kristallisiert: 1 mg Tetraeder, die sich beim Erhitzen zunächst in Nadeln umwandelten und dann bei 280–288° schmolzen. Mischprobe von **3** aus **1** mit **3** aus Scillarenon: 265–282°. Die Lage der Banden beider Acetylverbindungen im IR. stimmte überein.

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264. The Ring Expansion – Ring Contraction Dichotomy in Aromatic Nitrene and Carbene Reactions I. Arylcarbenes

Preliminary communication[1])

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(6. IX. 72)

Summary. Rearrangement experiments and energy calculations by the CNDO/2 and extended *Hückel* methods indicate that ring expansion and ring contraction in aromatic carbenes and nitrenes *can* be one-step processes which are governed by the stabilities of the primary products and the energies of the reactants.

It has generally been assumed that ring expansion/ring interconversion in aromatic nitrenes and carbenes (**1** ⇄ **2** ⇄ **3**, or **1** ⇄ **3**) involved the bicyclic intermediates **4**

Scheme 1

a: x = N̈,   y = CH
b: x = CH, y = N
c: x = CH, y = CH
d: x = N̈,   y = N̈
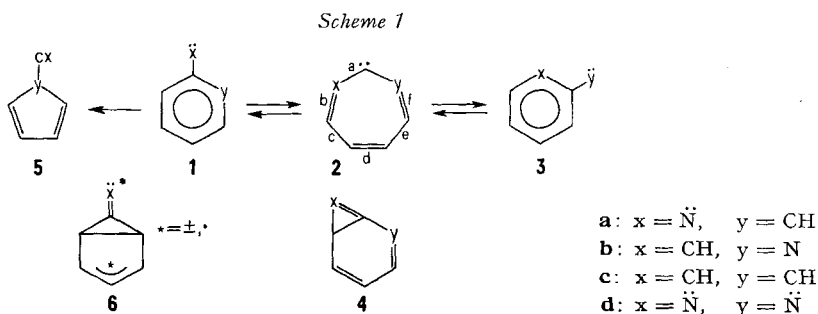
[1])   The full paper will be submitted to Helv.

[1]–[6], and similarly that ring contraction (1 → 5) involved the intermediates [7] or transition states [8] 6, and little has been known about the factors which influence expansion *versus* contraction [3] [5] [6].

Calculations of the total energies and binding energies of phenylnitrene (1a), 2-, 3- and 4-azatropylidene (2a, 7 and 8) and 2-, 3- and 4-pyridylcarbene (1b, 9 and 10) are presented in Table 1, and support the observation that of these isomers phenyl-nitrene is the most stable, to which all the others rearrange [2] [6]. These data also give an indication of the activation energy for ring contraction in phenylnitrene, since it is known that expansion occurs prior to contraction [5]. In order to provide this activation energy (> 3 eV) to phenylnitrene (from phenyl azide) or 2-pyridyl-carbene (from *vic*-triazolo[1,5-*a*]pyridine (7, Scheme 2)) it is necessary to perform an almost explosive shock-wave reaction [10] [11]. When, however, 2-pyridylcarbene is generated in a more energetic state, by elimination of two molecules of N_2 from 2-(5-tetrazolyl)-pyridine (8) [6] ring contraction becomes more facile. That it is indeed a low-energy pathway of phenylnitrene and 2-pyridylcarbene that leads to aniline and azobenzene [2] (contrast [6]) is indicated by our observation that 7 *gives* azo-benzene (16.6%), aniline (≤8%), and little 1-cyanocyclopentadiene (9) (≤3.4%) by gas-phase thermolysis under mild conditions [12] (400°, 10⁻³ Torr). Furthermore, this thermolysis gave an isolated 15.0% of *vic*-triazolo[1,5-*a*]pyridine (7), indicating step-wise loss of N_2 in 8 (Scheme 2). At high temperatures the intermediate diazo-com-pound 10 will possess enough vibrational energy to dissociate a further molecule of N_2 and get over the energy barrier to 9, which then becomes the major product.[2])

Scheme 2
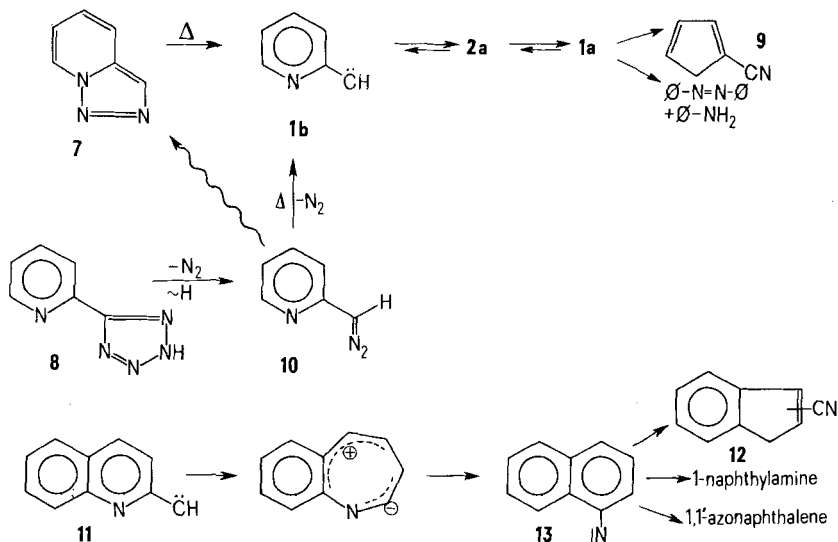
[2])   A direct comparison of 2-, 3-, and 4-pyridylcarbene is difficult when the precursors are different [6], but when three carbenes are generated from 5-tetrazolylpyridines, they do give similar reactions, in accord with the small calculated energy differences. In the phenyl-carbene-tropylidene system (Table 1) also, the low energy difference is in agreement with the observed expansion prior to contraction [5].

2-Quinolylcarbene (**11**) (from *vic*-triazolo[1,5-*a*]quinoline at 450°, 10⁻³ Torr) underwent ring contraction to 2- and 3-cyanoindene (**12**) (1:0.8 (*cf.* [13]), 7.2%), besides formation of 1-naphthylamine (37.6%) and 1,1'-azonaphthalene (5.9%); under similar conditions 1-naphthylnitrene itself (from 1-naphthyl azide) gave no detectable 2-cyanoindene, ≤0.01% 3-cyanoindene (by GC.), 1-naphthylamine (24%), and 1,1'-azonaphthalene (48%). A simple resonance consideration indicates that **11** is less stabilized relative to **1b** than the nitrene **13** relative to **1a** (*cf.* [14]), and the observed facility of ring contraction is again explained in terms of a relatively energetic carbene **11**[3]).

Table 1. *Total and binding energies of nitrenes and carbenes*[a])

Compound	$-E_{tot}$(CNDO/2)	$-E_{tot}$(EH)	$-E_{binding}$ (CNDO/2)
Phenylnitrene (**1a**)	1571.946	607.890	177.148
2-azatropylidene (**2a**)	1568.093	605.138	173.295
3-azatropylidene (**7**)	1568.088	604.452	173.290
4-azatropylidene (**8**)	1567.563	604.881	172.766
2-pyridylcarbene (**1b**)	1568.703	606.187	173.905
3-pyridylcarbene (**9**)	1568.616	606.135	173.818
4-pyridylcarbene (**10**)	1568.432	605.809	173.634
Phenylcarbene (**1c**)	1466.472	598.209	187.946
tropylidene (**2c**)	1465.970	597.497	187.445
benzo[b]tropylidene	2282.264	–	297.982
benzo[c]tropylidene	2281.423	–	297.140
benzo[d]tropylidene	2281.771	–	297.489

[a]) In eV. For methods of CNDO/2 and extended *Hückel* calculations, see [9]. All molecules assumed to be singlets; all C–C = C–N = 1.40 Å; all C–H = 1.1 Å. Exocyclic <C–C–H = 120°. Geometries are not minimized. Figures given are qualitative; only energy *differences* are important.

Table 2. *Products of gas-phase thermolysis of aryl-pyridyl-carbenes* **14a–d** (yields %)[a])

Carbene	R	R'	**17**	**18**	**19**
14a	OCH₃	H	95	–	–[b])
14b	Cl	H	26	–	–[b])
14c	H	NO₂	67.5[c])	–	–[b])
14d	—C₄H₄—		30	16	48[d])

[a]) Thermolysis [12] at 380°/10⁻³ Torr; products separated by chromatography on Al₂O₃/CHCl₃.
[b]) **18** and **19** not detectable by NMR. in trifluoroacetic acid [16].
[c]) Ca. 1:3 mixture of 1- and 3-nitrocarbazole.
[d]) By NMR. in trifluoroacetic acid.

The carbenes shown in Scheme 3 were generated from the corresponding *vic*-triazolo[1,5-*a*]azines[4]) in order to examine the mechanism of ring expansion. Results are given in Table 2.

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[3]) Nitrenoid ring contraction in carbenes (*e.g.* **1b** → **5a** → **9**) does not *necessarily* involve discrete nitrene intermediates (**3b** ≡ **1a**) since in a *Wolff*-type reaction it is the same bond that migrates whether **1a** → **5** or **2a** → **5**.

[4]) Details of the preparation of triazoloazines will be given in the full paper.

The non-occurrence of expansion of the benzene ring in carbenes **14a–c** taken with the small energy difference between 2-pyridylcarbene and 2-azatropylidene on the one hand, and phenylcarbene and tropylidene on the other hand (Table 1) indicates that there is a special reason for expansion of the pyridine ring; *viz.* conjugation of the vacant singlet carbene *p*-orbital with the benzene ring [15], and the occupied carbene σ-orbital with the more electrophilic pyridine ring. The orthogonality of the carbene-orbitals then renders the vacant one available for a *Wolff*-type expansion of the pyridine ring [4]. The undesirable non-bonded interaction between the nitrogen lone pair and the carbene σ-orbital favours this geometry; furthermore, the lowest π^*-MO in pyridine is of a lower energy than in benzene, and therefore a $\sigma\text{-}\pi^*$ interaction with the pyridine ring is favoured.

Scheme 3
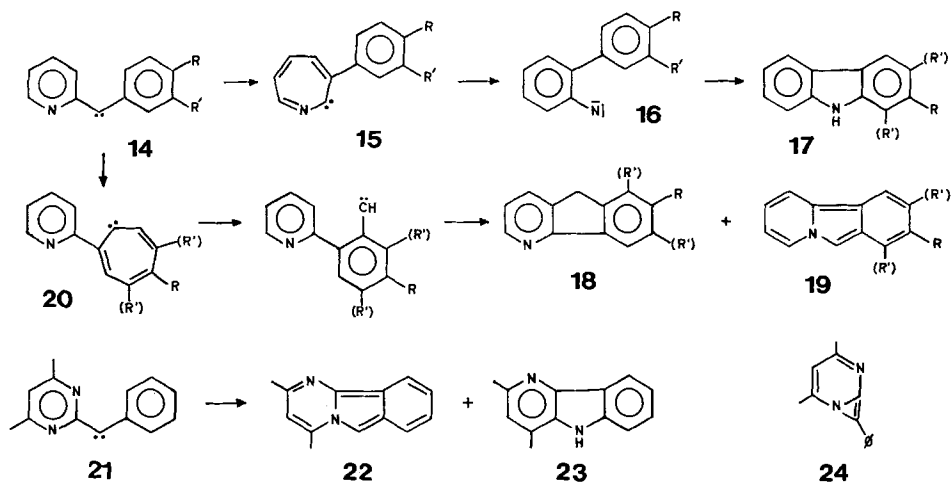
In the 2-naphthyl-2-pyridyl-carbene (**14d**), however, both the benzene ring and the pyridine ring expand, as evidenced by the formation of products **17d**, **18d** and **19d**[5]). Since the major product, **19d**, is thermodynamically very unstable, it is evidently not the stability of the final product that determines the reaction, but that of the primary product, the benzotropylidene **20d**, which has received additional stabilization by annelation (see Table 1), so that the reaction **14 → 15** becomes dis-favoured. Furthermore, the lowest π^*-MO in naphthalene is lower in energy than in benzene, and may be comparable with that in pyridine. In the analogous case of ring expansion in 1- and 2-naphthylcarbene [4], the selectivity was explained in terms of the order of the bond onto which the carbene adds in the formation of the *intermediate* **4c**. We feel that this is not the reason for the selectivity reported here, since on the bond-order principle the pyridine and the benzene rings in **14a–c** should be equally

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[5]   **17d**, **18d**, and **19d** were identified by high resolution mass measurement and spectroscopic data. Dark-red **19d** became colourless in acid solution (CH_2-signal in the NMR. spectrum at δ 5.56 in trifluoroacetic acid). The red **19d** precipitated again on basification, with con-comitant disappearance of the CH_2-signal (*cf.* [16]). **19d** could be chromatographed in the form of its trifluoroacetate.

attacked [17] [18]. Furthermore, the carbene **21** (Scheme 3) yielded the thermo-dynamically unstable product of benzene-ring expansion (**22**)[6] (72% by NMR.) and the stable product of pyrimidine-ring expansion (**23**)[7] (14.6%); the hypothetical intermediate of type **4** would be the anti-aromatic 1*H*-azirine (**24**) in the latter reaction. Rather than invoking this, we represent the ring-expansion reaction as a one-step process of the *Wolff*-rearrangement type [4] [20]. The rearrangements of 1- and 2-naphthylcarbenes [4] may equally well be explained in terms of the energy of the products (benzotropylidenes; Table 1) as of bond order[8]).

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[6]   Identified by high resolution mass measurement and spectroscopic data. NMR. ($CDCl_3$): δ 2.50 (*s*, 3H), 2.58 (*s*, 3H), 6.55 (*s*, H), 6.95–7.7 (*m*, 5H); in trifluoroacetic acid (*cf.* [3]): δ 2.95 (6H), 5.55 (*s*, 2H), 8.33–7.37 (5H).

[7]   Also prepared by photocyclization [19] [12] of 5-anilino-2,4-dimethylpyridine.

[8]   This point was discussed with Prof. *W. M. Jones* in Lausanne, October 1971.