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Rearrangements of 4-Quinolylcarbene, 3-Quinolylcarbene, and 2-Quinolylcarbene to 1-Naphthylnitrene and Cyanoindenes by Falling Solid Flash Vacuum Pyrolysis

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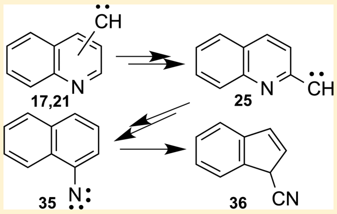
S *Supporting Information*

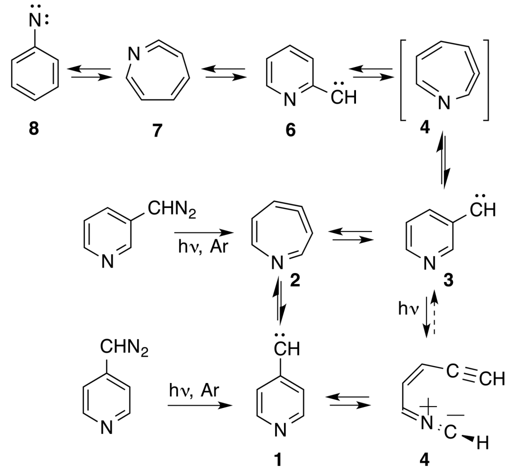


ABSTRACT: The relationship between 4-quinolylcarbene **17**, 3-quinolylcarbene **21**, 2-quinolylcarbene **25**, and 1-naphthylnitrene **35** has been explored experimentally and computationally. The diazomethylquinolines generated from (5-tetrazolyl)quinolines or 1,2,3-triazolo[1,5-*a*]quinoline by conventional flash vacuum pyrolysis (FVP) were observed by IR spectroscopy. The carbenes were generated by falling solid flash vacuum pyrolysis (FS-FVP). 4-Quinolylcarbene **17** was found to rearrange to 3-quinolylcarbene **21** and then to 2-quinolylcarbene **25**, and finally via 1-naphthylnitrene **35** to 1-cyanoindene **36**, which then isomerizes to 3- and 2-cyanoindenes **12** and **13**. The thermal rearrangement of 2-quinolylcarbene to 1-naphthylnitrene was verified by ESR spectroscopy. The reaction mechanism has been elucidated with the help of calculations of the structures and energies of the quinolylcarbenes and 1-naphthylnitrene and the intervening aza-benzobicyclo[4.1.0]heptatrienes, aza-benzocycloheptatetraenes, and aza-benzocycloheptatrienylidenes and the transition states connecting them at the B3LYP/6-31G* level. The nonobserved 1,2-hydrogen shifts in aza-benzocycloheptatetraenes/aza-benzocycloheptatrienylidenes are found to have very high activation barriers.

■ INTRODUCTION

The matrix photochemistry of several hetarylcarbenes and the isomeric (het)arylnitrenes has been reviewed recently,[1] and it has been established that nitrenes are generally thermodynamically more stable than the isosteric carbenes.[2] The rearrangement of 4-pyridylcarbene **1** to 3-pyridylcarbene **3** to 2-pyridylcarbene **6** and finally to phenylnitrene **8** has been investigated in great detail (Scheme 1).[3−6]

Scheme 1. Rearrangement of the Pyridylcarbenes 1, 3, and 6 to Phenylnitrene 8



Recent ^{13}C labeling studies have allowed the mechanisms of the ring contraction of phenylnitrene to cyanocyclopentadiene,[5] and of 1-isoquinolylcarbene **9** to 3- and 2-cyanoindenes **12** and **13** (Scheme 2)[7] to be elucidated.

Here we report the thermal rearrangements of the isomeric quinolylcarbenes **17**, **21**, and **25** to 1-naphthylnitrene **35** and cyanoindenes **12** and **13**.

■ RESULTS AND DISCUSSION

The tetrazoles **14**, **18**, and **22** were used as precursors for 4-quinolylcarbene **17**, 3-quinolylcarbene **21**, and 2-quinolylcarbene **25**, respectively (Scheme 3). 5-Substituted tetrazoles can elminate N_2 from the 2*H*-tautomer to yield nitrile imines $RC(^-)N(^+)NH$, but at high temperatures under FVP conditions the formation of diazo compounds and hence carbenes are preferred, probably because the 5*H*-tautomers of the tetrazoles are populated.[8] This reaction makes tetrazoles convenient precursors of carbenes in FVP reactions.[9] However, 5-substituted tetrazoles can also undergo a cycloreversion process to HN_3 and a nitrile, which are therefore very common byproducts. In the present case, nitriles **15**, **19**, and **23** are invariably obtained as byproducts in 50−60% yields.

When tetrazole **14** was pyrolyzed at 320 °C/10^{-5} hPa with deposition of the product on a KBr window cooled with liquid N_2, the diazomethane intermediate **16** was detected by an absorption at 2070 cm^{-1} in the IR spectrum of the solid film.

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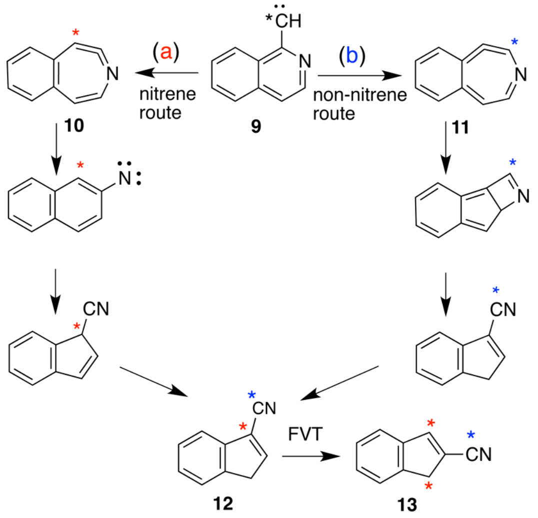
Scheme 2. Ring contraction of 1-Isoquinolylcarbene to Cyanoindenes 12 and 13[a]



[a]Two routes, a and b, yield different ^{13}C-labeling outcomes.

Similarly, the diazomethanes **20** and **24D** were detectable by absorptions at 2070 cm^{-1} following mild pyrolyses of tetrazoles **18** and **22** at 400 °C (see Scheme 3 and Figure S1a, Supporting Information). Compound **24D** has been generated photochemically and absorbs at 2089 cm^{-1} in an Ar matrix.[9] 1,2,3-Triazolo[1,5-*a*]quinoline **24T** is the stable form of diazo compound **24D**, and the two are thermally interconvertible.[9] The intensity of the diazo absorption of **24D** increased at 500 and 620 °C under conditions where 2-quinolylcarbene **25** is already being formed with consequential rearrangement to 2- and 3-cyanoindenes (see Figure S1b,c, Supporting Information). The diazo absorption disappeared on warming the cold pyrolyzate above −35 °C, and it was not observable following FVP at temperatures below 400 °C.

Because the tetrazoles have low vapor pressures, conventional FVP is slow and gives poor yields under preparative conditions. Therefore, we used the falling solid flash vacuum pyrolysis (FS-FVP).[10] Using this technique, tetrazole **14** was pyrolyzed at 650 °C/10^{-3}−10^{-1} hPa to yield a ca. 3:1 mixture of 3- and 2-cyanoindenes **12** and **13** (36%) together with 4-quinolinecarbonitrile **15** (61%) (see Schemes 3 and 4). Analogous pyrolyses of tetrazole **18** afforded analogous products, viz. a 3:1 mixture of 3- and 2-cyanoindenes **12** and **13** (40%) as well as 3-quinolinecarbonitrile **19** (57%). 3-Quinolylcarbene **21** has been generated previously by photolysis of the diazo compound **20** and characterized by its IR and UV−vis spectra,[11] and the ESR spectra of the 2-, 3-, and 4-quinolylcarbenes in propylene carbonate, methylcyclohexane, or ethanol matrices at 6 K have been reported.[12]

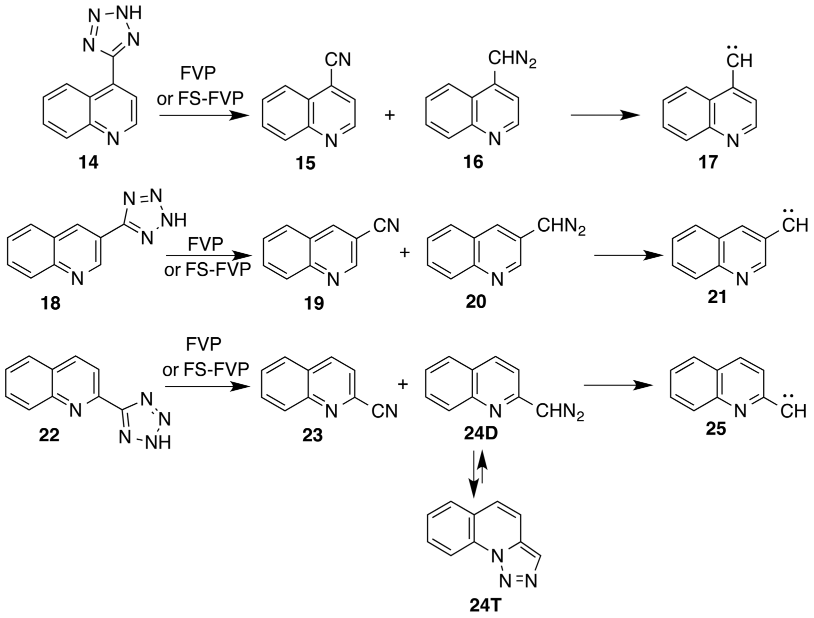
The ESR spectrum of 2-quinolylcarbene **25** (*Z* and *E* conformers) in Ar matrix at ∼12 K has been obtained photolysis of **24T**,[13] and this photolysis also affords a small amount of 1-naphthylnitrene[3] **35** (see Figure S2, Supporting Information). A strong ESR spectrum of **35** is obtained following FVP of 2-(5-tetrazolyl)quinoline **22** at 500−600 °C with deposition of the product in Ar matrix[13] (Figure S3, Supporting Information). The same ESR spectrum of **35** is obtained by FVP of **24T** or of 1-naphthyl azide at 500 °C (Figure S4, Supporting Information). A correlation between observed *D* values and calculated nitrene spin densities for several nitrenes, including 1-naphthylnitrene **35**, is reported in the accompanying publication.[7]

2-Quinolylcarbene **25** was generated previously[9] by conventional FVP of either the 2-(5-tetrazolyl)quinoline **22** or 1,2,3-triazolo[1,5-*a*]quinoline **24T** and yielded virtually the same results as described for **14** and **18**, viz. a ca. 3:1 mixture of 3- and 2-cyanoindenes **12** and **13** (Schemes 3 and 4).

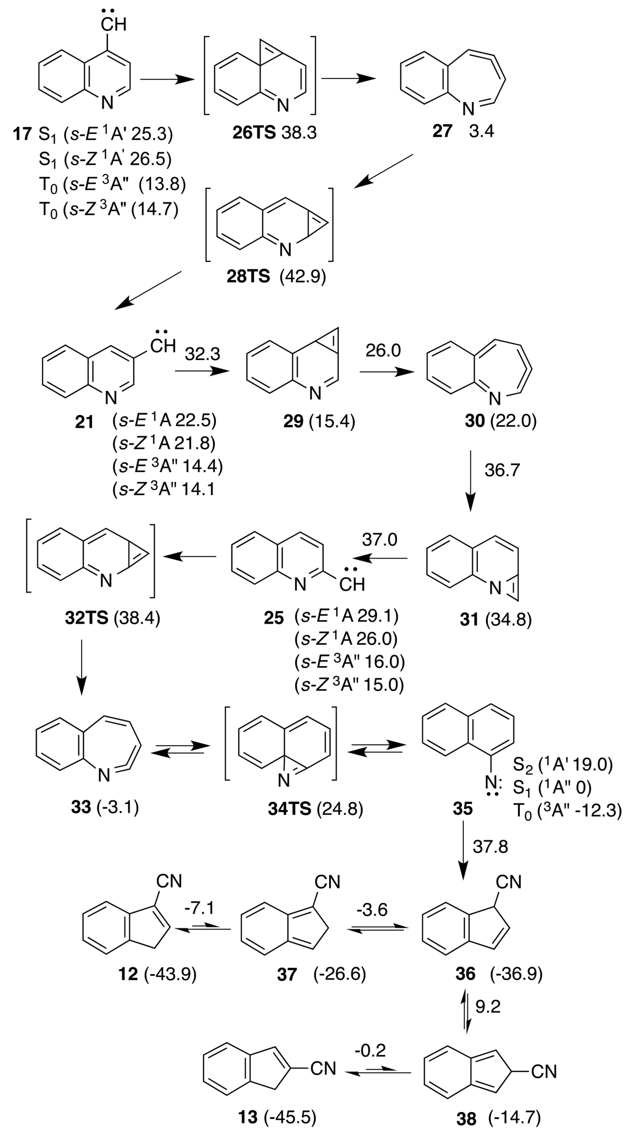
■ REACTION MECHANISM

The formation of the cyanoindenes **12** and **13** in all cases as well as the direct observation of 1-naphthylnitrene **35** in the FVP of **22**[13] indicate the occurrence of a deep-seated rearrangement, whereby 4-quinolylcarbene **17** and 3-quinolyl-

Scheme 3. Generation of Quinolylcarbenes by FVP or FS-FVP



Scheme 4. Rearrangements of 4-, 3-, and 2-Quinolylcarbenes to 1-Naphthylnitrene and Cyanoindenes[a]



[a]Calculated energies in kcal/mol at the B3LYP/6-31G* level relative to open-shell singlet nitrene **35** S_1 = 0.

carbene **21** enter the energy surface already known to connect 2-quinolylcarbene **25** and 1-naphthylnitrene **35**[14] (Scheme 4).

The energies shown in Scheme 4 are translated into the energy profiles shown in Figures 1 and 2, where it is seen that the activation energies for these rearrangements are all very modest, i.e., no more than ~20 kcal/mol with respect to the quinolylcarbenes and ~40 kcal/mol with respect to the 1-azabenzo[*f*]cycloheptatetraenes **27** and **33**. Such barriers are very easily accessed under FVP conditions. The open-shell singlet 1-naphthylnitrene **35** formed in this way can now undergo ring contraction to 1-cyanoindene **36** in a highly exothermic reaction with a calculated barrier of 38 kcal/mol, and **36** interconverts with 3-cyanoindene **12** and 2-cyanoindene **13** in a series of 1,5-shifts of H and CN as described previously[7,9] (Scheme 4 and Figure 2).

Although the triplet nitrene **35** T_0 is the lowest energy minimum prior to formation of the cyanoindenes, the 1-azabenzo[*f*]cycloheptatetraenes **27** and **33** are very close in energy to the singlet nitrene **35** S_1 (Figure 1). Compound **33** has been observed by IR spectroscopy under matrix photochemistry conditions from both the carbene side (**23**)[9] and the nitrene side (**27**),[15] but it is very difficult to observe intermediates of this type under FVP conditions because of the availability of favorable, exothermic reaction paths to the cyanoindenes. Furthermore, the FS-FVP method used here is not suitable for matrix-isolation of reactive intermediates.

Figures 1 and 2 present coherent and energetically feasible mechanism for the rearrangement of the quinolylcarbenes to cyanoindenes. Nevertheless, several other potential reactions will now be considered. They are numbered 1−6 below.

(1) Instead of cyclizing to the ring junction position, forming the transition state **26TS**, 4-quinolycarbene **17** could also cyclize onto the 3-position, forming the cyclopropene **39** (Scheme 5). Compound **39** has a relatively low energy virtually identical to that of **29**, 15 kcal/mol. Ring-opening of **39** would lead to the *ortho*-quinonoid aza-benzocycloheptatetraene **40**, which lies 21 kcal/mol above **35** S_1. The corresponding singlet azacycloheptatrienylidene **41** lies ca. 5 kcal/mol higher. Therefore, compounds **40** and **41** may well be formed in a reversible manner, but it is not obvious how this could lead to the observed products, the cyanoindenes.

(2) 1,2-Hydrogen shifts of the type **40**(**41**) → **27** (Scheme 6) would lead into the mechanism described in Scheme 4 and Figure 1, but there is no firm evidence for the occurrence of hydrogen shifts in cycloheptatetraenes/cycloheptatrienylidenes; if they were occurring, the several carbon and deuterium labeling experiments that have been conducted would have revealed them. Xie, Schreiner, and co-workers reported a very high, calculated, activation barrier, of the order of 80 kcal/mol, for a 1,2-H shift in a benzocycloheptatetraene (the all-carbon analogue of **30** → **33**), which is too high to make such shifts important.[16] We have located two transition states for the reaction **40**(**41**) → **27** (Scheme 6) lying at 68.3 and at 83.5 kcal/mol relative to **35** S_1 at the B3LYP/6-31G* level. These two transition states are interesting in their own right. In **40TS1** an intact benzene ring is preserved, whereas **40TS2** is *ortho*-quiononoid (Figure 3). Thus, these two transition states can be said to be bond-shift isomers. **40TS1** actually connects the cycloheptatrienylidene **41** and the allene **27**, whereas **40TS2** connects the two allenes **40** and **27**, whereby an inflection point on the IRC curve suggests the reaction passes through the carbene **27′** (see IRC curves in Figure S5, Supporting Information). Further theoretical work on these hypothetical H-shifts and transition states is planned, but the important outcome as regards Scheme 6 is that the H-shift **40** → **27** has a barrier of 50−65 kcal/mol (68−83 kcal/mol above **35** S_1), which is drastically higher than any of the barriers in Figures 1 and 2. This is illustrated energetically in Figure 4.

(3) 3-Pyridylcarbene, 3-pyridylnitrene, and 3-quinolylnitrene have all been shown to undergo ring opening to nitrile ylides.[4,11] It was therefore necessary to inquire whether 3-quinolylcarbene **21** could undergo analogous ring opening to the ylide **42** (Scheme 7).[11] While the reaction is computationally feasible, it would involve overall energies more than 10 kcal/mol higher than those in Figure 1, and we have no experimental evidence for its occurrence.

(4) Cycloheptatetraenes are known to undergo transannular cyclization en route to ring contraction to fulvenallene and benzofulvenallene,[5] and analogous mechanisms have been put forward for the rearrangements of 2-pyridylcarbene and 1-isoquinolylcarbene to cyanocyclopentadienes and cyanoin-

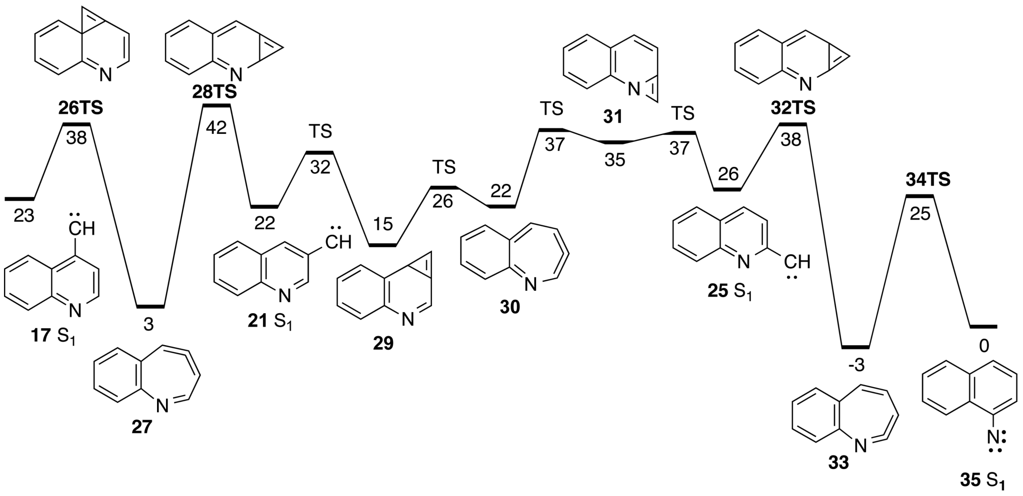


Figure 1. Singlet energy surface for the 4-, 3-, and 2-quinolylcarbenes **17**, **21**, and **25** and 1-naphthylnitrene **35** (relative energies in kcal/mol at the B3LYP/6-31G* level, see continuation of the energy surface in Figure 2).

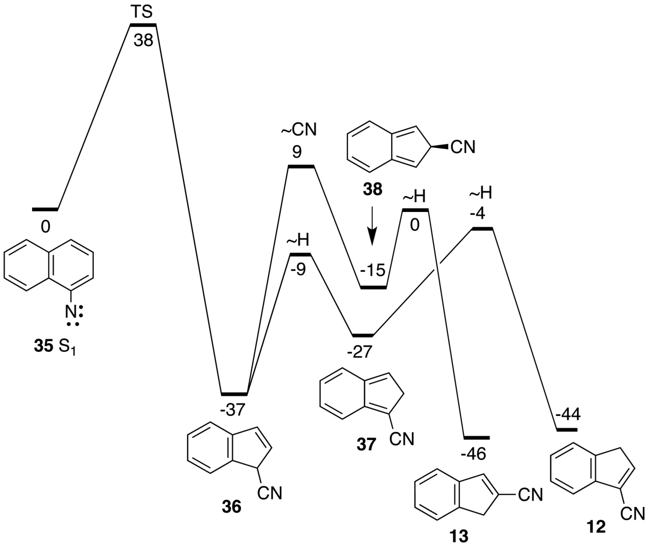
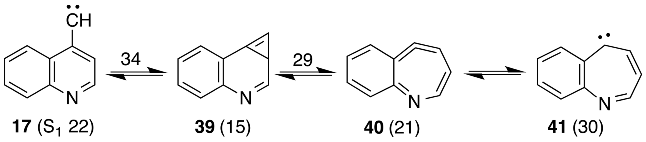


Figure 2. Ring contraction of 1-naphthylnitrene to cyanoindenes (relative energies in kcal/mol at the B3LYP/6-31G* level). For the interconversion of the cyanoindenes see refs7 and9

Scheme 5. Alternative Ring Expansion of 4-Quinolylcarbene 17[a]

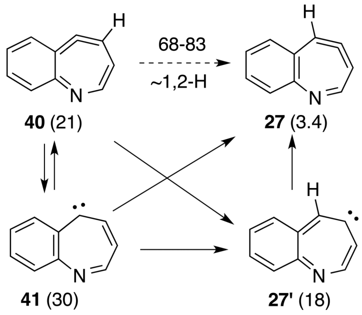


[a]Energies in kcal/mol at the B3LYP/6-31G* level relative to 1-naphthylnitrene **35** S_1.

denes, respectively.[5,7] The aza-benzocycloheptatetraene **30** could undergo a similar rearrangement to tricyclic compound **43** and then to the spiroazirine **44**, the biradical **45** and 1-cyanoindene **36** as a mechanism for forming the cyanoindenes **12** and **13**. The energies of the intermediates **44**, **45**, and **36** have been calculated previously[7] and are repeated in Scheme 8.

However, the first step in Scheme 8 requires a high activation energy of 54 kcal/mol relative to nitrene **35** S_1 (or 32 kcal/mol relative to **30**), which puts it considerably above all the barriers in Figures 1 and 2. It is in principle possible that this reaction could take place under high-temperature FVP conditions, but it is not energetically competitive, and we have no evidence for its occurrence.

Scheme 6. Hypothetical, Non-Observed 1,2-H Shifts Connecting 40 and 27[a]



[a]Energies in kcal/mol at the B3LYP/6-31G* level relative to 1-naphthylnitrene **35** S_1.

(5) There exists a second energy surface for 1-naphthylnitrene **35** S_1, which can be accessed photochemically and leads to the spectroscopically characterized zwitterionic cumulene **48** (a cyclic nitrile ylide) (Scheme 9 and Figure 5).[15] This rearrangement may well take place in a reversible manner under FVP conditions, since the required energies are quite low, and lower than the maximum energies in Figure 1, but this path has not been established in the present study—again because the exothermic rearrangement to the cyanoindenes drives the thermal reaction. An analogous situation pertains to 9-phenanthrylnitrene, which undergoes "normal" ring expansion to a dibenzoazacycloheptatetraene (analogous to **33**) on FVP but to a cyclic nitrile ylide (analogous to **48**) on photolysis.[17]

(6) The rearrangement of 1-isoquinolylcarbene **9** to 2-naphthylnitrene and to 3- and 2-cyanoindenes (Scheme 2)[7] is analogous to that of 2-quinolylcarbene to 1-naphthylnitrene and the cyanoindenes. The two energy surfaces are formally linked through 1-cyanoindene **36**, but otherwise there is no known connection between them. Whereas 1- and 2-naphthylcarbenes interconvert via ring expansion to benzocycloheptatetraene,[16] 1- and 2-naphthylnitrenes do not inter-

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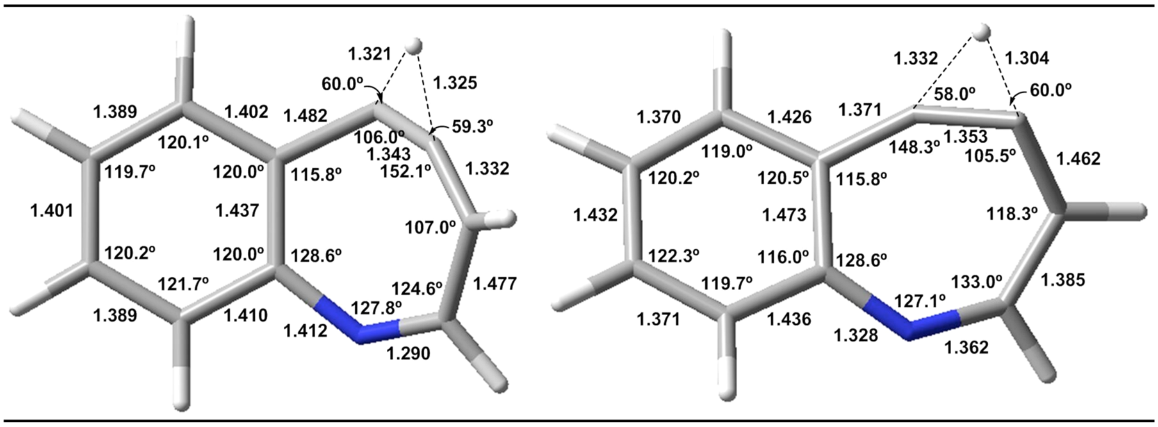


40TS1 **40TS2**

Figure 3. Calculated transition states for the hypothetical reactions **40**(**41**) → **27** (B3LYP/6-31G*). Left: transition structure **40TS1** is benzene-like; the internal reaction coordinate (IRC) graph connects carbene **41** with allene **27**. Right: transition structure **40TS2** is *o*-quinonoid; the IRC graph connects allene **40** with allene **27**. See Figure S5 (Supporting Information).

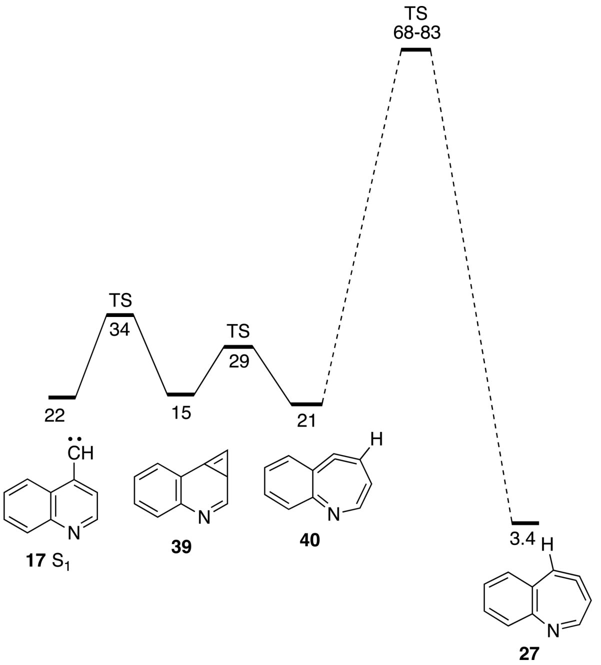
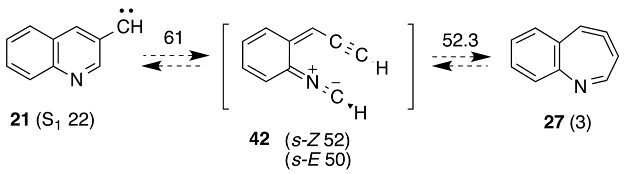


Figure 4. Carbene ring expansion **17** → **40** and the nonobserved 1,2-H shift **40** → **27** via **40TS1**/**40TS2** (energies in kcal/mol at the B3LYP/6-31G* level relative to 1-naphthylnitrene **35** S_1).

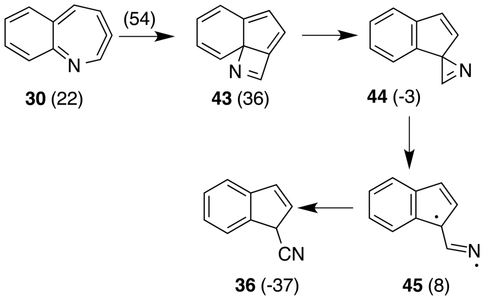
Scheme 7. Potential but Unobserved Ring Opening of 3-Quinolylcarbene 21 and 1-Aza-benzocycloheptatetraene 27[a]



[a] Energies in kcal/mol at the B3LYP/6-31G* level relative to 1-naphthylnitrene **35** S_1.

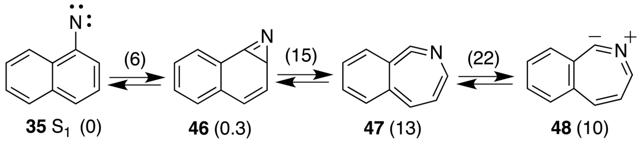
convert, just as phenylnitrene does not undergo a "ring-walk" process.[5]

Scheme 8. A Potential Route from 1-Aza-benzocycloheptatetraene 30 to Cyanoindenes[a]



[a] Energies in kcal/mol at the B3LYP/6-31G* level relative to 1-naphthylnitrene **35** S_1.

Scheme 9. Alternative Ring Expansion[15] of 1-Naphthylnitrene 35 S_1[a]



[a] Relative energies in kcal/mol at the B3LYP/6-31G* level.

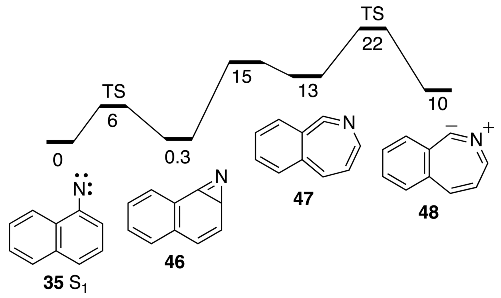


Figure 5. Singlet energy surface for the ring expansion of 1-naphthylnitrene **35** S_1 to the cyclic nitrile ylide **48**[15] (relative energies in kcal/mol at the B3LYP/6-31G* level).

■ CONCLUSION

The cyanoindenes **12** and **13** are the end products of the thermolysis reactions designed to generate the 4-, 3-, and 2-quinolylcarbenes. Calculations of the structures and energies of intermediates and transition states at the B3LYP/6-31G* level support the postulated rearrangement of 4-quinolylcarbene **17** to 3-quinolylcarbene **21** to 2-quinolylcarbene **25** to 1-naphthylnitrene **35** and then to 3- and 2-cyanoindenes **12** and **13**. The calculated activation barriers (Figures 1 and 2) are readily accessible under the flash vacuum pyrolysis conditions employed. In contrast, the potential 1,2-H shifts in aza-benzocycloheptatetraenes or aza-benzocycloheptatrienylidenes **40**, **41**, and **27** have very high calculated activation energies (Figures 3 and 4) and are not observed.

■ EXPERIMENTAL SECTION

Computational Method. All calculations were performed using the Gaussian 03 suite of programs.[18] Reported energies (298.15 K) include zero-point vibrational energy corrections. Transition states were verified by intrinsic reaction coordinate calculations. Imaginary frequencies are reported in the Supporting Information. The energies of the open-shell singlet nitrene **35** S_1 and carbenes **41** and **27′** were 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 wave function with an expectation value $< S^2> = 1$, and $E(T_0)$ is the energy of the triplet state.[19]

General. The apparatus used for conventional, preparative flash vacuum pyrolysis (FVP),[20] falling solid FVP (FS-FVP),[10,21] and FVP coupled to a liquid nitrogen cryostat for IR or ESR spectroscopic observation at 77 or 10 K[21] have been described and correspond to Figures 3b, 11, and 5, respectively, in ref 20. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra at 25 MHz. Mass spectra were obtained using electron ionization at 70 eV and recorded on a conventional sector instrument.

5-(3-Quinolyl)tetrazole 18. A mixture of 3-cyanoquinoline (4.5 g; 29.25 mmol), 1.9 g (29.25 mmol) NaN_3, and 1.35 g (29.25 mmol) NH_4Cl in 150 mL dry DMF was stirred under dry N_2 for 10 days at 120 °C, after which time the solvent was removed in vacuo, and the oily residue was treated with 100 mL 15% HCl with stirring. The tetrazole which precipitated was filtered and dried at 10^{-2} hPa at RT to yield 5.3 g (92%) of white crystals, mp 252 ° C (decomposition). ^{1}H NMR (DMSO-d_6) 9.67 (d, J = 2 Hz, 1H), 9.39 (d, J = 2 Hz, 1H), 8.28 (d, J = 8 Hz, 1H), 8.23 (d, J = 8 Hz, 1H), 8.01 (dt, J = 2 and 8 Hz, 1H), 7.83, t, J = 8 Hz, 1H), 5.7 (very broad, ca. 1H). ^{13}C NMR (DMSO-d_6) 153.9, 146.1, 143.8, 138.2, 133.0, 129.3, 128.9, 127.4, 125.7, 118.8. MS m/z (%) 198 (2), 197 ($M^{+\cdot}$, 17), 170 (4), 169 (35), 154 (7), 142 (8), 115 (9), 38 (99), 37 (11), 36 (100), 35 (39). IR (KBr) 3100–2100 (very broad), 1630 s, 1580 s, 1530 s, 1385 s, 1365 s, 1305 s, 1225 s, 1210 s, 1090 s, 1060 s, 1025 s, 940 s, 865 vs, 650 s, 765 s cm^{-1}. Anal. Calcd for $C_{10}H_7N_5$: C, 60.91; H, 3.58; N, 35.51. Found: C, 60.84; H, 3.44; N, 35.36.

Pyrolysis of 5-(3-Quinolyl)tetrazole 18. A sample of 1 g of the solid, powdered tetrazole was subjected to FS-FVP at 600 °C at a pressure varying between 10^{-3} and 10^{-1} hPa in the course of 60 min. The resulting products were separated by preparative GC (SE52, 160 °C isothermally) and identified by direct comparison of the ^{1}H NMR, IR, and mass spectra with those of the compounds isolated previously.[9,21] The following products were obtained (relative yields by GC): 3-cyanoquinoline **19** (57%), 2-cyanoindene **13** (12%), 3-cyanoindene **12** (28%). A trace of an additional compound (0.8%), possibly 1-cyanoindene, was also present.

*2-Cyanoindene **13**.* ^{1}H NMR ($CDCl_3$) 3.68 (d, J = 1.9 Hz, 2H), 7.60 (t, J = 1.9 Hz, 1H), 7.51–7.37 (m, 4H). IR (film on KBr) 2215 cm^{-1}. MS m/z (%) 142 (10), 141 ($M^{+\cdot}$, 100), 140, (54), 114 (22), 113 (10).

*3-Cyanoindene **12**.* ^{1}H NMR ($CDCl_3$) 3.62 (d, J = 2.0 Hz, 2H), 7.59 (t, J = 1.7 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.30 t, J = 2.0 Hz, 1H). IR (film on KBr) 2230 cm^{-1}. MS m/z (%) 142 (43), 141 ($M^{+\cdot}$, 100), 140 (100), 114 (72), 113 (34).

5-(4-Quinolyl)tetrazole 14. This compound was prepared from 4-cyanoquinoline (1.0 g; 6.5 mmol) in the same manner as described for **18** above and obtained as white crystals (1.0 g; 78%) after recrystallization from water–ethanol (1:1), mp 235 °C (decomposition). ^{1}H NMR (DMSO-d_6) 9.29 (d, J = 5.0 Hz, 1H), 9.03 (d, J = 8.7 Hz, 1H), 8.37 (d, J = 5.0 Hz, 1H), 8.35 (d, J = 8.7 Hz, 1H), 8.06 (dt, J = 8.7 Hz, 1H), 7.93, t, J = 8 Hz, 1H), 5.7 (very broad, ca. 1H). ^{13}C NMR (DMSO-d_6) 156.2, 146.4, 141.6, 136.4, 133.2, 130.0, 126.7, 124.3, 124.0, 121.2. MS m/z (%) 198 (10), 197 ($M^{+\cdot}$, 99), 170 (13), 169 (100), 168 (7), 154 (15), 143 (7), 142 (54), 141 (4), 140 (6), 129 (7), 128 (19), 127 (16), 115 (16), 101 (26), 84 (15), 75 (16), 63 (23), 38 (26), 36 (93). IR (KBr) 2900–2100 (very broad), 1625 m, 1595 s, 1540 m, 1380 s, 1320 m, 1270 m, 1225 s, 1210 s, 1020 s, 1005 s, 920 m, 830 s, 810 s, 755 s, 695 m cm^{-1}. Anal. Calcd for $C_{10}H_7N_5$: C, 60.91; H, 3.58; N, 35.51. Found: C, 61.07; H, 3.69; N, 35.41.

Pyrolysis of 5-(4-Quinolyl)tetrazole 14. A sample of 0.5 g of the solid, powdered tetrazole was subjected to FS-FVP at 600 °C at a pressure varying between 10^{-3} and 10^{-1} hPa in the course of 60 min. The resulting products were identified by direct comparison of the GC, ^{1}H NMR, IR, and mass spectral data with those obtained for the pyrolysis of **18**.[9,21] The product composition was nearly identical with that obtained in the FVP of **18**: 4-cyanoquinoline **19** (61%), 2-cyanoindene **13** (10%), 3-cyanoindene **12** (26%). A trace of an additional compound, possibly 1-cyanoindene, was also present.

Pyrolysis of 5-(2-Quinolyl)tetrazole 22 and 1,2,3-Triazolo-[1,5-*a*]quinoline 24T. The preparation and conventional FVP of **22** and **24T** were described previously.[9] Pyrolysis of **22** and **24T** in the apparatus for low temperature (77 K) IR spectroscopy[21] allowed the detection of an absorption ascribed to 2-diazomethylquinoline **24D** (2070 cm^{-1}; Figure S1a,b, Supporting Information), as well as 3- and 2-cyanoindenes **12** and **13** (2230 and 2215 cm^{-1}, respectively; Figure S1b,c). When **22** was the starting material, partial cycloreversion to HN_3 and 2-cyanoquinoline was also observed (Figure S1b).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00444.

> Figures showing IR absorption assigned to 2-diazomethylquinoline **24D**; ESR spectra of 2-quinolylcarbene **25** and 1-naphthylnitrene **35**; IRC graphs for **40** → **27** and **41** → **27**; computational method; Cartesian coordinates, energies, and imaginary frequencies, where relevant, of calculated structures (PDF)

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Notes

The authors declare no competing financial interest.

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