SYNTHESIS OF ENERGETIC MATERIALS IN IONIC LIQUIDS

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University of Maryland
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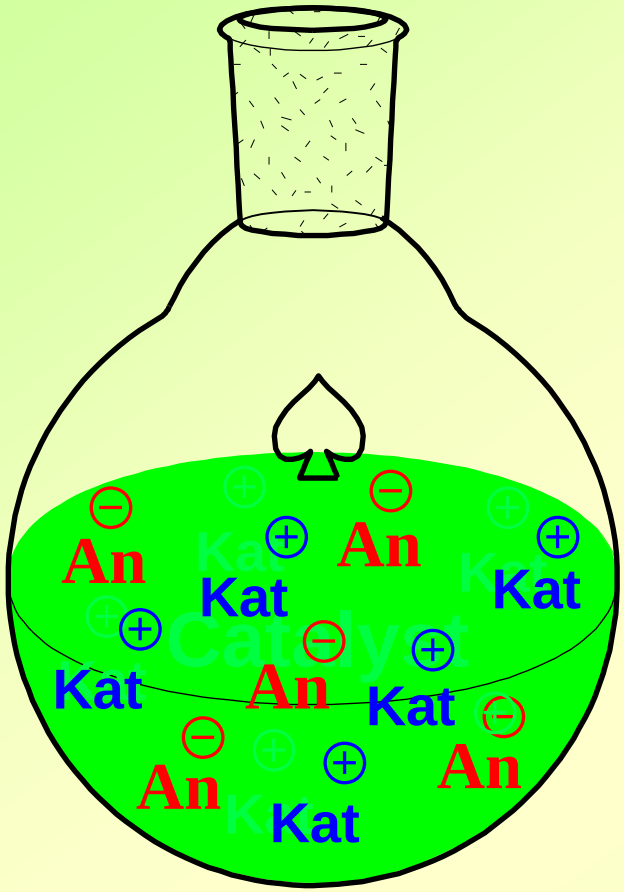
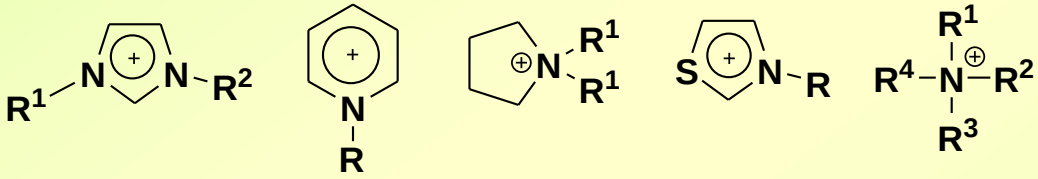
IONIC LIQUIDS – PERSPECTIVE SOLVENTS AND CATALYSTS FOR CHEMICAL REACTIONS



CATIONES



ANIONES

BF_4, PF_6, $AlCl_4$, HSO_4, CF_3SO_3, NTf_2, $N(CN)_2$, $PF_3(C_2F_5)_2$

([bmim][BF_4])

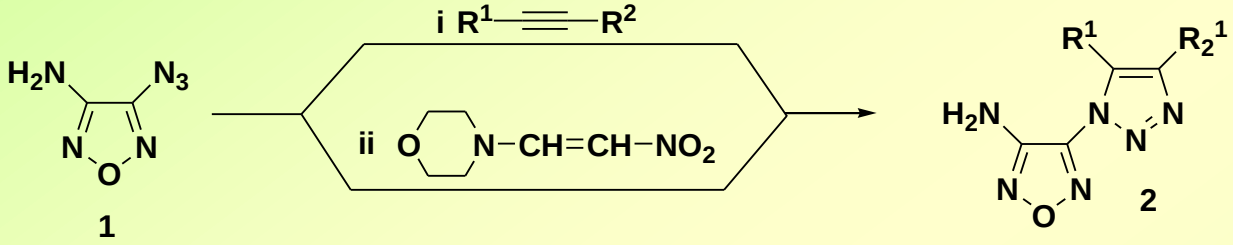
The main advantages of ionic liquids (ILs)
(green chemistry)

- ILs are incombustible
- ILs have very low volatility
- ILs can be regenerated and reused again
- ILs display catalytic activity

S. G, Zlotin, N.N. Makhova, *Mendeleev Commun*., 2010, 20, 63-71

S. G. Zlotin, N. N. Makhova, *Russ. Chem. Rev.,* 2010, 79, 543-583.

SYNTHESIS OF 1-(FURAZANYL)-1,2,3-TRIAZOLES AND 5-MONO- AND 1,5-DISUBSTITUTED TETRAZOLES IN ILs

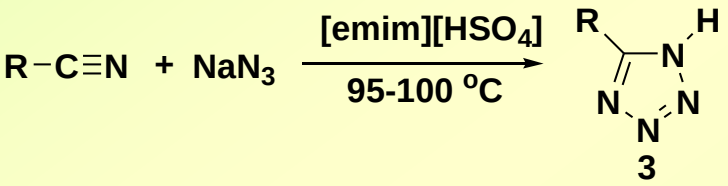


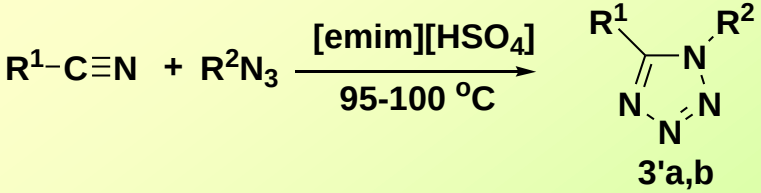
i. ILs = [bmim][BF_4], 80 °C, 6.5-7.5 h (lit. 80 °C, 30h)
ii. ILs = [bmim][PF_6], 70 °C, 12h (lit. 110 °C, 120h)

$R^1 = R^2 = CH_2OH$ (75%); $R^1 = H$, $R^2 = NO_2$ (35%)

a $R^1 = CH_2OH$, $R^2 = H$
b $R^1 = H$, $R^2 = CH_2OH$
} a : b = 4.5 : 1 (71%) (lit. a : b = 2.5 : 1)

I.V.Seregin, L.V.Batog, N.N.Makhova: *Mendeleev Commun.*, 2002, 83



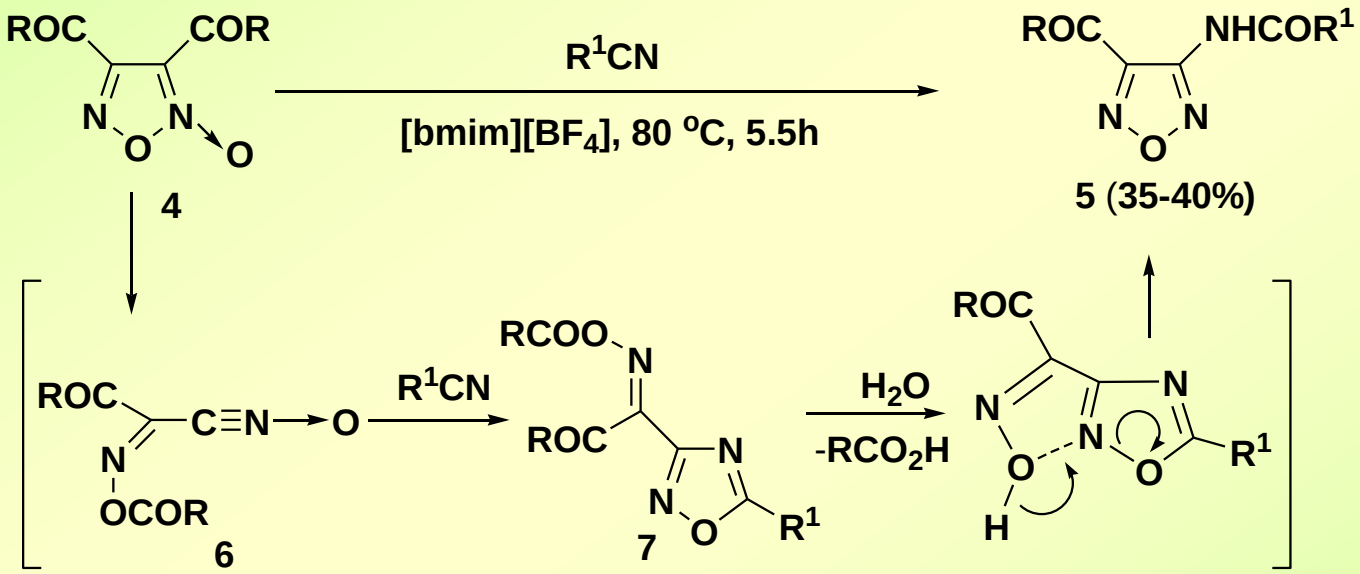


R	Time, h	yield, %
Ph	10	85
4-$NO_2C_6H_4$	3.5	99
3-Py	9	96
Bn	5	80

R^1	R^2	Time, h	yield, %
a			
EtO_2C	Bn	18	74
b			
PhCO	Bu	50	72

N. N. Makhova, A. S. Kulikov, M. A. Epishina, N. V. Ignat'ev, M. Schulte, Russ. Patent, 2010

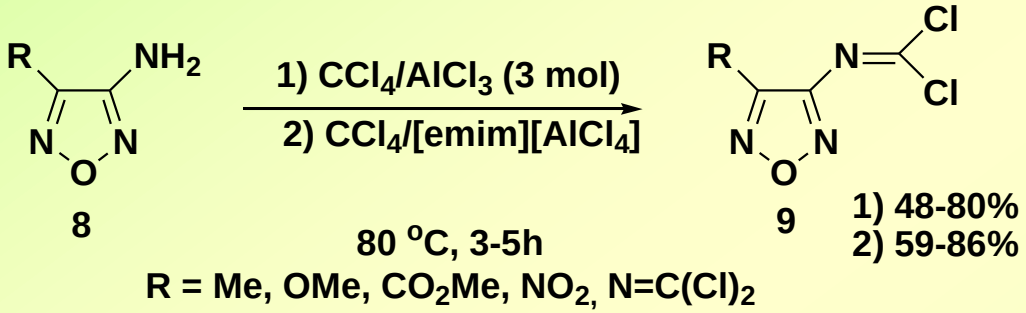
SYNTHESIS OF 3-ACYL-4-ACYLAMINOFURAZANS IN THE REACTION OF 3,4-DIACYLFUROXANS WITH NITRILES IN ILs



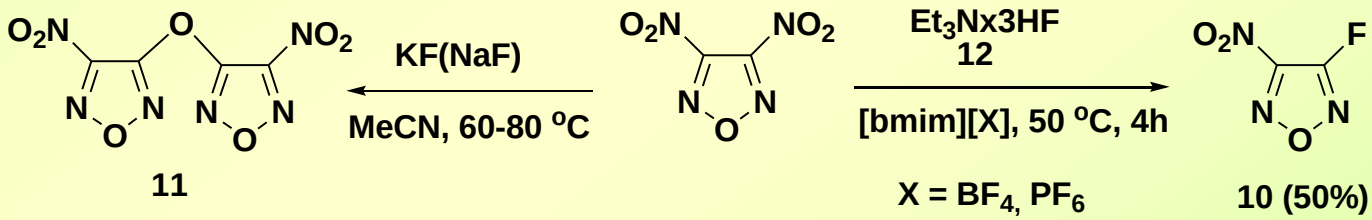
R = Me, cyclo-Pr; R^1 = CCl_3, $EtCO_2$

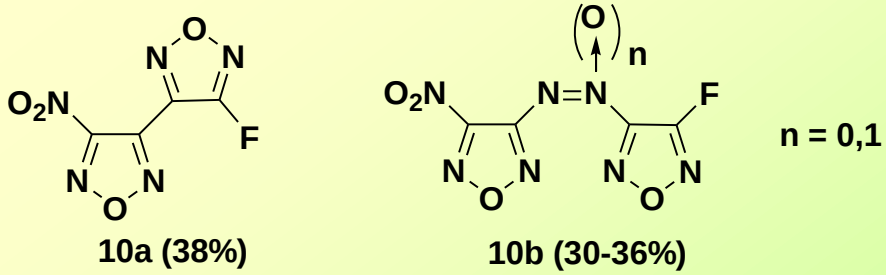
I. V. Seregin, I. V. Ovchinnikov, N. N. Makhova, D. V. Lyubetsky, K. A. Lyssenko, *Mendeleev Commun*., 2003, 230

SYNTHESIS OF DICHLOROIMINO- AND FLUOROFURAZANS IN ILs



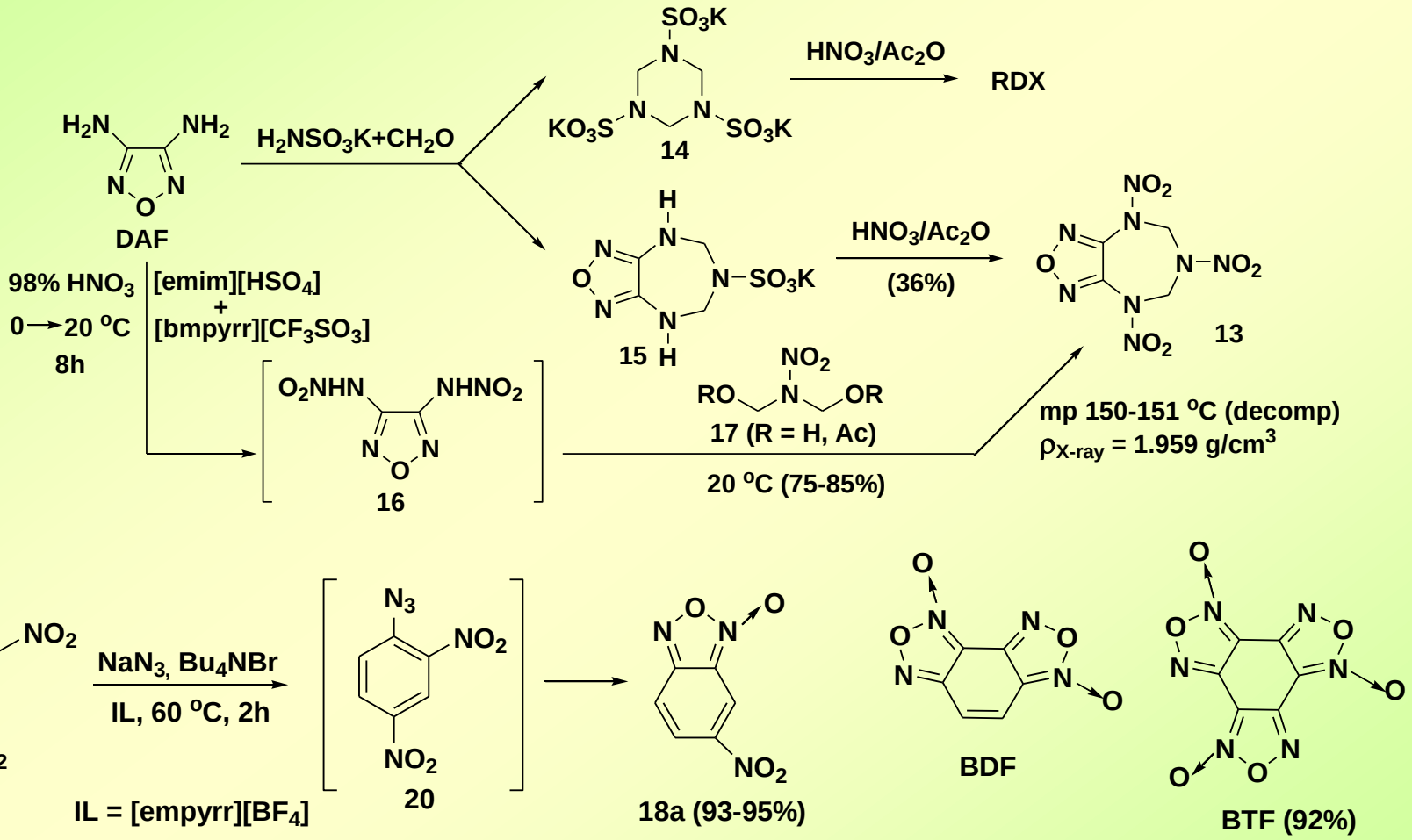
A.B.Sheremetev, N.S.Alexandrova, I.L. Yudin, *Mendeleev Commun*., 2003, 31





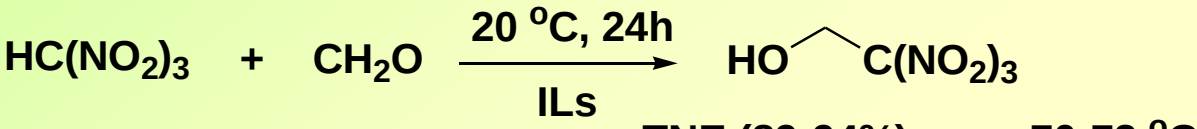
A.B.Sheremetev, N.S.Alexandrova, D.E.Dmitriev, *Mendeleev Commun*., 2006, 163

ONE-POT SYNTHESIS OF FURAZANO[3,4-*f*]-1,3,5-TRIAZEPINE AND BENZOFUROXANS IN ILs



A.B.Sheremetev, N.S.Alexandrova, K.Yu.Suponitsky, M.Yu.Antipin, V.A.Tartakovsky, *Mendeleev Commun.*, 2010, 20, 249.

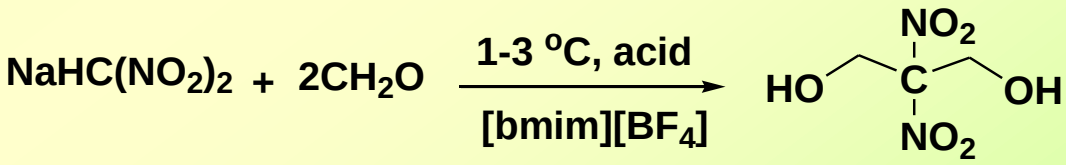
HENRY REACTION OF POLYNITROALKANES IN ILs



TNE (89-94%) mp = 70-72 °C

Synthesis of TNE in ILs

№	IL	Yield of TNE %
1	[bmim][BF_4]	80
2	[bmim][PF_6]	50
3	[emim][HSO_4]	89 (1), 86 (2), 83(3), 94 (4)

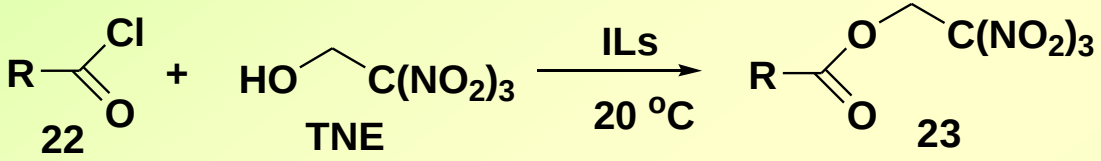


21 (40%)

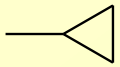
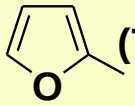
Acid = HCl, CF_3COOH, AcOH

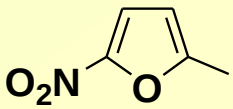
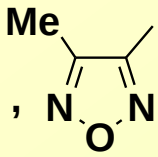
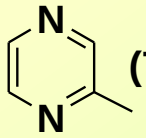
M.A.Epishina, I.V.Ovchinnikov, A.S.Kulikov, N.N.Makhova, V.A.Tartakovsky, *Mendeleev Commun*., 2011, 21, 21.

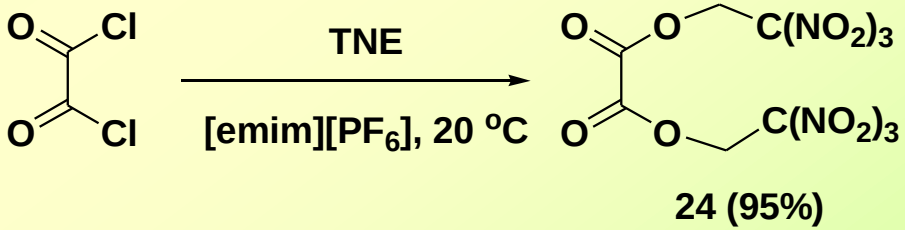
IONIC LIQUID-ASSISTED SYNTHESIS OF CARBOXYLIC ACIDS TRINITROETHYL ESTERS



ILs = [emim][X] X = BF_4, PF_6, $AlCl_4$

R = Ph (93%), 4-ClC_6H_4 (95%),  (85%),  (79%),

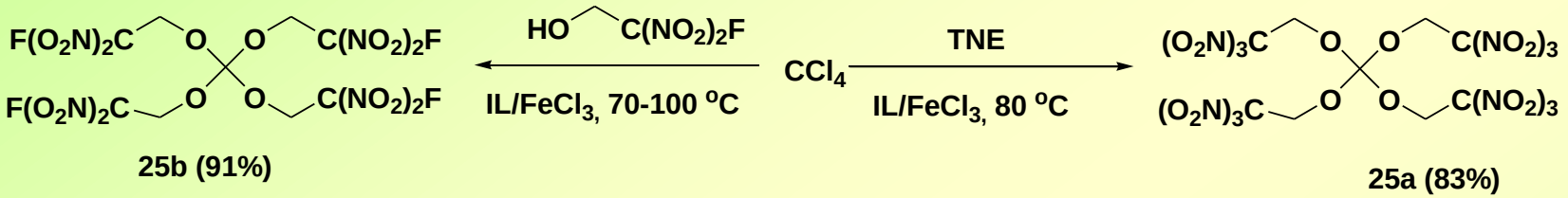
 (92%),  (95%),  (74%)



24 (95%)

A.B.Sheremetev, I.L.Yudin, K.Yu.Suponitsky: *Mendeleev Commun*., 2006, 264

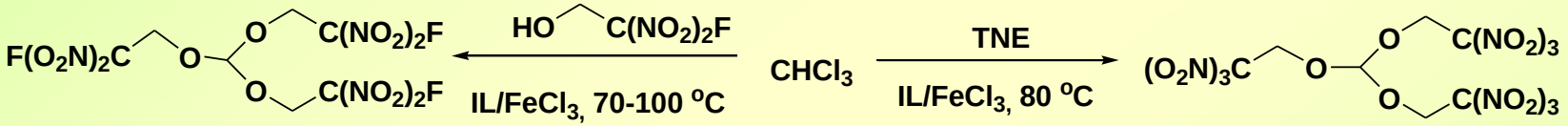
SYNTHESIS OF 2-R-2,2-DINITROETHANOL ORTHOESTERS IN ILs



25b (91%)

25a (83%)

*$K_{dec.}$ at 110 °C = 6.2×10^{-9} s^{-1}



26b (88%)

IL = $[emim][AlCl_4]$

26a (76%)

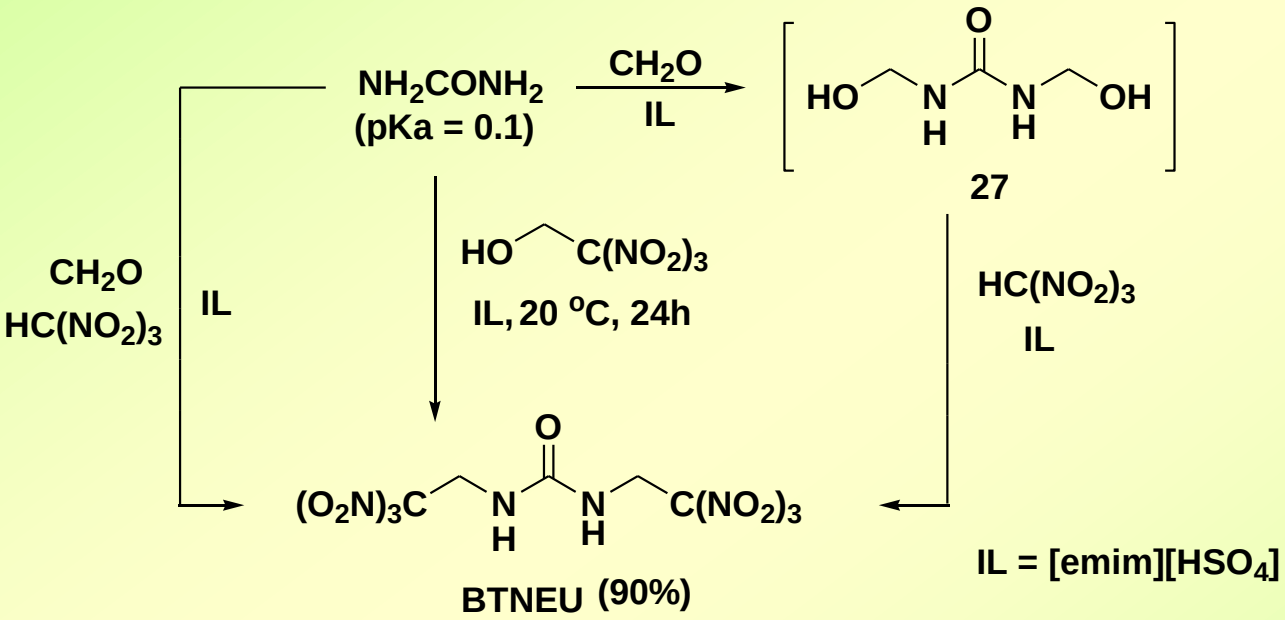
*$K_{dec.}$ at 110 °C = 2.9×10^{-8} s^{-1}

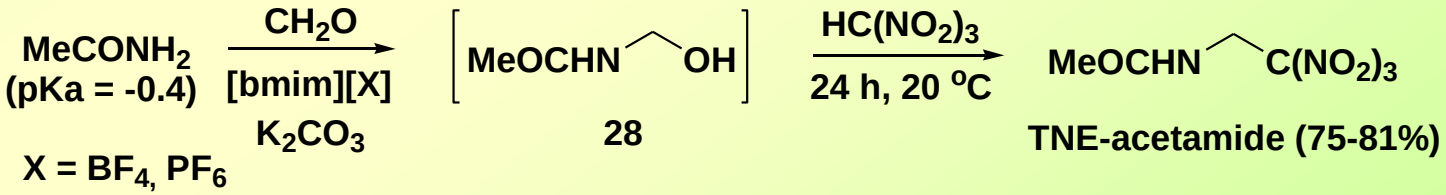
Synthesis of compound 25a in different ILs

N	IL	$FeCl_3$	Yield, %	N	IL	$FeCl_3$	Yield, %
1	[emim][Cl]	-	0	5	$[emim][PF_6]$	-	43
2	[emim][Cl]	5 mol %	41	6	$[emim][PF_6]$	5 mol %	79
3	$[emim][BF_4]$	-	35	7	$[emim][AlCl_4]$	-	54
4	$[emim][BF_4]$	5 mol %	72	8	$[emim][AlCl_4]$	5 mol %	83

A.B.Sheremetev, I.L.Yudin, *Mendeleev Commun.,* 2005, 204
*D.B. Lempert, G.B. Manelis, N.N. Makhova, Yu.M. Mikhailov, G.Nazin, G. Nechiporenko, Proceeding of 10th NTREM, 2007, 25

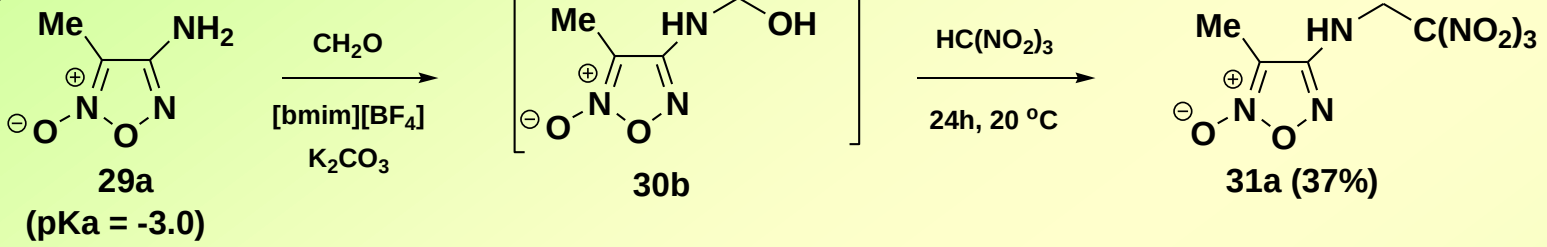
MANNICH REACTION OF UREA AND ACETAMIDE WITH TRINITROETHANOL (or CH_2O + TNM) IN ILs



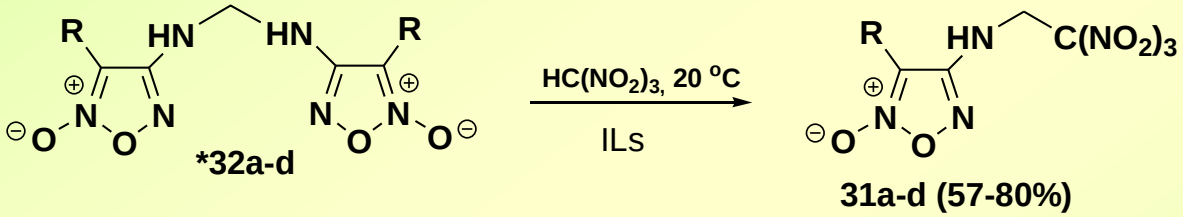


M.A.Epishina, I.V.Ovchinnikov, A.S.Kulikov, N.N.Makhova, V.A.Tartakovsky, *Mendeleev Commun*., 2011, 21, 21.

MANNICH REACTION OF AMINOFUROXANS WITH TRINITROETHANOL (or CH_2O + TNM) IN ILs

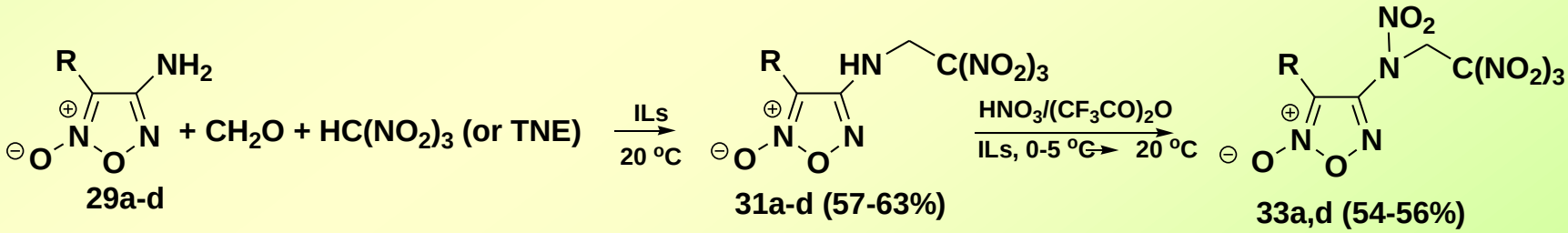


29a (pKa = -3.0) 30b 31a (37%)



*32a-d 31a-d (57-80%)

a R =Me, b R = MeCO, c R = CO_2Me, d R = Ph ILs = [bmim][HSO_4], [bmpyrr][CF_3SO_3]



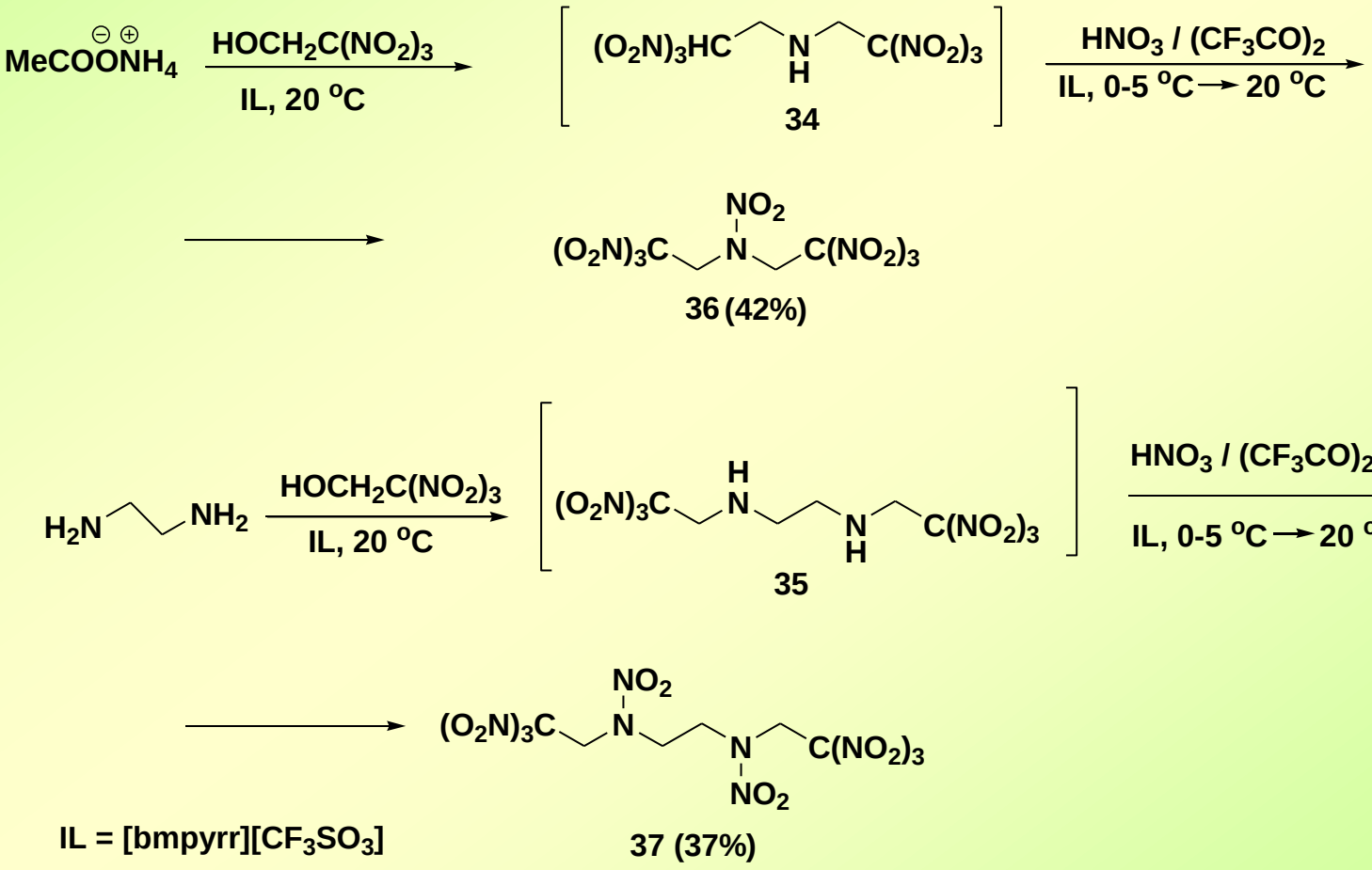
29a-d 31a-d (57-63%) 33a,d (54-56%)

a R =Me, b R = MeCO, c R = CO_2Me, d R = Ph ILs = [bmim][HSO_4], [bmpyrr][CF_3SO_3]

M.A.Epishina, I.V.Ovchinnikov, A.S.Kulikov, N.N.Makhova, V.A.Tartakovsky, *Russ. Chem. Bull. Int. Ed.*, 2011, (in press)

*A.O.Finogenov, M.A. Epishina, A.S. Kulikov, N.N. Makhova, I.V. Anan'ev, V.A. Tartakovsky, Izv. AN; Ser. Khim., 2010, 2054 (in Russian)

ONE-POT SYNTHESIS OF N,N-BIS(2,2,2-TRINITROETHYL)NITRAMINE AND N,N'-BIS(2,2,2-TRINITROETHYL)ETHYLENDINITRAMINE IN ILs



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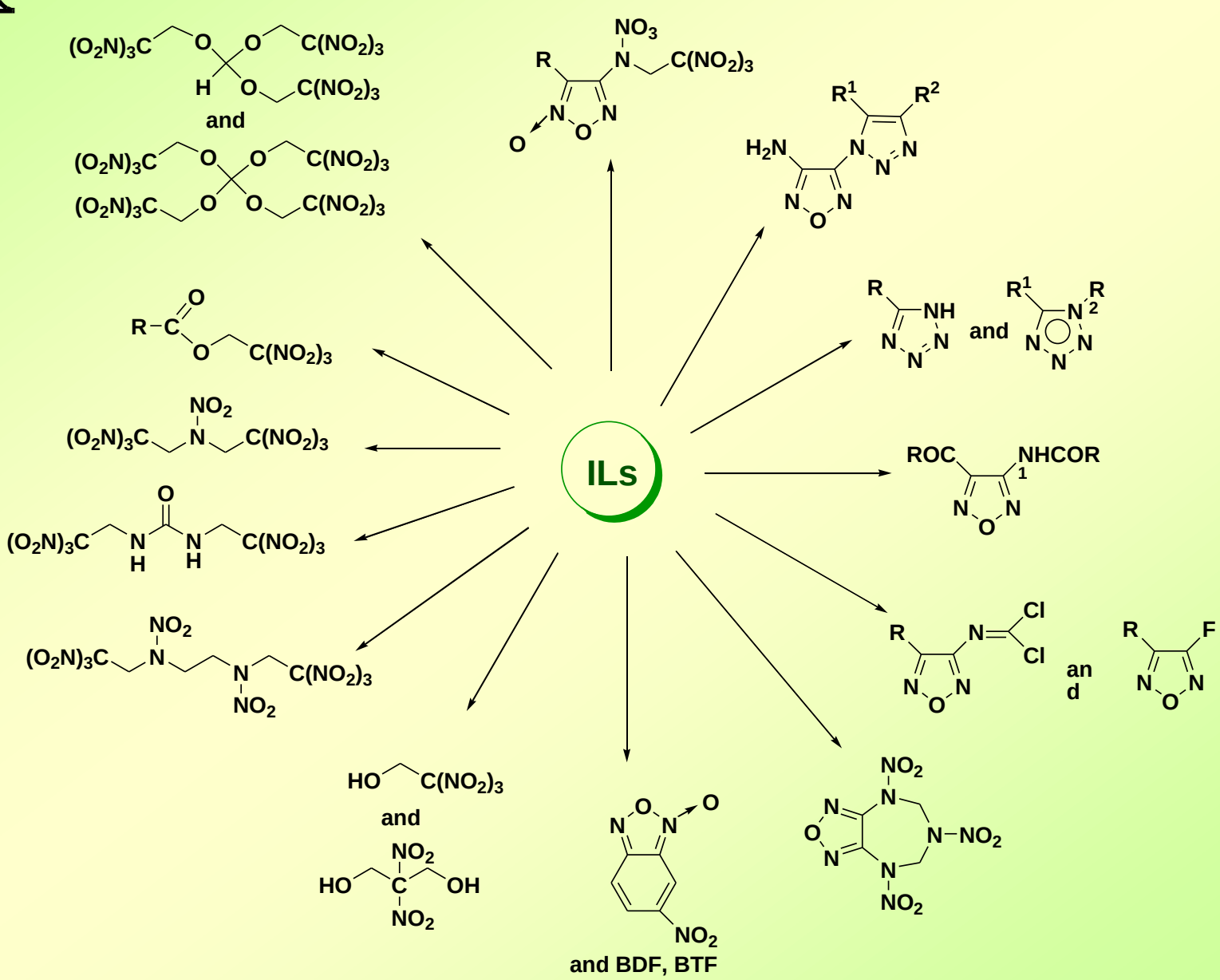
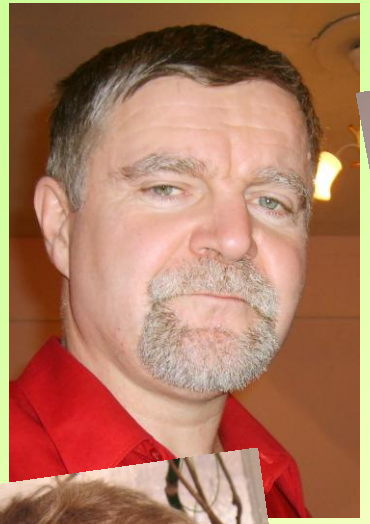
SUMMARY












THANK YOU FOR YOUR ATTENTION !