***N*-Methyl-*O*-methoxycarbonyl-*N*-nitrohydroxylamine (2b).** NO_2BF_4 (0.65 g, 48.94 mmol) was added to a solution of HA **2b** (1 g, 48.34 mmol) in 3 mL of anhydrous MeCN at −25 °C. The reaction mixture was stirred at −10 °C for 3 h. $NaHCO_3$ (0.94 g) in 10 mL of H_2O was added. The solution obtained was extracted with dichloromethane. After CH_2Cl_2 was removed, the residue was passed through a column with SiO_2 100/160 (CH_2Cl_2 as the eluent), and 0.66 g (91.6 %) of NHA **2b** was obtained as a colorless liquid. Found (%): C, 24.23; H, 3.38; N, 18.36. $C_3H_6N_2O_5$. Calculated (%): C, 24.01; H, 4.03; N, 18.68. IR, ν/cm^{-1}: 1360—1600 (NNO_2); 1805 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.55 (C, 3 H, NMe); 3.97 (s, 3 H, OMe).

***N*-Methyl-*N*-nitro-*O*-picrylhydroxylamine (2d).** NO_2BF_4 (0.34 g, 25.6 mmol) was added to a suspension of HA **1d** (0.6 g, 20.1 mmol) in 4 mL of anhydrous MeCN at −10 °C. The temperature was raised to 20 °C, and the reaction mixture was stirred for 2 h and then poured into water. The precipitate that sedimented was filtered off and washed with water, and 0.58 g (95 %) of NHA **2a** was obtained, m.p. 103—105 °C (decomp.). Ref. 2: m.p. 103—105 °C (decomp.).

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Formation of diamond from carbyne

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Highly disperse diamond (HDD) was obtained by heating amorphous carbyne in the presence of small amounts of HDD.

Key words: carbon, allotropic modifications, carbyne, diamond.

Consideration of carbon as a polymeric system consisting of C atoms allows one to distinguish three types of polymers: (1) spatial polymer (diamond); (2) "parquet" polymer (graphite); and (3) linear polymer (carbyne).

Polyynic carbon polymer, carbyne, has been obtained from acetylene used as the initial material (monomer).[1] Other allotropic forms of carbon can also be synthesized using benzene and adamantane as initial monomers. The first attempt to synthesize diamond from adamantane at normal pressures and temperatures was performed in 1976.[2] The authors of this work[2] have synthesized polyadamantane by bromination of adamantane followed by dehydrobromination. The data of X-ray diffraction analysis, electron diffraction, and IR spectroscopy made it possible to establish that the product of dehydropolycondensation of adamantane is a spatial carbon polymer in the form of adamantane cores "linked" by saturated C—C bonds.

A low-energy method for preparation of diamond from carbyne at a pressure of 5 GPa or lower without preliminary heating has been published recently.[3] The author of Ref. 3 believes that the use of carbyne as the initial material for the preparation of diamond allows one to decrease the high activation energy necessary for rearrangement of parquet layers of graphite into a spatial polymer.

It is likely that the mechanism of diamond formation is associated with the interaction of carbon chains (retained in the initial carbyne due to weak van der Waals bonds), which are transformed with explosion into diamond-like carbon. It was not merely accidental that

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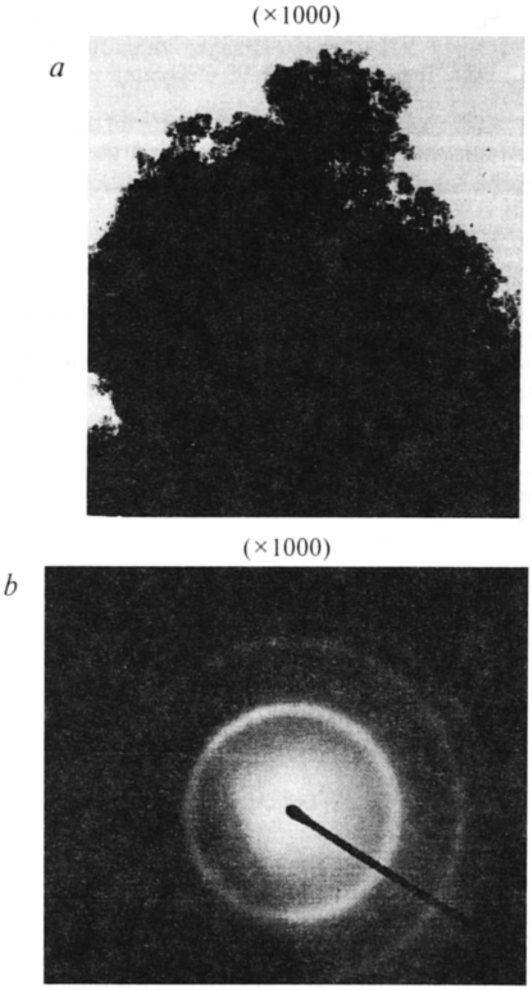

Fig. 1. Electron microphotograph (*a*) and microdiffraction pattern (*b*) of polycrystalline diamond sample.

Bayer, the pioneer in the field of synthesis of polyynes, supposed to obtain the carbon modification from them[4] that would be called "explosive diamond." The use of pressures (static or dynamic) favors the formation of diamond polycrystals.

The synthesis of diamond from carbyne at atmospheric pressure is discussed in this work. A sample of carbyne obtained by chemical dehydrochlorination of polyvinylidene chloride is readily transformed into diamond at atmospheric pressure and even at 350—400 °C in an argon flow, if highly disperse diamond (HDD) is used as a "seeding." The black carbyne powder is transformed into a white powder. The microphotograph of such a white polycrystalline sample is presented in Fig. 1, *a*, and the microdiffraction pattern of this sample is presented in Fig. 1, *b*. The X-ray-gram of diamond obtained from the carbyne powder is presented in Fig. 2. The X-ray-gram of the white powder exhibits the typical peaks of diamond at d = 2.05, 1.26, and 1.07 Å. Therefore, carbyne has transformed into diamond.

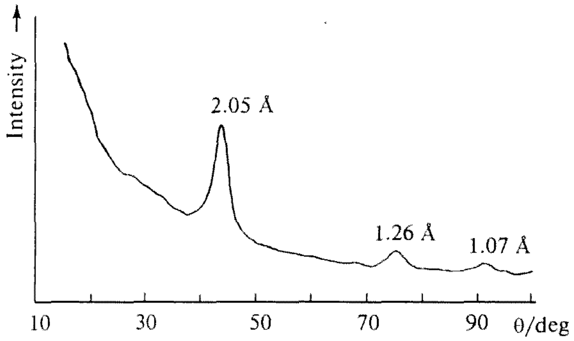

Fig. 2. X-ray-gram of diamond obtained from carbyne powder.

The electron-microscopic studies of the diamond powder have shown that the size of individual crystallites of diamond does not exceed 50 Å (see Fig. 1, *a*). The width of the diffraction maximum (see Fig. 1, *b*) also corresponds to the size of crystallites of 50 Å. It is noteworthy that the initial HDD consists of diamond particles 50 Å in size. Thus, the powder obtained is identical to HDD, which points to the phase transition of amorphous carbyne into highly disperse diamond.

It is likely that HDD particles are "nuclei" of crystallization of diamond and decrease substantially the energy barrier for the carbyne—diamond transition. According to the literature data,[3] the Berman—Simonov line on the refined diagram should be considerably lower for very small carbon clusters. Short chains are formed due to the destruction of carbyne chains, when they break in the sites of bending under the effect of active HDD particles. The release of the energy of saturated bonds accompanied by heating (without explosion) to 500—700 °C favors the transition of carbyne into diamond. New HDD particle formed produces the similar particle, *etc.*

The technological advantages of the method suggested are evident.

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