018 mmol) in anhydrous $CDCl_3$ (ca. 0.7 mL) for 5 min at −40 °C, the starting material was consumed completely, and a 1:1 mixture of *meso*- and *rac*-**22** was generated in 91% yield (^{1}H NMR spectroscopy).

Product rac-**22**: M.p. 144–146 °C (MeOH/H_2O), 147–149 °C (CCl_4/hexane); IR (CCl_4): $\tilde{\nu}$=3061, 1778 (C=N), 1438 (P−Ph), 1195 cm^{-1} (P=O); UV/Vis (CH_3CN): λ_{max} (lg ε)=212 (4.51), 225 nm (4.49); ^{1}H NMR ($CDCl_3$): δ=1.98 (s, 6H; Me), 7.32–7.55 (m, 12H; Ph), 7.61 (m, 4H; Ph), 7.92 ppm (m, 4H; Ph); ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ=13.75 (q, ^1J(^{13}C,^{1}H)=133 Hz), 36.62 (dd, ^1J(^{31}P,^{13}C)+^2J(^{31}P,^{13}C)=128.8 Hz; C-2), 128.24 (t, ^3J(^{31}P,^{13}C)+^6J(^{31}P,^{13}C)=11.4 Hz; *m*-Ph), 128.35 (t, ^3J(^{31}P,^{13}C)+^6J(^{31}P,^{13}C)=11.4 Hz; *m*-Ph), 130.37 (dd, ^1J(^{31}P,^{13}C)+^4J(^{31}P,^{13}C)=108 Hz; *i*-Ph), 131.83 (dd, ^1J(^{31}P,^{13}C)+^4J(^{31}P,^{13}C)=106.5 Hz; *i*-Ph), 131.62 (t, ^2J(^{31}P,^{13}C)+^5J(^{31}P,^{13}C)=9.6 Hz; *o*-Ph), 131.78 (s; *p*-Ph), 131.88 (s; *p*-Ph), 132.17 (t, ^2J(^{31}P,^{13}C)+^5J(^{31}P,^{13}C)=9.4 Hz; *o*-Ph), 167.42 ppm (q, ^2J(^{13}C,^{1}H)=9 Hz; C-3); the carbon atoms and both phosphorus atoms form several AXX' systems; another ^{13}C NMR spectrum was measured at 75.5 MHz to distinguish between close signals and ^{31}P,^{13}C coupling; ^{31}P NMR ($CDCl_3$): δ=32.59 ppm; ^{15}N NMR ($CDCl_3$): δ=−105.89 ppm (′t′, ^2J(^{31}P,^{15}N)+^3J(^{31}P,^{15}N)=5.4 Hz); MS (ESI): *m/z*: 509.2 [*M*$^+$+1]; elemental analysis calcd (%) for $C_{30}H_{26}N_2O_2P_2$ (508.49): C 70.86, H 5.15, N 5.51; found: C 70.20, H 5.05, N 5.29.

Product meso-**22**: M.p. 172–174 °C (benzene); ^{1}H NMR ($CDCl_3$): δ=2.01 (s, 6H; Me), 7.22–7.60 (m, 16H; Ph), 8.04 ppm (m, 4H; Ph); ^{13}C NMR ($CDCl_3$): δ=13.05 (Me), 37.46 (dd, ^1J(^{31}P,^{13}C)+^2J(^{31}P,^{13}C)=130.5 Hz; AXX' system, C-2), 127.7–128.5 (several signals), 130.04, 130.63, 131.2–132.2 (several signals), 166.63 ppm (C-3); ^{31}P NMR ($CDCl_3$): δ=31.66 ppm; MS (ESI): *m/z*: 509.2 [*M*$^+$+1]; elemental analysis calcd (%) for $C_{30}H_{26}N_2O_2P_2{\cdot}C_6H_6$ (586.62): C 73.71, H 5.50, N 4.77; found: C 73.18, H 5.13, N 4.64.

Thermolysis of *rac*- and *meso*-22: Solutions of 5–10 mg of *rac*- or *meso*-**22** in [D$_6$]DMSO (ca. 0.7 mL) were heated in sealed NMR tubes at 75 °C to monitor the thermolyses by ^{1}H NMR spectroscopy (see Figure 3). The maximum yield of **23** was 10%. After heating a solution of *rac*-**22** (1.50 g, 2.95 mmol) in DMSO (20 mL) at 120 °C for 3 h, the solvent including the formed MeCN was removed in vacuo (0.001 Torr) at ambient temperature. The product mixture (1.35 g) was treated with Et_2O, which led to a precipitate of the known[16] **24** as a beige solid. Filtration with suction gave nearly pure **24** (1.16 g, 92%), which contained only traces of **23**. The filtrate was purified by chromatography (silica gel, Et_2O/MeOH 10:1, yellow fraction). After removal of the solvent, addition of Et_2O gave **23** (48 mg, 3%) as a yellow solid.

4,5-Bis(diphenylphosphinoyl)-3,6-dimethylpyridazine (23): M.p. 258–260 °C (CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$): δ=2.53 (s, 6H; Me), 7.16–7.56 ppm (m, 20H; Ph); ^{13}C NMR ($CDCl_3$): δ=24.68, 128.05 (′t′, ^3J(^{31}P,^{13}C)+^6J(^{31}P,^{13}C)=12.6 Hz; *m*-Ph), 131.94 (d, ^1J(^{31}P,^{13}C)=110 Hz; *i*-Ph), 131.9–132.4 (several signals, *o*- and *p*-Ph), 138.48 (d, ^1J(^{31}P,^{13}C)=91 Hz; C-4/C-5), 159.27 (t, ^2J(^{31}P,^{13}C)+^3J(^{31}P,^{13}C)=6 Hz; C-3/C-6); several AXX′ systems; ^{31}P NMR ($CDCl_3$): δ=34.36 ppm; HRMS (ESI): *m/z*: calcd for $C_{30}H_{26}N_2O_2P_2$: 509.1542 [*M*+H]$^+$; found: 509.1558; elemental analysis calcd (%) for $C_{30}H_{26}N_2O_2P_2{\cdot}^1/_2H_2O$ (517.51): C 69.63, H 5.26, N 5.41; found: C 69.41, H 4.78, N 5.27.

Photolysis of *rac*- and *meso*-22: Irradiation of solutions of *rac*- or *meso*-**22** in $CDCl_3$ (ca. 0.02 mol L^{-1}) was performed at −40 °C and monitored by ^{1}H and ^{31}P NMR spectroscopy (see the Supporting Information). The maximum yield of **25** was ca. 22% (30–50% unreacted starting material) beside up to 3% **24** and MeCN. Very strict exclusion of moisture was necessary, otherwise completely different main products were formed (see the Supporting Information). After irradiating a solution of *meso*-**22** (500 mg, 0.983 mmol) in anhydrous $CHCl_3$ (100 mL, degassed and flushed with dry argon) at −40 °C for 35 min, the solvent was removed in vacuo, and the residue was purified by flash chromatography by using silica gel and Et_2O/MeOH 10:1. The fraction containing **25** was liberated from the solvent and treated with Et_2O/hexane (stirring for 1 h). This led to a precipitate of **25** (30 mg, 6%) as a yellow solid.

4,5-Bis(diphenylphosphinoyl)-2,6-dimethylpyrimidine (25): M.p. 221–223 °C (CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$): δ = 2.67 (s, 3H; Me), 2.76 (s, 3H; Me), 7.2–7.6 (m, 16H; Ph), 7.80 ppm (m, 4H; Ph); ^{13}C NMR ($CDCl_3$): δ = 25.51, 27.29, 127.76 (d, $^3J(^{31}P,^{13}C)$ = 13.2 Hz; *m*-Ph), 127.90 (d, $^3J(^{31}P,^{13}C)$ = 12.6 Hz; *m*-Ph), 128.92 (dd, $^1J(^{31}P,^{13}C)$ = 94.4, $^2J(^{31}P,^{13}C)$ = 18.3 Hz; C-5), 131.49 (d, $^4J(^{31}P,^{13}C)$ = 2.9 Hz; *p*-Ph), 131.59 (d, $^2J(^{31}P,^{13}C)$ = 9.2 Hz; *o*-Ph), 131.87 (d, $^4J(^{31}P,^{13}C)$ = 2.9 Hz; *p*-Ph), 131.94 (d, $^1J(^{31}P,^{13}C)$ = 106 Hz; *i*-Ph), 132.49 (d, $^2J(^{31}P,^{13}C)$ = 10.6 Hz; *o*-Ph), 132.53 (d, $^1J(^{31}P,^{13}C)$ = 110 Hz; *i*-Ph), 166.16 (d, $J(^{31}P,^{13}C)$ = 17.2 Hz; C-6), 166.62 (dd, $^1J(^{31}P,^{13}C)$ = 123.7, $^2J(^{31}P,^{13}C)$ = 10.3 Hz; C-4), 173.97 ppm (m; C-2); ^{31}P NMR ($CDCl_3$): δ = 22.77, 31.77 ppm; HRMS (ESI): *m*/*z*: calcd for $C_{30}H_{26}N_2O_2P_2$: 509.1542 $[M+H]^+$; found 509.1543.

4-*tert*-Butylcyclohexyl phenyl ketone *N,N*-dimethylhydrazone (27): By starting with ketone **26**[21] (9.00 g, 36.8 mmol), *N,N*-dimethylhydrazine (3.00 g, 49.9 mmol), sodium acetate (0.52 g, 6.3 mmol), and three drops of acetic acid, the product was prepared by using an analogous procedure from reference [26]. After recondensation at 130 °C/0.001 Torr, hydrazone **27** (6.70 g, 64 %) was isolated as a yellow oil, which was not purified but used directly for the next step. ^{1}H NMR ($CDCl_3$): δ = 0.78 (s, 9H; *t*Bu), 0.8–2.0 (m), 2.32 (s, 6H; Me), 7.10–7.60 ppm (m, 5H; Ph); ^{13}C NMR ($CDCl_3$): δ = 27.05 (t), 27.52 (q), 31.23 (t), 32.39 (s), 47.21 (d), 47.31 (q), 47.45 (d), 126.81 (d), 127.36 (d), 127.82 (d), 138.00 (s), 169.07 ppm (s).

4-*tert*-Butylcyclohexyl phenyl ketone *N,N,N*-trimethylhydrazonium iodide (28): By starting with hydrazone **27** (13.40 g, 46.78 mmol) and methyl iodide (12.50 g, 88.07 mmol) in anhydrous Et_2O (15 mL), the product was prepared by using an analogous procedure from reference [26]. The hydrazonium iodide **28** (16.90 g, 84 %) was isolated as a yellow solid, which was not purified but utilized directly for the next step. M.p. 134–137 °C; ^{1}H NMR ($CDCl_3$): δ = 0.80 (s, 9H; Me), 0.90–1.10 (m, 2H), 1.20–1.30 (m, 2H), 1.80–2.00 (m, 5H), 2.42 (m, 1H), 3.59 (s, 9H; Me), 7.20 (m, 2H; Ph), 7.50 ppm (m, 3H; Ph); ^{13}C NMR ($CDCl_3$): δ = 26.39 (t), 27.22 (q), 29.89 (t), 32.14 (s), 46.86 (d), 50.22 (d), 57.89 (q), 126.15 (d), 128.88 (d), 130.10 (d), 131.66 (s), 181.39 ppm (s).

6-*tert*-Butyl-2-phenyl-1-azaspiro[2,5]oct-1-ene (29): After reacting sodium (0.19 g, 8.3 mmol) with 2-propanol (25 mL), the resulting solution was used to treat **28** (3.80 g, 8.87 mmol) as described in an analogous procedure in reference [26]. Workup by recondensation (115 °C/0.001 Torr) gave crude products (1.90 g), which were purified and separated by flash chromatography (silica gel, Et_2O/hexane 1:4, elution order: *cis*-**29**, then *trans*-**29**) to yield both *cis*-**29** (418 mg, 20 %) and *trans*-**29** (532 mg, 25 %) as colorless crystals.

Product cis-**29**: M.p. 79–81 °C (hexane); IR (CCl_4): $\tilde{\nu}$ = 2943, 1727 cm^{-1} (C=N); ^{1}H NMR ($CDCl_3$): δ = 0.92 (s, 9H; Me), 1.14 (br d, $^2J_{4eq,4ax}$ = 13.5 Hz, 2H; 4*eq*-H), 1.20 (tt, $^3J_{6ax,5ax}$ = 12.0, $^3J_{6ax,5eq}$ = 3.0 Hz, 1H; 6*ax*-H), 1.56 (qd, $^2J_{5ax,5eq}$ = $^3J_{5ax,6ax}$ = $^3J_{5ax,4ax}$ = 12.5, $^3J_{5ax,4eq}$ = 3.8 Hz, 2H; 5*ax*-H), 1.81 (m, 2H; 5*eq*-H), 2.10 (td, $^2J_{4ax,4eq}$ = $^3J_{4ax,5ax}$ = 12.5, $^3J_{4ax,5eq}$ = 4.0 Hz, 2H; 4*ax*-H), 7.52 (m, 3H, Ph), 7.77 ppm (m, 2H, Ph); the assignment of *cis* stereochemistry was supported by ^{1}H NMR spectroscopic NOE experiments that indicated an interaction between 4*ax*-H and *ortho* protons; ^{13}C NMR ($CDCl_3$): δ = 25.30 (t; C-5 und C-7), 27.65 (q; *t*Bu), 32.69 (s), 35.05 (t; C-4 und C-8), 40.03 (s), 48.03 (d; C-6), 126.36 (s), 128.77 (d), 129.00 (d), 132.43 (d), 178.65 ppm (s; C-2); MS (ESI): *m*/*z*: 242.2 $[M^+ +1]$; elemental analysis calcd (%) for $C_{17}H_{23}N$ (241.38): C 84.59, H 9.60, N 5.80; found: C 84.29, H 9.55, N 5.68.

Product trans-**29**: M.p. 90–92 °C (hexane); IR (CCl_4): $\tilde{\nu}$ = 2943, 1725 cm^{-1} (C=N); ^{1}H NMR ($CDCl_3$): δ = 0.95 (s, 9H; Me), 1.10–1.40 (m, 5H; 6*ax*-H, 5*ax*-H, 4*ax*-H), 1.90–2.20 (m, 4H; 5*eq*-H, 4*eq*-H), 7.57 (m, 3H; Ph), 7.84 ppm (m, 2H; Ph); the assignment of *trans* stereochemistry was supported by ^{1}H NMR spectroscopic NOE experiments that indicated interactions between 4*eq*-H/5*ax*-H and *ortho* protons (see also Figure 4); ^{13}C NMR ($CDCl_3$): δ = 27.73 (q; *t*Bu), 28.79 (t; C-5, C-7), 32.43 (s), 35.71 (t; C-4, C-8), 40.88 (s), 47.61 (d; C-6), 125.81 (s), 129.06 (d), 129.11 (d), 132.55 (d), 179.46 ppm (s; C-2); MS (ESI): *m*/*z*: 242.2 $[M^+ +1]$; elemental analysis calcd (%) for $C_{17}H_{23}N$ (241.38): C 84.59, H 9.60, N 5.80; found: C 84.16, H 9.38, N 5.56.

Thermolysis of *cis*- and *trans*-29: Flash vacuum pyrolysis was performed at 400 °C and 10^{-5} Torr by utilizing a quartz glass apparatus described previously.[27] Before use, the tube was dried for 2 h at 450 °C and 10^{-5} Torr. Starting with *cis*-**29** (45 mg, 0.19 mmol), led to a 1:1 mixture of *cis*- and *trans*-**29** (43 mg, 95 %). By using *trans*-**29** (44 mg, 0.18 mmol), the same procedure gave also a 1:1 mixture of *cis*- and *trans*-**29** (41 mg, 93 %).

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