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230. On the Ring-Expansion in Aromatic Nitrenes and Carbenes

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(3. VII. 74)

Summary. The ring expansion, phenylnitrene (**1**) → azepinylidene (**3**) has been investigated using the CNDO/2 and Extended *Hückel* method. Both methods predict that the nitrene-nitrogen of **1** is moving out of the molecular plane on the path of minimum energy. Whether an intermediate **2** is formed or not, the net charge during the reaction indicates that an interaction between the filled nitrene p-orbital and an empty MO of the ring is important in lowering the transition state. The results are compared with experimental results of arylnitrenes and arylcarbenes. The rearrangement of tolylcarbenes to benzocyclobutene and styrene has been reexamined experimentally and interpreted in terms of the dynamics of the out of plane movement of the carbene during ring expansion.

The ring expansion of aromatic nitrenes (**1** → **3**) may be a direct process, or it may involve the intermediate **2** (equation (1)) [1–6]. Regardless of this question, the detailed movement of the atoms during this rearrangement is of interest; *i.e.* does the nitrene-N stay in the plane of the ring during the rearrangement, or does it move

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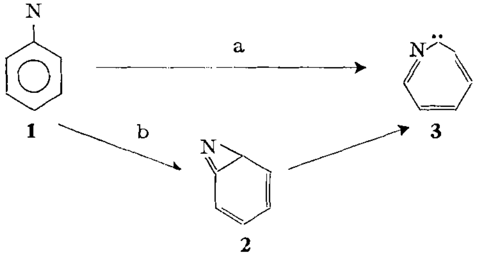
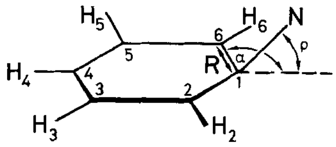
out of it? In the present paper we investigate this question using semiempirical methods of the Extended *Hückel* (EH) [7] and CNDO/2 [8] type. The conclusions derived from these calculations may also be applied, with due caution, to aromatic carbenes.



(1)

The whole potential surface of C_6H_5N spans 30 internal degrees of freedom. For a calculation chemically reasonable constraints must be applied to reduce this number to a magnitude which we can reasonably handle. We decided to leave the C–C and C–H bond lengths constant with the exception of the C(1)–C(6) distance. Furthermore we assumed always a singlet state for our species. For the calculation the following geometrical parameters were used: C–C = 1.38 Å, C–N = 1.42 Å, C–H = 1.05 Å, C–C–C angle = C–C–H angle = 120°.

To explore the reaction path for (1) the energy of the molecule was calculated as a function of the parameters R, α and ϱ. To vary R (C(1)–C(6) distance) the bond C(1)–C(6) was stretched and the angles C(1)–C(2)–C(3), C(2)–C(3)–C(4), C(3)–C(4)–C(5) and C(4)–C(5)–C(6) were equally widened to get the same angular tension at the carbon centers C(2) to C(5). The hydrogen centers H(2)–H(5) were placed on the bisection of the C–C–C angle of their respective carbon centers. H(6) was placed in the plane of the other H atoms on the bisection of the N–C(6)–C(5) angle, assuming N in the plane of the molecule ($\varrho = 0$). The values taken for R were 1.38, 1.8, 2.0, 2.2 and 2.56 Å.



Independently of the change in bond length the angles α and ϱ were varied in increments of 20°. From these variations it turned out with both methods used that for R = 1.38 Å it is more economical for the system to vary α and ϱ than R. This is indicated in the lower part of Fig. 1. For R ≥ 1.8 Å we found that the geometry of lowest energy is the one where the nitrogen atom is placed at equal distances between C(1) and C(6) (seven membered ring). Thus α becomes a function of R leaving R and ϱ as the only independent variables. These conditions are present in the upper part of Fig. 1. To derive the contours of the energy surface for the region in between the ones just described, we varied ϱ and α independently for a certain value of R. By this procedure we derived for each R an energy surface with the parameters ϱ and α. To get a good fit between the contours of the lower and upper part just described interpolation was used.

In Fig. 1 the potential energy surfaces obtained with the EH method (Fig. 1a) and the CNDO/2 method (Fig. 1b) are compared.

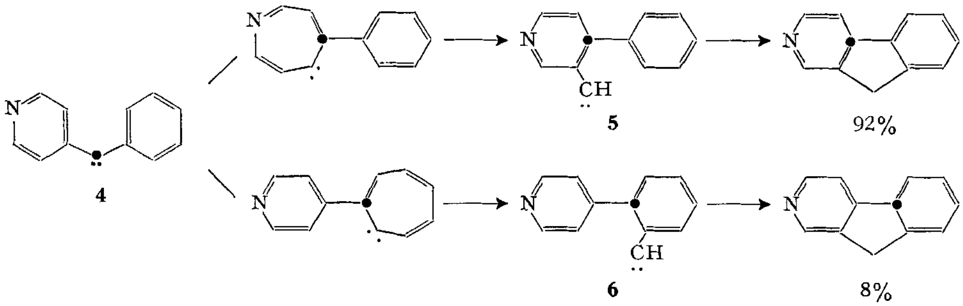
Both methods predict a minimum for **1** and **3**. A second common feature is the result that the in-plane path ($\varrho = 0$) from **1** to **3** is the one with the highest activation energy. The distinct difference between the methods used is that the CNDO/2 method predicts a minimum, **L**, at $R = 1.8$ Å, $\alpha = 51°$ and $\varrho = 70°$ whereas the EH method predicts a saddlepoint, **S**, in this region. The predicted minimum **L** corresponds approximately to a distorted non-planar azepinylidene. Since both methods show serious shortcomings in predicting strained species [9], the present study allows no conclusion as to the existence of the intermediate **2**. The thermochemistry indicates that the heat of formation of **2** cannot be much lower than that of **3** [6].

Even if the reaction (1) is concerted, it is possible that it could become stepwise if the intermediate **2** could be stabilized and/or the expanded carbene destabilized. This may be what happens in the benzoannelated cycloheptatrienylidenes studied by *Jones et al.* [10].

In Fig. 2 we have shown the net charges at the centers C(1), C(2), C(4) and at the nitrogen atom as a function of the reaction coordinate as obtained by both methods used. The net charges at the other centers were less pronounced and omitted for the sake of clarity. As can be seen from these drawings, both methods predict that the charges at C(2) and C(4) parallel each other, the net charge at C(1) is getting more negative and that at the N atom more positive. This result seems reasonable since the nitrene nitrogen is converted into an azepinylidene nitrogen while C(1) emerges as the carbene center of the seven membered ring and thus should be more negative [11]. Furthermore it is interesting to note that according to Fig. 2b for **L** ($R = 1.8$ Å, $\alpha = 51°$ and $\varrho = 70°$) we obtain a nearly equal charge distribution for the atoms in question.

The result that the nitrogen atom continues to lose electron density until the transition state has been reached, and **3** is almost formed, is in accord with experimental indications that the carbene-π ring-π^* interaction is an important stabilizing factor in the ring expansion of arylcarbenes; *i.e.* that the carbene shows partially nucleophilic properties [11] [12].

In line with this is the observation that arylnitrenes do not normally react with amines at nitrogen to give hydrazines [2], and also the reaction shown below. In



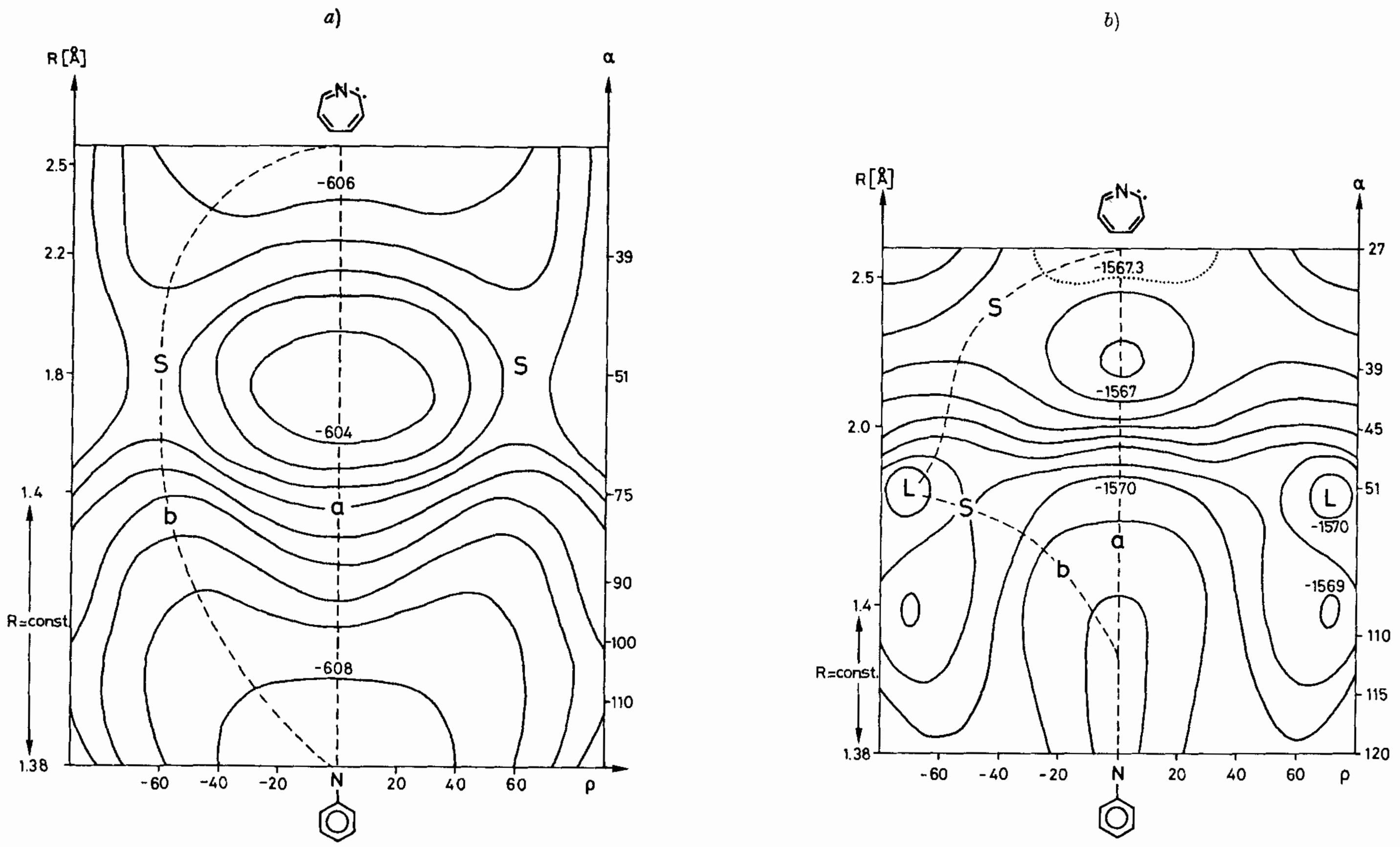


Fig. 1. *Potential energy surface obtained with the* EH *method a) and the* CNDO/2 *method b)*. The reaction path for $\varrho = 0$, **a**, and the path of minimum energy, **b**, are indicated. The contours are drawn every 0.5 eV

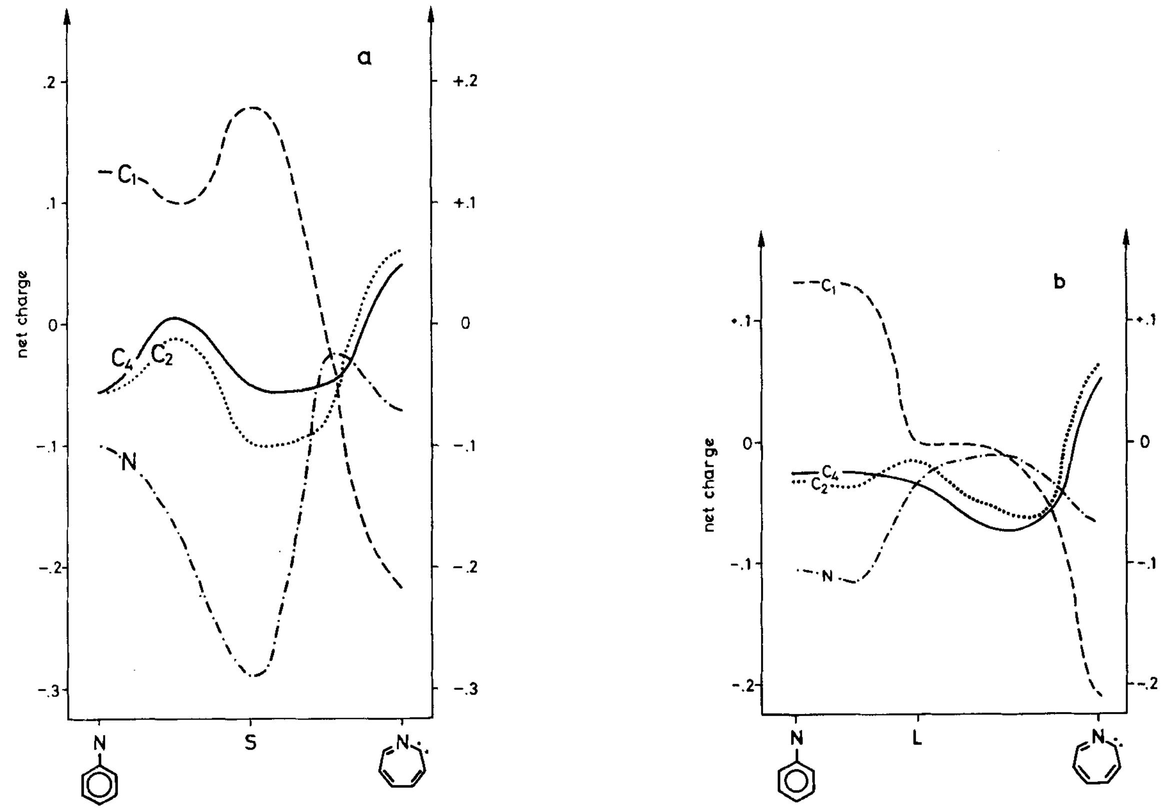
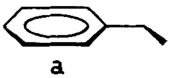


Fig. 2. *Net charges at C (1), C (2), C (4) and N for eq. (1) along the path of minimum energy.* The EH-result is shown in a), the CNDO/2 result in b). The points **S** and **L** refer to Fig. 1.

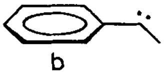
this latter example ^{14}C-labelling has revealed that phenyl-(4-pyridyl)-carbene (**4**) undergoes expansion of the pyridine ring *ca.* 11 times faster than of the benzene ring [13].

To extrapolate our results in part to phenylcarbene, we have compared the results of EH and CNDO/2 calculations on phenylnitrene and phenylcarbene[2]) in the singlet state.

According to the EH-calculations by *Hoffmann, Zeiss & Van Dine* [14] the phenylcarbene in conformation **a** is about 0.002 eV more stable than in conformation **b**. The CNDO/2 method on the other hand favours **b** by 0.45 eV over **a**.

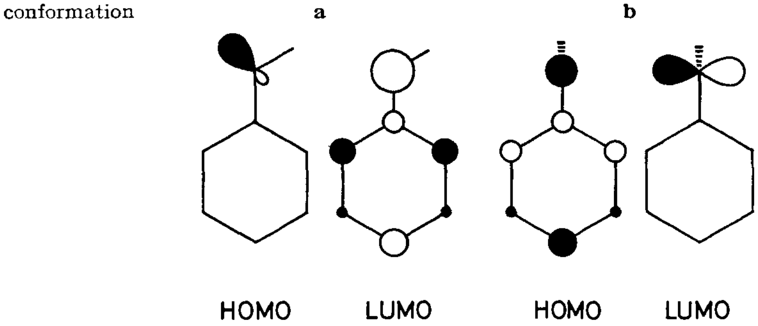


a

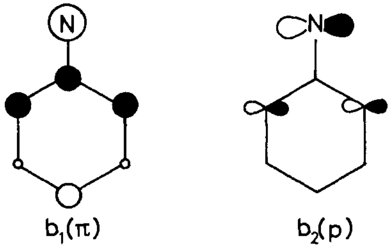


b

For both methods the predicted highest occupied molecular orbitals (HOMO's) and lowest unoccupied molecular orbitals (LUMO's) are shown below.



In the case of phenylnitrene EH-predicts $b_2(p)$ as HOMO and $b_1(\pi)$ as LUMO while CNDO/2 reverses this result. On bending the N-atom 10 degrees out of the molecular plane both methods predict the π-MO as HOMO and the 2p on N as LUMO.



$b_1(\pi)$ $b_2(p)$

The ordering of the MO's predicted by CNDO/2 for **1** (π as HOMO, 2p as LUMO) corroborates the observation that the nitrene-N can act as a nucleophile with respect to the ring by nitrene-π ring-π^* interaction. In Fig. 3 we have shown a plot [15] of the HOMO for **1** → **3** along the reaction coordinate according to the CNDO/2 results.

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[2]) For phenylcarbene we assumed the same bond length and angles as in ref. [14].

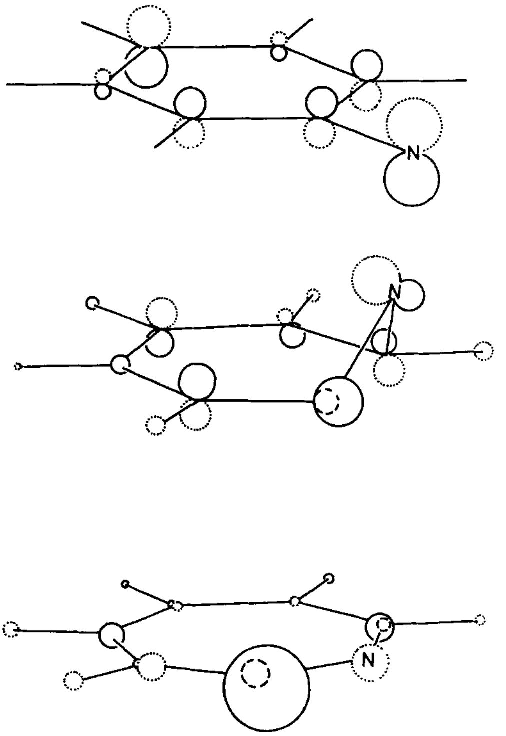


Fig. 3. *Plot of the* HOMO *for eq.* (*1*) *along the path of minimum energy based on* CNDO/2 *calculations*

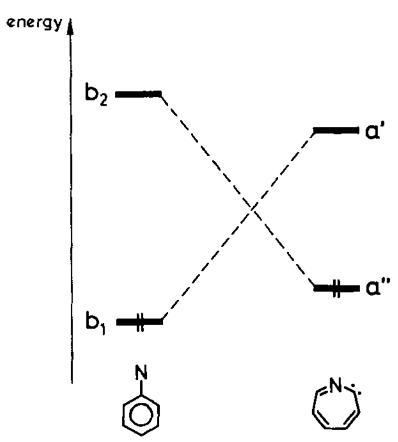
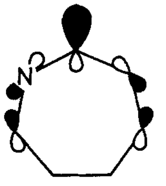


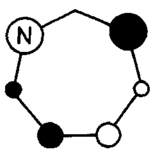
Fig. 4. *Level correlation diagram for eq.* (*1*)

Coming back to the questions put forward in the beginning we conclude that *both methods predict a path for the minimum energy in which the nitrogen atom moves out of the molecular plane.*

This result can be rationalized with the level correlation diagram for reaction (1) shown in Fig. 4. The relevant orbitals for **1** are the HOMO ($b_1(\pi)$) (Fig. 3 top), the LUMO ($b_2(p)$) and the σ-orbital corresponding to the C(1)–C(6) bond which is broken during reaction (1). The relevant levels for **3** are the HOMO (a″) (Fig. 3 bottom) the LUMO (a′(π)) and the σ-orbital corresponding to the C–N-bond which is formed during (1). The two σ-orbitals are omitted in Fig. 4. The HOMO (a″) and LUMO (a′) of **3** are shown below.



a″



a′

From Fig. 4 it is seen that the reaction (1) for $\varrho = 0$ is a symmetry forbidden process [16]. This is corroborated by Fig. 5 where we have plotted the total energy for (1) for $\varrho = 0$ and along the path of minimum energy.

With the conclusion that the nitrene-N must move out of the molecular plane during the reaction, a number of observations can be explained. While 2-pyridylnitrene and 4-pyrimidylnitrene expand very efficiently in the gas-phase [12] [18] 2-pyrimidylnitrenes (**7**) do not expand [5] and are less reactive than other hetarylnitrenes. In contrast to 4-pyrimidylnitrenes and pyrazinylnitrene, the yield of ring

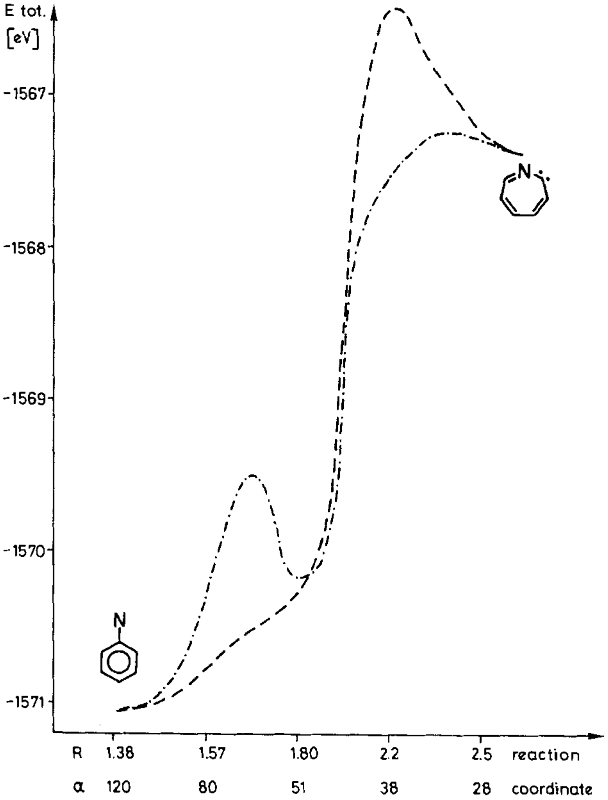
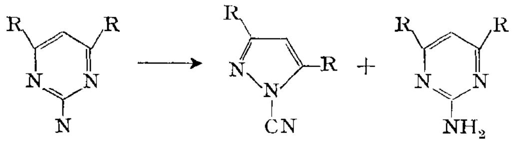
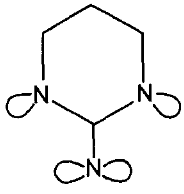


Fig. 5. *Total energy for eq. (1) along $\varrho = 0$ (– – –) and along the path of minimum energy (– · – · – ·) based on* CNDO/2 *calculations*



7 **8** **9**



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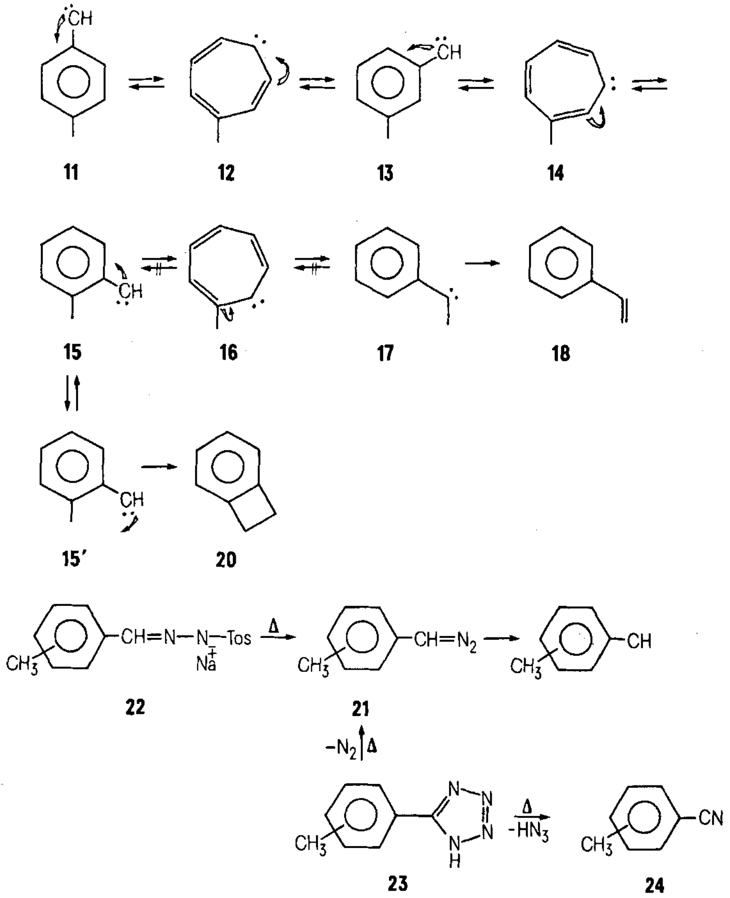
contraction product (**8**) is rather low and unusually high yields of amines (**9**) are formed instead [5] [19b].

This indicates that **7** has a prolonged lifetime which allows intersystem crossing to the triplet ground state with consequent hydrogen abstraction to yield amines **9** [19].

The singlet nitrene **7** may enjoy special stabilization by forming an electron rich three center bond [20] between the vacant p-orbital on the nitrene-N and the two lone pairs on the ring nitrogens as indicated in **10**. This additional interaction stabilizes the N-atom in the plane of the ring, preventing rearrangement. Reaction occurs mainly after intersystem crossing to the triplet. It should be noted that 2-pyrimidyl-carbenes do expand [6] [12a] [21]. Model calculations indicate that a replacement of the nitrene center by a carbene center makes the electron rich three center bond less favourable[3] [20] and furthermore, there is a thermodynamic driving force for the rearrangement [6]. It can further be predicted that 5-pyrimidyl-nitrene might show a through-bond stabilization of the in-plane vacant p-orbital in the singlet state.

Scheme 1



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[3] In the case of 2-pyrimidyl-carbene the EH-method favours **b** over **a** by 0.4 eV.

It is known that *o*-, *m*- and *p*-tolylcarbenes interconvert in the gas-phase, all rearranging eventually to benzocyclobutene (**20**) and styrene **18** (*Scheme 1*). The carbenes are generated by pyrolysis of the corresponding tolyldiazomethanes (**21**) or aldehyde tosylhydrazone salts (**22**) [22–25] or 5-(*x*-tolyl)tetrazoles (**23**).

In all cases aryldiazomethanes (**21**) are intermediates (see exper. part)[4]. A common observation is that *o*-tolylcarbene (**15**) always gives considerably more benzocyclobutene than do *m*- and *p*-tolylcarbenes, except under conditions of high energies (entries 7 and 9, Table 1) where benzocyclobutene itself is converted into styrene [25]. It has been proposed that the higher yield of benzocyclobutene from *o*-tolyldiazomethane could be due to a concerted reaction of the diazo-compound, or the formation of the carbene in a geometry especially favourable for insertion [23]. We wish to propose an explanation where we take advantage of the knowledge that the carbene-carbon atom must move out of plane during rearrangement.

From *Scheme 1* it can be seen that, when *o*-tolylcarbene (**15**) is formed by rearrangement from *p*- or *m*-tolylcarbene, it will initially be bent out of plane and in motion away from the methyl group in **15**. This motion will not stop at the geometry of **15**, but it will go on until a geometry favourable for ring expansion to the cycloheptatrienylidene **16** is reached. The energy necessary for this rearrangement will perforce be available since **15** was itself formed from such an intermediate (**14**): Thus the probability of *o*-tolylcarbene expanding – and hence rearranging to styrene – is high[5]. When, however, *o*-tolylcarbene is generated directly from *o*-tolyldiazomethane (**21**) or 5-(2-tolyl)tetrazole (**23**), the carbene in **15** has equal probabilities of motion towards and away from the methyl group. Furthermore, the carbene is not yet in motion out of the plane. Accordingly, the probability of reaction with the methyl group, leading to **20**, is high.

From the data in Tab. 1 it is apparent that the multiple rearrangement (*Scheme 1*) has an activation energy; *e.g.* *p*-tolylcarbene yields benzocyclobutene and styrene only above 400°; *o*-tolylcarbene yields these products already at 250°, and benzocyclobutene dominates strongly.

The activation energy for ring expansion (leading to styrene) can be supplied either by increased temperature (entries 1,4,6) or increased pressure at constant temperature (*cf.* entries 1–2, 4–5 and 9), or by photolysis (entry 10).

Such a pressure effect is not apparent for *p*-tolylcarbene. There is only a slight indication that the styrene yield increases with the energy (entries 18, 24, 25 and 27. In entry 25 benzocyclobutene may rearrange to styrene [25]). *p*-Tolylcarbene gives more styrene than benzocyclobutene, even though the activation energy for ring expansion appears to be higher than the one for ring closure of *o*-tolylcarbene to benzocyclobutene. This indicates that the rearranging carbene has a higher frequency factor for ring expansion than for ring closure, as required by *Scheme 1*.

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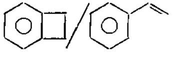
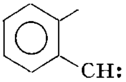
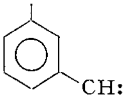
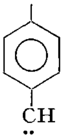
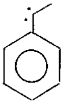
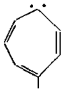
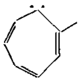
[4] The 5-tolyltetrazoles (**23**) and 5-phenyltetrazole also yield HN_3 and benzonitriles (**24**) in a competing reaction. 5-(o-Tolyl)tetrazole undergoes this reaction already on recrystallization from boiling water. The mass spectra of the tetrazoles also show stepwise loss of N_2, and a competing loss of HN_3 (see exper. part).

[5] This argument is independent of the question of involvment of a further intermediate like **2** in these reactions.

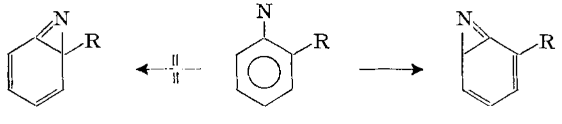
Table 1. *Rearrangement Products of Tolylcarbenes*

Carbene	Entry No.	Precursor	T°	P_{mm}	rel. yield 	Ref.
	1.	Tosylhydrazone	250	10^{-2}	6.0	a)
	2.	Tosylhydrazone	250	1	1.45	[22]
	3.	Tosylhydrazone	350	1	2.3–3.0	[22]
	4.	Tetrazole f)	420	10^{-2}	4.0	a)
	5.	Diazo	420	0.5	2.8	[23]
	6.	Tetrazole f)	610	$4 \cdot 10^{-2}$	1.65	a)
	7.	Tetrazole f)	800	$4 \cdot 10^{-2}$	0.37	a)
	8.	Diazo	700 b)	low	3.0	[24]
	9.	Diazo	150 c)	760	0.45	[22]
	10.	Diazo	30, hν	2	1.4	[17]
	11.	Diazo	420	0.5	~0.8 (1.1)	[23]([29])
	12.	Diazo	700 b)	low	0.80	[24]
	13.	Diazo	30, hν	2	0.7	[17]
	14.	Tosylhydrazone	250 d)	40	0:0	[17]
	15.	Tosylhydrazone	250 d)	0.4	0:0	a)
	16.	Tosylhydrazone	320 d)	0.3–0.4	0:0	a)
	17.	Tetrazole f)	320 e)	10^{-2}	0:0	a)
	18.	Tetrazole f)	420 e)	10^{-2}	0.75	a)
	19.	Tosylhydrazone	400 d)	0.3	0.9	a)
	20.	Tetrazole f)	420 e)	0.1–0.2	0.93	a)
	21.	Diazo	420	0.5	0.8 (1.1)	[23]([29])
	22.	Tetrazole f) g)	420	1	0.9	a)
	23.	Tetrazole f) g)	420	10	0.9	a)
	24.	Tetrazole f)	610	$3 \cdot 10^{-2}$	0.8	a)
	25.	Tetrazole f)	800	$5 \cdot 10^{-2}$–$6 \cdot 10^{-2}$	0.33	a)
	26.	Diazo	700 b)	low	0.83	[24]
	27.	Diazo	30, hν	2	0.5	[17]
	28.	Diazo	420	0.5	0:1	[23]
	29.	Tosylhydrazone	720	10^{-3}–10^{-2}	0:1	a)
	30.	Tosylhydrazone	450	6	~1	[17]
	31.	Tosylhydrazone	350	3	~0:1	[17]

a) This work.
b) 'Flash vacuum pyrolysis'. The contact times are shorter here than under our conditions, resulting in a lower effective temperature.
c) 'Violent', presumably explosive reaction.
d) Dimethylheptafulvalene and dimethylstilbene are formed.
e) Dimethylheptafulvalene not detectable.
f) Tetrazoles **23** always give benzonitriles **24** in a side-reaction.
g) *p*-Tolyldiazomethane isolated from the pyrolysate.

With a similar reasoning, one may understand why ortho-substituted phenylnitrenes (**24**) prefer to expand *away* from the substituent [3] (for clarity we write the bicyclic intermediates even if we do not know whether they are involved).

This ring expansion has an estimated activation energy $E_a > 25$ kcal/mol [6]. If the nitrene-nitrogen moves towards the substituent R (giving **25**), there is a high probability that it will react with R, or transfer vibrational energy to it, thereby losing the momentum necessary for ring expansion. The exclusive formation of **26** is not general [26] [27] and depends on other factors such as the nature of the reaction partner [26] and electronic effects [28].



25 **24** **26**

Experimental Part

1. *Preparation of compounds.* The 5-aryltetrazoles (**23**) were prepared by the procedure of *Finnegan et al.* [30]. Mass spectra (*CEC* 21-490 instrument with direct inlet; probe 110°, source 200°; 70 eV), listed as *m/e* followed by (relative abundance): 5-Phenyltetrazole, *m/e* 146 (M^+, 17%), 118 (100), 104 (5), 103 (13), 95–96 (m^* 146→118), 92 (3), 91 (36), 90 (3), 89 (12), 77 (28), 76 (7) 70 (m^* 118→91), 64 (8), 63 (18), 62 (8), 52 (3), 51 (12), 50 (9).

5(*o*-Tolyl)tetrazole, *m/e* 160 (M^+, 47%), 133 (16), 132 (79), 131 (100) 130 (m^* 132→131), 118 (10), 117 (67), 116 (18), 109 (m^* 160→132), 105 (7), 104 (33), 103 (15), 102 (13), 91 (9), 90 (17), 89 (19), 82 (m^* 132→104).

5-(*m*-Tolyl)tetrazole, *m/e* 160 (M^+, 15%), 133 (10), 132 (100), 131 (25), 130 (m^* 132→131), 118 (7.5), 117 (8.5), 116 (8.5), 109 (m^* 160→132), 105 (5.5), 104 (15), 103 (5.2), 102 (4.2), 91 (31), 90 (78), 89 (77), 82 (m^* 132→104).

5-(*p*-Tolyl)tetrazole, *m/e* 160 (M^+, 17%), 133 (8), 132 (100), 131 (50), 130 (m^* 132→131), 118 (6), 117 (8), 116 (6), 109 (m^* 160→132), 105 (3), 104 (8), 103 (4), 102 (3), 91 (23), 90 (5), 89 (4), 82 (m^* 132→104).

The aldehyde tosylhydrazone salts were essentially prepared according to [22] [17]. The use of THF as solvent [17] is not advisable, since it is impossible to free the precipitated salts from THF, even by prolonged pumping under high vacuum at room temperature. Subsequent pyrolysis then yields THF as the main product. The use of ether as solvent [22] is limited by the solubility of the tosylhydrazones. An ether/methanol mixture is convenient.

2. *Pyrolysis procedure.* The pyrolysis apparatus consisted of a 30 × 2 cm horizontal quartz tube, heated by a *Heraeus* oven, type Rok 3/30. Samples were sublimed in from a small flask with adaption for the introduction of carrier gas (N_2), where required. The pressure was recorded on a *Pirani* gauge. Runs at higher than 0.4 Torr used N_2 as carrier gas. Pressures between 10^{-5} and 0.4 Torr were regulated with the pumping efficiency. The products were trapped in a U-tube in liq. N_2 at the exit of the pyrolysis tube. After pyrolysis was completed, the system was filled with N_2, the pyrolysis tube disconnected, the system closed and evacuated, and the products distilled from the U-tube in two or three fractions. In the pyrolysis of 5-aryltetrazoles (**23**) the first fraction consisted mainly of HN_3 (identified by its NMR.- and IR.(gas)-spectra). The second fraction consisted mainly of benzocyclobutene (**20**) and styrene (**18**). The third fraction consisted of the aromatic nitrile (**24**) and aryldiazomethane (**21**), when present. The involatile rest contained, where indicated in Table 1, dimethylstilbene and dimethylheptafulvalene (identified by NMR. [17]), and was not investigated further. The presence of dimethylheptafulvalene was always probed by NMR.

The relative yields of benzocyclobutene and styrene (Table 1) were determined by NMR.-integration, and by gas-chromatography (*Hewlett-Packard* 5750; column 6 ft. 10% UCC W982 on chromosorb W; H_2 carrier at 30 ml/min; 80° isothermal). The benzonitriles **24** were estimated by NMR. and gas-chromatography. *p*-Tolyldiazomethane was estimated by NMR. [17] and identified by its UV.- [17] and IR.-spectra.

3. *Pyrolysis of 5-phenyltetrazole. a)* at 600°: 1.00 g 5-phenyltetrazole was sublimed at 150° nto the pyrolysis tube at 600°/0.10 Torr. After work-up, the first destillate was largely HN_3 ~10%), with at most a trace of fulvenallene/ethynyl-cyclopentadiene (*cf.* [6]). The second raction contained 260 mg benzonitrile (37%). Heptafulvalene was not detectable by NMR. [31];

b) at 800°/0.02–0.05 Torr, 0.800 g 5-phenyltetrazole yielded 0.126 g distillate, consisting of HN_3, benzonitrile, fulvenallene (*cf.* [4c]), ethynylcyclopentadiene, and toluene in the molar ratio 42:51:3.0:2.2:2.0. Heptafulvalene was not detectable.

c) at 400°/0.2 Torr, HN_3, toluene, benzonitrile (~9%), and at most a trace of heptafulvalene was formed.

4. *Pyrolysis of 5-*(o-*tolyl) tetrazole. a)* at 610°: 0.50 g of the tetrazole was sublimed at 135° into the pyrolysis tube at 610°/0.04 Torr. Much of the starting material decomposed in the sublimation flask. The first distillate (85 mg; 26%) consisted of benzocyclobutene and styrene in the molar ratio 1.65. The second fraction was *o*-tolunitrile (40 mg; 11%);

b) at 800°/0.04 Torr, 0.50 g tetrazole sublimed in at 120° yielded 26 mg (8%) of benzoclobutene and styrene in the ratio 0.37. The second fraction was *o*-tolunitrile (94 mg; 26%).

5. *Pyrolysis of 5-*(p-*tolyl)tetrazole a)* at 320°/0.01 Torr. 1.00 g Tetrazole was sublimed in at 150–160°. 0.85 g starting material was recovered. Benzocyclobutene and styrene were not detectable. 8 mg *p*-Tolunitrile (7%) was isolated. The presence of *p*-tolyldiazomethane was indicated by the red colour of the distillate (*vide infra*). Dimethylheptafulvalene [17] was not detectable; the same was true at 300°/0.1 Torr;

b) at 420°/0.01 Torr. 0.20 g Tetrazole was sublimed in at 117°. The first distillate (18 mg; 14%) was benzocyclobutene and styrene in the ratio 0.75. The second fraction (16 mg) was a red liquid, consisting mainly of *p*-tolunitrile. The presence of *p*-tolyl-diazomethane in this liquid was ascertained by the methyl-NMR.- [17] absorption (δ 2.25 (CCl_4)), and by the IR.- and UV. [17]-spectra (δ_{max} (CCl_4) 2070 cm^{-1}; λ_{max} (hexane) 276 nm). The red colour and the absorptions ascribed to *p*-tolyldiazomethane disappeared after addition of fumaronitrile. No trace of dimethylheptafulvalene was detectable; the same was true at 420°/0.2 Torr;

c) at 420°/1 Torr, with N_2 carrier. 0.50 g tetrazole sublimed in 10 h at 185°. There was obtained benzocyclobutene and styrene (19%; ratio 0.9), *p*-tolyldiazomethane (~9%) and *p*-tolunitrile (~9%);

d) at 420°/10 Torr, with N_2 carrier. From 0.4 g tetrazole was obtained benzocyclobutene and styrene (3%; ratio 0.9), *p*-tolyldiazomethane (13%), and *p*-tolunitrile (7%). *p*-Tolyldiazomethane: NMR. (CCl_4): δ 2.25 (*s*, 3H), 4.75 (*s*, H), 6,83 (*q*, $J = 8.5$ Hz, 4H);

e) at 400°/10^{-5} Torr results were similar to those described in *5b*, except that *p*-tolyldiazomethane was no longer detectable.

6. *Pyrolysis of the sodium salt of o-tolualdehyde tosylhydrazone* at 250°/0.01 Torr. 1.00 g of the salt was decomposed in the sublimation flask at 80–95°. The distillate (121 mg; 36%) contained benzocyclobutene and styrene in the ratio 6.0. There was only very little substance which could contain a dimethylheptafulvalene (NMR.: δ 1.85 and 5.8 (*cf.* [17j])).

7. *Pyrolysis of the sodium salt of* p-*tolualdehyde tosylhydrazone* at 250°/0.4 Torr. 1.00 g of the salt was decomposed at 80–90°. The red liquid distillate contained a little *p*-tolyldiazomethane (*cf.* *5b*). No benzocyclobutene or styrene was detectable by NMR. and GC. *p*-Tolyldiazomethane was detectable up to 400°/0.3 Torr. Benzocyclobutene and styrene appeared at 400°/0.3 Torr; ratio by GC. ≈ 0.9. The distillation residue consisted of a mixture of dimethylstilbene and dimethylheptafulvalene (*cf.* [17]); conditions, yield, ratio: 250°/0.4 Torr, 190 mg, ~1:1; 320°/0.3–0.4 Torr, 178 mg, ~1:2; 400°/0.3 Torr, 168 mg, ~1:1.

At 250°/0.4 Torr there deposited inside the pyrolysis tube some *p*-tolualdazine, m.p. 157° from EtOH [32].

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