Transformations of nitrates (nitro esters) of amino alcohols involving both functions

1. Reaction with alkali metal hydrogen carbonates

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The reaction of nitrates (nitro esters) of amino alcohols with alkali metal hydrogen carbonates yielding oxazolidin-2-ones and tetrahydro-1,3-oxazin-2-ones was discovered. A large number of both known and newly synthesized nitrates of amino alcohols with various structures were involved in this reaction, and the optimum reaction conditions were found. New oxazolidin-2-ones and tetrahydro-1,3-oxazin-2-ones were synthesized. Two more transformations were found for a few examples. One of the reactions gives nitramino alcohols, whereas another reaction affords polymers.

Key words: amino alcohols, *N*-acylation, *O*-nitration, nitrates (nitro esters) of amino alcohols, hydrogen carbonates, cyclization, oxazolidin-2-ones, tetrahydro-1,3-oxazin-2-ones, rearrangement, polymerization.

Nitro esters of amino alcohols,* which are generally prepared as nitrates by nitration of amino alcohols, have been studied primarily as energetic compounds.[1—5] Data on their chemical transformations or the use of these compounds in organic synthesis are scarce. As examples we refer to the reaction of diethanolamine dinitrate with formaldehyde giving rise to methylenediamine,[6] *N*-nitrosation of nitrates of amino alcohols containing the secondary amino group,[4,7] and *N*-acylation of aminoethanol nitrate.[8] The latter reaction was used in one of alternative procedures for the preparation of *N*-(2-nitroxyethyl)nicotinamide (Nicorandil), which is a new highly efficient cardiac drug.[9] In the above-cited examples, the reactions proceed with the involvement of only one of two reaction centers of amino alcohol nitrates, *viz.*, the amino group.

In the monograph,[10] it was hypothesized that nitrates of amino alcohols, like other derivatives of amines containing polar substituents (halogen atom or sulfate group) in the β position, can be subjected to cyclization involving both reaction centers to form ethyleneimines. The authors of the monograph[10] referred to the study of Japanese chemists[11] who examined the relationship between the reactivity of ephedrine derivatives and their three-dimensional structures. However, in the cited study, we found no data on cyclization of ephedrine nitrate. The cyclization reaction described in this study deals with a halogen derivative. Apparently, the idea suggested in the monograph[10] has not as yet been confirmed experimentally.

Therefore, to our knowledge, transformations of nitrates of amino alcohols involving the amino and nitrate groups are unknown. In our opinion, the discovery and study of these reactions may help in gaining a better insight into the nature of nitrates of amino alcohols and provide an approach to new compounds possessing useful properties.

When studying the behavior of one of the nitrates of amino alcohols, which we synthesized with the aim of searching for new compounds possessing cardiac activity, we found three types of transformations (Scheme 1).

The transformation (*a*) afforded the oxazolidine ring analogously to the transformation known for β-haloalkylamines[12,13] (Scheme 2).

Apparently, the transformation (*b*) belongs to a previously unknown type of rearrangements of nitrates of amino alcohols (if this reaction proceeds according to an intramolecular mechanism).

The transformation (*c*) is somewhat analogous to quaternization polymerization of *N*-(2-nitroxyethyl)nicotinamide described earlier[14] (Scheme 3).

According to the results of thermomechanical spectroscopy, compound **4** is a polymer with an amorphous-crystalline topological structure. In the temperature range

* Hereinafter, nitrates of amino alcohols.

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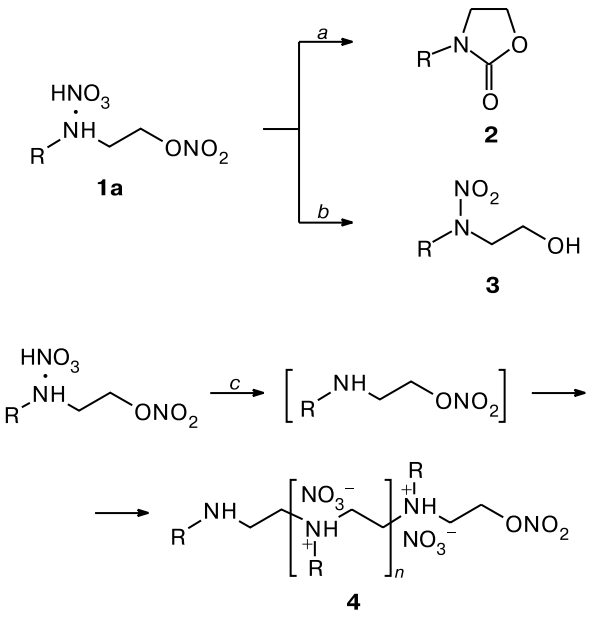
Scheme 1



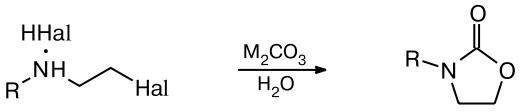
R = O_2N–C$_6$H$_4$–$CONHCH_2CH_2$–, *n* = 7

a. 2 equiv. of $KHCO_3$, H_2O; *b*. 2 equiv. of KOH, Pr^iOH, MeOH; *c*. 1 equiv. of KOH, MeOH

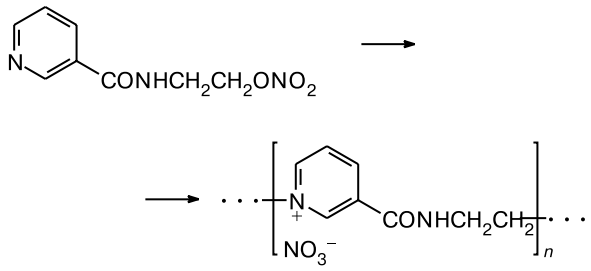
from −100 °C to 6 °C, compound **4** occurs in the crystalline glassy state. As the temperature is increased to 6 °C, the segmental mobility starts to freeze out. At 117 °C and 127 °C, crystal modifications with molecular weights of macromolecules of about $1 \cdot 10^3$ and $4 \cdot 10^3$, respectively, start to melt. The temperature of the onset of molecular flux is 141 °C.

In the present study, we examined primarily transformations of type (*a*), carried out reactions (*b*) and (*c*) (see Scheme 1), and established the structures of their reaction products.

Scheme 2



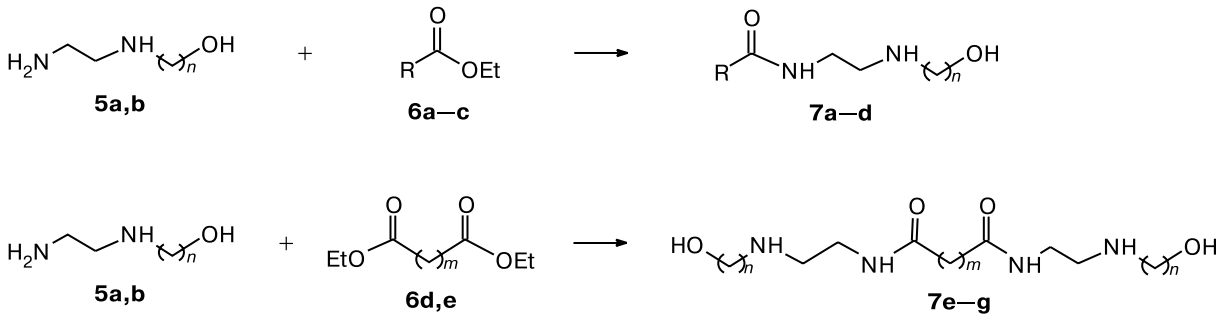
Scheme 3



Results and Discussion

We studied the reactions of nitrates of amino alcohols with potassium and sodium carbonates using both known and, predominantly, newly synthesized nitrates with different structures (Table 1). The differences in the molecular structures are associated with the position of the nitroxy group with respect to the amine nitrogen atom (β or γ), the number of nitroxy and amino groups, the nature of the amino group (primary or secondary), and the presence or absence of the third functional group (amide group). Compounds containing the amide group were synthesized not only with the aim of studying their

Scheme 4



n = 2 (**5a**), 3 (**5b**)

R = 4-$O_2NC_6H_4$ (**6a**), 4-$AcNHC_6H_4$ (**6b**),  (**6c**),

m = 0 (**6d**), 2 (**6e**)

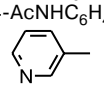
Compound	R	*n*	Compound	*n*	*m*
7a	4-$O_2NC_6H_4$	2	**7e**	2	0
7b	4-$O_2NC_6H_4$	3	**7f**	3	0
7c	4-$AcNHC_6H_4$	2	**7g**	2	2
7d		2			

Table 1. Characteristics of nitrates of amino alcohols and amido amino alcohols

Compound	Found / Calculated (%)			Molecular formula	^{1}H NMR (DMSO-d_6), δ (*J*/Hz)	IR, ν/cm^{-1}
	C	H	N			
1a	36.70 36.57	4.02 4.19	19.63 19.39	$C_{11}H_{15}N_5O_9$	3.25 (t, 2 H, C<u>H</u>$_2$NH, *J* = 5.3); 3.51 (t, 2 H, NHC<u>H</u>$_2$, *J* = 4.5); 3.63 (dt, 2 H, CONHC<u>H</u>$_2$, $J_{CH-CH} \cong J_{CH-NH} \cong 5.3$); 4.86 (t, 2 H, CH_2ONO_2, *J* = 4.5); 8.12 (d, 2 H, CH, *J* = 9.7); 8.38 (d, 2 H, CH, *J* = 9.7); 8.90 (br.s, NH·HNO_3); 9.03 (br.t, 1 H, CONH, $J_{NH-CH} \cong 5.3$)	1635, 1275, 870, 850 (ONO_2); 2885, 2795, 2745, 2430 (NH_2^+); 1380 (NO_3^-); 3385, 1670 sh, 1540 (NHCO); 1515, 1345 (NO_2); 2975, 2935, 2860, 1460, 1440, 1420 (CH_2); 1595, 1480, 1420, 870, 720 (Ar)
1b	38.55 38.40	4.56 4.57	18.42 18.66	$C_{12}H_{17}N_5O_9$	2.06 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 3.00—3.33 (br.m, 4 H, $C\underline{H}_2NH_2^+C\underline{H}_2$); 3.60 (m, 2 H, CONHC<u>H</u>$_2$); 4.60 (t, 2 H, CH_2ONO_2, $J \cong 6.3$); 8.20 (m, 4 H, CH, AB system, $\Delta\nu_{AB} \cong 40$); 8.70 (br.m, 2 H, NH·HNO_3); 9.00 (br.t, 1 H, CONH, $J \cong 5.0$)	1621, 1276, 852 (ONO_2); 3024, 2791 (NH_2^+); 1379 (NO_3^-); 3380, 1647, 1541 (NHCO); 1518, 1343 (NO_2); 2943, 2860, 1441 (CH_2); 1600, 1490, 870, 720 (Ar)
1e	25.20 25.11	4.98 4.64	23.59 23.42	$C_{10}H_{22}N_8O_{14}$	3.17 (br.t, 2 H, C<u>H</u>$_2$NH, $J \cong 5.9$); 3.43 (br.m, 2 H, NHC<u>H</u>$_2$); 3.49 (br.m, 2 H, CONHC<u>H</u>$_2$); 4.80 (br.t, 4 H, CH_2ONO_2, *J* = 4.3); 8.81 (br.s, 4 H, NH·HNO_3); 9.00 (br.t, 2 H, CONH, $J_{NH-CH} \cong 5.9$)	1640, 1280, 842 (ONO_2); 3000, 2800, 1650 (NH_2^+); 1380 (NO_3^-); 3395, 3275, 1675, 1555, 1510 (NHCO); 2955, 2840, 1460, 1435 (CH_2)
1f	28.17 28.46	5.17 5.18	22.06 22.13	$C_{12}H_{26}N_8O_{14}$	2.05 (m, 4 H, $CH_2C\underline{H}_2CH_2$); 3.11 (br.m, 8 H, CH_2NHCH_2); ~3.5 (m, 4 H, $CONHCH_2$); 4.58 (t, 4 H, CH_2ONO_2, $J \cong 6.0$); 8.60 (br.m, 4 H, NH·HNO_3); 8.93 (br.t, 2 H, CONH, $J_{NH-CH} \cong 5.7$)	1635, 1278, 878 (ONO_2); 2970 (NH_2^+); 1380 (NO_3^-); 3350, 1670, 1521 (NHCO); 2965, 2849 sh, 1436 sh (CH_2)
1g	17.62 17.46	5.27 4.76	25.76 25.45	$C_4H_{13}N_5O_9$	—	1637, 1273, 859, 847, 751 (ONO_2); 2937 (NH_3^+); 2791, 2739 (NH_2^+); 1384 (NO_3^-); 1474 (CH_2)
1i	24.19 24.49	4.87 5.14	21.50 21.42	$C_8H_{20}N_6O_{12}$	2.06 (m, 4 H, $CH_2C\underline{H}_2CH_2$); 3.13 (t, 4 H, C<u>H</u>$_2$NH, $J \cong 7.0$); 3.29 (s, 4 H, $NHC\underline{H}_2C\underline{H}_2NH$); 4.60 (t, 4 H, CH_2ONO_2, $J \cong 7.0$); 8.87 (br.s, 4 H, NH·HNO_3)	1361 sh, 1618, 1281, 875 (ONO_2); 3027, 2792, 2425 (NH_2^+); 1382 (NO_3^-); 2940, 2850 sh, 1474 sh (CH_2)

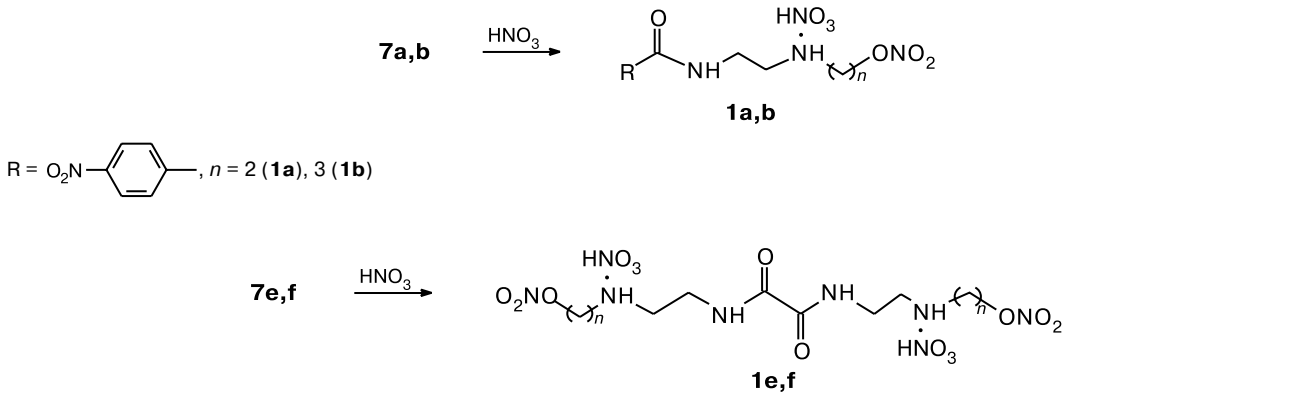
chemical properties but also for the purpose of using these compounds for the preparation of potentially biologically active compounds belonging to a series of amino amide derivatives. It is known[15] that many compounds belonging to amino amides, which can be represented as monoacylated diamines, possess high biological, including cardiac, activities. However, amino amides containing nitroxyalkyl substituents remained unknown.

The starting amino alcohols containing amide groups (amido amino alcohols) were synthesized by *N*′-acylation of *N*-(2-hydroxyethyl)ethylenediamine (**5a**) and *N*-(3-hydroxypropyl)ethylenediamine (**5b**) with 4-nitrobenzoic (**6a**), 4-acetamidobenzoic (**6b**), nicotinic (**6c**), oxalic (**6d**), and succinic (**6e**) esters (Scheme 4, Table 2).

Then alcohols **7a**—**g** were nitrated with nitric acid. It should be noted that the expected nitrates were prepared from alcohols **7a**,**b**,**e**,**f** in high yields (Scheme 5, Table 2), whereas the reactions with alcohols **7c**,**d**,**g** afforded mixtures of products, from which we failed to isolate individual compounds.

Two more new nitrates **1g,i** were synthesized by nitration of the known amino alcohols, *viz.*, the above-mentioned *N*-(2-hydroxyethyl)ethylenediamine (**5a**)[16]

Scheme 5



and *N*,*N*′-bis(3-hydroxypropyl)ethylenediamine (**5d**)[17] (Scheme 6, Table 1).

The nitrates presented in Table 1 and nitrates **1h**,[18] **1j**,[1,19] **1k**,[19] and **1l**[4] described earlier were used in the reactions with potassium (sodium) hydrogen carbonates in an aqueous medium. In all cases, the corresponding oxazolidin-2-ones or tetrahydro-1,3-oxazin-2-ones were prepared (Scheme 7, Table 3).

The maximum yields of the products (85—90%) were achieved under the following conditions: potassium (sodium) hydrogen carbonate was used in an excess of 25—50% with respect to the amount corresponding to the stoichiometric coefficients in the equations presented in Scheme 7, the temperature of the reaction mixture was 40—70 °C, and the reaction time was 20—60 min. The reaction can be carried out at room temperature if the

Table 2. Characteristics of amido amino alcohols

Compound	Found / Calculated (%)			Molecular formula	^{1}H NMR (DMSO-d$_6$), δ (*J*/Hz)	IR, ν/cm^{-1}
	C	H	N			
7a	52.40 52.17	6.11 5.97	16.39 16.59	$C_{11}H_{15}N_3O_4$	2.60 (t, 2 H, CH_2N, J = 5.5); 2.73 (t, 2 H, CH_2N, J = 6.0); 3.38 (unresolv. m, 2 H, CH_2NHCO); 3.45 (t, 2 H, CH_2O, $J \cong 5.5$); 3.50 (br.s, NH, OH); 8.07 (d, 2 H, CH, J = 8.1); 8.30 (d, 2 H, CH, J = 8.1); 8.79 (br.t, H, NHCO, $J_{NH-CH} \cong 5.0$)	3285, 1660, 1550 (NHCO); 3105 (NH); 2700 br, 1070 (OH, C—OH); 1515, 1340 (NO_2); 2930, 2855, 1445 (CH_2); 1595, 1480, 1425, 840 (Ar)
7b	53.81 53.92	6.13 6.41	15.30 15.72	$C_{12}H_{17}N_3O_4$	1.58 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 2.62 (t, 2 H, $NHC\underline{H}_2$, $J \cong 6.6$); 2.70 (t, $NHCH_2$, $J \cong 6.0$); 3.24—3.45 (m, $CONHC\underline{H}_2$, NH, OH); 3.47 (t, 2 H, CH_2OH, $J \cong 6.0$); 8.15 (m, 4 H, CH, AB, $\Delta\nu_{AB} \cong 40$); 8.74 (br.t, 1 H, CONH, $J \cong 5.0$)	3920, 1660, 1552 (NHCO); 3109 (NH); 3266, 1069 (OH, C—OH); 1517, 1340 (NO_2); 2901, 2852, 2821, 1436 (CH_2); 3032, 1598, 1486, 862, 722 (Ar)
7c	58.54 58.85	7.05 7.22	15.80 15.84	$C_{13}H_{19}N_3O_3$	2.06 (s, 3 H, CH_3CO); 2.55, 2.66 (t, 2 H each, CH_2NH, $J \cong 6.0$); 3.20—3.40 (m, $CONHC\underline{H}_2$, NH); 3.43 (t, 2 H, $C\underline{H}_2OH$, $J \cong 6.0$); 4.50 (br.s, 1 H, OH); 7.71 (m, 4 H, CH, AB, $\Delta\nu_{AB} \cong 40$); 8.29 (br.t, 1 H, $CO\underline{NH}CH_2$, $J \cong 5.0$); 10.15 (br.s, 1 H, CONHAr)	3245, 1670, 1635, 1525 (NHCO); 3305 (NH); 3305, 1065 (OH, C—OH); 2935, 2900, 2845, 2825, 1745, 1455 (CH_2); 1610, 1595, 1455, 855, 695 (Ar)

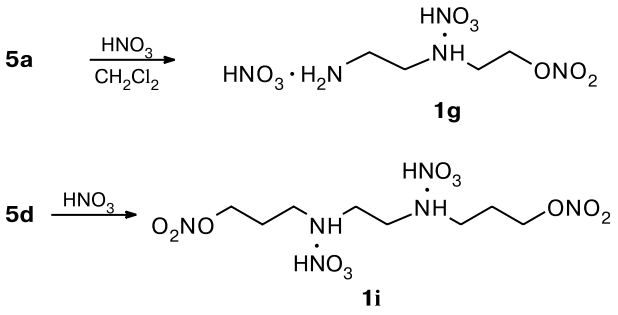
(*to be continued*)

Table 2 (*continued*)

Compound	Found / Calculated (%) C	H	N	Molecular formula	^{1}H NMR (DMSO-d_6), δ (*J*/Hz)	IR, ν/cm^{-1}
7d	57.33 57.40	7.49 7.22	20.11 20.08	$C_{10}H_{15}N_3O_2$	2.61 (t, 2 H, NHC$\underline{H}_2$CH$_2$OH, $J \cong 5.6$); 2.71 (t, 2 H, C$\underline{H}_2$NH, $J \cong 6.0$); 3.37 (dt, 2 H, CONHC$\underline{H}_2$, $J_{CH-CH} \cong J_{CH-NH} \cong 6.0$); 3.46 (t, 2 H, C$\underline{H}_2$OH, $J = 5.6$); 4.34 (br.s, 1 H, OH); 7.47 (dd, 1 H, CH(5), $^3J_{CH-CH} \cong 8.0$; $^3J_{CH-CH} \cong 5.0$); 8.17 (dt, 1 H, CH(4), $^3J_{CH-CH} \cong 8.0$; $^4J_{CH-CH} \cong {}^4J_{CH-CH} \cong 2.0$); 8.61 (br.t, 1 H, CONH, $J_{NH-CH} \cong 6.0$); 8.67 (dd, 1 H, CH(6), $^3J_{CH-CH} \cong 5.0$; $^4J_{CH-CH} \cong 2.0$); 8.99 (d, 1 H, CH(2), $^4J_{CH-CH} \cong 2.0$)*	3325, 1660, 1540 (NHCO): 3305 (NH); 1590, 1745, 1425, 705 (ring); 2935, 2850, 1440 (CH$_2$)
7e	45.44 45.79	8.68 8.45	21.49 21.36	$C_{10}H_{22}N_4O_4$	(DMFA-d_7) 2.66 (t, 4 H, NHC$\underline{H}_2$, $J = 5.3$); 2.77 (t, 4 H, NHC$\underline{H}_2$, $J \cong 5.7$); 3.32 (dt, 4 H, CONHC$\underline{H}_2$, $J_{CH-CH} \cong J_{CH-NH} \cong 5.7$); 3.5 (br.s, 4 H, NH, OH); 3.51 (t, 4 H, CH$_2$O, $J = 5.3$); 8.61 (br.t, NHCO, $J_{CH-NH} \cong 5.7$)	3275, 1675, 1655, 1520 (NHCO); 3295 (NH); 3480, 3270, 1060 (OH, C—OH); 2930, 2904, 2835, 1470, 1455, 1440 (CH$_2$)
7f	49.60 49.64	8.97 9.02	19.00 19.30	$C_{12}H_{26}N_4O_4$	1.50 (m, 4 H, CH$_2$C$\underline{H}_2$CH$_2$); 2.59 (m, 4 H, NHC$\underline{H}_2$); 2.65 (m, 4 H, NHC$\underline{H}_2$); 2.80—3.40 (m, CONHC$\underline{H}_2$, NH, OH); 3.49 (t, 4 H, C$\underline{H}_2$OH, $J \cong 6.0$); 8.54 (br.t, 2 H, CONH, $J_{CH-NH} \cong 5.0$)	3267, 1657, 1553 (NHCO); 3113 (NH); 3923, 1041 (OH, C—OH); 2948, 2887, 2825, 1484, 1442, 1370 (CH$_2$)
7g	49.42 49.64	8.83 9.02	19.49 19.30	$C_{12}H_{26}N_4O_4$	2.30 (s, 4 H, CH$_2$CO); 2.50 (m, 8 H, C$\underline{H}_2$NH); 3.10 (unresolv. m, 4 H, C$\underline{H}_2$NHCO); 3.42 (t, 4 H, CH$_2$O, $J \cong 5.4$); 3.5 (br.s, NH, OH); 7.85 (br.t, 2 H, NHCO, $J_{NH-CH} \cong 5.8$)	3250, 1650, 1615, 1555 (NHCO); 3190 (NH); 3250, 1055 (OH, C—OH)

* The signal for the proton of the NH group is not observed because of its broadening due to exchange.

Scheme 6

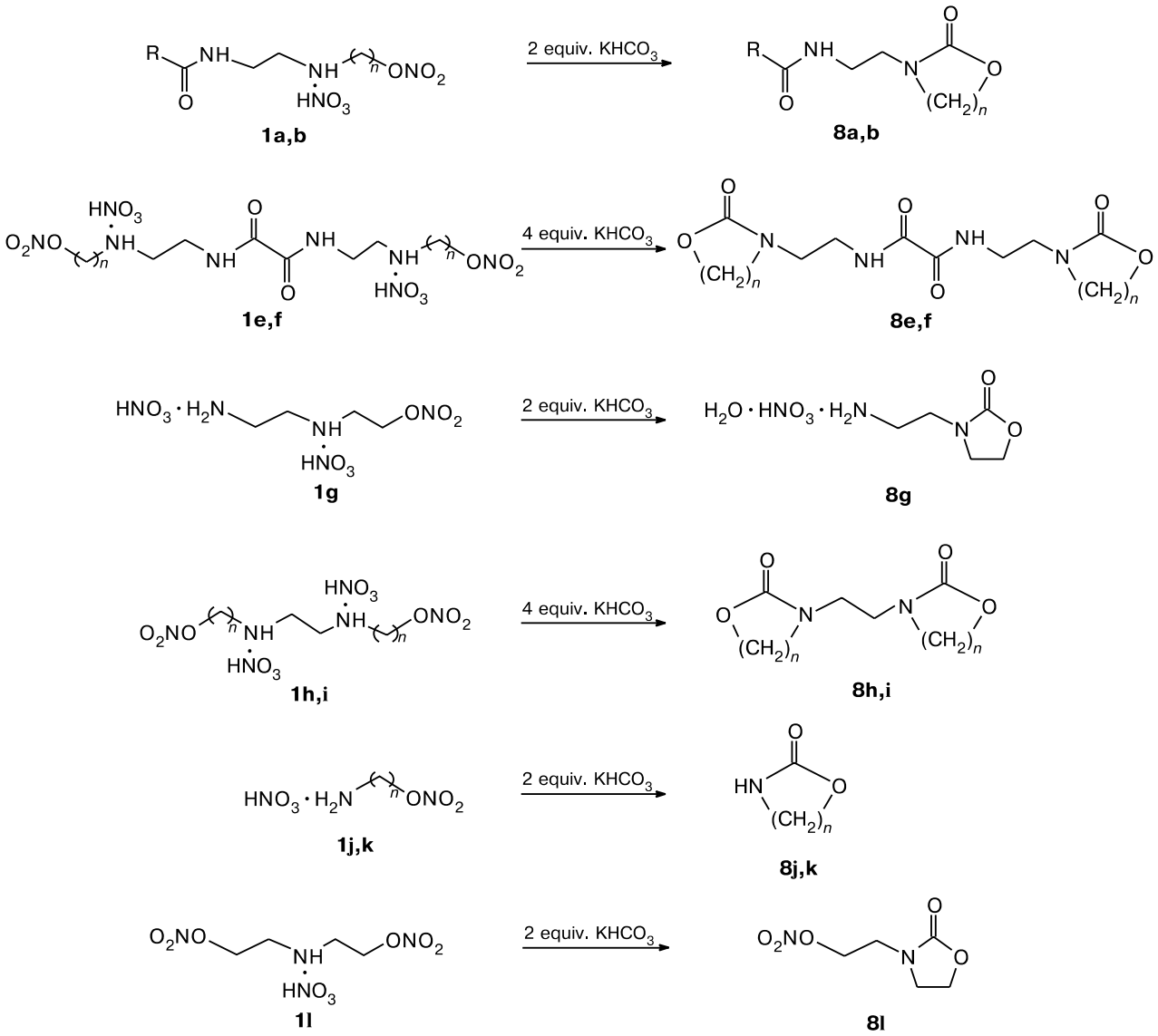


starting nitrates of amino alcohols are water-soluble. However, a small increase in the yield of the products (up to 5%) hardly compensates for time losses (an increase in the reaction time by several hours). The reactions with alkali metal carbonates (Na_2CO_3 or K_2CO_3) afforded products in somewhat lower yields.

The transformation, apparently, proceeds through the nucleophilic displacement of the nitroxy group by the anion of carbonic acid to form hydrogen carbonate of amino alcohol (Scheme 8) followed by the intramolecular nucleophilic attack of the nitrogen atom of the amino group on the carbon atom of the carbonate group. Elimination of the H_2O molecule gives rise to a new C—N bond resulting in cyclization of the molecule.

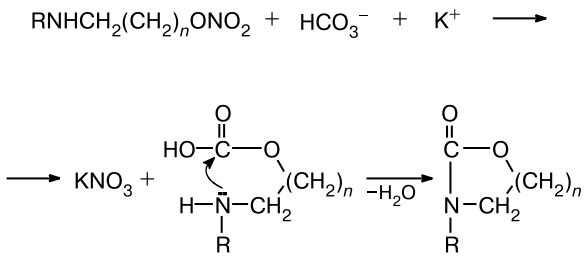
In conclusion, it should be noted that the main result of the present study is the discovery of the reac-

Scheme 7



R = 4-$O_2NC_6H_4$
1, 8: *n* = 2 (**a, e, h,** j); 3 (**b, f, i, k**)

Scheme 8



n = 1, 2

tion of nitrates of amino alcohols involving both reaction centers, which provides fresh insight into the reactivities of these compounds. Another result of our study is that a new procedure was developed for the synthesis of oxazolidin-2-ones and tetrahydro-1,3-oxazin-2-ones, which supplements the set of known methods.[21,22,23] The new method can sometimes be a procedure of choice due to its simplicity and the fact that it requires readily accessible starting compounds. In addition, in some cases the new method has no alternatives (for example, in the synthesis of compounds **8g** and **8l**; see Scheme 7).

Table 3. Characteristics of oxazolidin-2-ones and tetrahydro-1,3-oxazin-2-ones

Compound	Found / Calculated (%)			Molecular formula	^{1}H NMR (solvent), δ (*J*/Hz)	IR, ν/cm^{-1}
	C	H	N			
8a	51.33 51.61	4.57 4.69	15.35 15.05	$C_{12}H_{13}N_3O_5$	(DMSO-d_6) 3.40 (t, 2 H, CH_2NCO, $J \cong 5.6$); 3.45—3.56 (dt, 2 H, $NHCH_2$, $J_{CH-CH} \cong J_{CH-NH} \cong 5.6$); 3.65 (t, 2 H, $NHCH_2CH_2O$, $J \cong 7.6$); 4.28 (t, 2 H, CH_2O, $J \cong 7.6$); 8.04 (d, 2 H, CHC, $J = 8.5$); 8.31 (d, 2 H, $CHCNO_2$, $J = 8.5$); 8.95 (br.t, 1 H, CONH, $J_{NH-CH} \cong 5.6$)	3330, 1655, 1555 (NHCO); 2995, 1606, 1490, 870 (Ar); 2935, 2860, 1455, 1445 (CH_2); 1725, 1270, 1200, 1105 (C=O, C—O, C—N); 1520, 1430 (NO_2)
8b	53.16 53.24	4.97 5.15	13.96 14.33	$C_{13}H_{15}N_3O_5$	(DMSO-d_6) 1.93 (m, 2 H, $CH_2CH_2CH_2$); 3.20—3.60 (m, 6 H, $NHCH_2$, 2 NCH_2); 4.14 (t, 2 H, CH_2O, $J \cong 5.0$); 8.20 (m, 4 H, CH, AB system, $\Delta\nu_{AB} \cong 52$); 8.94 (br.t, 1 H, CONH, $J_{NH-CH} \cong 4.0$)	3316, 1644, 1552 (NHCO); 3048, 2295, 1598, 1490, 842 (Ar); 2960, 2925, 2855, 1455, 1440 (CH_2); 1671, 1266, 1150 (C=O, C—O, C—N); 1517, 1343 (NO_2)
8e	45.66 45.86	5.64 5.77	17.79 17.83	$C_{12}H_{18}N_4O_6$	(DMFA-d_7) 3.30—3.50 (m, 8 H, $NHCH_2CH_2N$); 3.71 (t, 4 H, NCH_2, $J = 7.8$); 4.30 (t, 4 H, CH_2O, $J = 7.8$); 8.90 (br.t, 2 H, CONH, $J \cong 5.0$)	3335, 1655, 1505 (NHCO); 2915, 2870, 1435 (CH_2); 1730, 1265, 1110 (C=O, C—O, C—N)
8f	49.00 49.12	6.40 6.48	16.30 16.36	$C_{14}H_{22}N_4O_6$	(DMSO-d_6) 1.91 (m, 4 H, $CH_2CH_2CH_2$); 3.24—3.36 (m, 12 H, NCH_2); 4.12 (t, 4 H, OCH_2, $J \cong 5.0$); 8.83 (br.t, 2 H, CONH, $J \cong 5.0$)	3351, 1672, 1507, 1496 (NHCO); 2949, 2873 sh, 1444, 1437 (CH_2); 1683, 1259, 1151 (C=O, C—O, C—N)
8g	28.64 28.44	6.13 6.20	20.05 19.90	$C_5H_{13}N_3O_6$	(DMSO-d_6) 3.02, 3.41 (t, 2 H each, $NCH_2CH_2NH_2$, $J \cong 5.8$); 3.55 (m, 2 H, NCH_2, BB′ portion of AA′BB′); 4.27 (m, 2 H, CH_2O, AA′ portion of AA′BB′); 7.98 (br.s, 5 H, $NH_2 \cdot HNO_3 \cdot H_2O$)	2974, 2927, 1629 (NH_3^+); 1382 (NO_3^-); 1485, 1428 (CH_2); 1734, 1269, 1148 (C=O, C—O, C—N)
8h[a]	48.05 48.00	6.17 6.04	13.78 13.99	$C_8H_{12}N_2O_4$	(DMSO-d_6) 3.34 (s, 4 H, NCH_2CH_2N); 3.57 (t, 4 H, CH_2NCO, $J = 7.9$); 4.23 (t, 4 H, CH_2O, $J = 7.9$)	3007, 2943, 2908, 2855, 1491, 1449 (CH_2); 1731, 1273, 1217, 1134, 1115 (C=O, C—O, C—N)
8i	52.42 52.62	6.90 7.07	12.20 12.27	$C_{10}H_{16}N_2O_4$	($CDCl_3$) 2.04 (m, 4 H, $CH_2CH_2CH_2$); 3.46 (t, 4 H, NCH_2, $J \cong 6.0$); 3.58 (s, 4 H, NCH_2CH_2N); 4.25 (t, 4 H, OCH_2, $J \cong 6.0$)	2972, 2943, 2914 sh, 2861, 1488, 1445, 1434 (CH_2); 1683, 1672, 1267, 1137, 1114 (C=O, C—O, C—N)
8j[b]	41.20 41.38	5.48 5.79	16.02 16.08	$C_3H_5NO_2$	($CDCl_3$) 3.65 (m, 2 H, NCH_2, BB′ portion of AA′BB′); 4.46 (m, 2 H, OCH_2, AA′ portion of AA′BB′); 6.77 (br.s, 1 H, CONH)	3275 (NH); 2995, 2931, 2855, 1485, 1411 (CH_2); 1729, 1254, 1084 (C=O, C—O, C—N)
8k[c]	47.35 47.52	6.87 6.97	13.64 13.85	$C_4H_7NO_2$	($CDCl_3$) 1.79 (m, 2 H, $CH_2CH_2CH_2$); 3.18 (td, 2 H, CH_2N, $J \cong 5.9$, $J_{CH-NH} \cong 2.3$); 4.10 (t, OCH_2, $J \cong 5.9$); 7.03 (br.m, 1 H, CONH)	3275 (NH); 2984, 2960, 2925, 2849, 1493, 1480, 1458, 1427 (CH_2); 1689, 1296, 1121, 1077 (C=O, C—O, C—N)
8l	33.98 34.10	4.37 4.58	15.84 15.90	$C_5H_8N_2O_5$	($CDCl_3$) 3.56 (t, 2 H, $NCH_2CH_2ONO_2$, $J \cong 5.1$); ~3.63 (m, 2 H, NCH_2, BB′ portion of AA′BB′); ~4.30 (m, 2 H, OCH_2, AA′ portion of AA′BB′); 4.59 (t, 2 H, CH_2ONO_2, $J \cong 5.1$)	(Film from acetone) 2995, 2925, 1486, 1436 (CH_2); 1749, 1202, 1119 (C=O, C—O, C—N); 1630, 1281, 849 (ONO_2)

[a] See Ref. 20.
[b] See Ref. 12.
[c] See Ref. 21.

Experimental

The ^{1}H NMR spectra of compounds **1a**,**e**, **7a**,**c**,**e**,**g**, and **8a**,**e**,**h** were recorded on an NMR spectrometer equipped with a superconducting magnet (294 MHz); the instrument was developed and built at the Institute of Problems of Chemical Physics in Chernogolovka of the Russian Academy of Sciences. The ^{1}H NMR spectra of all other compounds were measured on a Bruker DXP-200 spectrometer. The IR spectra were recorded on a Specord M-82 spectrophotometer in KBr pellets. The polymerization product of compound **1a** was analyzed on a UIP-70 thermomechanical analyzer.[24]

Commercial amino alcohols, such as **5a**,**c**, aminoethanol, 3-aminopropanol, and diethanolamine, and esters **6a—e** containing no less than 98% of the main compound were used as the starting reagents. Amino alcohols **5b,d** were synthesized according to known procedures.[17,25] Nitrates of amino alcohols **1g—l** were prepared according to procedures described earlier.[1,18,19] Nitration of amino alcohols was carried out with the use of freshly distilled HNO_3 (d = 1.51).

Synthesis of nitrates of amino alcohols 1a,b,e,f,i (general procedure). Amino alcohol (10 mmol) was added portionwise to HNO_3 (0.12—0.2 mol) with stirring and cooling to 0—4 °C. The reaction mixture was kept at 0—2 °C for 30—90 min and then poured onto ice (5 g per milliliter of the starting HNO_3). The precipitate that formed was filtered off, washed with ice water, dried, and recrystallized.

***N*-(5-Nitroxy-3-azoniapentyl)-4-nitrobenzamide nitrate (1a).** Reagents and conditions: HNO_3 (0.15 mol), 45 min. The yield was 94%, m.p. 143—145 °C (with decomp.). After recrystallization from H_2O, m.p. 148—150 °C (with decomp.).

***N*-(6-Nitroxy-3-azoniahexyl)-4-nitrobenzamide nitrate (1b).** Reagents and conditions: HNO_3 (0.12 mol), 1 h. The yield was 85%, m.p. 138—140 °C (with decomp.). After recrystallization from a 1 : 1.3 H_2O—Pr^iOH mixture, m.p. 139—140 °C (with decomp.).

***N*,*N*´-Bis(5-nitroxy-3-azoniapentyl)oxamide dinitrate (1e).** Reagents and conditions: HNO_3 (0.20 mol), 1 h. The yield was 82%, m.p. 144—146 °C (with decomp.). After recrystallization from a 1% HNO_3 aqueous solution, m.p. 152—153 °C (with decomp.).

***N*,*N*´-Bis(6-nitroxy-3-azoniahexyl)oxamide dinitrate (1f).** Reagents and conditions: HNO_3 (0.20 mol), 1.5 h. The yield was 86%, m.p. 156—157 °C (with decomp.). After recrystallization from a 1% aqueous HNO_3 solution, m.p. 157—158 °C (with decomp.).

***N*-(2-Nitroxyethyl)ethylenediammonium dinitrate (1g)** was prepared according to a procedure described earlier.[19] Reagents and conditions: **5a** (20 mmol), HNO_3 (80 mmol), CH_2Cl_2 (35 mL), Ac_2O (32 mmol). The yield was 58%, m.p. 116—120 °C (with decomp.). After recrystallization from MeOH, m.p. 125—127 °C (with decomp.).

***N*,*N*´-Bis(3-nitroxypropyl)ethylenediammonium dinitrate (1i).** Reagents and conditions: HNO_3 (0.20 mol), 30 min. The yield was 91%, m.p. 139—141 °C (with decomp.). After recrystallization from a 5% aqueous HNO_3 solution, m.p. 148—149 °C (with decomp.).

Synthesis of amido amino alcohols 7a—g (general procedure). A mixture of diamino alcohol, ester, and a solvent was refluxed with stirring and cooled. The reaction product was filtered off, washed, and recrystallized.

***N*-(5-Hydroxy-3-azoniapentyl)-4-nitrobenzamide (7a).** Reagents and conditions: **5a** (0.11 mol), **6a** (0.10 mol), Pr^iOH (20 mL), 80—85 °C, 7 h. The yield was 76%, m.p. 132—134 °C. After recrystallization from MeOH, m.p. 135—137 °C.

***N*-(6-Hydroxy-3-azoniahexyl)-4-nitrobenzamide (7b).** Reagents and conditions: **5b** (0.12 mol), **6a** (0.10 mol), Pr^iOH (20 mL), 80—85 °C, 7 h. The yield was 80%, m.p. 129—132 °C. After recrystallization from a CH_2Cl—CH_2Cl, m.p. 134—136 °C.

4-Acetamido-*N*-(5-hydroxy-3-azoniapentyl)benzamide (7c). Reagents and conditions: **5a** (0.15 mol), **6b** (0.10 mol), Bu^sOH (20 mL), 100—105 °C, 10 h; MeCN (100 mL) after cooling to −10 °C. The yield was 58%, m.p. 151—154 °C. After recrystallization from a 1 : 1.5 Bu^sOH—MeCN mixture, m.p. 160—162 °C.

***N*-(5-Hydroxy-3-azoniapentyl)nicotinamide (7d).** Reagents and conditions: **5a** (0.10 mol), **6c** (0.10 mol), without a solvent, 80—85 °C, 6.5 h. Volatile products were removed at 130—140 °C (1 Torr). The yield was 99.5%, m.p. 71—74 °C. After recrystallization from a 1 : 44 : 71 Pr^iOH—$CHCl_3$—CCl_4 mixture, m.p. 76—77 °C.

***N*,*N*´-Bis(5-hydroxy-3-azoniapentyl)oxamide (7e).** Reagents and conditions: **5a** (0.20 mol), **6d** (0.10 mol), MeOH (80 mL), 60 °C, 0.5 h (in the course of stirring of the components, the reaction mixture spontaneously warmed up to 40—50 °C). The yield was 80%, m.p. 127—129 °C. After recrystallization from a 1 : 4.4 MeOH—MeCN mixture, m.p. 133—134 °C.

***N*,*N*´-Bis(6-hydroxy-3-azoniahexyl)oxamide (7f).** Reagents and conditions: **5b** (0.20 mol), **6d** (0.10 mol), Pr^iOH (100 mL), 60 °C, 0.5 h (the reaction mixture spontaneously warmed up). The yield was 92%, m.p. 164—167 °C. After recrystallization from a 1 : 20 Pr^iOH—MeOH mixture, m.p. 169—171 °C.

***N*,*N*´-Bis(5-hydroxy-3-azoniapentyl)succinodiamide (7g).** Reagents and conditions: **5a** (0.25 mol), **6e** (0.10 mol), Bu^sOH (50 mL), 90—95 °C, 25 h, cooling to 0 °C. The yield was 54%, m.p. 112—114 °C. After recrystallization from a 1 : 4 MeOH—MeCN mixture, m.p. 115—116 °C.

Synthesis of oxazolidin-2-ones and tetrahydro-1,3-oxazin-2-ones 8a,b,e,f—l (general procedure). Potassium hydrogen carbonate (or $NaHCO_3$) was added portionwise with stirring and heating to a solution of nitrate of amino alcohol (10 mmol). The reaction mixture was kept at 20—60 min and then cooled to 20 °C. Compounds **8a**,**b**,**e**, which precipitated upon cooling, were filtered off, washed with ice water, dried, and recrystallized. Compounds **8f—l**, which are readily soluble in water, were isolated as follows: the reaction solution was concentrated to dryness (rotary evaporator, 10 Torr, 25 °C), the product was extracted from the residue with an organic solvent, the solvent was removed *in vacuo*, and the residue was recrystallized.

4-Nitro-*N*-[2-(2-oxooxazolidin-3-yl)ethyl]benzamide (8a). Reagents and conditions: H_2O (115 mL), 65—70 °C, $KHCO_3$ (25 mmol), 20 min. The yield was 89%, m.p. 182—184 °C. After recrystallization from a 1 : 5 CCl_4—MeCN mixture, m.p. 183—184 °C.

4-Nitro-*N*-[2-(2-oxotetrahydro-1,3-oxazin-3-yl)ethyl]benzamide (8b). Reagents and conditions: H_2O (75 mL), 50—60 °C,

$KHCO_3$ (30 mmol), 30 min. The yield was 90%, m.p. 205—207 °C. After recrystallization from MeCN, m.p. 207—209 °C.

***N,N´*-Bis[2-(2-oxooxazolidin-3-yl)ethyl]oxamide (8e).** Reagents and conditions: H_2O (120 mL), 50—55 °C, $KHCO_3$ (50 mmol), 30 min. The yield was 85%, m.p. 207—208 °C. After recrystallization from a 1 : 1 MeOH—H_2O mixture, m.p. 211—213 °C.

***N,N´*-Bis[2-(2-oxotetrahydro-1,3-oxazin-3-yl)-ethyl]oxamide (8f).** Reagents and conditions: H_2O (40 mL), 55—60 °C, $KHCO_3$ (50 mmol), 60 min, extraction with hot MeCN. The yield was 70%, m.p. 192—195 °C. After recrystallization from MeCN, m.p. 199—201 °C.

***N*-(2-Ammonioethyl)oxazolidin-2-one nitrate monohydrate (8g).** Reagents and conditions: H_2O (10 mL), 20 °C, $KHCO_3$ (20 mmol), 4 h. The reaction solution was concentrated and the residue was recrystallized from a 1 : 2 MeOH—$CHCl_3$ mixture. The yield was 55%, m.p. 97—99 °C.

1,2-Bis(2-oxooxazolidin-3-yl)ethane (8h). Reagents and conditions: H_2O (37 mL), 50—55 °C, $KHCO_3$ (50 mmol), 60 min, extraction with a 1 : 2 MeOH—CH_2Cl_2 mixture. The yield was 86%, m.p. 102—105 °C. After recrystallization from Pr^iOH, m.p. 107—108 °C (*cf.* lit. data[20]: m.p. 107 °C).

1,2-Bis(2-oxotetrahydro-1,3-oxazin-3-yl)ethane (8i). Reagents and conditions: H_2O (30 mL), 55—60 °C, $KHCO_3$ (50 mmol), 30 min, extraction with CH_2Cl_2. The yield was 79%, m.p. 129—131 °C. After recrystallization from a 1 : 3 $CHCl_3$—*n*-heptane mixture, m.p. 134—135 °C.

Oxazolidin-2-one (8j). Reagents and conditions: H_2O (8.5 mL), 50—55 °C, $KHCO_3$ (30 mmol), 20 min, extraction with CH_2Cl_2. The yield was 91%, m.p. 83—87 °C. After recrystallization from a 1 : 1 $CHCl_3$—CCl_4 mixture, m.p. 89—90 °C (*cf.* lit. data[12]: m.p. 90—91 °C).

Tetrahydro-1,3-oxazin-2-one (8k) was prepared analogously to compound **8j**. The yield was 87%, m.p. 79—81 °C. After recrystallization from a 1 : 5 $CHCl_3$—CCl_4 mixture, m.p. 82—84 °C (*cf.* lit. data[21]: m.p. 80 °C).

3-(2-Nitroxyethyl)oxazolidin-2-one (8l). Reagents and conditions: H_2O (14 mL), 40—45 °C, $KHCO_3$ (20 mmol), 60 min, extraction with CH_2Cl_2. The yield was 86%, m.p. 24—28 °C. After recrystallization from a 1 : 2 $CHCl_3$—CCl_4 mixture, m.p. 30—32 °C.

Transformation of 1a into nitramino alcohol *N*-(5-hydroxy-3-nitro-3-azoniapentyl)-4-nitrobenzamide (3). A solution of 85% KOH (0.66 g, 10 mmol) in MeOH (7 mL) was added dropwise with stirring to a mixture of compound **1a** (1.81 g, 5 mmol) and Pr^iOH (15 mL) at ~20 °C. Then the reaction mixture was heated to 50 °C and kept at 50—55 °C for 1 h. After cooling to 20 °C, the inorganic precipitate that formed was filtered off and washed with Pr^iOH. The filtrate was concentrated to dryness. The residue was washed with H_2O and dried. The yield of compound **3** was 1.34 g (90%), m.p. 107—109 °C. After recrystallization from Pr^iOH, m.p. 111—112 °C. Found (%): C, 44.46; H, 5.00; N, 18.44. $C_{11}H_{14}N_4O_6$. Calculated (%): C, 44.30; H, 4.73; N, 18.79. IR (in KBr pellets), ν/cm^{-1}: 1550, 1280, 1257 (NNO_2); 1511, 1345 (NO_2); 3413, 1076 (OH); 3357, 1537 sh, 1632 (CONH); 1595, 1495, 720 (Ar). ^1H NMR (DMSO-d_6), δ: 3.40 (t, 2 H, $CH_2N(NO_2)$, $J \cong 5.6$ Hz); 3.45—3.56 (dt, NHC$\underline{H}_2$, $J_{CH,CH} \cong J_{CH,NH} \cong 5.6$ Hz); 3.65 (t, 2 H, C$\underline{H}_2CH_2OH$, $J \cong 7.6$ Hz); 4.28 (t, 2 H, C$\underline{H}_2$OH, $J \cong 7.6$ Hz); 8.04 (d, 2 H, CHC, $J \cong 8.5$ Hz); 8.31 (d, 2 H, $CHCNO_2$, $J \cong 8.5$ Hz); 8.95 (br.t, 1 H, CONH, $J \cong 5.6$ Hz).

Polymerization of 1a. A solution of 85% KOH (0.2 g, 3 mmol) in MeOH (5 mL) was added dropwise with stirring and cooling to 15 °C to a mixture of compound **1a** (1.08 g, 3 mmol) and MeOH (10 mL). The reaction mixture was kept at 20 °C for 1 h. The inorganic precipitate that formed was filtered off and washed with MeOH. Dichloromethane (20 mL) was added to the filtrate and the inorganic precipitate that formed was filtered off. The filtrate was concentrated *in vacuo* to obtain a resinous yellow compound in a yield of 0.88 g. The compound solidified upon heating to 50 °C for 0.5 h. Then MeCN (25 mL) was added to the compound and the reaction mixture was refluxed. The resulting solution was filtered and the filtrate was cooled. The precipitate that formed was filtered off, washed with MeCN, and dried to obtain compound **4** in a yield of 0.64 g (72%). Found (%): C, 43.85; H, 4.85; N, 18.50. $(C_{11}H_{14}N_4O_6)_n$. Calculated (%): C, 44.30; H, 4.73; N, 18.78. For compound **4**, the "averaged" formula of the macromolecule is given; *n* was calculated based on the ^1H NMR spectroscopic data (DMSO-d_6), δ: 2.60—4.40 (br.m, 79 H, CH_2N, NH); 4.80 (br.t, 2 H, CH_2ONO_2, $J \cong 4.5$ Hz); 8.22 (m, 36 H, CH, AB system, $\Delta\nu_{AB} \cong 50.0$ Hz, $J_{AB} \cong 9.0$ Hz); 9.02 (br.t, 9 H, CONH, $J_{NH-CH} \cong 5.0$ Hz). IR (KBr pellets), ν/cm^{-1}: 3336, 1662, 1539 (NHCO); 3107, 3073, 1598, 836 (Ar); 2699, 2427 (NH_2^+); 2928, 2852, 1477, 1431 (CH_2); 1644 sh, 1294 (ONO_2); 1518, 1346 (NO_2); 1383 (NO_3^-).

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