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Ring Contraction in Arylcarbenes and Arylnitrenes; Rearrangements of 1- and 3-Isoquinolylcarbenes and 2-Naphthylnitrene to Cyanoindenes

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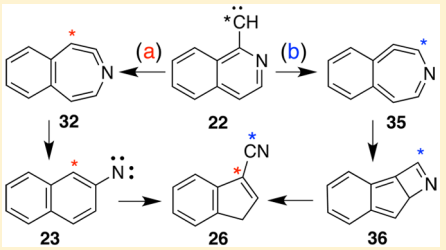
Supporting Information

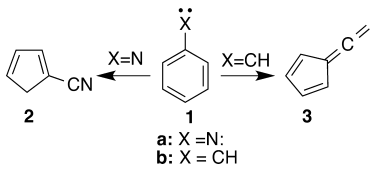
ABSTRACT: Flash vacuum pyrolysis (FVP) of 1-(5-^{13}C-5-tetrazolyl)isoquinoline **18** generates 1-(^{13}C-diazomethyl)isoquinoline **19** and 1-isoquinolyl-(^{13}C-carbene) **22**, which undergoes carbene−nitrene rearrangement to 2-naphthylnitrene **23**. The thermally generated nitrene **23** is observed directly by matrix-isolation ESR spectroscopy, but undergoes ring contraction to a mixture of 3- and 2-cyanoindenes **26** and **27** under the FVP conditions. The ^{13}C label distribution in the cyanoindenes was determined by ^{13}C NMR spectroscopy and indicates the occurrence of two parallel paths of ring contraction starting from 1-isoquinolylcarbene; path a via ring expansion to 3-aza-benzo[*c*]cyclohepta-1,2,4,6-tetraene **32** bifurcating to 2-naphthylnitrene **23** and 2-aza-benzobicyclo[3.2.0]heptatriene **39** (paths a1 and a2); and path b via ring closure of the carbene onto the ring nitrogen, yielding 1-aza-benzo[*d*]bicyclo[4.1.0]hepta-2,4,6-triene **34** and 3-aza-benzo[*d*]cyclohepta-2,3,5,7-tetraene **35**. Product studies demand that the major path is route a1 via 2-naphthylnitrene **23**, which then undergoes direct ring contraction to 1-cyanoindene; but the ^{13}C label distribution requires that the non-nitrene route b contributes significantly. The two reaction paths are modeled at the B3LYP/6-31G* level. The initially formed carbene **22** is estimated to carry chemical activation of some 40 kcal/mol. This allows both reaction channels to proceed simultaneously under low-pressure FVP conditions. FVP of 3-(5-tetrazolyl)isoquinoline **28** similarly generates 3-diazomethylisoquinoline **29** and 3-isoquinolylcarbene **30**, which rearranges to 3- and 2-cyanoindenes **26** and **27**.



INTRODUCTION

The mechanisms of ring contraction of phenylnitrene **1a** and phenylcarbene **1b** to cyanocyclopentadiene **2** and fulvenallene **3**, respectively (Scheme 1) have been elucidated by means of ^{13}C labeling experiments, matrix spectroscopy, and computational studies.[1]

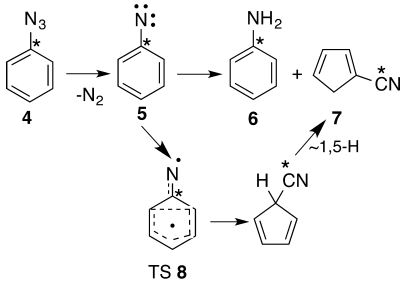
Scheme 1. Ring Contraction in Phenylnitrene and Phenylcarbene



Thus, high temperature flash vacuum pyrolysis (FVP) of 1-^{13}C-phenyl azide **4** affords phenylnitrene **5**, directly observable by matrix-isolation ESR spectroscopy, and the reaction products aniline **6** (labeled exclusively at C1) and 1-cyanocyclopentadiene **7** (labeled exclusively on the cyano group) (Scheme 2).[1]

The rearrangement of **5** to **7** can take place in a concerted manner via TS **8** (Scheme 2) with a calculated activation barrier

Scheme 2. Products of FVP of 1-^{13}C-phenyl azide[a]



[a]* = ^{13}C label.

of ca. 30 kcal/mol at the CASPT2//CASSCF level. A ring opening−ring closure mechanism is also possible.[1]

2-Pyridylcarbene **9** is isomeric with phenylnitrene **1a**, and FVP experiments have clearly demonstrated that carbene **9** rearranges very efficiently to the nitrene,[2] which is readily observed by ESR spectroscopy.[1,3] This rearrangement is understood to take place via ring expansion to 1-aza-cyclohepta-1,2,4,6-tetraene **10**.[4] However, the ^{13}C labeling

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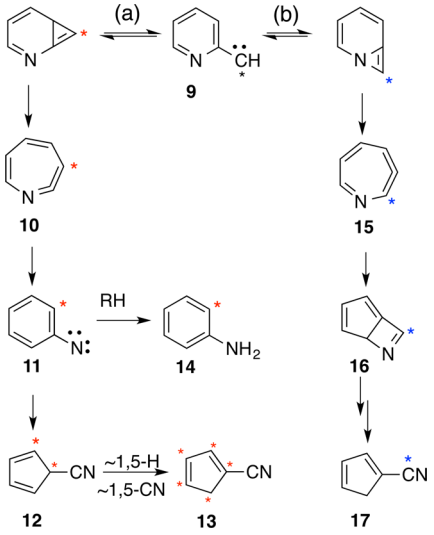
results demand that 2-pyridylcarbene **9** undergoes ring contraction to cyanocyclopentadiene **2** by two distinct mechanisms. Thus, one portion of 2-pyridylcarbene **9** rearranges to phenylnitrene **11** and then to cyanocyclopentadiene **13** (route a, Scheme 3). Another portion of the 2-

Scheme 3. Two Pathways for Ring Contraction of 2-Pyridylcarbene to Cyanocyclopentadiene[1a]

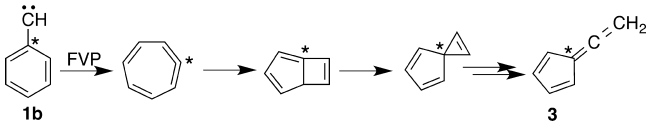


[a]* = ^{13}C label (a third computationally feasible route[1] yielding the same results as route a has been omitted for clarity.

pyridylcarbene undergoes ring expansion to the 4-azacyclohepta-1,2,4,6-tetraene **15** followed by transannular cyclization to **16** and ring opening to cyanocyclopentadiene **17** (route b, Scheme 3). (A third computationally feasible route[1] yielding the same results as route a has been omitted for clarity.) All ring carbon atoms and the cyano group become labeled by the operation of these two mechanisms (Scheme 3).[1]

Route b of the 2-pyridylcarbene ring contraction is analogous to the mechanism of ring contraction of phenylcarbene **1b** to fulvenallene **3** (Scheme 4), which has also been established by ^{13}C labeling.[1]

Scheme 4. Brief Mechanism of the Ring Contraction of Phenylcarbene to Fulvenallene[a]



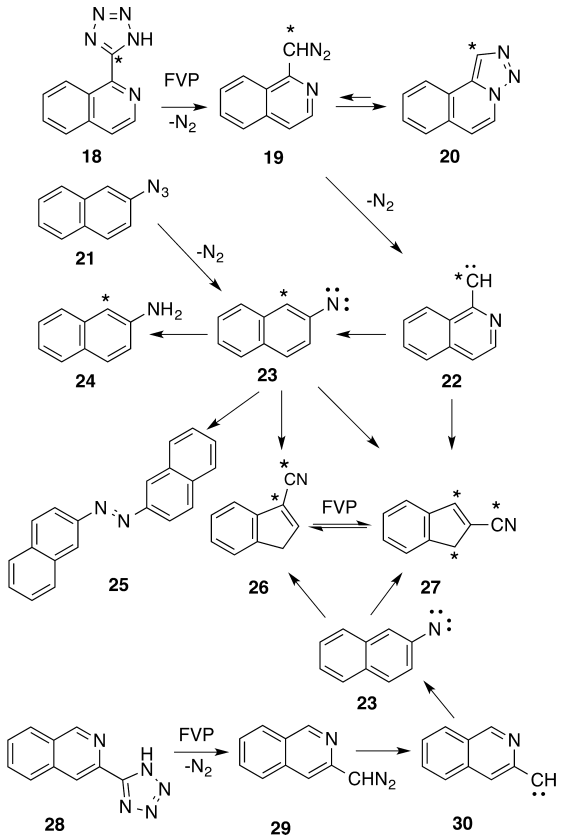
[a]* = ^{13}C label.

We now report a ^{13}C labeling study and calculations on the rearrangement of 1-isoquinolylcarbene to 2-naphthylnitrene and on to 3- and 2-cyanoindenes, which further supports the existence of parallel routes for ring contraction of heteroarylcarbenes.

RESULTS

Product Studies. 1-(5-Tetrazolyl)isoquinoline (unlabeled **18**), 1,2,3-triazolo[5.1-*a*]isoquinoline (unlabeled **20**), and 2-naphthyl azide **21** were prepared as described previously.[5] FVP of these three compounds yields the same products, namely 2-naphthylamine **24**, 2,2′-azonaphthalene **25**, 3-cyanoindene **26**, and 2-cyanoindene **27** at 400−800 °C/10^{-3} hPa (Scheme 5).[5]

Scheme 5. Products of Rearrangement of 1-Isoquinolyl-^{13}C-carbene 22, 1-^{13}C-2-Naphthylnitrene 23, and 3-Isoquinolylcarbene 30[a]



[a]* = ^{13}C or ^{12}C.

The 1-diazomethylisoquinoline **19** is a common intermediate from **18** and **20** and the immediate precursor of 1-isoquinolylcarbene **22**. Compound **19** can be detected by a weak-to-medium intensity diazo group absorption at 2080 cm^{-1} when the products of FVP of either **18** or **20** at 400−500 °C are isolated at 77 K for IR spectroscopy (Figure S1, Supporting Information). The cyanoindenes are already the major products at 500 °C. 3-Cyanoindene **26** is the principal ring contraction product in all cases, as revealed in experiments using N_2 as a carrier gas at ca. 1 hPa in order to deactivate the product collisionally.[5] This is very important, because the cyanoindenes interconvert thermally,[5,6] and the excess energy arising from the exothermicity of the ring contraction (see below) would accelerate such interconversion and obscure the labeling results. According to B3LYP/6-31G* calculations, 2-cyanoindene is thermodynamically a little more stable than 3-cyanoindene, so 2-cyanoindene will be the major product under thermodynamic equilibrium conditions.

The isomeric 3-(5-tetrazolyl)isoquinoline **28** was prepared from 3-cyanoisoquinoline and sodium azide. FVP of this compound at temperatures >400 °C yielded a mixture of 2- and 3-cyanoindenes **27** and **26** identified by GC-MS and IR comparison with the samples generated above (Scheme 5). The diazo compound **29** was detectable by a medium strength absorption at 2075 cm^{-1} in the 77 K IR spectrum, when the

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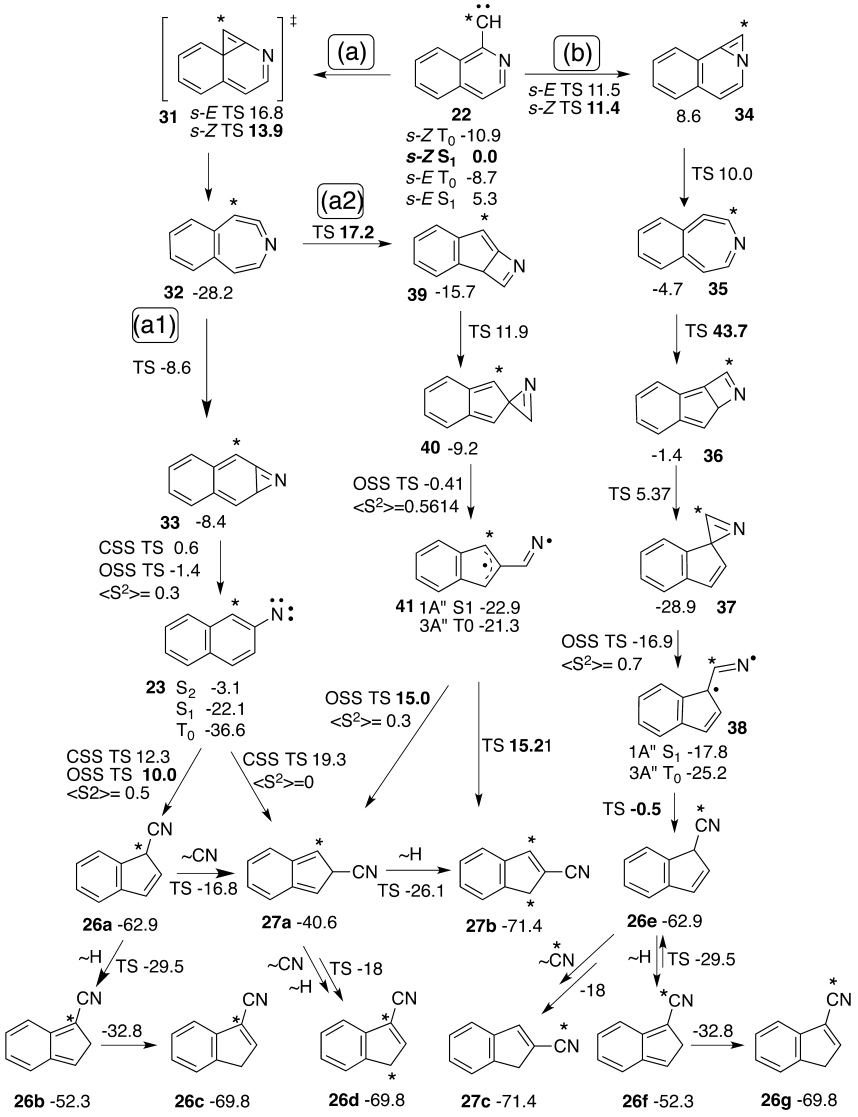
Scheme 6. Energies of Ground and Transition States (B3LYP/6-31G*, kcal/mol Relative to (*s*-*Z*)-1-Isoquinolylcarbene 22 *s*-*Z* S_1)[a]



[a]Compound numbers are in bold. Energy values in bold are for comparison. * = ^{13}C label.

pyrolysis was performed at 350 °C (Figure S2, Supporting Information). Both **18** and **28** underwent a minor degree of cycloreversion to HN_3 and 1- and 3-cyanoisoquinolines, respectively (see Figures S1 and S2).

The related FVP reactions of 1-naphthyl azide, 1,2,3-triazolo[1,5-*a*]quinoline, and 2-(5-tetrazolyl)quinoline are described elsewhere.[5,7]

ESR Spectroscopy. FVP of unlabeled **18**, unlabeled **20**, or 2-naphthyl azide **21** at 500 °C/10^{-3} hPa with Ar matrix isolation of the product at 15 K affords 2-naphthylnitrene (unlabeled **23**), clearly identified by its ESR spectrum (D/hc = 0.925 cm^{-1}; E/hc = 0.002 cm^{-1}) (Figure S3, Supporting Information). The ESR spectrum of 2-naphthylnitrene has been reported before,[8] but the high D value of 1.008 derived by Wasserman[8a] is unlikely for an arylnitrene with extended conjugation.

We have reported a linear correlation between the measured D values and the calculated spin densities ρ for over 100 nitrenes.[9] The D values of both 1- and 2-naphthylnitrenes fit the correlation exactly (1-naphthylnitrene: D/hc = 0.793; ρ = 1.450; 2-naphthylnitrene: D/hc = 0.925; ρ = 1.521) (see Figures S4–S7, Supporting Information). This supports our D value of 0.925 for 2-naphthylnitrene.

UV photolysis of Ar matrices containing **18** and **19** or **20** and **19** (all unlabeled) generates the ESR spectrum of 1-isoquinolylcarbene **22** (unlabeled; D/hc = 0.489 cm^{-1}; E/hc = 0.0245 cm^{-1}).[3] FVP of ^{13}C-labeled tetrazole **18** at 400 °C caused rearrangement to the ^{13}C-labeled 2-naphthylnitrene **23**, which had an ESR spectrum identical with that of the unlabeled material; a hyperfine splitting due to coupling with the ^{13}C label was not observed (Figure S6, Supporting Information).

^{13}C-Labeling Results. FVP of ^{13}C-labeled tetrazole **18** (91 atom-% ^{13}C) at 400 °C (1 hPa N_2 as carrier gas) with isolation of the products at 77 K followed by column and gas chromatography and ^{13}C NMR analysis of the separated products afforded 2-aminonaphthalene **24** (10% yield), which was labeled exclusively in the 1-position (Scheme 5 and Figure S8, Supporting Information).[10] 2,2′-Azonaphthalene **25** was not assayed. 3-Cyanoindene **26** (21% yield) was labeled on the CN group and on C3 (Figure S9, Supporting Information). At

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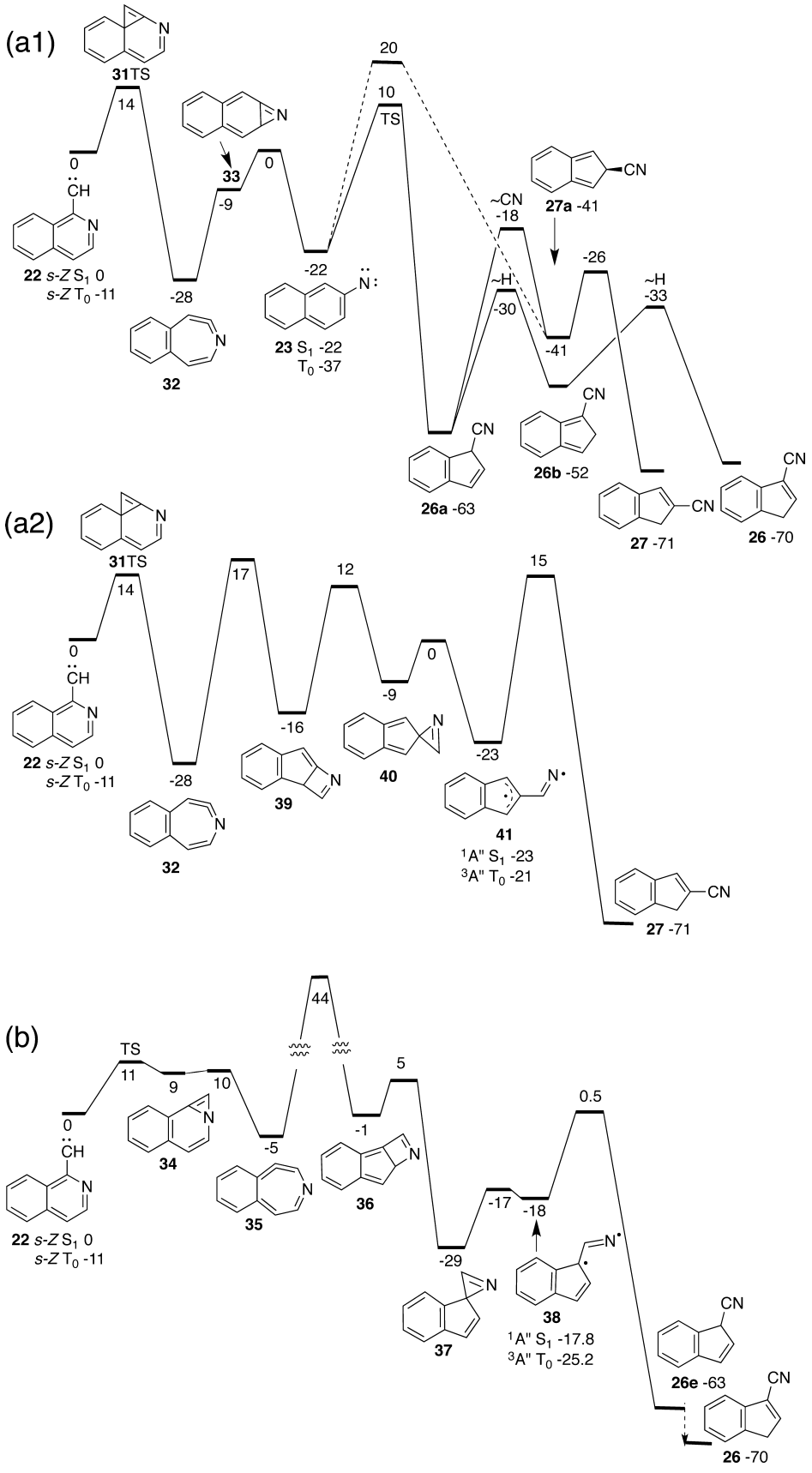

Figure 1. Routes a1, a2, and b (cf., Scheme 6). Energies in kcal/mol (including ZPVE) relative to **22** *s-Z* S_1 at the B3LYP/6-31G* level.

higher temperature (500 °C/10^{-3} hPa) increased ^{13}C label appeared at C1. 2-Cyanoindene **27** (3% yield at 400 °C/1 hPa N_2) was labeled on CN, C1, and C3 (Figure S10, Supporting Information). The label distribution between C1 and C3 was

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the same (1:1) as in the unlabeled material, but the proportion of label at C1 and C3 increased relative to that on the CN group at higher temperature (500 °C/10^{-3} hPa). Thus, one likely reaction pathway is the direct ring contraction of nitrene **23** to 3-cyanoindene **26** with the ^{13}C label at C3 (Scheme 5), but another mechanism puts a label on the CN group in both **26** and **27**.

The 1- and 3-positions in 2-cyanoindene **27** are interchangeable by consecutive 1,5-hydrogen shifts (and possibly also by bimolecular reactions or collisions with the quartz walls of the pyrolysis tube),[5] and these two positions carried equal amounts of label in 2-cyanoindene. The 2- and 3-cyanoindenes interconvert thermally,[5] and this process will place ^{13}C label at C1 and CN in 3-cyanoindene **26** at higher FVP temperatures. The pyrolysis was carried out with N_2 as carrier gas at 1 hPa in order to minimize both H and CN migration processes, but a mechanism is needed to explain the appearance of label on the CN carbon.

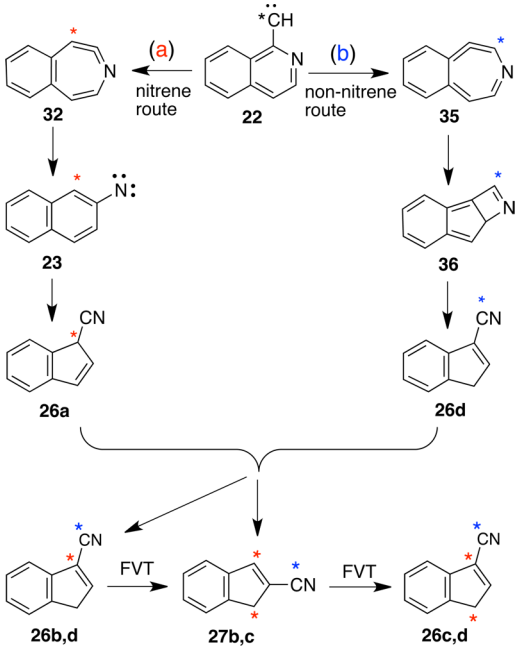
Reaction Mechanism. The mechanism put forward in Scheme 6 and Figure 1 is based on the previous FVP investigation of phenylnitrene and 2-pyridylcarbene[1] as well as a prior photochemistry study of 1- and 2-naphthylnitrenes and their rearrangements.[11] Calculations were carried out at the (U)B3LYP/6-31G* level, which has proved to be useful in many similar investigations,[1,9,11−13] and it is desirable to maintain this level of theory in order to be able to compare results. Calculations on the ring expansion of 1-naphthylnitrene at DFT and CASPT2/CASSCF levels have been published previously.[11] In analogy with Scheme 3, two principal routes of ring expansion of 1-isoquinolylcarbenes are considered (Scheme 6). In route a the nonaromatic cyclopropene **31** is a transition state. The alternate cyclization onto N to give azirine **34** (route b) is preferred by a few kcal/mol. The energy of the ring expansion product **35** (route b) is higher than that of **32** (route a), but the overall activation energy for the formation of **35** is lower. The transannular cyclization of **35** to **36** in route b has the highest activation barrier (43.7 kcal/mol), which is similar to that of the corresponding reactions in 2-pyridylcarbene and phenylcarbene (45−46 kcal/mol).[1]

A weak peak at 1910 cm^{-1} in the 77 K IR spectrum may be taken as direct evidence for the presence of the azabenzocycloheptatetraene **32** in route a (see Figure S1, Supporting Information). This compound has been characterized in detail in a previous photochemical investigation.[11] Route a can bifurcate at compound **32**, becoming routes a1 and a2 (Scheme 6 and Figure 1). Only route a1 yields the 2-naphthylnitrene **23**, which is a required intermediate according to the product studies. Routes a2 and/or a1 account for the equal label distribution over C1 and C3 in 2-cyanoindene **27b**. Route b is required to explain the appearance of label on the CN group. Thus, a combination of routes a1 and b accounts for the initial labeling of 3-cyanoindene **26** on C1 and CN (initially as **26a** and **26e**). Higher temperature causes migration of the CN group and the development of label at C1 in 3-cyanoindene **26d**. Energetically, routes a1 and a2 are preferred, but the activation barriers for all three routes are readily accessible under FVP conditions (see Scheme 6 and Figure 1).

DISCUSSION

The major features of the two mechanisms of formation of 3- and 2-cyanoindenes can be summarized as indicated in Scheme 7, where the contributions of route a2 are omitted for the sake of clarity. The data in Scheme 6 and Figure 1 show that routes

Scheme 7. Simplified Summary of the 1-Isoquinolylcarbene−2-Naphthylnitrene−Cyanoindene Rearrangements showing Nitrene and Non-Nitrene Routes[a]

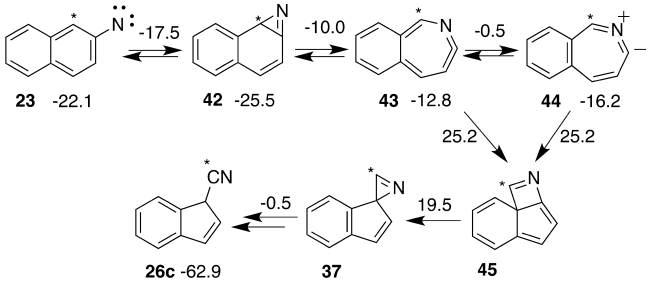


[a]Route a2 is omitted.

a1, a2, and b are all feasible under the FVP conditions applied, where experience has shown that activation barriers of the order of 50 kcal/mol are readily achievable.

There is a second intramolecular reaction path (Scheme 8) of 2-naphthylnitrene **23** that needs to be considered: the

Scheme 8. Calculated Energies (B3LYP/6-31G*) of Ground and Transition State Structures for the Potential but Unobserved Rearrangement via the Tricyclic Species 45 (kcal/mol Relative to Singlet 1-Isoquinolylcarbene 22 *s-Z* S_1)



cyclization to azirine **42** and ring expansion to the ketenimine **43** and the zwitterionic cumulene **44** (a cyclic nitrile ylide), which has been established experimentally and supported by detailed DFT and CASPT2 calculations (Scheme 8).[11] The calculated activation barriers to **42**, **43**, and **44** are quite low (Scheme 8), so that these intermediates may well be formed in a reversible manner under FVP conditions. The transannular cyclizations of azacycloheptatetraenes, such as **32** → **39**, have activation barriers of the order of 46−48 kcal/mol,[1,13] and for the formation of **45**, too, we calculate a transition state 38−41 kcal/mol above **43** and **44**, or 47 kcal/mol above nitrene **23** (Scheme 8). Therefore, this rearrangement is not likely to

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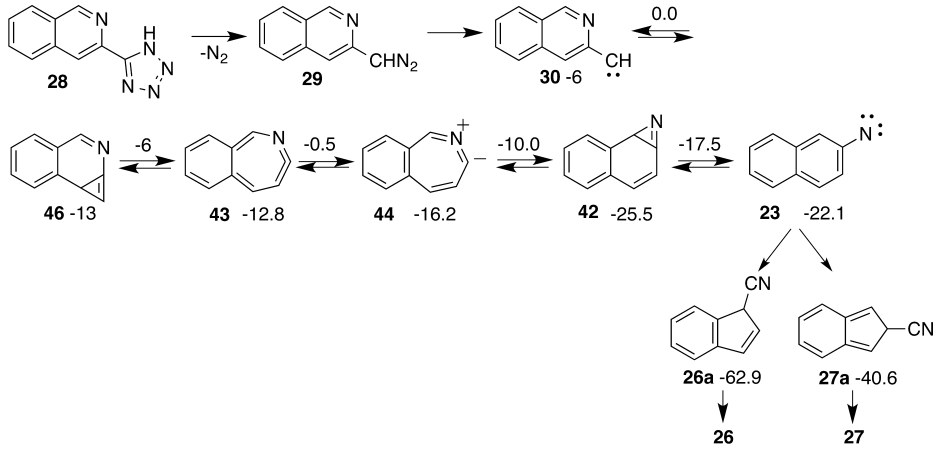
Scheme 9. 3-Isoquinolylcarbene−2-Naphthylnitrene−Cyanoindene Rearrangement



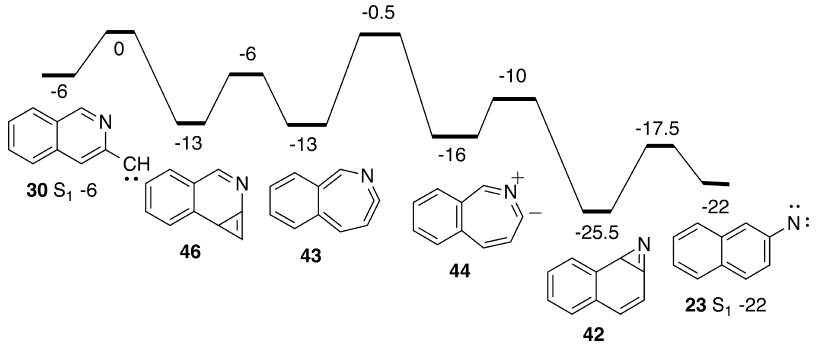


Figure 2. Energy profile for the rearrangement of 3-isoquinolylcarbene **30** to 2-naphthylnitrene **23**. Energies in kcal/mol (including ZPVE) relative to 1-isoquinolylcarbene **22** *s*-*Z* S_1 at the B3LYP/6-31G* level.

compete with the 32 kcal/mol barrier for the reaction **23** → **26a** (Scheme 6 and Figure 1a1), but it is potentially feasible under high-temperature FVP conditions, where it would provide an alternative route to CN-labeling in **26**. However, if a path analogous to Scheme 8 was applied to phenylnitrene, it would have resulted in the formation of ring-labeled cyanocyclopentadiene **7** from 1-^{13}C-phenylnitrene **5**, and the experimental labeling results exclude this process.[1]

The intermediates **42**−**44** must, however, be involved in the rearrangements of 3-isoquinolylcarbene **30** to the cyanoindenes (Scheme 9). The calculated activation energies for the rearrangements shown in Scheme 9 and Figure 2 are very modest indeed, below those for isomeric systems in Figure 1.

It must be noted that FVP conditions are not suitable for kinetic treatments in the Arrhenius sense.[14] Considering Scheme 6 and Figure 1, the proportion of nitriles formed by the nitrene route a) is complicated by the fact that those nitrenes that relax to the triplet ground state will lead to 2,2′-azonaphthalene and 2-aminonaphthalene. An excess of energy is required in order to ensure ring contraction in the singlet nitrene.[1] This problem is less important in the carbene route b because the singlet−triplet splittings in carbenes are smaller. There can be no doubt that route a is a major route, since the nitrene is directly detectable by ESR spectroscopy, and 2,2′-azanaphthalene and 2-aminonaphthalene can be obtained in a combined yield up to 74% under mild conditions (400 °C/1 hPa N_2).[5] In the case of phenylnitrene **1a**, azobenzene can be obtained in over 80% yield on FVP under mild conditions,[2c] but little or no cyanocyclopentadiene **2** is formed under those conditions.

It is also emphasized that all of the FVP reactions reported here are subject to chemical activation.[6,15] The heat of formation of 1-(5-tetrazolyl)isoquinoline **18** can be estimated[15] as 144 kcal/mol based on known heats of formation[16] of tetrazoles and group additivity. The experimental activation energies for decomposition of tetrazoles are in the range 32−44 kcal/mol.[17] The heat of formation of 3-cyanoindene can be estimated[18] as 70 kcal/mol. Thus, the energy of the transition state for decomposition of tetrazole **18** lies about 112 kcal/mol above 3-cyanoindene, or ∼42 kcal/mol above singlet isoquinolylcarbene **22**. While some of the excess energy is carried away by the N_2 molecules, the majority is available as chemical activation in low-pressure FVP reactions of the carbene and will allow all three reaction channels in Scheme 6 and Figure 1 to proceed at the same time.

■ CONCLUSION

1-Isoquinolylcarbene **22** rearranges thermally to 2-naphthylnitrene **23**. The thermolysis end products are 2-aminonaphthalene, 2,2′-azanaphthalene, and the 3- and 2-cyanoindenes **26** and **27**. ^{13}C-labeling studies support the ring contraction mechanisms put forward in Scheme 6. Calculations at the B3LYP level support the existence of two principal routes, a and b from the carbene to the cyanoindenes (Scheme 6 and Figure 1). There are two branches of route a, one (route a1) involving the direct ring contraction of 2-naphthylnitrene **23** to 3-cyanoindene **26**. A secondary route a2 bypasses the nitrene and involves a transannular cyclization (**32** → **39**) analogous to the phenylcarbene ring contraction route.[1] Route b involves an alternate ring expansion of the 1-isoquinolylcarbene **22** to 3-

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azacyclohepta-1,2,4,6-tetraene **35**, transannular cyclization to **36**, and ring opening. This route is also analogous to the phenylcarbene ring contraction.[1] 3-Cyanoindene **26** interconverts thermally with 2-cyanoindene **27**. 2-Cyanoindene is of slightly lower energy than 3-cyanoindene, but 3-cyanoindene is the major initial product under the mildest conditions (400 °C/1 hPa N_2 carrier gas). The overall activation barriers of the three ring contraction routes are easily accessible under FVP conditions. Routes a1 and a2 are energetically preferred, but route b is required in order to explain the ^{13}C-labeling results. All three routes are subject to chemical activation of the order of 40 kcal/mol carried by the singlet 1-isoquinolylcarbene **22**.

3-Isoquinolylcarbene **30** undergoes similar FVP rearrangement to 2-naphthylnitrene **23** and then 2- and 3-cyanoindenes as described in Scheme 9.

EXPERIMENTAL SECTION

Computational Method. Standard DFT calculations were performed using the Gaussian 03 suite of programs.[19] Geometry optimizations and frequency calculations were computed at the B3LYP/6-31G* level.

The energy of the open-shell singlet nitrene **23** (S_1, ^{1}A″) was computed at the UB3LYP/6-31G* level and corrected using the sum method of Cramer and Ziegler as $E(S_1) = 2\,E(50{:}50) - E(T_0)$, where $E(50{:}50)$ is the energy of the broken-symmetry unrestricted UB3LYP wave function with an expectation value $< S^2 >$ of 1, and $E(T_0)$ is the energy of the triplet state.[20] Zero point vibrational energy corrections have been applied in all calculations.

General. Apparatus for preparative FVP, FVP with product isolation at 77 K using a liquid nitrogen cryostat, FVP with product isolation in Ar matrix using a closed-cycle liquid helium cryostat for IR spectroscopy, and apparatus for FVP with ESR spectroscopy of the products were as described.[14,21] The apparatus shown in Figures 3b, 5, 6, and 7 in ref 14 were used. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra at 100 MHz. Mass spectra were obtained using electron ionization at 70 eV and recorded on a conventional sector instrument.

1-(5-^{13}C-5-Tetrazolyl)isoquinoline 18. The synthesis and preparative thermolyses of the unlabeled compound have been described earlier.[5,10] The labeled compound was prepared from 1-bromoisoquinoline (6.9 g; 33.2 mmol) and $Ba^{13}CO_3$ (90.8 atom-% ^{13}C; 5 g; 25.3 mmol) in the same manner as described for the unlabeled compound.[5] Yield 631 mg; mp 237−238 °C (lit.[5] 237−238 °C (unlabeled)).

FVP of 1-(5-^{13}C-5-Tetrazolyl)isoquinoline 18. FVP of unlabeled **18** at 500 °C with isolation of the products in the liquid nitrogen cryostat at 77 K for IR spectroscopy permitted the observation of a weak-to-medium intensity absorption at 2080 cm^{-1} ascribed to 1-diazomethylisoquinoline **19** (Figure S1, Supporting Information). The cyano groups of the cyanoindenes **26** and **27** were observable at 2230 and 2215 cm^{-1} (Figure S1). Small amounts of HN_3 (2130−2160 cm^{-1}) and 1-cyanoisoquinoline were also present (Figure S1). A weak signal at 1910 cm^{-1} is ascribed to a trace of benzoazacycloheptatetraene **32**.

For ESR spectroscopy, the ^{13}C-labeled tetrazole **18** was subjected to FVT at 600 °C with deposition of the product with Ar at 15 K. The XY_2-signal of 2-naphthylnitrene **23** was observed at 6662 G, D/hc = 0.925 cm^{-1}; E/hc = 0.00 cm^{-1} (Figure S3, Supporting Information). It was identical with the spectrum of the unlabeled nitrene.[3]

A sample of 200 mg of ^{13}C-labeled **18** was subjected to FVT at 400 °C/1 hPa N_2 as carrier gas. The starting material was held at 150 °C, and the product was isolated in a liquid N_2 trap. The 2-naphthylamine formed was isolated by column chromatography, and the cyanoindenes were separated and isolated by gas chromatography as described previously for the unlabeled compounds.[5] The ^{13}C-labeled 2-naphthylamine (10% yield) had mp 110−111 °C (lit. 113 °C (unlabeled)). ^{13}C NMR ($CDCl_3$, 25.2 MHz) δ: 108.3 (dt, $^1J_{CH}$ = 155.9, $^3J_{CH}$ = 5 Hz; C1). This spectrum (Figure S8, Supporting Information) showed that only C1 was labeled. The ^{13}C NMR assignments for unlabeled 2-naphthylamine in $CDCl_3$ were made on the basis of the ^{1}H-coupled spectrum in agreement with Ernst:[22] 143.7 (C2), 134.6 (C8a), 128.8 (C4), 127.4 (C5), 126.0, 125.5, 124 C4a, 122.1 C6, 118.0 C3, 108.3 (C1).

3-Cyanoindene (21% yield) showed predominant ^{13}C-labeling on C3 and the CN group with a minor amount of label on C1 (Figure S9, Supporting Information). Unlabeled 3-cyanoindene has the following signals: δ 39.2, 114.0, 116.9, 120.8, 23.8, 126.5, 139.9, 141.4, 146.7 ppm (see Figure S9, Supporting Information).

2-Cyanoindene (3% yield) showed ^{13}C-labeling principally on CN, C1, and C3, whereby C1 and C3 carried equal amounts of label (Figure S10, Supporting Information). Unlabeled 2-cyanoindene has the following signals: δ 40.4, 113.9, 116.6, 122.9, 123.7, 126.9 127.8, 141.0, 142.8, 145.6 ppm (see Figure S10, Supporting Information).

An analogous thermolysis of **18** was carried out at 500 °C/10^{-3} mbar. The 3-cyanoindene (37%) showed ^{13}C-labeling on CN, C1, and C3 (Figure S9, Supporting Information). 2-Cyanoindene (17%) also showed labeling on CN, C1, and C3, and the amount of label at C1 and C3 had increased relative to that at CN (Figure S10, Supporting Information).

3-(5-Tetrazolyl)isoquinoline 28.[23] *Caution: toxic HN_3 is evolved.* Isoquinoline-3-carbonitrile (3.0 g; 0.019 mol) was dissolved in 100 mL DMF, and solium azide (1.5 g; 0.023 mol) and ammonium chloride (1.2 g; 0.022 mol) were added. The mixture was heated at 90 °C for 100 h in a closed vessel. After cooling, the solvent was removed by vacuum distillation. The residue was suspended in water, and dilute NaOH was added until nearly all material had dissolved. This mixture was filtered and then acidified with 0.1 N HCl, and the resulting yellow solid was filtered and dried to yield 1.2 g (3%) of the product; mp 244−245 °C. ^{1}H NMR (DMSO-d_6) δ: 9.49 (s, 1H), 8.72 (s, 1H), 8.24 (d, J = 8 Hz, 1H), 8.19 (d, J = 8 Hz, 1H), 7.90 (t, J = 8 Hz, 1H), 7.80 (t, J = 8 Hz, 1H). A broad signal at 3.7 ppm is ascribed to water in the DMSO-d_6 (Figure S11, Supporting Information). For this reason a distinct NH signal for the tetrazole was not observed (but see the IR spectrum below). ^{13}C NMR (DMSO-d_6) δ: 155.4, 153.5, 137.3, 135.6, 132.1, 129.6, 129.1, 128.2, 127.8, 120.1, 118.3 ppm (Figure S12, Supporting Information). IR (KBr) 3060 m, 3700−1800 (broad), 1642 m, 1612 s, 1555 m, 1465 m, 1450 m, 1405 s, 1370 m, 1289 m, 1058 m, 952 m, 891 s, 760 s, 738 m cm^{-1}. MS m/z (%) 198 (4), 197 (M^+., 40), 169 (3), 156 (4), 155 (37), 154 (6), 142 (13), 141 (100), 140 (23), 129 (4), 128 (36), 127 (5), 122 (2), 117 (7), 115 (9), 114 (39), 113 (14), 101 (11), 88 (11), 87 (6), 77 (13), 76 (5), 75 (9), 74 (5), 70 (7), 64 (6), 63 (15), 62 (8), 51 (10), 50 (9), 39 (9), 36 (10). Anal. Calcd for $C_{10}H_7N_5$ C, 60.91; H, 3.58; N, 35.51. Found: C, 60.58; H, 3.58; N, 35.35.

FVP of 3-(5-Tetrazolyl)isoquinoline 28. FVP at 350 °C with isolation of the products at 77 K for IR spectroscopy gave rise to a medium-strength absorption at 2075 cm^{-1} ascribed to 3-diazomethylisoquinoline **29** (Figure S2, Supporting Information). FVP at 450 °C yielded a mixture of 3- and 2-cyanoindenes **26** and **27** (2230 and 2215 cm^{-1}) as well as a small amount of HN_3 (2130−2160 cm^{-1}) (Figure S2, Supporting Information). The GC-MS properties of the cyanoindenes were identical with those of the samples isolated previously.[5]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00442.

IR spectrum showing diazo group absorption of **19** and **29**; ESR spectra of 1-isoquinolylcarbene **22** and 2-naphthylnitrene **23**; D-ρ correlation for arylnitrenes; ^{1}H and ^{13}C NMR spectra of **28**; ^{13}C NMR spectra of ^{13}C-labeled 2-aminonaphthalene **24**, 3-cyanoindene **26**, and 2-cyanoindene **27**; and computational data (PDF)

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Notes

The authors declare no competing financial interest.

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