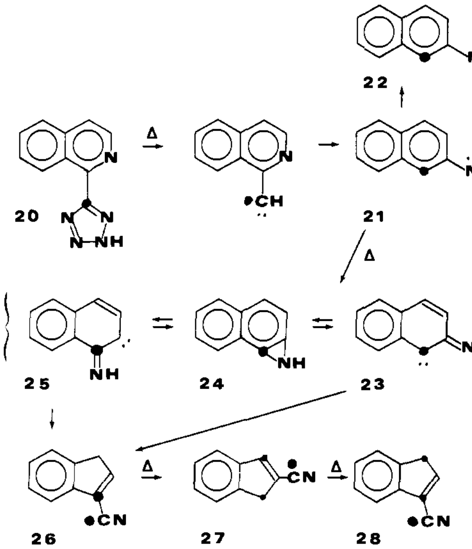
Scheme III



for insertion it is triangular.[19] The direct insertion of phenylnitrene to form 1*H*-benzazirine (**12** → **16**) thus seems most attractive.

The problem of the sigmatropic shifts of the cyano group, which randomizes all ring-carbon atoms, can be avoided by substitution. Thus, a CN-group migration in 3-cyanoindene gives 2-cyanoindene.[10] It is known that 2-naphthylnitrene contracts predominately to 3-cyanoindene under mild conditions.[20] Therefore, by using the same mechanism as developed above, the labeled nitrene **21** should give rise to the 3-cyanoindene **26** (Scheme III). This indeed was found to be the case. The nitrene **21** was generated in a carbene-nitrene rearrangement[14] by pyrolysis[9] of **20** at 400° (1 mm N_2) (Scheme III), and the products were separated by gas chromatography. 2-Aminonaphthalene (**22**) (7.5%)[21] was exclusively labeled in the 1-position. 1-Aminonaphthalene was not detectable. 3-Cyanoindene (**26**) (20.6%)[21] was labeled on CN and C-3, with a very small amount of label on C-1; the degree of labeling at C-1 increased with the temperature. 2-Cyanoindene (**27**) (3.4%)[21] was equally labeled on C-1 and C-3, and these two positions are interchanged by hydrogen shifts. A small amount of CN-migration, **27** → **28**, explains the temperature dependent development of label in the 1-position of 3-cyanoindene (**28**). The labeling ratio C-3/CN in **26** was ca. 2.3 at 400°, and decreased to ca. 1.7 at 800°, indicating that (i) the interconversion of the iminocarbenes **23** and **25** is incomplete, but increasing in importance with the temperature, or (ii) the interconversion of the iminocarbenes is complete, but some of the nitrenes (**21**) undergo direct contraction to 3-cyanoindene with consequent exclusive labeling in the 3-position. The latter possibility will apply if the nitrene reacts by the direct insertion pathway, **21** → **24** (vide supra).

In conclusion, the gas-phase Wolff rearrangement of iminocarbenes is preceded by 1*H*-benzazirine formation. It may be inferred that some Wolff-rearrangements of oxocarbenes, which do *not* cyclize to oxirenes in solution,[5,6] may well do so in the gas phase. We hope to report later on such a study.

The labeling pattern observed in the ring contraction of arylnitrenes is consistent with rate-determining isomerization of the nitrenes to 1*H*-benzazirines and iminocarbenes. Thus, there are just two intramolecular reactions of phenylnitrene: (i) addition to the π-system, which results in ring expansion[22] (**12** → **11**), and (ii) reaction with the ortho-CH bond, which results in ring contraction.[23]

References and Notes

(1) This work was supported by the Schweizerischer Nationalfonds, project No. 2.258.074.
(2) K.-P. Zeller, H. Meier, H. Kolshorn, and E. Müller, *Chem. Ber.*, **105**, 1875 (1972); J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Am. Chem. Soc.*, **95**, 124 (1973); S. A. Matlin and P. G. Sammes, *J. Chem. Soc., Perkin Trans 1*, 2623 (1972).
(3) A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, **96**, 6768 (1974); P. G. Mente and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 418 (1972); G. N. Schrauzer and H. Kisch, *J. Am. Chem. Soc.*, **95**, 2501 (1973).
(4) T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1 (1975); T. L. Gilchrist, C. W. Rees, and C. Thomas, *ibid.*, 8 (1975).
(5) Z. Majerski and C. S. Redvanly, *J. Chem. Soc., Chem. Commun.*, 694 (1972).
(6) K.-P. Zeller, *J. Chem. Soc., Chem. Commun.*, 317 (1975).
(7) C. Wentrup, *Helv. Chim. Acta*, **55**, 1613 (1972).
(8) Prepared from aniline-*1*-^{13}C (60% enriched) adapting the method of C. S. Marvel and G. S. Hiers, "Organic Syntheses", Coll. Vol. 1, Wiley, New York, N.Y., 1948, p 327.
(9) Pyrolyses were carried out using the apparatus described by R. Gleiter, W. Rettig, and C. Wentrup, *Helv. Chim. Acta*, **57**, 2111 (1974). Labeling results were assayed by Fourier-transform ^{13}C NMR spectroscopy using a Bruker HX-90 or WP-60 instrument.
(10) C. Wentrup and W. D. Crow, *Tetrahedron*, **26**, 3965 (1970); **27**, 880 (1971).
(11) The reason why the toluidines from the methylisatins showed only 10–12% intermediacy of benzazirines[7] may be that only the diradicals (**2**) undergo abstraction, and the iminocarbenes (**3** and **5**) do not, or only to a small extent, return to diradicals **2**. If the *singlet* iminocarbenes were to revert to singlet diradicals, they would have to do so by way of the doubly excited (σ,p) singlet states of the iminocarbenes.
(12) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 4379 (1967).
(13) W. D. Crow and M. N. Paddon-Row, *Tetrahedron Lett.*, 2231 (1972); W. D. Crow, A. N. Khan, M. N. Paddon-Row, and D. S. Sutherland, Abstracts, Fourth International Congress of Heterocyclic Chemistry, University of Utah, Salt Lake City, Utah, 1973, p 279.
(14) C. Wentrup, *Tetrahedron*, **30**, 1301 (1974).
(15) From 2-pyridyllithium and $^{13}CO_2$ (91% ^{13}C), followed by conversion of the picolinic acid to be nitrile, and addition of HN_3.
(16) For the ^{13}C NMR spectrum of azobenzene, see L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, N.Y., 1972.
(17) G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961); G. Smolinsky and B. I. Feuer, *ibid.*, **31**, 3882 (1966).
(18) J. H. Hall, J. W. Hill, and J. M. Fargher, *J. Am. Chem. Soc.*, **90**, 5313 (1968).
(19) C. D. Gutsche, G. L. Bachman, W. Odell, and S. Bauerlein, *J. Am. Chem. Soc.*, **93**, 5172 (1971); P. F. Alewood, P. M. Kazmaier, and A. Rauk, *ibid.*, **95**, 5466 (1973); H. F. Schaefer, III, *Chem. Brit.*, **11**, 227 (1975).
(20) C. Wentrup, *Top. Curr. Chem.*, in press.
(21) The yields were determined using unlabeled **20** (Nguyen Mong Lân, unpublished work).
(22) C. Wentrup, *Chem. Commun.*, 1386 (1969).
(23) Note Added in Proof: The mechanism presented in Scheme II has been corroborated by generation of 4-pyridylcarbene-^{13}C, which yielded aniline-4-^{13}C and cyanocyclopentadiene. The latter was equally labeled on all ring carbon atoms, *but carried no detectable label on the CN group.* Thus, phenylnitrene does definitely *not* undergo carbon scrambling.

Célestin Thêtaz, Curt Wentrup*
Institute of Organic Chemistry
University of Lausanne
CH-1005 Lausanne, Switzerland

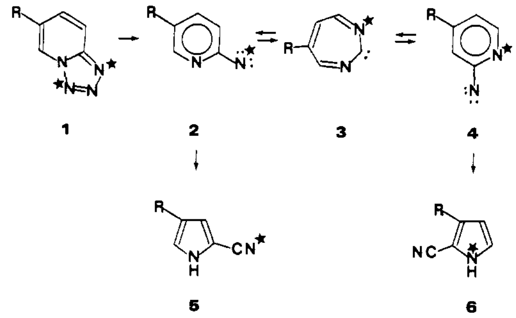
Received November 17, 1975

Pyridylnitrenes. Mechanism of Ring Contraction to Cyanopyrroles[1]

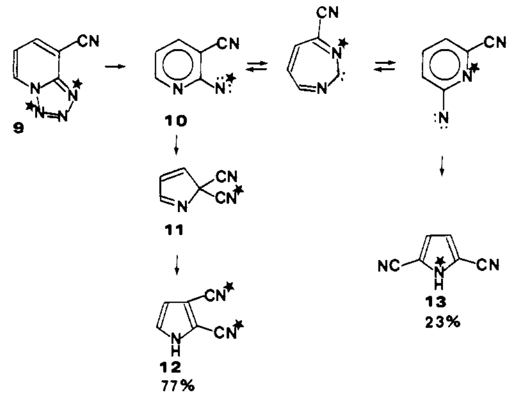
Sir:

The ring contraction of phenylnitrene to cyanocyclopentadiene[3] has been shown not to be a direct process of the nitrene, but to be preceded by an isomerization, most probably to iminocyclohexadienylidene and 1*H*-benzazirine.[4] Likewise, phenylcarbene appears to isomerize to methylenecyclohexadienylidene, which then contracts to fulvenallene.[5] We now report a series of 2-pyridylnitrenes which undergo ring expansions and ring contractions, the contraction products being formed, at least in one case, directly from the nitrenes.

Scheme I

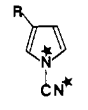


Scheme II

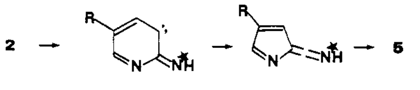


^{15}N-Labeled 6-methyltetrazolo[1,5-*a*]pyridine (**1**, R = CH_3) was obtained from 2-bromo-5-methylpyridine and potassium azide-*1*(*3*)-^{15}N using a known method.[6] Thermolysis of tetrazolopyridines results in tetrazole-azide tautomerism[7] and subsequent nitrene formation.[8] Gas-phase pyrolysis[9] of **1** at 365°, using 1 mm of N_2 as carrier gas, gave the ^{15}N-labeled nitrene **2**, which is in equilibrium with the isomeric nitrene **4** by means of the intermediate **3**.[8] The mixture of cyanopyrroles formed was analyzed and separated by gas chromatography (20% Carbowax 20M on Chromosorb W) and identified as **5** and **6** (R = CH_3) by comparison with known (unlabeled) samples.[10] The ratio **5**:**6** was 62:38. **5** was exclusively labeled on the cyano group, as shown by hydrolysis to 4-methylpyrrole-2-carboxylic acid which had lost all the label. Similarly, it was shown that **6** was labeled exclusively on the pyrrole nitrogen (Scheme I).[11]

The above results prove that the individual nitrenes **2** and **4** (R = CH_3) contract without any scrambling process intervening in the contraction step. The products are *not* formed via initial contraction to 1-cyanopyrroles (**7**), which would have resulted in identical labeling patterns in **5** and **6**. The absence of **7** contrasts the behavior of pyrazinylnitrenes and 2-pyrimidylnitrenes, which contract to 1-cyanoimidazoles and -pyrazoles, respectively.[2,12,13] The results do not exclude ring contraction via iminocarbenes[4] (eq 1), but such a mechanism can be excluded in the pyrolysis of the labeled tetrazole **9** (Scheme II).



7



(1)

9 at 365° (1 mmN_2) gave two dinitriles, **12** and **13**, which were separated by thick layer chromatography (SiO_2-$CHCl_3$), and the position of label was determined by Raman spectroscopy. **13** showed no displacement of the CN absorption, while the mass spectrum indicated that **13** carried a full label. The label must therefore be on the pyrrole-nitrogen. However, **12** showed a displacement of the two CN-absorptions by ca. 25 cm^{-1}, in agreement with ^{15}N-labeling. Since there is no way in which the initial nitrene **10** can undergo a hydrogen shift of the type depicted in eq 1, yielding the observed product, **12**, the latter must be formed by direct ring contraction to **11** (Scheme II).

There are thus at least two mechanisms of ring contraction in arylnitrenes: direct and indirect. The *direct* contraction can give either C-nitriles, as observed in **10**, or N-nitriles, as observed in pyrazinylnitrenes and 2-pyrimidylnitrenes.[2,12,13] The *indirect* contraction takes place via iminocarbenes, as observed in phenylnitrene and 2-naphthylnitrene.[4] The *rates* of the ring contractions follow the order: phenylnitrene < 2-pyridylnitrene < pyrazinylnitrene.[14] The rate increase can be ascribed to the increased electrophilicities of the hetarylnitrenes. This lowers the activation energies for ring contraction so much that the isomerization to iminocarbenes[4] cannot compete. The naphthylnitrenes contract in good yields at 480°, i.e., not quite as easily as the pyridylnitrenes, and it is possible that they constitute a borderline case, reacting by both the direct and the indirect contraction mechanism.[4]

References and Notes

(1) Part VI of the series "Hetarylnitrenes". Part V: see ref. 2. This work was supported by the Schweizerischer Nationalfonds, project No. 2.258.074. We thank S. Ruzicka for help with the Raman spectra.
(2) C. Wentrup, *Helv. Chim. Acta*, **55**, 565 (1972).
(3) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 4379 (1967).
(4) C. Thétaz and C. Wentrup, *J. Am. Chem. Soc.*, preceding paper in this issue.
(5) C. Wentrup, *Tetrahedron*, **30**, 1301 (1974).
(6) J. H. Boyer and R. F. Reinisch, *J. Am. Chem. Soc.*, **82**, 2218 (1960).
(7) C. Wentrup, *Tetrahedron*, **26**, 4969 (1970); R. Huisgen, K. v. Fraunberg, and H. J. Sturm, *Tetrahedron Lett.*, 2589 (1969).
(8) W. D. Crow and C. Wentrup, *Chem. Commun.*, 1387 (1969).
(9) The pyrolysis apparatus is described by R. Gleiter, W. Rettig, and C. Wentrup, *Helv. Chim. Acta*, **57**, 2111 (1974).
(10) We thank Dr. R. A. Jones, University of East Anglia, Norwich, for providing NMR spectra of methylcyanopyrroles.
(11) An analogous study of 6-cyanotetrazolo[1,5-*a*]pyridine-*1*(*3*)-^{15}N (**1**, R = CN) yielded a mixture of dinitriles **5** and **6** (R = CN) in which only 8% of the label was on the pyrrole nitrogen. The ratio **5**:**6** determined by NMR spectroscopy was 92:8, indicating that only **6** (R = CN) was ring labeled, whereas **5** (R = CN) was labeled on the CN group (A. Chollet, Diploma Thesis, University of Lausanne, 1974).
(12) C. Wentrup, C. Thétaz, and R. Gleiter, *Helv. Chim. Acta*, **55**, 2633 (1972).
(13) C. Wentrup, *Top. Curr. Chem.*, in press.
(14) The evidence is that phenylnitrene requires an almost explosive reaction,[3,5] the pyridylnitrenes contract already at 365° in the gas phase, and pyrazinylnitrenes contract even in solution.[2,12,13]

Raymond Harder, Curt Wentrup*
Institute of Organic Chemistry
University of Lausanne
CH-1005 Lausanne, Switzerland

Received November 17, 1975

Experimental Evidence for Geometrical Variations in the Transition State of the SN2 Reaction

Sir:

The success of the transition state theory of reaction rates has led to several attempts to predict the structure of the transition state. In particular, the changes in bond lengths and bond orders of the transition state accompanying minor structural changes in the reactants have been the subject of theoretical interest. Among these predictions the Hammond postulate,[1] the Thornton rules,[2] and the rules of Harris and Kurz[3] are perhaps the best known.

Rather few unambiguous experimental measures of tran-