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Development and synthesis of novel representatives of polyazido-substituted *N*-(alkoxymethyl)nitramines

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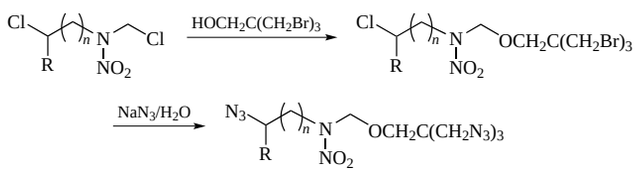
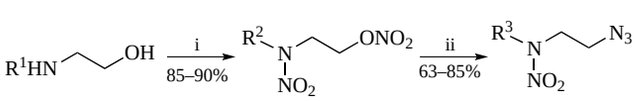
α,ω-Dichloro-β-nitrazaalkanes on treatment with (poly)halo alcohols undergo chemoselective substitution in the activated *N*-chloromethyl moiety. The thus prepared polyhalo derivatives are converted into the corresponding polyazido compounds which can be the promising energetic plasticizers and monomers.



Keywords: nitramines, α,ω-dichloro-β-nitrazaalkanes, halo alcohols, *N*-(alkoxymethyl)nitramines, azides, azidation, formation enthalpy.

Compounds containing nitramino and azido functional groups belong to the class of high-energy compounds, and studies aimed at creating new representatives of this class of compounds, as well as development of methods for their synthesis are being actively performed in many countries. In terms of applicability as an energy-intensive functional in plasticizer formulations, the nitramine group has a number of advantages such as the presence of active oxygen, positive heat of formation, thermal and chemical resistance, high nitrogen content, good solvating ability toward polar polymers as well as a high contribution to the density of compounds. However, the nitramine group makes a very significant undesirable contribution to the melting point. Ways to solve this problem involve combining nitramines with other explosophoric groups such as the nitroxy- and/or azido groups.

Historically, a number of *N*-alkyl-*N*-(2-nitroxyethyl)-nitramines of the NENA series (MeNENA, EtNENA, BuNENA, DINA) was obtained in good yields by nitration of the corresponding *N*-alkyl-*N*-(2-hydroxyethyl)amines with HNO_3/Ac_2O under zinc chloride catalysis[1–3] (Scheme 1). These compounds are interesting because they are either liquids or low-melting solids, and can act as active plasticizers of cellulose nitrates and synthetic rubbers. They are used as ballistic-type energy-intensive plasticizers in solid propellants and high-power artillery powders (in the case of DINA, EtNENA)[3,4] or are considered for use for this purpose (in the case of MeNENA[3,4] and BuNENA[5]). Further azidation of the nitroxy groups gave the corresponding azido-substituted nitramines such as MeAENA,[3] EtAENA,[3] BuAENA[6] and DANPE[7,8] (see Scheme 1). In spite of the loss in the content of some active oxygen in the composition and a slight decrease in density on transition from nitroxy- to azido-substituted compounds (by 0.1–0.15 g ml^{-1} on average),[3] a cardinal increase in the formation enthalpy, lower melting temperatures, and an increase in the thermal stability of the corresponding nitramino azides were achieved.[3,4] To date, all azido-substituted nitramines (AENA series) presented in Scheme 1 became the standard energy-intensive plasticizers in ballistic solid rocket fuels and in high-power artillery powders.[3,4]



R^1 = Me, Et, Bu, $(CH_2)_2OH$

MeNENA	R^2 = Me;	MeAENA	R^3 = Me	DINA	$R^2 = (CH_2)_2ONO_2$
EtNENA	R^2 = Et;	EtAENA	R^3 = Et	DANPE	$R^3 = (CH_2)_2N_3$
BuNENA	R^2 = Bu;	BuAENA	R^3 = Bu		

Scheme 1 *Reagents and conditions*: i, $HNO_3/Ac_2O/ZnCl_2$; ii, NaN_3, DMF.

Thus, combining nitramino and azido groups in a compound is most suitable for the creation of promising energy-intensive plasticizers, since along with a high formation enthalpy and a good thermal stability, the azido group, due to its polar nature, like the nitramino group, has a high ability to solvate a polymer matrix without making a high contribution to the increase in the melting point of a compound. Still, elevating the energy-mass characteristics of newly created compounds of the *N*-(azidoalkyl)-nitramine series even further remains a relevant goal. Obviously, the energy parameters can be improved both due to the number of explosophore groups and their density in a molecule by minimizing the supporting carbon skeleton.

In this work, the functionalization of nitramines was performed by the reaction of α,ω-dichloro-substituted nitraza-alkanes with halogen-containing alcohols occurring at the chlorine atom in the activated *N*-chloromethyl moiety followed by replacement of halogen atoms with azido groups. Due to the broad pool of available halo alcohols, this approach allowed one to obtain a wide range of polyazido-substituted *N*-(alkoxyalkyl)-nitramines by traditional procedures.

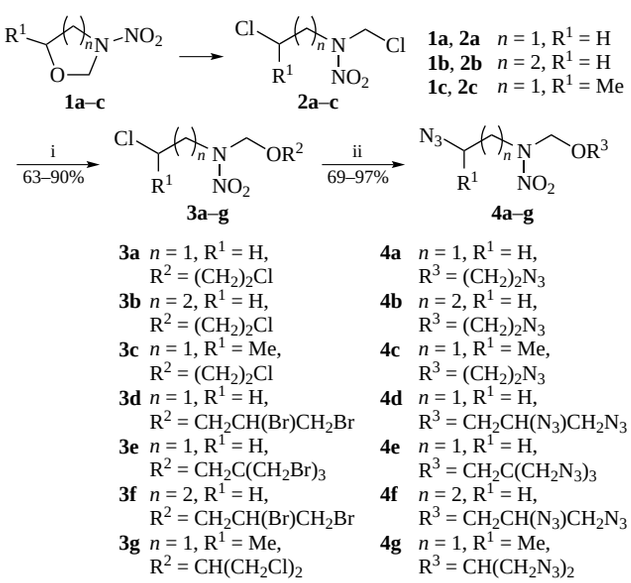
Examples of generating α-alkoxy groups in *N*-alkyl-*N*-(chloroalkyl)nitramines by mixing them directly with the corresponding alcohols (in the case of simple alcohols) or by prolonged (~120 h) refluxing in dichloroethane (in the case of halo alcohols)[6] were previously mentioned.[9] In the latter case, a number of *N*-[(haloalkoxy)alkyl]nitramines were obtained. However, the content of the target product in the crude material was ~60% and its subsequent isolation implied a laborious chromatographic separation. A different patented[10] synthesis of such compounds in ~90% yields implied the reaction of *N*-alkyl-*N*-(chloromethyl)-nitramines with epoxides in the presence of Lewis acids, however, that method required final fractional distillation.

Our team has previously developed[11] a general method for the synthesis of α,ω-dichloro-β-nitrazaalkanes **2a–c** based on

N-nitrooxazolidines or *N*-nitroperhydro-1,3-oxazines **1a–c** (see Scheme 1). The presence of two chlorine atoms considerably differing in reactivity within the same molecule opened up prospects for the extensive chemoselective functionalization of those compounds. Thus, the goal of this work was to develop a convenient method, easily scalable for industrial use, for synthesizing a large variety of azido-substituted *N*-alkylnitramines based on commercially available starting materials.

First, a series of new (poly)halo-substituted *N*-(alkoxymethyl)-nitramines **3a–g** was prepared by the improved procedure from previously obtained α,ω-dichloro-β-nitrazaalkanes **2a–c** and halo alcohols. In this case, the components were taken either in equimolar amounts or with a small (⩽ 10%) excess of nitramines **2a–c**. ^{1}H NMR monitoring showed that refluxing for 37 h in 1,2-dichloroethane was generally sufficient for exhaustive conversion. Compounds **3c** and **3e**,**g** were exceptions which required 70 and 90 h processing, respectively, probably due to steric factors. As a result, the content of halo-substituted *N*-(alkoxymethyl)nitramines **3** in the reaction mixtures was ⩾ 90%, while the conversion with respect to a halo alcohol (the component which is more difficult to remove) approached 100%. The unreacted starting nitramine **2**, the only admixture, could be efficiently removed by treatment of the crude emulsion with aqueous $NaHCO_3$ and then with diluted HCl. Thus, a series of halo-substituted *N*-(alkoxymethyl)nitramines **3a–g** was obtained in overall yields of 63–90% (Scheme 2).

At the next step, we performed further functionalization of compounds **3a–g** by replacement of the halogen atoms therein with azido groups. Mostly, such transformations comprised treatment with NaN_3 at 80–85 °C in DMF[3,6,8] or in DMSO,[3] and the target azides were isolated by dilution of the reaction mixture with water followed by extraction with a hydrophobic solvent and repeated washing of the organic phase with water from DMF or DMSO residues.[3,6,8] In this work, we performed azidation of *N*-(haloalkoxymethyl)nitramines **3a–g** by the method reported for similar compounds[11] under heterophase conditions in a boiling aqueous solution of NaN_3 in the presence of Bu_4NBr as the phase-transfer catalyst (see Scheme 2). This approach features a simple processing and isolating the product. The yields of the corresponding polyazido-substituted derivatives **4a–g** were rather high (69–97%), and they appeared as mobile liquids. The properties of new polyhalo and polyazido derivatives **3** and **4** are given in Table 1.



3a $n = 1$, $R^1 = H$, $R^2 = (CH_2)_2Cl$
3b $n = 2$, $R^1 = H$, $R^2 = (CH_2)_2Cl$
3c $n = 1$, $R^1 = Me$, $R^2 = (CH_2)_2Cl$
3d $n = 1$, $R^1 = H$, $R^2 = CH_2CH(Br)CH_2Br$
3e $n = 1$, $R^1 = H$, $R^2 = CH_2C(CH_2Br)_3$
3f $n = 2$, $R^1 = H$, $R^2 = CH_2CH(Br)CH_2Br$
3g $n = 1$, $R^1 = Me$, $R^2 = CH(CH_2Cl)_2$

4a $n = 1$, $R^1 = H$, $R^3 = (CH_2)_2N_3$
4b $n = 2$, $R^1 = H$, $R^3 = (CH_2)_2N_3$
4c $n = 1$, $R^1 = Me$, $R^3 = (CH_2)_2N_3$
4d $n = 1$, $R^1 = H$, $R^3 = CH_2CH(N_3)CH_2N_3$
4e $n = 1$, $R^1 = H$, $R^3 = CH_2C(CH_2N_3)_3$
4f $n = 2$, $R^1 = H$, $R^3 = CH_2CH(N_3)CH_2N_3$
4g $n = 1$, $R^1 = Me$, $R^3 = CH(CH_2N_3)_2$

Scheme 2 *Reagents and conditions*: i, R^2OH, 1,2-dichloroethane, reflux, 36–38 h for **3a**,**b**,**f**; 70 h for **3c**; 90 h for **3e**,**g**; ii, $NaN_3/Bu_4NBr/H_2O$, reflux, 12 h for **4a**,**b**,**e**; 20 h for **4c**,**d**,**f**,**g**.

Table 1 Properties of polyhalo- and polyazido-substituted *N*-(alkoxymethyl)nitramines **3** and **4**.

Compound	Yield (%)	n_D^{20}	$T_{decomp.}$[a]/°C	ΔH_f (calc.)/kcal mol^{-1}	Hydrogen content (%)	Ω (%)[b]
3a	63	1.4994	n.d.	n.d.	4.64	n.d.
3b	73	1.5004	n.d.	n.d.	5.23	n.d.
3c	81	1.4935	n.d.	n.d.	5.23	n.d.
3d	75	1.5506	n.d.	n.d.	3.13	n.d.
3e	90	1.5607	n.d.	n.d.	3.06	n.d.
3f	73	1.5453	n.d.	n.d.	3.56	n.d.
3g	69	1.5056	n.d.	n.d.	4.69	n.d.
4a	94	1.5112	185–186	104.5	4.38	–83.41
4b	96	1.5093	164–166	98.0	4.95	–98.28
4c	86	1.5043	167–169	97.5	4.95	–98.28
4d	83	1.5304	142–144	174.0	3.89	–81.34
4e	97	1.5362	169–171	233.5	3.98	–90.32
4f	69	1.5275	144–146	167.5	4.38	–93.57
4g	85	1.5199	170–171	167.0	4.38	–93.57

[a] Stuart SMP-10 instrument (2 K min^{-1}). [b] Oxygen balance based on CO_2, for a compound $C_aH_bN_cO_d$, Ω (%) = 1600 × (d – 2a – b/2)/MW; MW – molecular weight.

To summarize, a convenient protocol for the synthesis of a wide range of azido-substituted *N*-(alkoxymethyl)nitramines of type **4** based on commercially available starting substances has been suggested. The simplicity of the procedure and the standard equipment make it possible to speak on the scalability of the process. A representative series of azido-substituted *N*-(alkoxymethyl)nitramines **4** that are liquids under ordinary conditions have been synthesized. The compounds obtained may be of interest both as plasticizers of cellulose nitrates and synthetic rubbers and as monomers in the synthesis of energy-intensive polymers.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.11.004.

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