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Highly Strained 2,3-Bridged 2*H*-Azirines at the Borderline of Closed-Shell Molecules**

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Dedicated to Professor Stefan Spange on the occasion of his 60th birthday

Abstract: Substituted 1-azidocyclopentenes and 1-azidocyclohexenes were photolyzed to generate 2,3-bridged 2*H*-azirines. In the case of bridgehead azirines with a six-membered carbocycle, detection by NMR spectroscopic analysis was possible, whereas even kinetically stabilized bridgehead azirines with a five-membered ring could not be characterized by low-temperature NMR spectroscopic analysis. Thus, a recent report on the latter heterocycles was corrected. Depending on the substitution pattern, irradiation of 1-azidocyclopentenes either led to products that can be explained on the basis of short-lived 2,3-bridged 2*H*-azirines, or gave secondary products generated from triplet nitrenes. The diverse photoreactivity of 2,3-bridged 2*H*-azirines was also studied by quantum chemical methods (DFT, CCSD(T), CASSCF(6,6)) with respect to the singlet and triplet energy surfaces. The ring-opening processes leading to the corresponding vinyl nitrenes were identified as key steps for the observed reactivity.

Keywords: azides · nitrogen heterocycles · photolysis · quantum chemical calculations · reactive intermediates

Introduction

Strained compounds are of special interest because of their increased energy content and the enhanced reactivity that frequently results from this. The 2,3-bridged 2*H*-azirines **2** include considerable ring strain and can be easily generated by photolysis or thermolysis of cyclic vinyl azides **1** (Scheme 1).[1–3] The stability of the heterocycle **2a** allowed this compound to be to distilled in vacuo.[4] In contrast to such stability, the more strained compounds of type **2** with a six-[4a,5,6] or a five-membered[6] ring were produced only in situ; the existence of such species were proved by trapping reactions such as addition of nucleophiles at the C=N bond. However, the bridgehead azirines **2b–d** could be generated in solution by irradiation of **1b–d** at low temperature and have recently been detected in 83–91% yield by IR and NMR spectroscopic analysis even at ambient temperature.[7] Especially in the presence of wet organic solvents, subsequent reaction led to the formation of the dimers **3b–f**, and products with R=H were quickly oxidized to the corresponding pyrazines **4b**, **4c**, and **4e** when oxygen was not rigorously excluded. Nevertheless, highly strained azirines such as **2b–d** can undergo addition and cycloaddition reactions that are not possible for simple 2*H*-azirines. For example, 2-cyanoaziridines **5b–d** were available from **2b–d** by addition of hydrogen cyanide at −50°C, whereas less strained azirines did not react with this reagent even at 90°C and long reaction times. Tricyclic compounds **6b** and **6c** were generated by 1,3-dipolar *exo* cycloaddition of diazomethane at **2b** and **2c**, respectively, and characterized at low temperature because cycloreversion took place at temperatures above

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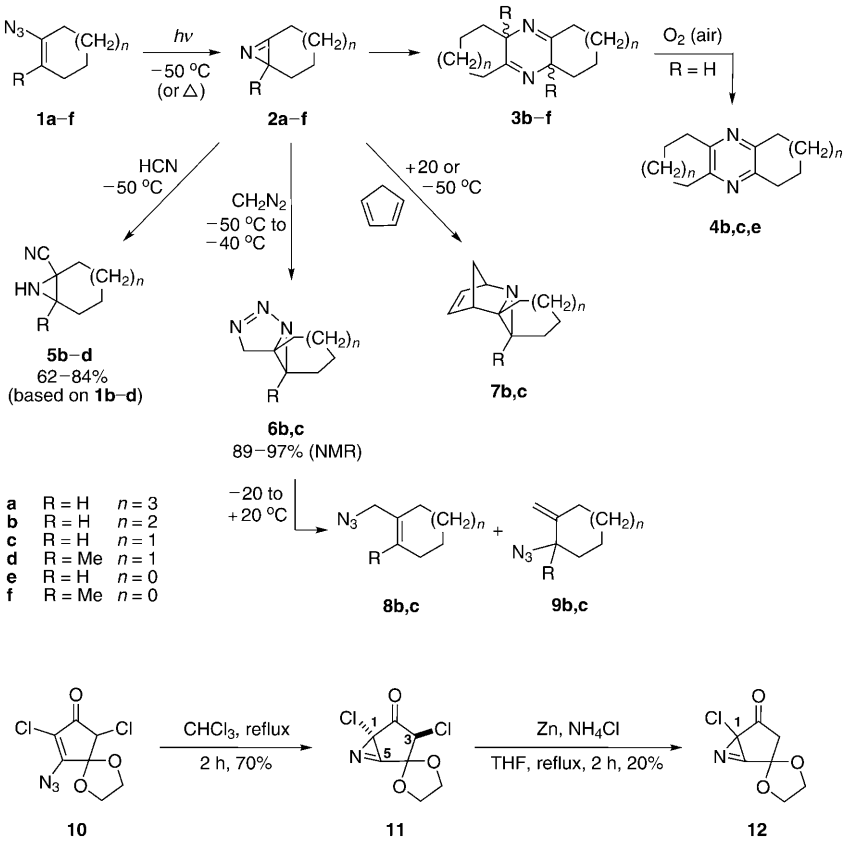


Scheme 1. Synthesis and reaction behavior of 2,3-bridged 2*H*-azirines.

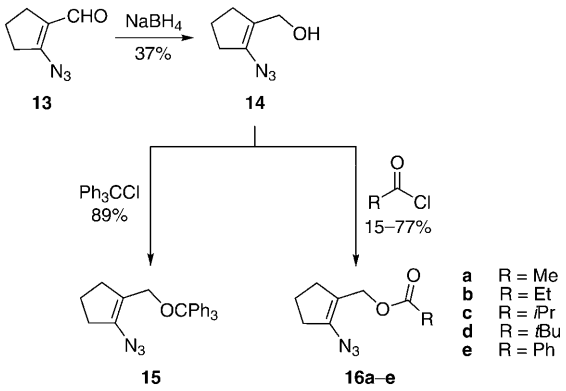
−20 °C to yield the allyl azides **8b/c** and **9b/c**. Thus, intermediates with a 1,2,3-triazabicyclo[3.1.0]hex-2-ene substructure were detected for the first time.[7] Such species were only postulated in the known reaction of simple azirines with diazo compounds,[8] which also resulted in the slow formation of allyl azides at room temperature. Whereas alkyl- or aryl-substituted azirines without an electron-withdrawing group did not react with cyclopentadiene,[1b] the heterocycles **2b** and **2c** underwent Diels–Alder reaction under mild conditions to give stereoselectively the cycloadducts **7b** and **7c**, respectively.[7]

Even upon irradiation of **1e** or **1f** at −120 and −80 °C, respectively, and NMR spectroscopic analysis at the same temperatures, it was not possible to detect 2,3-bridged 2*H*-azirines with a five-membered ring, such as **2e** or **2f**, because, at best, only strongly broadened signals of the starting materials were observed. Nevertheless, the photolyzed solutions yielded dimers of type **3** or the corresponding aromatic pyrazine derivatives **4** after thawing.[7] Thus, intermediates **2e** and **2f** are plausible, but too short lived to allow observation by spectroscopic methods in solution. Surprisingly, synthesis of bridgehead azirine **11** by simply heating a solution of vinyl azide **10** in chloroform to reflux was reported recently.[9] Treatment of **11** with zinc and ammonium chloride in boiling tetrahydrofuran was claimed to yield the product **12**. Both 2,3-bridged 2*H*-azirines **11** and **12** with a five-membered carbocycle were isolated and characterized by elementary analyses as well as on the basis of IR, ^{1}H, and ^{13}C NMR spectroscopic data.[9] The unexpectedly high stability of **11** and **12** may be caused by kinetic stabilization due to the sterically demanding substituents. For example, comparison of the properties of **2c** with those of **2d** shows that an additional methyl group at the bridgehead increases the kinetic stability of the azirines significantly.[7]

Herein, we report the syntheses of 1-azidocyclopentenes with sterically bulky substituents and on our attempts to generate and detect kinetically stabilized bridgehead azirines of type **2** ($n=0$). Furthermore, a structural corrigendum of compound **11** is presented. Finally, through the use of additional photochemical reactions of cyclic vinyl azides and by quantum chemical calculations, we show that highly strained 2,3-bridged azirines are located at the borderline of closed-shell molecules and diradical triplet nitrenes.

Results and Discussion

We prepared the ether **15** and the esters **16a–e** from alcohol **14**, which was easily accessible by reduction of the known aldehyde **13**[10] (Scheme 2). Unfortunately, we could not detect any NMR signals arising from a 2,3-bridged azirine of type **2** ($n=0$), when the azides **13**, **15**, or **16a–e** were photo-

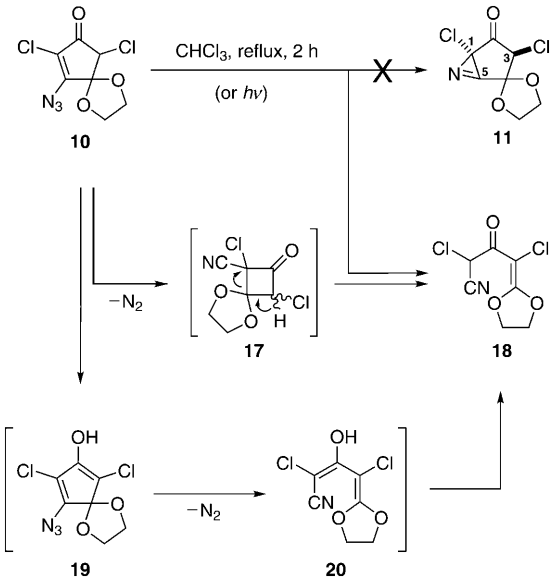


Scheme 2. Synthesis of 1-azidocyclopentenes with substituents in position 2.

lyzed in chloroform at −50 °C. Even irradiation at −120 °C in deuterated dichlorofluoromethane and NMR spectroscopic analysis at the same temperature led to the same negative result, which is in sharp contrast to the formation and stability of the highly strained azirines **11** and **12**. We assume that the ring strain of bridgehead azirines of type **2** ($n=1$) is considerably lower if compared with that of ring-contracted compounds **2** ($n=0$). Whereas in the latter case the kinetic stabilization by the bulky substituents was not sufficient, the same substituents are able to raise the stability of the former azirines significantly.[11]

Our results cast doubt upon the claimed structures of the products **11** and **12**.[9] Furthermore, we estimated the ^{13}C NMR spectroscopic data that would result from these structures on the basis of other 2,3-bridged 2*H*-azirines[7,11] and 2-chloro-2*H*-azirines[12] with a carbonyl group of an ester or a ketone in position 2. Thus, we calculated shift values of $\delta=50$–60 ppm for C-1 of **11** and **12**, whereas shifts of $\delta=85.48$ and 87.49 ppm, respectively, were reported.[9] Moreover, azirines[1b] and especially bridgehead azirines,[7] show a characteristic IR absorption band, for example, at 1743 cm^{-1} for **2c**, that is missing in the case of **11**. These discrepancies encouraged us to prepare azide **10** and its secondary product **11** so that the structure of the latter could be clarified. After heating **10** in boiling chloroform, a substance was isolated in 67% yield that was identical to previously described **11**[9] according to its melting point as well as its ^1H and ^{13}C NMR spectroscopic data. In the $^{13}C,^1H$ long-range correlation 2D-NMR spectrum optimized to geminal and vicinal coupling with $J=5$ Hz, however, the cross-signal of bridgehead carbon C-5 ($\delta=166$ ppm) and 3-H was missing, and a clear correlation between the carbon at $\delta=166$ ppm and the CH_2 protons was found. This is not compatible with the structure of **11**, and the carbon signal with $\delta=166$ ppm cannot be assigned to either the C=N unit or the carbonyl group of **11**. Instead, it should result from an sp^2-hybridized carbon at position 2 of a 1,3-dioxolane ring. Therefore, we considered the isomeric alternative structure **18**, which includes a nitrile group (with $\delta=114$ ppm) and a push–pull substituted olefin that was in agreement with all spectroscopic data (Scheme 3). Final concerns about the structure of **18** were resolved by single-crystal X-ray diffraction analysis (Figure 1). Compound **18** was also formed by photolysis of **10** in chloroform (maximum yield ca. 40%) along with several other products. However, even at low temperature, irradiation of **10** did not lead to a set of NMR signals that were consistent with the corresponding 2,3-bridged azirine.

The generation of **18** from **10** can be explained by invoking the help of intermediate **17**, because ring contraction of 3-azidocycloalk-2-en-1-ones to yield 2-cyanocycloalkanones is a well-known transformation.[3b,13] After deprotonation, cleavage of the four-membered ring, and reprotonation, compound **17** should afford the final product **18**. Alternatively, keto–enol tautomerism of **10** may produce the 1-azidocyclopentadiene **19**, which should undergo ring fission to furnish 1-cyanobuta-1,3-diene **20**.[14] This intermediate will tautomerize to give the ketone **18**.



Scheme 3. Generation of nitrile **18** from azide **10**.

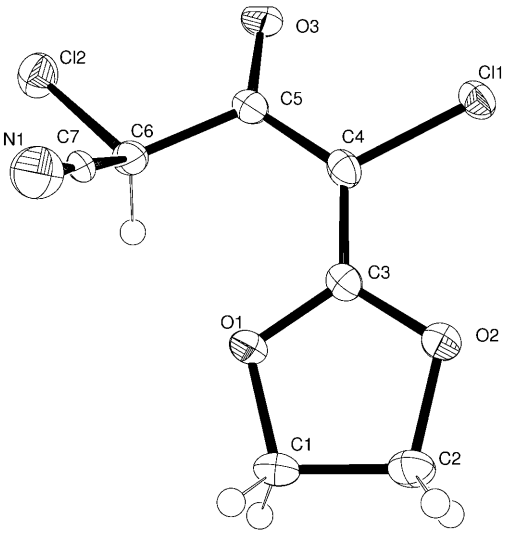
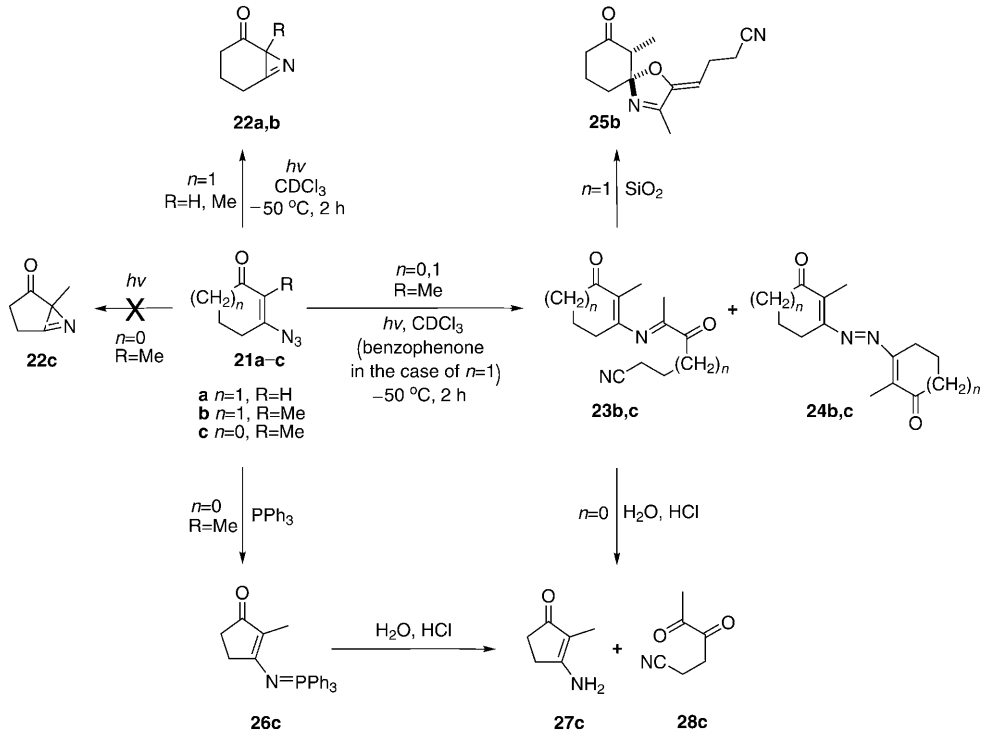


Figure 1. Molecular structure of **18** determined by single-crystal X-ray diffraction analysis.

When solutions of azides **21a**[5f] or **21b**[5f,6] were irradiated in anhydrous CD_2Cl_2 at −80 °C or in anhydrous $CDCl_3$ at −50 °C with a mercury high-pressure lamp, bridgehead azirines **22a** (22%) and **22b** (65%), respectively, were formed (Scheme 4). These compounds could be characterized even at ambient temperature by ^1H and ^{13}C NMR spectroscopic analysis and on the basis of their IR spectra. However, photolysis of the starting material **21c**[6] in chloroform at −50 °C did not lead to 2*H*-azirine **22c** or to dimeric compounds similar to **3f**. Surprisingly, quite different products, namely, nitrile **23c** and azo compound **24c**, were generated and isolated by chromatography in 41 and 15% yield, respectively. The structure of **23c** was established not only by the usual spectroscopic methods, but also by hydrolysis to produce the



Scheme 4. Photolysis of azides **21a–c**.

enamine **27c** and the diketone **28c**. The former compound was prepared for comparison through the Staudinger reaction of azide **21c** followed by hydrolysis of the resulting iminophosphorane **26c**. When a solution of **21b** in chloroform was irradiated at −50 °C, in the presence of the photosensitizer benzophenone, no azirine **22b** could be detected, and the dimeric compound **23b** as well as a trace amount of **24b** were observed instead. Attempts to purify **23b** by chromatography resulted in a rearrangement reaction, and the spiro compound **25b** was isolated in 30 % yield (based on **21b**).

The product **25b** was characterized not only by the usual spectroscopic methods, but also by single-crystal X-ray diffraction analysis, which confirmed the structure and especially the stereochemistry (Figure 2).

A possible mechanism for the formation of compounds **23b**, **23c**, **24b**, **24c**, and **25b** assumes the initial formation of the triplet nitrenes ^{3}**29b** and ^{3}**29c**, which is probably induced either by the ketone unit of **21c** as an intramolecular photosensitizer[15] or, in the case of azide **21b**, by the sensitizer benzophenone (Scheme 5). Dimerization of ^{3}**29** can lead to the formation of side product **24**. Processes that lead to the creation of azo compounds are well known for aromatic azides and the corresponding triplet nitrenes.[16,17] Another dimerization reaction of ^{3}**29** can generate the diradical **30**, which gives rise to nitrile **23** by ring cleavage. In the case of **23b**, the isomerization to yield spiro compound **25b** can be explained by keto–enol tautomerism to intermediate **31b**, followed by an intramolecular nucleophilic addition.

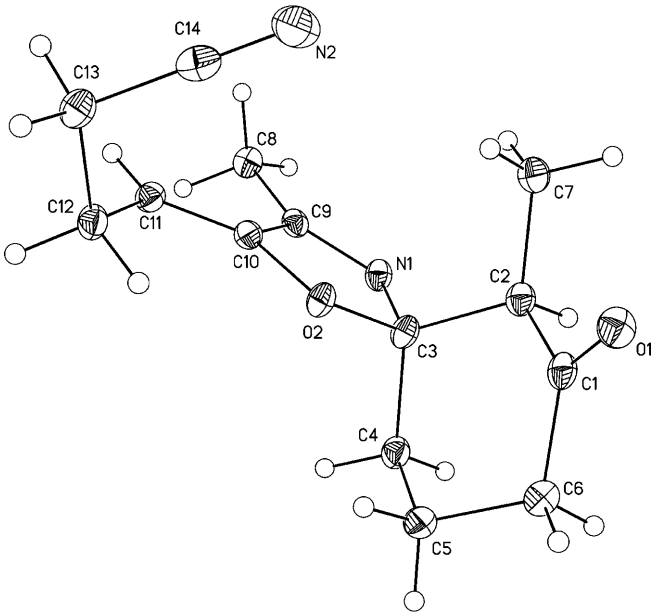
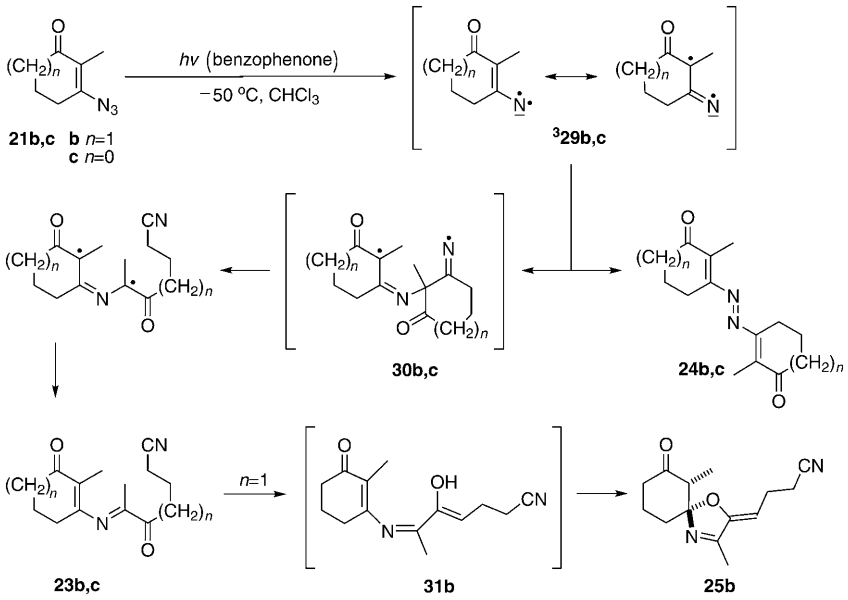


Figure 2. The molecular structure of compound **25b**.

It is remarkable that quite different products result from simple photolysis of homologous azides **21b** and **21c**. Because we were not able to detect intermediates such as **22c** and ^{3}**29** directly, quantum chemical calculations were performed to further analyze the reaction.



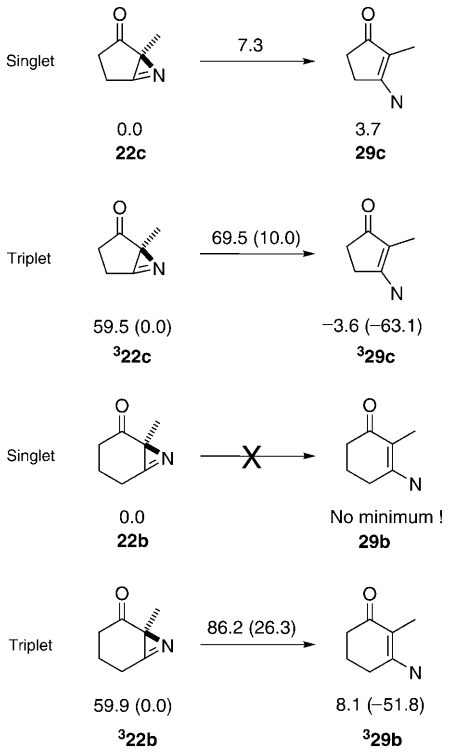
Scheme 5. Postulated mechanisms to explain the formation of **23b**, **23c**, **24b**, **24c**, and **25b**.

Quantum chemical calculations: To study the nature of the intermediates resulting from irradiation of the azides and their dependence on the ring size, quantum chemical calculations were performed. At first, DFT calculations using the PBE/TZVP and PBE/TZVPP method (Turbomole 6.0)[18] and B3LYP/6-31+G(d) (Gaussian 03)[19] were performed to localize the appropriate structures on the energy hypersurface. Then, to appropriately treat both open-shell as well as closed-shell species, CASSCF(6,6) calculations using the 6-31G(d) basis set, as implemented in the Gaussian 03 package of programs, were used. In the CASSCF treatment of **22c**, the correlated orbitals refer to the σ and π bonds of the three-membered ring and their anti-bonding counterparts (for a typical plot see the Supporting Information). For the triplet species ^{3}**29c** the active space consists of the orbitals of the σ and π bonds of the C–N-part of the molecule, the corresponding antibonding combinations, and the formally singly occupied lp orbitals that result from the broken sigma molecular orbital.

CCSD(T)/6-31+G(d) single-point calculations were further utilized to verify the CASSCF(6,6) results. All stationary points were checked by frequency analyses. The DFT as well as the CASSCF(6,6) and CCSD(T) relative energies qualitatively agree reasonably well (see the Supporting Information, Tables S1 and S2). In the following discussions CASSCF values are used with the CCSD(T) data given in parentheses.

For the five-membered system, we were able to identify minima on the singlet hypersurface for the azirine **22c** (E_{rel} = 0.0 kcal mol^{-1}) as well as for the (open shell) vinyl nitrene structure **29c** (3.7 kcal mol^{-1} (5.1 at CCSD(T)), Scheme 6). The transition state for the respective ring-opening process has a calculated energy of 7.3 (12.0) kcal mol^{-1} relative to **22c**, thus making this reaction very facile. The azirine triplet structure ^{3}**22c** is, as expected, high in energy (59.5 (44.8) kcal mol^{-1}). Passing a transition state for the ring-opening reaction (69.5 (56.4) kcal mol^{-1}, i.e., 10.0 (11.6) kcal mol^{-1} more than the azirine triplet) a very favorable triplet vinyl nitrene ^{3}**29c** structure with a relative energy of −3.6 (−6.0) kcal mol^{-1} was found.

The calculations for the six-membered ring systems **22b** predict a different reactivity. Two closed-shell conformers (twist-boat and twist-chair) for the bicyclic azirine system **22b** could be localized, the latter being 7.4 (4.6) kcal mol^{-1} lower in energy (E_{rel} = 0.0 kcal mol^{-1}).



Scheme 6. Results of the quantum chemical calculations for the ring-opening reactions of compounds **22c** and **22b**. Singlet and triplet electronic states were considered. The relative energies [kcal mol^{-1}] given refer to the CASSCF(6,6)/6-31G(d) calculations. Data in parenthesis in the case of the triplet reactions refer to the reaction energies on the triplet hypersurface.

No minimum for a singlet vinyl nitrene structure **29b** upon widening of the C–N-bond was found. Two energy-rich triplet azirine conformers for ^{3}**22b** (59.9 (62.0) and 60.2

(62.6) kcal mol^{-1}) were found, which open through a transition state with an energy of 86.2 (72.6) kcal mol^{-1} to produce a minimum structure for the corresponding triplet vinyl nitrene ^{3}**29b** with a relative energy of 8.1 (10.3) kcal mol^{-1}.

We interpret these results to be a consequence of the different ring strain in both systems. Thus, in the case of the six-membered ring system, the less pronounced ring strain significantly disfavors the vinyl nitrene structure, making the 2,3-bridged azirine in its two conformers the only minima on the singlet hypersurface. In contrast, in the case of the five-membered ring system, the azirine structure is less stable due to higher ring strain and leads easily to a singlet vinyl nitrene structure of comparable energy (3.7 (5.1) kcal mol^{-1}).

The (photochemical) singlet–triplet excitation energies were calculated to be of comparable energy, with a significantly higher barrier for ring opening in the case of the six-membered ring system. For the five-membered ring system, the triplet vinyl nitrene is calculated to correspond to the global minimum (3.6 (6.0) kcal mol^{-1} better than the singlet azirine), whereas the six-membered triplet nitrene is predicted to be less stable than the corresponding singlet azirine by 8.1 (10.3) kcal mol^{-1}.

Conclusion

Clearly, ring strain plays a dominant role when cyclic vinyl azides lose dinitrogen to generate the corresponding 2,3-bridged 2*H*-azirines or short-lived nitrenes. Based on this fact, and strongly supported by quantum chemical calculations, the formation of quite different products upon photolysis of homologous 3-azidocycloalk-2-enones **21b** and **21c** can be explained. However, the substitution pattern of the vinyl azides is also important, as shown by comparison of the different reactions **1e,f**→**3e,f**, **10**→**18**, and **21c**→**23c**+**24c**. The reaction mechanism postulated for these transformations, and recent studies on similar thermal or photochemical reactions,[3,5–7,20] demonstrate the manifold chemistry of cyclic vinyl azides.

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 or as KBr pellets. ^{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 data were recorded at 75 and 100 MHz. NMR signals were referenced to TMS ($\delta=0$ ppm) or solvent signals and recalculated relative to TMS. The multiplicities of ^{13}C NMR signals were determined with the aid of DEPT135 experiments. GC-MS spectra were acquired with a Shimadzu quadrupole mass spectrometer (EI, 70 eV) linked to a Shimadzu GC-17A gas chromatograph with thermal conductivity detector and DB-1 column (30 m). HRMS (ESI) spectra were recorded with an Applied Biosystems Mariner 5229 mass spectrometer or a 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.

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) or cooling with a mixture of 2-methylbutane and liquid nitrogen (−120 °C). Most of these photolyses were monitored by NMR spectroscopic analysis utilizing anhydrous $CDCl_3$ (−50 °C), CD_2Cl_2 (−80 °C), or $CDCl_2F$[21] (−120 °C). A solution of the appropriate starting material was irradiated in an NMR tube. To exclude oxygen, the solution was flushed with argon in an ultrasonic bath prior to irradiation. Dioxane was used as a standard to determine yields based on ^{1}H NMR spectroscopic data.

Single-crystal X-ray diffraction analysis: Data were collected with an Oxford Gemini S diffractometer at 110 K using $Mo_{K\alpha}$ ($\lambda=0.71073$ Å) (**18**) and $Cu_{K\alpha}$ ($\lambda=1.54184$ Å) (**25b**) radiation. The structures were solved by direct methods and refined by full-matrix least-square procedures on F^2.[22] All non-hydrogen atoms were refined aniosotropically and a riding model was employed in the refinement of the hydrogen atom positions. CCDC-790143 (**18**) and 790144 (**25b**) 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.

(2-Azidocyclopent-1-en-1-yl)methanol (14): At 0 °C, a solution of $NaBH_4$ (125 mg, 3.3 mmol) in water (0.4 mL) was added dropwise to a solution of **13**[10] (361 mg, 2.63 mmol) in THF (5 mL) and Et_2O (5 mL). The mixture was continuously stirred for 1 h at 0 °C and for 24 h at RT. Thereafter, the solvents were removed under reduced pressure, and the residue was treated with saturated aqueous NaCl (10 mL). This mixture was extracted with Et_2O (3×5 mL), and the combined layers were washed with water (5 mL) and dried over $MgSO_4$. After removal of the solvent under reduced pressure, **14** remained as a yellow oil (134 mg, 37 %). ^{1}H NMR ($CDCl_3$): $\delta=1.67$ (br s, 1H; OH), 1.96 (m, 2H; CH_2), 2.46 (m, 2H; CH_2), 2.61 (m, 2H; CH_2), 4.13 ppm (s, 2H; CH_2OH); ^{13}C NMR ($CDCl_3$): $\delta=$ 20.25 (t, CH_2), 31.08 (t, CH_2), 32.13 (t, CH_2), 58.00 (t, CH_2OH), 125.72 (s), 132.89 ppm (s); IR ($CDCl_3$): $\tilde{\nu}=3612$ (OH), 2113 (N_3), 1280 cm^{-1} (N_3).

(2-Azidocyclopent-1-enyl)methyl triphenylmethyl ether (15): Trityl chloride (130.3 mg, 0.467 mmol) was added to a solution of **14** (50 mg, 0.359 mmol) in a 1:1:1 mixture (1 mL) of pyridine, THF, and CH_2Cl_2 and stirred at RT for 48 h. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (silica gel; Et_2O/hexane, 1:10) to give **15** as a light-yellow oil (122 mg, 89 %). ^{1}H NMR ($CDCl_3$): $\delta=1.99$ (m, 2H; CH_2), 2.60 (m, 4H; 2×CH_2), 3.70 (s, 2H; CH_2O), 7.24–7.36 (m, 9H; ArH), 7.51 ppm (m, 6H; ArH); ^{13}C NMR ($CDCl_3$): $\delta=20.18$ (t, CH_2), 30.95 (t, CH_2), 32.56 (t, CH_2), 59.10 (t, CH_2O), 86.59 (s, *C*Ph$_3$), 124.30 (s), 126.85 (d, ArC), 127.67 (d, ArC), 128.67 (d, ArC), 132.31 (s), 144.12 ppm (s); IR ($CDCl_3$): $\tilde{\nu}=2100$ cm^{-1} (N_3).

General procedure for the synthesis of esters 16a–e: At 0 °C, the corresponding acyl chloride (0.719 mmol) was added dropwise to a solution of **14** (50 mg, 0.359 mmol) and triethylamine (72.8 mg, 99.9 μL, 0.719 mmol) in CH_2Cl_2 (2 mL). The mixture was continuously stirred at RT for 16 h. Thereafter, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica gel; Et_2O/hexane, 1:10) to give the ester **16** as a yellowish oil.

(2-Azidocyclopent-1-enyl)methyl 2-methylpropanoate (16c): Yield 77 %; ^{1}H NMR ($CDCl_3$): $\delta=1.14$ (d, $^3J=7.0$ Hz, 6H; CH_3), 1.95 (m, 2H; CH_2), 2.39 (m, 2H; CH_2), 2.53 (sept., $^3J=7.0$ Hz, 1H; CH), 2.60 (m, 2H; CH_2), 4.57 ppm (s, 2H; CH_2O); ^{13}C NMR ($CDCl_3$): $\delta=18.95$ (q, CH_3), 20.11 (t, CH_2), 30.99 (t, CH_2), 32.13 (t, CH_2), 33.92 (d, CH), 58.85 (t, CH_2O),

121.24 (s), 135.27 (s), 176.95 ppm (s, C=O); IR ($CDCl_3$): $\tilde{\nu}$ = 2104 (N_3), 1729 cm^{-1} (-CO_2-).

Photolysis of 13, 15, and 16: Solutions of **15** or **16c** (ca. 0.1 mmol) in $CDCl_2F$ (0.6 mL) were irradiated at −120 °C, and degradation of the starting materials were monitored by NMR spectroscopic analysis at the same temperature. No set of product signals could be detected, and this negative result was also found when solutions of the azides **13** or **16a**,**b**,**d**,**e** (see the Supporting Information) in $CDCl_3$ were photolyzed at −50 °C.

2,4-Dichloro-4-dioxolan-2-ylidene-3-oxobutanenitrile (18): As described previously,[9] a solution of **10** in chloroform was heated to reflux for 2 h. After concentration of the solution under reduced pressure, crystallization started on cooling. The resulting crystals were washed with *n*-hexane/ethyl acetate (9:1) to give the colorless compound **18** (67 %). The melting point (126–127 °C) as well as the ^1H and ^{13}C NMR spectroscopic data measured in [D_6]acetone were identical with the data described for **11**.[9] ^1H NMR ($CDCl_3$): δ = 4.73 (m, 2H; CH_2O), 4.88 (m, 2H; CH_2O), 5.60 ppm (s, 1H; CHCl); ^{13}C NMR ($CDCl_3$): δ = 45.10 (d, CHCl), 67.08 (t, CH_2O), 70.56 (t, CH_2O), 86.15 (s, CCl), 113.39 (s, CN), 168.31 (s, OCO), 175.55 ppm (s, C=O); IR (KBr): $\tilde{\nu}$ = 1588 (C=O), 1088 cm^{-1}.

X-ray crystal data for 18: $C_7H_3Cl_2NO_3$; M = 222.02 g mol^{-1}; crystal dimensions 0.45 × 0.22 × 0.04 mm; T = 110 K; triclinic; $P\bar{1}$; a = 5.2694(4), b = 8.2771(6), c = 10.1159(9) Å, α = 95.829(6), β = 99.430(7), γ = 101.196(6)°; V = 422.89(6) $Å^3$; Z = 2; ρ_{calcd} = 1.744 g cm^{-3}; μ = 0.736 mm^{-1}; θ range = 3.04–26.00°; reflections collected: 2692, independent: 1639 (R_{int} = 0.0172), R_1 = 0.0337, wR_2 = 0.0867 [$I > 2\sigma(I)$].

Photolysis of 21a: A solution of **21a**[5f] (10 mg, 0.073 mmol) in CD_2Cl_2 (0.7 mL) was irradiated at −80 °C, and the reaction was monitored by NMR spectroscopic analysis at the same temperature. After 30 min, compound **22a** was generated in 22 % yield whereas 47 % of **21a** remained unchanged. The highly unstable azirine **22a** decomposed on extended irradiation.

7-Azabicyclo[4.1.0]hept-6-en-2-one (22a): ^1H NMR ($CDCl_3$, −50 °C): δ = 1.79–2.30 (m, 4H), 2.89 (s, 1H), 3.30 (m, 1H; 5-H), 3.47 ppm (m, 1H; 5-H).

Photolysis of 21b: A solution of **21b**[5f,6] (50 mg, 0.33 mmol) in $CDCl_3$ (0.7 mL) was irradiated at −50 °C for 4.5 h. The product **22b** was generated in 65 % yield.

1-Methyl-7-azabicyclo[4.1.0]hept-6-en-2-one (22b): ^1H NMR ($CDCl_3$): δ = 1.53 (s, 3H), 1.58–2.65 (m, 4H), 3.15 (m, 1H; 5-H), 3.36 ppm (m, 1H; 5-H); ^{13}C NMR ($CDCl_3$): δ = 13.73 (q), 18.77 (t), 26.91 (t), 39.89 (t), 41.28 (s, C-1), 174.25 (s, C-6), 207.38 ppm (s, C=O); IR ($CDCl_3$): $\tilde{\nu}$ = 1763 (C=N), 1696 cm^{-1} (C=O).

Photolysis of 21b in the presence of benzophenone: A solution of **21b** (150 mg, 1.0 mmol) and benzophenone (180 mg, 1.0 mmol) in chloroform (ca. 2.1 mL) was irradiated at −50 °C for about 7 h. Thereafter, the solvent was removed under reduced pressure, and the oily residue was separated by flash chromatography (silica gel; Et_2O/CH_2Cl_2, 1:1) to give first a red fraction, which was composed of benzophenone and trace amounts of **24b**. The second fraction gave **23b** as a yellow oil. On attempts to purify **23b** by repeated chromatography (silica gel; *n*-hexane/ethyl acetate, 9:1), the rearrangement product **25b** was formed. After crystallization (*n*-hexane/ethyl acetate, 9:1), product **25b** was isolated as a white solid. When **21b** was irradiated in $CDCl_3$ without benzophenone but in the presence of acetone, acetophenone, or thioxanthone, either **22b** was generated exclusively or mixtures of **22b**, **23b**, and **24b** were obtained.

6-(2-Methyl-3-oxocyclohex-1-enylimino)-5-oxoheptanenitrile (23b): ^1H NMR ($CDCl_3$): δ = 1.49 (t, J = 1.7 Hz, 3H; CH_3), 1.93 (s, 3H; CH_3), 1.96–2.11 (m, 4H; CH_2), 2.37 (m, 2H; CH_2), 2.46 (m, 4H; CH_2), 3.10 ppm (t, J = 7.0 Hz, 2H; CH_2); ^{13}C NMR ($CDCl_3$): δ = 9.40 (q, CH_3), 14.92 (q, CH_3), 16.56 (t, CH_2), 19.54 (t, CH_2), 21.84 (t, CH_2), 28.42 (t, CH_2), 34.82 (t, CH_2), 36.99 (t, CH_2), 114.97 (s), 119.12 (s), 161.30 (s), 161.71 (s), 197.90 (s, C=O), 199.17 ppm (s, C=O); IR (CCl_4): $\tilde{\nu}$ = 2245 (C≡N), 1706 (C=O), 1644 cm^{-1} (C=N).

(*E*)-Bis(2-methyl-3-oxocyclohex-1-enyl)diazene (24b): ^1H NMR ($CDCl_3$): δ = 2.05 (m, 4H; CH_2), 2.30 (t, J = 1.8 Hz, 6H; CH_3), 2.56 (m, 4H; CH_2), 2.62 ppm (m, 4H; CH_2); ^{13}C NMR ($CDCl_3$): δ = 9.99 (q, CH_3), 20.96 (t, CH_2), 23.31 (t, CH_2), 38.15 (t, CH_2), 140.01 (s), 161.62 (s), 201.82 ppm (s, C=O).

2-[(*Z*)-3-Cyanoproylidene]-3,*cis*-6-dimethyl-1-oxa-4-azaspiro[4.5]dec-3-en-7-one (25b): Yield 30 %; m.p. 87–88 °C; ^1H NMR ($CDCl_3$): δ = 0.76 (d, J = 6.8 Hz, 3H; Me at C-6), 1.75 (br d, J = 14.4 Hz, 1H; 10-H_{eq}), 1.96–2.04 (m, 2H; 9-H), 2.13 (s, 3H; Me at C-3), 2.29 (br td, J = 13.2, 5.6 Hz, 1H; 10-H_{ax}), 2.33–2.55 (m, 6H; 8-H, 2′-H, 3′-H), 2.97 (q, J = 6.8 Hz, 1H; 6-H), 4.80 ppm (m, 1H; 1′-H); ^{13}C NMR ($CDCl_3$): δ = 6.00 (q, *Me*-C-6), 14.02 (q, *Me*-C-3), 16.99 (t, C-2′ or C-3′), 21.88 (t, C-9), 21.70 (t, C-2′ or C-3′), 35.33 (t, C-10), 40.51 (t, C-8), 52.09 (d, C-6), 95.65 (d, C-1′), 113.71 (s, C-5), 119.23 (s, CN), 156.03 (s, C-2 or C-3), 162.96 (s, C-2 or C-3), 208.25 ppm (s, C-7); IR (CCl_4): $\tilde{\nu}$ = 2249 (CN), 1723 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{14}H_{18}N_2O_2$ (246): C 68.27, H 7.37, N 11.37; found: C 67.76, H 7.27, N 11.07.The assignment of the signals was confirmed by NOE, HSQC, and HMBC experiments. Especially, the *Z* configuration was proved by NOE experiments with irradiation at the frequencies of 1-H′ and *Me*-C-3.

X-ray crystal data for 25b: $C_{14}H_{18}N_2O_2$; M = 246.30 g mol^{-1}; crystal dimensions 0.30 × 0.30 × 0.08 mm; T = 110 K; monoclinic; $P2_1/n$, a = 7.2881(2); b = 7.8659(2), c = 22.7567(5) Å, β = 95.321(2)°, V = 1298.96(6) $Å^3$; Z = 4; ρ_{calcd} = 1.259 g cm^{-3}; μ = 0.685 mm^{-1}; θ range = 5.95–62.49°; reflections collected: 4401, independent: 2050 (R_{int} = 0.0209), R_1 = 0.0397, wR_2 = 0.1066 [$I > 2\sigma(I)$].

Photolysis of 21c: A solution of **21c**[6] (700 mg, 5.10 mmol) in chloroform (ca. 30 mL) was irradiated at −50 °C for about 23 h. Thereafter, the solvent was removed under reduced pressure, and the oily residue was separated by flash chromatography (silica gel; Et_2O/CH_2Cl_2, 1:1) to give first **24c** (85 mg, 15 %) as reddish-brown crystals, and then **23c** as a yellow oil (227 mg, 41 %).

(*E*)-5-(2-Methyl-3-oxocyclopent-1-enylimino)-4-oxohexanenitrile (23c): ^1H NMR ($CDCl_3$): δ = 1.49 (t, ^5J = 1.7 Hz, 3H; 2′-Me), 1.99 (s, 3H; 6-H), 2.55 (m, 2H; 4′-H or 5′-H), 2.62 (m, 2H; 4′-H or 5′-H), 2.66 (t, J = 7.1 Hz, 2H; 2-H), 3.33 ppm (t, J = 7.1 Hz, 2H; 3-H). The *E* configuration was confirmed by NOE experiments. ^{13}C NMR ($CDCl_3$): δ = 7.17 (q), 11.61 (t, C-2), 15.38 (q), 27.61 (t), 32.71 (t), 33.57 (t), 118.74 (s), 120.79 (s), 162.26 (s), 172.67 (s), 196.00 (s, C=O), 205.47 ppm (s, C=O); IR ($CDCl_3$): $\tilde{\nu}$ = 1700 cm^{-1} (C=O); GC-MS: m/z (%): 218 (5) $[M]^+$, 136 (56), 95 (77), 67 (100), 53 (32), 41 (69), 39 (49); HRMS (ESI): m/z: calcd for $C_{12}H_{15}N_2O_2$: 219.1128 $[M+H^+]$; found: 219.1098.

(*E*)-Bis(2-methyl-3-oxocyclopent-1-enyl)-diazene (24c): M.p. 157–165 °C (Et_2O/CH_2Cl_2); ^1H NMR ($CDCl_3$): δ = 2.22 (t, ^5J = 1.9 Hz, 3H), 2.60 (m, 2H), 2.79 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 8.27 (q), 22.98 (t), 33.95 (t), 146.19 (s), 173.33 (s), 208.47 ppm (s, C=O); IR ($CDCl_3$): $\tilde{\nu}$ = 1686 cm^{-1} (C=O); GC-MS: m/z (%): 218 (43) $[M]^+$, 55 (64), 54 (92), 53 (88), 52 (85), 41 (93), 39 (100); HRMS (ESI): m/z: calcd for $C_{12}H_{15}N_2O_2$: 219.1128 $[M+H^+]$; found: 219.1103.

Hydrolysis of 23c: At 0 °C, aqueous HCl (1 M, 5 mL) was added to **23c** (236 mg, 1.08 mmol). The mixture was continuously stirred for 48 h at RT and then extracted with Et_2O. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to give **28c** as a yellow oil (74 mg, 55 %). The acidic aqueous phase (see above) was made alkaline with diluted sodium hydroxide and extracted repeatedly with $CHCl_3$. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to afford **27c** as a white solid (13 mg, 11 %), which was purified by recrystallization from $CHCl_3$/hexane.

3-Amino-2-methylcyclopent-2-enone (27c): M.p. 131–135 °C; ^1H NMR ($CDCl_3$): δ = 1.57 (t, ^5J = 1.4 Hz, 3H), 2.37 (m, 2H), 2.49 (m, 2H), 5.05 ppm (br s, NH_2); ^{13}C NMR ($CDCl_3$): δ = 5.98 (q), 26.47 (t), 33.19 (t), 109.24 (s, C-2), 171.90 (s, C-3), 203.98 ppm (s, C=O); IR ($CDCl_3$): $\tilde{\nu}$ = 3521, 3419 (NH_2), 1601 cm^{-1} (C=O); elemental analysis calcd (%) for C_6H_9NO (111): C 64.84, H 8.16, N 12.60; found: C 64.42, H 7.97, N 12.51.

4,5-Dioxohexanenitrile (28c): ^1H NMR ($CDCl_3$): δ = 2.36 (s, 3H), 2.60 (t, J = 7.1 Hz, 2H), 3.14 ppm (t, J = 7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.97 (t, C-2), 23.47 (q, C-6), 31.92 (t, C-3), 118.39 (s, C≡N), 194.53 (s, C=O), 195.87 ppm (s, C=O); IR (CCl_4): $\tilde{\nu}$ = 1721 cm^{-1} (C=O); elemental

analysis calcd (%) for $C_6H_7NO_2$ (125): C 57.59, H 5.64, N 11.19; found: C 57.55, H 5.75, N 11.07.

***N*-(2-Methyl-3-oxocyclopent-1-enyl)-triphenyl-iminophosphorane (26c)**: At 0°C under a nitrogen atmosphere and with stirring, a solution of triphenylphoshine (383 mg, 1.46 mmol) in anhydrous Et_2O (ca. 20 mL) was added dropwise to a solution of **21c** (200 mg, 1.46 mmol) in Et_2O (15 mL). The mixture was stirred at RT for 2 h. Thereafter, the solvent was removed under reduced pressure to give **26c** as a yellow solid (542 mg, 100%), which was purified by recrystallization from $CHCl_3$/Et_2O to yield a white solid. M.p. 195–199°C; ^{1}H NMR ($CDCl_3$): δ = 1.86 (s, 3H), 1.94 (m, 2H), 2.20 (m, 2H), 7.45–7.79 ppm (m, 15H; Ph); ^{13}C NMR ($CDCl_3$): δ = 7.41 (q), 31.37 (t and d, ^3J(P,C) = 9 Hz; C-5), 33.82 (t, C-4), 119.79 (s and d, ^3J(P,C) = 22 Hz; C-2), 128.73 (d and d, ^3J(P,C) = 13 Hz; *m*-Ph), 129.54 (s and d, ^1J(P,C) = 100 Hz; *i*-Ph), 132.23 (d and d, ^2J(P,C) = 10 Hz; *o*-Ph), 132.29 (d and d, ^4J(P,C) = 2 Hz; *p*-Ph), 180.94 (s, C-1), 205.22 ppm (s, C=O); IR ($CDCl_3$): $\tilde{\nu}$ = 1555 (C=O), 1419 cm^{-1} (N=P); elemental analysis calcd (%) for $C_{24}H_{22}NO_2P$ (387): C 77.61, H 5.97, N 3.77; found: C 77.68, H 6.16, N 3.66.

Synthesis of 27c by hydrolysis of 26c: At 0°C, aqueous HCl (1M, 20 mL) was added to **26c** (542 mg, 1.46 mmol). The mixture was stirred for 48 h at RT and then washed repeatedly with Et_2O. The acidic aqueous phase was made alkaline with concentrated sodium hydroxide and extracted repeatedly with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was recrystallized from $CHCl_3$/hexane to give **27c** as a white solid (31 mg, 19%), which was identical to **27c** obtained from hydrolysis of **23c**.

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