265. The Ring Expansion - Ring Contraction Dichotomy in Aromatic Nitrene and Carbene Reactions II. Hetarylnitrenes

Preliminary communication[1])

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(6. IX. 72)

Summary. ^{15}N-labelling experiments and energy calculations on nitreno-azines and -diazines are in agreement and lead to the theory that both ring contraction and ring expansion in hetaryl-nitrenes *can* be one-step processes which are governed mainly by the energy differences between the reacting species and the products.

In the preceding paper [1] we showed that ring expansions in aromatic carbenes are largely determined by the energy difference between the first reacting species and the product. We report here similar observations on ring contractions and ring expansions in heteroaromatic nitrenes.

Calculations of total and binding energies for several nitrenes and isomeric carbenes by the CNDO/2 [2] and extended Hückel method [3] are presented in the Table. As it is known that 2-pyridylnitrene (**1**) and 2,7-diazatropylidene (**2**) interconvert completely in the gas-phase [4], a *calculated* energy difference of ca. 3.5 eV can be taken as a lower limit for the excess energy of the reacting nitrene. The calculated energies for 4-pyrimidylnitrene (**5a**), 2,4,7-triazatropylidene (**4**), and pyrazinylnitrene (**3**) now indicate an energy barrier of ca. 7 eV between **4** and **3**, and 2–4 eV between **5** and **4**. These calculated energy differences are borne out by experiment, for we find that pyrazinylnitrene is indeed the most stable of the three isomers, and that **5** converts to **3** *via* **4**.

Total and binding energies of hetarylnitrenes and isomeric species[a])

| Compound	$-E_{tot}$ (CNDO/2)	$-E_{tot}$ (EH)	$-E_{binding}$ (CNDO/2)
2-pyridylnitrene (**1**)	1674.036	615.877	162.965
2,7-diazatropylidene (**2**)	1670.660	613.355	159.590
pyrazinylnitrene (**3**)	–	628.843	–
4-pyrimidylnitrene (**5a**)	1776.318	623.580	148.975
2,4,7-triazatropylidene (**4a**)	1772.331	621.495	144.998

[a]) In eV. All calculations are for singlet molecules; all C–C = C–N = 1.40 Å; C–H = 1.1 Å. Geometries are not minimized.

Figures given are qualitative; only energy *differences* are important.

Tetrazolo[1,5-*a*]pyrazine (**6**)[5] and 5,7-dimethyltetrazolo[1,5-*c*]pyrimidine (**7b**) [5] labelled with ^{15}N on N(1) and N(3) were prepared from the corresponding chloro-

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1) The full paper will be submitted to Helv.

diazines and potassium azide-1,3-^{15}N in dimethylformamide. Gas-phase thermolysis at 375°/10⁻³ Torr gives the ring-contraction products, 1-cyanoimidazoles (8) in almost quantitative yield [6] (see Scheme 1). The position of the label in 8 was determined by hydrolysis to the corresponding imidazoles (9). It was found [2]) that pyrazinylnitrene (3) completely lost its label (formation of unlabelled 9a), whereas the pyrimidyl-nitrene 5b retained its label ($\geqslant 98\%$) in the formation of 9b. This means that the

Scheme 1
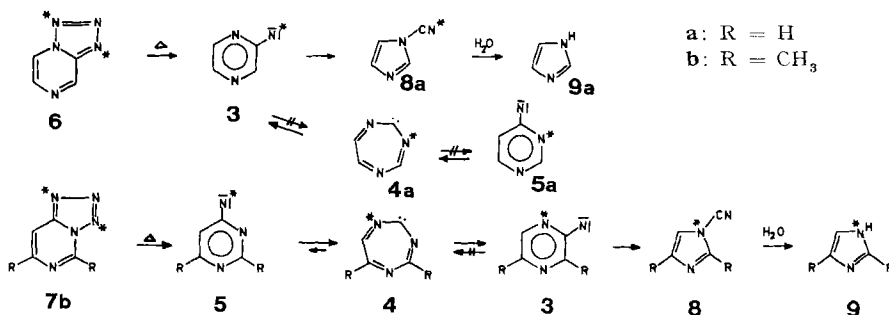
hypothetical equilibrium 3 ⇄ 4 ⇄ 5 is completely to the side of 3, so that 4-pyrimidyl-nitrene (5) contracts only after expansion *via* 4, but pyrazinylnitrene (3) contracts directly. This makes it understandable that 3 contracts already in solution [7] (with no intermediate) while 5 does not[3]).

A lowering of the activation energy for formation and/or contraction of a 4-pyri-midylnitrene[3]) is found in 5-phenyl-tetrazolo[1,5-*c*]quinazoline (10), which yields the nitrene 11 and the consequent ring-contraction product 12 already in solution (ben-zene, 70 h, 180°, 50%; cf. [7]); in this case we found no chemical evidence for inter-conversion with the corresponding quinoxalylnitrene 13, generated from 4-phenyl-tetrazolo[1,5-*a*]quinoxaline (14) (Scheme 2). Solution thermolysis of 14 (benzene, 87 h, 180°) gave 12 in 88% yield[4]); gas-phase thermolysis at 380°/10⁻³ Torr gave 12 (92%), and indolo[2,3-*b*]quinoxaline (16) (8%) [10]. Under the same gas-phase conditions 10 gave 12 in 99% yield[5]), and thin-layer chromatography and spectroscopy of the product did not reveal the presence of 16, thereby excluding any *significant* conversion of 11 to 13 *via* ring expansion (Scheme 2).

Photolysis of 14 in trifluoroacetic acid (which facilitates azide-tautomerization [5] [11]) (75 W *Hanovia* lamp, Pyrex, 85 h) produced also ring contraction, in the form

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[2])   Isotopic abundances were determined on a *CEC* 21-490 mass spectrometer. All measurements were corrected for naturally occurring isotopes.

[3])   The tetrazole/azide tautomerization is easier in 6 than in 7b [5]; hence more energy is re-quired for the formation of 5a than for 3. If this energy, and the energy of activation for ring concentration is lowered, as in 6-methyl-2-methylthio-4-pyrimidylnitrene [7], then it may be expected that ring contraction can take place directly in a 4-pyrimidylnitrene. We will report on this in the full paper.

[4])   All new products were identified by microanalysis, spectroscopic data, and in the case of 12 hydrolysis to known [8] 2-phenylbenzimidazole.

[5])   Above 700° a new kind of nitrene degeneracy appeared: ring opening [9] of 11 followed by disengagement of benzonitrile to yield the products of 2-cyanophenylnitrene. The isomeric 4-phenylquinazolyl-2-nitrene gave 1-cyano-3-phenylindazole (62.5%) at 380°.

Scheme 2

10   11   17   13   14

15   12   16
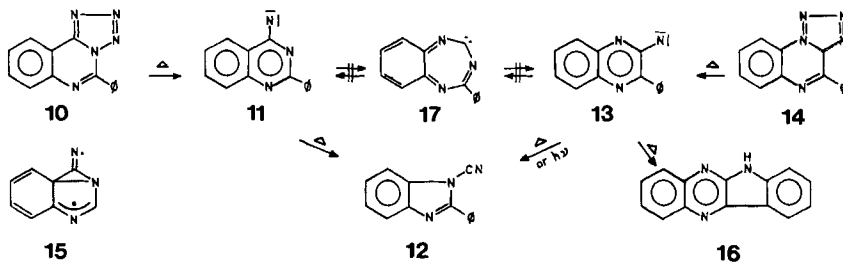
of 2-phenylbenzimidazole, which can be formed by reaction of **12** with the acid [7]. Little if any indoloquinoxaline **16** was formed. This is in marked contrast to the reported photocyclization of 5-phenyl-4-pyrimidylnitrene [11] and supports the conclusion that ring contraction is much faster (transition state lower) in pyrazinylnitrene than in 4-pyrimidylnitrene; in **13** ring contraction is faster than the intramolecular (triplet state) cyclization, which for 2-biphenylylnitrene has $t_{1/2} = 8 \cdot 10^{-4}$ s [12].

It might be thought that the reason for the non-occurrence of ring expansion in **11** was due to a difficulty in migrating the 1,8a-bond and/or an instability of the ring-expanded product, **17** (*cf.* [1]), but this is hardly the case since 2-quinolylcarbene [1], 2-quinolylnitrene and 9-phenanthridylnitrene do expand prior to contraction (*vide infra*). It is rather the aromatic stabilization of the 1-cyanoimidazoles which lowers the transition state for ring contraction (*cf.* [13]); such a stabilization is not obtained in the primary ring-contraction products of phenylnitrene, phenylcarbene, and the pyridylnitrenes, which is an additional reason why expansion occurs prior to contraction ([1] [4] [14]) in these systems[6]). If ring contraction is governed by the stability of the product, then there is no *intermediate* in the reaction. The traditional intermediate [1] in the ring-contraction reactions is of the type **15** which fails to explain why **11** contracts so easily.

We have verified the specific rearrangement of 2-quinolylnitrene to 1-isoquinolylnitrene [9] [16] by thermolysis of 9-phenyltetrazolo[1,5-*a*]quinoline (**18**), which gave a single compound, $C_{15}H_{10}N_2$ (73% at 510°/10^{-3} Torr); IR. (KBr, cm^{-1}): no $\nu_{C \equiv N}$, ν_{NH} 3240, ν_{max} 1640–1660; NMR. (DMSO-d$_6$): δ 10.9 (NH), 8.45–6.8 (10 H, aromatic), to which is ascribed the formula **19** (Scheme 3). Reasons for this specific rearrangement are found in the higher delocalization of 1-isoquinolylnitrene [17], the instability of the hypothetical 1-cyanoindole[6]), and the stability of the products of 1-isoquinolylnitrene [9].

Furthermore, ^{15}N-labelling of 9-phenanthridylnitrene (**20**) (by thermolysis of tetrazolo[1,5-*d*]phenanthridine-1,3-^{15}N at 800°/10^{-3} Torr) resulted in scrambling ($> 70\%$) of the label between the two nitrogens in the products [9] **21** and **22** (Scheme 3), as shown by hydrolysis[2]). Thus, like 2-pyridylnitrene itself [4], **20** expands prior to

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[6])   1-Cyanopyrroles were previously unknown. Treatment of pyrrolylpotassium with BrCN at − 50° gives 1-cyano-2,3,4,5-tetrabromopyrrole, which is very unstable. However, the aromatic stabilization in 1-cyanopyrroles must be higher than in 2-cyano-2H-pyrroles, for which reason we prefer primary ring contraction to 1-cyanopyrroles in 2-pyridylnitrenes [15] [16].

Scheme 3

18   **19**

20   **23**

24

21   **22**
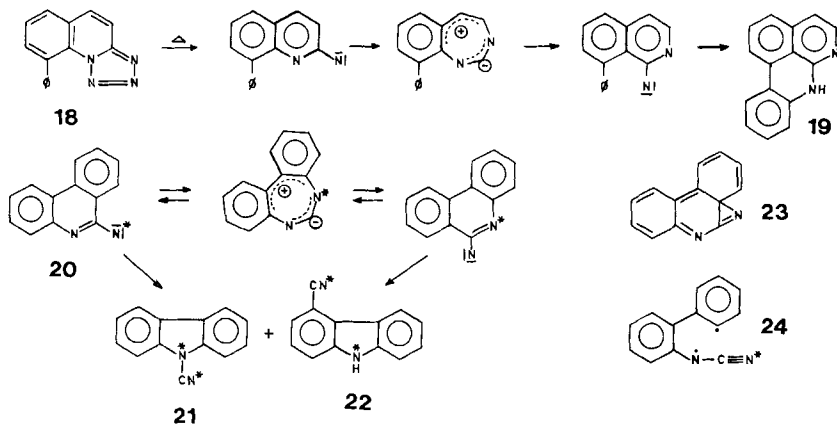
contraction. The traditional intermediate [1] in this reaction would be **23**, which must be discarded. Nor can ring expansion take place *via* ring-opening to a biradical **24**, for in this case the product **21** would be formed with an enrichment in the cyano-group. The corrollary is that ring expansion in aromatic nitrenes can be a one-step process of the *Wolff*-rearrangement type, and therefore, the order of the bond into which the nitrene 'inserts' need not be important (*cf.* [18])[7].

REFERENCES

[1] C. Wentrup, C. Mayor & R. Gleiter, Helv. 55, 2628 (1972).
[2] J. A. Pople & G. A. Segal, J. chem. Physics 44, 3289 (1966).
[3] R. Hoffmann, J. chem. Physics 39, 1397 (1963); 40, 2745 (1964).
[4] W. D. Crow & C. Wentrup, Chem. Commun. 1969, 1387.
[5] C. Wentrup, Tetrahedron 26, 4969 (1970).
[6] C. Wentrup & W. D. Crow, Tetrahedron 26, 4915 (1970).
[7] C. Wentrup, Helv. 55, 565 (1972).
[8] R. Walter & T. v. Pulawski, J. prakt. Chem. [2], 59, 251 (1899).
[9] C. Wentrup, Tetrahedron 27, 367 (1971).
[10] G. M. Badger & P. J. Nelson, J. chem. Soc. 1962, 3926.
[11] J. A. Hyatt & J. S. Swenton, J. Heterocycl. Chem. 9, 409 (1972).
[12] A. Reiser, F. W. Willets, G. C. Terry, V. Williams & R. Marley, Trans. Faraday Soc. 64, 3265 (1968).
[13] M. J. S. Dewar, Adv. chem. Physics III, 65 (R. Daudel, editor, Interscience, London 1964).
[14] W. D. Crow & M. N. Paddon-Row, Tetrahedron Letters 1972, 2231; J. Amer. chem. Soc. 94, 4746 (1972).
[15] W. D. Crow & C. Wentrup, Chem. Commun. 1968, 1082.
[16] R. F. C. Brown & R. J. Smith, Austral. J. Chem. 25, 607 (1972).
[17] Cf. G. Smolinsky, L. C. Snyder & E. Wasserman, Rev. Modern Physics 35, 576 (1963).
[18] T. Mitsuhashi & W. M. Jones, J. Amer. chem. Soc. 94, 677 (1972).
[19] C. Wentrup, to be published.

[7]   The degeneracy/specificity of hetarylnitrene rearrangements reported in the present paper is also reflected in the mass-spectrometric decompositions [19].