

*Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

FLOW-VACUUM PYROLYSIS OF POLYCYCLIC COMPOUNDS.
27.¹ PYROLYSIS OF 8,9-DIHYDRO-14*H*-
TETRAZOLO[1,5*a*]DIBENZO[*c,f*]AZONINE
AND 6,7,8,9-TETRAHYDRO-TETRAZOLO[1,5*a*]BENZO[*c*]AZOCINE

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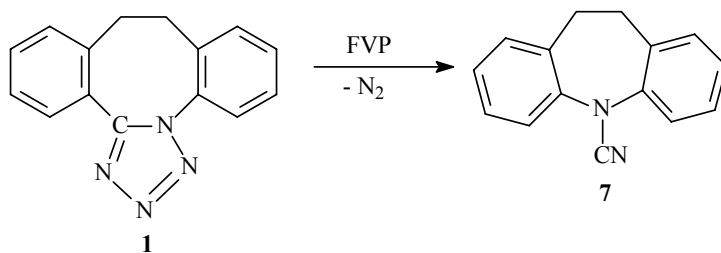
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The flow-vacuum pyrolysis (FVP) of 8,9-dihydro-14*H*-tetrazolo[1,5*a*]dibenzo[*c,f*]azonine (**13**) and 6,7,8,9-tetrahydro-tetrazolo[1,5-*a*]benzo[*c*]azocine (**14**) in quartz tube, inert atmosphere, between 300-550°C in vacuum was investigated using GC/MS. The corresponding cyanoderivatives (**19** and **21**) as stable reaction products, were separated and characterized by IR, ¹H-, ¹³C-NMR and mass spectroscopy. A radical mechanism explaining the formation of above mentioned reaction products was suggested.

INTRODUCTION

The substituted tetrazoles were detailed investigated²⁻⁴ in comparison with the benzoannulated ones. Flow-vacuum pyrolyses of such compounds were however thoroughly investigated by Wentrup research group.⁵⁻⁸ The scarcity of literature information about thermal behaviour of the annulated tetrazoles with benzocycloalkane skeleton was a reason for starting

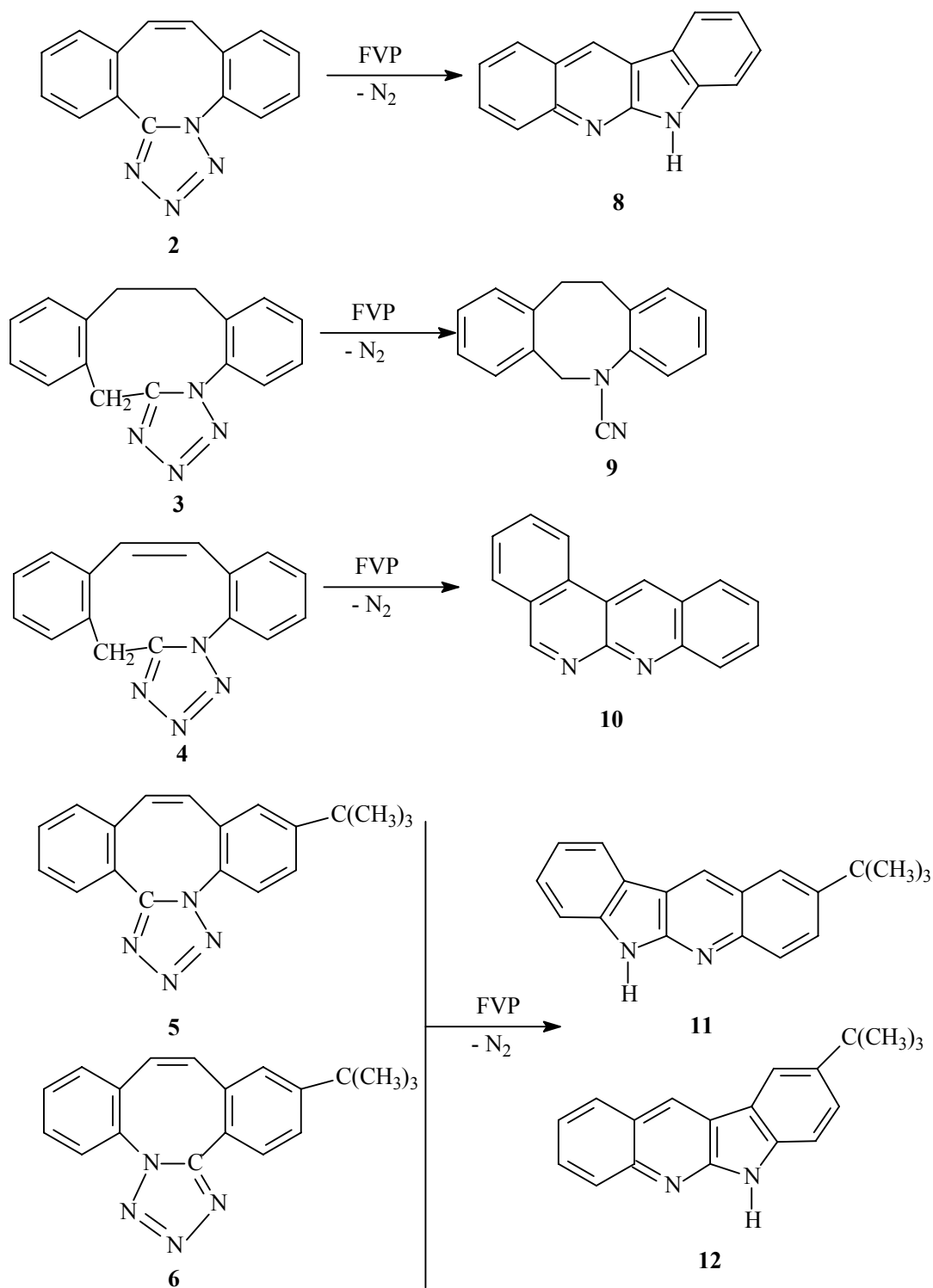
our study. In our previous work we observed a different thermal behaviour between the tetrazoles **1**,⁹ **3**,¹⁰ respectively **2**,⁹ **4**,¹⁰ **5**¹¹ and **6**.¹¹ Whereas tetrazoles **1** and **3**, with a saturated middle ring, afford as main products of pyrolysis the corresponding ring-contracted N-cyanoderivatives **7** and **9**, the middle ring unsaturated tetrazoles **2**, **4**, **5**, **6** allowing an extended conjugation gave quinindolines **8**, **11**, **12** and dibenzonaphthyridine **10** (Scheme 1).



Scheme 1

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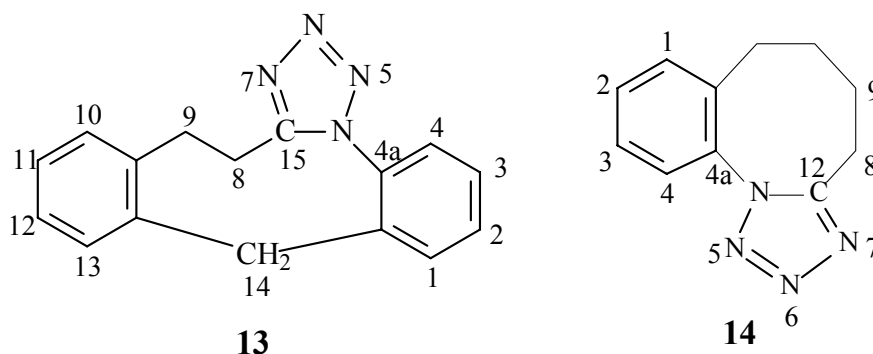
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Scheme 1 (continued)

In order to obtain new evidences concerning the thermal behaviour of benzocycloalkane annelated tetrazoles in pyrolysis reaction, we present herein the study of the flow-vacuum pyrolysis of title

tetrazoles: 8,9-dihydro-14*H*-tetrazolo[1,5*a*]dibenzo[*c,f*]azonine (**13**) and 6,7,8,9-tetrahydrotetrazolo[1,5*a*]benzo[*c*]azocine (**14**):



RESULTS and DISCUSSION

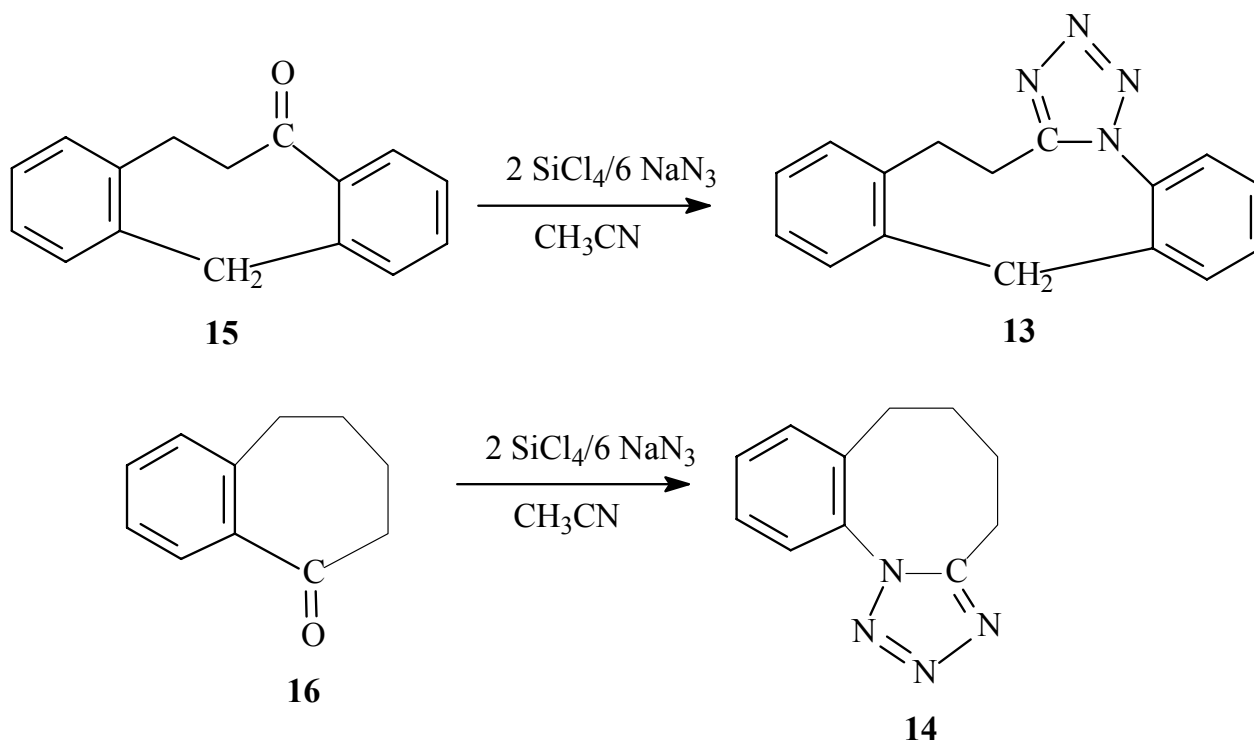
1. Syntheses

The compounds **13** and **14** were obtained by reaction of the corresponding ketone with triazidochlorosilane¹² generated *in situ* from silicon tetrachloride and sodium azide, at 25°C in anhydrous acetonitrile (Scheme 2).

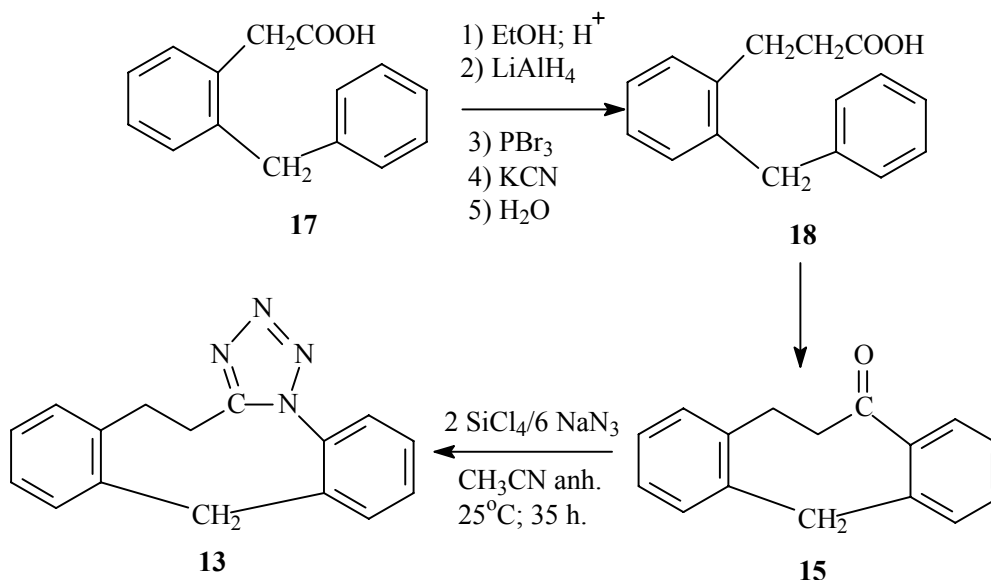
The synthesis of 8,9-dihydro-14*H*-tetrazolo[1,5*a*]dibenzo[*c,f*]azonine (**13**) was achieved using the reactions outlined in Scheme 3. Usual homologation of *o*-(benzyl)phenylacetic acid (**17**)¹³ conducted to the key-intermediate 5[2'-(benzyl)phenyl]propionic acid (**18**) (m.p. = 84-86°C) with identical spectral data to the published ones.¹⁴ Cyclisation of the acid **11** in presence of the

polyphosphoric acid, using previously described procedure¹⁴ afforded with 84% yield the 5*H*-11,12-dihydrodibenzo[*a,d*]cycloocten-10-one (**15**), m.p. 93-95°C, with all spectral data similar with reported ones.¹⁴ Treatment of ketone **15** with triazidochlorosilane generated *in situ* (molar ratio: ketone: SiCl₄: NaN₃ 1: 2: 6)^{12a} conducted to tetrazole compound **13** (m.p. 116-118°C, yield = 85%) after 35 hours, by magnetical stirring at 25°C. The spectral analyses IR and NMR were in agreement with proposed structure (*see* Experimental).

The synthesis of 6,7,8,9-tetrahydro-tetrazolo[1,5*a*]benzo[*c*]azocine (**14**) was performed from the corresponding ketone **16** using the same method and the spectral data were identical with the reported ones by us.^{12a}



Scheme 2



2. Pyrolyses

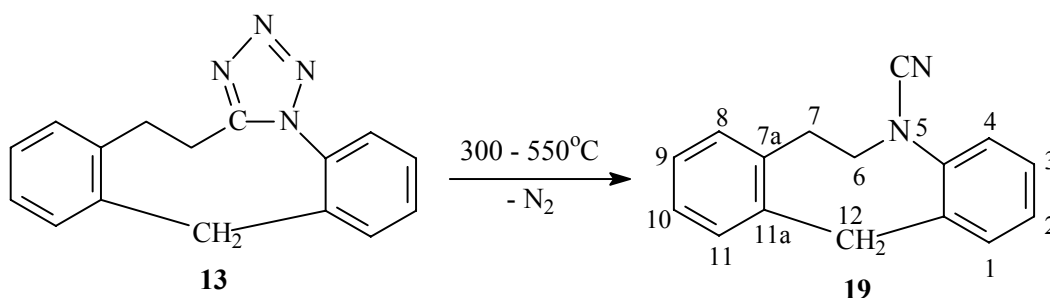
2.1. General procedure

For a good correlation of experimental data between the previous and present results, we performed the flow-vacuum pyrolyses of tetrazole derivatives **13**, **14** in the same described conditions:⁹ the pyrolysis quartz tube (60 cm length, 10 mm internal diameter) was filled with quartz chips on 30 cm length; this zone was heated with a cylindrical electric oven. The temperature was continuously measured by a thermocouple and the pressure (1-2 mm Hg) with a McLeod manometer. The sample (usually ~ 30 mg) was sublimed under argon flow (4 mL/min) in the pyrolysis tube. The reaction products were dissolved in dichloromethane, the solvent was evaporated *in vacuum* and the residue was analysed by GC/MS (*see* Experimental). Analytical pyrolyses at optimal temperature were followed by preparative runs in order to isolate the main products. The spectral analyses IR and NMR were used for characterisation of the structures of the isolated pyrolysis products.

2.2. Pyrolysis of 8,9-dihydro-14H-tetrazolo[1,5a]dibenzo[c,f]azonine (**13**)

The flow-vacuum pyrolyses of **13** were performed between 350-550°C, the crude reaction product (80% yield) was analyzed by GC/MS and 12*H*-6,7-dihydro-dibenzo[*b,e*]azocine-5-carbo-nitrile **19** (Scheme 4) was formed as major product (92%; only minor unidentified components were observed along with **19**). After recrystallisation from ethanol was obtained a solid product (m.p. 140 – 141°C) and the spectral data (IR and NMR, *see* Experimental) are in agreement with the proposed structure for **19**.

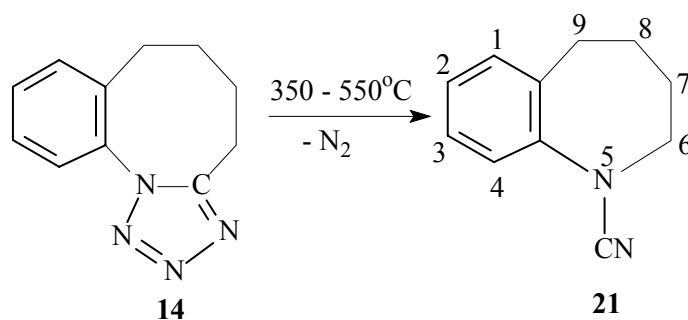
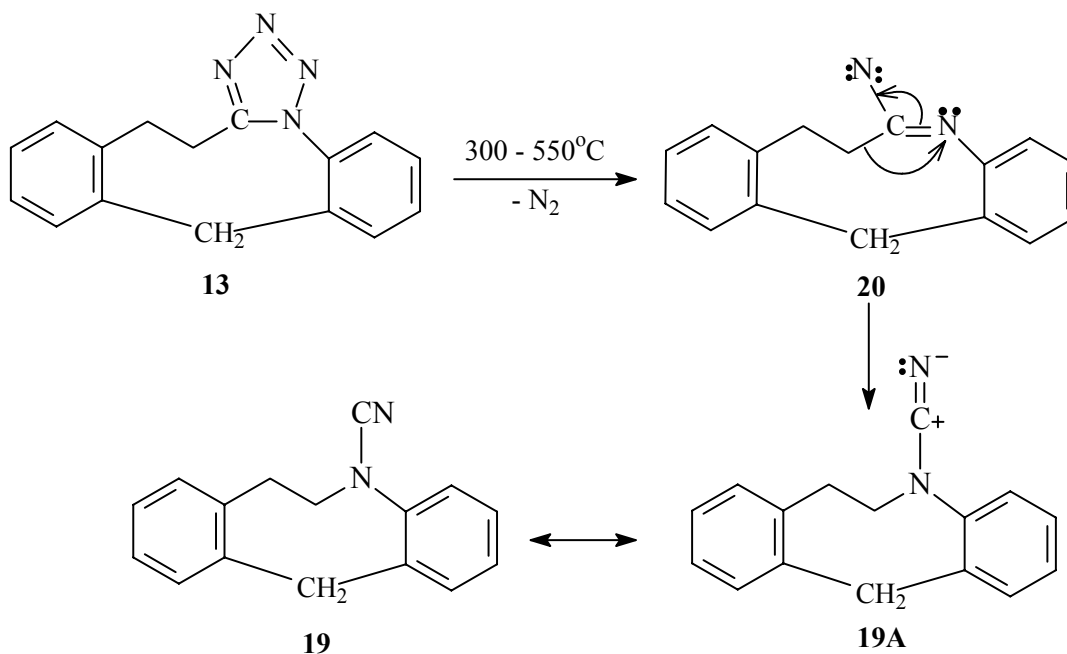
Formation of N-cyanoderivative **19** during flow-vacuum pyrolysis (FVP) of the tetrazole compound **13** could be explained by the radical reaction mechanism presented in Scheme 5, which is analogous to those proposed by us for generation of **7** from **1**⁹ and **9** from **3**.¹⁰ Thermal elimination of a nitrogen molecule affords the nitrene **20** which is prone to rearrangement into **19A**; this is a mesomeric form of the N-cyanoderivative **19**. The observation of Dreiding stereomodels shows the sterical easiness of the rearrangement step: **20** to **19A**.



2.3. Pyrolysis of 6,7,8,9-tetrahydro-tetrazolo[1,5a]benzo[c]azocine (**14**)

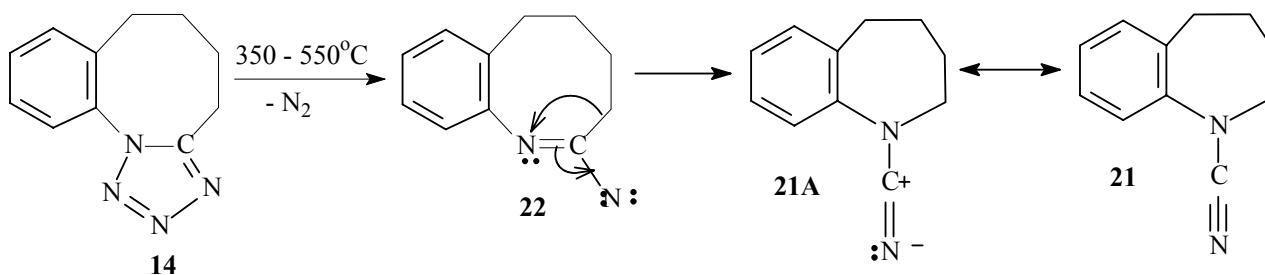
The thermal behaviour of the tetrazole ring annelated with monobenzoazocine was realized between 350 and 550°C in the same FVP conditions as presented for the tetrazole derivative **13**. We

separated the corresponding N-cyanoderivative **21** as main reaction product (yield 83%): white solid, m.p. 119-120°C after recrystallisation from methanol (Scheme 6). The spectral data IR and NMR were in agreement with the structure **21** (see Experimental).



The formation of N-cyanoderivative **21** is explained by the radicalic mechanism depicted in

Scheme 7 which is similar with those described in Scheme 5 for the thermal decomposition of **13**.



The first step is the elimination of a nitrogen molecule when is formed the nitrene **22**. This unstable intermediate suffers a rapid rearrangement into **21A**, a mesomeric form of the N-cyanoderivative **21**.

EXPERIMENTAL

1. Apparatus for physical analyses

Melting points are uncorrected. IR spectra were registered on a Bruker Equinox 55 spectrometer. The NMR spectra were registered at 300 MHz (^1H -) and 75 MHz (^{13}C -) on a Varian Gemini 300 apparatus using TMS as internal standard. The GC/MS analyses for pyrolyses of compounds **13** and **14** were performed on a QMD 1000 gas-chromatograph with split/splitless injector, coupled with Carlo Erba Instruments mass-spectrometer provided with quadrupole; a capillary factor four VF5ms column (30 m length, 0.25 mm internal diameter) was used. The analysis conditions were: injector temperature: 250°C; temperature program: 60°C for 2 minutes, 60-320°C at 10°C/min; carrier gas: helium (flow-rate of 1 mL/min); temperature of transfer line: 270°C; electron ionisation: 70 eV.

2. Syntheses

2.1. Synthesis of 8,9-dihydro-14H-tetrazolo[1,5a]dibenzo[*c,f*]azonine (**13**)

A mixture of corresponding ketone **15** (1 g, 4.5 mmoles), silicon tetrachloride (1.5 g, 8.95 mmoles) and sodium azide (1.7 g, 26.4 mmoles) in 20 mL anhydrous acetonitrile was magnetically stirred for 35 hours at 25°C. The reaction mixture was decomposed with crushed ice (30 g), 10% sodium carbonate solution was added until neutral pH and extracted with chloroform (3 x 25 mL). The combined organic layers were washed with water, dried over anhydrous magnesium sulfate, filtered and evaporated *in vacuo*. The solid residue was recrystallized from methanol: ethanol mixture (1: 1) affording the tetrazole **13**, 1.1 g (85% yield), m.p. 116-118°C.

IR spectrum (KBr, ν , cm^{-1}): 1081m (tetrazole ring); 1263w (N-N=N); 1496s; 1600w ($\nu\text{C}=\text{N}$); 2850w; 3025w; 3070w. (w – weak, m – medium, vi – very intense).

$^1\text{H-NMR spectrum}$ (CDCl_3 , δ , ppm), 62 °C: 2.20 (sl, 1H, H^8); 2.81 (m, 1H, H^8); 3.13 (m, 1H, H^9); 3.30 (m, 1H, $\text{H}^{9(9)}$); 4.10 (sl, 1H, $\text{H}^{14(14)}$); 4.33 (d, 15.1, $\text{H}^{14(14)}$); 6.80 – 7.60 (m, 8H_{arom}).

$^{13}\text{C-NMR spectrum}$ (CDCl_3 , δ , ppm), 62 °C: 28.49 (C^8); 30.78 (C^9); 34.57 (C^{14}); 126.89 (CH); 127.42 (CH); 127.47 (CH); 128.00 (CH); 130.08 (CH); 130.51 (CH); 130.88 (CH); 131.18 (CH); 132.25 (Cq); 132.64 (2Cq); 140.59 (Cq); 154.32 (C^{15}).

MS spectrum (m/e, relative abundance %): 39 (10); 51 (12); 63 (10); 77 (15); 78 (24); 89 (10); 91 (5); 104 (100, BP); 116 (8); 117 (9); 178 (5); 193 (5); 206 (5); 218 (30); 219 (17); 233 (65); 234 (49); 236 (6.5); 262 (0.2; M).

2.2. Synthesis of 6,7,8,9-tetrahydro-tetrazolo[1,5a]benzo[*c*]azocine (**14**)

The compound **14** was obtained by literature data^{12a} using the same method as described above for the tetrazole **13**: mixture of the benzosuberone **16** (3.4 g; 20 mmoles), silicon tetrachloride (6.8 g; 4.5 mL; 40 mmoles) and sodium azide (7.8 g; 120 mmoles) in 70 mL anhydrous acetonitrile was magnetically stirred for 35 hours at 25°C. After usual work-up, the compound **14** was obtained in 80% yield, m.p. 119-120°C

after recrystallization from methanol. The IR and NMR spectral data were similar with those described in literature.^{12a} The undetermined mass spectral data are presented here: 39 (12); 41 (15); 50 (20); 51 (30); 63 (30); 65 (15); 70 (12); 75 (13); 76 (26); 77 (38); 78 (26); 89 (78); 90 (50); 91 (31); 102 (39); 103 (44); 104 (21); 115 (93); 116 (100; BP); 117 (88); 118 (21); 127 (27); 128 (87); 129 (93); 130 (32); 131 (25); 143 (59); 144 (80); 145 (14); 171 (43); 172 (13); 200 (34; M).

3. Pyrolyses

3.1. Pyrolysis of 8,9-dihydro-14H-tetrazolo[1,5a]dibenzo[*c,f*]azonine (**13**)

The preliminary qualitative experiments were performed in a flow system using a previously described apparatus¹⁵ at variable temperature between 350 and 550°C and 1-2 mm Hg. At 550°C, the tetrazole was completely transformed. In order to establish the yield of this transformation, a sample of 40 mg tetrazole **13** was pyrolyzed at 550°C and the reaction product, a light yellow solid, was dissolved in dichloromethane and the solvent was evaporated. The GC/MS analysis of the residual product (28.4 mg, 80% yield) indicated as major product (92%) N-cyanoderivative **19**. Preparative runs permitted the separation of this compound with m.p. 140 – 141°C after recrystallisation from ethanol.

IR spectrum (KBr, ν , cm^{-1}): 759m; 1459m; 1497m; 1679m; 2113vi; 2867w; 2934m; 3068w.

$^1\text{H-NMR spectrum}$ (CDCl_3 , δ , ppm): 1.78 (m, 2H, $\text{H}^{7,7}$); 1.83 (m, 2H, $\text{H}^{8,8}$); 2.9 (t, 2H, $\text{H}^{9,9}$); 3.55 (t, 2H, $\text{H}^{6,6}$); 6.95 – 7.14 (m, 4H, H_{arom}).

$^{13}\text{C-NMR spectrum}$ (CDCl_3 , δ , ppm): 25.90 (C^7); 29.78 (C^8); 32.57 (C^9); 49.24 (C^6); 124.66 (CH); 124.98 (CH); 127.59 (CH); 130.18 (CH); 138.18 (CN).

MS spectrum (m/e, relative abundance %): 51 (10); 77 (12); 89 (15.7); 90 (15.5); 91 (13); 103 (16.4); 104 (10); 115 (13); 116 (31.6); 117 (71); 118 (28); 130 (17.6); 131 (28); 132 (10); 143 (22); 144 (78); 145 (21); 171 (100, BP); 172 (52; M); 173 (5.2; M+1); 174 (0.4; M+2).

3.2. Pyrolysis of 6,7,8,9-tetrahydro-tetrazolo[1,5a]benzo[*c*]azocine (**14**)

The azocine **14** was pyrolysed in the same described conditions for azonine **13**. At 550°C, the azocine **14** was total decomposed and the corresponding N-cyanoderivative **21** was separated as main reaction product (yield 83%): white solid, m.p. 119-120°C after recrystallisation from methanol.

The spectral data for N-cyanoderivative **21**:

IR spectrum (KBr, ν , cm^{-1}): 759m; 1459m; 1678w; 2113 vi (CN); 2934m;

$^1\text{H-NMR spectrum}$ (CDCl_3 , δ , ppm): 1.78 (m, 2H, $\text{H}^{7,7}$); 1.83 (m, 2H, $\text{H}^{8,8}$); 2.9 (t, 2H, $\text{H}^{9,9}$); 3.55 (t, 2H, $\text{H}^{6,6}$); 7.1 (m, 4H, H_{arom}).

$^{13}\text{C-NMR spectrum}$ (CDCl_3 , δ , ppm): 25.9 (C^7); 29.78 (C^8); 32.57 (C^9); 49.24 (C^6); 124.66 (CH); 124.98 (CH); 127.59 (CH); 130.71 (CH); 138.18 (CN).

MS spectrum (m/e, relative abundance %): 39 (59); 41 (18.5); 50 (23); 51 (35); 63 (26); 65 (16); 77 (35); 89 (45); 90 (29); 91 (20); 103 (37); 115 (24); 116 (39); 117 (61); 130 (37); 131 (22); 143 (24); 144 (78); 145 (12); 171 (100, BP); 172 (M, 25); 173 (M+1, 2).

CONCLUSIONS

In this work we presented the synthesis of 8,9-dihydro-14H-tetrazolo[1,5a]dibenzo[*c,f*]azonine (**13**)

and a comparison between the thermal behaviour in flow-vacuum pyrolysis of two tetrazoles annelated with dibenzoazonine (**13**) and respectively benzoazocine (**14**) skeleton. It was proved that the annelated tetrazoles **13** and **14** with the saturated dibenzoazonine middle ring and respectively with benzotetrahydroazocine moiety have a similar thermal behaviour with the saturated analogs **1**⁹ and **3**.¹⁰ The main pyrolysis reaction products were the corresponding N-cyanoderivatives (**19** and respectively, **21**). The first step of the thermal decomposition in FVP conditions of tetrazole derivatives **13** and **14** is the elimination of a nitrogen molecule when are formed the corresponding nitrenes (**20**, and respectively, **22**). By rearrangement, these unstable intermediates form the corresponding N-cyanoderivatives, **19** and **21**, as stable compounds, in good yields (80% and respectively, 83% as major pyrolysis reaction products). The observation of Dreiding stereomodels shows the sterical easiness of the rearrangement step **20** to **19A** and respectively, **22** to **21A**.

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REFERENCES

1. Part 26 in this series: D. Istrati, A. Popescu, L. Părvulescu, E. Andrei, C. Drăghici and C. Ciuculescu, *Rev. de Chimie (Bucuresti)*, **2008**, *59*, 564-568.
2. R.N. Butler, in A.R.Katritzky, C.W. Rees (Eds.), "Comprehensive Heterocyclic Chemistry", vol.5, Pergamon Press, Oxford, 1984, p. 628, 791 – 838.
3. R.N. Butler, *Adv. Heterocyclic Chem.*, **1977**, *21*, 323 – 435.
4. R.F.C. Brown, "Pyrolytic Methods in Organic Chemistry", Academic Press, New York, 1980, 153 – 158.
5. W.D. Crow and C. Wentrup, *Chem. Commun.*, **1968**, 1082.
6. C. Wentrup, *Tetrahedron*, **1971**, *27*, 367 - 374.
7. C. Wentrup, *Top. Curr. Chem.*, **1976**, *62*, 173- 251.
8. C. Wentrup, *Adv. Heterocycl. Chem.*, **1981**, *28*, 231-361.
9. M.D. Banciu, A. Popescu, A. Simion, C. Drăghici, C. Mangra, D. Mihăiescu and M. Pocol, *J. Anal. Appl. Pyrolysis*, **1999**, *48*, 129 – 146.
10. A. Popescu, D. Istrati, C. Drăghici, A. Banciu, D. Mihăiescu, C. Ciuculescu, A. Britchi and M.D. Banciu, *Rev. Roum. Chim.*, **2001**, *46*, 181 – 186.
11. A. Popescu, A. Lari, A. Banciu, C. Drăghici, D. Ciuculescu, D. Istrati and M. D. Banciu, *Rev. Roum. Chim.*, **2006**, *51*, 345-350.
12. a) M.D. Banciu, C. Drăghici, A. Popescu, A. Banciu and A. Simion, *Rev. Roum. Chim.*, **1998**, *43*, 649; b) A.A.S. El-Ahl, S.S. Elmorsy, H. Soliman and F.A. Amer, *Tetrahedron*, **1995**, 7337 – 7340.
13. J. Fouche, J.C. Blondel, R. Horelois, C. James, A. Leger and G. Poignet, *Bull. Soc. Chim. France*, **1972**, 3113.
14. M.D. Banciu, L. Părvulescu, A. Banciu, A. Simion, C. Costea, C. Drăghici, M. Pop and D. Mihăiescu, *J. Anal. Appl. Pyrolysis*, **2001**, *57*, 261-274.
15. M.D. Banciu, E. Olteanu, C. Drăghici, A. Petride, M. Dănilă, *J. Anal. Appl. Pyrolysis*, **1996**, *37*, 151.

