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STUDIES IN THE FIELD OF CHEMISTRY OF NITRO COMPOUNDS (TO 100TH BIRTHDAY ANNIVERSARY OF S. S. NOVIKOV)

One-Pot Method for Synthesis of 2-Substituted 1,1-Di(methoxy-NNO-azoxy)ethanes

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Abstract—One-pot method was developed for synthesis of 2-substituted 1,1-di(methoxy-NNO-azoxy)ethanes from 2,2-di(methoxy-NNO-azoxy)ethanol in three chemical stages.

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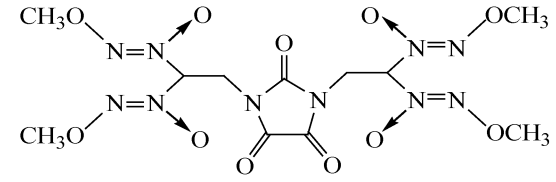
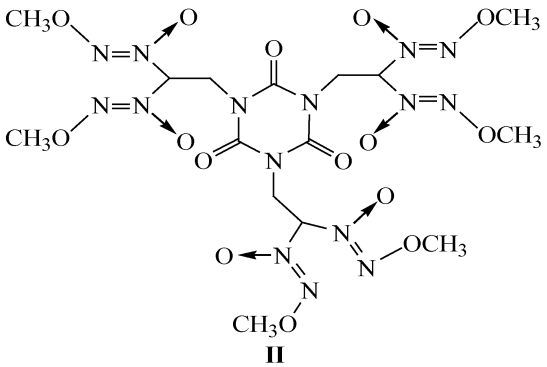
Alkoxy diazenoxides [R–(NO)=N–O–R'] (ADO) have been known since the end of the XIX century. During the last 30 years, some representatives of this poorly understood class of compounds have been studied as potential components of energetic materials with increased stability and low reactivity (components of gas-generating formulations) [1]. According to the results of calculations [1], of particular interest among these compounds are 1,1di(methoxy-NNO-azoxy)ethyl derivatives of low-enthalpy imide heterorings (cyanuric and parabanic acids), e.g., the as yet unknown compounds **I** and **II**:



I



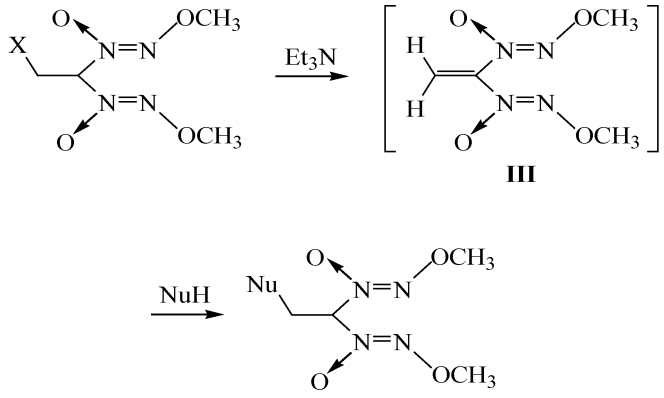
II

Two methods are known for introduction of 1,1-di-(methoxy-NNO-azoxy)ethyl group. The first of these is the reaction of acetate, nitrate, or methanesulfonate of 2,2-di(methoxy-NNO-azoxy)ethanol with nucleophiles in the presence of a base [2, 3]. In [2], it was suggested that an intermediate, 1,1-di(methoxy-NNO-azoxy)ethene (**III**) is formed, but its existence was not confirmed (Scheme 1).

Recently, olefin **III** has been found and isolated in pure form [4], which made it possible to develop the second method: addition of strong acids to this olefin by Michael without catalysis by bases [4, 5] (Scheme 2).

The synthesis and isolation of the starting compounds

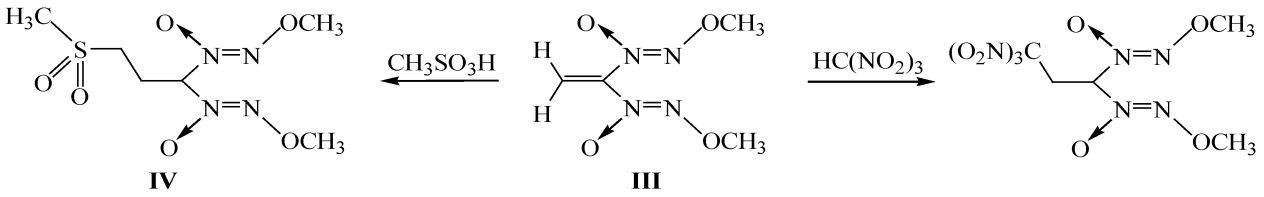
Scheme 1.



III

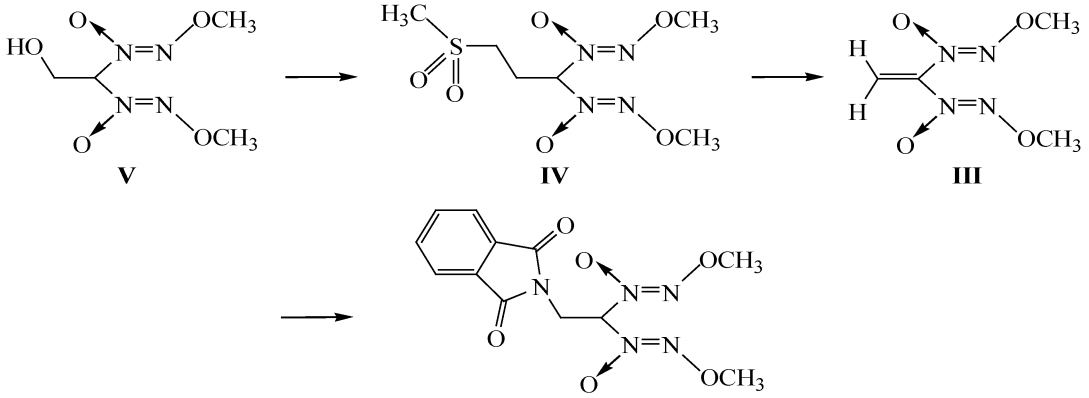
X = Ac, ONO_2, OSO_2Me; Nu = Et_2N, CN, Py, $CH_3N(NO_2)$, $[-CH_2N(NO_2)_2]_2$, CH_3O, C_2H_5OH.

Scheme 2.



IV **III**

Scheme 3.



V **IV** **III**

VI

III and **IV** involve some difficulties [4]. Therefore, to obtain structures of the types **I** and **II**, a one-pot method was developed in the present study for synthesis of 2-substituted 1,1-di(methoxy-NNO-azoxy)ethanes from 2.2-di(methoxy-NNO-azoxy)ethanol (**V**). The previously unknown 1,1-di(methoxy-NNO-azoxy)-2-(*N*-phthalimido)ethane (**VI**) was chosen as a model (Scheme 3).

The overall yield of compound **VI** in terms of alcohol **V** was 69%. Compound **VI** has the form of colorless crystals with mp 161–162°C. Its structure was confirmed by an elemental analysis and ^{1}H and ^{13}C NMR spectroscopy.

Compound **VI** can serve as a starting compound for synthesis of 2,2-di(methoxy-NNO-azoxy)ethylamine and its derivatives, which may prove valuable as energetic materials.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker AM 300 NMR spectrometer in DMSO-d_6. Metanesulfonic anhydride and diisopropylethylamine were purchased from Aldrich. 2,2-Di(methoxy-NNO-azoxy)ethanol (**V**) was synthesized by the method described in [5]. The reaction course and the chromatography were monitored by TLC (Silufol, AcOEt–C_6H_6, 1 : 1 by volume).

1,1-Di(methoxy-NNO-azoxy)-2-(*N*-phthalimido)-ethane (VI). To a solution of 2,2-di(methoxy-NNO-azoxy)ethanol (**V**) (1.94 g, 10 mmol) and methanesulfonic anhydride (2.09 g, 12 mmol) in 15 ml of dry acetonitrile was added diisopropylethylamine (4.3 ml, 3.2 g, 25 mmol) and the mixture was agitated for 0.5 h until compound **V** disappeared [according to TLC (R_f 0.14)] because of being converted to sulfonate **IV** (R_f 0.42) with an admixture of olefin **III** (R_f 0.54). Then, phthalimide was added (1.48 g, 10 mmol) and the mixture was agitated for 2 h at 40°C. The resulting homogeneous solution was evaporated in a vacuum. The residue was dissolved in AcOEt, washed with a 3% HCl solution saturated with NaCl, and evaporated in a vacuum. The residue was chromatographed on silica gel (Sapelko, 40–60 μm, 30 g) with a $CHCl_3$–AcOEt mixture (5 : 1 to 2 : 1 by volume). After the solvent was evaporated, the fraction with R_f 0.58 was crystallized from isopropanol to give 2.03 g of compound **VI**, mp 161.2–162.0°C. ^{1}H NMR spectrum (300 MHz), δ (ppm): 4.04 s (6H, OMe), 4.55 d (2H, CH–2CH, J 6.3 Hz), 6.69 t (1H, CH_2CH–, J 6.3 Hz), 7.86–7.96 symmetric m (4H, Ar). ^{13}C NMR spectrum (75 MHz), δ (ppm): 36.12 (NCH2), 62.48 (CH3O), 89.45

(CHN_2), 123.91 (3,6-C_6), 131.68 (4,5-C_6), 135.31 (1,2-C_6), 167.37 (C=O). Found: C 44.54, H 3.70, N 21.58. Calculated (%): C 44.59, H 4.05, N 21.66.

CONCLUSIONS

1,1-Di(methoxy-NNO-azoxy)-2-(*N*-phthalimido)-ethane was obtained in an overall yield of 69% by one-pot synthesis of 2-substituted 1,1-di(methoxy-NNO-azoxy)ethanes from 2.2-di(methoxy-NNO-azoxy)ethanol.

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