ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 10, pp. 1829−1831. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © I.N. Zyuzin, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 10, pp. 1677−1679.

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

Safe Method for Synthesis of Methoxy-NNO-Azoxyethene

I. N. Zyuzin

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia

Received July 13, 2009

Abstract—Safe method for synthesis of methoxy-NNO-azoxyethene by pyrolysis of 1,1-di(methoxy-NNO-azoxy)ethane in high yield was developed. The method is based on use of dibutyl phthalate as phlegmatizer and polyphenols as inhibitors of radical polymerization.

DOI: 10.1134/S1070427209100152

A method developed for synthesis of methoxy-NNO-azoxyethene (**I**) by vacuum pyrolysis of 1,1-di(methoxy-NNO-azoxy)ethane (**II**) in a melt in evacuated ampules at 220–285°C with an analytical yield of 75% and preparative yield of 53% was described in [1] (see the Scheme).

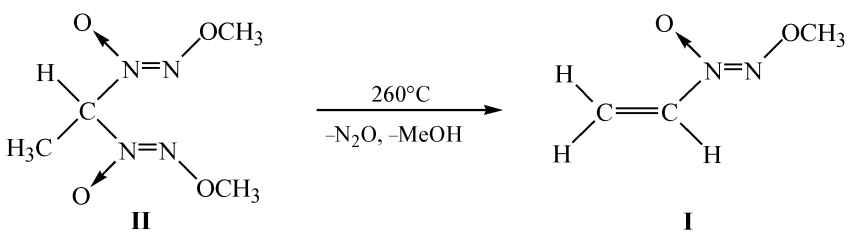
Olefin **I** has been suggested as a monomer for polymeric energetic materials [2]. It can also serve as a starting compound for synthesis of a number of methoxy-NNO-azoxy compounds by functionalization of the C=C bond.

The ampule method is unacceptable for obtaining large amounts of olefin **I** because of the explosion hazard: the starting compound **I** has a positive enthalpy of formation (ΔH_f° +21.0 kJ mol^{-1}) [3] and, according to estimates, is comparable in the heat of explosion with TNT. The explosion hazard becomes even more pronounced because of the increase in the heat content of compound **II** via melting (ΔH_m° 27 kJ mol^{-1} [4]) and heating of the melt to the pyrolysis point.

The problem was solved by performing pyrolysis in an inert organic solvent serving as a phlegmatizer. Dibutyl phthalate was chosen as the solvent on the basis of its following parameters: optimal boiling point (340°C, 190°C/7 mm Hg, 147°C/1 mm Hg), sufficient thermal stability and chemical inertness, easy availability, and low toxicity. High-boiling aliphatic hydrocarbons are of little use for this purpose because they poorly dissolve compound **II** and cannot be mixed with its melt. An additional advantage of the method suggested consists in continuous evaporation of the forming olefin **I** by a flow of methanol and N_2O at P = 60–100 mm Hg. This diminishes the loss of olefin **I** for polymerization whose possibility in principle has been demonstrated previously [2]. Olefin **I** was obtained in an analytical yield of 73%, which nearly coincides with the best yield provided by the ampoule method [1].

The loss of olefin **I** for polymerization could be additionally diminished by using radical polymerization inhibitors and, in particular, hydroquinone. In a run with 1.6 mol % hydroquinone, the analytical yield exceeded 90%, with about 5% starting compound **II** found in the

Scheme 1.



II **I**

distillation products and still bottoms. Lowering the hydroquinone fraction of 0.8 mol % resulted in a decrease in the analytical yield to 78.5%. Under the severe pyrolysis conditions hydroquinone is nearly completely oxidized to benzoquinone, which is evaporated together with the reaction products and colors yellow the condensate dropping from the reflux condenser. According to this indirect indication, hydroquinone was completely consumed in run B by approximately the middle of the reaction. On replacing hydroquinone with quinizarin (0.74 mol %), the yield was 81.9%, i.e., at a close molar fraction, quinizarin is comparable in efficiency with hydroquinone. Unfortunately, quinizarin is also oxidized to benzoquinone contaminating the product and has no advantage over hydroquinone in this regard.

At the very beginning of the reaction, the temperature of the reaction solution exceeded by 2° the bath temperature (210°C). Presumably, the decomposition reaction of compound **II** has a small exothermic effect, provided that olefin **I** remains in the liquid phase. A possible reason for the subsequent decrease in temperature is that the steady-state concentration of olefin **I** in solution is reached and heat is consumed for its evaporation (ΔH°_{ev} 48 kJ mol^{-1} [5]).

In recovery of olefin **I**, benzoquinone was reduced with hydrazine to hydroquinone (bp 286.5°C, 163.5°C/10 mm Hg), which remains in still bottoms in distillation. After two vacuum distillations, the yield of olefin **I** with n_D^{20} 1.4898–1.4900 was 61.3%, and the total yield of all fractions, 71.1%.

EXPERIMENTAL

1,1-Di(methoxy-NNO-azoxy)ethane (**II**) was produced by the method described in [1]. Dibutyl phthalate was distilled in a vacuum. The yield of compound **I** was determined by GLC (LKhM-8MD instrument, columns packed with 15% carbowax-20M on Chromaton N-AW DMCS, carrier-gas N_2, 30 ml min^{-1}, column temperature 150°C, evaporator temperature 200°C, retention time τ 6.6 min, PhCN as internal standard with τ 5.25 min. Compound **II** was determined by LC (Millikhrom-1A instrument, column with a reversed C-18 phase, 5000 theoretical plates, 3 : 10 MeOH : H_2O as eluent, 50 μl min^{-1}, UV detector 240 nm). The retention time τ was 5.8 min for **II** and 7.3 min for **I**; 2,2-di(methoxy-NNO-azoxy)propane as internal standard [6] with τ 8.9 min.

A one-piece-soldered 750-ml Claisen flask equipped with a herringbone dephlegmator (20 cm) and a reflux condenser served as a reactor for preparative pyrolysis. The dephlegmator of the reactor is equipped with a neck for the upper thermometer and a jacket through which hot water (80°C) is pumped by a thermostat. The flask of the reactor is equipped with two necks (ground joint 14) for a submersible thermometer (0–250°C) and argon supply through a capillary. To the condenser are successively connected via ground joints a receiver cooled by dry ice and salt (–20°C) spiral tap cooled by dry ice with acetone, T-joint to a gage, two high washing vessels with sulfuric acid and total pressure drop of 65 mm Hg, and water-jet pump. A bath with a Wood alloy, equipped with a thermometer (0–360°C), heater, and contact thermometer providing adjustment of the bath temperature with an accuracy of ±2°C, was used for heating. The pressure in the system was controlled by passing the gas flow through one or two washing vessels with sulfuric acid and by inclining these vessels.

A. Preparative pyrolysis of 1,1-di(methoxy-NNO-azoxy)ethane (II). Compound **II** (100 g, 0.561 mol) and hydroquinone (1 g, 0.0091 mol, 1.6 mol %) were dissolved in dibutyl phthalate (150 ml) under heating and the solution was placed in the reactor for preparative pyrolysis. The reactor was bubbled with argon, evacuated (residual pressure 70 mm Hg), and lowered into the bath (210°C). In 5 min, the temperature in the flask became equal to that of the bath (210°C), and in 10 min, somewhat exceeded it (212°C). There was an abundant flow of a gas through the washing vessels, with the pressure adjusted within the range 60–100 mm Hg. The condensate dripped from the condenser at a rate of 1–2 drops per second. In 20 min, the temperature in the flask decreased to 205°C, and that of the bath increased to 220°C. In 1 h after the beginning of the process, the gas-release rate decreased, the temperature in the flask was gradually raised to 245°C during the following 1.5 h. The yield of olefin **I** was 51.8 g (90.3%) according to GLC. The combined distillation products from the receiver and trap also contained methanol, dibutyl phthalate, and starting **II** (3.8 g, 3.8%). The distillation products were colored yellow by benzoquinone. The still bottoms were mostly composed of dibutyl phthalate and contained trace amounts of the starting **II** (1.1 g, 1.1%).

B. Pyrolysis was performed as in run A, but with two times smaller amount of hydroquinone (0.5 g, 0.0045 mol, 0.8 mol %). According to GLC data, the yield of olefin **I** was 45.0 g (78.5%).

Distillation balance

Fraction (distillation)	bp, °C/P, mm Hg	n_D^{20}	Yield	
			g	%
1(1)	40–64/8	1.4845	12.1	5.3
1(2)	53–62/7.5	1.4869	10.3	4.5
2(2)	63–64/7.5	1.4898	120.8	52.7
3(2)	65–68/7.5	1.4900	19.8	8.6
According to [1]	66–68/8	1.4898	–	–
Overall yield			163.0	71.1

C. Pyrolysis was performed as in run A, but with quinizarin (1 g, 0.0042 mol, 0.74 mol %) as inhibitor, instead of hydroquinone. According to GLC data, the yield of olefin **I** was 46.9 g (81.9%). As in runs A and B, the distillation products are colored yellow by benzoquinone.

D. Pyrolysis was performed as in run A, but without an inhibitor. According to GLC data, the yield of olefin **I** was 41.9 g (73.1%). The distillation products were colorless.

Methoxy-NNO-azoxyethene (I). Combined distillation products from runs A–D, containing a total of 185 g of olefin **I**, were diluted with chloroform (50 ml) and hydrazine hydrate was added (1.5 g, 0.025 mol). The solvents were evaporated under atmospheric pressure (bp 64–65°C; in the flask, up to 110°C). The residue was distilled in a vacuum, with two fractions taken. The still bottoms contained 3.8 g of olefin **I** and 15.4 g of compound **II**. Crystallization from ether and isopropanol yielded 12.1 g of compound **II**, mp 74.7–75.2°C (mp 75–75.5°C [1, 6]). Fraction no. 2 (167.7 g, bp 64–69°C/8 mm Hg, n_D^{20} 1.4888) was repeatedly distilled in a vacuum (see table).

CONCLUSIONS

(1) A safe method was developed for synthesizing methoxy-NNO-azoxyethene by pyrolysis of 1,1-di(methoxy-NNO-azoxy)ethane dissolved in dibutyl phthalate.

(2) With hydroquinone used as inhibitor of radical polymerization, the analytical yield of 1,1-di(methoxy-NNO-azoxy)ethane increases from 73 to 90%.

REFERENCES

1. Zyuzin, I.N., Lempert, D.B., and Nechiporenko, G.N., *Izv. Akad. Nauk, Ser. Khim.*, 2002, no. 6, pp. 1354–1356.
2. Zyuzin, I.N., Baturina, A.A., Grachev, V.P., et al., *Materialy Vserossiiskoi nauchnoi konferentsii "Energeticheskie kondensirovannye sistemy",* Chernogolovka, 28–31 oktyabrya 2002 (Proc. All-Russia Conf. "Energetic Condensed Systems," October 28–31, 2002), Chernogolovka, 2002, p. 38.
3. Kirpichev, E.P., Zyuzin, I.N., Avdonin, V.V., et al., *Zh. Fiz. Khim*., 2006, vol. 80, no. 9, pp. 1543–1546.
4. Garkushina, M.P., Zyuzin, I.N., Lempert, D.B., and Prokudin, V.G., *XVI Int. Conf. on chemical thermodynamics in Russia (RCCT 2007),* Suzdal, July 1–6, 2007, Ivanovo, 2007, vol. I, p. 2S-180.
5. Zyuzin, I.N., Lempert, D.B., and Prokudin, V.G., *XVI Int. Conf. on chemical thermodynamics in Russia (RCCT 2007),* Suzdal, July 1–6, 2007, Ivanovo, 2007, vol. I, pp. 2S-144–2S-145.
6. Atovmyan, L.O., Golovina, N.I., and Zyuzin, I.N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, no. 6, pp. 1309–1312.