

2-Quinoly- and 1-Isoquinolynitrenes: Ring Expansion and Ring Opening in Heteroarylnitrenes

Chris Addicott, Ales Reisinger, and Curt Wentrup*

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

wentrup@uq.edu.au

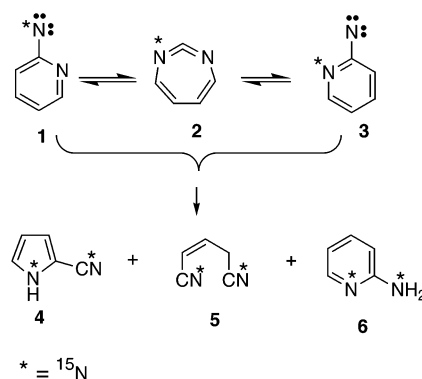
Received September 11, 2002

Argon matrix photolysis of tetrazolo[1,5-*a*]quinoline **8** and tetrazolo[5,1-*a*]isoquinoline **7** causes nitrogen elimination and ring expansion to 1,3-diazabenzocyclohepta-1,2,4,6-tetraene **13**. The photolysis of tetrazolo[5,1-*a*]isoquinoline **7** also causes ring opening to *o*-cyanophenylketenimine **22**. Mechanisms of ring opening of heteroarylnitrenes are discussed.

Introduction

The interconversion of 2-pyridylnitrenes **1** and **3** via 1,3-diazacyclohepta-1,2,4,6-tetraenes **2** under conditions of flash vacuum thermolysis (FVT) has been established by ^{15}N and substituent labeling.^{1,2} In particular, complete nitrogen scrambling is observed in the 2-cyanopyrrole (**4**), glutacononitrile (**5**), and 2-aminopyridine (**6**) products following FVT of ^{15}N -labeled 2-pyridyl azide. 2-Cyanopyrrole **4** is the major product of this reaction, but some 3-cyanopyrrole is often obtained as a result of thermal 1,5-sigmatropic shifts of H and CN groups in **4**. Compound **5** is a minor product, but the analogous ring opening of isoquinolynitrene is important, as demonstrated in the present paper. 2-Aminopyridine **6** is due to hydrogen abstraction by the (triplet) nitrene, and hence its yield is pressure dependent. Seven-membered-ring carbodiimides of type **2** can be isolated at low temperatures (77 K suffices in many cases) following these FVT reactions, and they can also be photochemically generated in low-temperature matrices. They have been directly observed and characterized by IR spectroscopy.^{3–5} The dibenzo derivative of **2** was shown to dimerize at $-40\text{ }^\circ\text{C}$ to afford a diazete derivative, which was characterized by X-ray crystallography.³ Formation of the triplet nitrene **1** under both FVT and matrix photolysis conditions has been ascertained by ESR

spectroscopy.⁶ The ring expansion of **1** to **2** under solution photolysis conditions is of synthetic value as a means of preparation of diazepine derivatives.⁷



The benzologues of **1**, 2-quinolynitrene **12** and 1-isoquinolynitrene **11**, can be generated by FVT of the tetrazoles **7** and **8**. First, mild FVT of **7** and **8** at $150\text{ }^\circ\text{C}$ with isolation of the products at 77 K affords the azides **9** and **10**, respectively, which are readily observed by IR spectroscopy. At $380\text{ }^\circ\text{C}$ a new absorption near 2000 cm^{-1} assigned to carbodiimide **13** appeared.³ Above $500\text{ }^\circ\text{C}$ this species started disappearing again, being replaced by the final products **15** and **16**,³ and these were isolated in 40 and 25% yields, respectively.⁸ The formation of these two products in the same ratio from both precursors (**7** and **8**) suggests the presence of a common intermediate, presumably isoquinolynitrene **11**, which subsequently ring opens to the vinyl nitrene **14** at temperatures above $500\text{ }^\circ\text{C}$. A 1,2-H shift in **14** would lead to *o*-cyanophenylacetone nitrile **15** (perhaps via the ketenimine **22**; see

(1) For reviews of carbene and nitrene rearrangements, see: (a) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173–251. (b) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 231–361. (c) Wentrup, C. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: New York, 1984; Chapter 8, pp 395–433. (d) Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487–492. (e) Gritsan, N. P.; Platz, M. *Adv. Phys. Org. Chem.* **2001**, *36*, 255–304.

(2) Crow, W. D.; Wentrup, C. *Chem. Commun.* **1969**, 1387.

(3) Wentrup, C.; Winter, H.-W. *J. Am. Chem. Soc.*, **1980**, *102*, 6159.

(4) Wentrup, C.; Thétaz, C.; Tagliaferri, E.; Lindner, H. J.; Kitschke, B.; Reisenauer, H. P.; Winter, H.-W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 566.

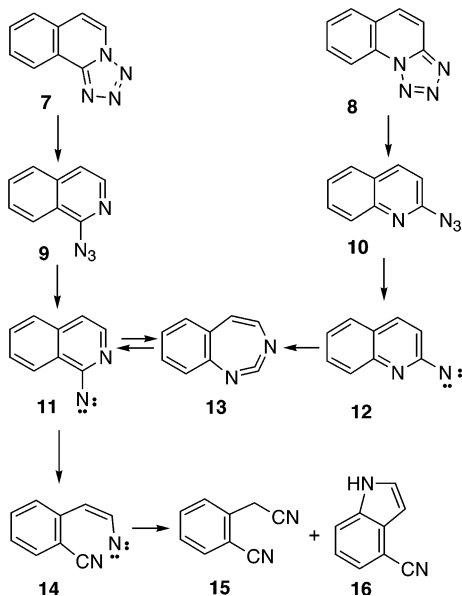
(5) Evans, R. A.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 4009.

(6) Kuzaj, M.; Lüerssen, H.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 480.

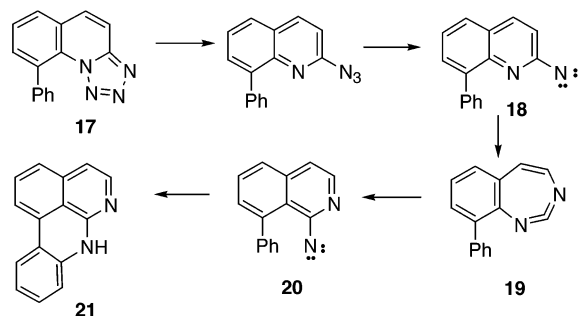
(7) Reisinger, A.; Koch, R.; Wentrup, C. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2247.

(8) Wentrup, C. *Tetrahedron* **1971**, *27*, 367.

below), and aromatic CH insertion to **16**.



Further evidence for the conversion of a quinolynitrene (**18**) to an isoquinolynitrene (**20**) was given by FVT of 8-phenyl tetrazolo[1,5-*a*]quinoline **17**. The product **21** was isolated in 73% yield, and it is reasonable to formulate its formation via ring expansion to the cyclic carbodiimide **19**.⁹



The triplet nitrenes **11** and **12** have been observed by Ar matrix ESR spectroscopy in both the FVT reactions and the matrix photolysis reactions of the corresponding tetrazoles **7** and **8**. Further photolysis of these matrices caused the development of ESR signals typical of a *carbene*, which may have been the triplet benzodiazacycloheptatrienylidene (a triplet state of **13**).⁶

We have now investigated the matrix photochemistry of **7** and **8** in detail and report that both undergo ring expansion to carbodiimide **13**, and 1-isoquinolynitrene **11** undergoes ring opening as well.

Results

Matrix Photolysis of Tetrazolo[5,1-*a*]isoquinoline 7. Compound **7** exists in the tetrazole form in the solid form in KBr as evidenced by the absence of IR absorptions due to the azido group in the 2100-cm⁻¹ region.

(9) Wentrup, C.; Thétaz, C.; Gleiter, R. *Helv. Chim. Acta* **1972**, *55*, 2633. See also: Brown, R. F. C.; Smith, R. *J. Aust. J. Chem.* **1972**, *25*, 607.

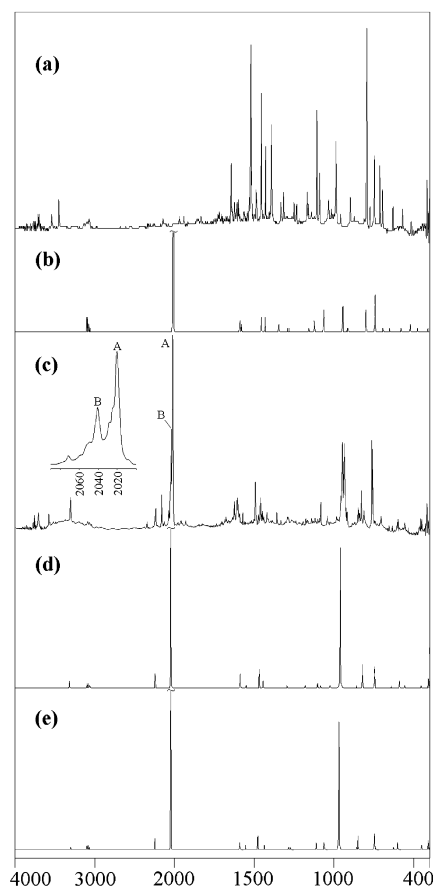


FIGURE 1. (a) IR spectrum of tetrazolo[5,1-*a*]isoquinoline in Ar matrix; (b) calculated IR spectrum of 1,3-diazabenzocyclohepta-1,2,4,6-tetraene **13** (A) (the peak at 2016 cm⁻¹ is attenuated by a factor of 2); (c) result of 2 h of broadband irradiation of the matrix in part a. Calculated IR spectra of (d) *s-Z*- and (e) *s-E*-2-(2-iminovinyl)benzonitrile **22** (B) (the peaks at 2047 and 2043 cm⁻¹ are attenuated by 20% and 10%, respectively). All calculations are at the B3LYP/6-31G* level, scaled by 0.9613. Inset: 2010–2070 cm⁻¹. A = 2020 cm⁻¹. B = 2041 cm⁻¹. Shoulders are present at 2049, 2052, 2059, and 2071 cm⁻¹. Abscissa in wavenumbers.

Simple sublimation with Ar matrix isolation affords the matrix-isolated tetrazole (Figure 1a), and only at temperatures above 150 °C is the azide **9** obtained. Photolysis of **7** ($\lambda > 260$ nm) gave rise to new absorptions at 2020, 2041, 2071, 2158, 2238, and 3305 cm⁻¹ (Figure 1c). New bands in the fingerprint region appeared as well (757, 763, 932, 936, and 948 cm⁻¹). This spectrum is analyzed as the composite of two compounds, the cyclic carbodiimide **13** (2020 cm⁻¹) and the open-chain ketenimine **22** (inter alia 2041, 2238, and 3305 cm⁻¹). The experimental IR spectra are in good agreement with the calculated spectra of **13** and the *s-Z* and *s-E* forms of **22** (Figure 1b,d,e). As shown below, it is possible to obtain **13** almost pure from tetrazoloquinoline.

The absorption at 2041 cm⁻¹ is characteristic of an acyclic ketenimine.¹⁰ The shoulders on the 3305- (NH) and 2041-cm⁻¹ (C=C=NH) bands suggest that the matrix may contain more than one conformer of **22**. The 2238-

(10) Jacox, M. E.; Milligan, D. E. *J. Am. Chem. Soc.* **1963**, *85*, 278. Jacox, M. E. *Chem. Phys.* **1979**, *43*, 157. Finnerty, J.; Mitschke, U.; Wentrup, C. *J. Org. Chem.* **2002**, *67*, 1084.

TABLE 1. Experimental and Calculated IR Bands (cm⁻¹) for **22 (B3LYP/6-31G*, scaled by 0.9613)**

exptl	calcd for <i>s-Z-22</i>	calcd for <i>s-E-22</i>
417 w, 421 w	400, 409	411
452 w, 458 w	455	451
557 w, 559 w	559	554
605 w, 609 w	591	603
635 w, 636 w	-	627
763 m	748	747
826 w, 830 w	823	
837 w, 843 w		850
932 m, 936 m, 938 m, 941 m, 948 m	962	969
1043 w	1027	1063
1121 w	1104	1111
1166 w, 1169 w	1182	
1293 w	1295	1274, 1283
1460 w	1444	1434
1493 w	1469	1477
1573 w		1553
1605 w	1589	1591
2041 m, 2049 w, 2059 w, 2071 w	2047	2043
2238 w	2245	2246
3295 w, 3301 w, 3305 w, 3308 w, 3309 w	3319	3301

TABLE 2. Experimental and Calculated IR Bands (cm⁻¹) for **13 (B3LYP/6-31G*, scaled by 0.9613)**

exptl	calcd	exptl	calcd
420 w	411	1141 w	1122
467 w	455	1178 w	1158
485 w	476	1207 w	1192
535 w	521	1257 w	1239
598 w	579	1285 w	1277
668 w	651	1296 w	1290
705 w	691	1358 w	1346
757 m	743	1448 w	1431
815 w	799	1473 w	1454
841 w	822	1599 w	1578
958 w	944	1603 w	1590
1039 w	1026	2020 s	2016
1085 w, 1089 w	1064		

cm⁻¹ band (CN) is slightly broadened, probably for the same reason. All calculations were performed at the B3LYP/6-31G* level of theory, and no significant changes occurred for **22** at the B3LYP/6-311++G** level. The data are compiled in Tables 1 and 2.

Matrix Photolysis of Tetrazolo[1,5-*a*]quinoline **8.** As in the previous case, sublimation and co-deposition with Ar at 25 K afforded the matrix-isolated tetrazole **8** (Figure 2a), and sublimation through an oven at 150 °C gave the azide **10**.³ Photolysis of **8** with $\lambda > 260$ nm for 1 h produced carbodiimide **13** as shown by the excellent agreement between experimental and calculated IR bands (Figure 2 and Table 2).

Weak bands are seen at 2041, 2047, and 2060 cm⁻¹ in Figure 2. These correspond to the wavenumbers assigned to **22** in Figure 1, but the relative intensities are different, possibly because a different mixture of conformers and/or sites is produced. The weakness of these bands makes a firm assignment impossible, but since we know from FVT chemistry that the nitrenes do interconvert thermally (see the Introduction), a partial rearrangement of **12** to **11** via **13** and consequential ring opening to **22** would not be surprising under photolysis conditions.

Only a few weak bands remain unassigned in the spectra of photolysis of **7** and **8**. Very weak bands at 2124 and 2128 cm⁻¹ (especially from the quinoline) and a

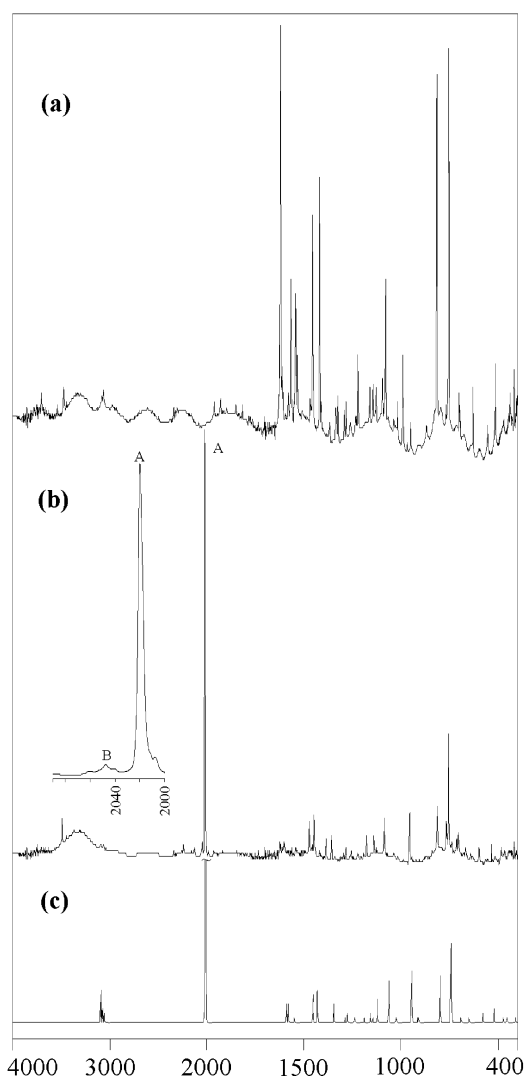


FIGURE 2. (a) IR spectrum of tetrazolo[1,5-*a*]quinoline in Ar matrix; (b) results of 1 h of broadband irradiation; and (c) calculated spectrum of 1,3-diazabenzocyclohepta-1,2,4,6-tetraene **13** (A) at the B3LYP/6-31G* level, scaled by 0.9613 (the peak at 2016 cm⁻¹ is attenuated by a factor of 2). Inset: 2000–2090 cm⁻¹. A = 2020 cm⁻¹. B = 2047 cm⁻¹. Two slightly weaker peaks are present at 2041 and 2060 cm⁻¹. Abscissa in wavenumbers.

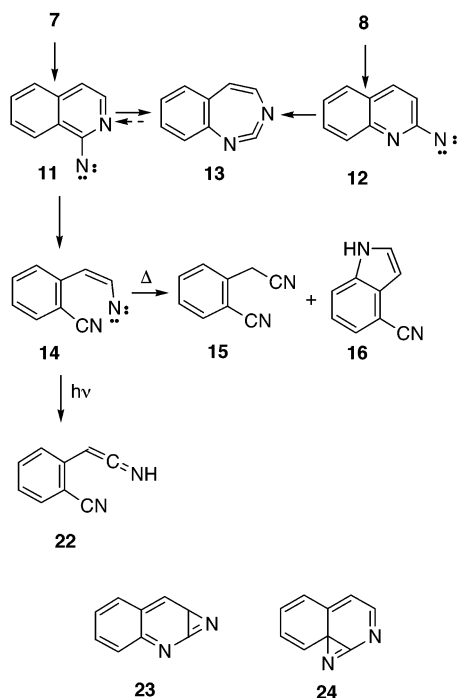
different species absorbing at 2158 cm⁻¹ (especially from the isoquinoline) suggests the presence of isocyanide functions. *C*-(*o*-Isocyanophenyl)ketenimine, formed by ring cleavage of **13**, is a possibility for the former set of bands. The calculated spectra are given in the Supporting Information. *o*-(Isocyanomethyl)benzocyanide, formed by photoisomerization¹¹ of **22**, is a possibility for the 2158-cm⁻¹ species. However, the weakness of these minor peaks makes any assignment hazardous.

Thermally Produced Carbodiimide **13.** We have ascertained that the same carbodiimide **13** is produced thermally and photochemically by carrying out Ar matrix isolations of the products of FVT of **7** and **8** over the temperature range 430–730 °C. The absorptions of **13** were identical with those reported in Table 2. The results obtained previously³ with neat isolation at 77 K were confirmed.

Carbodiimide **13** absorbs at 2007 cm^{-1} in the neat state at 77 K . ^{15}N labeling of the carbodiimide function is expected to result in a significant lowering of the wave-number.¹² We prepared the 1(3)- ^{15}N labeled tetrazoles **7** and **8** by reactions of 2-chloroquinoline and 1-chloroisoquinoline with potassium azide labeled on one terminal nitrogen atom.¹³ FVT of these compounds afforded the carbodiimide **13**, absorbing at $1999.5 \pm 1\text{ cm}^{-1}$ when produced from labeled **7**, and at $1998.5 \pm 1\text{ cm}^{-1}$ when produced from labeled **8** (neat, 77 K). FVT of a mixture of labeled **7** and **8** confirmed that the absorption maxima of the two ^{15}N -isotopomeric carbodiimides, 1- and 3- ^{15}N -**13** are separated by 1 cm^{-1} , in excellent agreement with the calculated difference (1 cm^{-1} at the B3LYP/6-31G* level). The calculated spectra are shown in the Supporting Information.

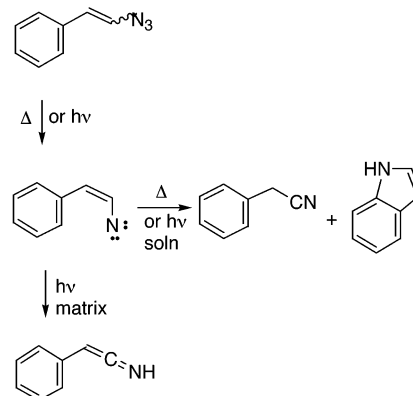
Discussion

The results clearly show that both the quinolyl and the isoquinolyl systems give rise to the ring-expanded carbodiimide **13**, presumably via the nitrenes **11** and **12** which can be observed (in their triplet states) by ESR spectroscopy.⁶ In analogy with calculations on related systems,¹⁴ the ring expansion of the quinolynitrene may take place via the azirine **23**, but the azirine **24** derived from isoquinolynitrene is expected to be a transition state rather than an intermediate. Both **23** and **24** are expected to be significantly higher in energy than **13**,¹⁴ and we have no direct experimental evidence for either of them.



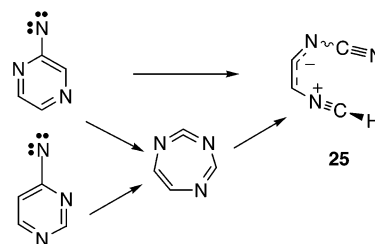
The formation of ketenimine **22** suggests ring opening of isoquinolynitrene to the vinylnitrene **14** followed by a 1,2-H shift. Under thermal conditions in the gas phase, **22** would rearrange to the observed FVT product **15**. The thermolysis of β -styryl azide is known to afford phenylacetone nitrile and indole.¹⁵ The solution photolysis produces phenylacetone nitrile via 3-phenyl-2-azirine.¹⁵ A mechanism

with initial formation of β -styrylnitrene and *C*-phenylketenimine was proposed.^{15a} We have shown that the matrix photolysis of β -styryl azide in Ar matrix at 313 nm for 30 min indeed produces a ketenimine absorbing at 2023 cm^{-1} .¹⁶



The formation of **15**, **16**, and **21** from the appropriate quinolines **8** and **18** demonstrates that the cyclic carbodiimide **13** can isomerize to 1-isoquinolynitrene **11**, at least under FVT conditions. Since at most traces of **22** are formed in the matrix photolysis of **8**, the reaction essentially stops at the ring expansion stage, **13**, under matrix photolysis conditions.

We have recently discovered an important type of ring opening (Type 1) involving nitrile ylide intermediates and taking place in heteroarylnitrenes and heteroarylcarbenes or their ring-expanded equivalents under matrix photolysis conditions, e.g. **25** in the 2-pyrazinylitrene/4-pyrimidinylitrene/1,3,5-triazacyclohepta-1,2,4,6-tetraene system:¹⁷



Analogous Type 1 ring-opening reactions also take place in 2-quinoxalynitrene,¹⁸ 1-quinazolynitrene,¹⁸ 3-quinolynitrene, and other nitrenes and carbenes,¹⁹ as well as 3-pyridazinylitrene where the ring-opened ylide is a stable diazo compound, 3-diazo-2-butenic nitrile.²⁰ Type 1 ring opening is energetically very favorable because ylides are relatively stable intermediates, and it always takes place under matrix photolysis conditions whenever

(11) Keteneimine undergoes matrix photochemical isomerization to methyl isocyanide. Maier, G.; Schmidt, C.; Reusenauer, H. P.; Endlein, E.; Becker, D.; Eckwert, J.; Hess, B. A., Jr.; Schaad, L. J. *Chem. Ber.* **1993**, *126*, 2337.

(12) Donnelly, T.; Dunkin, I. R.; Norwood, D. S. D.; Prentice, A.; Shields, C. J.; Thomson, P. C. P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 307.

(13) Wentrup, C.; Thétaz, C. *Helv. Chim. Acta* **1976**, *59*, 256.

(14) Kuhn, A.; Vosswinkel, M.; Wentrup, C. *J. Org. Chem.*, **2002**, *67*, 9023.

(15) (a) Boyer, J. H.; Krueger, W. E.; Mikol, G. J. *J. Am. Chem. Soc.* **1967**, *89*, 5504. (b) Isomura, K.; Kobayashi, S.; Taniguchi, S. *Tetrahedron Lett.* **1968**, 3499.

it is structurally possible. Type 1 ring opening to a nitrile ylide is not structurally possible in **11**, **12**, or **13**, and also not in 2-pyridylnitrene **1**. Therefore, the energetically more expensive ring opening via vinylnitrene-type intermediates, e.g. **14** (Type 2), occurs instead. This is also a major reaction channel in 3-isoquinolyl nitrene,¹⁸ where it succeeds ring expansion, and in 2-pyrimidyl nitrenes.¹⁹ Ring opening now emerges as a common ultimate fate of heteroaromatic nitrenes, and sometimes carbenes, especially under photolysis conditions, where it may compete with or follow ring expansion. Ring contraction is a common ultimate fate under thermal conditions, sometimes with ring opening competing and reversible ring expansion occurring.

Computational Details

Standard DFT calculations were performed with the Gaussian 98 suite of programs.²¹ Vibrational spectra were computed with the B3LYP/6-31G* method. A scaling factor of 0.9613 was used for frequencies.²²

Experimental Section

General. The starting tetrazoles **7** and **8** and the ¹⁵N-labeled **8** were prepared according to the literature.^{23–25} The apparatus for matrix isolation was as previously described.²⁶ A 1000-W high-pressure Xe/Hg lamp was used for photolysis.

Matrix Isolation and Photolyses: Tetrazolo[5,1-*a*]isoquinoline **7.** This compound was sublimed at 55–56 °C in a stream of Ar for 25 min onto a KBr window at 31 K. The matrix was cooled to 10 K and the infrared spectrum recorded: IR (Ar, 10 K) (cm⁻¹) 3541 w, 3449 w, 3136 w, 3100 w, 3086 w, 3070 w, 2150 w, 2141 w, 1971 w, 1942 w, 1915 w, 1859 w, 1832 w, 1726 w, 1719 w, 1647 m, 1600 w, 1566 w, 1562 w, 1532 w, 1522 s, 1517 m, 1488 w, 1485 w, 1456 s, 1430 m, 1407 w, 1400 w, 1393 m, 1383 w, 1332 w, 1315 w, 1301 w, 1292 w, 1263 w, 1256 w, 1251 w, 1240 w, 1236 w, 1220 w, 1218 w, 1209 w, 1203 w, 1168 w, 1163 w, 1162 w, 1142 w, 1140 w, 1124 w, 1122 w, 1114 w, 1112 w, 1109 w, 1107 m,

1090 m, 1038 w, 1034 w, 1033 w, 1025 w, 1018 w, 1015 w, 1009 w, 1003 w, 999 w, 993 w, 989 w, 988 m, 985 w, 958 w, 902 w, 899 w, 897 w, 876 w, 811 w, 809 w, 796 s, 795 s, 775 w, 752 w, 748 m, 712 m, 696 w, 633 w, 571 w, 569 w, 518 w, 517 w, 507 w, 417 m, 409 w.

Irradiation ($\lambda > 260$ nm, 2 h) gave rise to **13** and **22**: IR (Ar, 10 K) (cm⁻¹) 3579 w, 3575 w, 3568 w, 3309 w, 3308 w, 3305 w, 3301 w, 3295 w, 3088 w, 3072 w, 3068 w, 3045 w, 2238 w, 2161 w, 2158 w, 2153 w, 2150 w, 2140 w, 2128 w, 2123 w, 2071 w, 2059 w, 2053 w, 2049 w, 2041 m, 2028 m, 2025 m, 2020 s, 2008 w, 1992 w, 1983 w, 1978 w, 1959 w, 1955 w, 1949 w, 1929 w, 1919 w, 1676 w, 1605 w, 1594 w, 1573 w, 1561 w, 1555 w, 1502 w, 1493 w, 1486 w, 1473 w, 1465 w, 1464 w, 1460 w, 1458 w, 1453 w, 1448 w, 1442 w, 1437 w, 1418 w, 1412 w, 1386 w, 1357 w, 1331 w, 1314 w, 1308 w, 1304 w, 1296 w, 1293 w, 1289 w, 1286 w, 1285 w, 1270 w, 1268 w, 1266 w, 1262 w, 1257 w, 1251 w, 1240 w, 1225 w, 1222 w, 1219 w, 1213 w, 1211 w, 1208 w, 1198 w, 1194 w, 1178 w, 1173 w, 1169 w, 1166 w, 1141 w, 1129 w, 1121 w, 1114 w, 1102 w, 1097 w, 1092 w, 1089 w, 1085 w, 1043 w, 1025 w, 1021 w, 1017 w, 984 w, 983 w, 979 w, 976 w, 971 w, 964 w, 958 w, 948 m, 941 m, 938 m, 936 m, 932 m, 927 w, 920 w, 918 w, 885 w, 872 w, 869 w, 850 w, 843 w, 840 w, 837 w, 830 w, 826 w, 818 w, 815 w, 814 w, 810 w, 807 w, 773 w, 766 w, 763 m, 757 m, 749 w, 747 w, 744 w, 742 w, 740 w, 715 w, 708 w, 705 w, 657 w, 636 w, 635 w, 609 w, 605 w, 598 w, 559 w, 557 w, 554 w, 535 w, 467 w, 464 w, 458 w, 452 w, 428 w, 421 w, 417 w.

Tetrazolo[1,5-*a*]quinoline **8.** This compound was sublimed at 60–64 °C in a stream of Ar for 10 min onto a KBr window at 31 K. The matrix was cooled to 10 K and the infrared spectrum recorded: IR (Ar, 10 K) (cm⁻¹) 3475 w, 3081 w, 3066 w, 1963 w, 1929 w, 1897 w, 1849 w, 1816 w, 1627 m, 1620 s, 1612 w, 1579 w, 1566 m, 1543 m, 1533 w, 1468 w, 1464 w, 1459 w, 1455 m, 1452 w, 1419 m, 1412 w, 1370 w, 1367 w, 1335 w, 1326 w, 1292 w, 1282 w, 1261 w, 1235 w, 1231 w, 1223 w, 1222 w, 1164 w, 1162 w, 1144 w, 1133 w, 1129 w, 1095 w, 1081 w, 1067 w, 1039 w, 1020 w, 991 w, 970 w, 949 w, 869 w, 817 s, 815 s, 768 w, 755 s, 702 w, 698 w, 697 w, 630 w, 556 w, 515 w, 472 w, 440 w, 418 w.

Irradiation ($\lambda > 260$ nm, 1 h) gave rise to predominantly **13**: IR (Ar, 10 K) (cm⁻¹) 3492 w, 2240 w, 2158 w, 2128 w, 2123 w, 2060 w, 2047 w, 2041 w, 2020 s, 2008 w, 1992 w, 1965 w, 1918 w, 1603 w, 1599 w, 1473 w, 1448 w, 1386 w, 1358 w, 1314 w, 1305 w, 1296 w, 1291 w, 1289 w, 1285 w, 1257 w, 1251 w, 1245 w, 1222 w, 1207 w, 1196 w, 1193 w, 1178 w, 1141 w, 1129 w, 1124 w, 1089 w, 1085 w, 1039 w, 1018 w, 988 w, 958 w, 945 w, 923 w, 841 w, 815 w, 808 w, 767 w, 762 w, 757 m, 740 w, 738 w, 715 w, 705 w, 668 w, 662 w, 643 w, 598 w, 570 w, 566 w, 535 w, 485 w, 467 w, 420 w, 418 w.

Tetrazolo[5,1-*a*]isoquinoline-1(3)-¹⁵N (50 atom % ¹⁵N). To a mixture of 1-chloroisoquinoline (19.3 mg; 0.118 mmol) and terminally ¹⁵N-labeled sodium azide¹³ (8.2 mg; 0.126 mmol; 50 atom % ¹⁵N) was added 1 mL of 50% aqueous EtOH and two drops of 10% aqueous EtOH containing 78 mmol of HCl per 100 mL. The solution was stirred in a closed flask at 100 °C for 20 h. Colorless crystals separated on cooling to room temperature, yield 7.8 mg (39%), mp 142–145 °C (mp of the corresponding unlabeled material: 145–146 °C).

Acknowledgment. The support of this work by the Australian Research Council is gratefully acknowledged. We thank Hans-Wilhelm Winter for the experiments on the ¹⁵N-labeled tetrazoles.

Supporting Information Available: Tables of Cartesian coordinates, absolute energies, and IR spectra of all calculated compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(16) Freiermuth, B.; Wentrup, C. Unpublished results, The University of Queensland, 1989.

(17) Addicott, C.; Wong, M. W.; Wentrup, C. *J. Org. Chem.* **2002**, *67*, 8538.

(18) Vosswinkel, M. PhD Thesis, Universities of Queensland and Bochum, 2003, in preparation.

(19) Bednarek, P.; Mitschke, U.; Wentrup, C. Unpublished results, The University of Queensland, 2000–2002.

(20) Wentrup, C.; Crow, W. D. *Tetrahedron* **1970**, *26*, 4915. Wentrup, C.; Crow, W. D. *Tetrahedron* **1971**, *27*, 1566.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; J. A. Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(22) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391. Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(23) Reimlinger, H.; Lingier, W. R. F.; Vandewalle, J. T. M. *Chem. Ber.* **1975**, *108*, 3780. Reimlinger, H. *Chem. Ber.* **1970**, *103*, 1900.

(24) Reynolds, G. A.; Van Allan, J. A. *J. Org. Chem.* **1959**, *24*, 1478.

(25) Thétaz, C.; Wehrli, F. W.; Wentrup, C. *Helv. Chim. Acta* **1976**, *59*, 259.

(26) Kuhn, A.; Plüg, C.; Wentrup, C. *J. Am. Chem. Soc.* **2000**, *122*, 1945. Kappe, C. O.; Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1995**, *60*, 1686.