Rearrangement of 2-Quinolyl- and 1-Isoquinolylcarbenes to Naphthylnitrenes

Nguyen Mong Lân,[1a] Riko Burgard,[1b] and Curt Wentrup*

Chemistry Department, School of Molecular and Microbial Sciences, The University of Queensland, Brisbane, Qld 4072, Australia

wentrup@uq.edu.au

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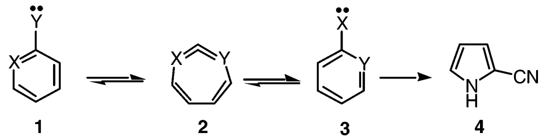
2-Quinolylcarbene **23** and 1-isoquinolylcarbene **33** are generated by flash vacuum thermolysis (FVT) of the corresponding triazolo[1,5-*a*]quinoline and triazolo[5,1-*a*]isoquinoline **19** and **29**, as well as 2-(5-tetrazolyl)quinoline and 1-(5-tetrazolyl)isoquinoline **20** and **30**, respectively. These carbenes rearrange to 1- and 2-naphthylnitrene **21** and **31**, respectively, and the nitrenes are also generated by FVT of 1- and 2-naphthyl azides **18** and **28**. The products of FVT of both the nitrene and carbene precursors are the 2- and 3-cyanoindenes **26** and **27** together with the nitrene dimers, viz. azonaphthalenes **25** and **35**, and the H-abstraction products, aminonaphthalenes **24** and **34**. All the azide, triazole, and tetrazole precursors yield 3-cyanoindene **26** as the principal ring contraction product under conditions of low FVT temperature (340−400 °C) and high pressure (1 Torr N_2 as carrier gas for the purpose of collisional deactivation). This ring contraction reaction is strongly subject to chemical activation, which caused extensive isomerization of 3-cyanoindene to 2-cyanoindene under conditions of low pressure (10^{-3} Torr). 2-Cyanoindene is calculated to be ca. 1.7 kcal/mol below 3-cyanoindene in energy; accordingly, high-temperature FVT of these cyanoindenes always gives mixtures of the two compounds with the 2-cyano isomer dominating. Photolysis of trizolo[1,5-*a*]quinoline **19** and triazolo[5,1-*a*]isoquinoline **29** in Ar matrixes causes partial ring opening to the corresponding 2-diazomethylquinoline **19′** and 1-diazomethylisoquinoline **29′**. The photolysis of the former gives rise to a small amount of the cyclic ketenimine **22**, the intermediate connecting 2-quinolylcarbene and 1-naphthylnitrene.

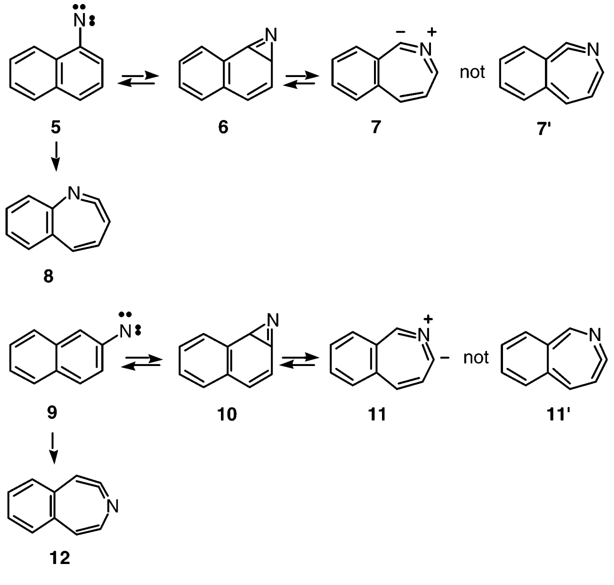
Introduction

The ring expansion and ring contraction of arylcarbenes and arylnitrenes (e.g., **1** and **3**) is a subject of longstanding and continuing interest.[2]



X,Y = CH or N:

The 1- and 2-naphthylnitrenes **5** and **9** are particularly interesting because, as has been shown recently, their photochemistry in Ar matrixes leads to ring closure to azirines **6** and **10** as well as ring expansion to the novel ylidic cyclic cumulenes **7** and **11**, which are distinct energy minima of lower energies than their *o*-quinoid ketenimine bond-shift isomers **7′** and **11′**.[3] Prolonged photolysis leads to the formation of the "aromatic" ketenimines **8** and **12**, which are the global energy minima among the isomers shown.[3]



The triplet naphthylnitrenes are directly observable by UV and IR spectroscopy under matrix isolation conditions.[3] These triplet nitrenes have also been observed by ESR spectroscopy under both photochemical[4,5] and thermal[5] conditions; i.e., photolysis of the matrix isolated

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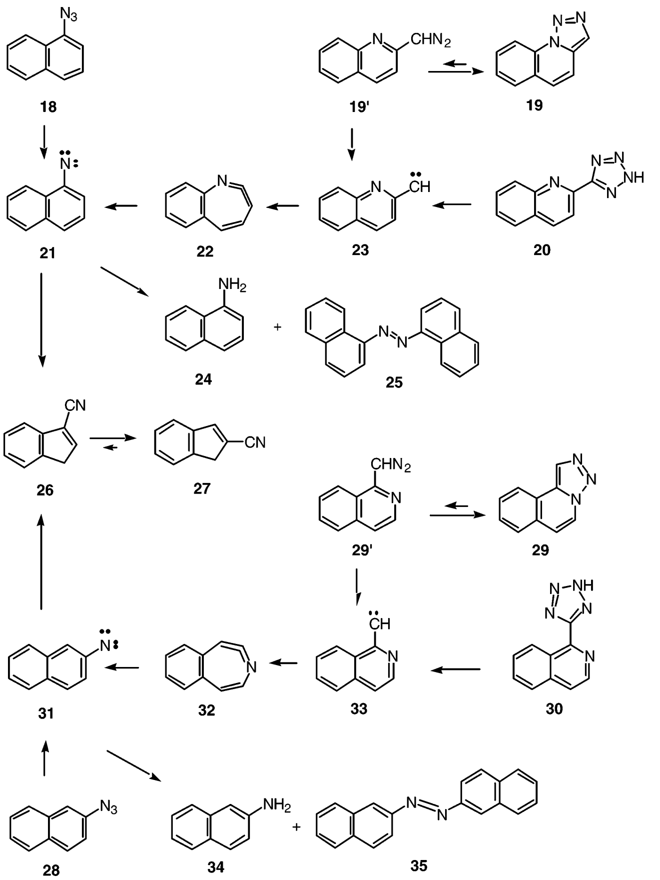
SCHEME 1



naphthyl azides as well as flash vacuum thermolysis (FVT) of the azides with isolation of the thermolysates in Ar matrixes at ca. 10 K leads to intense ESR spectra of the nitrenes.[5] The ground states of the nitrenes are the triplet electronic states. The open-shell singlet states of the 1- and 2-naphthylnitrenes lie 14−17 kcal/mol higher in energy.[3] Although the singlet nitrenes have not been observed directly, it is assumed that the nitrene rearrangements take place on the singlet energy surface.

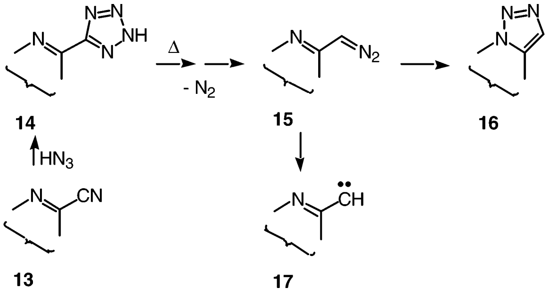
Importantly, the 1- and 2-naphthylnitrenes can also be produced in the thermal rearrangements of 2-quinolyl- and 1-isoquinolylcarbenes **23** and **33**, respectively (see Scheme 1). The carbenes are generated by FVT of 1,2,3-triazolo[1,5-*a*]quinoline **19** and 1,2,3-triazolo[5,1-*a*]isoquinoline **29** as well as 2-(5-tetrazolyl)quinoline **20** and 1-(5-tetrazolyl)isoquinoline **30** as described below. These reactions are carbene−nitrene rearrangements,[2a] formally taking place via the same seven-membered ring ketenimines **22** (**8**) and **32** (**12**) as observed in the matrix photolysis work.[3] It has been elucidated elsewhere that nitrenes are intrinsically (thermodynamically) more stable than the isomeric carbenes.[2a,c,6,7] Accordingly, thermal generation of the carbenes is expected to lead to rearrangement to the nitrenes and formation of nitrene-derived products.

The triplet 1- and 2-naphthylnitrenes were directly observed by Ar matrix ESR spectroscopy in the FVT reactions of the triazoles and tetrazoles.[5] The 2-quinolylcarbene and 1-isoquinolylcarbene were directly observed by ESR spectroscopy on Ar matrix photolysis of the triazoles.[5] Here too, although the singlet nitrenes have not been observed, it is assumed that the carbene-nitrene rearrangements take place on the singlet energy surface. However, it is not excluded that photochemical carbene-nitrene interconversion can take place on triplet energy surfaces as well.

In this paper, we report the preparative FVT experiments on the rearrangements of 2-quinolyl- and 1-isoquinolylcarbenes to 1- and 2-naphthylnitrenes, respectively, the detection of the diazomethyl valence isomers of the triazoles (**19′** and **29′**), and of the ketenimine **22** connecting 2-quinolylcarbene and 1-naphthylnitrene.

Results and Discussion

Two types of carbene precursor were used, 1,2,3-triazoloazines and 5-tetrazolylazines. Tetrazolylazines **14** are readily obtained by addition of HN_3 to cyanoazines **13**.[8] These tetrazoles exist as tautomeric mixtures of the 1*H* and 2*H* tautomers, whereby the 2*H* tautomer is the preferred tautomer in the gas phase.[9] Flash vacuum thermolysis (FVT) of tetrazoles **14** leads to transient diazomethylazines **15** either via the 5*H*-tetrazole tautomers or via initially formed nitrilimines.[9,10] The diazomethylazines **15** cyclize to the lower energy triazoloazines **16**, and the mild thermolysis of tetrazoles can therefore sometimes be used as a convenient synthesis of 1,2,3-triazoloazines.[10] FVT of triazoles **16** again generates diazomethylazines **15** as transient intermediates.[11] If the temperature is sufficiently high, the diazo compounds **15** will decompose by N_2 loss, and both the tetrazoles **14** and the triazoles **16** will serve as precursors of carbenes **17**.



Flash Vacuum Thermolysis. FVT of 1-naphthyl azide **18**, triazoloquinoline **19**, and 2-(5-tetrazolyl)quinoline **20** afforded the same products (but not always in

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(11) (a) The cyclization of diazomethylazines to triazoloazines can be described as a pseudopericyclic reaction.[11b] Accordingly, the activation barrier is expected to be low, and as a consequence it is difficult to detect the higher energy diazo compounds in equilibrium with the triazoles. (b) Fabian, W. M. F.; Barkulev, V. A.; Kappe, C. O. *J. Org. Chem.* **1998**, *63*, 5801.

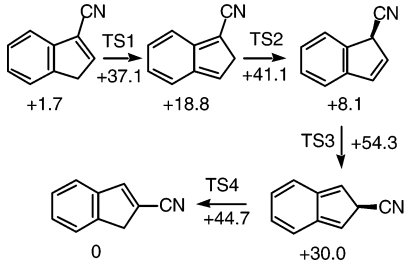
TABLE 1. FVT Products Yields of Products[a]

precursor	*T*/*P* (°C/Torr)	3-CN **26**	2-CN **27**	1-NH_2 **24**	2-NH_2 **34**	1-azo **25**	2-azo **35**
20	400/1 N_2	10.3	2.7	20	–	13	–
	340/10^{-3}	1[b]	3[b]	–	–	–	–
19	400/1 N_2	3.2	0.8	17	–	33	–
	510/10^{-3}	12	28	6	–	5	–
18	480/10^{-3}	5.4	4.6	12.6	–	2.4	–
30	400/1 N_2	20.6	3.4	–	7.5	-	6.4
	340/10^{-3}	1[b]	20[b]	–	–	–	–
29	400/1 N_2	3.2	0.8	–	41	–	33
	500/10^{-3}	24	14	–	7.7	–	8
28	500/10^{-3}	11	10.6	–	7.8	–	14
26	800/10^{-3}	4[c]	6[c]	–	–	–	–
	1000/10^{-3}	2[d]	8[d]	–	–	–	–

[a] The absolute yields are given unless otherwise indicated. [b] Relative yields of 3- and 2-cyanoindene, determined by gas chromatography, are given. The absolute yields are very low. [c] Relative yields of 3- and 2-cyanoindene are given. [d] Relative yields of 3- and 2-cyanoindene are given. 4-, 5-, 6-, and 7-cyanoindenes are formed as well.[13]

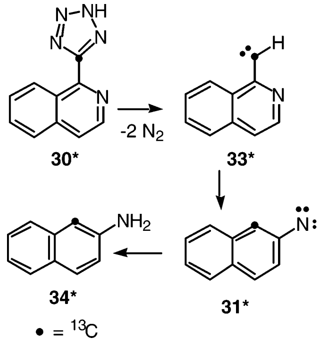
the same ratios) expected from 1-naphthylnitrene **21**, viz. 1-aminonaphthalene **24**, 1,1′-azonaphthalene **25**, and a mixture of 2- and 3-cyanoindenes **26** and **27** (Scheme 1 and Table 1). Similarly, 2-naphthyl azide **28**, triazoloisoquinoline **29**, and 1-(5-tetrazolyl)isoquinoline **30** all afforded the products expected from 2-naphthylnitrene **31**, i.e., 2-aminonaphthalene **34**, 2,2′-azonaphthalene **35**, and the mixture of 2- and 3-cyanoindenes **26** and **27** (Scheme 1 and Table 1). It is seen that the triazoles **19** and **29** are particularly good precursors, affording the highest overall yields.

Experiments at different temperatures and pressures reveal that the product ratios are strongly affected by chemical activation.[6] The rearrangements of the naphthylnitrenes to cyanoindenes **26** and **27** are strongly exothermic. The calculated energies of 3- and 2-cyanoindene are 40.2 and 41.9 kcal/mol below cumulene **22**, respectively (B3LYP/6-31+G* energies corrected by zero-point vibrational energies).[12] The potential energy surfaces for the 1- and 2-naphthylnitrenes and the corresponding azirines, cyclic ketenimines and ylidic cumulenes as well as the transition states connecting them have been calculated previously at the B3LYP/6-31+G* level and, for the nitrenes and some of the other species, CASPT2//CASSCF(12,12)/6-31G* levels.[3] Comparison with these energy profiles put the energies of 3- and 2-cyanoindene ca. 69 and 71 kcal/mol, respectively, below the transition state for the rearrangement of ketenimine **22** to 1-naphthylnitrene **21** (see Scheme 1). To this must be added any additional activation energy required for the ring contraction reactions **21** → **26** and **31** → **26**. When these reactions are conducted in the low-pressure gas phase, the excess vibrational energy will cause interconversion of the cyanoindenes. While 2-cyanoindene is of lowest energy, both can interconvert by means of a series of 1,5-shifts of H and CN as illustrated in the scheme below (B3LYP/6-31+G* energies of ground and transition states in kcal/mol).



These rearrangements have the characteristics of sigmatropic shifts. The highest activation barrier in this scheme, ca. 53 kcal/mol above the energy of 3-cyanoindene, corresponds to the 1,5-shift of CN, where the carbon atom of the migrating cyano group is bonded to both C3 and C2 in the transition state TS3. As shown in Table 1, experimentally, 2-cyanoindene usually predominates at low pressure (10^{-3} Torr), regardless of the precursor, as expected from the thermochemistry. Increasing the pressure to 1 Torr by using N_2 as a carrier gas causes collisional deactivation, and 3-cyanoindene now becomes the principal ring contraction product in all cases. This implies that both 1- and 2-naphthylnitrenes afford 3-cyanoindene as the principal ring contraction product. When pure, isolated samples of 2- or 3-cyanoindenes are subjected to FVT (i.e., in the absence of chemical activation), their interconversion requires higher temperatures (800–1000 °C), as expected from the high energy of TS3 (see Table 1).[13]

The results outlined in Scheme 1 are corroborated by a ^{13}C labeling experiment with 1-(5-tetrazolyl-5-^{13}C)isoquinoline **30*** which on FVT at 400 °C afforded 2-aminonaphthalene **34*** labeled exclusively in the 1-position as determined by ^{13}C NMR spectroscopy.[14]



Ring contraction to five-membered nitriles is a common fate of aryl- and heteroarylnitrenes under FVT conditions.[2a,b] The mechanisms of ring contraction are complicated, and different mechanisms may apply in different systems.[2a,14,15] The mechanism of ring contraction to cyanoindenes was discussed in the light of the ^{13}C-labeling experiment.[14] Recent work has demonstrated the existence of two types of ring opening in heteroarylnitrenes, both of which can lead to subsequent ring closure to five-membered ring nitriles.[16]

Matrix Photolysis. Photolysis of triazoloquinoline **19** isolated in an Ar matrix at 20 K resulted in the develop-

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[12] Absolute energies (HF + ZPE) at the B3LYP/6-31+G* level [B3LYP/6-31G* values in brackets]: 3-cyanoindene, −439.884367 [−439.868193] hartree; 2-cyanoindene, −439.887047 [−439.870795] hartree. Full computational data for the cyanoindenes and the transition states TS1-TS4 for their interconversion are given in the Supporting Information

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ment of a new, sharp, weak-to-medium intensity absorption band at 2089 cm^{-1}. The best wavelength for the formation of this band was 222 nm. This band is ascribed to the 2-diazomethylquinoline **19′**, but since diazo compounds usually have very high extinction coefficients, it can be concluded that the photolysis was very inefficient.[11] Similar photolysis of triazoloisoquinoline **29** produced a new, weak and sharp band at 2092 cm^{-1} assigned to 1-diazomethylisoquinoline **29′**. In photolyses where **19′** was present, a new multiplet was also present at 1913−1926 cm^{-1}. The characteristic band structure identifies the carrier as the cyclic ketenimine **22** (**8**), whose IR spectrum has been described in detail elsewhere.[3] The amount of diazo compound **29′** formed from triazoloisoquinoline **29** was insufficient to allow a firm identification of the cyclic ketenimine **32**. We have experienced difficulty in photolyzing matrix-isolated triazoloazines in other cases.[17] The tetrazolylazines are generally inert under matrix photolysis conditions. As mentioned in the Introduction, photolysis of the matrix-isolated triazoles in the cavity of an ESR spectrometer easily allows the observation of the triplet carbenes **23** and **33**,[5] and FVT of the triazoles and tetrazoles with matrix isolation of the products in the ESR cryostat allows the direct observation of the triplet nitrenes **21** and **31**.[5] Thus, most of the intermediates involved in the quinolyl- and isoquinolylcarbene-to-naphthylnitrene rearrangements have now been observed.[18]

Conclusion

FVT of 1,2,3-triazolo[1,5-*a*]quinoline **19** and 1,2,3-triazolo[5,1-*a*]isoquinoline **29** as well as 2-(5-tetrazolyl)quinoline **20** and 1-(5-tetrazolyl)isoquinoline **30** generates 2-quinolylcarbene **23** and 1-isoquinolylcarbene **33**, respectively, which rearrange to 1- and 2-naphthylnitrenes **21** and **31**, respectively. The nitrenes undergo H-abstraction to afford aminonaphthalenes, dimerization to azonaphthalenes, and ring contraction, initially to 3-cyanoindene **26**. The highly exothermic ring contraction reaction causes chemical activation of 3-cyanoindene, which therefore undergoes thermal interconversion with the lower energy 2-cyanoindene **27**.

Matrix photolysis of the triazoles permits the detection of the higher energy diazomethylquinoline and -isoquinoline valence isomers **19′** and **29′** as well as the cyclic ketenimine **22** connecting 2-quinolylcarbene and 1-naphthylnitrene.

Computational Method

The calculations of structures and energies of ground and transition states reported here were carried out at the B3LYP/6-31+G* and B3LYP/6-31G* levels of theory, using the Gaussian94 suite of programs.[19] Each of he transition structures had one imaginary vibrational frequency, but their locations of the reaction coordinates were not corroborated by intrinsic reaction coordinate calculations. The IR spectra of 2- and 3-cyanoindene were also calculated. The reliability of these computational methods for the present purposes has been amply demonstrated.[2d,3] There was no significant difference between the structures and relative energies obtained with the two basis sets.

Experimental Section

The procedures used for flash vacuum thermolysis and matrix isolation have been published.[20] A 1000 W high-pressure Hg/Xe lamp equipped with a monochromator and appropriate filters, and an excimer lamp operating at 222 nm (25 mW/cm^2) were used for the photolyses.

The 1- and 2-naphthyl azides[21] **18** and **28**, 1,2,3-triazolo-[1,5-*a*]quinoline[22,23] **19**, and 1,2,3-triazolo[5,1-*a*]isoquinoline[22] **29** were prepared according to literature methods. The 1- and 2-aminonaphthalenes were obtained from a commercial supplier, and the azonaphthalenes were prepared by the method of Hantzsch and Schmiedel.[23]

2-(5-Tetrazolyl)quinoline 20. A mixture of 3.08 g (20 mmol) of 2-cyanoquinoline, 1.43 g (22 mmol) of sodium azide, and 1.15 g (21.5 mmol) of ammonium chloride in 30 mL of absolute DMF was heated at 100 °C with magnetic stirring for 5 h. After the mixture was cooled to room temperature, the inorganic salts were filtered off, and the solution was evaporated to dryness. The residue was taken up in 5 mL of water and acidified to pH = 2. The resulting beige precipitate was recrystallized from ethyl acetate to yield 3.6 g (92%) of white needles: mp 192−193 °C dec. Anal. Calcd for $C_{10}H_7N_5$ C, 60.91; H, 3.58; N, 35.51. Found: C, 61.10; H, 3.40; N, 35.50.

1-(5-Tetrazolyl)isoquinoline 30 was prepared analogously from 1-cyanoisoquinoline: yield 80%; mp 237−238 °C. Anal. Calcd for $C_{10}H_7N_5$ C, 60.91; H, 3.58; N, 35.51. Found: C, 61.03; H, 3.72; N, 35.33.

Preparative FVT Experiments. Portions of ca. 400 mg of the precursors were subjected to FVT at the appropriate temperature in a dynamic vacuum of 10^{-3} Torr or at 1 Torr by using N_2 as a carrier gas. The thermolysis products were isolated in a liquid nitrogen cooled cold trap, dissolved in absolute ether or chloroform after the end of the thermolysis, evaporated to dryness, and weighed. The cyanoindenes were assayed by gas chromatography (10% Carbowax 20M, 165 °C, carrier gas H_2 at 30 mL /min) and ^1H NMR spectroscopy. The aminonaphthalenes and azonaphthalenes were separated by column chromatography (SiO_2/chloroform). All products were characterized by direct comparison with authentic samples. The results are collected in Table 1.

Acknowledgment. This work was supported by the Australian Research Council. We thank Mr. Michael Vosswinkel for assistance with the DFT calculations.

Supporting Information Available: Computed Cartesian coordinates, energies and vibrational data for 3- and 2-cyanoindenes, and the transition states for their interconversion at the B3LYP/6-31+G* level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) (a) Annelated cyclopropenes may connect **23** with **22** and **33** with **32**. These are expected to be high energy, shallow minima or transition states.[3,18b] The same is true of the azirines connecting **22** with **21** and **32** with **31**.[3] (b) Kuhn, A.; Vosswinkel, M.; Wentrup, C. *J. Org. Chem.* **2002**, *67*, 9023.

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