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Experimental and Theoretical Characterization of the Valence Isomerization of Bi-2*H*-azirin-2-yls to Diazabenzenes**

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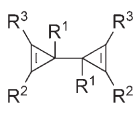
Abstract: 3,4-Diazidocyclobutenes **16** were prepared from the corresponding dihalides. Some of these diazides, such as parent compound **16d** and phenyl-substituted derivatives **16c**,**f**, underwent spontaneous stereoselective electrocyclic ring opening below room temperature, whereas the tetraalkyl derivatives of **16** had to be heated to force the same reaction. In most cases, the resulting 1,4-diazidobuta-1,3-dienes **8** were isolated to study their photochemical transformation into bi-2*H*-azirin-2-yls **9** via intermediate monoazirines **17**. Except for starting materials with a low number of substituents such as **9d** and **9f**, title compounds **9** underwent a thermal valence isomerization which led exclusively to pyridazines **18** at surprisingly low temperatures. Based on quantum-chemical calculations for the parent bi-2*H*-azirinyl-2-yl **9d** at the UB3LYP/6-31+G(d) and MR-MP2/TZV(2df,2p) levels, the valence isomerization process is best explained by simultaneous homolytic cleavage of both C–N single bonds of **9** to generate energetically favorable *N*,*N*′ diradicals **26**, which cyclize to **18**. The theoretical studies indicate also that one stereoisomer of **9**, namely, the *rac* compound, should undergo valence isomerization more easily than the other, which is in conformity with different rates of these rearrangement reactions found experimentally. For the tetramethyl-bi-2*H*-azirin-2-yls **9g**, which are better models for the experimentally studied compounds, simultaneous homolytic cleavage of both C–N single bonds is also predicted by the calculations, although the intermediate diradicals **26g** are significantly higher in energy than those of the parent system **9d**.

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

Introduction

The extremely strained bicycloprop-2-enyl **5a** was isolated first by Billups et al.[1] in 1989 as the last remaining valence isomer of benzene (**1**). This compound, which was calculated to be the highest in energy of the $(CH)_6$ species **1**–**4** and **5a**,[2,3] polymerizes above −10 °C.[1] Thirty years before, Breslow et al.[4] discovered that the highly substituted derivative **5b** undergoes valence isomerization to give hexaphenylbenzene on heating. Less substituted starting materials, for ex-

1 **2** **3** **4**



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a $R^1=R^2=R^3=H$
b $R^1=R^2=R^3=Ph$
c $R^1=R^3=H$, $R^2=Me$
d $R^1=Me$, $R^2=R^3=H$

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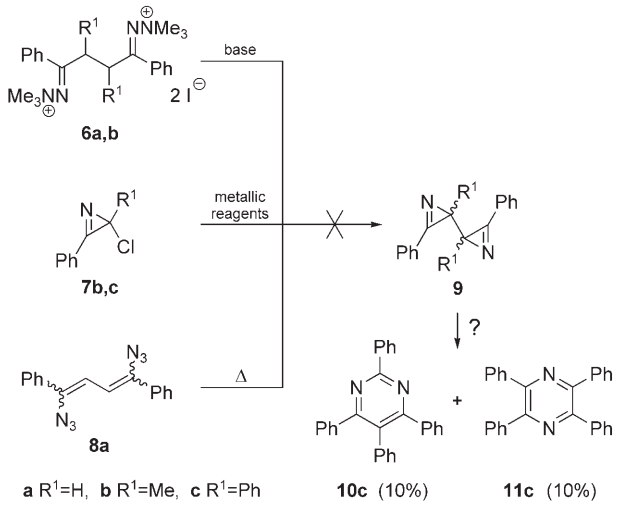
ample, *meso*-**5c**, *rac*-**5c**, and **5d**, rearrange at 160–200 °C in the gas phase each to give mixtures of *o*-, *m*-, and *p*-xylenes.[5] Several mechanisms were proposed to explain these aromatization reactions,[5b,6] which are accompanied by Cope rearrangements such as the isomerization **5d**→**5c**.[5c]

Up to now, all attempts to prepare the diaza analogues of **5**, namely, the heterocycles **9**, failed (Scheme 1).[7] Neither the double Neber reaction of hydrazonium salts **6a**,**b** or similar starting materials nor the coupling reaction of 2-chloro-2*H*-azirine **7b** with various reagents generated the bi-2*H*-azirin-2-yls **9**.[8a] Later, Storr and Gallagher[9] reported the treatment of **7c** with lithium in THF, which was said to lead to pyrimidine **10c** (10% yield) and pyrazine **11c** (10%) but not to tetraphenylpyridazine (**18c**). The authors postulated the intermediate **9c**, which could not be observed. Attempts to generate **9a** from diazide **8a** failed immediately because the starting material **8a** could not be prepared.[5] To the best of our knowledge, 1,4-diazidobuta-1,3-dienes are unknown.[7]

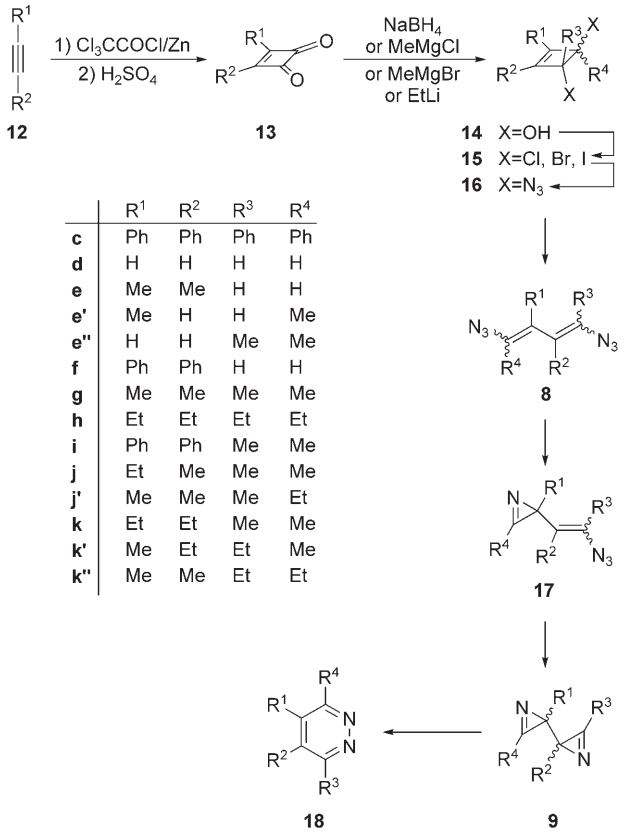


Scheme 1.

Nevertheless, we consider access via azides to be the most promising approach to investigate highly strained heterocycles of type **9** and their valence isomerization to yield diazabenzenes. If compounds **9** are unstable at room temperature, the reaction **8**→**9** can be performed not only by thermolysis but also by photolysis at low temperature. We describe here the synthesis of diazides **8c**–**g**,**j**,**k** and their transformation into biazirinyls **9c**,**d**,**f**,**g**,**j**,**k**, as well as their aromatization and the theoretical characterization of the last-named process.

Results and Discussion

Results in the literature[8,10] but also of our own efforts indicated quickly that classical methods[11] to prepare vinyl azides are unsuited to the synthesis of diazides of type **8**. Thus, we planned to generate these compounds by conrotatory ring opening of cyclobutenes of type **16** (Scheme 2). To prepare such 3,4-diazidocyclobutenes, we used the known

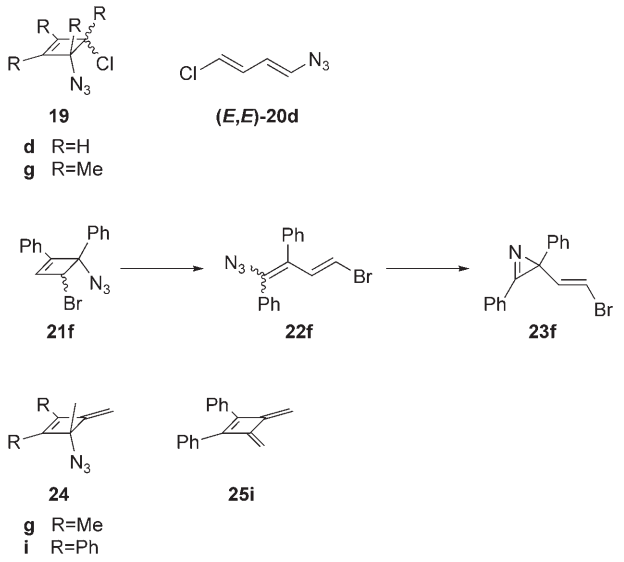


	R1	R2	R3	R4
c	Ph	Ph	Ph	Ph
d	H	H	H	H
e	Me	Me	H	H
e'	Me	H	H	Me
e''	H	H	Me	Me
f	Ph	Ph	H	H
g	Me	Me	Me	Me
h	Et	Et	Et	Et
i	Ph	Ph	Me	Me
j	Et	Me	Me	Me
j'	Me	Me	Me	Et
k	Et	Et	Me	Me
k'	Me	Et	Et	Me
k''	Me	Me	Et	Et

Scheme 2.

dihalides **15c**[12] (X=Br), *cis*-**15d** (X=Cl), *trans*-**15d**[13] (X=Cl, Br, I), a mixture[14] of the dibromides **15e**, **15e**′, and **15e**″, or **15f**[15] (X=Br) as well as **15g**,[16] **15i**,[17] **15j**,[18] and **15k**[18] (all X=Cl). Alternatively to the procedure of Brune et al.[18,19] via bis(methylene)cyclobutenes, some of these known and several new compounds were accessible more conveniently from alkynes **12** via cyclobutenediones **13**[20] and diols **14**,[21] which were transformed into dihalides **15** (X=Cl, Br, I) on treatment with $SOCl_2$, PBr_3, or PI_3. We prepared **15f** (X=I), **15h** (X=Br), and **15i** (X=Cl, Br) as pure substances, whereas **15j** (X=Cl, Br) and **15k** (X=Cl, Br) resulted each as mixtures with dihalides **15j**′ or **15k**′ and **15k**″, respectively. The equilibration of 3,4-dihalocyclobut-1-enes substituted with alkyl groups is notorious as a rapid process.[18,19] The synthesis of **15c** (X=Br) was performed by a different literature method.[12]

When the commercially available dichloride *cis*-**15d**[22] was treated with NaN_3, LiN_3, or tributylhexadecylphosphonium azide (QN_3)[23] under different conditions, we got only mixtures of *cis*-**16d**, *cis*-**19d**, (*E*,*E*)-**20d**, and **18d** (Scheme 3, Table 3). After isolation of the diazide *cis*-**16d**, we were not



Scheme 3.

able to perform electrocyclic ring opening by heating a solution of this compound. However, the reaction of the dibromide or the analogous diiodide *trans*-**15d** with a concentrated solution of QN_3 in chloroform gave, in addition to small amounts of the diazide *cis*-**16d** (7 and 6%, respectively), only the diazide (*E*,*E*)-**8d** (89 and 62%, respectively). Clearly, ring opening of *trans*-**16d** was very rapid, and therefore this intermediate was not detected by NMR spectroscopic monitoring of the substitution reaction. Nevertheless, the products of monosubstitution, 3-azido-4-bromocyclobut-1-ene and the analogous iodo compound, could be observed as intermediates. Evidently, the azido groups accelerate electrocyclic ring opening as effectively as other donor substituents such as alkoxyl groups. As shown by the work of Kirmse, Houk, and Rondan,[24] the maximum effect could be expected if the conrotatory process allows both donors to rotate "outward". The parent diazide (*E*,*E*)-**15d** could not be prepared with the help of alternative reagents, for example, sodium azide in DMSO, or by starting with less reactive dihalides. On treatment with QN_3 at 20°C, dichloride *trans*-**15d** gave a mixture of (*E*,*E*)-**20d** (62% yield) and **18d** (10%). Obviously, the second nucleophilic substitution could not compete with the rapid conrotatory ring opening generating monoazide (*E*,*E*)-**20d**.

However, different reaction conditions, such as sodium azide or lithium azide in DMSO or QN_3 in chloroform, proved to be appropriate to transform a mixture of dibromide **15e** and allyl isomers **15e′** and **15e″** into the open-chain product (*E*,*E*)-**8e** (34–37%) in addition to *cis*-**16e** (yield ca. 16%). Similar procedures were not optimal in the case of starting material **15f** (X = Br) because the synthesis of (*E*,*E*)-**8f** is accompanied by formation of monoazide **22f** and its succeeding product **23f**. The intermediate **21f**, which is generated by S_N2' reaction from dibromide **15f** and is a precursor of **22f**, was detected by NMR spectroscopic monitoring in an amount of up to 60%. The best yield (70%) and highest purity of (*E*,*E*)-**8f** were achieved when diiodide **15f** had been treated with QN_3.

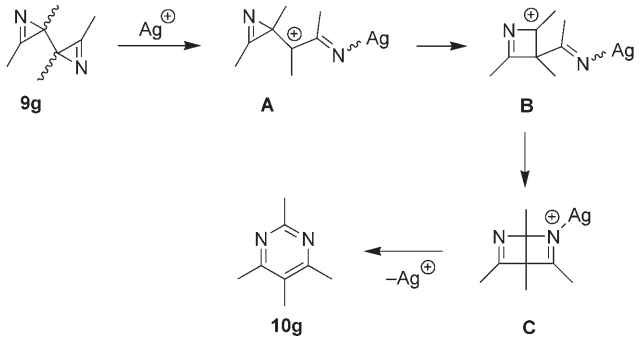
On photolysis in dichloromethane or chloroform at −50 to −85°C, diazides (*E*,*E*)-**8d**, (*E*,*E*)-**8e**, and (*E*,*E*)-**8f** led to mono-2*H*-azirines (*E*)-**17d** (up to 60%), (*E*)-**17e** (up to 37%), and (*E*)-**17f** (up to 18%), respectively (Scheme 2). At first, we achieved the formation of bi-2*H*-azirin-2-yls **9** only in the case of irradiation of (*E*,*E*)-**8f**. Thus, both diastereomers of **9f** were generated in 20% yield in a ratio of 1.2:1. Small amounts of the very unstable compound **9d** (8% yield, 3:2 mixture of diastereomers) could only be detected by ^1H and ^{13}C NMR spectroscopy when (*E*,*E*)-**8d** was irradiated in the presence of the sensitizing agent 9,10-dicyanoanthracene in chloroform at −50°C. On warming this mixture of products from photolysis, **9d** degraded to furnish at best traces of **18d**. Different stabilities of the diastereomers of **9f** were observed by NMR spectroscopy at room temperature. The minor isomer of **9f** decomposed completely after a few minutes, whereas the major isomer could be detected even after several hours. Just like hydrocarbon **5a**, **9d** and also **9f** did not tend to aromatization.

To synthesize more stable diazides of type **8** and bi-2*H*-azirin-2-yls **9**, we tried to prepare tetrasubstituted 3,4-diazidocyclobut-1-enes **16**. Unfortunately, even when different reagents and conditions were used, dichloride **15i** as well as dibromides **15h** and **15i** could not be transformed into diazides, because elimination instead of substitution occurred. For example, the reaction of **15i** (X = Br) with QN_3 produced monoazide **24i** (18% yield) and the known hydrocarbon **25i**[25] (48%). However, treatment of *trans*-**15g** (X = Cl) with a concentrated solution of QN_3 in chloroform at 20°C gave a mixture of diazides *trans*-**16g** (55% yield) and *cis*-**16g** (9%) as well as the monoazides **19g** (5%, 3:2 mixture of diastereomers) and **24g** (17%). After separation by chromatography, *trans*-**16g** could be isolated, since the conrotatory electrocyclic ring opening to afford (*E*,*E*)-**8g** is strongly decelerated by inward rotation of the methyl groups. The target compound (*E*,*E*)-**8g** was generated only on warming in benzene (80°C), whereby the secondary products (*E*)-**17g** and known **18g**[26] are also formed. Prolonged heating led exclusively to **18g** (88% yield). On incomplete thermolysis of *trans*-**16g**, (*E*,*E*)-**8g** could be isolated in 14% yield based on the amount of converted starting material. We were not able to prepare **8g** by ring opening of *cis*-**16g**.

The *E* configuration of (*E*)-**17e**,**g** was determined from two-dimensional ^1H NMR nuclear Overhauser spectroscopy (2D-NOESY) experiments and nuclear Overhauser enhancement (NOE) difference spectra. Thus the configuration of (*E*,*E*)-**8e**,**g** is also confirmed. The *trans* structure of *trans*-**16g** was established by the signals of the ^1H NMR spectra, which exhibited very small low-field shifts in the presence of [Eu(fod)$_3$] (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato). The analogous spectra of the compounds *cis*-**16d**,**e**,**g** showed changes of the chemical shifts at least 300 times greater, since these diazides are able to interact with the shift reagent in a chelating[27] manner.

The synthesis of more unsymmetrical tetraalkyl-substituted (*E*,*E*)-1,4-diazidobuta-1,3-dienes **8** was performed like that of (*E*,*E*)-**8g**. Thus, mixtures of the chlorides **15j** and **15j′** or, alternatively, mixtures of the corresponding bromides were treated with QN_3 to afford 1:1 mixtures of the azides *trans*-**16j** and *trans*-**16j′** in 73–75% yield. Both the bromides **15k**, **15k′**, and **15k″** as well as the analogous mixture of allylic chlorides led similarly to a 1:2:1 mixture of the azides *trans*-**16k**, *trans*-**16k′**, and *trans*-**16k″** with 51 and 62% yield, respectively. Partial separation of the constitutional isomers of these *trans*-diazidocyclobutenes was possible. On heating, however, thermal electrocyclic ring opening competed with scrambling of the allylic isomers by [3,3] sigmatropic rearrangement[28] of the azido group. Therefore, mixtures of (*E*,*E*)-**8j** and (*E*,*E*)-**8j′** as well as mixtures of (*E*,*E*)-**8k**, (*E*,*E*)-**8k′**, and (*E*,*E*)-**8k″**, which unfortunately both could not be separated, were produced.

As expected, (*E*,*E*)-**8g** was transformed via (*E*)-**17g** into **18g** with high yield (97%) on thermolysis. However, the photochemical reaction of (*E*,*E*)-**8g** in $CDCl_3$ at −60°C, which proceeded also via (*E*)-**17g** with a proportion of up to 61%, led quantitatively to a 1:1 mixture of *meso*-**9g** and *rac*-**9g**. On warming the irradiated solution, both stereoisomers were converted to **18g** in quantitative first-order reactions. One of these valence isomerizations occurred already with $k = 3.65 \times 10^{-4}\ s^{-1}$ at −25°C, and the other with $k = 1.73 \times 10^{-4}\ s^{-1}$ at +10°C. In the presence of silver(I) tetrafluoroborate at −25°C, the more stable diastereomer of **9g** was slowly (7 d) but completely transformed into known[29] **10g**, whereas the other stereoisomer gave **18g** again. A mechanism including the intermediates **A**, **B**, and **C** may be responsible for formation of **10g** (Scheme 4). Similar mechanisms were discussed for the reaction of bicycloprop-2-enyls to benzene derivatives. In the case of the latter transformation, Dewar benzenes were proved as intermediates or even isolated.[1a,6b] Photolysis of (*E*,*E*)-**8g** in the more UV transparent CD_3CN using quartz equipment at −40°C furnished (*E*)-**17g** and **9g** first and then, after prolonged irradiation, a mixture of **10g** (40%) and **18g** (22%) as well as the fragmentation products but-2-yne (3–4%) and acetonitrile (3–4%). As shown in control experiments, **10g** and **18g** were photochemically stable also under these conditions. Similar prolonged photolysis of the diazides *cis*-**16g** and *trans*-**16g** in CD_3CN proceeded via **9g** and resulted in the formation of both aromatics **10g** (15% in both cases) and **18g** (33 and 41%, respectively) as well as traces of but-2-yne and acetonitrile.



Scheme 4.

To investigate whether the aromatization **9**→**18** is accompanied by the Cope rearrangement of **9**, which would exchange the "inner" (R^1,R^2) and the "outer" substituents (R^3,R^4), we included starting materials with different alkyl substituents such as (*E*,*E*)-**8j** and (*E*,*E*)-**8k**. Because we were only able to use (*E*,*E*)-**8j** as an inseparable mixture with (*E*,*E*)-**8j′** as well as (*E*,*E*)-**8k** as a mixture with (*E*,*E*)-**8k′** and (*E*,*E*)-**8k″**, we could not prove strictly that the transformation of one constitutional isomer of **8** led exclusively to one isomer of **18** without any scrambling of the substituents. However, the ratio (*E*,*E*)-**8j**:(*E*,*E*)-**8j′** agreed with the ratio **9j**:**9j′** after quantitative photochemical reaction, and these ratios correspond also to the ratio **18j**:**18j′** after quantitative thermal aromatization. Concerning the analogous quantitative transformations, the same held true for the ratios (*E*,*E*)-**8k**:(*E*,*E*)-**8k′**:(*E*,*E*)-**8k″**, **9k**:**9k′**:**9k″**, and **18k**:**18k′**:**18k″**, easily measured by ^1H NMR spectroscopy. Therefore, scrambling of the substituents during the isomerization **9**→**18** seems to be unlikely.

We monitored the reaction of **15c** (X = Br) with QN_3 in $CDCl_3$ by NMR spectroscopy at low temperature. Even in the range of −50 to −25°C, nucleophilic substitution and electrocyclic ring opening proceeded so rapidly that only some of the signals of **8c** could be assigned with certainty. At +5°C, slow evolution of nitrogen started, in the course of which one geometrical isomer of **17c** with a maximum amount of 87% and after that both stereoisomers of **9c**, generated in a ratio of 2:1, could be detected unequivocally. This *thermal* formation of bi-2*H*-azirin-2-yls was not surprising, because there are several reports in the literature on thermal transformation of other 1-azido-1,2-diphenylethenes into 2*H*-azirines, which occurred already at low temperatures.[30] After prolonged reaction times or after slight warming of the reaction mixture including **9c**, only the known aromatic compound **18c**[31] was found with 87% NMR yield based on dibromide **15c**. Although we prepared the known heterocycles **10c**[32] and **11c**[33] for comparison, they could not be detected as thermal secondary products of **9c**. This should exclude the postulated[9] bi-2*H*-azirin-2-yl **9c** being intermediate during the transformation **7c**→**10c**+**11c** assuming that the presence of the generated lithium chloride did not change the thermal successive reactions of **9c** dramatically. When a reaction mixture with a large amount of **8c** resulting from **15c** (X = Br) and QN_3 was irradiated at low temperature, pyrimidine **10c** was formed in 44% yield, whereas **11c** and **18c** could not be detected.

The thermal valence isomerization **9**→**18** showed some remarkable singularities, which deserve special attention with regard to its reaction mechanism. Compared to thermal reactions of simple 2*H*-azirines,[34] the low temperature at which the aromatization **9**→**18** could be performed was sur-

prising, especially when compared to the temperatures which were necessary for analogous valence isomerization of bicycloprop-2-enyls.[5,6] The very different reactivities of *meso*- and *rac*-**9** or *unlike*- and *like*-**9**, respectively, are also noteworthy. Furthermore, the exclusive thermal transformation of **9** to yield pyridazines **18** should be explained, since bicycloprop-2-enyls such as **5c** or **5d** led to mixtures of *o*-, *m*-, and *p*-xylenes.[5] The formation of pyridazines from two molecules of simple 2*H*-azirines was observed only in rare cases and with very low yield.[35] On the other hand, similar dimerizations to yield pyrazine derivatives were reported several times.[34]

Quantum-Chemical Calculations

To elucidate the mechanisms of the thermal biazirinyl ring-opening processes and to understand the experimental results, we investigated parts of the energy hypersurface of the parent system **9d** and that of the tetramethyl-substituted biazirinyls **9g**. All optimizations were performed at the UB3LYP/6-31+G* level using the Gaussian 98 program,[36] and the stationary points were characterized as transition states or minima by harmonic frequency analyses. All reported relative energies are corrected for zero-point vibrational energies (ZPVE) as obtained from the DFT calculations (unscaled).

In the DFT calculations, the guess=mix keyword was employed to enforce convergence of the SCF procedure to a spin- and spatial-symmetry broken solution (BS-UDFT). For the biradicals or transition states with significant biradical character, $\langle S^2\rangle$ values between 0.4 and 1.1 were found (see Table 1).[37,38] In view of the thus-introduced uncertainty and the complexity of the electronic structure problem, we decided to check the most relevant species by single-point calculations at the MR-MP2[39] and UCCSD(T) levels. Note that the Hartree–Fock solutions (on which CCSD(T) is based) suffer even more from spin contamination than DFT, as is evident from $\langle S^2\rangle$ values between 1.22 and 1.98. We also applied the spin-correction procedure proposed by Ya-

Table 1. Relative energies $E_{rel(0\,K)}$ [kcal mol^{-1}] with respect to *rac-syn*-**9d** from UB3LYP/6-31+G*, spin-corrected (SC) UB3LYP/6-31+G*,[40] MR-MP2/TZV(2df,2p), and UCCSD(T)/TZVP calculations, and $\langle S^2\rangle$ values from UB3LYP and UHF calculations (which are the basis for the UCCSD(T) treatment) for the species **9d**, **18d**, **26d**, **27d**, **28d**, **29d**, and the related transition states.

	$E_{rel(0\,K)}$ (UB3LYP/6-31+G*)	$\langle S^2\rangle$ (UB3LYP)	$E_{rel(0\,K)}$ [UB3LYP/6-31+G* (SC)]	$E_{rel(0\,K)}$ [MR-MP2/TZV (2df,2p)]	$E_{rel(0\,K)}$ [UCCSD(T)/TZVP-(d,p)]	$\langle S^2\rangle$ (UHF)
rac-syn-**9d**	0.0	0.0000	0.0	0.0	0.0	0.0000
rac-anti-**9d**	0.1	0.0000		0.6		
TS *rac-syn*-**9d**→*rac-anti*-**9d**	2.1	0.0000				
meso-gauche-**9d**	1.2	0.0000				
meso-anti-**9d**	−0.1	0.0000				
TS *meso-gauche*-**9d**→*meso-anti*-**9d**	1.2	0.0000				
18d	−70.8	0.0000		−63.3		
cis-**26d**	−9.2	1.0429	−9.7	−6.4	0.3	1.9880
trans-**26d**	−11.7	1.0437		−6.4		
TS *cis*-**26d**→*trans*-**26d**	29.0	2.0718				
TS *rac-syn*-**9d**→*cis*-**26d**	17.4	0.4431	11.6	13.4	24.4	1.5461
TS *rac-anti*-**9d**→*trans*-**26d**	18.6	0.4271	13.1	14.8	26.0	1.5476
TS *meso-anti*-**9d**→*trans*-**26d**	19.9	0.5256				
TS *cis*-**26d**→**18d**	−2.1	1.0244	−2.2	3.6	3.2	1.8060
syn-**27d**	16.1	1.1014	22.4	27.0	29.7	1.1790
anti-**27d**	15.1	1.0148	20.8		22.6	1.2615
TS *rac-anti*-**9d**→*anti*-**27d**	19.7	0.6658				
TS *rac-syn*-**9d**→*syn*-**27d**	19.5	0.7337	16.3	25.3	25.8	1.2278
TS *meso-anti*-**9d**→*anti*-**27d**	20.0	0.6705				
TS *meso-gauche*-**9d**→*syn*-**27d**	21.4	0.6433				
TS *syn*-**27d**→*cis*-**26d**	15.8	1.0200	20.6	26.4	23.2	1.4195
TS *anti*-**27d**→*trans*-**26d**	14.7	1.0201				
TS *syn*-**27d**→*anti*-**27d**	21.9	0.9938				
28d	−62.6	0.0000				
TS *cis*-**26d**→**28d**	−4.9	1.0253	−4.9	1.1	1.5	1.8250
trans-**26d′**	−9.1	1.0507		−3.4		
trans-**26d″**	−7.7	1.0562				
TS *trans*-**26d**→***trans*-26d′**	−5.7	1.0229				
TS *trans*-**26d′**→***trans*-26d″**	−3.4	1.0261				
s-*trans*-**29d+HCN**	20.7	0.9587		20.6		
s-*cis*-**29d+HCN**	23.2	0.9391				
TS *trans*-**26d′**→s-*trans*-**29d+HCN**	26.2	0.9914		23.5		
TS *trans*-**26d″**→s-*cis*-**29d+HCN**	28.4	1.0006				
HCCH+2HCN	−13.2	0.0000				
TS s-*trans*-**29d+HCN**→**HCCH+2HCN**	22.9	0.5047		18.2		
TS *trans*-**26d**→**HCCH+2HCN**	35.4	0.0000		25.9		

maguchi, Jensen, Dorigo, and Houk,[40] using the UB3LYP wavefunction. For diradicals ($\langle S^2\rangle \approx 1$), we found corrections ranging from +0.1 to +6 kcal mol^{-1}, and for systems with less spin contamination ($\langle S^2\rangle \approx 0.5$) corrections of −3.2 to −5.5 kcal mol^{-1} that disagree with the results from the MR-MP2 method. Table 1 compares the relative energies from the three mentioned methods for the selected set of stationary points. The qualitative picture of the energetics is the same for all methods, although significant differences are noted, for example, between DFT or MR-MP2 and CCSD(T) for the transition state **TS** *rac-anti*-**9d**→*trans*-**26d** as well as between DFT and MR-MP2 or CCSD(T) for *syn*-**27d** and **TS** *syn*-**27d**→*cis*-**26d**. However, for the most important question whether the reaction proceeds via intermediate **27d** or directly from *rac*-**9d** to *cis*-**26d**, all methods agree qualitatively, that is, the barrier *rac-syn*-**9d**→*syn*-**27d** is higher than that between *rac-syn*-**9d** and *cis*-**26d**. If we consider the MR-MP2 results as most accurate (because it is not spin-symmetry broken and accounts for static and dynamic electron correlation effects), the difference between these two barriers is more than 10 kcal mol^{-1} in favor of the concerted mechanism.

Parent bi-2*H*-azirin-2-yls 9d: As aforementioned, the biazirinyls exist in two diastereomeric forms (*rac* and *meso*), each in two rotational conformations. The structures of the potential energy minima of the parent biazirinyls, C_2-symmetric *rac-syn*-**9d** and *rac-anti*-**9d,** as well as *meso-gauche*-**9d** (C_1) and *meso-anti*-**9d** (C_i), are plotted in Figure 1. These structures have similar energies (within 1.3 kcal mol^{-1}) and there is only a small barrier for rotation around the central C–C single bond (about 2.1 kcal mol^{-1}, see Table 1).

There are two obvious reaction paths to trigger thermal isomerization of *rac*- and *meso*-**9d**: breaking either the C–C or the C–N single bonds in the azirine rings. For the parent azirine, it is experimentally well known that fission of a C–N single bond is much easier than C–C bond breaking.[34] Our calculations are well in accord with these observations. For the thermal C–C breakage of azirine to yield the nitrile ylide, an activation energy of 46.7 kcal mol^{-1} (UB3LYP/6-31+G*, resulting in the closed-shell transition state) and 52.2 kcal mol^{-1} [MR-MP2/TZV(2df,2p)] was calculated. However, for the C–N breakage of azirine an open-shell transition state (24.8 kcal mol^{-1} at UB3LYP, 27.3 kcal mol^{-1} at MR-MP2) was localized to give diradicaloid vinylnitrene (19.9 kcal mol^{-1} at UB3LYP, open-shell singlet with some mixing in of the triplet state, and 31.4 kcal mol^{-1} at MR-MP2, open-shell singlet).

Heterolytic C–C bond breaking of bi-2*H*-azirin-2-yls **9d**, with calculated activation energies of 40–47 kcal mol^{-1} (all UB3LYP calculations give closed-shell species), is comparably unfavorable.[41] Here, in the first step, C–C bond fission of one of the two azirine rings would lead to a nitrile ylide. This could either attack the second azirine ring at the nitrogen atom to produce pyrimidine or, after thermal opening of the second ring, could give a bis(nitrile ylide), which would aromatize immediately to pyrazine. We could not detect a reaction pathway with simultaneous C–C breaking of both azirine rings (see below).

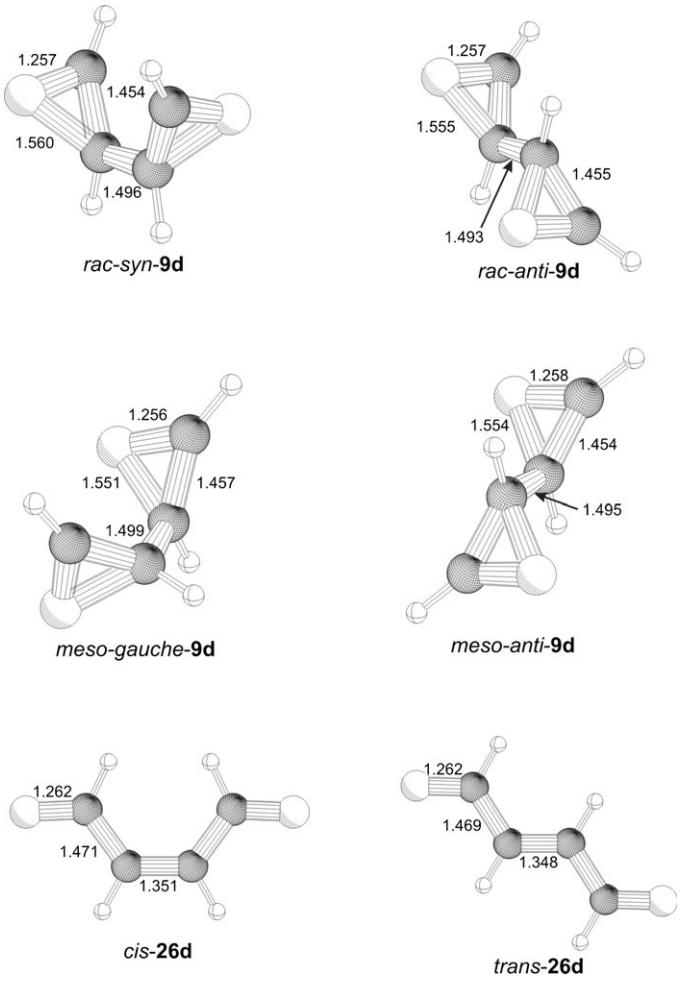


Figure 1. UB3LYP/6-31+G* optimized structures for bi-2*H*-azirin-2-yls **9d** and *N,N′* diradicals **26d** (bond lengths in Å).

To break the two C–N single bonds in both azirine rings of **9d** homolytically, there are in principle two reaction pathways: breaking of the C–N single bonds one after the other or simultaneous breaking of both bonds (two-stage or concerted). Both reactions lead to *N,N′* diradicals. From *rac-syn*-**9d** and *meso-gauche*-**9d**, the *Z* diradical *cis*-**26d** is formed, while *rac-anti*-**9d** and *meso-anti*-**9d** give rise to the *E* diradical *trans*-**26d** (Figure 1). With $\Delta H^{\neq}$ in the range of 19.5–21.4 kcal mol^{-1}, the activation barriers for the first step of the two-stage reaction pathway (**9d**→**27d**→**26d**) are much lower than those of C–C bond cleavage (Figure 2). Upon including the zero-point energy, the energy of the transition state (**TS** *syn*-**27d**→*cis*-**26d**) drops below those of the intermediate *C,N* diradicals *syn*-**27d** and *anti*-**27d**. Therefore, this reaction pathway is concerted (unsymmetrical) rather than stepwise. On the other hand, there is also a synchronous pathway with symmetric cleavage of both C–N bonds (*rac-syn*-**9d**→*cis*-**26d**, *rac-anti*-**9d**→*trans*-**26d**) with slightly lower activation energy of 17.4 or 18.6 kcal mol^{-1}. At the more reliable MR-MP2/TZV(2df,2p) level of theory, the

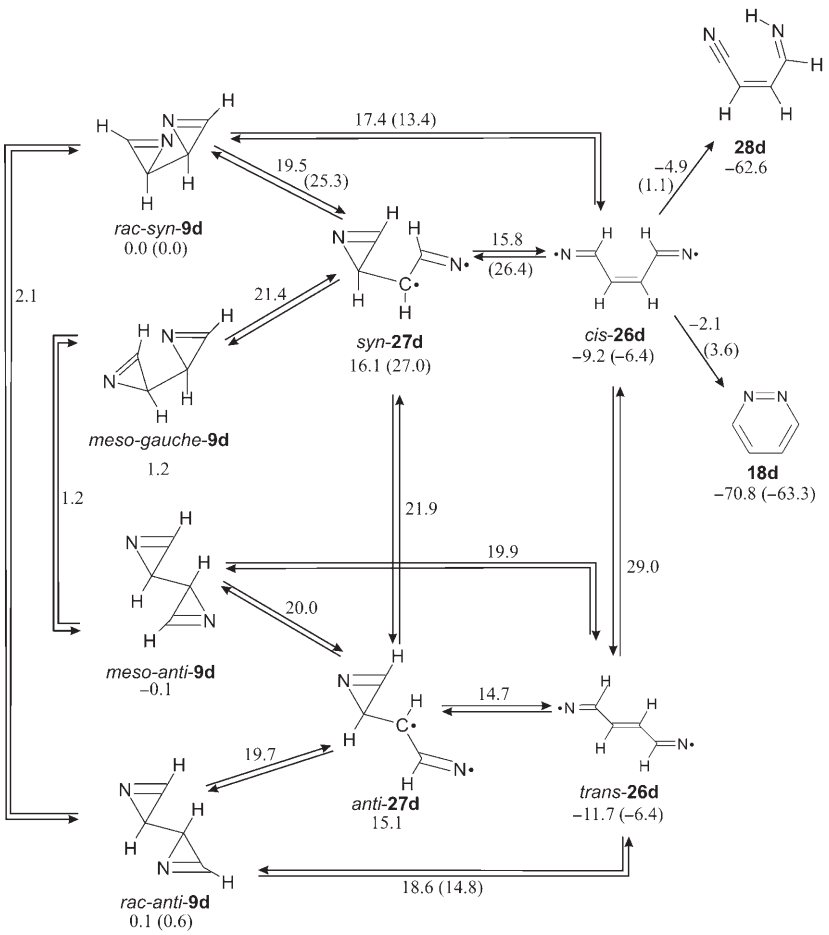


Figure 2. Reactions of the parent biazirinyls **9d** that are triggered by C–N bond breaking: Energies at UB3LYP/6-31+G* (ZPVE corrected) relative to *rac-syn*-**9d** are given in kcal mol^{-1}. Relative energies of transition states are given at the corresponding arrows; relative energies (ZPVE-corrected), calculated at the MR-MP2/TZV(2df,2p) level, are given in parentheses.

following barriers for the symmetrical cleavage were obtained: 13.4 and 14.8 kcal mol^{-1}. Interestingly, the diradicals *cis*-**26d** and *trans*-**26d** are more stable than the closed-shell (but highly strained) biazirinyls [−9.2 and −11.7 kcal mol^{-1} at UB3LYP/6-31+G* and −6.4 kcal mol^{-1} for both at MR-MP2/TZV(2df,2p)]. The stability of the diradicals probably arises from the planar geometry and hence effective conjugation of the π system. Summing up, it can be stated, that there is a low energy pathway, either concerted or even synchronous (operative at room temperature), that converts the parent biazirinyls *rac*- and *meso*-**9d** to the diradicals *cis*-**26d** and *trans*-**26d**, respectively.

To obtain information on the fate of the diradicals in the experimental setup, we performed additional calculations on the $C_4H_4N_2$ energy hypersurface starting from *cis*-**26d** and *trans*-**26d**. Rotation of one or both C=N$^{\bullet}$ groups around the C–C single bonds of *cis-N,N′* diradical *cis*-**26d** leads to nitrile **28d** via a 1,5-H shift or to pyridazine **18d**, respectively, via aromatization. Both reactions have low activation energies (*cis*-**26d**→**28d** 4.3 kcal mol^{-1}, *cis*-**26d**→**18d** 7.1 kcal mol^{-1}).

Led by the observation that in case of other substituted biazirinyl systems thermal fragmentation to alkynes and nitriles was observed as the dominant process,[42] we also investigated this pathway for the parent system. There is no such pathway for *Z* diradical *cis*-**26d**, but all rotational isomers of *E* diradical *trans*-**26d** (Figure 3) can undergo fragmentation. Ethyne and two molecules of hydrocyanic acid are either eliminated simultaneously from *trans*-**26d** or in two stages from *trans*-**26d′** and *trans*-**26d″**. Both pathways have relatively high barriers (*trans*-**26d**→C_2H_2+2HCN 47.1, *trans*-**26d′**→s-*trans*-**29d** 35.3, *trans*-**26d″**→s-*cis*-**29d** 36.1 kcal mol^{-1}).

Elimination of hydrogen cyanide leads to unstable *C,N* diradicals s-*trans*-**29d**, which form ethyne and a second hydrogen cyanide molecule with activation energies of about 2 kcal mol^{-1}. Again, comparison of the energies at the UB3LYP/6-31G* and MR-MP2/TZV-(2df,2p) levels gives evidence that the DFT method is appropriate to describe these structures. Both methods agree that the activation barriers for the fragmentation are too high to be overcome at experimental ambient conditions in the parent system.

Tetramethylbi-2*H*-azirin-2-yls 9g: We extended our calculations further to the tetramethylbiazirinyls **9g**, which serve as models for the experimentally studied alkyl-substituted derivatives. We were especially interested to learn about the substituent effect of the methyl groups on the course of the ring-opening process. Due to the presence of the methyl groups, we were not able to localize all the transition states which interconnect the various species involved in the rearrangement. Tetramethylbiazirinyl **9g** exhibits similar configurations and conformations to the parent system (Figure 4). We found that simultaneous homolytic C–N bond breaking of both azirine rings is preferred in comparison to sequential homolytic opening of the three-membered rings. Compared to the parent system, the activation barriers for the simultaneous cleavage of the C–N bonds are here somewhat lower for the *rac* isomers but higher for the *meso* isomers (Table 2).

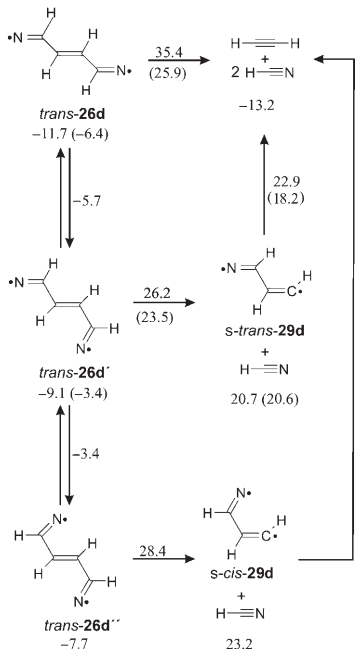


Figure 3. Fragmentation pathways for the *E* diradical *trans*-**26d**: Energies at UB3LYP/6-31+G* level (ZPVE corrected) in kcal mol^{-1} are relative to biazirinyl *rac-syn*-**9d**. Energies of transition states are given at the corresponding reaction arrows; relative energies (ZPVE-corrected), calculated at the MR-MP2/TZV(2df,2p) level, are given in parentheses.

However, the geometries and energies of the tetramethyl *N*,*N*′ diradicals **26g** formed by the initial bond-breaking process are markedly different. They are nonplanar because of steric hindrance of the methyl groups. In comparison to the parent system, where diradicals **26d** are more stable than bisazirinyls **9d**, here tetramethyl *N*,*N*′ diradicals **26g** are 7–10 kcal mol^{-1} less stable than tetramethylbiazirinyls **9g**. The C–C single bonds of the tetramethyl diradicals are longer (1.51 Å) than in the parent system (1.47 Å), and this indicates reduced conjugation and thus destabilization, while the central C=C bond is similar in length in both systems. Being nonplanar, the tetramethyl *N*,*N*′ diradicals are more easily converted to tetramethylpyridazine **18g**, which in turn also suffers from steric interaction of the methyl groups. Thus, we explain the different chemical behavior of the methyl-substituted biazirinyls **9g** mainly as a result of steric repulsion of the methyl groups in diradicals **26g** and cyclic compound **9g** in comparison to the parent biazirinyls **9d**.

Conclusion

Electrocyclic ring opening of 3,4-diazidocyclobutenes **16** is a successful strategy to prepare 1,4-diazidobuta-1,3-dienes **8**, which were unknown before. By irradiation of the latter, long-sought[8,9] bi-2*H*-azirin-2-yls **9** are accessible for the first time. The postulated[8] valence isomerization of these heterocycles can indeed be realized, but the thermal transformation does not lead to pyrimidines and pyrazines as was suggested.[9] Pyridazines **18** are produced instead. On the basis of quantum-chemical calculations, their formation is explained by short-lived but energetically favorable *N*,*N*′ diradicals **26**, which are generated by simultaneous homolytic cleavage of both C–N bonds of the azirine rings. Assuming these intermediates, the low barrier for the aromatization process **9**→**18**, which excludes any competitive diaza Cope rearrangement, can easily be rationalized. The more rapid reaction of the *rac* stereoisomers of **9** compared to the corresponding *meso* compounds is also explained by the theoretical studies. Furthermore, the missing formation of aromatic compounds **18** in the case of heterocycles **9** with a low number of substituents is interpreted by competitive reactions of the involved intermediates **26**.

Presently, we are trying to prepare more stable bi-2*H*-azirin-2-yls which will allow experimental assignment of their stereochemistry and direct correlation of their rates of valence isomerization.

Experimental Section

Caution: Care must be taken in handling azides, which are explosive. Especially neat (*E*,*E*)-**8d** can lead to heavy explosions on friction.

Instrumentation and measurement: Melting points were determined with a Pentakon Dresden Boetius apparatus and are uncorrected. FTIR spectra were recorded on a BRUKER IFS 28 FTIR spectrophotometer. IR measurements were made on solutions in KBr cuvettes. UV/Vis spectra were acquired by using a Carl Zeiss Jena SPECORD UV/Vis spectrophotometer in cuvettes of 1 cm thickness. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 300 and 75 MHz, respectively. NMR signals were referenced to TMS ($\delta=0$) or solvent signals and recalculated relative to TMS. The multiplicities of ^{13}C NMR signals were determined with the aid of gated spectra and/or DEPT135 experiments. GC-MS spectra were acquired with a Hewlett-Packard model 5989 quadrupole mass spectrometer. Ionization was performed by EI (70 eV). For the previous separation, a Hewlett-Packard model 5890 series II gas chromatograph with thermal conductivity detector was used (column: HP-MS 5 (60 m), carrier gas: helium). HRMS (ESI) spectra were recorded on an Applied Biosystems Mariner 5229 mass spectrometer. The elemental analyses were performed with a Vario EL elemental analyzer from Elementar Analysensysteme GmbH Hanau. Elemental analyses of explosive azides and highly unstable azirines could not be performed. The gas chromatograms were recorded with a Hewlett-Packard model 5890 series II gas chromatograph with flame ionization detector (column: HP-MS 5 capillary column (5% phenylmethylsilicone gum), carrier gas: nitrogen). Preparative GC separations were carried out with a Shimadzu model GC 8A gas chromatograph. Separation conditions and columns used are given at the separated compounds. 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 separations were carried out under isocratic flow with distilled and degassed solvents. A KNAUER model 64 HPLC pump equipped with MERCK LiChrospher Si 60, 5 μm (∅ 20 mm, $l=20$ cm) column and UV detector ($\lambda=254$ nm) was used.

General instructions for photolysis: Irradiation was conducted at −40 to −60 °C by using a high-pressure mercury lamp (TQ150, Heraeus GmbH) supplied with glass or quartz equipment and an ethanol cryostat. Most of these photolyses were monitored by NMR spectroscopy. Thus, the solution of the appropriate starting material was irradiated in an NMR tube. To exclude oxygen, this solution was flushed with argon in an ultrasonic bath prior to irradiation. Dioxane was used as standard to determine yields based on ^{1}H NMR data. When a photosensitizer was employed, sa-

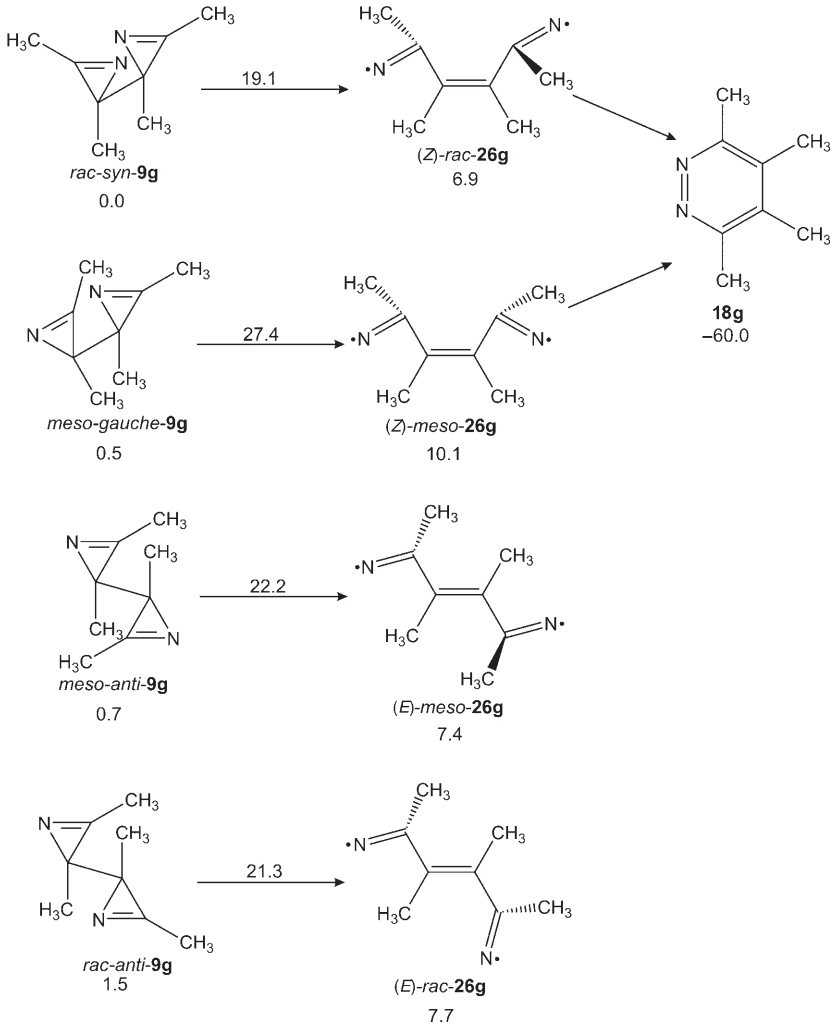


Figure 4. Reactions of tetramethyl-bi-2*H*-azirin-2-yls **9g**: Energies at UB3LYP/6-31+G* level (ZPVE-corrected) relative to tetramethylbiazirinyl *rac-syn*-**9g** are given in kcal mol^{-1}. Energies of transition states are given above the corresponding arrows.

turated solutions of the sensitizer were used as solvent. Exact conditions are given at the compounds irradiated.

3-Ethyl-4-methylcyclobut-3-ene-1,2-dione (13j): Using a known procedure,[20] pent-2-yne (**12j**) was treated with activated zinc powder and trichloroacetyl chloride to give regioisomeric 4,4-dichloroethylmethylcyclobut-2-enones, which were hydrolyzed in the presence of sulfuric acid to yield **13j** as a pale yellow liquid (see Supporting Information for details). IR ($CDCl_3$): $\tilde{\nu}$ = 1771 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 1.29 (t, ^3J = 7.7 Hz, 3H; 2′-H), 2.34 (t, ^5J = 1.0 Hz, 3H; Me), 2.75 (qq, ^3J = 7.7 Hz, ^5J = 1.0 Hz, 2H; 1′-H); ^{13}C NMR ($CDCl_3$): δ = 10.13 (q), 11.14 (q), 19.88 (t, C-1′), 198.58 (s), 199.12 (s), 199.63 (s), 204.10 (s); MS (ESI): *m*/*z* (%): 125.0535 (0.3) [*M*+H$^+$; calcd 125.0597], 249.1092 (100) [2*M*+H$^+$; calcd 249.1121]; elemental analysis calcd (%) for $C_7H_8O_2$: C 67.73, H 6.50; found: C 67.65, H 6.57.

***cis*-3,4-Diphenylcyclobut-3-ene-1,2-diol (*cis*-14f)**: Cyclobutenedione **13f** was treated with $LiAlH_4$ to prepare *cis*-**14f** in 23% yield.[21a] We found that the yield could be increased to 71% by using $NaBH_4$/$CeCl_3$ instead of $LiAlH_4$, analogously to a known procedure.[43]

1,2,3,4-Tetraethylcyclobut-3-ene-1,2-diol (14h): A solution of ethyllithium[44] (0.75 M, 100 mL, 75 mmol) in Et_2O was cooled to −60 °C. Thereafter a solution of 3,4-diethylcyclobut-3-ene-1,2-dione (**13h**=**13k**)[20] (2.76 g, 20.0 mmol) in anhydrous Et_2O was added dropwise at a temperature not above −55 °C. The reaction mixture was stirred at −60 °C for 1 h and then added slowly at a temperature not above −55 °C (**caution**: strongly exothermic reaction) to a previously prepared mixture of glacial acetic acid (6.00 g, 100 mmol) and anhydrous Et_2O (200 mL), which was cooled to −60 °C. After the addition was finished, stirring was continued for 30 min. Then the reaction mixture was washed (1×H_2O, 2×aq $NaHCO_3$, 2×H_2O) and dried ($MgSO_4$). After removing the solvent under reduced pressure, **14h** (3.64 g, 18.4 mmol, 92%) was obtained as a yellow oil which was recondensed in vacuum and crystallized (hexane, −25 °C) to give a white solid, m.p. 69 °C (hexane). IR ($CDCl_3$): $\tilde{\nu}$ = 3479 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ = 1.03 (t, ^3J = 7.4 Hz, 6H; CH_3CH_2 at C-3/C-4), 1.06 (t, ^3J = 7.8 Hz, 6H; CH_3CH_2 at C-1/C-2), 1.71 (m, 4H; CH_2 at C-3/C-4), 2.08 (br q, ^3J = 7.8 Hz, 4H; CH_2 at C-1/C-2), 4.40 ppm (br s, 2H; OH); ^{13}C NMR ($CDCl_3$): δ = 8.53 (q), 12.99 (q), 18.00 (t, CH_2 at C-1/C-2), 27.74 (t, CH_2 at C-3/C-4), 84.79 (s, C-1/C-2), 147.51 ppm (s, C-3/C-4); MS (ESI): *m*/*z* (%): 181.1601 (100) [*M*−OH$^-$; calcd 181.1587]; elemental analysis calcd (%) for $C_{12}H_{22}O_2$: C 72.68, H 11.18; found: C 72.40, H 10.85. If hydrolysis of the reaction mixture obtained after treatment of the dione with ethyllithium was performed at higher temperature (0 °C) with ice/H_2O, open-chain diketones were found as main products (see Supporting Information for details).

3-Ethyl-1,2,4-trimethylcyclobut-3-ene-1,2-diol (14j) and 3,4-diethyl-1,2-dimethylcyclobut-3-ene-1,2-diol (14k): Treatment of 3-ethyl-4-methylcyclobut-3-ene-1,2-dione (**13j**=**13k**′) or 3,4-diethylcyclobut-3-ene-1,2-dione (**13h**=**13k**) with methylmagnesium bromide was carried out analogously to a known procedure[21b] to get **14j** and **14k**, respectively.

14j: Yield 86%, white solid, m.p. 40 °C (hexane); IR ($CDCl_3$): $\tilde{\nu}$ = 3396 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, ^3J = 7.7 Hz, 3H; 2′-H), 1.20 (s, 3H), 1.23 (s, 3H), 1.54 (t, ^5J = 1.1 Hz, 3H; Me-4), 2.00 (qq, ^3J = 7.7 Hz, ^5J = 1.1 Hz, 2H; 1′-H), 3.10 ppm (br s, 2H; OH); ^{13}C NMR ($CDCl_3$): δ = 7.93 (q), 12.17 (q), 17.58 (t, C-1′), 18.35 (q), 19.11 (q), 79.71 (s), 80.04 (s), 143.18 (s), 149.04 ppm (s); MS (ESI): *m*/*z* (%): 139.1144 (18) [*M*−OH$^-$; calcd 139.1117], 179.1051 (100) [*M*+Na$^+$; calcd 179.1043], 335.2185 (44) [2*M*+Na$^+$; calcd 335.2193]; elemental analysis calcd (%) for $C_9H_{16}O_2$: C 69.19, H 10.32; found: C 68.96, H 10.24.

14k: Yield 82%, white solid, m.p. 85–86 °C (hexane); IR (CCl_4): $\tilde{\nu}$ = 3386 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ = 1.08 (t, ^3J = 7.7 Hz, 6H; 2′-H), 1.30 (s, 6H; 1-Me/2-Me), 2.07 (q, ^3J = 7.6 Hz, 2H; 1′-H), 2.08 (q, ^3J = 7.7 Hz, 2H; 1′-H), 2.45 ppm (br s, 2H; OH); ^{13}C NMR ($CDCl_3$): δ = 12.60 (q, C-2′), 17.66 (t, C-1′), 19.19 (q, Me-1/Me-2), 79.85 (s, C-1/C-2), 148.37 ppm (s, C-3/C-4); MS (ESI): *m*/*z* (%): 153.1267 (80) [*M*−OH$^-$; calcd 153.1274], 193.1213 (100) [*M*+Na$^+$; calcd 193.1199], 363.2471 (57) [2*M*+Na$^+$; calcd 363.2506]; elemental analysis calcd (%) for $C_{10}H_{18}O_2$: C 70.55, H 10.66; found: C 70.72, H 10.90.

Table 2. Relative energies $E_{rel(0\,K)}$ [kcal mol^{-1}] from UB3LYP/6-31+G* calculations for the species **9g**, **18g**, and **26d** and the related transition states.

	$E_{rel(0\,K)}$
rac-syn-**9g**	0.0
rac-anti-**9g**	1.5
meso-gauche-**9g**	0.5
meso-anti-**9g**	0.7
TS *rac-syn*-**9g**→(*Z*)-*rac*-**26g**	19.1
TS *rac-anti*-**9g**→(*E*)-*rac*-**26g**	21.3
TS *meso-anti*-**9g**→(*E*)-*meso*-**26g**	22.2
TS *meso-gauche*-**9g**→(*Z*)-*meso*-**26g**	27.4
(*Z*)-*rac*-**26g**	6.9
(*E*)-*rac*-**26g**	7.7
(*E*)-*meso*-**26g**	7.4
(*Z*)-*meso*-**26g**	10.1
18g	−60.0

Table 3. Product distribution after treatment of *cis*-**15d** (X=Cl) with azide-transfer reagents.

Reagent	Solvent	*t*/*T* [h/°C]	*cis*-**15d** (X=Cl) [%]	*cis*-**19d** [%]	*cis*-**16d** [%]	(*E*,*E*)-**20d** [%]	**18d** [%]
NaN_3	[D_6]DMSO	72/50	15	17	20	12	34
LiN_3	CD_3OD	72/70	27	6	––	––	traces
QN_3	C_6D_6	75/50	33	31	13	5	12
QN_3	molten	23/50	21	12	18	12	4

3,4-Diiodo-1,2-diphenylcyclobutene [15f (X=I)]: A solution of diol *cis*-**14f** (2.14 g, 8.99 mmol) in dry $CHCl_3$ (100 mL) was added to a solution of PI_3 (3.80 g, 9.22 mmol) in dry $CHCl_3$ (200 mL) at −50 °C. The reaction mixture was kept for 4 days at this temperature, then warmed to room temperature slowly, and stirred for 2 days. After washing (H_2O, aq $NaHCO_3$, aq $Na_2S_2O_3$, H_2O), the organic layer was separated and dried ($MgSO_4$). Evaporating the solvent under reduced pressure led to a residue which was recrystallized (Et_2O/hexane) to yield **15f** (X=I) (3.18 g, 6.94 mmol, 77%) as a pale beige crystalline solid, m.p. 127 °C (Et_2O/hexane). ^{1}H NMR ($CDCl_3$): δ=5.59 (s, 2H; 3-H/4-H), 7.41–7.46 (m, 6H), 7.53–7.58 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): δ=27.51 (d, C-3/C-4), 127.53 (d), 128.65 (d), 129.66 (d, *p*-Ph), 131.31 (s, *i*-Ph), 139.19 ppm (s, C-1/C-2); elemental analysis calcd (%) for $C_{16}H_{12}I_2$: C 41.95, H 2.64; found: C 41.93, H 2.81.

Reaction of *cis*-3,4-dichlorocyclobutene [*cis*-15d (X=Cl)] with azide-transfer reagents: *Reaction with NaN_3:* Finely powdered NaN_3 (101.3 mg, 1.56 mmol) was dissolved in [D_6]DMSO in an NMR tube with warming. Then the solution was allowed to cool to room temperature, and *cis*-**15d** (X=Cl) (52.2 mg, 0.42 mmol) was added. After 72 h at 50 °C the reaction mixture showed the composition given in Table 3. Separation was carried out by preparative GC on a nonpolar column (1 m, OV-101) at a column temperature of 80 °C. *Reaction with LiN_3*: Finely powdered LiN_3 (101.3 mg, 1.56 mmol) was dissolved in CD_3OD in an NMR tube. Then *cis*-**15d** (X=Cl) (52.2 mg, 0.42 mmol) was added. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 70 h at 70 °C the reaction was stopped. The composition of the mixture is given in Table 3. *Reaction with QN_3*: a) Hexadecyltributylphosphonium azide (QN_3, 165.3 mg, 0.352 mmol) was solved in C_6D_6 in an NMR tube and *cis*-**15d** (X=Cl) (14.0 mg, 0.114 mmol) was added. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 75 h at 50 °C the reaction was stopped. The composition of the mixture is given in Table 3. b) QN_3 (580 mg, 1.23 mmol) was melted and *cis*-**15d** (X=Cl) (50.0 mg, 0.41 mmol) was added at 50 °C. After 23 h at 50 °C the reaction mixture was recondensed in oil-pump vacuum to yield a colorless oil (34.6 mg) composed as given in Table 3.

***cis*-3-Azido-4-chlorocyclobutene (*cis*-19d)**: Colorless liquid; IR ($CDCl_3$): $\tilde{\nu}$=2108 cm^{-1} (N_3); ^{1}H NMR ($CDCl_3$): δ=4.44 (br d, J=2.8 Hz, 1H), 5.15 (m, 1H), 6.33 (m, 1H), 6.42 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): δ=62.57 (d), 64.25 (d), 138.16 (d), 142.83 ppm (d).

***cis*-3,4-Diazidocyclobutene (*cis*-16d)**: Colorless liquid; IR ($CDCl_3$): $\tilde{\nu}$=2109 cm^{-1} (N_3), 1261 (N_3); ^{1}H NMR ($CDCl_3$): δ=4.53 (br s, 2H; 3-H/4-H), 6.40 ppm (t, J=1.1 Hz, 2H; 1-H/2-H); ^{13}C NMR ($CDCl_3$): δ=65.26 (d, C-3/C-4), 140.24 ppm (d, C-1/C-2).

(*E*,*E*)-1-Azido-4-chlorobuta-1,3-diene ((*E*,*E*)-20d): Pale yellow liquid; IR ($CHCl_3$): $\tilde{\nu}$=2111 cm^{-1} (N_3), 1261 (N_3); ^{1}H NMR ($CDCl_3$): δ=5.90 (ddd, $^3J_{trans}$=13.3 Hz, ^3J=11.2 Hz, ^4J=0.6 Hz, 1H; 2-H), 6.14 (ddd, $^3J_{trans}$=13.1 Hz, J=0.8 Hz, J=0.6 Hz, 1H; 4-H), 6.20 (br d, $^3J_{trans}$=13.3 Hz, 1H; 1-H), 6.39 ppm (ddd, $^3J_{trans}$=13.1 Hz, ^3J=11.2 Hz, ^4J=0.6 Hz, 1H; 3-H); ^{13}C NMR ($CDCl_3$): δ=116.1 (d), 119.6 (d), 129.6 (d), 129.8 ppm (d). The assignment of ^{1}H NMR signals was possible by means of the greater peak width at half-height of the signal of 1-H.

(*E*,*E*)-1,4-Diazidobuta-1,3-diene ((*E*,*E*)-8d): QN_3 (2.0 g, 4.3 mmol) was melted with $CHCl_3$ (1 mL) to a homogenous solution. After cooling to room temperature, *trans*-**15d** (X=Br)[13] or *trans*-**15d** (X=I)[13] (1.5 mmol) was added. After 20 h [*trans*-**15d** (X=Br)] or 80 min [*trans*-**15d** (X=I)] at room temperature, the reaction mixture was separated by chromatography (Et_2O/hexane, silica gel). The first fraction contained butadiene (*E*,*E*)-**8d** [89% from *trans*-**15d** (X=Br) and 62% from *trans*-**15d** (X=I)]. As the second fraction *cis*-**16d** [7% from *trans*-**15d** (X=Br) and 6% from *trans*-**15d** (X=I)] was eluted. (*E*,*E*)-**8d**: Explosive yellow needles (hexane), m.p. (decomp). IR ($CDCl_3$): $\tilde{\nu}$=2099 cm^{-1} (N_3), 1257 (N_3); UV/Vis (CH_3CN): λ_{max} ($\lg\varepsilon$)=296 nm (4.52); ^{1}H NMR ($CDCl_3$): AA′XX′ system, δ_A=5.87 (m, 2H; 2-H/3-H), δ_X=6.12 ppm (m, 2H; 1-H/4-H); $^3J_{AX}$=$^3J_{A'X'}$=13.3 Hz, $^3J_{AA'}$=11.5 Hz, $^5J_{XX'}$=1.0 Hz, $^4J_{AX'}$=$^4J_{A'X}$=−0.5 Hz (coupling constants obtained by spectrum simulation); ^{13}C NMR ($CDCl_3$): δ=116.39 (d), 127.97 ppm (d).

Reaction of *trans*-3,4-dichlorocyclobutene [*trans*-15d (X=Cl)] with QN_3: QN_3 (1.0 g, 2.13 mmol) was melted with $CHCl_3$ (1 mL) to a homogenous solution. After cooling to room temperature, *trans*-**15d** (X=Cl)[13] (88.0 mg, 0.72 mmol) was added. After 24 h at room temperature, the reaction mixture was recondensed in vacuum and the solvent removed from the condensate under reduced pressure to yield a mixture of (*E*,*E*)-**20d** (62%) and **18d** (10%) as a light yellow oil.

Reaction of dibromides 15e, 15e′, and 15e″ with azide-transfer reagents: a) A mixture of isomeric dibromides **15e**, **15e′**, and **15e″**[14] (1.00 g, 4.17 mmol) in DMSO (5 mL) was added dropwise to a solution of NaN_3 (1.08 g, 16.6 mmol) in DMSO (40 mL) at room temperature. The reaction mixture was stirred for 45 min at 50 °C. After cooling, it was poured onto ice/H_2O and extracted with Et_2O. The organic layer was washed (H_2O), dried ($MgSO_4$), and the solvent was removed in vacuum. A mixture of (*E*,*E*)-**8e** and *cis*-**16e** (650 mg, ratio (*E*,*E*)-**8e**:*cis*-**16e**=1.8:1) and a small amount of unconverted bromides was obtained. Crystallization (CH_2Cl_2 at −25 °C) yielded (*E*,*E*)-**8e** (230 mg, 34%) as orange-yellow crystals. From the remaining solution, some more (*E*,*E*)-**8e** and *cis*-**16e** (108 mg, 16%, yellow oil) could be obtained by HPLC (Et_2O/hexane 1/40). b) A mixture of isomeric dibromides **15e**, **15e′**, and **15e″** (1.00 g, 4.17 mmol) in DMSO (5 mL) was added dropwise to a solution of LiN_3 (820 mg, 16.7 mmol) in DMSO (40 mL) at room temperature. The reaction mixture was stirred for 2 h at 40 °C. Workup followed the procedure described under a) to yield (*E*,*E*)-**8e** (250 mg, 37%) as orange-yellow crystals. c) A mixture of isomeric dibromides **15e**, **15e′**, and **15e″** (650 mg, 2.71 mmol) in $CHCl_3$ (2 mL) was added dropwise to a solution of QN_3 (3.80 g, 8.09 mmol) in $CHCl_3$ (3 mL) at room temperature. The reaction mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure, and the residue was separated by chromatography (silica gel, Et_2O). Crystallization (hexane) yielded (*E*,*E*)-**8e** (152 mg, 34%) as orange-yellow crystals.

(*E*,*E*)-1,4-Diazido-2,3-dimethylbuta-1,3-diene ((*E*,*E*)-8e): M.p. 48 °C (hexane, decomp); IR ($CDCl_3$): $\tilde{\nu}$=2100 cm^{-1} (N_3), 1258 (N_3); UV/Vis (cyclohexane): λ_{max} ($\lg\varepsilon$)=297 nm (4.46); ^{1}H NMR ($CDCl_3$): δ=1.75 (d, ^4J=1.1 Hz, 6H; Me), 6.26 ppm (q, ^4J=1.1 Hz, 2H; 1-H/4-H); ^{13}C NMR ($CDCl_3$): δ=11.97 (q, Me), 123.14 (d, C-1/C-4), 125.13 ppm (s, C-2/C-3).

***cis*-3,4-Diazido-1,2-dimethylcyclobutene (*cis*-16e)**: IR ($CDCl_3$): $\tilde{\nu}$ = 2101 cm^{-1} (N_3), 1241 (N_3); ^1H NMR ($CDCl_3$): δ = 1.74 (d, ^4J = 0.7 Hz, 6H; Me), 4.24 ppm (brs, 2H; 3-H/4-H); ^{13}C NMR ($CDCl_3$): δ = 11.48 (q, Me), 64.75 (d, C-3/C-4), 141.49 ppm (s, C-1/C-2).

Reaction of 3,4-diiodo-1,2-diphenylcyclobutene [15f (X = I)] with QN_3: 3,4-Diiodo-1,2-diphenylcyclobutene **15f** (X = I) (1.15 g, 2.51 mmol) was dissolved in a solution of QN_3 (4.20 g, 8.94 mmol) in $CHCl_3$ (5 mL). The reaction mixture was stirred at room temperature for 12 h and the color changed to bright yellow. The phosphonium salts were separated by chromatography (Et_2O/hexane), and the organic solvents were removed from the eluate in vacuum. Recrystallizing (Et_2O/hexane) the residue yielded 1,4-diazido-2,3-diphenylbuta-1,3-diene [(*E*,*E*)-**8f**] (508 mg, 1.76 mmol, 70%), yellow crystalline solid, m.p. 80°C (Et_2O/hexane, decomp). IR ($CDCl_3$): $\tilde{\nu}$ = 2096 cm^{-1} (N_3), 1269 (N_3); ^1H NMR ($CDCl_3$): δ = 6.01 (s, 2H), 7.25–7.48 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): δ = 126.61 (d), 127.91 (d), 128.41 (d, 2C), 129.74 (d, 2C), 131.55 (s), 135.24 ppm (s).

Reaction of 3,4-dibromo-3,4-dimethyl-1,2-diphenylcyclobutene [15i (X = Br)] with QN_3: Treatment of dibromide **15i** (X = Br) with QN_3 was carried out as described for the analogous transformation of **15j** (X = Br); see Table 4. However, the reaction did not yield the wanted diazidocyclobutene but led to **24i** (18%) and the known[25] bis(methylene)cyclobutene **25i** (48%).

3-Azido-3-methyl-4-methylene-1,2-diphenylcyclobutene (24i): Colorless oil; IR ($CDCl_3$): $\tilde{\nu}$ = 2101 cm^{-1} (N_3), 1246 (N_3); ^1H NMR ($CDCl_3$): δ = 1.62 (s, 3H; Me), 4.88 (d, ^2J = 1.4 Hz, 1H), 4.98 (d, ^2J = 1.4 Hz, 1H), 7.30–7.64 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): δ = 20.73 (q, Me), 70.89 (s, C-3), 95.53 (t, =CH_2), 126.93 (d), 127.66 (d), 128.59 (d), 128.63 (d), 128.75 (d, *p*-Ph), 129.04 (d, *p*-Ph), 131.48 (s), 131.92 (s), 149.31 (s), 150.86 ppm (s), one signal (s) was hidden by another.

Reaction of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene [15g (X = Cl)] with QN_3: **15g** (X = Cl)[16] (1.79 g, 10 mmol) was added to a solution of QN_3 (11.0 g, 23.4 mmol) in $CHCl_3$ (50 mL) under cooling with water. The reaction mixture was evaporated in vacuum after 20 h of stirring. The residue was separated by chromatography (Et_2O, silica gel) to remove the phosphonium salts. After removal of the solvent under reduced pressure, a pale yellow oil (2.04 g) was obtained. NMR analyses indicated that *trans*-**16g** (55%, 5.5 mmol), *cis*-**16g** (9%, 0.9 mmol), **24g** (17%, 1.7 mmol), **19g** (major isomer, 3%, 0.3 mmol), and **19g** (minor isomer, 2%, 0.2 mmol) were formed in an overall yield of 86%. The products could be separated by flash chromatography (hexane/Et_2O, silica gel) with the following order of elution: *trans*-**16g**, **24g**, *cis*-**16g**, **19g** (minor isomer), **19g** (major isomer).

***trans*-3,4-Diazido-1,2,3,4-tetramethylcyclobutene (*trans*-16g)**: Colorless oil; IR ($CDCl_3$): $\tilde{\nu}$ = 2093 cm^{-1} (N_3), 1251 (N_3); UV/Vis (CH_3CN): λ_{max} (lgε) = 208 nm (3.74); ^1H NMR ($CDCl_3$): δ = 1.42 (s, 6H; 3-Me/4-Me), 1.64 ppm (s, 6H; 1-Me/2-Me); ^{13}C NMR ($CDCl_3$): δ = 8.75 (q, Me-1/Me-2), 17.91 (q, Me-3/Me-4), 72.67 (s, C-3/C-4), 141.24 ppm (s, C-1/C-2).

***cis*-3,4-Diazido-1,2,3,4-tetramethylcyclobutene (*cis*-16g)**: Colorless oil; IR ($CDCl_3$): $\tilde{\nu}$ = 2102 cm^{-1} (N_3), 1248 (N_3); UV/Vis (Ch_3CN): λ_{max} (lgε) = 205 nm (3.75); ^1H NMR ($CDCl_3$): δ = 1.29 (s, 6H; 3-Me/4-Me), 1.63 ppm (s, 6H; 1-Me/2-Me); ^{13}C NMR ($CDCl_3$): δ = 8.80 (q, Me-1/Me-2), 17.55 (q, Me-3/Me-4), 73.41 (s, C-3/C-4), 141.94 ppm (s, C-1/C-2).

3-Azido-1,2,3-trimethyl-4-methylencyclobutene (24g): Yellow oil; IR ($CDCl_3$): $\tilde{\nu}$ = 2096 cm^{-1} (N_3), 1247 (N_3); ^1H NMR ($CDCl_3$): δ = 1.36 (s, 3H; 3-Me), 1.70 (q, ^5J = 1.2 Hz, 3H; 2-Me), 1.77 (m, 3H; 1-Me), 4.50 (brs, 1H), 4.54 ppm (brs, 1H); ^{13}C NMR ($CDCl_3$): δ = 8.95 (q), 9.10 (q), 19.35 (q, 3-Me), 71.30 (s, C-3), 90.85 (t, =CH_2), 142.76 (s), 150.04 (s), 153.09 ppm (s). The assignment of the ^1H NMR signals of the methyl groups was performed by double resonance experiments.

3-Azido-4-chloro-1,2,3,4-tetramethylcyclobutene [19g (major isomer)]: Colorless oil; IR ($CDCl_3$): $\tilde{\nu}$ = 2099 cm^{-1} (N_3), 1255 (N_3); ^1H NMR ($CDCl_3$): δ = 1.26 (s, 3H), 1.36 (s, 3H), 1.58 (q, ^5J = 1.2 Hz, 3H), 1.61 ppm (q, ^5J = 1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 7.59 (q), 8.57 (q), 16.10 (q), 18.94 (q), 73.78 (s, C-3), 80.48 (s, C-4), 140.36 (s), 145.72 ppm (s).

3-Azido-4-chloro-1,2,3,4-tetramethylcyclobutene [19g (minor isomer)]: Colorless oil; IR ($CDCl_3$): $\tilde{\nu}$ = 2089 cm^{-1} (N_3), 1252 (N_3); ^1H NMR ($CDCl_3$): δ = 1.34 (s, 3H), 1.37 (s, 3H), 1.58 (q, ^5J = 1.2 Hz, 3H), 1.61 ppm (q, ^5J = 1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 7.52 (q), 8.66 (q), 17.63 (q), 20.28 (q), 73.03 (s, C-3), 81.26 (s, C-4), 140.19 (s), 143.55 ppm (s).

The assignment of the signals of C-3 and C-4 of both isomers of **19g** was possible by comparison with NMR data of **15g** (X = Cl), *trans*-**16g**, and *cis*-**16g**.

Table 4. Synthesis of *trans*-3,4-diazidocyclobutenes from dihalides.

Dihalides	QN_3	*trans*-3,4-Diazidocyclobutenes
15j (X = Cl) and **15j′** (X = Cl) (1.13 g, 5.85 mmol) in $CHCl_3$ (5 mL)	11.0 g (23.4 mmol)	*trans*-**16j**:*trans*-**16j′** ≈ 1:1 (0.90 g, 4.39 mmol, 75%)
15j (X = Br) and **15j′** (X = Br) (1.46 g, 5.18 mmol) in $CHCl_3$ (5 mL)	10.8 g (23.0 mmol)	*trans*-**16j**:*trans*-**16j′** ≈ 1:1 (0.78 g, 3.78 mmol, 73%)
15k (X = Cl), **15k′** (X = Cl), and **15k″** (X = Cl) (1.48 g, 7.14 mmol) in $CHCl_3$ (2 mL)	10.0 g (21.3 mmol)	*trans*-**16k**:*trans*-**16k′**:*trans*-**16k″** ≈ 1:2:1 (914 mg, 4.43 mmol, 62%)
15k (X = Br), **15k′** (X = Br), and **15k″** (X = Br) (1.84 g, 6.22 mmol) in $CHCl_3$ (5 mL)	10.2 g (21.7 mmol)	*trans*-**16k**:*trans*-**16k′**:*trans*-**16k″** ≈ 1:2:1 (696 mg, 3.16 mmol, 51%)

Reactions of tetraalkyl-3,4-dichlorocyclobutenes and tetraalkyl-3,4-dibromocyclobutenes 15j and 15j′ as well as 15k, 15k′, and 15k″ with QN_3: The appropriate dihalides were dissolved ($CHCl_3$) and added with stirring to molten QN_3 at room temperature. Stirring was continued for 12 h at room temperature. After adding Et_2O (100 mL), the reaction mixture was filtered over silica gel by eluting with Et_2O. The solvent was evaporated under reduced pressure, and the crude product was purified by chromatography (hexane/Et_2O 2/1, silica gel) to yield mixtures of the isomeric *trans*-3,4-diazidocyclobutenes as yellow liquids (Table 4).

***trans*-3,4-Diazido-1-ethyl-2,3,4-trimethylcyclobutene (*trans*-16j)**: Colorless liquid; IR ($CDCl_3$): $\tilde{\nu}$ = 2094 cm^{-1} (N_3), 1247 (N_3); ^1H NMR ($CDCl_3$): δ = 1.10 (t, ^3J = 7.6 Hz, 3H; 2′-H), 1.41 (s, 3H), 1.45 (s, 3H), 1.67 (t, ^5J = 1.2 Hz, 3H; 2-Me), 2.09 ppm (qq, ^3J = 7.6 Hz, ^5J = 1.2 Hz, 2H; 1′-H); ^{13}C NMR ($CDCl_3$): δ = 9.15 (q), 11.71 (q), 17.08 (q), 18.39 (t, C-1′), 18.69 (q), 72.52 (s), 72.67 (s), 140.51 (s, C-2), 146.28 ppm (s, C-1).

***trans*-3,4-Diazido-3-ethyl-1,2,4-trimethylcyclobutene (*trans*-16j′)**: Colorless liquid; IR ($CDCl_3$): $\tilde{\nu}$ = 2096 cm^{-1} (N_3), 1254 (N_3); ^1H NMR ($CDCl_3$): δ = 1.04 (t, ^3J = 7.4 Hz, 3H; 2′-H), 1.42 (s, 3H; 4-Me), 1.67 (q, ^5J = 1.2 Hz, 3H), 1.70 (q, ^5J = 1.2 Hz, 3H), 1.65–1.85 ppm (m, 2H; 1′-H); ^{13}C NMR ($CDCl_3$): δ = 8.75 (q), 8.98 (q), 10.23 (q), 18.28 (q, Me-4), 26.52 (t, C-1′), 72.69 (s, C-4), 76.61 (s, C-3), 141.16 (s), 142.43 ppm (s).

Mixture of *trans*-**16k**, *trans*-**16k′**, and *trans*-**16k″** (1:2:1): IR ($CDCl_3$): $\tilde{\nu}$ = 2096 (N_3), 1252 cm^{-1} (N_3).

***trans*-3,4-Diazido-1,2-diethyl-3,4-dimethylcyclobutene (*trans*-16k)**: Colorless liquid; ^1H NMR ($CDCl_3$): δ = 1.10 (t, ^3J = 7.5 Hz, 6H; 2′-H), 1.46 (s, 6H; 3-Me/4-Me), 2.12 ppm (q, ^3J = 7.5 Hz, 4H; 1′-H); ^{13}C NMR ($CDCl_3$): δ = 12.18 (q, C-2′), 18.48 (t, C-1′), 18.75 (q, Me-3/Me-4), 72.66 (s, C-3/C-4), 145.87 ppm (s, C-1/C-2).

***trans*-3,4-Diazido-1,4-diethyl-2,3-dimethylcyclobutene (*trans*-16k′)**: Colorless liquid; ^1H NMR ($CDCl_3$): δ = 1.03 (t, ^3J = 7.4 Hz, 3H; CH_3CH_2 at C-4), 1.13 (t, ^3J = 7.7 Hz, 3H; CH_3CH_2 at C-1), 1.42 (s, 3H; Me-3), 1.71 (t, ^5J = 1.4 Hz, 3H; Me-2), 1.65–1.85 (m, 2H; CH_2 at C-4), 2.12 ppm (brq, ^3J = 7.7 Hz, 2H; CH_2 at C-1); ^{13}C NMR ($CDCl_3$): δ = 8.85 (q), 9.25 (q), 11.78 (q), 18.17 (q, Me-3), 19.24 (t, CH_2 at C-1), 26.79 (t, CH_2 at C-4), 72.49 (s, C-3), 76.76 (s, C-4), 141.56 (s, C-2), 146.29 ppm (s, C-1).

***trans*-3,4-Diazido-3,4-diethyl-1,2-dimethylcyclobutene (*trans*-16k″)**: Colorless liquid; ^1H NMR ($CDCl_3$): δ = 1.04 (t, ^3J = 7.5 Hz, 6H; 2′-H), 1.60–

1.90 (m, 4H; 1′-H) 1.73 ppm (s, 6H; 1-Me/2-Me); ^{13}C NMR ($CDCl_3$): δ = 8.89 (q), 9.98 (q), 26.38 (t, C-1′), 76.64 (s, C-3/C-4), 142.14 ppm (s, C-1/C-2).

Thermal ring opening of *trans*-3,4-diazidotetraalkylcyclobutenes: Thermolyses of the 3,4-diazidotetraalkylcyclobutenes *trans*-**16g** or the mixture of *trans*-**16j** and *trans*-**16j′** as well as mixtures of *trans*-**16k**, *trans*-**16k′**, and *trans*-**16k″** were performed in benzene at 70–80 °C and monitored by NMR spectroscopy. The reactions were stopped when the amount of (*E*,*E*)-**8g**, (*E*,*E*)-**8j**, and (*E*,*E*)-**8j′**, as well as (*E*,*E*)-**8k**, (*E*,*E*)-**8k′**, and (*E*,*E*)-**8k″** reached a maximum. The resulting mixtures were separated by flash chromatography (Et_2O/hexane, silica gel) which allowed also the isolation of unconverted starting materials. In a typical experiment, (*E*,*E*)-**8g** was obtained in 6% yield based on applied starting material *trans*-**16g**, which correspond to 14% yield related to the amount of converted *trans*-**16g**. Monitoring the thermolysis of (*E*,*E*)-**8g** by NMR spectroscopy showed a maximum amount of (*E*)-**17g** (42%) after 50 min at 80 °C in $CDCl_3$. In the case of the azides *trans*-**16j** and *trans*-**16j′** as well as *trans*-**16k**, *trans*-**16k′**, and *trans*-**16k″**, separation of isomeric 1,4-diazidobuta-1,3-dienes was not possible (10% yield of (*E*,*E*)-**8j** and (*E*,*E*)-**8j′** based on applied azides *trans*-**16j** and *trans*-**16j′** as well as 10% yield of (*E*,*E*)-**8k**, (*E*,*E*)-**8k′**, and (*E*,*E*)-**8k″** based on applied azides *trans*-**16k**, *trans*-**16k′**, and *trans*-**16k″**). However, changing the ratio of the mixture of the 3,4-diazidocyclobutenes *trans*-**16k**, *trans*-**16k′**, and *trans*-**16k″** led to product mixtures with different distribution of (*E*,*E*)-**8k**, (*E*,*E*)-**8k′**, and (*E*,*E*)-**8k″**, although electrocyclic ring opening competed with scrambling of the allylic isomers of the starting material (see Supporting Information). These different product mixtures were used for assignment of NMR signals and also for irradiation to give different distributions of **9k**, **9k′**, and **9k″**.

(*E*,*E*)-2,5-Diazido-3,4-dimethylhexa-2,4-diene ((*E*,*E*)-8g): Yellow liquid; IR ($CHCl_3$): $\tilde{\nu}$ = 2108 cm^{-1} (N_3), 1287 (N_3); UV/Vis (Ch_3CN): λ_{max} ($\lg\varepsilon$) = 255 nm (4.08); ^{1}H NMR ($CDCl_3$): δ = 1.66 (q, ^5J = 1.5 Hz, 6H; 3-Me/4-Me), 1.86 ppm (q, ^5J = 1.5 Hz, 6H; 1-H/6-H); ^{13}C NMR ($CDCl_3$): δ = 14.31 (q), 15.78 (q), 123.00 (s), 126.33 ppm (s). The assignment of the ^{1}H NMR signals was possible by comparison of the ^{1}H NMR signals of (*E*,*E*)-**8g**, (*E*,*E*)-**8j**, (*E*,*E*)-**8j′**, (*E*,*E*)-**8k**, (*E*,*E*)-**8k′**, and (*E*,*E*)-**8k″**. Methyl groups in positions 2 and 3 of the 1,4-diazidobuta-1,3-dienes showed chemical shifts in the range of 1.65–1.70 ppm, in contrast to methyl groups in positions 1 and 4 with values in the range of 1.85–1.90 ppm.

2-[(*E*)-2-Azido-1-methylprop-1-enyl]-2,3-dimethyl-2*H*-azirine ((*E*)-17g): Unstable, not isolable; ^{1}H NMR ($CDCl_3$): δ = 1.28 (s, 3H; 2-Me), 1.63 (q, ^5J = 1.5 Hz, 3H; 1′-Me), 2.12 (q, ^5J = 1.5 Hz, 3H; 3′-H), 2.44 ppm (s, 3H; 3-Me); ^{13}C NMR ($CDCl_3$): δ = 12.58 (q), 13.40 (q), 14.39 (q), 22.39 (q, Me-2), 36.13 (s, C-2), 124.75 (s), 127.61 (s), 174.49 ppm (s, C-3). The assignment of the ^{1}H NMR signals of 1′-Me and 3′-H was proved by a NOESY NMR experiment.

(*E*,*E*)-2,5-Diazido-3-ethyl-4-methylhexa-2,4-diene ((*E*,*E*)-8j), (*E*,*E*)-2,5-diazido-3,4-dimethylhepta-2,4-diene ((*E*,*E*)-8j′): Mixture (*E*,*E*)-**8j**:(*E*,*E*)-**8j′** = 1:2.3, yellow liquid; IR ($CDCl_3$): $\tilde{\nu}$ = 2104 (N_3), 1285 cm^{-1} (N_3); ^{1}H NMR ($CDCl_3$, (*E*,*E*)-**8j**): δ = 0.86 (t, ^3J = 7.6 Hz, 3H; 2′-H), 1.647 (q, ^5J = 1.5 Hz, 3H; 4-Me), 1.86 (t, ^5J = 0.9 Hz, 3H; 1-H), 1.87 (q, ^5J = 1.5 Hz, 3H; 6-H), 2.1–2.4 ppm (m, 2H; 1′-h); ^{1}H NMR ($CDCl_3$, (*E*,*E*)-**8j′**): δ = 1.08 (t, ^3J = 7.6 Hz, 3H; 7-H), 1.65 (t, ^5J = 0.9 Hz, 3H; 4-Me), 1.66 (q, ^5J = 1.5 Hz, 3H; 3-Me), 1.88 (q, ^5J = 1.5 Hz, 3H; 1-H), 2.1–2.4 ppm (m, 2H; 6-H); ^{13}C NMR ($CDCl_3$, (*E*,*E*)-**8j**): δ = 12.45 (q), 14.43 (q), 14.67 (q), 16.26 (q), 22.87 (t), 121.62 (s), 125.84 (s), 127.33 (s), 129.15 ppm (s); ^{13}C NMR ($CDCl_3$, (*E*,*E*)-**8j′**): δ = 12.67 (q), 14.55 (q), 16.19 (q), 16.46 (q), 22.55 (t), 122.90 (s), 123.02 (s), 126.32 (s), 132.35 ppm (s).

(*E*,*E*)-2,5-Diazido-3,4-diethylhexa-2,4-diene ((*E*,*E*)-8k), (*E*,*E*)-2,5-diazido-4-ethyl-3-methyl-hepta-2,4-diene ((*E*,*E*)-8k′), (*E*,*E*)-3,6-diazido-4,5-dimethylocta-3,5-diene ((*E*,*E*)-8k″): Mixture (*E*,*E*)-**8k**:(*E*,*E*)-**8k′**:(*E*,*E*)-**8k″** = 1:2:1, yellow liquid; IR ($CDCl_3$): $\tilde{\nu}$ = 2107 (N_3), 1285 cm^{-1} (N_3); ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, ^3J = 7.6 Hz, 2′-H, (*E*,*E*)-**8k**), 0.88 (t, ^3J = 7.6 Hz, 2′-H, (*E*,*E*)-**8k′**), 1.08 [t, ^3J = 7.6 Hz, 7-H ((*E*,*E*)-**8k′**) + 1-H/8-H ((*E*,*E*)-**8k″**)], 1.66 (q, ^5J = 1.5 Hz, 3-Me, (*E*,*E*)-**8k′**), 1.67 (t, ^5J = 0.8 Hz, 4-Me/5-Me, (*E*,*E*)-**8k″**), 1.87 (s, 1-H/6-H, (*E*,*E*)-**8k**), 1.89 (q, ^5J = 1.5 Hz, 1-H, (*E*,*E*)-**8k′**), 1.9–2.4 ppm [m, 1′-H ((*E*,*E*)-**8k**) + 6-H ((*E*,*E*)-**8k′**) + 1′-H ((*E*,*E*)-**8k′**) + 2-H/7-H ((*E*,*E*)-**8k″**)]; ^{13}C NMR ($CDCl_3$, (*E*,*E*)-**8k**): δ = 12.38 (q), 14.76 (q), 22.72 (t), 126.78 (s), 127.52 ppm (s); ^{13}C NMR ($CDCl_3$, (*E*,*E*)-**8k′**): δ = 12.48 (q), 12.74 (q), 15.05 (q), 17.18 (q), 22.62 (t), 23.52 (t), 121.55 (s), 127.10 (s), 128.80 (s), 131.87 ppm (s); ^{13}C NMR ($CDCl_3$, (*E*,*E*)-**8k″**): δ = 12.86 (q), 16.86 (q), 22.71 (t), 122.76 (s), 132.30 ppm (s).

Photolyses of (*E*,*E*)-1,4-diazidobuta-1,3-diene ((*E*,*E*)-8d): (*E*,*E*)-**8d** (18.6 mg, 0.023 mmol) and dioxane (3 μL, as standard) were dissolved in a saturated and degassed solution of 9,10-dicyanoanthracene (DCA) in $CDCl_3$. The NMR tube was irradiated at −50 °C, and the progress of the reaction was monitored by NMR spectroscopy at −50 °C. The maximum yield of **9d** (8%, determined by NMR spectroscopy) was reached after 95 min of irradiation. Formation of (*E*)-**17d** (up to 24%) as an intermediate could also be observed. Without DCA, irradiation of (*E*,*E*)-**8d** led to (*E*)-**17d** in up to 60% yield.

2-[(*E*)-2-Azidoethenyl]-2*H*-azirine ((*E*)-17d): Unstable, not isolable; ^{1}H NMR ($CDCl_3$, −50 °C): δ = 2.40 (dd, ^3J = 8.5 Hz, ^3J = 2.1 Hz, 1H; 2-H), 4.89 (ddd, $^3J_{trans}$ = 13.7 Hz, ^3J = 8.5 Hz, ^4J = 0.6 Hz, 1H; 1′-H), 6.25 (d, $^3J_{trans}$ = 13.7 Hz, 1H; 2′-H), 10.07 ppm (dd, ^3J = 2.1 Hz, ^4J = 0.6 Hz, 1H; 3-H); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 26.70 (d, C-2), 119.81 (d), 128.65 (d), 164.95 ppm (d, C-3).

***meso*-/*rac*-Bi-2*H*-azirin-2-yl (*meso*-9d/*rac*-9d)**: Unstable, not isolable; ^{1}H NMR ($CDCl_3$, −50 °C): δ = 1.68 (s, 2H; 2-H, major isomer), 1.98 (s, 2H; 2-H, minor isomer), 9.91 (s, 2H; 3-H, minor isomer), 10.09 ppm (s, 2H; 3-H, major isomer); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 28.32 (d, C-2), 28.70 (d, C-2), 165.75 (d, C-3), 166.89 ppm (d, C-3). The ratio of diastereomers was 3:2. Assignment of *meso* and *rac* isomers could not be performed.

Photolyses of (*E*,*E*)-1,4-diazido-2,3-dimethyl-1,3-butadiene ((*E*,*E*)-8e): A solution of (*E*,*E*)-**8e** in $CDCl_3$ was irradiated in an NMR tube at −50 °C. The progress of the reaction was monitored by NMR spectroscopy at −50 °C. The maximum yield of (*E*)-**17e** (37%, determined by NMR spectroscopy) was reached after 20 min of irradiation. When DCA was used as sensitizer, no new products could be found, but the maximum yield of (*E*)-**17e** decreased to 26%.

2-[(*E*)-2-Azido-1-methylethenyl]-2-methyl-2*H*-azirine ((*E*)-17e): Unstable, not isolable; ^{1}H NMR ($CDCl_3$, −50 °C): δ = 1.14 (d, ^4J = 1.3 Hz, 3H; 1′-Me), 1.31 (d, ^4J = 1.5 Hz, 3H; 2-Me), 6.20 (qd, ^4J = 1.3 Hz, ^5J = 0.8 Hz, 1H; 2′-H), 10.26 ppm (qd, ^4J = 1.5 Hz, ^5J = 0.8 Hz, 1H; 3-H); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 13.65 (q, Me-1′), 20.73 (q, Me-2), 33.65 (s, C-2), 122.48 (d, C-2′), 128.31 (s, C-1′), 172.53 ppm (d, C-3). The ^{1}H NMR signal assignment of the methyl groups of (*E*)-**17e** was performed by double resonance experiments. The configuration of (*E*)-**17e** was proved by NOE difference spectroscopy. When the signal of 2′-H was irradiated, only one NOE of 5.3% could be observed at the signal of 2-Me.

Photolysis of 1,4-diazido-2,3-diphenylbuta-1,3-diene ((*E*,*E*)-8f): In an NMR tube, (*E*,*E*)-**8f** (44.6 mg, 0.155 mmol) was dissolved in $CDCl_3$ (700 μL) and irradiated at −50 °C. The reaction was monitored by NMR spectroscopy at this temperature. The maximum percentage of (*E*)-**17f** (18%) was determined after 25 min of irradiation. Isomers **9f** (20%, ratio of more stable isomer:less stable isomer = 1.2:1) were detected after 40 min of photolysis. The less stable diastereomer was no longer detectable after 20 min at room temperature, whereas complete decomposition of the more stable isomer could be observed only after a few hours at room temperature.

2-[(*E*)-2-Azido-1-phenylethenyl)]-2-phenyl-2*H*-azirine ((*E*)-17f): Not isolable; ^{1}H NMR (−50 °C, $CDCl_3$): δ = 6.70 (s, 1H), 7.20–7.70 (m, 10H), 10.08 ppm (s, 1H); ^{13}C NMR (−50 °C, $CDCl_3$): δ = 39.06 (s, C-2), 126.78 (d), 126.84 (d, 2C), 127.60 (s), 127.64 (d), 128.01 (d, 2C), 128.12 (d, 2C), 128.33 (d, 3C), 133.97 (s), 141.01 (s, *i*-Ph at C-2), 162.93 ppm (d, C-3).

***meso*-/*rac*-2,2′-Diphenylbi-2*H*-azirin-2-yl (*meso*-9f/*rac*-9f)**: Unstable, not isolable; more stable isomer: ^{1}H NMR (−50 °C, $CDCl_3$): δ = 7.20–7.60 (m, 10H), 9.85 (s, 2H); ^{13}C NMR (−50 °C, $CDCl_3$): δ = 39.09 (s, C-2), 126.42 (d), 127.12 (d, *p*-Ph), 128.24 (d), 139.35 (s, *i*-Ph), 158.16 (d, C-3); less stable isomer: ^{1}H NMR (−50 °C, $CDCl_3$): δ = 7.20–7.60 (m, 10H), 9.80 (s, 2H); ^{13}C NMR (−50 °C, $CDCl_3$): δ = 38.59 (s, C-2), 126.15 (d), 127.08 (d, *p*-Ph), 128.19 (d), 139.75 (s, *i*-Ph), 157.20 (d, C-3).

Photochemical syntheses of tetraalkylbi-2*H*-azirin-2-yls 9g, 9j, and 9j′ as well as 9k, 9k′, and 9k″: The photochemical transformations of butadienes (*E*,*E*)-**8g**, (*E*,*E*)-**8j**, and (*E*,*E*)-**8j′** as well as (*E*,*E*)-**8k**, (*E*,*E*)-**8k′**, and (*E*,*E*)-**8k″** were carried out in solution ($CDCl_3$) at temperatures between −50 and −60 °C. The yields were quantitative. The ratios of **9j**:**9j′** obtained after photolysis were in accordance with the ratios of the starting material (*E*,*E*)-**8j**:(*E*,*E*)-**8j′**. The same held true for the ratios **9k**:**9k′**:**9k″** and (*E*,*E*)-**8k**:(*E*,*E*)-**8k′**:(*E*,*E*)-**8k″**.

2,2′,3,3′-Tetramethylbi-2*H*-azirin-2-yl (9g) (more stable isomer, most probably *meso* compound): IR ($CDCl_3$): $\tilde{\nu}$ = 1753 cm^{-1} (C=N); ^1H NMR ($CDCl_3$, −50 °C): δ = 0.93 (s, 6H; 2-Me/2′-Me), 2.47 ppm (s, 6H; 3-Me/3′-Me); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 14.53 (q, Me-3/Me-3′), 19.78 (q, Me-2/Me-2′), 38.95 (s, C-2/C-2′), 176.25 ppm (s, C-3/C-3′).

2,2′,3,3′-Tetramethylbi-2*H*-azirin-2-yl (9g) (less stable isomer, most probably *rac* compound): ^1H NMR ($CDCl_3$, −50 °C): δ = 1.16 (s, 6H; 2-Me/2′-Me), 2.38 ppm (s, 6H; 3-Me/3′-Me); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 14.71 (q, Me-3/Me-3′), 20.25 (q, Me-2/Me-2′), 38.93 (s, C-2/C-2′), 173.75 ppm (s, C-3/C-3′).

2-Ethyl-2′,3,3′-trimethylbi-2*H*-azirin-2-yl (9j) (more stable isomer, most probably *unlike* compound): ^1H NMR ($CDCl_3$, −50 °C): δ = 0.49 (t, ^3J = 7.6 Hz, 3H; CH_3CH_2), 0.97 (s, 3H; 2′-Me), 1.48–1.60 (m, 2H; CH_2), 2.44 (s, 3H), 2.45 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 10.30 (q, CH_3CH_2), 14.32 (q), 15.13 (q), 19.80 (q, Me-2′), 24.00 (t, CH_2), 38.54 (s, C-2′), 43.81 (s, C-2), 174.93 (s), 175.66 ppm (s).

2-Ethyl-2′,3,3′-trimethylbi-2*H*-azirin-2-yl (9j) (less stable isomer, most probably *like* compound): ^1H NMR ($CDCl_3$, −50 °C): δ = 0.61 (t, ^3J = 7.5 Hz, 3H; CH_3CH_2), 1.18 (s, 3H; 2′-Me), 1.70–1.84 (m, 2H; CH_2), 2.37 (s, 3H), 2.40 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 10.20 (q, CH_3CH_2), 14.60 (q), 15.38 (q), 20.49 (q, Me-2′), 24.77 (t, CH_2), 38.01 (s, C-2′), 43.45 (s, C-2), 172.03 (s), 172.80 ppm (s).

3-Ethyl-2,2′,3′-trimethylbi-2*H*-azirin-2-yl (9j′) (more stable isomer, most probably *unlike* compound): ^1H NMR ($CDCl_3$, −50 °C): δ = 0.93 (s, 3H), 0.94 (s, 3H), 1.26 (t, ^3J = 7.4 Hz, 3H; CH_3CH_2), 2.46 (s, 3H; Me-3′), 2.76 (q, ^3J = 7.4 Hz, 1H; CH_2), 2.78 ppm (q, ^3J = 7.4 Hz, 1H; CH_2); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 8.59 (q, CH_3CH_2), 14.53 (q, Me-3′), 19.79 (q), 20.04 (q), 21.96 (t, CH_2), 39.01 (s), 39.84 (s), 176.29 (s, C-3′), 179.83 ppm (s, C-3).

3-Ethyl-2,2′,3′-trimethylbi-2*H*-azirin-2-yl (9j′) (less stable isomer, most probably *like* compound): ^1H NMR ($CDCl_3$, −50 °C): δ = 1.16 (s, 3H), 1.17 (s, 3H), 1.22 (t, ^3J = 7.4 Hz, 3H; CH_3CH_2), 2.34 (s, 3H; Me-3′), 2.66 ppm (q, ^3J = 7.4 Hz, 2H; CH_2); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 8.33 (q, CH_3CH_2), 14.69 (q, Me-3′), 20.31 (q), 20.57 (q), 22.08 (t, CH_2), 38.86 (s), 39.78 (s), 173.53 (s, C-3′), 177.16 ppm (s, C-3).

2,2′-Diethyl-3,3′-dimethylbi-2*H*-azirin-2-yl (9k), 2,3-diethyl-2′,3′-dimethylbi-2*H*-azirin-2-yl (9k′), 3,3′-diethyl-2,2′-dimethylbi-2*H*-azirin-2-yl (9k″) (more stable isomers, most probably *meso* or *unlike* compounds): ^1H NMR ($CDCl_3$, −50 °C): δ = 0.52 (t, ^3J = 7.3 Hz, CH_3CH_2, **9k**), 0.54 (t, ^3J = 7.4 Hz, CH_3CH_2 at C-2, **9k′**), 0.94 (s, 2-Me/2′-Me, **9k″**), 1.01 (s, 2′-Me, **9k′**), 1.29 [t, ^3J = 7.5 Hz, CH_3CH_2 at C-3 (**9k′**) + CH_3CH_2 (**9k″**)], 1.4–1.9 (m, CH_2 (**9k**) + CH_2 at C-2 (**9k′**)), 2.46 (s, 3′-Me, **9k′**), 2.47 (s, 3-Me/3′-Me, **9k**), 2.7–2.9 ppm [m, CH_2 at C-3 (**9k′**) + CH_2 (**9k″**)]; ^{13}C NMR ($CDCl_3$, −50 °C): δ = 8.56 (q), 8.72 (q), 10.23 (q), 10.32 (q), 14.22 (q), 14.89 (q), 19.71 (q), 19.99 (q), 21.86 (t), 22.25 (t), 24.00 (t), 24.29 (t), 38.47 (s), 39.88 (s), 43.37 (s), 44.85 (s), 174.31 (s), 175.43 (s), 178.50 (s), 179.69 ppm (s).

2,2′-Diethyl-3,3′-dimethylbi-2*H*-azirin-2-yl (9k), 2,3-diethyl-2′,3′-dimethylbi-2*H*-azirin-2-yl (9k′), 3,3′-diethyl-2,2′-dimethylbi-2*H*-azirin-2-yl (9k″) (less stable isomers, most probably *rac* or *like* compounds): ^1H NMR ($CDCl_3$, −50 °C): δ = 0.677 (t, ^3J = 7.8 Hz, CH_3CH_2 at C-2, **9k′**), 0.683 (t, ^3J = 7.5 Hz, CH_3CH_2, **9k**), 1.21 (s, 2-Me/2′-Me, **9k″**), 1.23 (s, 2′-Me, **9k′**), 1.24 (t, ^3J = 7.3 Hz, CH_3CH_2, **9k″**), 1.27 (t, ^3J = 7.5 Hz, CH_3CH_2 at C-3, **9k′**), 1.4–1.9 (m, CH_2 (**9k**) + CH_2 at C-2 (**9k′**)), 2.39 (s, 3′-Me, **9k′**), 2.42 (s, 3-Me/3′-Me, **9k**), 2.7–2.9 ppm (m, CH_2 at C-3 (**9k′**) + CH_2 (**9k″**)); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 8.33 (q), 8.35 (q), 10.09 (q), 10.15 (q), 14.50 (q), 15.13 (q), 20.54 (q), 20.59 (q), 21.98 (t), 22.45 (t), 25.04 (t), 25.10 (t), 37.72 (s), 39.64 (s), 42.27 (s), 44.29 (s), 171.17 (s), 172.38 (s), 175.47 (s), 176.85 ppm (s).

Thermal reactions of tetraalkylbi-2*H*-azirin-2-yls 9g, 9j, and 9j′ as well as 9k, 9k′, and 9k″: After photolyses of the corresponding diazides (*E*,*E*)-**8** at −50 to −60 °C, the resulting solutions of **9g**, **9j**, and **9j′** as well as **9k**, **9k′**, and **9k″** were warmed to temperatures in the range of −25 to 20 °C to yield the pyridazines **18** quantitatively. The ratio of the starting materials **9j** and **9j′** were in accordance with the ratio of the thermal products **18j** and **18j′**. The same held true for the ratios **9k**:**9k′**:**9k″** and **18k**:**18k′**:**18k″**. The heterocyclic aromatic products were isolated by removing the solvent in vacuo. However, if $AgBF_4$ is present, the reaction mixture must first be washed with aqueous NaBr. Products **18g** and **10g** resulting from thermal, silver-ion-induced, or photochemical reactions were identified by comparing their ^1H NMR and ^{13}C NMR data to those of independently prepared[26,29] samples. These sets of data can be unequivocally distinguished from each other and from those of **11g**, which was also synthesized[45] for control experiments including photostability.

1:2 Mixture of 4-ethyl-3,5,6-trimethylpyridazine (18j) and 3-ethyl-4,5,6-trimethylpyridazine (18j′): Colorless liquid; MS (ESI): *m*/*z* (%): 151.1229 (100) [*M*+H$^+$; calcd 151.1230], 323.2129 (17) [2*M*+Na$^+$; calcd 323.2206]; elemental analysis calcd (%) for $C_9H_{14}N_2$: C 71.96, H 9.39, N 18.65; found: C 71.48, H 9.07, N 18.87.

18j: ^1H NMR ($CDCl_3$): δ = 1.11 (t, ^3J = 7.6 Hz, 3H; 2′-H), 2.21 (s, 3H; Me-5), 2.57 (s, 3H), 2.61 (s, 3H), 2.63 ppm (q, ^3J = 7.6 Hz, 2H; 1′-H); ^{13}C NMR ($CDCl_3$): δ = 12.43 (q), 13.69 (q), 20.01 (q), 20.77 (q), 21.52 (t, C-1′), 133.56 (s, C-5), 139.37 (s, C-4), 156.85 (s), 157.88 ppm (s).

18j′: ^1H NMR ($CDCl_3$): δ = 1.28 (t, ^3J = 7.5 Hz, 3H; 2′-H), 2.19 (s, 3H), 2.22 (s, 3H), 2.58 (s, 3H; 6-Me), 2.93 ppm (q, ^3J = 7.5 Hz, 2H; 1′-H); ^{13}C NMR ($CDCl_3$): δ = 12.93 (q), 13.78 (q), 14.39 (q), 20.79 (q, Me-6), 27.31 (t, C-1′), 133.55 (s), 134.52 (s), 157.16 (s, C-6), 161.40 ppm (s, C-3).

1:2:1 Mixture of 4,5-diethyl-3,6-dimethylpyridazine (18k), 3,4-diethyl-5,6-dimethylpyridazine (18k′), and 3,6-diethyl-4,5-dimethylpyridazine (18k″): Colorless liquid; MS (ESI): *m*/*z* (%): 165.1377 (100) [*M*+H$^+$; calcd 165.1386]; elemental analysis calcd (%) for $c_{10}H_{16}N_2$: C 73.13, H 9.82, N 17.06; found: C 72.75, H 9.79, N 17.24.

18k: ^1H NMR ($CDCl_3$): δ = 1.17 (t, ^3J = 7.7 Hz, 6H; 2′-H), 2.65 (s, 6H; 3-Me/6-Me), 2.65 ppm (q, ^3J = 7.7 Hz, 4H; 1′-H); ^{13}C NMR ($CDCl_3$): δ = 13.50 (q, C-2′), 20.07 (q, Me-3/Me-6), 21.11 (t, C-1′), 138.82 (s, C-4/C-5), 157.44 ppm (s, C-3/C-6).

18k′: ^1H NMR ($CDCl_3$): δ = 1.14 (t, ^3J = 7.6 Hz, 3H; CH_3CH_2 at C-4), 1.34 (t, ^3J = 7.5 Hz, 3H; CH_3CH_2 at C-3), 2.23 (s, 3H; Me-5), 2.60 (s, 3H; Me-6), 2.67 (q, ^3J = 7.6 Hz, 2H; CH_2 at C-4), 2.94 ppm (q, ^3J = 7.5 Hz, 2H; CH_2 at C-3); ^{13}C NMR ($CDCl_3$): δ = 13.31 (q), 13.80 (q), 13.85 (q), 20.87 (q, Me-6), 20.94 (t, CH_2 at C-4), 26.46 (t, CH_2 at C-3), 133.78 (s, C-5), 138.78 (s, C-4), 157.64 (s, C-6), 161.08 ppm (s, C-3).

18k″: ^1H NMR ($CDCl_3$): δ = 1.34 (t, ^3J = 7.5 Hz, 6H; 2′-H), 2.25 (s, 6H; 4-Me/5-Me), 2.96 ppm (q, ^3J = 7.5 Hz, 4H; 1′-H); ^{13}C NMR ($CDCl_3$): δ = 12.84 (q), 13.91 (q), 27.29 (t, C-1′), 133.86 (s, C-4/C-5), 161.14 ppm (s, C-3/C-6).

Reaction of *trans*-3,4-dibromo-1,2,3,4-tetraphenylcyclobutene [15c (X = Br)] with QN_3: In a typical experiment, **15c** (X = Br)[12] (21.5 mg, 43.3 μmol) and dioxane (2 μL as standard) were dissolved in $CDCl_3$ (0.7 mL). To this mixture, a solution of QN_3 (50.0 mg, 0.106 mmol) in $CDCl_3$ (0.3 mL) was added at −50 °C. The reaction was monitored by NMR spectroscopy while increasing the temperature stepwise from −50 °C to 60 °C. Tetraphenylpyridazine **18c** (87%) was obtained as the stable final product and identified by comparing its ^1H NMR and ^{13}C NMR data to those of an independently prepared[51] sample. These data can be unequivocally distinguished from those of **10c**[32] and **11c**,[33] which were also synthesized for control experiments including photostability. The azirine **17c** as well as bi-2*H*-azirin-2-yls *meso*- and *rac*-**9c** could be observed as intermediates by NMR spectroscopy. The maximum amount of **17c** was 87%.

2-(2-Azido-1,2-diphenylethenyl)-2,3-diphenyl-2*H*-azirine (17c): IR ($CDCl_3$): $\tilde{\nu}$ = 2110 cm^{-1} (N_3), 1738 (C=N), 1255 (N_3); ^1H NMR ($CDCl_3$): δ = 6.88–7.63 ppm (m); ^{13}C NMR ($CDCl_3$): δ = 44.78 (s, C-2), 123.50 (s), 126.11 (d), 126.37 (d), 127.24 (d), 127.68 (d) 127.75 (d), 128.25 (d), 128.40 (d), 128.53 (d), 128.95 (d), 129.09 (d), 129.75 (d), 131.86 (d), 133.26 (s), 137.63 (s), 139.04 (s), 142.19 (s), 165.51 ppm (s, C-3), one signal (s) was

hidden by another. The formation of only one stereoisomer could be observed.

***meso*-/*rac*-2,2′,3,3′-Tetraphenylbi-2*H*-azirin-2-yl (*meso*-9c/*rac*-9c)**: ^{1}H NMR ($CDCl_3$): $\delta = 6.80$–7.80 ppm (m); ^{13}C NMR ($CDCl_3$): $\delta = 45.49$ (s, C-2/C-2′), 45.55 (s, C-2/C-2′), 122.73 (s), 123.14 (s), 126.40 (d), 126.69 (d), 126.80 (d) 127.25 (d), 127.93 (d), 128.10 (d), 128.80 (d), 129.12 (d), 129.61 (d), 129.63 (d), 132.87 (d), 132.97 (d), 139.77 (s), 140.70 (s), 163.72 (s, C-3/C-3′), 163.98 ppm (s, C-3/C-3′).

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