mit Calciumchlorid bei 0° getrocknet, filtriert und 2 Std. unter Rückfluss gekocht. Dann dampft man das Benzol ab und destilliert das Produkt bei 59°/0,15 Torr: 70 g **5c** (80%). n_D^{20}: 1,5200. IR. (fl.): 4,35, 14,03. UV. (C_6H_{12}): 2650 (4200). NMR. ($CDCl_3$): 1,53/*s* gem. CH_3-; 2,34/*d*, J = 7,1 CH_2-7; 5,24–5,48/*m* CH-6; 6,05–6,30/*m* CH-2 und CH-5; 6,53/*m* CH-3 und CH-4.

$C_{11}H_{13}NO$ (175,2) Ber. C 75,40 H 7,48 N 7,99% Gef. C 75,31 H 7,55 N 7,87%

2-(1-Cycloheptatrienyl)-isopropylamin (**5d**). Eine Suspension von 52,5 g (0,3 Mol) 2-(1-Cycloheptatrienyl)-isopropylisocyanat in 200 ml konzentrierter Salzsäure wird unter Rühren auf 40° erwärmt. Es entwickelt sich CO_2 und die Temperatur steigt auf 52° an (Kühlung). Man hält etwa 10 Min. auf 45°, bis die CO_2-Entwicklung beendet ist, giesst dann die Lösung in 600 ml Eiswasser und extrahiert viermal mit Äther. Das Wasser und die Salzsäure werden im rotierenden Verdampfer bei höchstens 60° Badtemperatur im Vakuum abgedampft, bis ein dickes Öl und wenig Wasser zurückbleiben. Man gibt 400 ml 2N Natronlauge hinzu, extrahiert viermal mit Äther und trocknet die ätherische Lösung mit Magnesiumsulfat. Dann dampft man das Lösungsmittel ab und destilliert das Amin bei 46°/0,4 Torr: 39,6 g **5d** (88,6%). n_D^{20}: 1,5327. IR. (fl.): 14,03. UV. (C_6H_{12}): 2670 (4000). NMR. ($CDCl_3$): 1,27/*s* gem. CH_3-; 1,32/*s* $-NH_2$; 2,30/*d*, J = 7,0 CH_2-7; 5,21–5,45/*m* CH-6; 6,03–6,28/*m* CH-2 und CH-5; 6,50/*m* CH-3 und CH-4.

$C_{10}H_{15}N$ (149,2) Ber. C 80,49 H 10,09 N 9,39% Gef. C 80,44 H 10,21 N 9,59%

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59. Hetarylnitrenes V.[1]) Reactions of Tetrazolopyrazine Ring Contraction of Nitrenodiazines in Solution

Preliminary communication[2])

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(3 I 72)

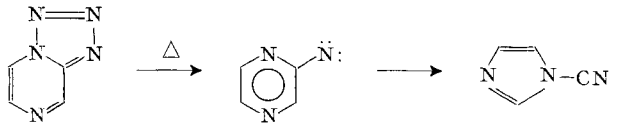
Summary. Thermolysis of tetrazolopyrazine (**1**) in organic solvents gives pyrazinylnitrene (**2**) which undergoes ring contraction to 1-cyanoimidazole (**3**). 7-Methyl-5-methylthio-tetrazolo[1,5-*c*]-pyrimidine (**4**) likewise gives 1-cyano-2-methylthio-4-methyl-imidazole (**6**). The two tetrazoles also undergo ring contraction to 1-cyanoimidazoles by gas chromatography, and **1** gives a low yield of **3** by photolysis. Thermolysis of **1** and **4** in cyclohexane gives aminopyrazine (**7**) and 6-amino-4-methyl-2-methylthio-pyrimidine (**8**), respectively. Tetrazolo[1,5-*a*]pyrimidines (**9**) give only 2-aminopyrimidines (**10**).

1-Cyanoimidazole, formed by thermolysis of **1** in acetic acid, reacts further to give 1-acetylimidazole, which with more acetic acid gives imidazole and acetic anhydride. An earlier report [2] of ring expansion of pyrazinylnitrene in acetic acid is discredited.

In protic deuteriated solvents (D_2O, CH_3OD), tetrazolopyrazine reacts as an enamine, specifically exchanging H—C(6) for deuterium.

[1]) Part IV: see [1].
[2]) A full paper will be submitted to Helv.

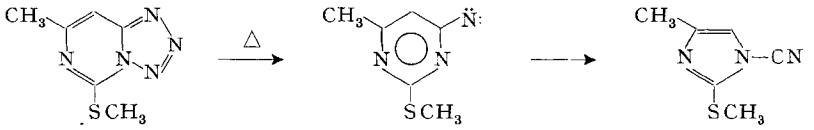
Aromatic and heteroaromatic nitrenes undergo ring contraction in the gas-phase [1] [3] [4], *e.g.*



1 **2** **3**

In some cases the formation of amines by hydrogen abstraction confirms the existence of nitrene intermediates [3] [4], but when the reaction is clean it is difficult or impossible to prove that a nitrene is involved. We now report the first examples of nitrene ring contraction in solution, which allow a closer inspection of the reacting species and investigation of the kinetics of its formation.

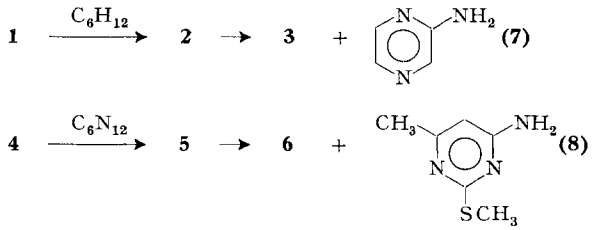
Thermolyses of tetrazolodiazines in solution (35–45 mg/ml) were performed in sealed NMR. tubes, and the progress of reaction followed by NMR. After reaction was complete the tubes were opened, the content extracted with $CHCl_3$, filtered from insoluble polymer, the filtrate evaporated, and the composition of the product checked by IR., gas chromatography, and mass spectrometry. Results are presented in the Table. Tetrazolopyrazine (**1**) and 7-methyl-5-methylthio-tetrazolo[1,5-*c*]pyrimidine (**4**) gave 1-cyanoimidazoles **3** and **6**, respectively.



4 **5** **6**

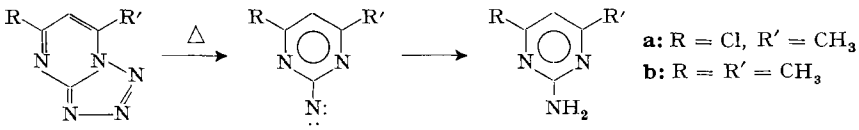
The same two products resulted from gas chromatography of **1** and **4**, respectively, above 200° (see Table and [3]). By direct photolysis of **1**, ring contraction occurred in low yield (see Table), but the main product was a yellow, insoluble compound (mp. > 330°) which showed IR.-bands at 1700–1600 and 3400–3200 cm^{-1}, and presumably is formed by poly-condensation of the nitrene **2**. It was insufficiently volatile for a mass spectrum to be obtained with a direct insertion probe at 250°.

Evidence for the involvement of nitrenes **2** and **5** was found by thermolysis in cyclohexane, which gave both the cyanoimidazoles **3** and **6**, and the amines **7** and **8**.



The yields were low in this reaction because the products (*e.g.* **3** and **7**) react with each other, as was established by separate experiments, although no definite secondary products have been isolated. Insertion of pyrazinylnitrene (**2**) into a C–H bond of

cyclohexane to give 2-cyclohexylamino-pyrazine was not observed. It is noteworthy that gas-phase thermolysis of **1** and **4** did not give detectable amounts of amines **7** and **8**, thus making it uncertain that nitrenes were actually involved [3].



9 **11** **10**

Solution thermolysis of tetrazolo[1,5-*a*]pyrimidines (**9**) (**9a** is the most easily tautomerized into the azido-form [5]) gave only the amino-pyrimidines **10** (*cf.* [6]); by gas-phase thermolysis of tetrazolo[1,5-*a*]pyrimidines the aminopyrimidines are also predominant, besides 1-cyanopyrazoles [3]. Formation of **10b** from **9b** in $CDCl_3$ was accompanied by formation of **10**-d_2 and $CHCl_3$, indicating D-abstraction by the nitrene **11**, giving rise to CCl_3 radicals, which with a proton source gave $CHCl_3$.

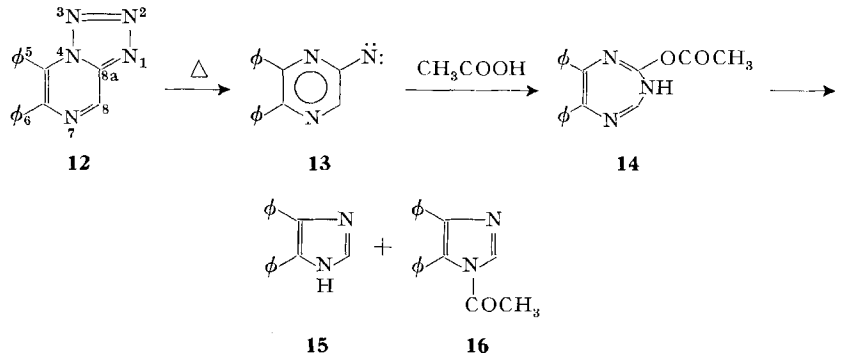
Sasaki et al. reported recently [2] that thermolysis of 5,6-diphenyl-tetrazolo[1,5-*a*]pyrazine (**12**) in acetic acid resulted in the corresponding imidazole (**15**) and 1-acetylimidazole (**16**), for which they postulated *ring expansion* of the nitrene

Thermolyses and Photolyses of Tetrazolodiazines

Compound	Reaction conditions			Solvent	Products (yield %)
1	Δ	125°	112 h	$CDCl_3$	**3** (4), **1** (12)
1	Δ	180°	6 h	C_6H_6	**3** (40)
1	Δ	125°	96 h	C_6H_{12}	**3** (trace), **7** (8), **1** (25)
1	*hν*[a])	20°	36 h	$CDCl_3$	**3** (1), **1** (67), polymer (32 by weight)
1	*hν*	20°	48 h	C_6H_6	**3** (1), **1** (74), polymer (25 by weight)
1	GC.[b])	300°			**3** (50), **1** (50)
1	Δ	125°	120 h	CH_3COOH	**19** (30), $(CH_3CO)_2O$ (30), **1** (70)
1	Δ	125°	48 h	CH_3OD	**20** (99+)
1	Δ	110°	16 h	D_2O	**20** (99+)
4	Δ	125°	70 h	$CDCl_3$	**6** (40), **4** (55)
4	Δ	125°	48 h	C_6H_6	**6** (50)
4	Δ	125°	72 h	C_6H_{12}	**6** (trace), **8** (10)
4	GC.	300°			**6** (100) [3]
9a	Δ	190°	168 h	$CDCl_3$	**10a** (10), **9a** (25), HCl
9b	Δ	190°	72 h	$CDCl_3$	**10b** (60), **9b** (6)

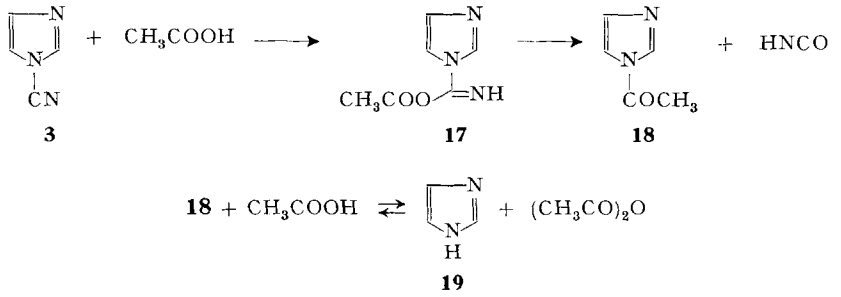
a) *hν*: 75 W high-pressure Hg-lamp, Wycor glass.
b) Gas chromatography on 20% carbowax on Chromosorb W, column temp. 180°; injection port temp. stated.

13 to a triazepine (*e.g.* **14**). We have shown that this postulate is not valid: the products are readily explained by primary *ring contraction* to 1-cyanoimidazole, as in the reaction **1** → **3**. Thermolysis of tetrazolopyrazine (**1**) in acetic acid gave imidazole and acetic anhydride (see Table). When 1-cyanoimidazole (**3**) (50 mg) was dissolved in acetic acid (1 ml), and the reaction monitored by NMR., a rapid transformation



12 **13** **14** **15** **16**

into 1-acetylimidazole (**18**) was observed ($t_{1/2}$ (40°) $\leqslant$ 30 s); **18** (50 mg) in acetic acid (1 ml) was further transformed into imidazole (**19**) and acetic anhydride ($t_{1/2}^{initial}$ (40°) $\simeq$ 4 min) (*cf.* [7]):

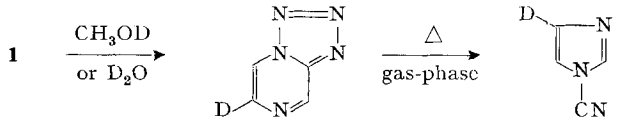


3 **17** **18** **19**

The rate of this latter reaction slowed down as reaction progressed, and it was still not complete after heating at 125° for 24 h. This is because the reaction is reversible [8] and the concentration of **18** thus depends on the concentration of acetic acid, in accord with the observations of *Sasaki et al.* [2] for the formation of **15** and **16** from **12**.

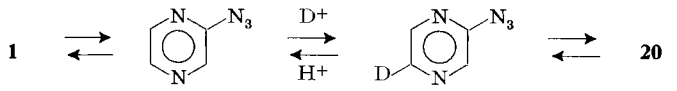
When equivalent amounts of **3** and acetic acid were reacted in CCl_4 at 60–65° for $22^1/_2$ h, NMR. of the soluble fraction showed that it consisted of **18** ($\geqslant$ 98%) with little acetic anhydride ($\leqslant$ 1.5%). HNCO was isolated in the form of its trimer, isocyanuric acid, by expelling it from the solution by a stream of N_2 during reaction. The reaction is formulated as passing through an intermediate isoimide (**17**), by analogy with a scheme put forward [9] for the reaction of aminonitriles with carboxylic acids. Our reaction differs from the latter, however, in that the isoimide **17** *does not* react with acid to give an N-carboxamide and acid anhydride.

An attempt to thermolyse **1** in CH_3OD resulted in complete and specific exchange of H–C(6):

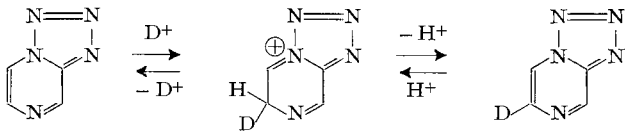


20 **21**

The reaction was faster in D_2O, and proceeded at temperatures where the product **20** does not decompose (see Table). It is generally accepted that an annelated tetrazole ring is electron withdrawing, while the tautomeric azido group is electron donating [10] [11]. It might therefore be assumed that the formation of **20** proceeds *via* the azido-form in analogy with the exchange of *o,p*-protons in anilines [12]:



This mechanism was ruled out, however, since aminopyrazine failed to exchange on heating with D_2O at 135° for 7 days (the amino group is a stronger electron donator than the azido group, *cf.* [11]). The exchange must therefore be a reaction of the tetrazole, reacting as an enamine:



It was reported recently that enamines exchange with acetone-d_6 [13]. **1** did not exchange noticeably with acetone-d_6 at 135°, and can therefore be qualitatively classed as a very weak enamine.

20 was identified by comparison of its IR., NMR., and mass spectra with those of **1** [5], and by the reversal to **1** on treatment with H_2O. Gas-phase thermolysis of **20** (*cf.* [3]) gave 1-cyanoimidazole-4-d (**21**).

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