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169. [1,2,3]Triazoloazine/(Diazomethyl)azine Valence Tautomers from 5-Azinyltetrazoles

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(13.II.78)

Summary

[1,2,3]Triazoloazines are formed by thermolysis of 5-azinyltetrazoles in the gas-phase or in solution. Thus, 5-(2-pyridyl)tetrazole (**7**) and 5-(2-pyrazinyl)tetrazole (**11**) yield [1,2,3]triazolo[1,5-*a*]pyridine (**9**) and [1,2,3]triazolo[1,5-*a*]pyrazine (**13**), respectively, at 400°/10^{-3}–10^{-5} Torr. 5-(2-Phenyl-4-quinazolinyl)tetrazole (**15**) gives 5-phenyl[1,2,3]triazolo[1,5-*c*]quinazoline (**17**) in 75% yield by heating under reflux in mesitylene solution. 2-(Diazomethyl)pyridine (**8**), a valence tautomer of **9**, can be trapped by fumaronitrile, leading to 3-(2-pyridyl)-1,2-cyclopropanedicarbonitrile (**19**). The [1,2,3]triazoloazines undergo base catalysed H/D-exchange in D_2O solution.

Due to their highly interesting biological properties, the synthesis of compounds possessing purine-like ring systems has received much attention recently [1]. Although a large number of such structures has been prepared, relatively few [1,2,3]-triazolo[1,5-*a*]azines of the general formula **1** are known.

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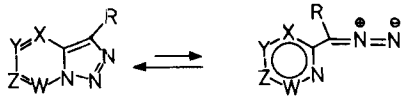
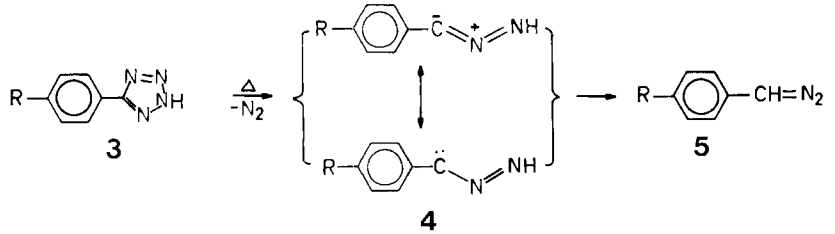


1 2

X, Y, Z, W = CR or N

In this paper, a new synthetic approach to this class of compounds, together with evidence for valence tautomeric equilibria of **1** with the diazomethylazines **2** is presented. 1,2,3-Triazole/*α*-diazoalkylideneamine valence tautomerism has been known in monocyclic triazoles since the work of *Dimroth* [2], but was only recently established in a condensed system of the type **1**, namely in [1,2,3]triazolo[1,5-*a*]-pyrimidines [3].

1. Syntheses. – The synthetic approach to **1** is based on the observation [4] that 5-aryltetrazoles **3** upon thermolysis in the gas-phase eliminate one molecule of N_2 with the formation of aryldiazomethanes **5**, *e.g.*:



3 4 5

When the reaction conditions were sufficiently mild (400°/1 Torr of N_2 as carrier gas) **5** can be isolated; at higher temperatures, decomposition to arylcarbenes occurred [4].

Although there is still no conclusive evidence for arenecarbonitrile imine (**4**, R = H), this intermediate has been invoked previously in the solution thermolysis and photolysis of 5-phenyltetrazole (**3**, R = H) [5–8]. The main product under these conditions was 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine, formally a dimer of **4** (R = H) [5] [8]. **4** is not trappable by 1,3-dipolar cycloaddition when generated photochemically [7] [8], although it was shown by labelling that only N(3)–N(4) was eliminated from **3** (R = H) [8]. It was postulated that **3** reacts as a hydrogen-bonded dimer or higher polymer, thereby leading initially to a nitrile imine associated with a molecule of tetrazole. Further reaction of this associate could lead to the dihydrotetrazines [8]. When **4** was generated thermally from **3** in solution, it could, however, be trapped by aromatic nitriles leading to 1,2,4-triazoles [5].

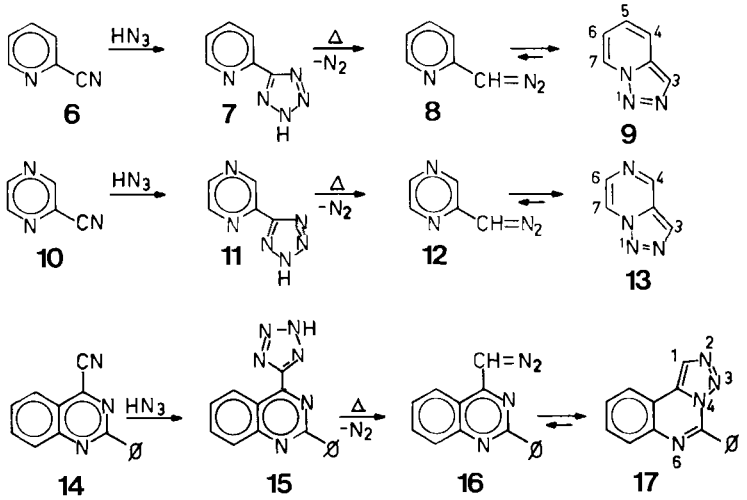
In view of these results, we formulate the above formation of aryldiazomethanes **5** in terms of a [1,3]-*H*-shift in the nitrile imines **4**, although it is emphasized that it cannot at this time be excluded that other tautomers of **3** also undergo thermolysis[2]). The nitrile imines **4** are formulated as hybrids of bent dipolar and carbenic structures in agreement with the calculations of *Caramella & Houk* [10].

The 5-(heteroaryl)tetrazoles **7**, **11**, and **15** were readily prepared by addition of HN_3 to the corresponding nitriles **6**, **10**, and **14** using the procedure of *Finnegan et al.* [11] (see *Scheme 1*).

[2]) The 1*H*-tautomer of **3** could lose N_2 forming a C-iminonitrene which, after recyclization to 3-aryldiazirine could re-open to the intermediate **4**. Such a process was not observed in the photochemical labelling work [8], however. Thermolysis of the 5*H*-tautomer of **3** could lead directly to **5**, but the population of this tautomer appears energetically unlikely. The thermolysis of 2,5-diaryltetrazoles leads to nitrile imines in solution as well as in the gas-phase [9].

The thermolysis of 5-(2-pyridyl)tetrazole (**7**) at 400°/10^{-3} Torr resulted in [1,2,3]triazolo[1,5-*a*]pyridine (**9**) in 15% isolated yield. Since **9** is a known compound, easily accessible by the oxidation of the hydrazone of pyridine-2-carboxaldehyde [12], no attempts were made to optimize the yield. The formation of **9** indicates, however, that the tetrazole **7** eliminates one molecule of N_2 to yield 2-(diazomethyl)pyridine (**8**), the latter cyclizing to the more stable triazole **9** as shown in *Scheme 1*.

Scheme 1



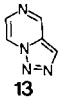
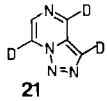
The same procedure was applied to the synthesis of the novel heterocyclic system [1,2,3]triazolo[1,5-*a*]pyrazine (**13**), a hitherto unknown isomer of purine. The highest yield of **13** (20%) was obtained by thermolysis of 5-(2-pyrazinyl)tetrazole (**11**) at 400°/10^{-5} Torr. The structure of **13** is fully corroborated by its NMR. and mass spectra and elemental analysis, as well as the deuterium exchange experiments to be described in Section 4. In particular, the NMR. spectrum of **13** (see *Table*) is very similar to that of tetrazolo[1,5-*a*]pyrazine (**22**, *Table*). The additional signal for H–C(3) of **13** appears at 8.3 ppm ($CDCl_3$); the corresponding signal of **9** is at 8.1 ppm (see *Table*). H–C(3) of **9** and **13** both show a long-range coupling of $J \approx 1$ Hz with the *epi*-proton H–C(7). This coupling disappeared when H–C(7) was exchanged for deuterium (*cf.* Section 4). *Epi*-couplings of this kind have been observed also in indene [13], benzofuran [14], indole [14], and other aromatic systems [15].

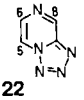
5-Phenyl[1,2,3]triazolo[1,5-*c*]quinazoline (**17**) was obtained in low yield by gas-phase thermolysis of the tetrazole **15**. A much higher yield of **17** (75%) was achieved by heating **15** in mesitylene at 160° for 78 h. **17** is the first [1,2,3]triazolo[1,5-*c*]-quinazoline reported.

Unfortunately, thermolysis of the tetrazoles **7** and **11** in solution cannot be used for the preparation of the smaller [1,2,3]triazolo[1,5-*a*]azines **9** and **13**, these decomposing at the temperatures required to thermolyse **7** and **11**. Thus, the activation energy for the decomposition of **9** is only *ca.* 6 kcal/mol higher than the one for **7** in

diphenyl ether solution (*cf.* Section 3). Apparently, the activation energy difference is higher in the larger, condensed systems **15** and **17**, thereby allowing the synthesis of **17** in solution. The preparation of other condensed [1,2,3]triazolo[1,5-*a*]azines by this method is currently under investigation.

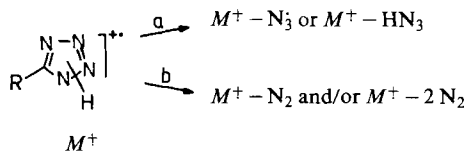
Table. ^{1}*H-NMR. Spectra of Triazolo- and Tetrazoloazines*[a])

	Chemical shifts of					$J_{(3,7)}$	$J_{(4,5)}$	$J_{(4,6)}$	$J_{(4,7)}$	$J_{(5,6)}$	$J_{(5,7)}$	$J_{(6,7)}$
	H–C (3)	H–C (4)	H–C (5)	H–C (6)	H–C (7)							
 **9**	8.05	7.7	7.2	7.0	8.7	0.8	9.0	~1.25	~1.0	~6.5	~1.0	7.0
 **20**	–	7.7	7.2	7.0	8.7	–	9	~1.25	~1.0	~6.5	~1.0	7
 **13**	8.3	9.3	–	8.00	8.6	1	–	–	1.3	–	–	5.0
 b)	8.3	9.3	–	8.01	–	–	–	–	–	–	–	–
 **21**	–	–	–	8.01	–	–	–	–	–	–	–	–

	Chemical shifts of			$J_{(5,8)}$	$J_{(5,6)}$
	H–C (8)	H–C (6)	H–C (5)		
 **22**	9.6	8.3	8.8	1.6	4.7
 **23**	9.6	8.3	–	–	–

a) Measured in $CDCl_3$ solutions using *Varian* A-60A or XL-100 instruments. Chemical shifts δ in ppm; coupling constants J in Hz, corroborated by spin decoupling and computer simulation.
b) Not isolated.

2. Comparison of the thermal, photochemical, and mass spectral fragmentations of 5-aryltetrazoles. – The mass spectra of the tetrazoles **7**, **11**, and **15** are listed in the experimental part. There are two major modes of fragmentation of the molecular ions: path a) is a cycloreversion in which N_3 or HN_3 is eliminated, path b) parallels the thermal process, in which either N_2 or 2 N_2, or both, are extruded:



A metastable ion is observed for the simultaneous loss of $2\,N_2$, which appeared also in the mass spectra of other 5-(2-azinyl)tetrazoles to be reported elsewhere. 5-Phenyl- and the 5-tolyltetrazoles also fragment according to the two general pathways a) and b) [4], but do not show a metastable $M^+ - 2\,N_2$ peak.

Huisgen et al. [5] reported that 5-phenyltetrazole thermolyses in solution by two pathways corresponding to the paths a) (formation of HN_3 and benzonitrile) and b) (formation of N_2 and benzonitrile imine). Similar paths were observed in the gas-phase thermolysis of 5-phenyl- and the 5-tolyltetrazoles [4]. In contrast, *Scheiner* [7] [8] found that photolysis of 5-phenyltetrazole involves only the path corresponding to b) above (loss of N_2).

The thermolyses reported in Section 1 proceed exclusively by loss of N_2, and this appears to be general for (heteroaryl)tetrazoles. However, under somewhat more energetic conditions, pyridyltetrazoles fragment thermally in the gas-phase by the two routes corresponding to a) and b) [16].

3. Trapping of 2-(diazomethyl)pyridine (8). - [1,2,3]Triazolo[1,5-*a*]pyridine (**9**) decomposed in diphenyl ether solution in the temperature range of 180–220°. The rate of N_2 evolution followed first order kinetics, *e.g.* $k\,(\mathbf{9}) = 3.52 \cdot 10^{-6}\,s^{-1}$ at 180.5°. The *Arrhenius* parameters were $E_a(\mathbf{9}) = 48 \pm 1$ kcal/mol and $\log A = 18$ [17] (for a preliminary measurement see [18]). When the decomposition of **9** was carried out in the presence of fumaronitrile, evolution of N_2 occurred at a measurable rate already at 130°, *e.g.* $k_{obs}(\mathbf{9}) = 3.61 \cdot 10^{-4}\,s^{-1}$ at 150° at a concentration of fumaronitrile of 0.167 mol/l (ten-fold excess)[3]), and 3-(2-pyridyl)-1,2-cyclopropanedicarbonitrile (**19**) was isolated in 32% yield as a mixture of two geometric isomers. These were identified by elemental analysis and spectral data (see experimental part).

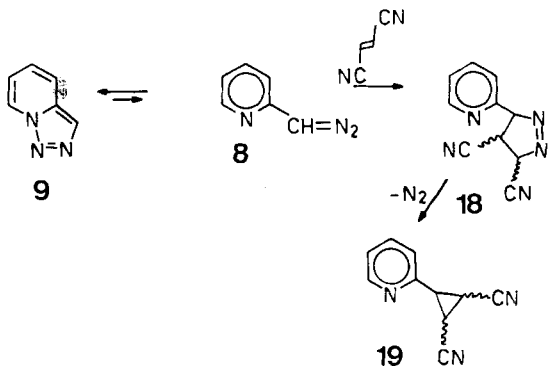
The mechanism shown in *Scheme 2* is consistent with the above observations. Although the concentration of **8** was too low for direct detection, a 1,3-dipolar cycloaddition of **8** to fumaronitrile would be rapid at the reaction temperature. The resulting 1-pyrazoline **18** is expected to decompose under the reaction conditions [19] yielding the observed product **19**. Since the reaction shown in *Scheme 2* is faster than the decomposition of **9** in the absence of fumaronitrile, a carbene route can be excluded.

5-(2-Pyridyl)tetrazole (**7**) also decomposed according to first order kinetics in diphenyl ether solution. In the temperature range of 180–220° the activation parameters $E_a(\mathbf{7}) = 41.6 \pm 1$ kcal/mol and $\log A = 15.2$ were obtained. The rate was independent of added fumaronitrile. However, the TLC. of the product mixtures resulting from the thermolysis of either **7** or **9** in the presence of fumaronitrile were

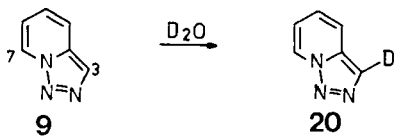
[3]) A detailed kinetic analysis of this reaction will be published separately.

identical. This suggests that **7** is transformed quantitatively to **8**⇌**9**, which then undergo faster subsequent reactions.

Scheme 2



4. Hydrogen/Deuterium exchange. – Heating of [1,2,3]triazolo[1,5-*a*]pyridine (**9**) in D_2O solution above 100° caused exchange of H–C(3) for deuterium, *e.g.* $t_{1/2}(150°) \approx 20$ min. On long exposure, a slower exchange of H–C(7) was also observable. The exchange of both protons was strongly catalysed by added NaOD, but not by D_2SO_4. It is known that H/D-exchange in *α*-position to the nitrogen atom

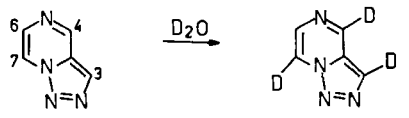


in pyridine *N*-oxides and *N*-substituted pyridinium ions occurs *via* a carbanion mechanism [20]. In pyridine and the diazines exchange is faster at the positions *β* and *γ* to the ring nitrogen atoms, but all positions are activated; *e.g.* H–C(2) in pyrazine exchanges *ca.* 100 times faster than H–C(2) in pyridine at 165° [21]. Similar observations were made with [1,2,4]triazolo[4,3-*b*]pyridazine, which underwent both acid and base catalysed exchange [22]. On the basis of these reports, one might expect that a carbanion mechanism would result in a more rapid exchange of H–C(7) than of H–C(3) in **9**.

An alternative mechanism for the exchange of H–C(3) in **9** would involve 2-(diazomethyl)pyridine (**8**) which, as shown in Section 3, is reversibly formed at the temperature of the H/D-exchange experiment. *α*-Carbonyldiazo-compounds are known to undergo base catalysed H/D-exchange [23]. In contrast, simple aryldiazomethanes do not exchange, but are irreversibly protonated in acidic media [24], that is, further reaction of the benzyldiazonium ions is faster than deprotonation.

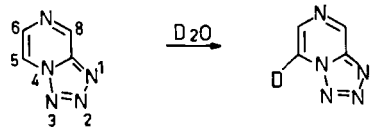
Thus, while exchange of H–C(3) in **9** *via* **8** seems quite plausible, it cannot be excluded at present that the reaction occurs by deprotonation of **9** itself.

Heating of [1,2,3]triazolo[1,5-*a*]pyrazine (**13**) in D_2O at 100° caused exchange of three protons. By monitoring the reaction by NMR. spectroscopy (*cf.* the *Table*) the relative rates of exchange could be determined: H–C(7) > H–C(3) > H–C(4) ≫ H–C(6). The approximate half-lives at 100° were: $t_{1/2} \approx 24$ h for H–C(7), $t_{1/2} \approx 40$ h for H–C(3), and $t_{1/2} \approx 50$ h for H–C(4).



13 **21**

The fastest exchanging proton H–C(7) of **13** finds a parallel in H–C(5)[4]) of tetrazolo[1,5-*a*]pyrazine (**22**), which exchanged rapidly in D_2O yielding **23** ($t_{1/2} \approx 12$ h at 94°). The exchange was instantaneous when a small amount of NaOD was added to the D_2O solution of **22**. The reaction even took place in pure CH_3OD, being completed in 48 h at 125°.



22 **23**

Thus summarizing, the exchange of the triazole ring proton in [1,2,3]triazolo-[1,5-*a*]azines may take place *via* the (diazomethyl)azines, or by a carbanion mechanism in the triazoles themselves. Exchange of the six-ring protons probably occurs *via* a carbanion mechanism in most cases.

This work was supported in Lausanne by the *Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung*, and in Marburg by the *Fonds der Chemischen Industrie.*

Experimental Part

General. Mass spectra (MS.) were recorded on a *CEC* 21-490 instrument using direct inlet at a source temp. of 200° and ionizing voltage of 70 eV, and are reported as *m/e* value followed by the relative abundance (% of base peak) in parenthesis. ^{1}H-NMR. spectra were recorded on a *Varian* A-60A or XL-100 instrument: chemical shift δ in ppm, coupling constants J in Hz. IR. absorptions are given in cm^{-1}, and λ_{max} of UV. spectra in nm (ε). Elemental analyses were performed by Mr. *Pfeiffer* of the microanalytical service of the *Fachbereich Chemie*, Marburg.

5-(2-Pyridyl)tetrazole (7) [27] was prepared by the method of *Finnegan et al.* [11]. MS.: 147 (M^+, 3.8), 119 ($M^+ - N_2$, 7.8), 105 ($M^+ - N_3$, 8.0), 104 ($M^+ - HN_3$, 2.2), 92 (8.3), 91 ($M^+ - 2\,N_2$, 100), 78 (25), 65 (10), 64 (32), 63 (20), 52 (14), 51 (20), 50 (19); m^* 56.5 ($M^+ - 2\,N_2$).

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[4]) In a preliminary communication [25] the exchanging proton of **22** was erroneously designated as H–C(6), although the NMR. spectrum of **22** had been correctly analysed previously [26].

Thermolysis of **7** (0.50 g) was carried out at 400°/10^{-3} Torr using the apparatus previously described [4]. Extraction of the thermolysate with cold ether gave a fraction containing cyclopentadienecarbonitrile [28] (≤3.4% yield) and aniline [28] (≤8% yield) together with non-identified aromatics. Column chromatography of the residue from the ether extraction (Al_2O_3; $CHCl_3$/MeOH 9:1) yielded azobenzene [28] (16.6% isolated yield), *[1,2,3]triazolo[1,5-a]pyridine* (**9**; 15%), and starting material **7** (10%). **9** was identified by comparison of its IR. and NMR. spectra and GC. retention time with those of an authentic sample [12].

5-(2-Pyrazinyl)tetrazole (**11**). A mixture of pyrazine-2-carbonitrile (**10**; 10.5 g, 0.10 mol), ammonium chloride (5.88 g, 0.11 mol), and sodium azide (7.16 g, 0.11 mol) in 100 ml of abs. dimethylformamide was stirred magnetically at 100° for 5.5 h. The solvent was distilled in vacuum, the residue dissolved in the minimum amount of water, and the resulting solution acidified to pH = 2 and then evaporated to dryness at 50–100°. The residue was extracted with boiling methanol, the extract evaporated, and the residue recrystallized from ethyl acetate, yielding 7.1 g (48%) of **11** as white crystals of m.p. 183° ([29]: 182–184°). – MS.: 148 (M^+, 100), 120 ($M^+ - N_2$, 34), 106 ($M^+ - N_3$, 26), 105 ($M^+ - HN_3$, 10), 93 (26), 92 ($M^+ - 2\,N_2$, 48), 79 (44), 78 (9), 68 (9), 67 (17), 66 (33), 65 (56), 64 (22), 63 (7), 53 (19), 52 (73), 51 (28), 41 (26), 40 (18), 39 (27), 38 (85), 37 (48); m^* 57 (148→92), 58 (148→93), 46 (92→65); doubly charged ions: 32.5 and 46.

$C_5H_4N_6$ (148.15) Calc. C 40.53 H 2.72 N 56.74% Found C 40.67 H 2.61 N 56.75%

[1,2,3]Triazolo[1,5-a]pyrazine (**13**). 2.4 g (0.016 mol) of **11** were thermolysed at 400°/10^{-5} Torr being sublimed into the thermolysis tube at 70°. The product was chromatographed on silica gel with $CHCl_3$/MeOH 9:1. The product of Rf 0.33 (TLC. on 0.20 mm SiO_2 60F 254, 'Alurolle', *Merck*) was sublimed at 100°/10^{-2} Torr and recrystallized from ethyl acetate, yielding **13** as colourless prisms of m.p. 126–126.5°. – UV. (96% EtOH): 274 (4860), 283 (4935), 300 sh. – IR. (KBr): 3010, 1640, 1530, 1490, 1460, 1365, 1335, 1280, 1225, 1190, 1180, 1105, 1030, 975, 905, 845, 820, 790, 750, 680, 650, 585, 435, 405. – NMR.: see the *Table*. – MS.: 121 ($M^+ + 1$, 5.8), 120 (M^+, 59), 93 (5.6), 92 ($M^+ - N_2$, 100), 66 (5.4), 65 (59), 64 (10), 52 (11.5), 51 (4.4), 41 (16), 40 (4.6), 39 (9.5), 38 (60), 37 (9); m^* 70.5 (120→92), 46 (92→65); doubly charged ions: 46 and 32.5.

$C_5H_4N_4$ (120.13) Calc. C 49.99 H 3.36 N 46.65% Found C 49.76 H 3.74 N 46.88%

2-Phenylquinazoline-4-carbonitrile (**14**). To a solution of 13 g (54 mmol) of 4-chloro-2-phenylquinazoline in 160 ml of abs. toluene were added 7 g of gaseous trimethylamine. The flask was stoppered and kept at RT. for one week, after which the precipitate was filtered off and dried in a desiccator: 11 g (36.7 mmol; 68%) of (2-phenyl-4-quinazolinyl)-trimethylammonium chloride, m.p. 155° (dec.) was obtained. This material was not examined further but added to a mixture of 14 g of acetamide and 8.6 g of potassium cyanide which had been previously fused at 130°. The resulting mixture was kept at 90° for 2 h, then diluted with water, and extracted several times with ether. After drying and evaporation of the solvent, the residue was recrystallized from ethanol yielding 6.8 g (80%) of **14**, m.p. 162–165°. Repeated recrystallization furnished a sample of m.p. 166–167° ([30]: 166–167°).

5-(2-Phenyl-4-quinazolinyl)tetrazole (**15**). A mixture of 5.1 g (22.1 mmol) of **14**, 1.6 g (24.6 mmol) of sodium azide, and 1.3 g (24.3 mmol) of ammonium chloride in 50 ml of abs. dimethylformamide was stirred magnetically at 100° for 5 h. The mixture was filtered, and the solution evaporated to dryness in high vacuum. The residue was dissolved in 10 ml of water and acidified to pH 2, which caused precipitation. Recrystallization from ethanol afforded 3.2 g (53%) of **15** as white crystals of m.p. 199–200° (dec.). – IR. (KBr): 3350 br., 1550, 1500, 1450, 1420, 1350, 1060, 870, 770, 710. – MS.: 275 ($M^+ + 1$, 15), 274 (M^+, 92), 246 (44), 232 (26), 231 (18), 219 (30), 218 (100), 206 (26), 205 (136); m^* 173.5 ($M^+ - 2\,N_2$), 194.5 ($M^+ - HN_3$).

$C_{15}H_{10}N_6$ (274.30) Calc. C 65.67 H 3.68 N 30.64% Found C 65.70 H 3.47 N 30.60%

5-Phenyl[1,2,3]triazolo[1,5-c]quinazoline (**17**). 250 mg (0.91 mmol) of **15** dissolved in 50 ml of abs. mesitylene were heated under reflux at 160° for 78 h. The solution was evaporated to dryness in high vacuum and the residue chromatographed on aluminium oxide 90 (activity II–III, *Merck*) with $CHCl_3$. Recrystallization from ethanol afforded 169 mg (75%) of **17** as white needles of m.p. 192–193° (dec.). – IR. (KBr): 1630, 1500, 1470, 1400, 1350, 1270, 1240, 970, 830, 780, 690. – NMR. ($CDCl_3$): 7.3–8.7 (*m*, arom. H); 8.4 (sharp peak, disappeared on stirring with D_2O at 135–145° (heterogeneous mixture) for

50 h, H–C(1)). – MS.: 247 ($M^+ + 1$, 9), 246 (M^+, 62), 219 (15), 218 (100), 217 (9), 190 (19), 115 (43), 114 (17), 88 (3); *m** 193 ($M^+ - N_2$), 165 ($M^+ - 2\,N_2$).

$C_{15}H_{10}N_4$ (246.27) Calc. C 73.16 H 4.09 N 22.75% Found C 72.97 H 3.70 N 22.87%

3-(2-Pyridyl)-1,2-cyclopropanedicarbonitrile (**19**). A solution of 1.298 g (10.91 mmol) of **9** and 8.109 g (103.96 mmol) of fumaronitrile in 545 g of diphenyl ether was heated at 164° until the evolution of N_2 had ceased (3 h). The solvent was distilled *in vacuo*, and the excess of fumaronitrile removed at 100–180° in high vacuum. The residue was extracted with boiling ether, the extract evaporated, and the remaining solid recrystallized from ether yielding 0.6 g (32%) of **19** as white crystals of m.p. 160°. – IR. (KBr): 3040*w*, 3005*s*, 2215*s*, 1580*s*, 1460*s*, 1440*s*, 1395*m*, 1300*m*, 1205*m*, 1070*m*, 1030*m*, 835*m*, 750*s*, 515*m*. – NMR. ($CDCl_3$; *ca.* 1:1 mixture of *cis/trans* isomers): 2.5–2.7 and 3.1–3.25 (*m*, 3 H, H–C(1), H–C(2), H–C(3)); 7.3 (*m*, H–C(5′)); 7.42 (*m*, $J_{(3',4')} = 7.5$, $J_{(3',5')} \approx J_{(3',6')} \approx 1$, H–C(3′)); 7.7 (*m*, $J_{(3',4')} \approx J_{(4',5')} \approx 7.5$, $J_{(4',6')} \approx 1.5$, H–C(4′)); 8.45 (*d*×*d*, $J_{(5',6')} = 5$, $J_{(3',6')} \approx 1$, $J_{(4',6')} \approx 1.5$, H–C(6′) of one isomer); 8.57 (*d*×*d*, $J_{(5',6')} = 5$, $J_{(4',6')} \approx 1$, H–C(6′) of one isomer). By spin decoupling it was shown that the pyridyl and cyclopropyl protons did not mutually couple, and that the two low-field absorptions at 8.45 and 8.57 belong to two different isomers. For chemical shifts of similarly substituted cyclopropanes, see [31]. – MS.: 170 ($M^+ + 1$, 11), 169 (M^+, 91), 168 (91), 143 ($M^+ - CN^\cdot$, 93), 142 ($M^+ - HCN$, 100), 118 (17), 115 ($M^+ - HCN - HCN$, 19), 93 (14), 78 (51), 64 (14), 63 (20), 62 (9), 52 (24), 51 (40), 50 (19); *m** 121 (168 → 142 or 169 → 143), 93 (142 → 115), 33 (78 → 51).

$C_{10}H_7N_3$ (169.20) Calc. C 70.98 H 4.18 N 24.84% Found C 71.21 H 4.27 N 24.79%

3-[^{2}H]-[1,2,3]Triazolo[1,5-a]pyridine (**20**). A solution of 45.5 mg (0.38 mmol) of **9** in 0.5 ml (25 mmol) of D_2O (99.7%) in a sealed NMR. tube was heated at 130° for 70 h. The signal corresponding to H–C(3) in the NMR. spectrum *(Table)* disappeared completely. The deuterated compound **20** was isolated by removal of the solvent *in vacuo*, and purified by column chromatography on *Florisil* with $CHCl_3$/ether 8:2. The process was reversed by a similar treatment of **20** with H_2O. – MS.: 121 (13), 120 (57), 119 (1.9), 93 (23), 92 (100), 91 (5.7). – MS. of unlabelled **9**: 120 ($M^+ + 1$, 10), 119 (M^+, 61), 92 (10), 91 (100).

3,4,7-[^{2}H]$_3$-[1,2,3]Triazolo[1,5-a]pyrazine (**21**). A solution of 52 mg (0.43 mmol) of **13** in 0.5 ml (25 mmol) of D_2O (99.7%) was heated in a sealed NMR. tube at 100°. The decrease of the signals of H–C(3), H–C(4), and H–C(7) was followed by NMR.; they had disappeared completely after 7 days. – NMR.: see the *Table*.

5-[^{2}H]-Tetrazolo[1,5-a]pyrazine (**23**). 45 mg (0.37 mmol) of **22** (m.p. 89–91° [26]) were heated in D_2O at 110° for 16 h, or in CH_3OD at 125° for 48 h. Evaporation of the methanol solution gave 45 mg of **23** as crystals of m.p. 86–89°. – NMR.: see the *Table*. – MS.: 123 ($M^+ + 1$, 4.3), 122 (M^+, 39), 121 (3.9), 95 (6.7), 94 ($M^+ - N_2$, 67), 93 (7.4), 67 (22), 66 ($M^+ - N_2 -$ DCN, 100), 65 (3.5), 54 (6.9), 53 (22), 52 (5.6), 47 ($M^{2+} - N_2$, 2.4), 42 (13), 41 (22), 40 (33), 39 (43), 38 (13). – MS. of unlabelled tetrazolo[1,5-*a*]pyrazine (**22**): 122 (1), 121 (M^+, 5), 94 (2.6), 93 (44), 92 (3), 67 (6), 66 (100), 65 (6), 53 (18), 52 (10), 51 (5), 46.5 ($M^{2+} - N_2$, 0.1), 42 (1.6), 41 (8.8), 40 (19), 39 (43), 38 (16).

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