Энергоемкие производные пиразина: синтез и свойства

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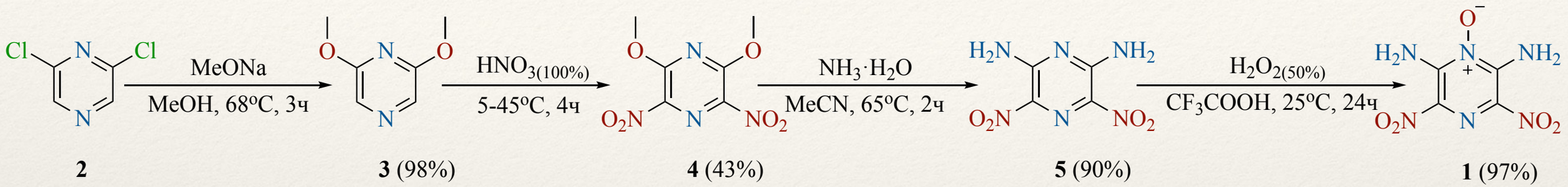
Москва, 2025

Глава 1.
Замещенные производные пиразина

1

LLM-105: подходы к синтезу

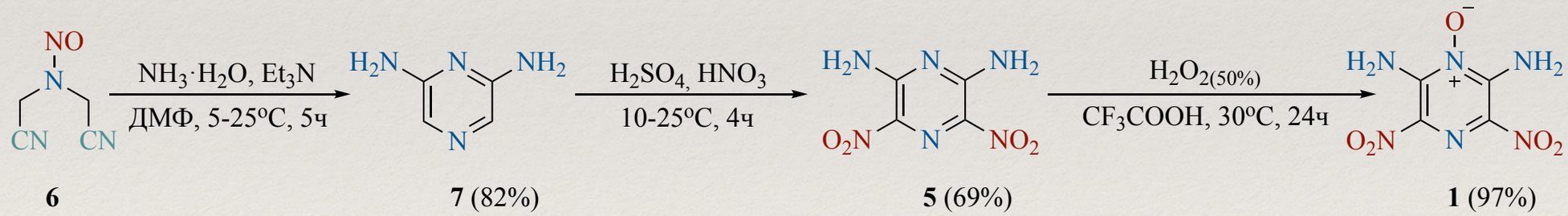
Метод А (1995 год)



2 **3** (98%) **4** (43%) **5** (90%) **1** (97%)

Суммарный выход **LLM-105** = 36%

Метод Б (2013 год)



6 **7** (82%) **5** (69%) **1** (97%)

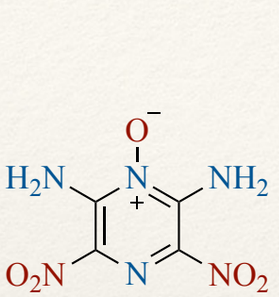
Суммарный выход **LLM-105** = 53%

Метод А: Pagoria P. F. Synthesis of LLM-105 //Propellants Explos. Pyrotech. – 1995. – Т. 20. – No. 1. – С. 38-42.

Метод Б: Zhao X., Liu Z. An improved synthesis of 2, 6-diamino-3, 5-dinitropyrazine-1-oxide //Journal of Chemical Research. – 2013. – Т. 37. – No. 7. – С. 425-426.

2

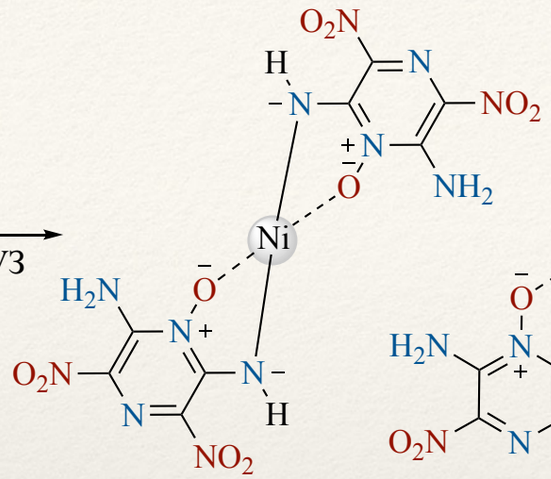
LLM-105: в составе комплексных соединений



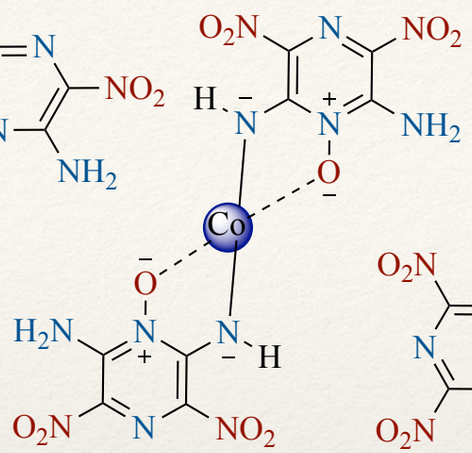
1

$M(NO_3)_n$

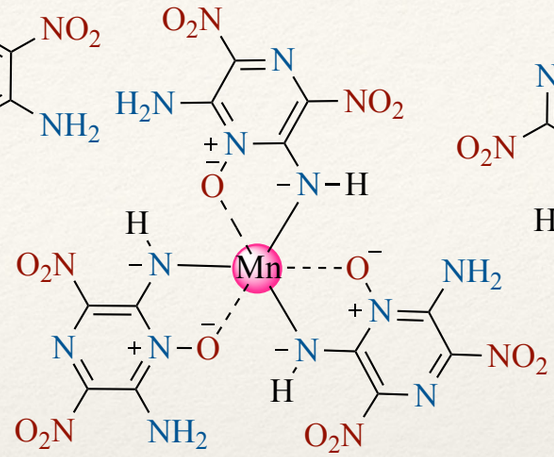
ДМФ, 60°C, УЗ



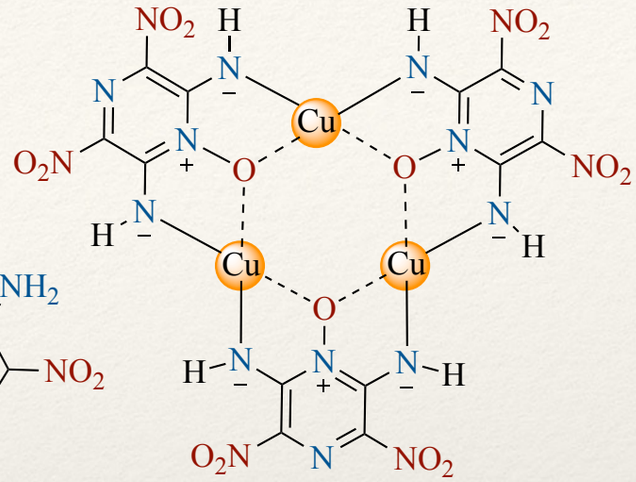
8 (M = Ni)



9 (M = Co)

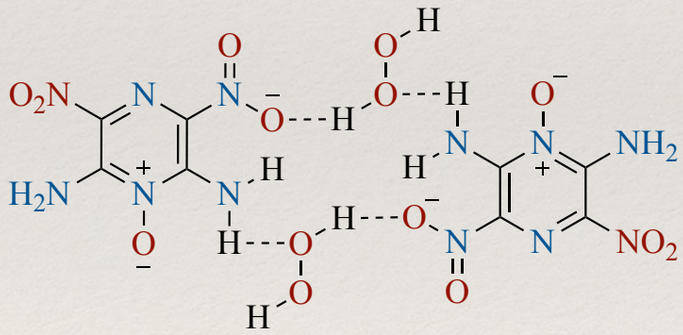


10 (M = Mn)

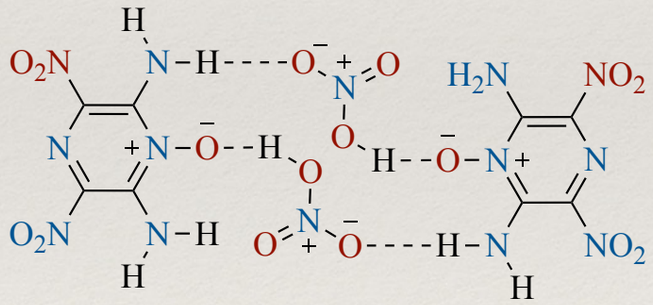


11 (M = Cu)

действительно синтезированные соединения



12



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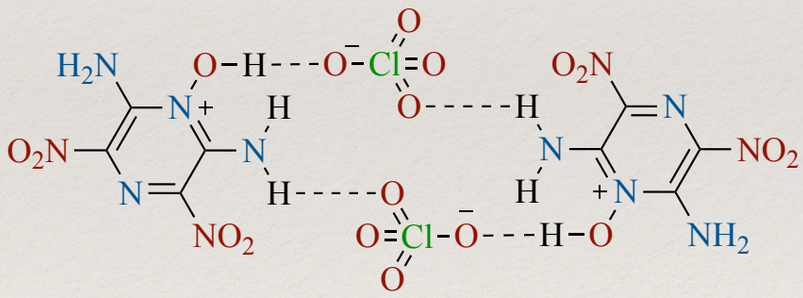


14

теоретическая расчетная работа

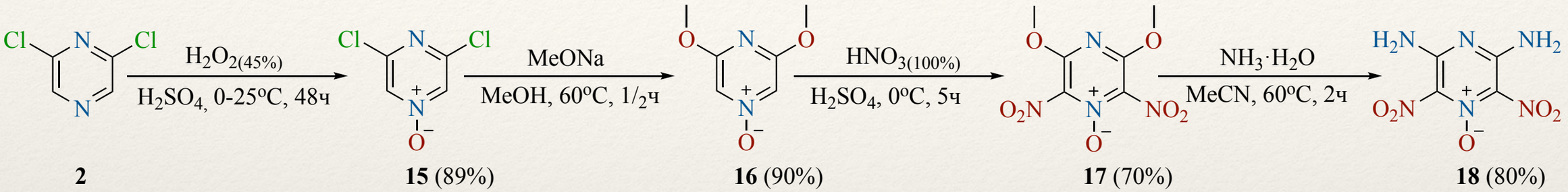
8-11: Xiao Y. et al. Construction of Energetic Complexes Based on LLM-105 and Transition Metal Cations (Ni, Co, Mn, and Cu) //Crystals. – 2023. – Т. 13. – No. 11. – С. 1587.

12-14: Ji J., Wang K., Zhu W. Prediction of the crystal structure and properties of energetic LLM- 105: oxidant cocrystals: A theoretical study //Journal of the Chinese Chemical Society. – 2022. – Т. 69. – No. 4. – С. 618-629.

3

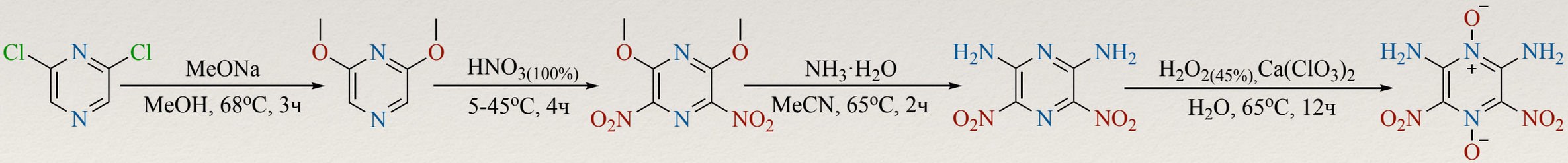
LLM-105: изомеры и модификации

3,5-диамино-2,6-динитропиразин-3-оксид



2 **15** (89%) **16** (90%) **17** (70%) **18** (80%)

3,5-диамино-2,6-динитропиразин-1,3-диоксид



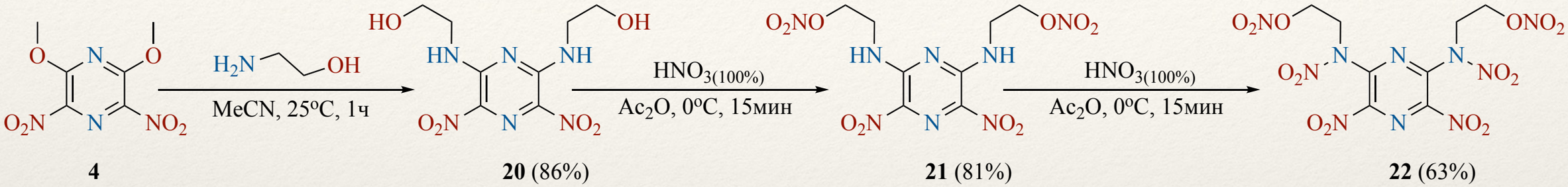
2 **3** (98%) **4** (43%) **5** (90%) **19** (99%)

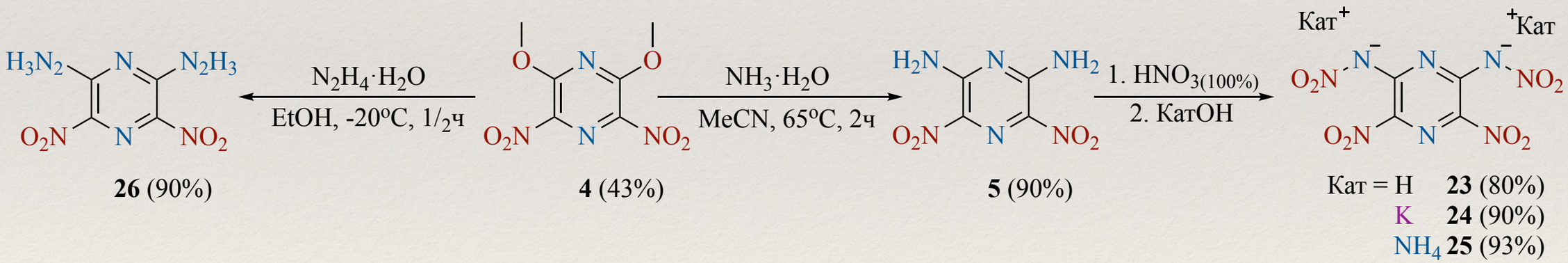
15-18: Wenquan Z. / Compound 3,5-diamino-2,6-dinitropyrazine-1-oxide and preparation method thereof. 2015 Patent **CN105294580A**

19: Gökçınar E., Klapötke T. M., Bellamy A. J. Computational study on 2, 6-diamino-3, 5- dinitropyrazine and its 1-oxide and 1, 4-dioxide derivatives //Journal of Molecular Structure: THEOCHEM. – 2010. – T. 953. – No. 1-3. – C. 18-23.

4

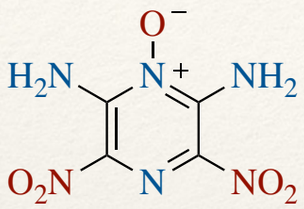
LLM-105: родственные соединения



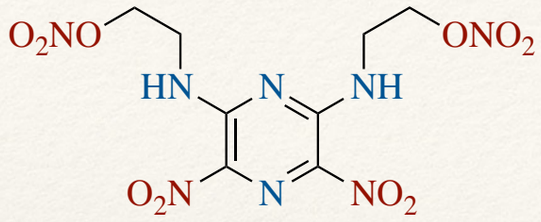


15-18: Chen F. et al. Modifying polynitro benzene and pyrazine skeletons with flexible nitratoethyl substituents towards new energetic melt-castable materials //Chemical Engineering Journal. – 2022. – Т. 435. – С. 135053.
23-25: Singh J. et al. Energetic salts of sensitive N, N′-(3, 5-dinitropyrazine-2, 6-diyl) dinitramide stabilized through three-dimensional intermolecular interactions //Inorganic Chemistry. – 2022. – Т. 61. – No. 41. – С. 16493-16500.
26: Yadav A. K. et al. Symmetric refunctionalization of diaminodinitropyrazine with hydrazine and aminotetrazole: strategy for enhancing detonation performance and safety in energetic materials //Inorganic Chemistry. – 2024. – Т. 63. – No. 32. – С. 15144-15153

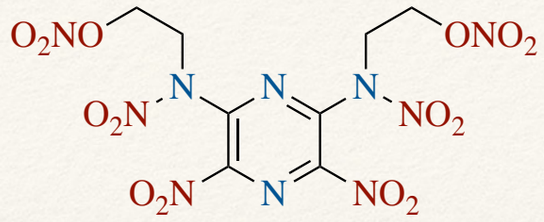
5 Физико-химические параметры и специальные свойства



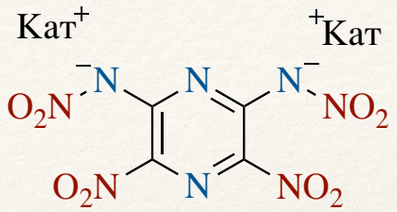
1



21



22



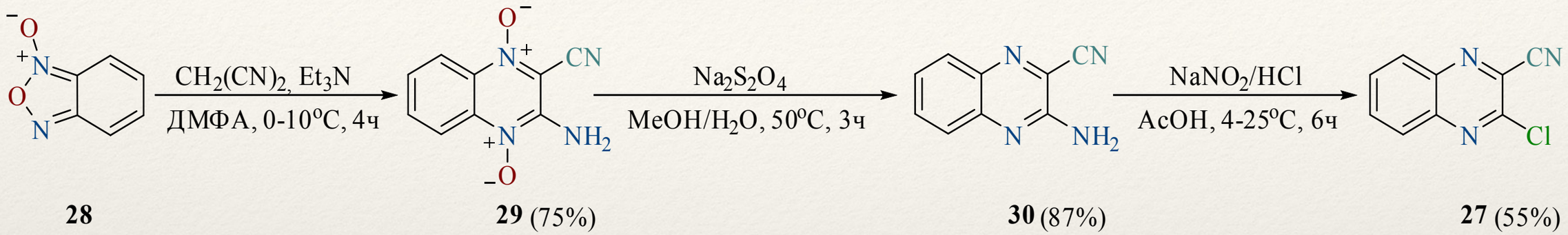
Кат = H **23**
K **24**
NH_4 **25**

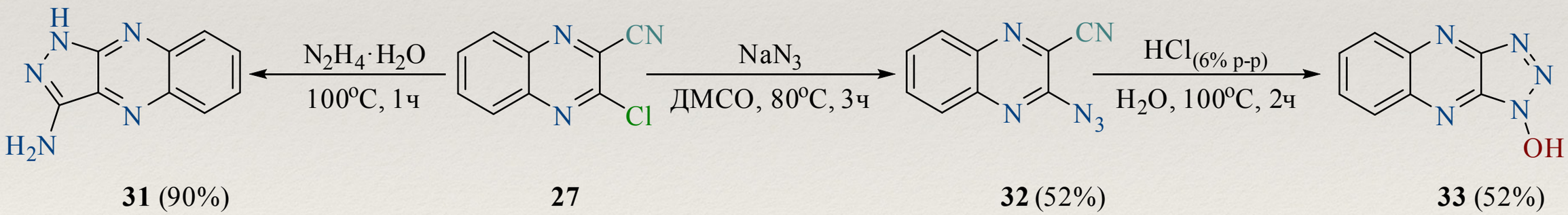
Параметр/Соединение	TNT	1	21	22	23	24	25	26
ΔH^0_f[КДж·моль$^{-1}$]	-59	-13	-162	-5	246	-107	179	219
ρ [г·см$^{-3}$]	1,65	1,93	1,68	1,80	1,89	2,10	1,73	1,84
IS [Н]	15	100	20	16	Н/Д	4	5	40
FS [Дж]	360	360	160	84	Н/Д	40	60	360
T_m [^{o}C]	81	—	170	129	Н/Д	Н/Д	Н/Д	Н/Д
T_d [^{o}C]	295	352	205	153	103	220	155	205
V [км·с$^{-1}$]	6,8	8,3	7,8	7,8	9,2	8,3	8,6	8,7
D [ГПа]	19,4	32	24,7	32,3	36,8	29,9	30,8	31,6

Глава 2.

Аннелированные производные пиразина

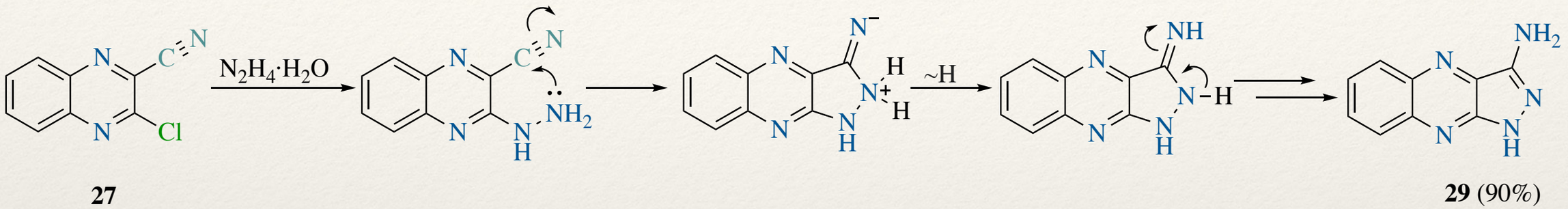
6 Производные хиноксалина



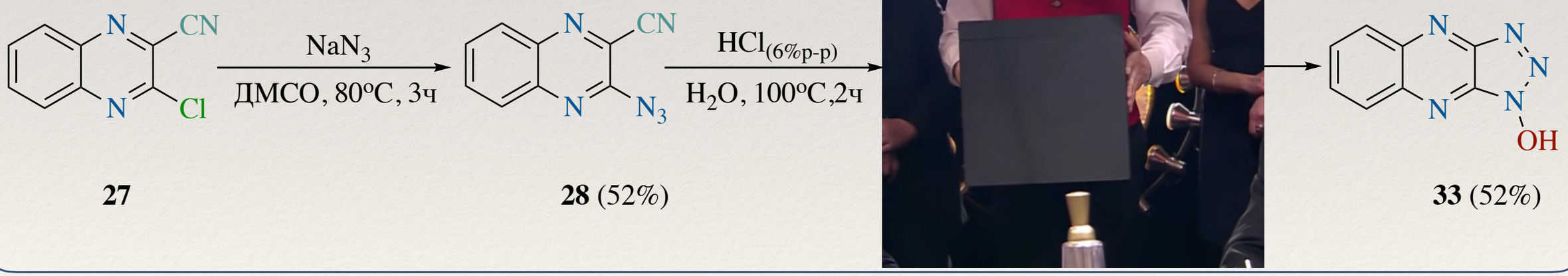


28: Leyva E. et al. One-pot methodology for conversion of o-halogen nitrobenzenes to benzofuroxans //Synthetic Communications. – 2017. – Т. 47. – №. 6. – С. 604-608.
29-33: Monge A. et al. 3-Amino-2-quinoxalinecarbonitrile. New fused quinoxalines with potential cytotoxic activity //Journal of heterocyclic chemistry. – 1994. – Т. 31. – №. 5. – С. 1135-1139

Механизмы циклизации



27 **29** (90%)

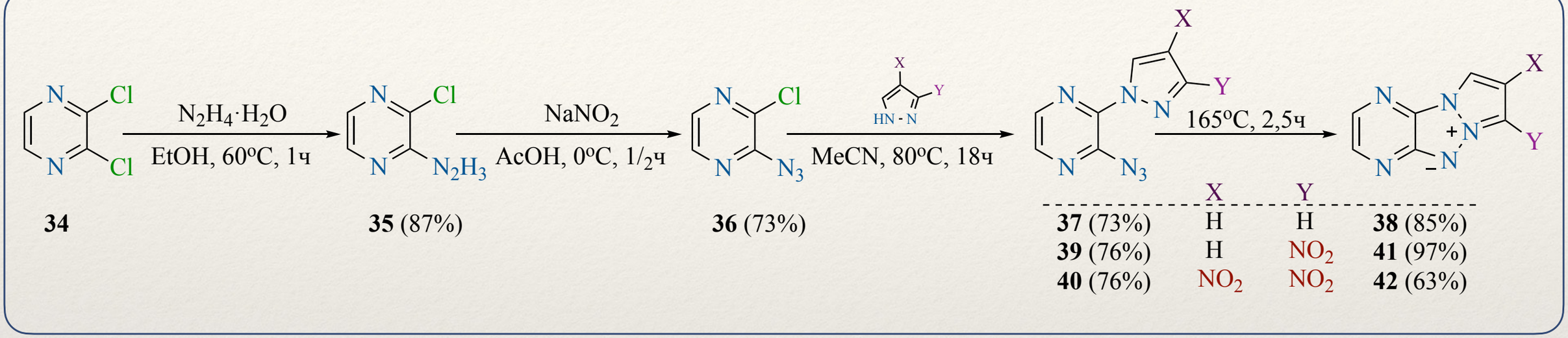


27 **28** (52%) **33** (52%)

28: Leyva E. et al. One-pot methodology for conversion of o-halogen nitrobenzenes to benzofuroxans //Synthetic Communications. – 2017. – Т. 47. – №. 6. – С. 604-608.
29-33: Monge A. et al. 3-Amino-2-quinoxalinecarbonitrile. New fused quinoxalines with potential cytotoxic activity //Journal of heterocyclic chemistry. – 1994. – Т. 31. – №. 5. – С. 1135-1139

8

Трансформация 2,3-дихлорпиразина

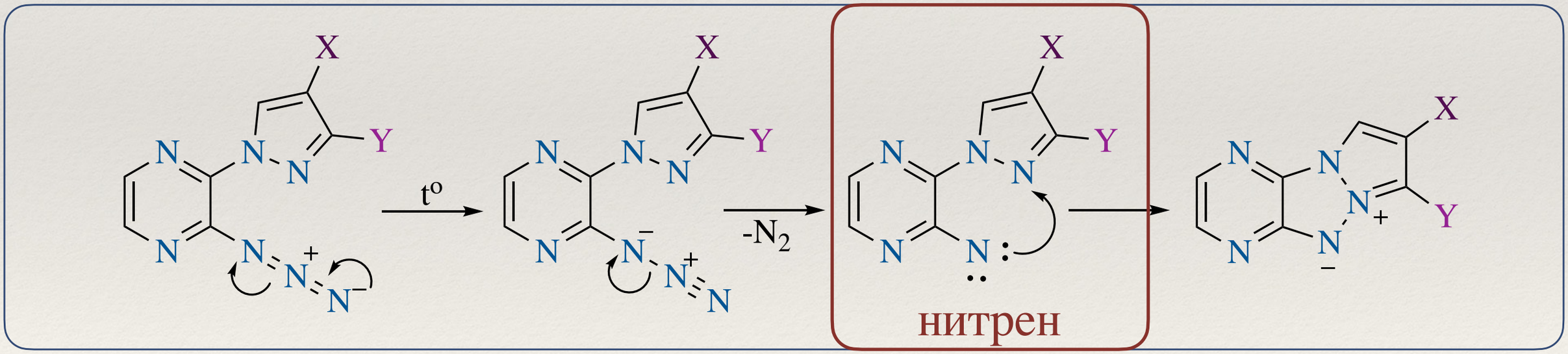


34

35 (87%)

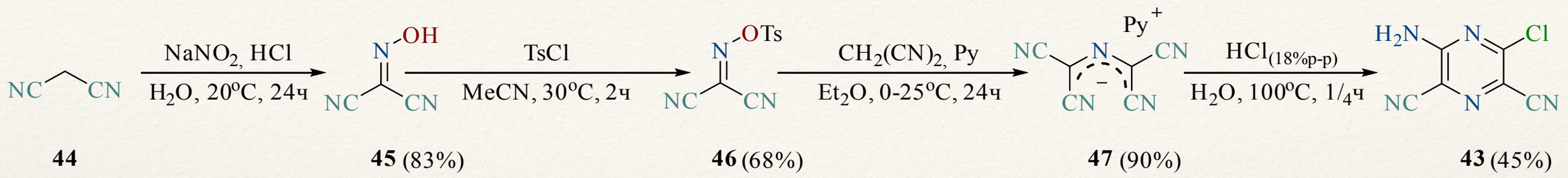
36 (73%)

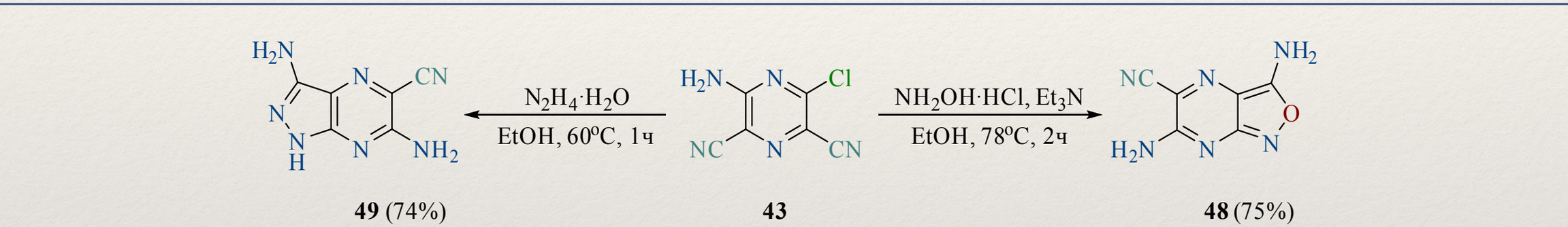
	X	Y	
37 (73%)	H	H	**38** (85%)
39 (76%)	H	NO_2	**41** (97%)
40 (76%)	NO_2	NO_2	**42** (63%)

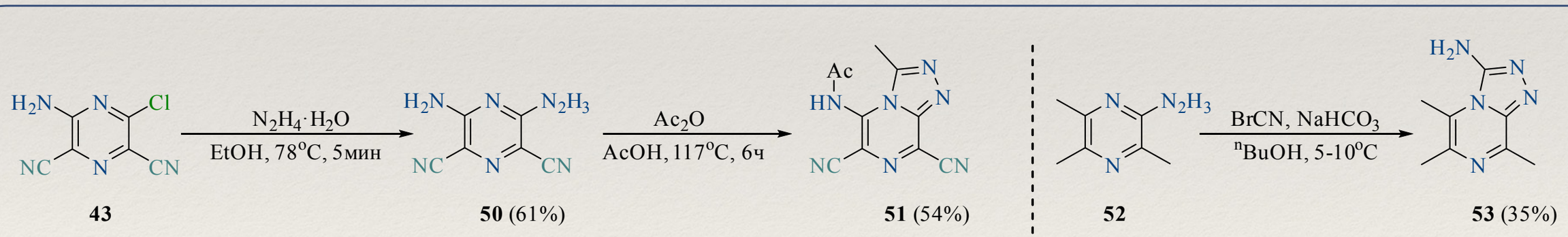


34: Tam H. D. et al. Synthesis of C-Nucleosides. 17. s-Triazolo [4, 3-a] pyrazines //The Journal of Organic Chemistry. – 1979. – Т. 44. – №. 7. – С. 1028-1035.
35: Sirbu D. et al. An original class of small sized molecules as versatile fluorescent probes for cellular imaging //Chemical Communications. – 2019. – Т. 55. – №. 54. – С. 7776-7779.
36-42: Nyffenegger C. et al. Synthesis of nitro-functionalized polynitrogen tricycles bearing a central 1, 2, 3-triazolium ylide //Synlett. – 2009. – Т. 2009. – №. 08. – С. 1318-1320

Азолопиразины

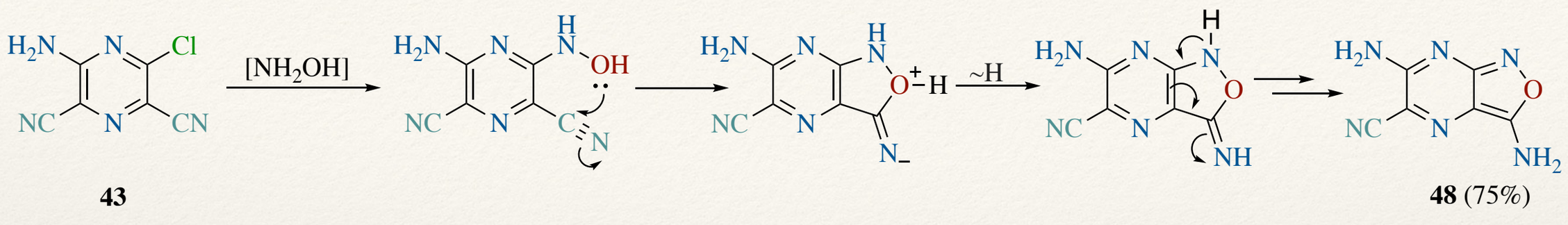


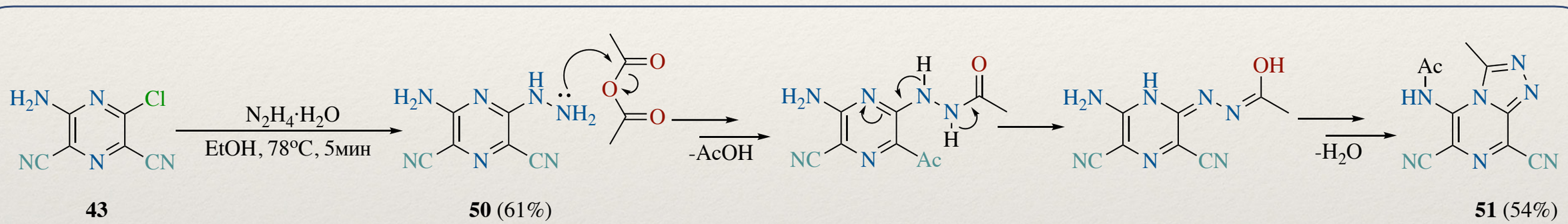


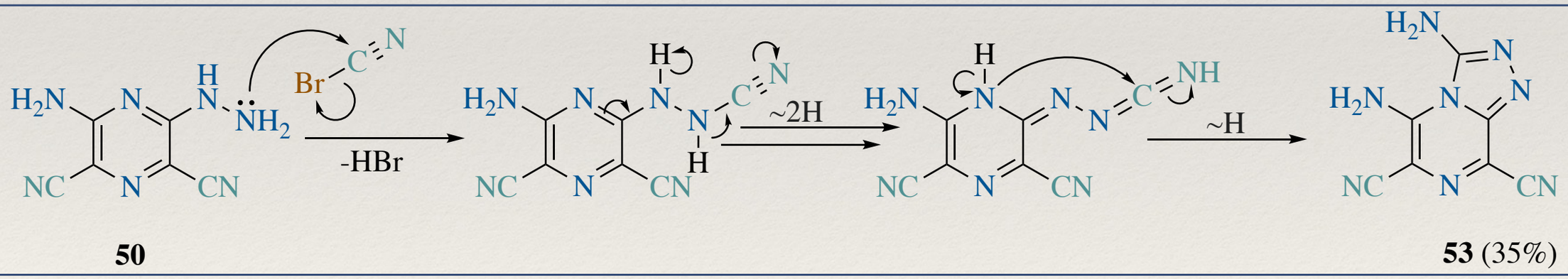


43-47: Lang M. et al. Aza-2-dièmes-1, 3 3. Nouvelles voies d'accès à des amino-2-pyrazines substituées //Helvetica chimica acta. – 1986. – Т. 69. – №. 4. – С. 793-802.
48-49: El-Shafei A. K. et al. Synthesis and reactions of some pyrazine derivatives //Synthetic communications. – 1994. – Т. 24. – №. 13. – С. 1895-1916.
50-53: Maguire J., Paton D., Rose F. L. s-Triazolopyrazines //Journal of the Chemical Society C: Organic. – 1969. – №. 11. – С. 1593-1597.

Механизмы циклизации

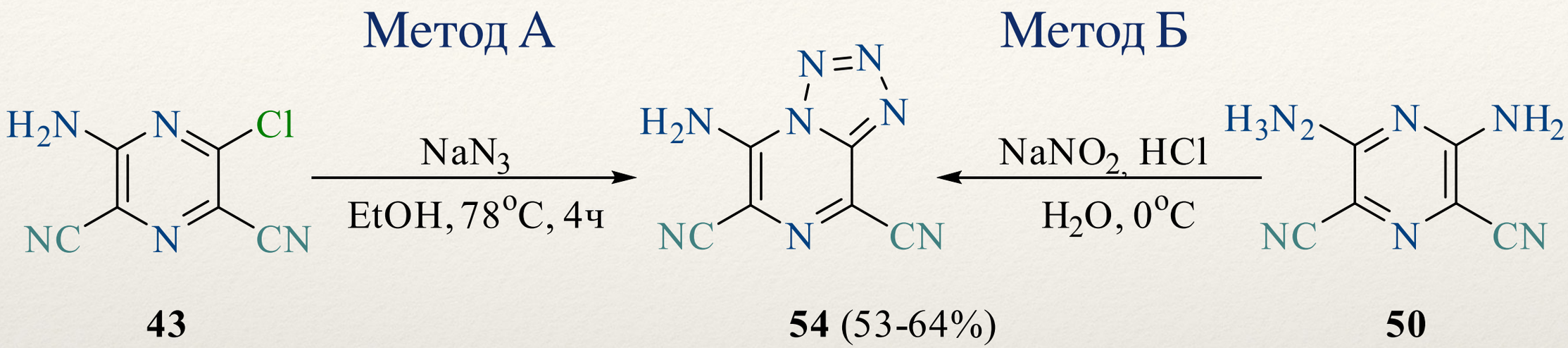


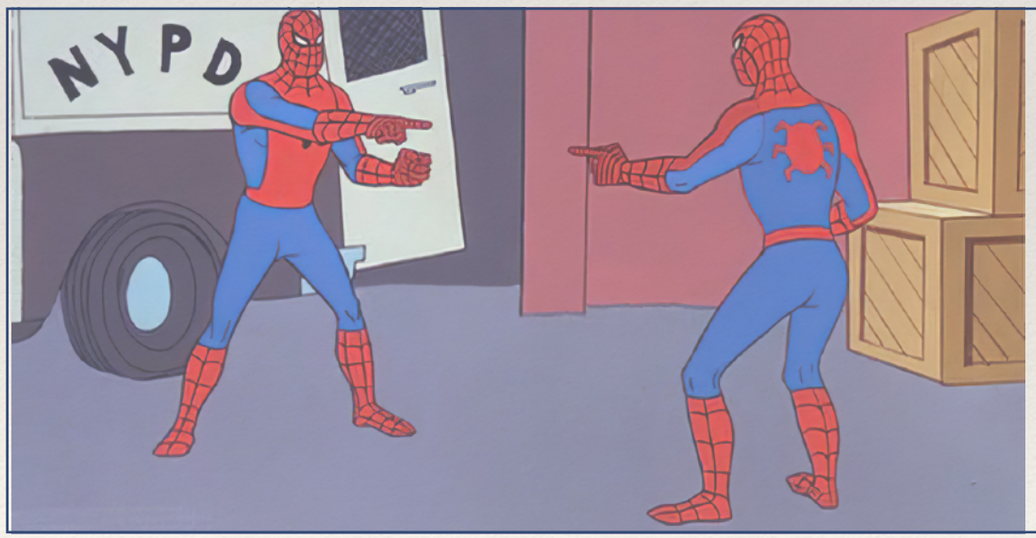


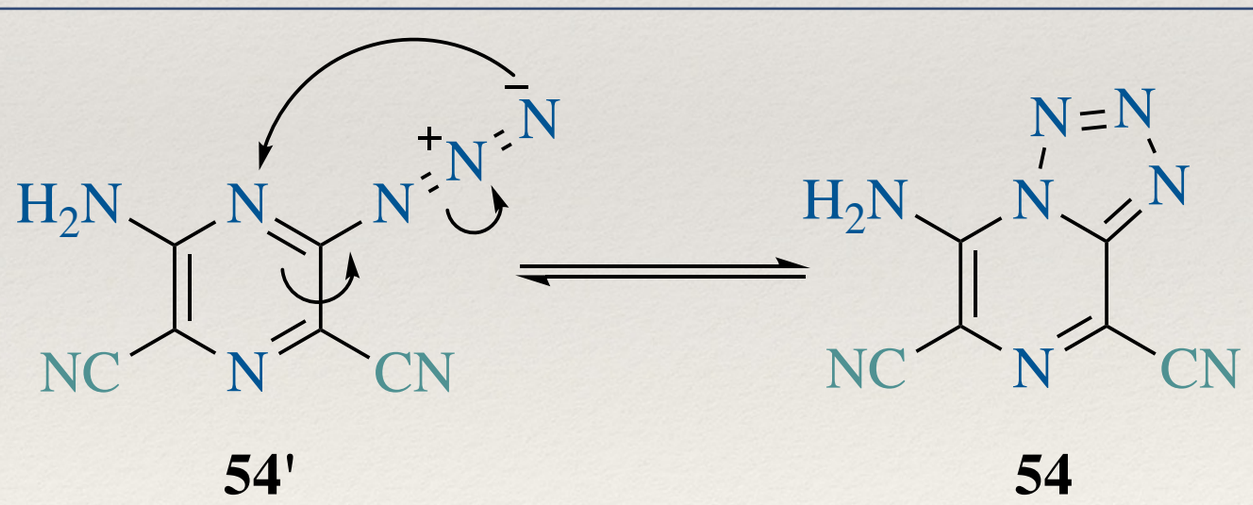


44-43: Lang M. et al. Aza-2-diènes-1, 3 3. Nouvelles voies d'accès à des amino-2-pyrazines substituées //Helvetica chimica acta. – 1986. – Т. 69. – №. 4. – С. 793-802.
48-49: El-Shafei A. K. et al. Synthesis and reactions of some pyrazine derivatives //Synthetic communications. – 1994. – Т. 24. – №. 13. – С. 1895-1916.
50-53: Maguire J., Paton D., Rose F. L. s-Triazolopyrazines //Journal of the Chemical Society C: Organic. – 1969. – №. 11. – С. 1593-1597.

Азид-тетразол и методы его синтеза

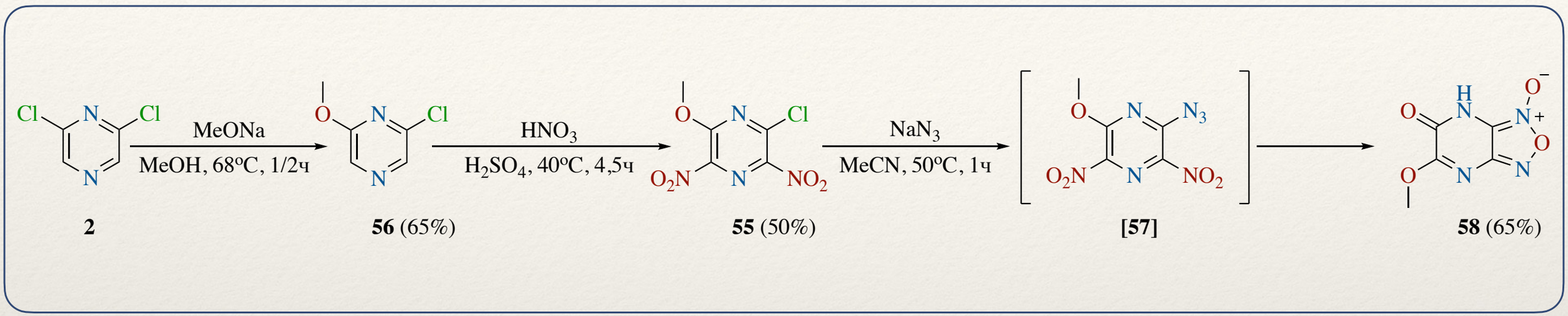


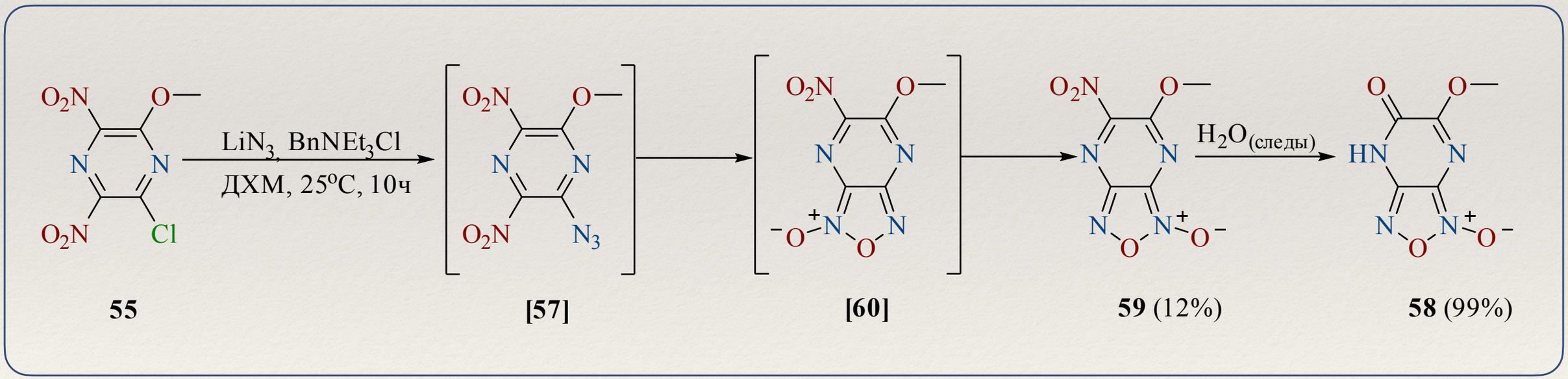




Метод А: El-Shafei A. K. et al. Synthesis and reactions of some pyrazine derivatives //Synthetic communications. – 1994. – Т. 24. – №. 13. – С. 1895-1916.
Метод Б: Maguire J., Paton D., Rose F. L. s-Triazolopyrazines //Journal of the Chemical Society C: Organic. – 1969. – №. 11. – С. 1593-1597.

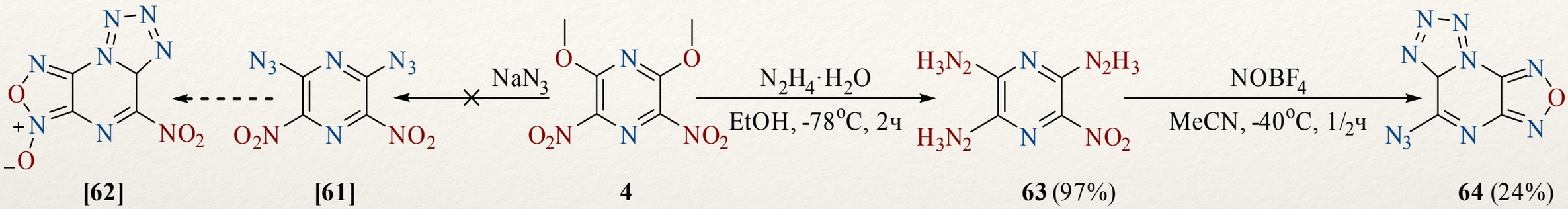
Фуроксанопиразины





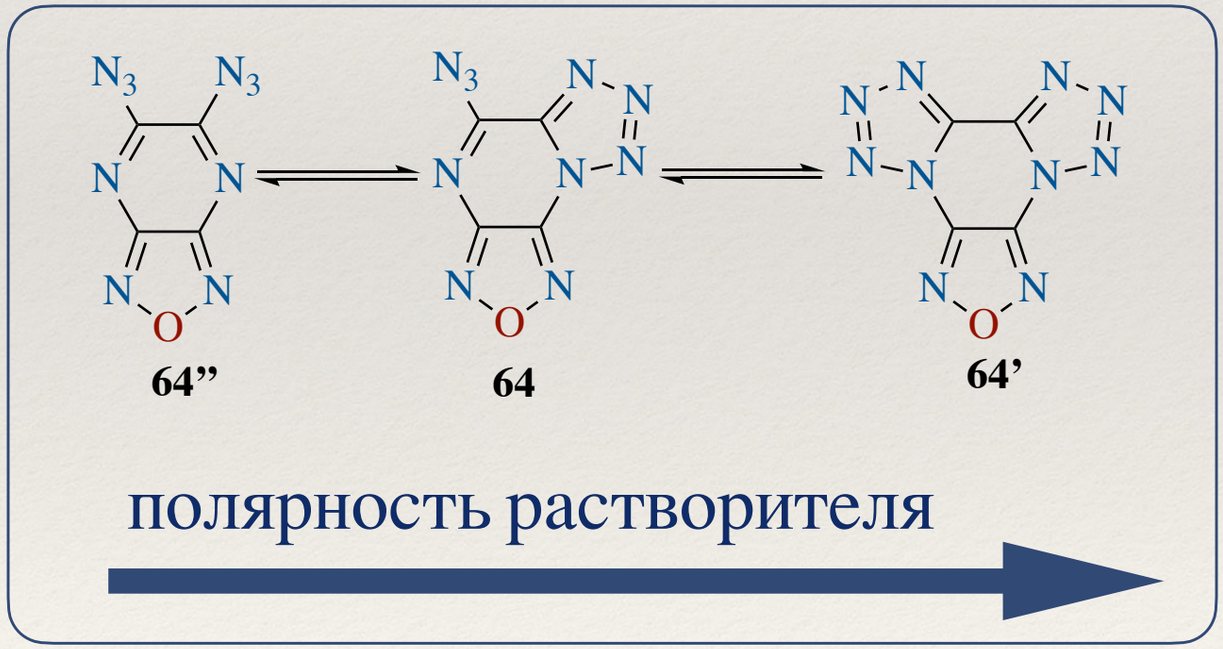
56-58: Yudin I. L. et al. Furoxano [3, 4-b] pyrazines: The first synthesis and x-ray structure //Journal of heterocyclic chemistry. – 2005. – Т. 42. – №. 4. – С. 691-694.

Фуроксанопиразины (почти)



[62] **[61]** **4** **63** (97%) **64** (24%)

Хотели как лучше… … а получилось тоже ничего

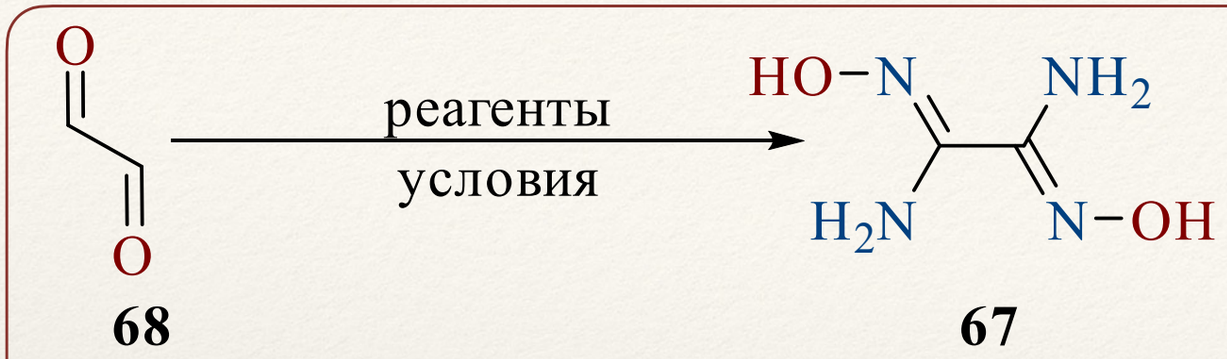


64” **64** **64’**

64-64: Guillou S. et al. An unexpected synthesis of 7-azidofurazano [3, 4-b] tetrazolopyrazine //Tetrahedron. – 2009. – Т. 65. – №. 43. – С. 8891-8895.

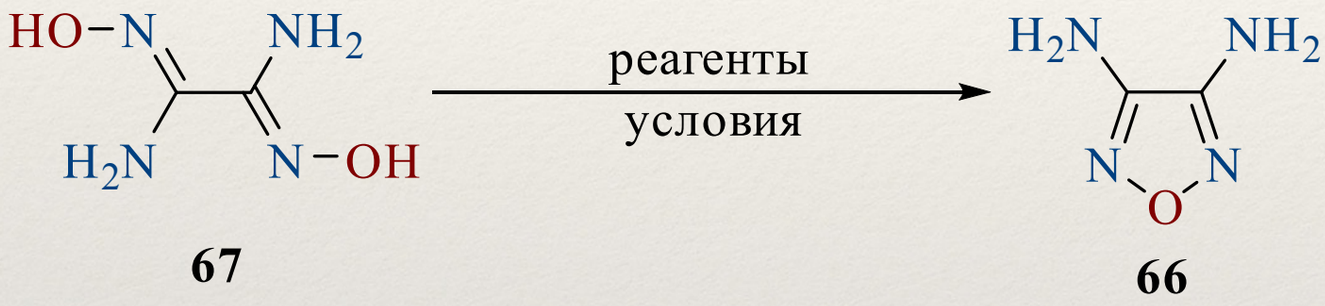
Глава 3.
Фуразано[3,4-*b*]пиразины

Синтез ДАФ



68 **67**

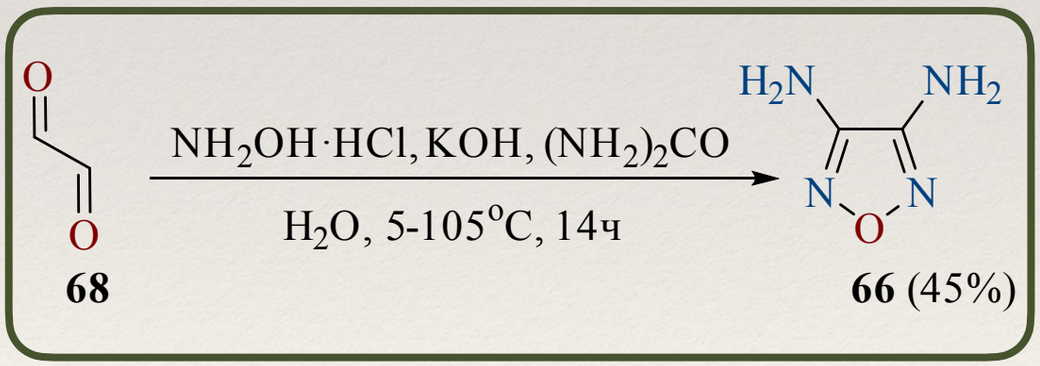
Реагенты	Условия	Выход **68**
$NH_2OH \cdot HCl$	5-95°C, 5ч	52%
$NH_2OH_{(50\%р\text{-}р)}$	25-95°C,5д	80%



67 **66**

Реагенты	Условия	Выход **66**
$NaOH, H_2O$	140°C, 4ч	20%
KOH, H_2O	170°C, 2ч	50%
KOH, H_2O	180°C, 2ч	70%
KOH, H_2O	МВИ, 20мин	71%

Исторический двухстадийный подход



68 **66** (45%)

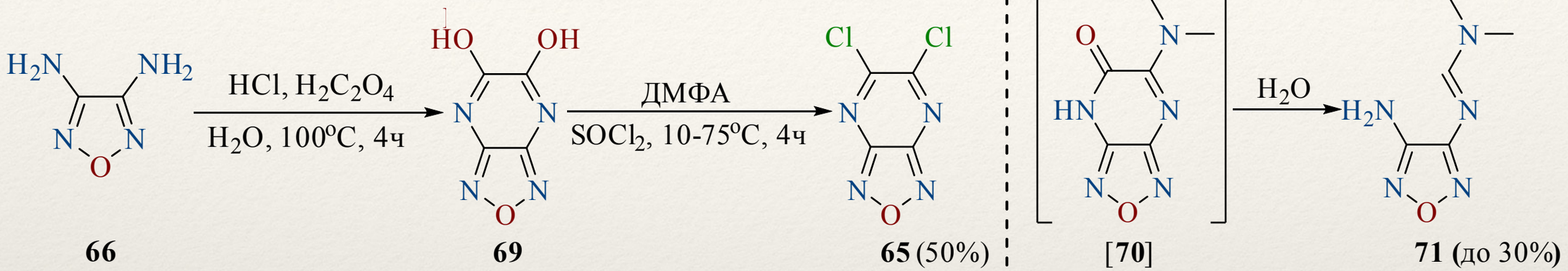
One-pot by Shreeve and Co.

67: Zelenin A. K., Trudell M. L. A two-step synthesis of diaminofurazan and synthesis of N-monoarylmethyl and N, N′-diarylmethyl derivatives //Journal of heterocyclic chemistry. – 1997. – Т. 34. – №. 3. – С. 1057-1060. / Johnson E. C., Sabatini J. J., Zuckerman N. B. A Convenient and Safer Synthesis of Diaminoglyoxime //Organic process research & development. – 2017. – Т. 21. – №. 12. – С. 2073-2075.

66: Gunasekaran A. et al. A convenient synthesis of diaminoglyoxime and diaminofurazan: Useful precursors for the synthesis of high density energetic materials //Journal of heterocyclic chemistry. – 1995. – Т. 32. – №. 4. – С. 1405-1407. / Kusurkar R. S. et al. Microwave mediated fast synthesis of diaminoglyoxime and 3, 4-diaminofurazan: key synthons for the synthesis of high energy density materials //Journal of Chemical Research. – 2005. – Т. 2005. – №. 4. – С. 245-247. / Zhang J., Shreeve J. M. 3, 3′-Dinitroamino-4, 4′-azoxyfurazan and its derivatives: an assembly of diverse N–O building blocks for high-performance energetic materials //Journal of the American Chemical Society. – 2014. – Т. 136. – №. 11. – С. 4437-4445.

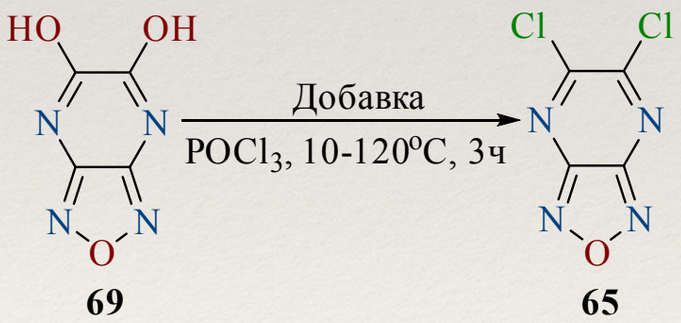
Синтез 5,6-дихлорфуразано[3,4-*b*]пиразина

Метод А

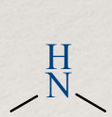
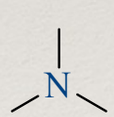
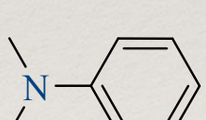
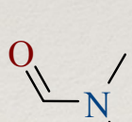
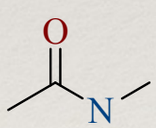
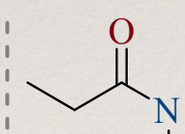


66 → **69** → **65** (50%) → [**70**] → **71** (до 30%)

Метод Б



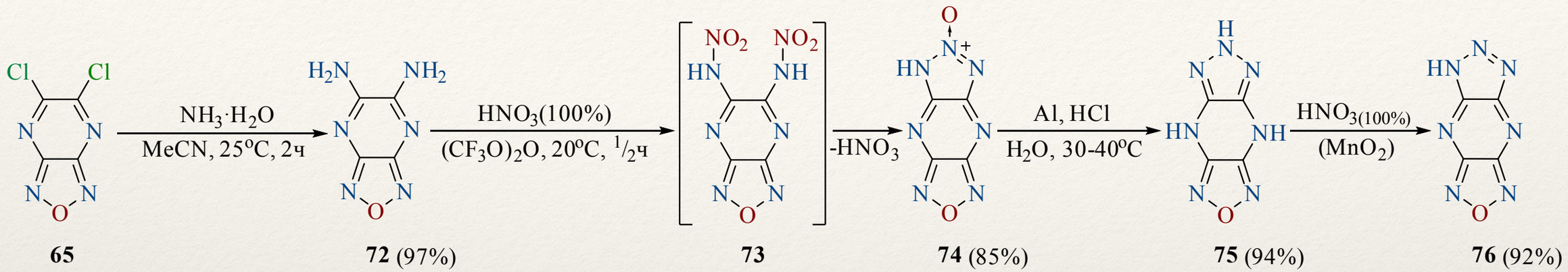
69 → **65**

Добавка	-	PCl_5						
Выход **65**	следы	69%	52%	47%	50%	45%	62%	53%

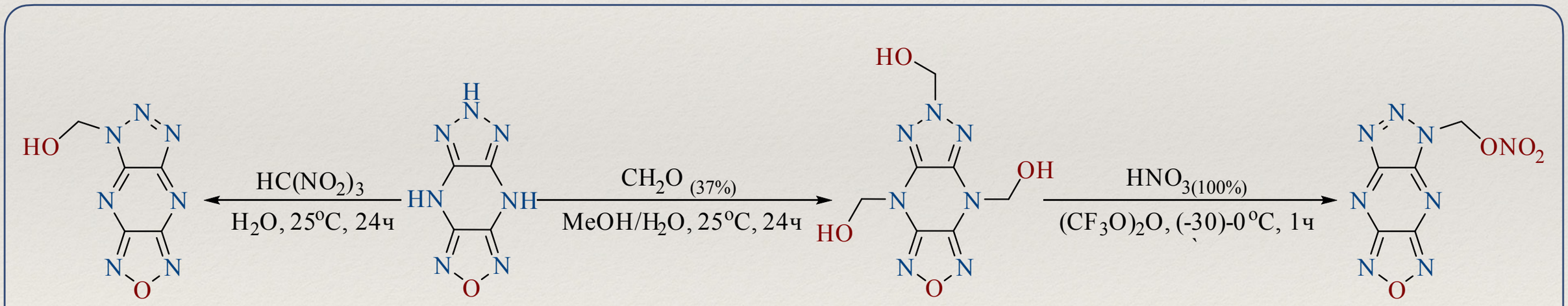
69: Khisamutdinov G. K. et al. Synthesis and properties of 1, 2, 4-triazolo [4, 3-d]-1, 2, 4-triazolo-[3, 4-f] furazano [3, 4-b] pyrazines //Russian Chemical Bulletin. – 1993. – Т. 42. – С. 1700-1702.
Метод А: Starchenkov I. B., Andrianov V. G. Chemistry of furazano [3, 4-b] pyrazines: 3. Method for the synthesis of 5, 6-disubstituted furazano [3, 4-b] pyrazines //Chemistry of Heterocyclic Compounds. – 1997. – Т. 33. – №. 10. – С. 1219-1233.
Метод Б: Sun Z. et al. Practical and Scalable Synthesis of 5, 6-Dichlorofurazano [3, 4-b] pyrazine //Organic Process Research & Development. – 2023. – Т. 27. – №. 9. – С. 1662-1666.

16

1,2,3-триазоло[4,5-*b*]фуразано[4,5-*e*]пиразины



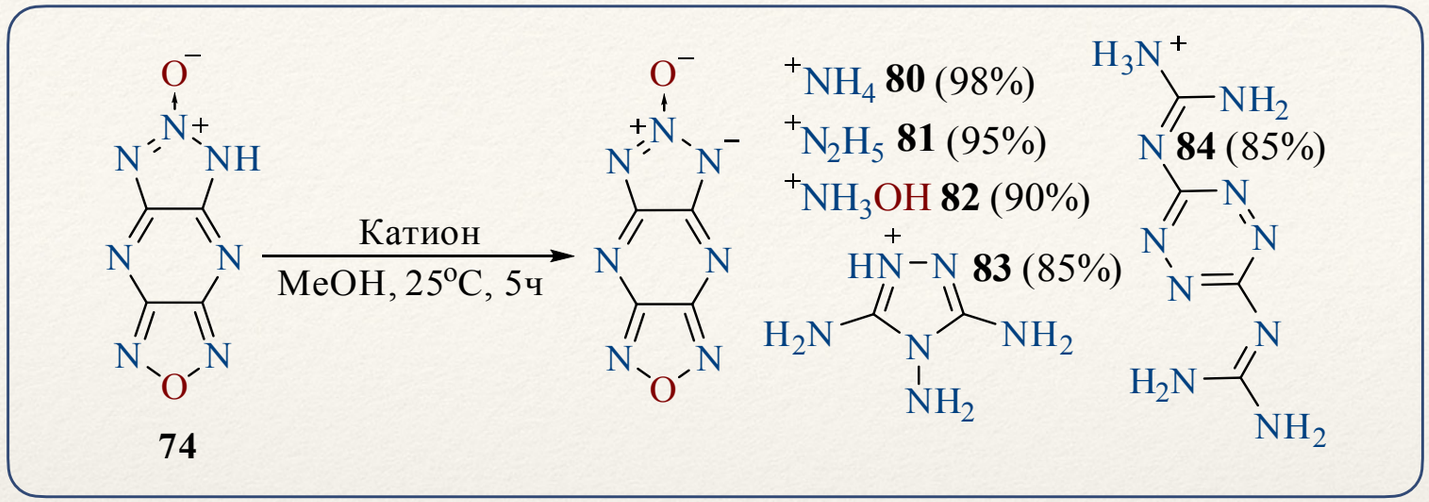
65 **72** (97%) **73** **74** (85%) **75** (94%) **76** (92%)



79 (85%) **75** **77** (82%) **78** (82%)

72-79: Starchenkov I. B., Andrianov V. G., Mishnev A. F. Chemistry of furazano [3, 4-b] pyrazine 6. 1, 2, 3-triazolo [4, 5-b] furazano [3, 4-b] pyrazines //Chemistry of Heterocyclic Compounds. – 1998. – Т. 34. – №. 9. – С. 1081-1085.

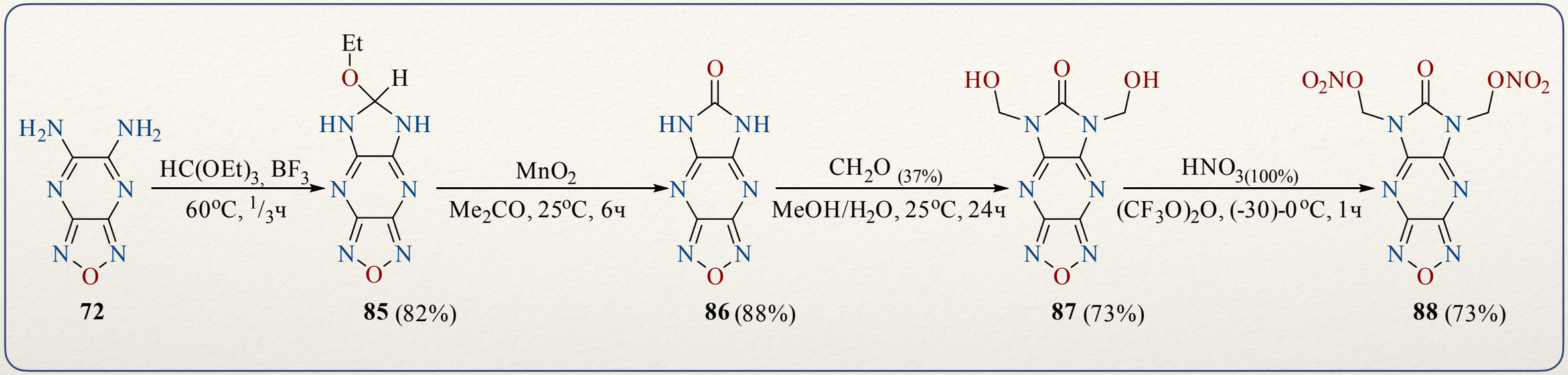
Энергоемкие соли ТФПО

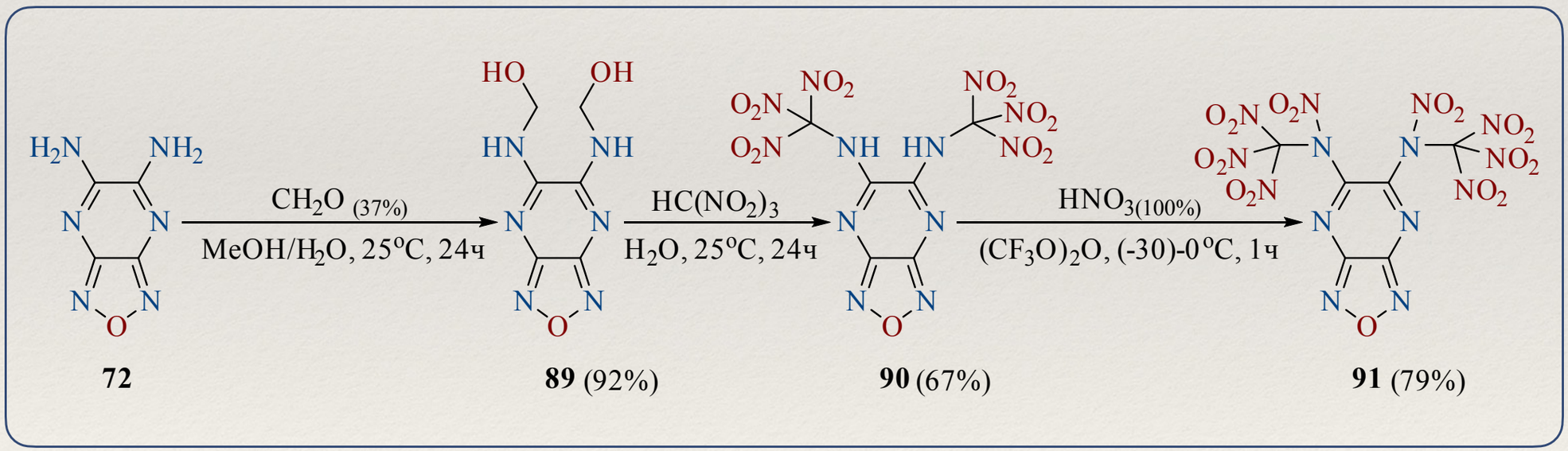


Параметр/Соединение	74[42]	80[42]	81[42]	82[42]	83[42]	84[42]	TNT[42]	RDX[42]
ΔH^0_f[КДж·моль$^{-1}$]	597	476	641	542	794	1070	-67	92
T_d [°C]	281	270	141	157	274	301	295	210
ρ [г·см$^{-3}$]	1,85	1,73	1,76	1,74	1,70	1,69	1,65	1,82
V [км·с$^{-1}$]	8,5	8,1	8,4	8,5	8,0	7,9	8,4	8,9
D [ГПа]	32,4	26,3	30,0	30,3	25,0	24,0	32,1	35,4
IS [Н]	32	>40	38	35	>40	>40	7	7

80-84: Thottempudi V. et al. 1, 2, 3-Triazolo [4, 5,-e] furazano [3, 4,-b] pyrazine 6-oxide–a fused heterocycle with a roving hydrogen forms a new class of insensitive energetic materials //Chemistry–A European Journal. – 2014. – Т. 20. – №. 2. – С. 542-548.

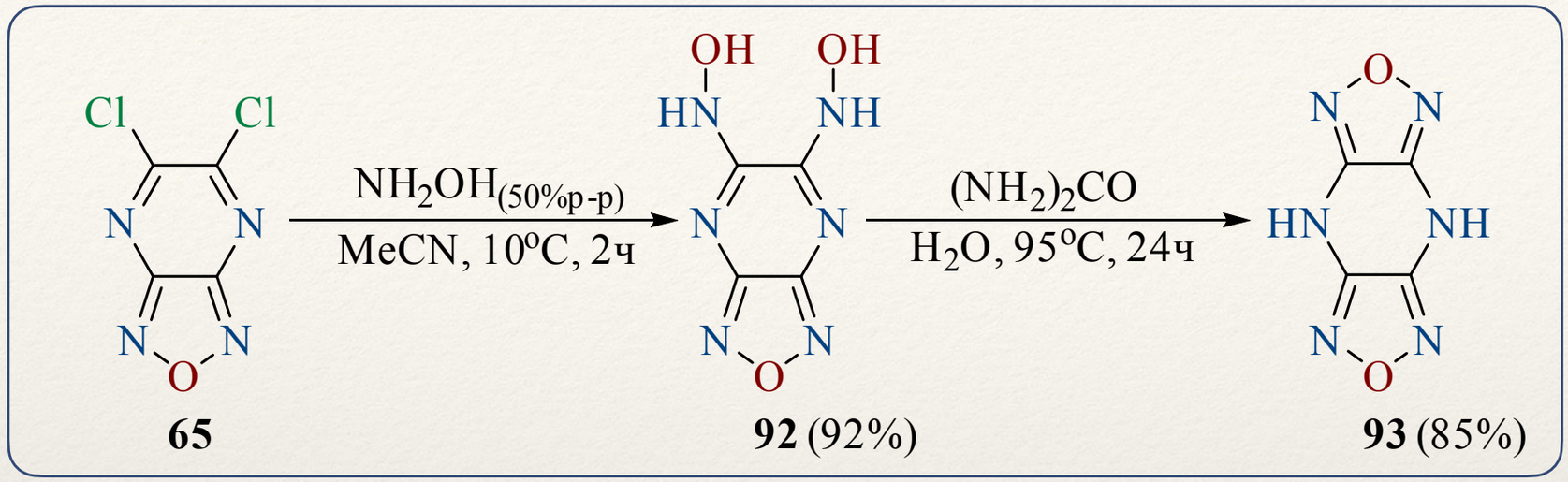
Полинитиропроизводные ДАФП

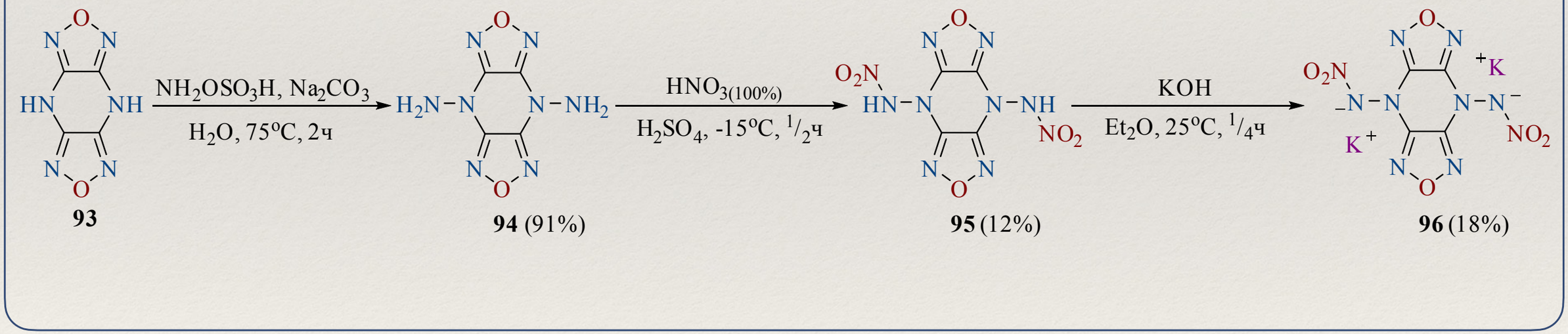




85-91: Starchenkov I. B., Andrianov V. G., Mishnev A. F. The chemistry of furazano-[3, 4-b] pyrazine. 7. Properties of 5, 6-diamino-and 5, 6-dihydrazino-furazano [3, 4-b] pyrazine //Chemistry of Heterocyclic Compounds. – 1999. – Т. 35. – №. 4. – С. 499-508.

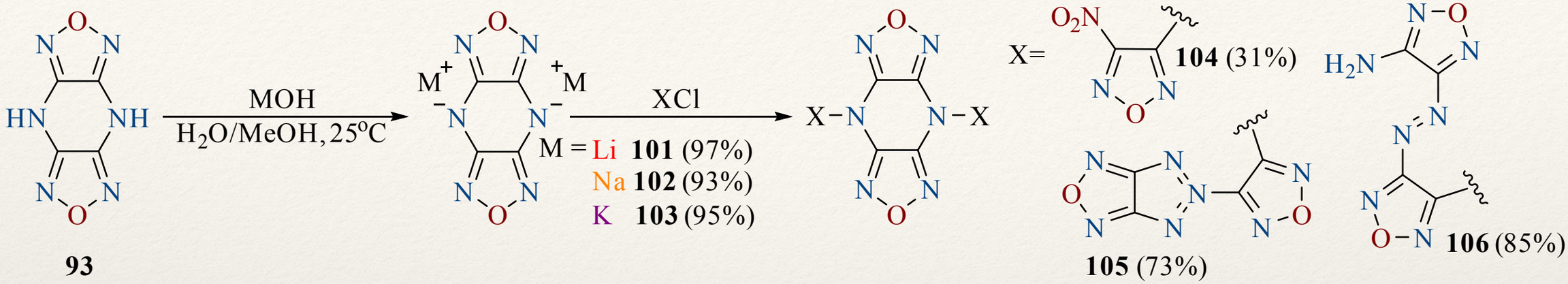
N-функционализированные бисфуразанопиразины I



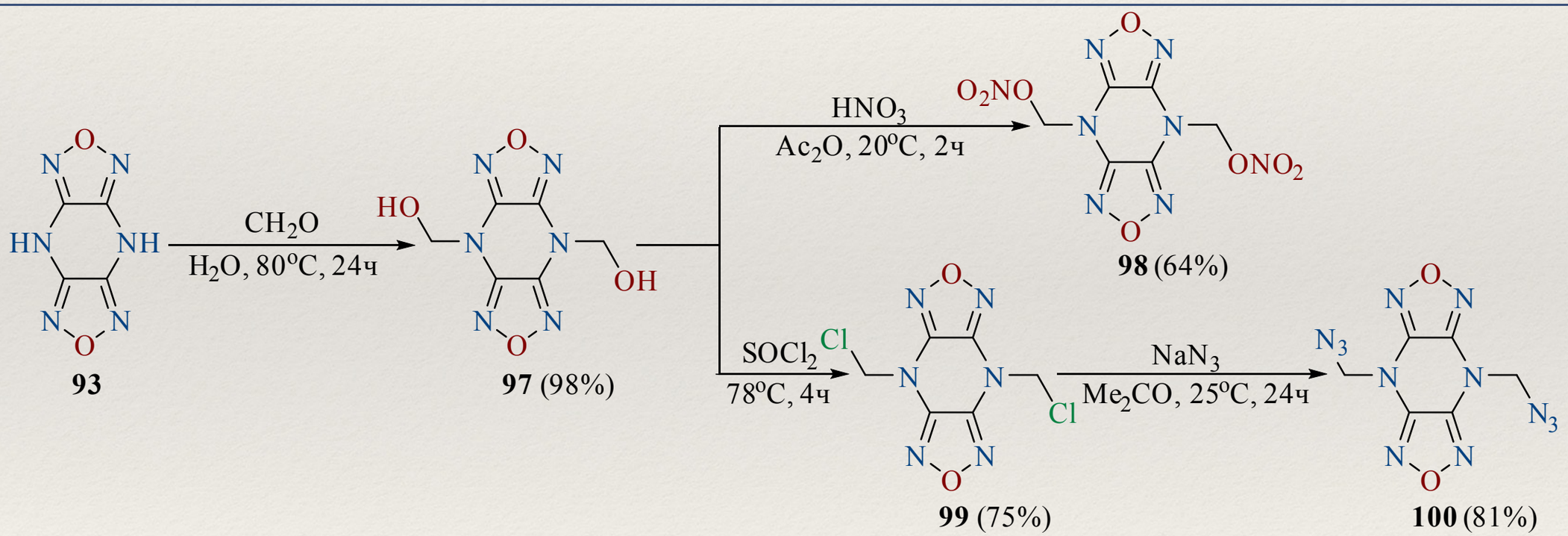


92-96: Li W. et al. Construction of a thermally stable and highly energetic metal–organic framework as Lead-free primary explosives //Crystal Growth & Design. – 2018. – Т. 18. – №. 3. – С. 1896-1902.

20 N-функционализированные бисфуразанопиразины II



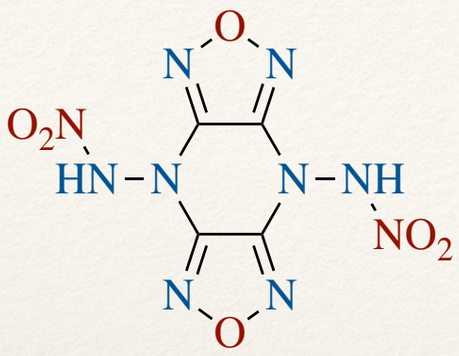
93



104-106: Fischer J. W., Nissan R. A., Lowe-Ma C. K. Synthesis of 4, 8-disubstituted 4H, 8H-bis [1, 2, 5] oxadiazolo [3, 4–6: 3′, 4′-e] pyrazines //Journal of heterocyclic chemistry. – 1991. – Т. 28. – №. 7. – С. 1677-1681

97-100: Zhang J. et al. N-functionalized nitroxy/azido fused-ring azoles as high-performance energetic materials //Journal of Materials Chemistry A. – 2016. – Т. 4. – №. 19. – С. 7430-7436.

Физико-химические параметры и специальные свойства



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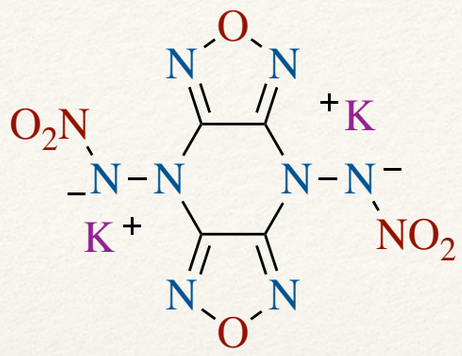

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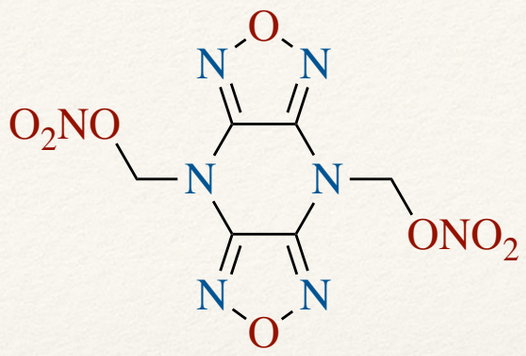

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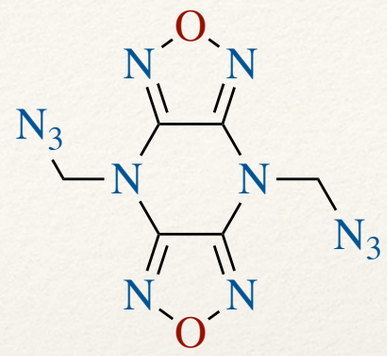
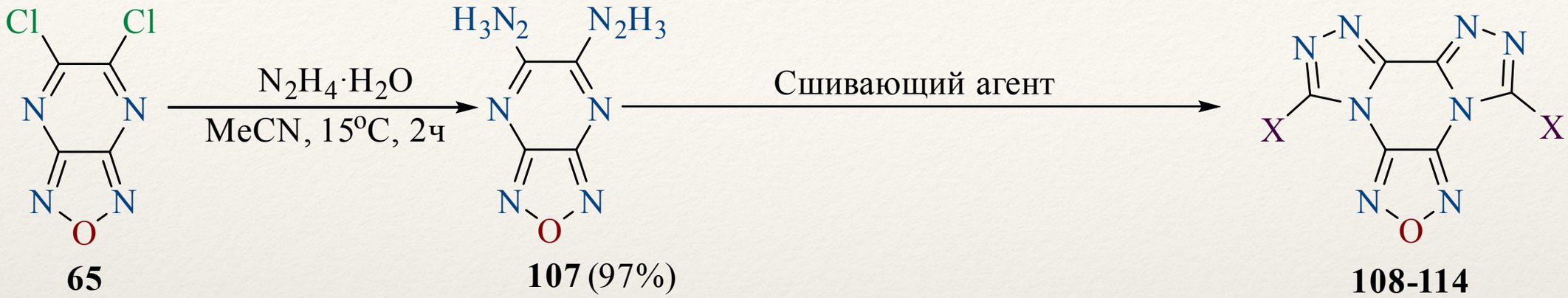
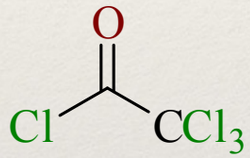
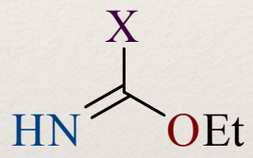
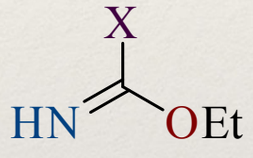
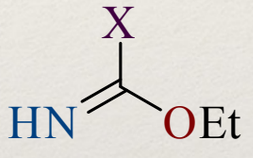
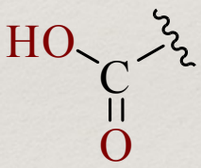
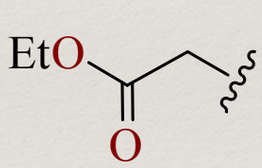
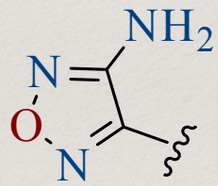
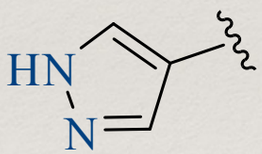


101

Соединение/Параметр	95	96	98	100	$Pb(N_3)_2$	TNT	RDX
ΔH^0_f[КДж·моль$^{-1}$]	750	277	276	1100	450	-67	80
T_m [^{o}C]	-	-	128	122	-	81	-
T_d [^{o}C]	74	292	196	188	315	295	204
ρ [г·см$^{-3}$]	1,80	2,1	1,84	1,68	4,8	1,65	1,86
V [км·с$^{-1}$	9,2	9,7	8,6	8,3	5,9	8,4	8,7
D [ГПа]	36,5	36,8	33,4	27,8	33,4	32,1	35,2
IS [Н]	1	2	18	18	2,5	15	7
FS [Дж]	24	1	240	120	1	360	120

Бис(1,2,4-триазоло)фуразанопиразины



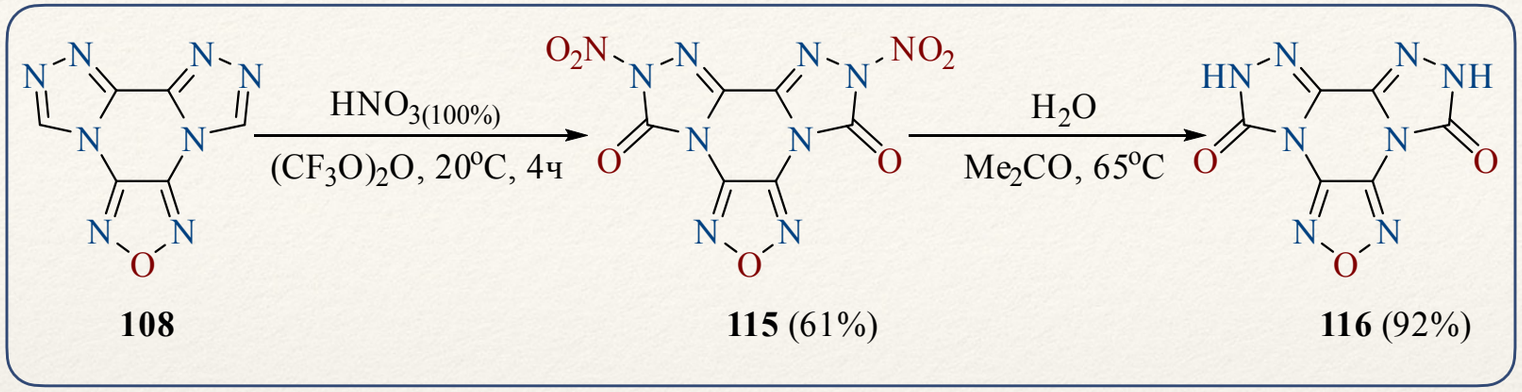
Реагент	HCOOH	Ac_2O	BrCN				
Группа X	H	Me	NH_2				
Соединение	**108** (76%)	**109** (93%)	**110** (75%)	**111** (23%)	**112** (70%)	**113** (56%)	**114** (42%)

108,109, 111-113: Khisamutdinov G. K. et al. Synthesis and properties of 1, 2, 4-triazolo [4, 3-d]-1, 2, 4-triazolo-[3, 4-f] furazano [3, 4-b] pyrazines //Russian Chemical Bulletin. – 1993. – Т. 42. – С. 1700-1702.

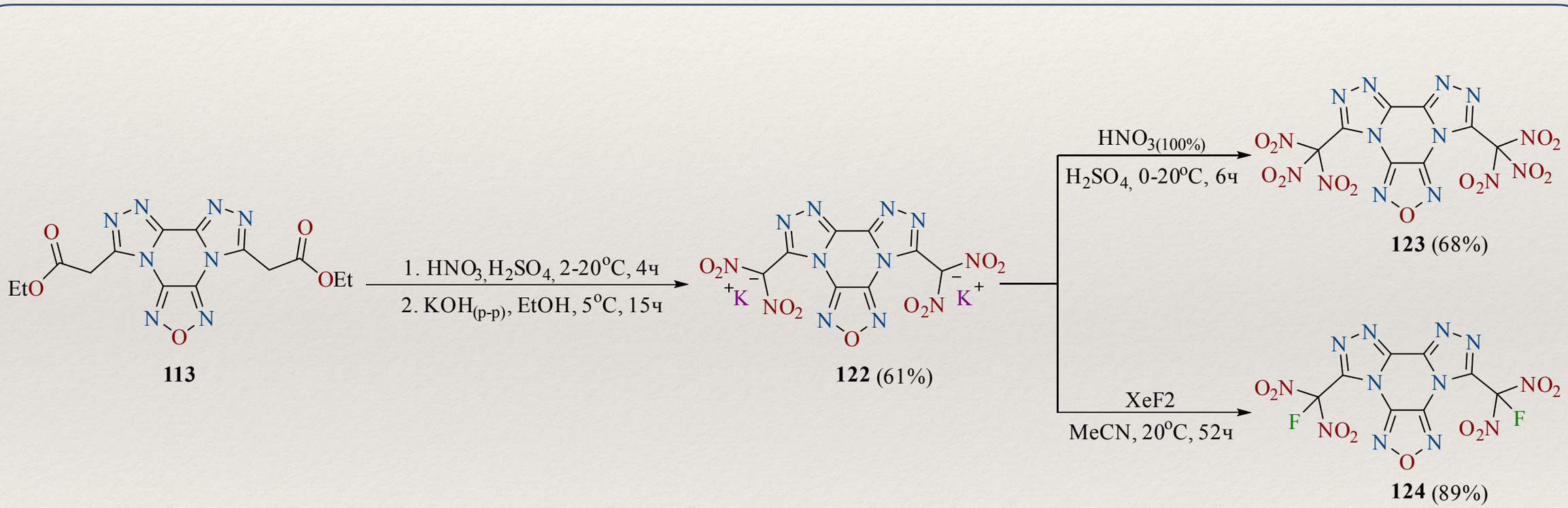
110: Lei C. et al. Toward high-energy and low-sensitivity energetic materials based on a fused [5, 5, 5, 6]-tetracyclic backbone //Organic Letters. – 2023. – Т. 25. – №. 19. – С. 3487-3491.

114: Zhu T. et al. Preparation of novel heat-resistant and insensitive fused ring energetic materials //Journal of Materials Chemistry A. – 2024. – Т. 12. – №. 8. – С. 4678-4683.

Нитрование тетрациклических каркасов I



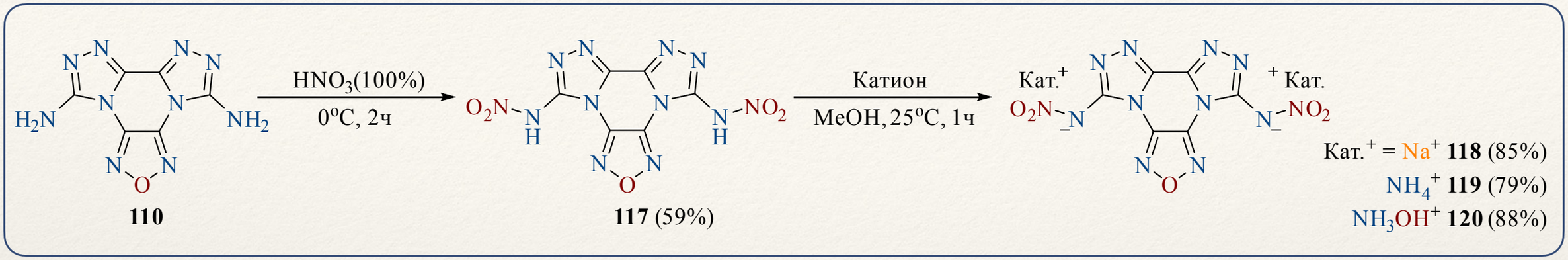
108 **115** (61%) **116** (92%)



113 **122** (61%) **123** (68%) **124** (89%)

115-116 и 122-124: Khisamutdinov G. K. et al. Synthesis and properties of 1, 2, 4-triazolo [4, 3-d]-1, 2, 4-triazolo-[3, 4-f] furazano [3, 4-b] pyrazines //Russian Chemical Bulletin. – 1993. – Т. 42. – С. 1700-1702.

Физико-химические параметры и специальные свойства



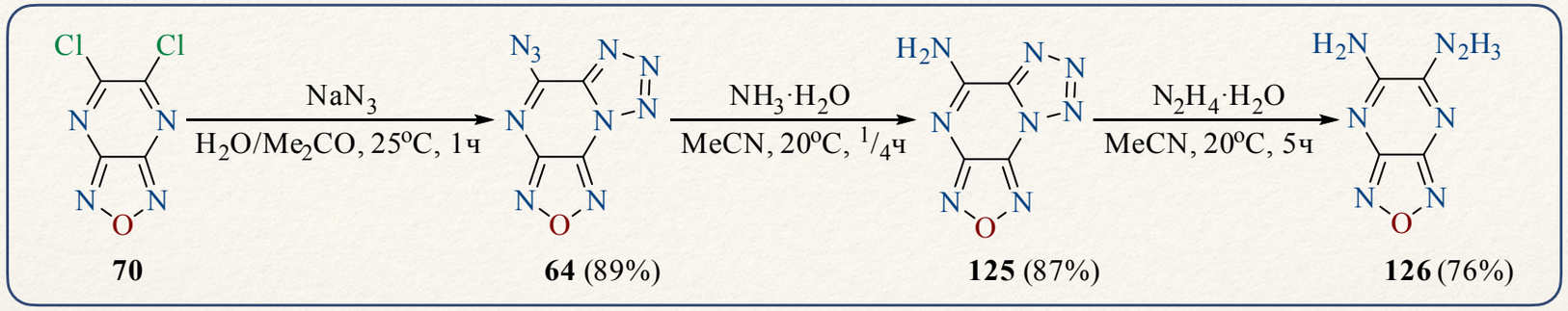
110 **117** (59%)

Соединение/Параметр	110	117	118	119	120	RDX
ΔH^0_f[КДж·моль$^{-1}$]	792	966	917	772	907	70
T_d [^{o}C]	238	151	276	198	171	204
ρ [г·см$^{-3}$]	1,75	1,92	2,00	1.76	1.82	1,86
V [км·с$^{-1}$	8,0	9,2	7,8	8,8	9,0	8,7
D [ГПа]	23,7	37,8	26,9	33,0	35,2	35,2
IS [Н]	40	10	6	24	26	7
FS [Дж]	360	144	108	288	300	120

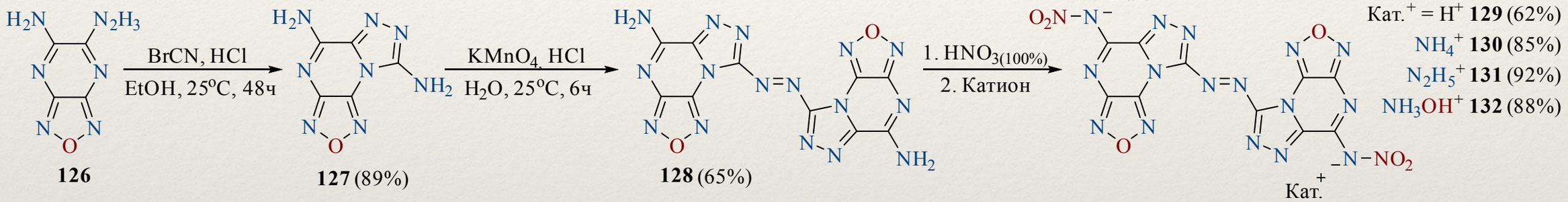
117-120: Lei C. et al. Toward high-energy and low-sensitivity energetic materials based on a fused [5, 5, 5, 6]-tetracyclic backbone //Organic Letters. – 2023. – Т. 25. – №. 19. – С. 3487-3491.

25

Превращения 5-азидотетразолофуразанопиразина

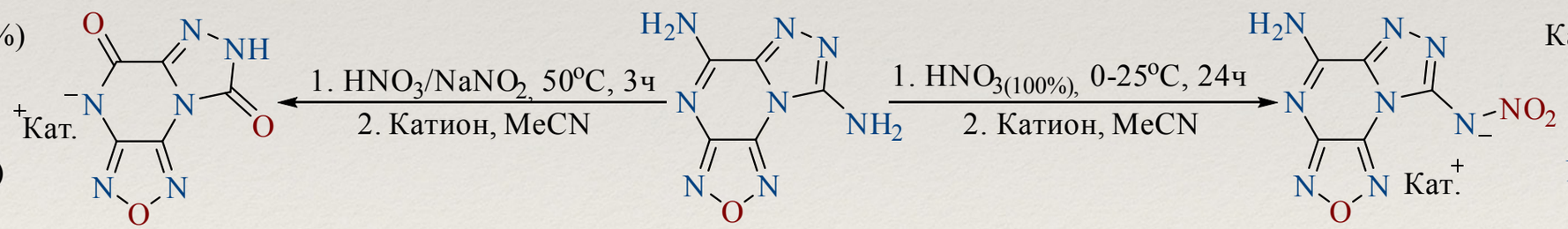


70 **64** (89%) **125** (87%) **126** (76%)



126 **127** (89%) **128** (65%)

Кат.$^+$ = H^+ **129** (62%)
NH_4^+ **130** (85%)
$N_2H_5^+$ **131** (92%)
NH_3OH^+ **132** (88%)



Кат.$^+$ = H^+ **134** (84%)
NH_4^+ **138** (78%)
$N_2H_5^+$ **139** (73%)
NH_3OH^+ **140** (80%)

128

Кат.$^+$ = H^+ **133** (64%)
NH_4^+ **135** (72%)
$N_2H_5^+$ **136** (85%)
NH_3OH^+ **137** (81%)

125-126: Andrianov V. G., Starchenkov I. B., Mishnev A. F. Chemistry of furazano [3, 4-b] pyrazines. 2. Nucleophilic substitution of the azido group in furazano [3, 4-b] pyrazines //Chemistry of Heterocyclic Compounds. – 1997. – Т. 33. – №. 8. – С. 977-981.

127-132: Zhu T. et al. High-Energy and Thermally Stable Energetic Materials Based on an Azo-Fused Dinitramino Compound //Organic Letters. – 2024. – Т. 26. – №. 39. – С. 8430-8434.

133-140: Zhu T. et al. [5, 6, 5]-Tricyclic Energetic Compounds with Piperazine, Triazole, and 1, 2, 5-Oxadiazole Rings in Framework //Crystal Growth & Design. – 2024. – Т. 24. – №. 21. – С. 8847-8854.

Физико-химические параметры и специальные свойства

Соединение/Параметр	ΔH^0_f [КДж·моль$^{-1}$]	T_d [^oC]	P [г·см$^{-3}$]	V [км·с$^{-1}$]	P [ГПа]	IS [Н]	FS [Дж]
127	547	238	1,73	7,9	22,7	40	360
128	1043	283	1,76	7,6	22,7	40	360
129	1918	193	1,88	9,1	36,1	14	48
130	1544	238	1,81	8,7	31,1	20	84
131	1821	205	1,83	8,9	33,4	15	72
132	1668	211	1,86	9,0	35,8	16	80
133	603	200	1,83	8,5	27,3	26	288
134	111	304	1,84	7,9	24,9	22	252
135	575	208	1,75	8,4	27,3	40	360
136	708	211	1,79	8,7	31,5	30	288
137	634	204	1,78	8,7	29,0	34	324
138	109	228	1,76	7,8	22,6	40	360
139	243	218	1,79	8,0	25,0	38	360
140	168	207	1,8	8,1	25	40	360
RDX	80	204	1,8	8,8	33,6	7	120
HNS	78	318	1,75	7,6	24,3	5	240

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