ХИМИЧЕСКИЕ НАУКИ / CHEMICAL SCIENCES
Оригинальная статья / Original article
УДК 547.796.1, 547.772.1
DOI: 10.21285/2227-2925-2017-7-1-9-18

ОДНОРЕАКТОРНЫЙ МЕТОД СИНТЕЗА ПРОИЗВОДНЫХ 5-(ПИРАЗОЛ-1-ИЛ)-ТЕТРАЗОЛА ИЗ 5-АМИНОТЕТРАЗОЛА

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Рассмотрены реакции конденсации 5-гидразинотетразола с β-дикарбонильными соединениями (малоновый диальдегид и ацетилацетон). Синтезировано и описано 12 новых соединений. Для получения 5-гидразинотетразола использована реакция окисления коммерчески доступного 5-аминотетразола перманганатом калия в водно-щелочном растворе до пентагидрата 5,5'-азотетразолата с последующим проведением реакции разложения полученного соединения в кислой среде до 5-гидразинотетразола. Предложен однореакторный метод проведения стадии получения производных 5-(пиразол-1-ил)тетразолов из 5-аминотетразола. Согласно предложенному методу после проведения реакции конденсации с β-дикарбонильным соединением реакционная масса обрабатывалась эквимолекулярным количеством брома, целевые соединения выделялись из реакционной массы в виде соответствующих малорастворимых в воде 4-бромпроизводных 5-(пиразол-1-ил)тетразола. Наличие атома брома в полученных соединениях существенно облегчает процессы их выделения, перекристаллизации и проведения реакций алкилирования тетразольного цикла. Дебромирование осуществлялось гидрированием водородом с использованием палладиевого катализатора при умеренных давлениях. Для получения 4-нитропроизводных 5-(пиразол-1-ил)тетразола использовано нитрование в системе HNO_3/H_2SO_4. Восстановлением нитрогруппы гидрированием над палладиевым катализатором получены соответствующие 4-аминопроизводные-5-(пиразол-1-ил)тетразола.
Ключевые слова: тетразол, пиразол, нитрование, бромирование, дебромирование, гидрирование.

Формат цитирования: Степанова Е.В., Степанов А.И. Однореакторный метод синтеза производных 5-(пиразол-1-ил)тетразола из 5-аминотетразола // Известия вузов. Прикладная химия и биотехнология. 2017. Т. 7, N 1. С. 9–18. DOI:10.21285/2227-2925-2017-7-1-9-18

ONE-POT SYNTHESIS OF 5-(4-PYRAZOLE-1-YL)TETRAZOLE DERIVATIVES FROM 5-AMINOTETRAZOLE

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Condensation reactions of 5-hydrazinotetrazole with malonic dialdehyde and acetylacetone are considered. 12 new derivatives of 5-(pyrazole-1-yl)tetrazoles were synthesized and characterized. Commercially available 5-aminotetrazole was oxidized by potassium permanganate in aqueous alkaline solution yielding 5,5'-azotetrazolate pentahydrate which was decomposed in acidic media to 5-hydrazinotetrazole. One-pot procedure is suggested to prepare the 5-(pyrazole-1-yl)tetrazole derivatives from 5-aminotetrazole. According to introduced method after carrying out condensation with β-carbonyl compounds reaction mixture was treated by an equivalent amount of bromine. Target products were separated from the reaction mixture as corresponding 4-bromoderivatives of 5-(pyrazole-1-yl)tetrazoles. The presence of a bromine atom in structure of synthesized compounds greatly facilitates processes of their isolation, purification and further alkylation of tetrazole ring. Debromination was realized by hydrogenation over palladium catalyst by hydrogen at

moderate pressure. For synthesis of 4-nitroderivatives of 5-(pyrazole-1-yl)tetrazoles nitration in system HNO_3/H_2SO_4 was used. 5-(4-amino-3,5-dimethylpyrazole-1-yl)tetrazole was prepared by the reduction of 5-(4-nitro-3,5-dimethylpyrazole-1-yl)tetrazole.
Keywords: tetrazole, pyrazole, nitration, bromination, debromination, hydrogenation

For citation: Stepanova E.V., Stepanov A.I. One-pot synthesis of 5-(4-pyrazole-1-yl)tetrazole derivatives from 5-aminotetrazole. *Izvestiya Vuzov. Prikladnaya Khimiya i Biotekhnologiya* [Proceedings of Universities. Applied Chemistry and Biotechnology]. 2017, vol. 7, no. 1, pp. 9–18. DOI: 10.21285/2227-2925-2017-7-1-9-18 (in English).

INTRODUCTION

For the first time chemical compounds with terazole ring were synthesized in 1885 [1]. At the present time interest in tetrazole chemistry is called forth due to the possibility of widespread usage of these compounds as corrosion inhibitors, plant protection products, analytical reagents, materials for photochemistry [2], or as components of gas generating compositions and as energetic materials [3, 4].

Nevertheless analysis of the current chemical literature shows certain lack of attention for the studying of the chemical properties of 5-hydrazinotetrazole (**1**), which is largely restricted by the works of the close of 19th century. Thus, in papers by Thiele there were described hydrazones formation reactions of compound **1** with benzaldehyde [5], acetophenone and acetone [6], acetoacetic ester [5], preparation of 1-(tetrazol-5-yl)semicarbazide, triacetyl derivative of 5-hydrazinotetrazole [6], 5-azidotetrazole [6] (see also ref. [7]). In latter works, the condensation of hydrazinotetrazole **1** with formaldehyde [8], some carbonyl compounds [9–14] as well as the reaction with dicyandiamide (DCADA) [15] were discussed (Fig.1).

Now 5-hydrazinotetrazole (**1**) is considered mainly as a constituent of energy rich high enthalpy compounds, for example, as a cationic constituent in a number nitrogen rich energetic salts [16], as a ligand in complex salts for priming explosives with heavy metals [17–19].

Condensation reactions of 5-aminotetrazole with *β*-dialdehydes and *β*-diketones result in pyrazole ring formation have not previously been considered. The aim of present work is to develop on the basis of chemistry of 5-aminotetrazole accessible methods for the synthesis of derivatives of 5-(pyrazol-1-yl)tetrazole.

RESULTS AND DISCUSSION

For the synthesis of 5-(pyrazol-1-yl)tetrazoles we used condensation reaction of 5-hydrazinotetrazole **1** with *β*-dicarbonyl compounds: acetylacetone and malonic dialdehyde (Scheme 2). Due to a low stability of malonic dialdehyde we used in the condensation reaction its diacetal – 1,1,3,3-tetramethoxypropane (Scheme 2).

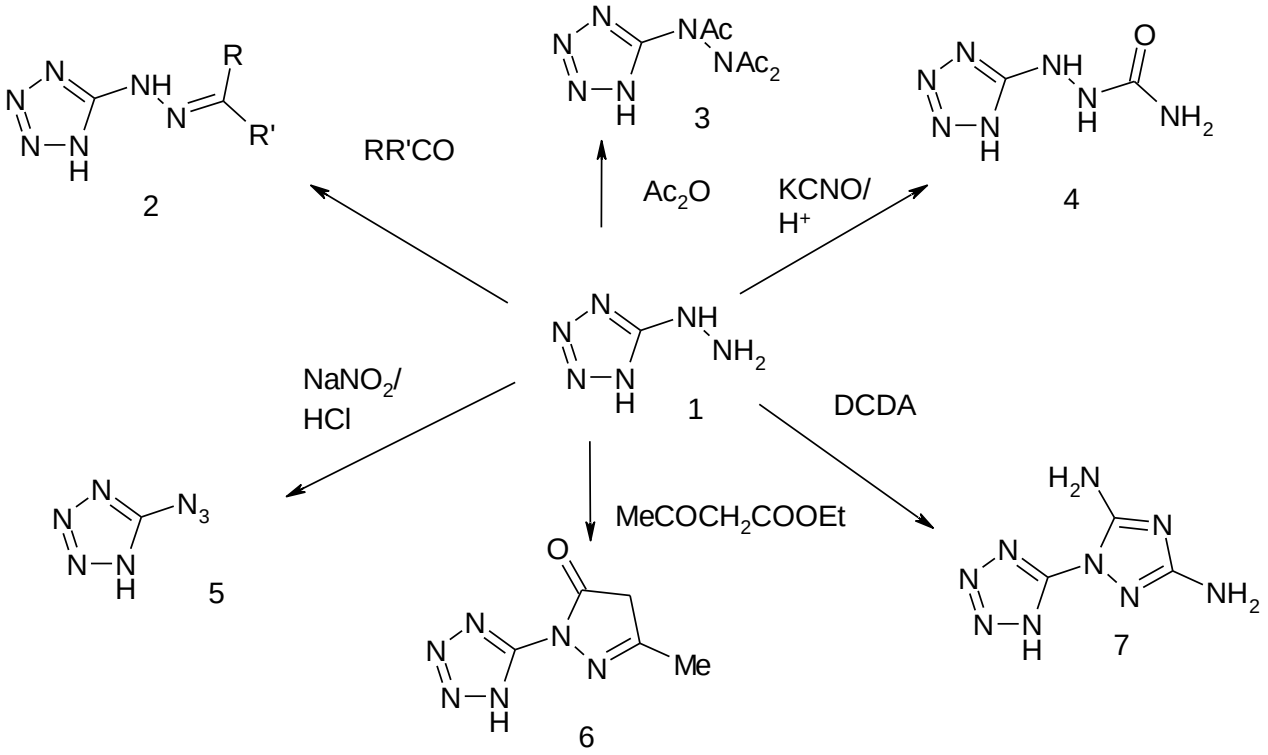

Fig. 1. Compounds derived from 5-hydrazinotetrazole (1)

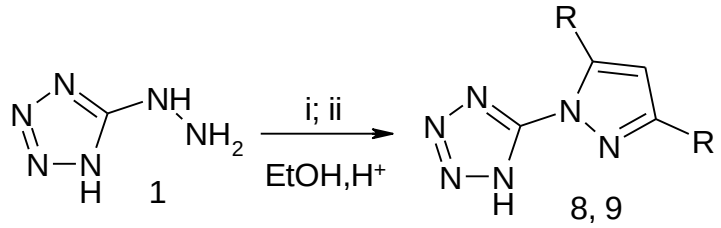

Fig. 2. Reaction of 5-hydrazinotetrazole (1) with β-dicarbonyl compounds (8, i $(MeO)_2CH_2(OMe)_2$; 9, ii $MeCOCH_2COMe$)

It should be noted, that in *praesenti* the only acceptable synthetic route for 5-hydrazinotetrazole is based on Thiele method [20] from 5-aminotetrazole (**10**) (Fig. 3). Due to high water solubility, the procedure for isolation of target product **1** from reaction mass is quite laborious and includes distillation of water from the reaction mixture in *vacuo* followed by separation of the target product by extraction of solid residual with hot methanol.

Since the main byproducts in the synthesis of

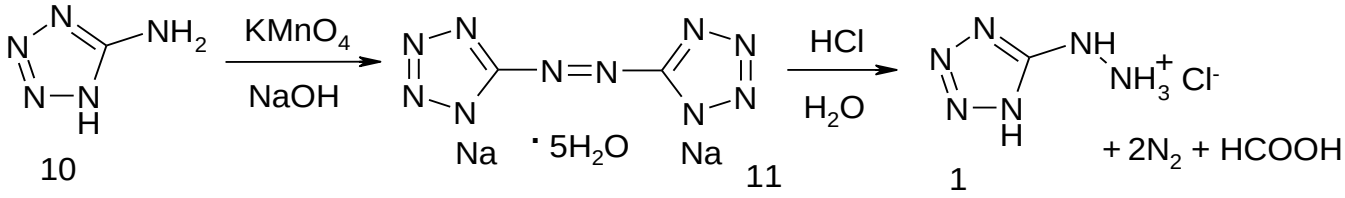

Fig. 3. Preparation of 5-hydrazinotetrazole (1)

5-hydrazinotetrazole (**1**) includes only inorganic salts and formic acid we considered the possibility of involving compound **1** in synthesis without its isolation from reaction mixture. As a result of our studies it was found that pyrazoles **8**, **9** could be obtained with good preparative yields directly from 5-aminotetrazole and corresponding *β*-dicarbonyl compounds bypassing the steps of 5-hydrazinotetrazole (**1**) isolation and purification. The stages of 5-aminotetrazole oxidation, hydrolysis of intermediate azobistetrazole **11** and the coupling reaction were carried out by one-pot synthesis. However, rather high water solubility of thus prepared pyrazoles **8**, **9** sets up certain difficulties in their separation from reaction mixture. In this case, addition of one mole of bromine to the reaction mixture allows isolating the corresponding pyrazoles in a form of sparingly soluble in water 4-bromoderivatives **12**, **13** with near quantitative yields (Fig. 4). In the sequel pyrazoles **8**, **9** may be recovered from 4-bromoderivatives **12**, **13** by catalytic hydrogenation by hydrogen in an alcohol (Fig. 5).

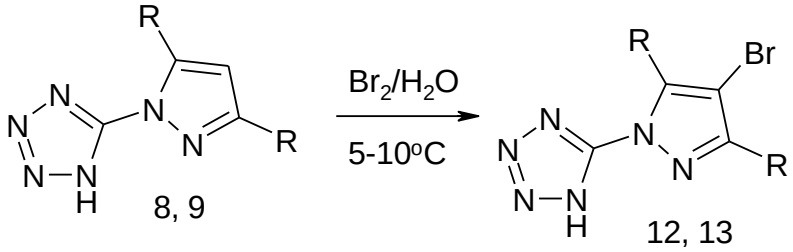

Fig. 4. Bromination of 5-(pyrazole-1-yl)tetrazoles 8, 9 (8, 12 R = H; 9, 13 R = Me)

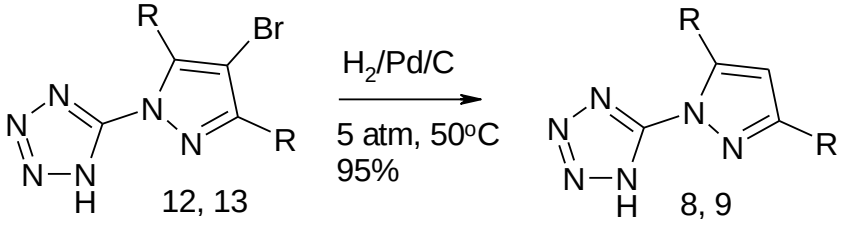

Fig. 5. Hydrogenation of 5-(4-bromopyrazole-1-yl)tetrazoles 12, 13 (8, 12 R = H; 9, 13 R = Me)

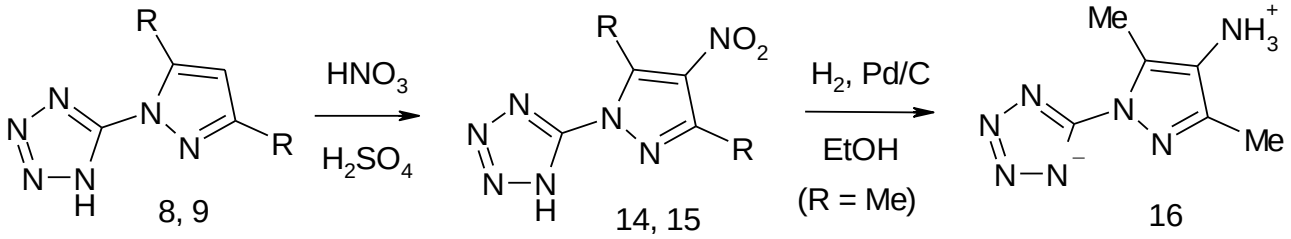

Fig. 6. Nitration of 5-(pyrazole-1-yl)tetrazoles 8, 9 (8, 14 R = H; 9, 15, 16 R = Me)

Compounds **8**, **9** readily undergo electrophilic nitration reactions at position C-4 of the pyrazole ring. Reduction of nitro group in compound **15** was used in the synthesis of 5-(4-amino-3,5-dimethylpyrazole-1-yl)tetrazole **16**. According NMR data compound **16** forms internal salt (Fig. 6). We did not succeed isolation from reaction mixture hydrogenation product of compound **14** because of its rapid oxidation by atmospheric oxygen.

It is well known that alkylation of tetrazoles passes through *N*-1 and *N*-2 atoms of tetrazole ring [21]. Alkylation of compounds **8**, **9** proved certain difficulties in the separation of alkylated isomeric compounds by crystallization. Contrariwise, the alkylation of bromoderivative **13** by chloroacetamide, ethylene chlorohydrin proceeds relatively selectively on *N*-2 atom of tetrazole ring (Fig. 7). The content of isomeric alkylation byproducts according to ^1H NMR spectroscopy data was 3–5%. Protons signals of N1-CH2 group of the second regioisomer are shifted in a strong field at 0.15–0.20 ppm.

Hydrogenation of compound **17** results in replacement of bromine atom by hydrogen one. It should be noted that the presence in its structure bromine atom greatly facilitates the process of isolation from reaction mixture and carrying out further purification by recrystallisation due to decreasing the solubility of parent compound **17** in common organic solvents, and this way is probably more convenient method for the synthesis of *N*-alkylated derivatives of tetrazolylpyrazoles **8**, **9** in comparison with their direct alkylation. Similarly, the separation of initial pyrazoles **8**, **9** through the steps of bromination and subsequent hydrogenation of bromoderivatives **12**, **13** increases the yield by 10–15% in comparison of their direct isolation from the reaction mixture after condensation of 5-hydrazinotetrazole with dicarbonyl compounds.

Spectral data of the obtained compounds are presented in Table.

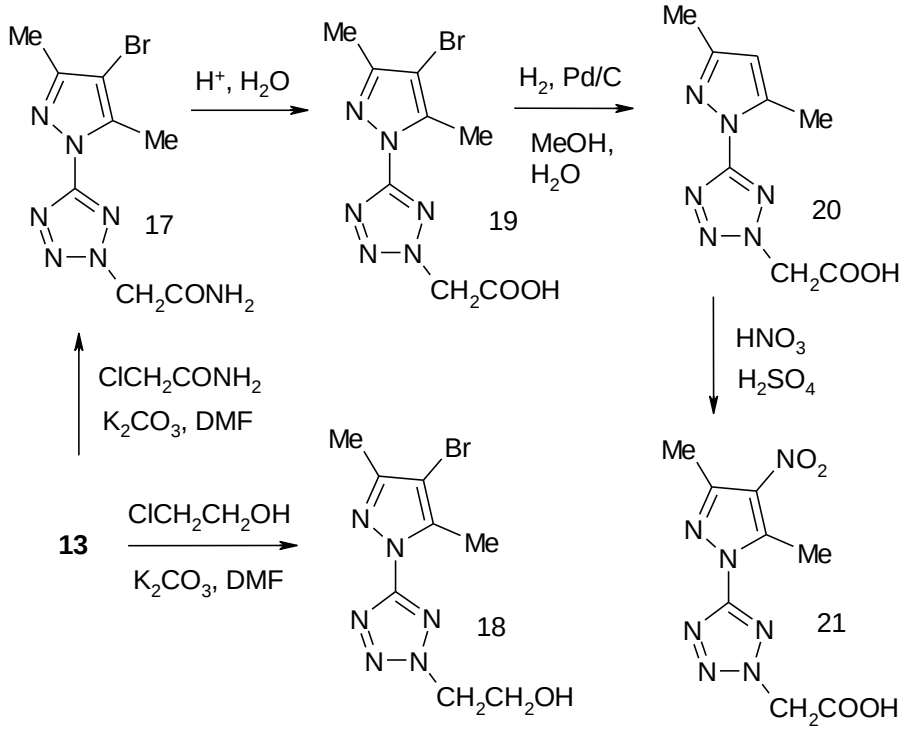

Fig. 7. Alkylation of 5-(4-bromo-3,5-dimethylpyrazole-1-yl)tetrazole 13

NMR and MS spectral data of 5-hydrazinotetrazole derivatives

Compound, No	NMR-^{13}C, δ, ppm,				NMR-^{1}H, δ, ppm.	MS, *m/z* (I_{rel}, %)
	tetrazole ring	pyrazole ring (*C*3, *C*4, *C*5)	*R*, *R* (pyrazole ring)	*N*2-*R*' (tetrazole ring)		
1	158.8	–	–	–	8.29	–
8	155.2	144.4; 110.0; 131.0	–	–	8.53 (1H, *d*, *J*2.51 *Hz*, C5H); 8.00 (1H, *d*, *J*2.51 *Hz*, C3H); 6.70 (1H, *m*, C4H)	108 (3) $[M - N_2]^+$; 79 (15); 54 (11); 53 (100); 52 (99); 51 (52); 41(45); 40 (40); 39 (74); 38 (85); 37 (29); 28 (100) $[N_2]^+$
9	153.8	152.7; 110.0; 142.9	13.62; 12.90	–	6.24 (1H, *s*, C4H); 2.56 (3H, *s*, $C5CH_3$); 2.24(3H, *s*, $C3CH_3$)	165 (0.6) $[M + 1]^+$; 164 (7) $[M]^+$; 136(1) $[M - N_2]^+$; 95 (52.4) [3,5-diMe-pyrazole]$^+$; 93 (12); 67(16); 66(53); 65 (20); 52 (15); 51 (13); 42 (44); 41 (49); 40 (44); 39 (100); 38 (21); 29 (37)
12	155.9	144.5; 97.35; 131.1	–	–	8.82 (1H, *s*, C5H); 8.14 (1H, *s*, C3H)	216 (9) $[M(^{81}Br)]^+$; 214 (9) $[M(^{79}Br)]^+$; 188 (5) $[M(^{81}Br) - N_2]^+$; 186 (4) $[M(^{79}Br) - N_2]^+$; 106 (25); 104 (24); 81 (12); 79 (28); 53 (30); 52 (70); 51 (90); 41 (35); 39 (30); 38 (100); 37 (25); 28 (73) $[N_2]^+$
13	154.5	150.9; 99.01; 140.6	12.60; 12.25	–	2.55 (3H, *s*, $C5CH_3$); 2.24 (3H, *s*, $C3CH_3$)	175 (5) [4-Br-3,5-Me_2-pyrazole]$^+$; 135 (10); 95 (18); 67 (13); 66 (20); 65 (54); 64 (24); 63 (19); 52 (16); 51 (14); 42 (36); 41 (42); 40 (27); 39 (100); 38 (26); 29 (76); 28 (17) $[N_2]^+$
14	157.3	139.1; 137.9; 131.0	–	–	13.2-12.2, 12.1-10.7 (0.3H + 0.7H, br.*s*, NH); 9.56, 9.55 (0.7 + 0.3H, *s*, C5H); 8.72, 8.71 (0.7H + 0.3H, *s*., C3H)	182 (5) $[M + 1]^+$; 181 (42) $[M]^+$; 153 (100) $[M - N_2]^+$; 79 (10); 52 (14); 51 (10); 30 (22); 29 (31)
15	155.9	148.5; 133.2; 144.4	14.25; 12.86	–	12.0-9.50 (1H, br.*s*, NH); 2.86 (3H, *s*, $C5CH_3$); 2.52 (3H, *s*, $C3CH_3$)	209 (2) $[M]^+$; 192(3); 181(3) $[M - N_2]^+$; 67 (15); 66 (18); 65 (57); 64 (16); 63 (18); 53 (19); 52 (22); 51 (15); 46(29) $[NO_2]^+$; 43 (21); 42 (69); 41 (52); 40 (31); 39 (100); 38 (23); 30 (96); 28 (20) $[N_2]^+$
16	155.3	144.4; 127.3; 124.7	–	11.43; 10.47	8.30-5.5 (3H, s, NH_3^+); 2.41(3H, s, $C5CH_3$); 2.18 (3H, s, $C3CH_3$)	180 (1.3) $[M + 1]^+$; 179(14) $[M]^+$; 111 (13); 110 (24) [4-NH_2-3,5-Me_2-pyrazole]$^+$; 109 (26); 70 (20); 54 (27); 53 (19); 43 (24); 42 (100); 41 (28); 29 (21); 28 (51) $[N_2]^+$
17	160.8	150.1; 98.24; 140.3	11.62; 11.97	166.1 (C=O); 55.72 (CH_2)	7.88, 7.59 (2H, *s*, NH_2); 5.50 (2H, *s*, CH_2); 2.48 (3H, *s*, $C5CH_3$); 2.24 (3H, *s*, $C3CH_3$)	302 (3) $[M(^{81}Br)+1]^+$; 301 (23) $[M(^{81}Br)]^+$; 300 (3) $[M(^{79}Br)+1]^+$; 299 (20) $[M(^{81}Br]^+$; 229 (11); 227 (13); 201 (19); 199 (18); 176 (35) [4-^{81}Br-3,5-Me_2-pyrazole)]$^+$; 174 (35) [4-^{81}Br-3,5-Me_2-pyrazole)]$^+$; 65 (20); 44 (100) $[H_2NCO]^+$; 42 (33) $[CH_2CO]^+$; 39 (31); 30 (40)
18	160.8	149.9; 98.11; 140.2	12.59; 11.93	59.39 (CH_2); 57.01 (CH_2)	4.76 (2H, *t*, *J*5.27 *Hz*, CH_2); 3.96 (2H, *d*, *J*5.14 *Hz*, CH_2); 2.48 (3H, *s*, $C5CH_3$); 2.23 (3H, *s*, $C3CH_3$)	289 (3) $[M(^{81}Br) + 1]^+$; 288 (26)$[M(^{81}Br)]^+$; 287 (3) $[M(^{79}Br) + 1]^+$; 286 (25) $[M(^{79}Br)]^+$; 229 (22); 227 (20); 201 (34); 199 (30); 176 (85); 174 (87); 148 (20); 120 (19); 80 (20); 67 (39); 66 (20); 65 (24); 45 (60); 43 (32); 42 (41); 39 (70); 31 (100) $[CH_2OH]^+$; 29 (53); 27 (67)
19	160.9	150.2; 98.35; 140.3	12.62; 11.97	167.5 (COOH); 54.71 (CH_2)	5.78 (2H, *s*, CH_2); 2.49 (3H, *s*, $C5CH_3$); 2.24 (3H, *s*, $C3CH_3$)	303 (2) $[M(^{81}Br) + 1]^+$; 302 (27) $[M(^{81}Br)]^+$; 301 (3) $[M(^{79}Br) + 1]^+$; 300 (27) $[M(^{79}Br)]^+$; 201 (22); 199 (23); 176 (77) [4-^{81}Br-3,5-Me_2-pyrazole]$^+$; 174 (83) [4-^{79}Br-3,5-diMe-pyrazole]$^+$; 95 (17); 79 (16); 67 (57); 65 (22); 64 (21); 59 (28); 45 (65); 43 (20); 42 (44);

						40 (22); 39 (71); 38 (20); 31 (100) $[CH_2OH]^+$; 29 (20); 28 (29); 27 (30)
20	161.3	151.6; 109.2; 142.3	13.68; 12.57	167.6 (COOH); 54.59 (CH_2)	6.21 (1H, *s*, C4H); 5.74 (2H, *s*, CH_2); 2.46 (3H, *s*, $C5CH_3$); 2.21 (3H, *s*, $C3CH_3$)	223 (3) $[M + 1]^+$; 222 (23) $[M]^+$; 149 (20); 122 (28); 96 (100); 95 (33) $[3,5\text{-}Me_2\text{-pyrazole}]^+$; 81 (18); 67 (50); 66 (20); 45 (37); 42 (46); 40 (18); 39 (54); 31 (54); 28 (31)
21	159.7	148.4; 133.1; 144.4	14.23; 12.71	167.4 (COOH); 55.97 (CH_2)	5.85 (2H, *s*, CH_2); 2.80 (3H, *s*, $C5CH_3$); 2.51 (3H, *s*, $C3CH_3$)	268(1) $[M + 1]^+$; 267(7) $[M]^+$; 141 (29); 124 (61); 80 (39); 67 (35); 45 (33); 44 (24); 43 (100) $[CH_3CO]^+$; 42 (45); 39 (25); 31 (46); 30 (45) $[NO]^+$; 28 (31)

CONCLUSIONS

Thus, we have shown that the condensation of 5-hydrazinotetrazole with malonic dialdehyde and acetylacetone and affords the corresponding derivatives of 5-(pyrazol-1-yl)tetrazole. The readiness of pyrazole ring bromination, and further separation of thus obtained bromoderivatives allows to map out one-pot synthesis strategy of 5-(4-bromopyrazole-1-yl) tetrazoles from commercially available 5-aminotetrazole. The hydrogenation by hydrogen at 5-10 atm in the presence of a palladium catalyst was used for debromination.

EXPERIMENTAL

1. Materials and Methods

All the reagents and chemicals were procured from commercial sources (Acros Organics, Belgium; Alfa Aesar, Germany; Sigma-Aldrich, USA) and used without any further purification. 5-Hydrazinotetrazole **1** was prepared from 5-aminotetrazole according to [20]. The IR spectra were recorded in pellets with KBr on FSM-1201 Fourier spectrometer. The ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Bruker DRX-400 spectrometer (400 and 100 MHz, respectively). The ^1H and ^{13}C chemical shifts were determined with reference to the solvent signal (δ 2.51 and 39.96 ppm, respectively). The mass spectra were recorded on a Finnigan MAT INCOS 50 spectrometer (EI, 70 eV). Elemental analysis was performed on a Perkin-Elmer 2400 elemental analyzer. The melting points were determined on a Kofler hot bench.

2. Synthesis of tetrazole derivatives

5-(Pyrazole-1-yl)tetrazole (8) and 5-(3,5-dimethylpyrazole-1-yl)tetrazole (9)

a) Preparation from solid 5-hydrazinotetrazole hydrochloride. To 50 ml of acetic acid sequentially with stirring were added 12.5 g (0.1 mol) of 5-hydrazinotetrazole hydrochloride, 22.0 g (0.1 mol) of 1,1,3,3-tetraethoxypropane (for pyrazole **8**) or 12.5 g (0.1 mol) of acetylacetone (for pyrazole **9**); the resulting mixture was heated to 90 °C and stirred at this temperature for 1 h. The solvent was distilled off in *vacuo* and 25 ml of hot water were added to the residue, the mixture was cooled to room temperature, the precipitate was filtered off and recrystallized from methanol.

Pyrazole **8**. Yield 8.4 г (68%), m.p. 172-173 °C (MeOH). IR spectrum, *v*, cm^{-1}: 3438; 3328; 3154; 3135; 2933; 2791; 1621; 1401; 1289; 1209; 1099; 1066; 1010; 941; 795; 725; 690; 595; 568; 498. Calculated, %: C 35.30, H 2.96, N 61.74. $C_4H_4N_6$. Found, %: C 35.11, H 3.08, N 61.89.

Pyrazole **9**. Yield 13.1 г (80%), m.p. 164-165 °C (MeOH). IR spectrum, *v*, cm^{-1}: 2923; 1624; 1573; 1444; 1402; 1302; 1264; 1185; 1135; 1097; 1001; 796; 755; 726; 569; 535; 442. Calculated, %: C 43.90, H 4.91, N 51.19. $C_6H_8N_6$. Found, %: C 43.63, H 4.76, N 51.38.

b) Hydrogenation of bromopyrazoles **12** and **13**

In a 100 cm^3 autoclave 70 ml of ethanol, 10 g (0.046 mol) of (4-bromopyrazole-1-yl)tetrazole (**12**) or 10 g (0.041 mol) (4-bromo-3,5-dimethylpyrazole-1-yl)tetrazole (**13**) and 0.1 g of 10%-Pd/C catalyst were filled. The reaction mass was hydrogenated at 50-60 °C at a pressure of 5-10 atm until the end of hydrogen absorption (3-4 h). The reaction mass was filtered hot, neutralized by adding crumbled $NaHCO_3$ to pH 5 and filtered from inorganic salts. The solvent was distilled off in *vacuo* and the residue was recrystallized from methanol. Yield 5.9 g (95%) of pyrazole **8** and 6.5 g (97%) of pyrazole **9**.

5-(4-Bromopyrazole-1-yl)tetrazole (12) and the 5-(4-bromo-3,5-dimethylpyrazole-1-yl)tetrazole (13)

a) Preparation by bromination of compounds **8** and **9.** To 10 ml of AcOH 2.0 g (0.016 mol) of pyrazole **8** or 2.6 g (0.016 g) pyrazole **9** were added. To thus obtained solutions at temperature 10-15 °C a solution of 2.6 g (0.016 mol) Br_2 in 5 ml of AcOH was added dropwise. Then the mixture was diluted with 30 ml of cold water, neutralized to pH 5 by adding a crystalline sodium acetate; the precipitate was separated by filtration and recrystallized from methanol.

Bromopyrazole **12**. Yield 3.1 g (90%), m.p. 172-173 °C (MeOH). IR spectrum, *v*, cm^{-1}: 3138; 3108; 2923; 2854; 1585; 1489; 1386; 1200; 1170; 1137; 1037; 1010; 960; 895; 818; 743; 599; 523; 419. Calculated, %: C 22.34, H 1.41, N 39.09.

$C_4H_3BrN_6$. Found, %: C 22.55, H 1.68, N 38.85.

Bromopyrazol **13**. Yield 91%, m.p. 216-217 °C (*i*-PrOH). IR spectrum, *v*, cm^{-1}: 3151; 2923; 1572; 1454; 1316; 1225; 1171; 1136; 1102; 1065; 1035; 1019; 855; 779; 746; 572; 481. Calculated, %: C 29.65, H 2.90, N 34.58. $C_6H_7BrN_6$. Found, %: C 29.92, H 3.01, N 34.04.

b) One-pot synthesis from 5,5'-azobistetrazole (**11**). To 200 ml (0.66 mol) of vigorously stirred 3.3*N* hydrochloric acid aqueous solution 50 g (0.167 mol) disodium salt of 5,5'-azobistetrazole pentahydrate [20] (**11**) were added by 2-3 g portions maintaining the temperature in the reaction mixture below 50 °C. The resulting solution was heated to 80 °C, kept at this temperature for 30 minutes and cooled to 30 °C. At this temperature 10.5 g (0.064 mol) of 1,1,3,3-tetramethoxypropane (for compound **12**) or 6.5 g (0.065 mol) pentane-2,4-dione (for compound **13**) were added dropwise. Then the mixture was slowly heated to 90–100 °C, maintained at this temperature for 30 min and cooled to 10-15 °C. At this temperature 12 g of Br_2 (0.075 mol) were added dropwise. The mixture was allowed to stand at room temperature overnight, cooled to 10 °C, the precipitate was filtered off and washed by 100 ml of cold water. Yield of bromopyrazole **12** 11.5 g (64%) and of bromoprazole **13** 12.4 g (61%).

c) One pot synthesis from 5-aminotetrazole (**10**). In 500 ml of 3.0N water solution of KOH (1.5 mol) 51.5 g (0.5 mol) of 5-aminotetrazole (**10**) were dissolved. The solution was heated to 90-95 °C and at 95-100 °C 79 g (0.5 mol) of $KMnO_4$ were added in portions by 5-6 g. An excess of permanganate was removed by adding of 2-3 g of oxalic acid. The reaction mass was filtered hot from precipitated MnO_2. The residue was washed by 2x100 ml of hot water, cooled to room temperature and added dropwise to 1 l of 8*N* solution of hydrochloric acid (8 mol) maintaining the temperature of reaction mixture below 50 °C. The resulting solution was heated to 80 °C, kept at this temperature for 30 minutes and cooled to 30 °C. Thus obtained solution of 5-hydrazinotetrazole was divided into two equal portions. The first portion was subsequently treated by 14.8 g (0.09 mol) of 1,1,3,3-tetramethoxypropane and then by 14.4 g (0.09 mol) of bromine as described above. Analogously the second part of the solution was treated by 9 g (0.09 mol) of pentane-2,4-dione and then by 14.4 g (0.09 mol) of bromine. The precipitates were filtered off and washed by 100 ml of cold water and recrystallized from propanol-2. Yield of bromopyrazole **12** 16.1 g (60%) and of bromopyrazole **13** 17.9 g (59%).

5-(4-Nitropyrazole-1-yl)tetrazole (14)

In 5 ml of HNO_3 (d1.5) 1.35 g (0.01 mol) of pyrazole **8** were dissolved by cooling to the temperature below 5 °C. To the obtained solution 5 ml of H_2SO_4 (d1.86) were added dropwise by an external cooling to 5-10 °C. Reaction mixture was kept at room temperature for 8 h and poured into 20 g of crushed ice. The precipitate was filtered off and recrystallized from methanol. Yield 1.4 g (79%), m.p. 184-185 °C (MeOH). IR spectrum, *v*, cm^{-1}: 2920; 2852; 1626; 1510; 1426; 1408; 1346; 1295; 1236; 1075; 1033; 948; 857; 818; 754; 502; 481; 420. Calculated, %: C 26.53, H 1.67, N 54.14. $C_4H_3N_7O_2$. Found, %: C 26.91, H 1.82, N 54.68.

5-(2,5-Dimethyl-4-nitropyrazole-1-yl)tetrazole (15)

Nitropyrazole **15** was prepared similar to compound **14** by nitration of 1.6 g (0.01 mol) of pyrazole **8**. Yield 1.7 g (82%), m.p. 196-197 °C (MeOH). IR spectrum, *v*, cm^{-1}: 3081; 2920; 2853; 1577; 1504; 1469; 1411; 1378; 1359; 1313; 1227; 1164; 1029; 844; 789; 763; 745; 446. Calculated, %: C 34.45., H 3.37, N 46.88. $C_6H_7N_7O_2$. Found, %: C 34.19, H 3.51, N 46.53.

5-(4-Amino-3,5-dimethylpyrazole-1-yl)tetrazole (16)

In a 100 cm^3 autoclave 70 ml of ethanol, 10 g (0.48 mol) of 5-(3,5-dimethyl-4-nitropyrazole-1-yl)tetrazole (**15**) and 0.1 g of 10% -Pd/C catalyst were filled. The reaction mass was hydrogenated at 50-60 °C at a pressure of 5-10 atm until the end of hydrogen absorption (3-4 h). The reaction mass was cooled to room temperature, filtered and the precipitate was extracted with 30 ml of hot (90-100 °C) DMF. The mother liquor was poured into 100 ml of cold water; the precipitate was separated by filtration and recrystallized from DMF/*i*-PrOH (1 : 1 V/V). Yield 7.9 g (92%), m.p. 284-286 °C (dec.) (DMF/*i*-PrOH). IR spectrum, *v*, cm^{-1}: 3076; 2920; 2852; 2744; 2585; 1645; 1611; 1585; 1550 1504; 1401; 1238 1201; 1146; 1111; 1086; 1041; 1029; 798; 719; 668; 571; 465; 408. Calculated, %: C 40.22, H 5.06, N 54.72. $C_6H_9N_7$. Found, %: C 39.97, H 5.19, N 54.46.

2-(5-(4-Bromo-3,5-dimethylpyrazole-1-yl)-2-tetrazol-2-yl)acetamide (17)

To 30 ml of DMF 5.8 g (0.02 mol) bromopyrazole **13**, 2.1 g (0.022 mol) of chloroacetamide and 4.1 g (0.03 mole) of anhydrous finely grinded K_2CO_3 were added. The mixture was stirred at 60 °C for 8 h, poured into 100 ml of cold water; the precipitate was separated by filtration and recrystallized from AcOH. Yield 4.7 g (79%), m.p. 252-253 °C (AcOH). IR spectrum, *v*, cm^{-1}: 3351; 3175; 3006; 2957; 2922; 2852; 1707; 1570; 1455; 1408; 1377; 1323; 1303; 1203; 1157; 1073; 1045; 1020; 824; 782; 743; 643; 626; 542; 480; 413. Calculated, %: C 32.02, H 3.36, N 32.67. $C_8H_{10}BrN_7O$. Found, %: C 32.41, H 3.42, N 32.38.

2-(5-(4-Bromo-3,5-dimethylpyrazole-1-yl)-2-tetrazol-2-yl)ethanol (18)

To 20 ml of DMF 3.0 g (0.012 mol) bromopyrazole **13**, 2.0 g, (0.025 mol) ethylenechlorohydrine

and 2.8 g (0.02 mole) of anhydrous finely grinded K_2CO_3 were added. The mixture was stirred at 50-60 °C for 10 h. After cooling to a room temperature the solvent was distilled off in *vacuo*. The dry residue was extracted 2x20 ml of boiling ethanol and the filtrate was poured into 50 ml of cold water, the precipitate was separated by filtration and recrystallized from methanol. Yield 21 g (62%), m.p. 98-99 °C. IR spectrum, *v*, cm^{-1}: 2920; 1632; 1576; 1450; 1413; 1319; 1080; 1051; 1019; 781; 739; 570; 512; 469; 442; 416; 405. Calculated, %: C 33.47, H 3.86, N 29.27. $C_8H_{11}BrN_6O$. Found, %: C 33.83, H 4.01, N 29.02.

2-(5-(4-Bromo-3,5-dimethylpyrazole-1-yl)-2-tetrazol-2-yl)acetic acid (19)

To 50 ml of 1% water solution of NaOH 2.9 g (0.01 mol) of acetamide **17** were added. Reaction mass was stirred at 90-95 ^oC for 5 h. Then the solution was acidified to pH 1 by conc. HCl and cooled to 5-10 ^oC. The precipitate was separated by filtration and recrystallized from AcOH-H_2O (1 : 1 V/V). Yield 2.5 g (86%), m.p. 186-187 °C (AcOH/H_2O). IR spectrum, *v*, cm^{-1}: 2920; 1576; 1450; 1413; 1319; 1171; 1151; 1079; 1051; 1019; 960; 865; 781; 740; 586; 570; 513; 467. Calculated, %: C 31.91, H 3.01, N 27.91. $C_8H_9BrN_6O_2$. Found, %: C 31.69, H 3.42, N 27.72.

(5-(3,5-Dimethylpyrazol-1-yl)-2-tetrazol-2-yl)acetic acid (20)

In a 50 cm^3 autoclave 30 ml of ethanol, 2.2 g (7.6 mmol) of bromoderivative **19** and 0.05 g of 10% Pd/C were filled The reaction mass was hydrogenated at 50-60 °C at a pressure of 5-10 atm until the end of hydrogen absorption (3-4 h). The reaction mixture was cooled to room temperature, alkalized by addition of 6 ml of 10% NaOH water solution and filtered from catalyst. The solvent was removed in *vacuo*. The residue was dissolved in 10 ml of water and acidified with conc. HCl to pH1. The precipitate was separated by filtration and recrystallized from water. Yield 1.4 g (88%), m.p. 182–183 ^oC (H_2O). IR spectrum, *v*, cm^{-1}: 3018; 2921; 2852; 1737; 1573; 1410; 1320; 1224; 1052; 828; 623; 569. Calculated, %: C 43.24, H 4.54, N 37.82. $C_8H_{10}N_6O_2$. Found, %: C 43.55, H 4.83, N 37.59.

2-(5-(3,5-Dimethyl-4-nitropyrazole-1-yl)-2-tetrazol-2-yl)acetic acid (21)

In 5 ml of HNO_3 (*d*1.5) 2.22 g (0.01 mol) of pyrazole **20** were dissolved at temperature below 5 ^oC. To obtained solution by external cooling to 5–10 ^oC 5 ml of H_2SO_4 (d1.86) were added. Reaction mixture was kept at room temperature 8 h and poured into 20 g of crushed ice. The precipitate was filtered of and recrystallized from methanol. Yield 2.3 g (85%), m.p. 184–185 ^oC (MeOH). IR spectrum, *v*, cm^{-1}: 3536; 3508; 3464; 3442; 3415; 3401; 1737; 1725; 1568; 1504; 1417; 1383; 1361; 1232; 1189; 825; 797; 663; 416. Calculated, %: C 35.96, H 3.39, N 36.69. $C_8H_9N_7O_4$. Found, %: C 36.12, H 3.48, N 36.33.

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Критерии авторства

Степанова Е.В., Степанов А.И. выполнили экспериментальную работу, на основании полученных результатов провели обобщение и написали рукопись. Степанова Е.В., Степанов А.И. имеют на статью равные авторские права и несут равную ответственность за плагиат.

Конфликт интересов

Авторы заявляют об отсутствии конфликта интересов.

Contribution

Stepanova E.V., Stepanov A.I. carried out the experimental work, on the basis of the results summarized the material and wrote the manuscript. Stepanova E.V., Stepanov A.I. have equal author's rights and bear equal responsibility for plagiarism.

Conflict of interest

The authors declare no conflict of interests regarding the publication of this article.

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Поступила 18.10.2016

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Received 18.10.2016