

Communications to the Editor

1*H*-Benzazirines. Intermediates in the Ring Contraction of Iminocyclohexadienylienes and Arylnitrenes¹

Sir:

Recent work on oxocarbenes,² thioxocarbenes,³ and iminocarbenes⁴ has demonstrated that the Wolff rearrangements in these species are often preceded by isomerization to oxirenes, thiirenes, and 1*H*-azirines, respectively. However, such isomerizations were absent in some cyclic oxocarbenes where the annelated oxirenes would have been highly strained, e.g., in homoadamantane⁵ and naphthalene⁶ derivatives.

It is now reported that iminocyclohexadienylienes (e.g., **3**) interconvert quantitatively with 1*H*-benzazirine (**4**) prior to ring contraction to cyanocyclopentadiene (**8**).

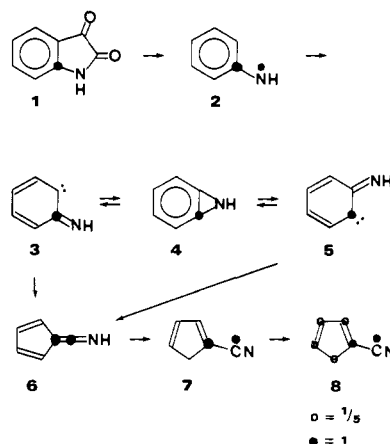
The gas-phase pyrolysis of isatin yields aniline and 1-cyanocyclopentadiene.⁷ Experiments with methylisatins gave mixtures of toluidines compatible only with a 10–12% interconversion of diradicals (CH₃-**2**) via methyl-1*H*-benzazirines (CH₃-**4**).⁷ This study allowed no conclusion as to the involvement of **4** in the formation of the main pyrolysis product of isatin, 1-cyanocyclopentadiene. The ¹³C-labeled isatin⁸ **1** has now been pyrolyzed at 715° (0.15 mm), and found to yield 1-cyanocyclopentadiene (**8**) in which all ring carbon atoms are equally labeled, but with the labeling ratio CN/C_{ring} = 5.⁹

The complete interconversion **3** ⇌ **4** ⇌ **5** (Scheme I) would lead to the initial Wolff-rearrangement products **6** and **7** in which the labeling ratio CN/C-1 = 1. Since it is well documented that the cyano group in **7** undergoes facile sigmatropic migrations around the ring under the reaction conditions,¹⁰ the label at C-1 will become distributed over the five ring-carbons. Accordingly, the CN group will be five times as much labeled as each of the ring carbons, as observed.¹¹

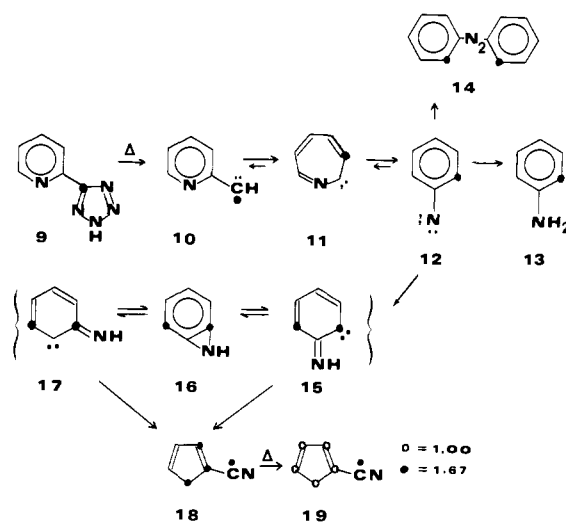
Let us now consider the ring contraction in phenylnitrene, which also yields cyanocyclopentadiene,¹² and in which some degree of carbon scrambling occurs.¹³ We have postulated¹⁴ that this reaction takes place via iminocyclohexadienyliene (e.g., **12** → **15**). If this is correct, a labeling study should conform to the mechanism given in Scheme I. We therefore prepared the ¹³C-labeled 2-pyridylcarbene precursor **9**¹⁵ which, on gas-phase pyrolysis at 400° in the presence of 1 mm of N₂ as carrier gas, gives the phenylnitrene **12**.¹⁴ Under these conditions, the nitrene dimerizes to azobenzene (**14**) which was found to be exclusively labeled in the ortho positions.¹⁶ The nitrene **12** was, therefore, also labeled in the ortho position only. The conversion of **9** to **12** as formulated in Scheme II is in accord with previous studies of the carbene–nitrene rearrangement.¹⁴

The pyrolysis of **9** at higher temperatures results in the formation of cyanocyclopentadiene, but by using N₂ carrier gas it is possible to deactivate some of the nitrenes, which then give aniline and azobenzene.¹⁴ Repetition of the pyrolysis of **9** at 610° (1 mm N₂) gave **13** and **14** which, again, were exclusively labeled in the ortho positions, but the cyanocyclopentadiene (**19**) was labeled on all carbon atoms (vide infra). Since **13** and **14** were specifically labeled, the scrambling cannot occur in phenylnitrene itself, or any intermediate which can revert to phenylnitrene. Otherwise, at least partially scrambled aniline and azobenzene should re-

Scheme I



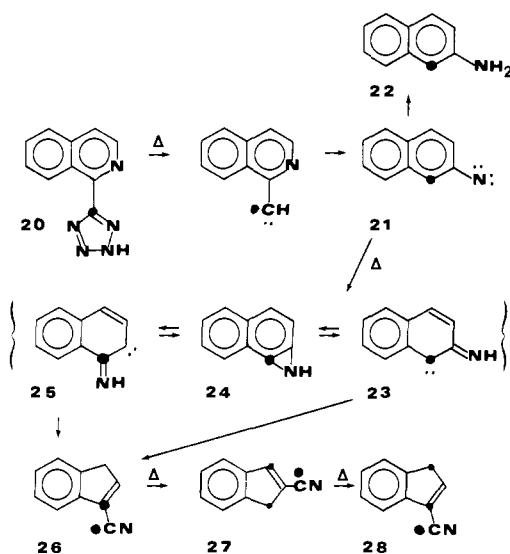
Scheme II



sult. The degree of ¹³C-labeling in **9** was 90.8%, and we can therefore ascertain that no more than natural abundance ¹³C was present in the meta and para positions in azobenzene (**14**).

An irreversible isomerization of **12** to **15** and/or **16**, interconversion of **15** and **17**, and a Wolff-type ring contraction in **15** and **17** would furnish the cyanocyclopentadiene **18** with the indicated atoms equally labeled (Scheme II). Subsequent CN migrations¹⁰ will give the final product, **19**, in which the labeling ratio CN/C_{ring} = 1:3/5 = 1.67. The ratio found experimentally (pyrolysis of **9** at 670° (10⁻³ mm)) was 1.7. The results thus strongly support the postulate that ring contraction in phenylnitrene is not a direct process, but takes place after isomerization to iminocyclohexadienyliene. This isomerization may be looked upon as an internal hydrogen abstraction by the nitrene (**12** → **15**), or an insertion into the ortho-CH bond (**12** → **16**). There is precedence for intramolecular C–H insertion of singlet aryl nitrenes in the gas phase.¹⁷ Intermolecular hydrogen abstraction has been reported for triplet phenylnitrenes in solution.^{17,18} Both theoretical and experimental evidence indicate that the transition state for abstraction is linear, while

Scheme III



for insertion it is triangular.¹⁹ The direct insertion of phenyl nitrene to form 1*H*-benzazirine (12 \rightarrow 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-naphthyl nitrene 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 rearrangement¹⁴ by pyrolysis⁹ of **20** at 400° (1 mm N₂) (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** \rightarrow **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** \rightarrow **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 aryl nitrenes is consistent with rate-determining isomerization of the nitrenes to 1*H*-benzazirines and iminocarbenes. Thus, there are just two intramolecular reactions of phenyl nitrene: (i) addition to the π -system, which results in ring expansion²² (12 \rightarrow 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).
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- (6) K.-P. Zeller, *J. Chem. Soc., Chem. Commun.*, 317 (1975).
- (7) C. Wentrup, *Helv. Chim. Acta*, **55**, 1613 (1972).
- (8) Prepared from aniline-1-¹³C (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 ¹³C 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 methylsatisins showed only 10–12% intermediacy of benzazirines⁷ 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.
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- (14) C. Wentrup, *Tetrahedron*, **30**, 1301 (1974).
- (15) From 2-pyridyllithium and ¹³CO₂ (91% ¹³C), followed by conversion of the picolinic acid to be nitrile, and addition of HN₃.
- (16) For the ¹³C NMR spectrum of azobenzene, see L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, N.Y., 1972.
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- (21) The yields were determined using unlabeled **20** (Nguyen Mong Lan, 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-¹³C, which yielded aniline-4-¹³C and cyanocyclopentadiene. The latter was equally labeled on all ring carbon atoms, but carried no detectable label on the CN group. Thus, phenyl nitrene does definitely not undergo carbon scrambling.

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Pyridyl nitrenes. Mechanism of Ring Contraction to Cyanopyrroles¹

Sir:

The ring contraction of phenyl nitrene to cyanocyclopentadiene³ has been shown not to be a direct process of the nitrene, but to be preceded by an isomerization, most probably to iminocyclohexadienyliene and 1*H*-benzazirine.⁴ Likewise, phenyl carbene appears to isomerize to methylenecyclohexadienyliene, which then contracts to fulvenallene.⁵ We now report a series of 2-pyridyl nitrenes which undergo ring expansions and ring contractions, the contraction products being formed, at least in one case, directly from the nitrenes.