Reductive debenzylation of hexabenzylhexaazaisowurtzitane — the key step of the synthesis of polycyclic nitramine hexanitrohexaazaisowurtzitane

A. P. Koskin, I. L. Simakova, * and V. N. Parmon

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 5 prosp. Akad. Lavrent 'eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383) 330 8056. E-mail: simakova@catalysis.ru

Main features of the reductive debenzylation of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane were studied. This process is the key step of the synthesis of 2,4,6,8,10,12-hexaatetracyclo[$5.5.0.0^{3,11}.0^{5,9}$]dodecane (hexanitrohexaazaisowurtzitane, CL-20), a compound with unique energetic and explosive characteristics. The use of the latter is restricted so far by the high cost of the two-step process of debenzylation during which the compound is rapidly deactivated. The expensive Pd/C catalyst is deactivated in the first step of the process, which limits the use of this polycyclic nitramine. The influence of the solvent nature; loadings of the reactants, catalyst, and cocatalyst; the hydrogen pressure and reaction temperature on the general features of the process and the yield of the target precursor of CL-20 was studied.

Key words: hexanitrohexaazaisowurtzitane, 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[$5.5.0.0^{3,11}.0^{5,9}$]dodecane, debenzylation, palladium-containing catalyst, deactivation of Pd/C.

In the recent decades, much attention in the area of high-energy materials chemistry has been given to investigation of the properties of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[$5.5.0.0^{3,11}.0^{5,9}$]dodecane (hexanitrohexaazaisowurtzitane, CL-20) and search for efficient methods for the synthesis of this polycyclic nitramine.^{1,2} The studies of the explosive and detonation properties of CL-20 and related compositions showed that presently this compound is the most powerful stable explosive.^{3,4} However, due to the absence of an economical industrial method of the synthesis of CL-20 its wide use is limited.¹

The best known method for the synthesis of CL-20 is presented in Scheme 1. Based on this protocol, in 1990 the Thiokol corporation (USA) made a pilot unit for the synthesis of CL-20.⁵ The first step of the synthesis is the construction of the hexaazaisowurtzitane framework using the condensation of glyoxal 1 with benzylamine, and the second step is the substitution of the benzyl groups at the nitrogen atom for the nitro group. The direct nitration of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazatetra $cyclo[5.5.0.0^{3,11}.0^{5,9}]$ dodecane (2) does not afford CL-20, because the hexaazaisowurtzitane framework desintegrates by nitrozative debenzylation. Therefore, the intermediate step of the synthesis of precursors of nitramine CL-20 is necessary. This step is effected by means of the simultaneous hydrodebenzylation-acetylation process during which the C-N bonds are hydrogenolyzed on the palladium catalysts followed by the acetylation of the forming amines with acetic anhydride $(2 \rightarrow 3)$. The benzyl groups

Scheme 1



Reagents, conditions, and yield: *i*. PhCH₂NH₂, MeCN, H⁺, 80%; *ii*. Pd/C, H₂, Ac₂O; *iii*. Pd/C, H₂, HCOOH; *iv*. HNO₃, NH₄NO₃.

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 12, pp. 2290-2295, December, 2007.

1066-5285/07/5612-2370 © 2007 Springer Science+Business Media, Inc.

at the nitrogen atoms of the six-membered ring (N(4)) and N(10)) are more stable in this process, and the second step of hydrodebenzylation is carried out to substitute them under more severe conditions $(3 \rightarrow 4)$. The subsequent nitration of the synthesized 4,10-diformyl-2,6,8,12tetraacetyl-2,4,6,8,10,12-hexaazatetracyc- $10[5.5.0.0^{3,11}.0^{5,9}]$ dodecane (4) affords CL-20 in high yield.⁶ At present the methods for the synthesis of the polycyclic framework^{7,8} and nitration of the polyacetyl hexaazaisowurtzitane derivatives⁹ have been studied rather well and it is not difficult to use them. At the same time, two catalytic steps of the process $2 \rightarrow 3 \rightarrow 4$, which are most complicated and most expensive in the synthesis of CL-20, are studied to considerably less extent. The main problem of practical realization of these steps is the fast deactivation of the Pd/C catalyst.

The purpose of this work is to study the catalytic steps of the debenzylation process and to search for a possibility to enhance the yield of compound **4**, *viz*., target precursor of CL-20, and improve the stability of the Pd/C catalyst.

Experimental

The palladium catalysts for debenzylation were synthesized by the method of palladium ion adsorption from an aqueous solution of $H_2[PdCl_4]$ (1 mol L⁻¹) on the Sibunit carbon support (granular size 50–100 μ m, specific BET surface $S_{sp}(N_2) =$ 320 m² g⁻¹, pore volume $V_s = 0.86$ mL g⁻¹, maximum in the size pore distribution curve at 4 nm) at room temperature followed by the reduction to metallic palladium with a solution of sodium formate. The content of the noble metal in the catalyst was ~4, ~6, and ~10 wt.%. The percentage content of the metal on the carbon support was determined by the X-ray spectral method on a VRA-30 fluorescence analyzer with the Cr anode of the X-ray tube. The palladium catalysts were studied by transmission electron microscopy (TEM) on a JEM-2010 instrument (JEOL, Japan) with an accelerating voltage of 200 kV and a limiting resolution by the lattice of 0.14 nm. The average size of the palladium particles was estimated from the histograms of the palladium particle size distribution constructed by processing TEM microphotographs.

Dimethylacetamide (DMA), DMF, and *N*-methylpyrrolidone were dried over CaH₂ and distilled *in vacuo*. Acetic anhydride was purified collecting the fraction with b.p. 139–140 °C.

The catalytic debenzylation of compound **2** was carried out in a temperature-controlled $(0-100 \,^{\circ}\text{C})$ stainless steel autoclave (volume 150 mL) equipped with an electromagnetic stirrer (800-1000 rpm) and a system of gaseous hydrogen supply. The volume of the absorbed gas was quantitatively measured using a Sapfir-22 instrument (OOO "Neotekhnologiya," Russia) and computation of the experimental data. Catalytic experiments were performed according to a described procedure.¹⁰ The stability of the catalyst in deactivation processes was studied loading the spent Pd/C catalyst after two debenzylation steps ($2 \rightarrow 3 \rightarrow 4$) into the next cycle. For this purpose, the spent catalyst separated from the reaction mixture was successively washed with formic acid, a 1% solution of Na₂CO₃, and distilled water and dried *in vacuo*, and the catalytic activity was studied using a standard procedure. The relative rate of hydrogen absorption (v) was expressed as the amount of hydrogen absorbed within the first hour of the process referred to the amount of loaded compound **2**.

The composition of the components in the liquid reaction mixture was determined by GC/MS on a VG-7070 GC/MS instrument (VG Analytical) on a quartz capillary column (30 m × 0.2 mm) (Silicone SE-30). The structures of the reaction products were determined by ¹H and ¹³C NMR spectroscopy. The spectra were recorded on a Bruker AC-200 instrument (¹H NMR, 200.13 MHz; ¹³C NMR, 50.32 MHz) in CDCl₃ and DMSO-d₆. The chemical shifts are presented in the δ scale relative to Me₄Si.

2,4,6,8,10,12-Hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (2) was presented by the Institute of Problems of Chemical Energetic Technologies, Siberian Branch of the Russian Academy of Sciences (Biisk, Russia), m.p. 152–153 °C. ¹H NMR (CDCl₃), δ : 3.62 (s, 2 H, CH); 4.13 (br.d, 8 H, PhC<u>H₂</u>); 4.08 (s, 4 H, PhC<u>H₂</u>); 4.20 (s, 4 H, CH); 7.20–7.30 (m, 30 H, Ph). ¹³C NMR (CDCl₃), δ : 56.3, 57.0 (both t, PhCH₂ each); 77.0, 80.7 (both d, CH); 126.8, 126.9 (both d, *p*-C_{Ph}); 128.2, 128.3 (both d, *m*-C_{Ph}); 128.7, 129.3 (both d, *o*-C_{Ph}); 140.9 (s, *ipso*-C_{Ph}).

2,6,8,12-Tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{3,11}.0^{5,9}]dodecane (3) was synthesized by the reaction of compound **2** (3.4 g) and HCOOH (5 mL) in DMF (10 mL) and PhBr (0.06 mL) in the presence of the Pd(10%)/C catalyst (0.34 g) and molecular hydrogen (4 bar). The yield was 2.12 g (86%), m.p. 318-321 °C. ¹H NMR (DMSO-d₆), δ : 2.1 (m, 12 H, Me); 4.12 (s, 4 H, CH₂); 5.51 (br.s, 4 H, CH); 6.58 (br.s, 2 H, CH); 7.34–7.44 (m, Ph, 10 H).

2,6,8,12-Tetraacetyl-4,10-diformyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0. 3,11 . 0,5,9]dodecane (4) was synthesized by the reaction of compound 3 (2.12 g) and HCOOH (10.6 mL) in the presence of the Pd(10%)/C catalyst (0.34 g) and molecular hydrogen (4 bar). The yield was 1.29 g (84%), m.p. 291–295 °C. ¹H NMR (DMSO-d₆), δ : 2.1 (m, 12 H, Me); 6.4 (br.d, 4 H, CH); 6.49 (s, 2 H, CH); 8.34 (s, 2 H, CHO).

Results and Discussion

Identification of the step of the debenzylation process making the main contribution to the deactivation of the Pd/C catalyst. The initial substrate of debenzylation (2) is unstable and decomposes easily at elevated temperatures in acids and upon the interaction with acetic anhydride. When crystalline compound 2 is dissolved in acetic anhydride (or is heated in DMF), the solution darkens rapidly. The ¹H NMR analysis of the obtained mixture indicates a decrease in the intensity of signals at δ 3.5–4.5. This interval contains the signals of the CH groups characteristic of the hexaazaisowurtzitane framework. This process is accelerated upon the addition of the Pd/C catalyst to the solution; however, the mixture remains colorless, because the colored products of the destruction of compound 2 are sorbed by the catalyst. In this case, the catalyst stored in a mixture of compound 2 with acetic anhydride and DMF for 1 day was completely deactivated.

We carried out separately the reactions $2 \rightarrow 3$ and $3 \rightarrow 4$ on two samples of the same Pd/C catalyst. The

hexaazaisowurtzitane products obtained after hydrogenolysis were isolated from the reaction mixture, their yield was calculated, and the samples of the Pd/C catalyst were washed, dried, and loaded into the reactor to undergo the repeated cycle of hydrogenolysis. It turned out that the hydrogenation of compound 3 to compound 4 on the same catalyst can be carried out at least three times, whereas the hydrogenation of compound 2 to compound 3 can't be repeated (Table 1). Therefore, the main contribution to the catalyst deactivation is made by the first debenzylation step. In the second debenzylation step, the destruction of the hexaazaisowurtzitane framework occurs much less intensively, because compound 3 is substantially more stable than compound 2. In fact, the higher stability of the framework of compound 3 makes it possible to use more drastic reaction conditions for the replacement of the benzyl groups by the formyl groups at the N(4) and N(10)atoms and even to carry out the synthesis of CL-20 by the nitrozative debenzylation of compound 3 as shown in Ref. 11.

We studied the composition of the liquid phase of the reaction mixture after the first hydrodebenzylation step by GC/MS. Benzylacetamide and several nonidentified nitrogen-containing admixtures were found in addition to the residual peaks of the reactants and the group of peaks of the expected products of debenzylation (toluene, benzene, and acetic acid). Benzylacetamide is formed due to the hexaazaisowurtzitane framework opening followed by the acylation of the destruction products.¹² It is known that benzylacetamide can form stable complexes with palladium, and the leading role of this compound in the deactivation of the palladium catalyst was repeatedly pointed out in the literature.⁶ The preliminary treatment of the Pd/C catalyst with benzylacetamide (synthesized by the counter synthesis) results, in fact, in the complete deactivation of the catalyst (0.34 g of the palladium catalyst was

Table 1. Determination of the contribution of the debenzylation

 steps to the deactivation of the palladium catalyst

Reaction	Yield of target product (%)				
	Fresh	First	Second		
$2 \rightarrow 3^{a}$	82	0	_		
$3 \rightarrow 4^{b}$	85	77	75		
$2 \rightarrow 3 \rightarrow 4$ ^c	69	0	—		

^{*a*} Loadings of the reactants: 3.4 g of compound **2**, 0.34 g of Pd(6%)/Sibunit, 5 mL of Ac_2O , 0.06 mL of PhBr, and 10 mL of DMF. The hydrogen pressure of 4 bar, and the temperature was 25 °C.

^{*b*} Loadings of the reactants: 1.97 g of compound **3**, 0.34 g of Pd(6%)/Sibunit, and 9.8 mL of HCOOH (88%). The hydrogen pressure of 4 bar, and the temperature was 25 °C.

^c Yield of compound **4** synthesized in the two-step cycle of hydrodebenzylation with respect to compound **2**.

treated with 0.05 g of benzylacetamide). Nevertheless, when performing the hydrodebenzylation $2 \rightarrow 3$, we observed no correlation between the amount of benzylacetamide in the reaction mixture (determined by GC/MS) and the degree of deactivation of the catalyst (estimated by the depth of the debenzylation process). It is most likely that benzylacetamide is not the single and strongest catalytic poison for the Pd/C catalyst formed in the reaction mixture. Earlier¹² more than five different nitrous residues of the hexaazaisowurtzitane framework formed by hydrogenolysis have been identified. Each of the residues can deactivate the Pd/C catalyst to this or another extent.

Effect of the solvent nature and metal loadings of the reactants, cocatalyst, and catalyst on the course of the process and the yield of the target precursor of CL-20. The catalytic debenzylation of compound 2 proceeds stepwise, which was shown¹³ by the analysis of the reaction mixture using HPLC and GC. Bromobenzene (PhBr) is added to the reaction mixture to accelerate the first debenzylation step. Bromobenzene is the source of hydrogen bromide, which is the cocatalyst of the hydrogenolysis of the C–N bond. The examples of the kinetic curves of hydrogen absorption by the reaction mixture for the Pd/C catalysts with different amounts of the active metal are shown in Fig. 1. The acceleration of the process in the initial debenzylation step is presumably related to the accumulation of acids in the reaction mixture. As known, the acids, namely, HBr and AcOH, promote the hydrogenolysis of the C-heteroatom bond.14 Then the rate of hydrogen absorption decreases, because solubility of H₂ in DMF decreases with the substitution of the benzyl groups for the acetyl groups in the hexaazaisowurtzitane substrate and, hence, the hydrogenolysis rate decreases. In addition the Pd/C catalyst is gradually deactivated.



Fig. 1. Kinetic curves of hydrogen absorption by the reaction mixture during the process on the Pd(6%)/Sibunit (*I*) and Pd(10%)/Sibunit (*2*) catalysts under a hydrogen pressure of 4 bar and a temperature of 25 °C. Composition of the mixture: 3.4 g of compound **2**, 0.34 g of the catalyst, 10 mL of DMF, 5 mL of Ac₂O, and 0.06 mL of PhBr.



P are the destruction products of the polycyclic framework of compound 2 (more than five compounds)

Reagents and conditions: i. Pd/C, H₂, PhBr, DMF; ii. Ac₂O, DMF; iii. Ac₂O, acids, H₂O.

Hydrogen can be absorbed by the reaction mixture *via* several paths: hydrogenation of acetic anhydride and bromobenzene, hydrogenolysis of internal and external C–N bonds of the hexaazaisowurtzitane framework, and hydrogenation of residues of the framework. The consideration of Scheme 2 shows that an increase in the rate v_1 of the target hydrogenolysis reaction should increase the v_1/v_2 ratio and, therefore, should decrease the amount of the destruction products, whose formation is a reason for catalyst deactivation.

We experimentally studied the influence of the concentrations of the substrate and acylating agent and the hydrogen pressure on the course of the process and the yield of the target product (Table 2). It was found that the effect of the acetic anhydride concentration is dual: on the one hand, acylating agent excess accelerates side processes and, on the other hand, its deficiency results in a decrease in the v_4 acylation rate of unstable amine **6**, which is also unacceptable. The replacement of acetic

Table 2. Influence of the loadings of the reactants and cocatalyst on the rate of hydrogen absorption and the yield of the target product in the first step of debenzylation*

Volume /mL		/mole of H_2	Yield of 3 (%)	
Ac ₂ O	DMF	PhBr	(mole of 2) ^{-1} h ^{-1}	
5	10	0	0.3	0
5	10	0.06	1.5	82
5	10	0.12	1.7	60
15	0	0	0.2	0
15	0	0.06	1.6	0
8	7	0.06	1.4	54

* Debenzylation was carried out on the Pd(6%)/Sibunit catalyst under a hydrogen pressure of 4 bar and at a reaction temperature of 25 °C; m = 3.4 g. anhydride (Ac₂O) by acetyl chloride (AcCl) resulted in the resinification of the reaction mixture, and the use of benzoic anhydride ((PhCO)₂O) revealed no advantages in the debenzylation processes. The most productive was the use of solvents containing the amide groups. The solvents DMF (on the Pd(6%)/C catalyst, the yield of compound 3 was 82%), DMA (80%), and N-methylpyrrolidone (50%) accelerate the acylation reaction due to the basicity of the amide nitrogen atom. When ethers and hydrocarbons are used, the yield of the target precursor of CL-20 was substantially lower. The results obtained for the process on the Pd/Sibunit catalyst samples prepared by us confirm the known published data, according to which PhBr is the optimum source of HBr and its optimum amount is 1/8 molar fraction with respect to the substrate.¹¹ The absence of bromobenzene substantially retards the hydrogenolysis of the C–N bond and prevents this reaction to occur at room temperature.

From the viewpoint of the yield of the final product and the reaction rate, a hydrogen pressure of 4 bar is optumum to perform the debenzylation process. The reduction of the hydrogen pressure considerably decreases the v_1 rate of debenzylation. An increase in the hydrogen pressure increases the contribution of the side pathways of transformation of the components of the reaction medium, which results in the disappearance of compound **3** in the reaction products.

We carried out a series of experiments with the variation of the amount of the Pd(4%)/Sibunit catalyst at the same concentrations of the reactants and cocatalyst, hydrogen pressure, and stirring factor (Fig. 2). The rate of hydrogen absorption by the reaction mixture increased with an increase in the catalyst load. The highest rate of hydrogen absorption was observed when 0.85 g of the catalyst (per 3.4 g of the substrate, weight ratio catalyst/ substrate = 1/4) was charged; however, the yield of compound **3** decreased, being 71%. For the viewpoint of the



Fig. 2. Effect of the weight of the loaded Pd(4%)/Sibunit catalyst (*m*) on the rate of hydrogen absorption v (*I*) and the yield of compound **3** (*2*) under a hydrogen pressure of 4 bar and at a temperature of 25 °C. The composition of the mixture: 3.4 g of compound **2**, 10 mL of DMF, 5 mL of Ac₂O, and 0.06 mL of PhBr.

yield of the target product, the catalyst/substrate loading in the weight ratio 1/5 was optimum. With larger loadings of the Pd/C catalyst (larger than the weight ratio 1/5), the acceleration of the target reaction of C—N bond hydrogenolysis is accompanied by an increase in the rates of the side reactions.

Testing of the hydrogenation catalysts in the debenzylation of compound 2. We tested a series of the hydrogenation catalysts of different nature (Table 3) to find a more stable catalytic system for the debenzylation of compound 2. Unfortunately, the screening performed revealed no system comparable in catalytic activity with the Pd/C samples. The samples with a high content of the noble

Table 3. Catalytic systems of hydrogenation in the debenzylation of compound **2** at 25 (I) and 50 °C (II)

Catalyst ^a	d ^b /nm	v /(mole of H ₂) (mole of 2) ⁻¹ h ⁻¹		Yield of 3 (%)	
		Ι	II	Ι	II
Pd(6%)/C, ICT-3-23 ^c	5	1.0	3.2	56	80
Pd(10%)/C, E101 NE/W ^c	6	1.5	3.3	61	80
Pd(4%)/Sibunit	1.0	_	2.8	0	0
Pd(6%)/Sibunit (3 nm)	_	1.5	3.7	82	0
Pd(10%)/Sibunit	1.8	_	3.8	86	0

^{*a*} The catalyst was tested in the hydrodebenzylation of compound **2**. Loadings of the reactants: 3.4 g of compound **2**, 0.34 g of Pd/C, 5 mL of Ac₂O, 0.06 mL of PhBr, and 10 mL of DMF. The hydrogen pressure was 4 bar, and the reaction temperature was 25 °C.

^b Average size of the palladium particles.

^c Commercially available catalysts.

metal should be used to accelerate the debenzylation by the Pd/C catalysts. The use of the Pd(4%)/Sibunit catalyst (loading of the catalyst/substrate in the weight ratio 1/10) did not allow us to obtain the target precursor of CL-20 in the stepwise reaction. In this case, due to the deactivation processes, the moment when the debenzylation rate becomes lower than the rate of irreversible side processes associated with opening of the framework of compound **2**, preceded the step of formation of compound **3**. The ¹H NMR study of the reaction mixture indicates that the process ceases at the step of formation of the diacetyl hexaazisowurtzitane products. An increase in the loading of the Pd(4%)/Sibunit sample to the weight ratio catalyst/substrate = 1/5 was needed for the complete transformation of compound **2** into **3**.

Temperature dependences of the activity and selectivity of the debenzylation catalysts. Unlike the earlier known prototypes of the catalysts, namely, Pd(10%)/C (E101 NE/W, Degussa), Pd(20%)(OH)₂/C (Pearlman catalyst), and Pd(5%)/C (ICT-3-23), the debenzylation process on the Pd(4-10%)/Sibunit catalyst samples prepared by us should be carried out at room temperature. Even an insignificant rise of the reaction temperature to 40-50 °C resulted in a substantial decrease in the selectivity of C-N bond hydrogenolysis and the yield of the target product. At the same time, the activity of the mentioned prototypes of catalysts is insufficient for the debenzylation process to occur at room temperature. Possibly, the difference observed in the properties of the catalysts is caused by differences in the size of the metallic palladium particles in the catalyst samples prepared by us and in the known prototypes. According to the TEM data, metal particles 3 nm in size predominate in the Pd(6%)/Sibunitcatalyst, whereas the 6-nm particles prevail in Pd(10%)/C(Degussa) (see Table 3). The activity of the Pd/C catalysts increases with a decrease in the average particle size and, hence, an increase in the active surface area; however, their selectivity in C-N bond hydrogenolysis decreases. A possibility to perform the process at lower (room) temperature has several advantages, the main of which is the partial suppression of destruction processes of the hexaazaisowurtzitane framework that occur at elevated temperatures.

Thus, the results of the present study indicate that the Pd/C catalyst is deactivated during the first step of the debenzylation process. The dependences of the yield of the target product on the solvent nature, loadings of the reactants, catalyst, and cocatalyst, and hydrogen pressure were found for the reaction on the Pd/Sibunit catalysts. The optimum conditions were selected for the synthesis of compound **3**. The increase in the dispersity of the metal particles in the Pd/C catalyst was found to substantially enhance the catalytic activity, which makes it possible to perform the process under mild conditions at room temperature.

The authors are grateful to A. V. Golovin for help in recording ¹H and ¹³C NMR spectra and to V. A. Utkin for GC/MS analysis of compositions of the reaction mixture.

References

- S. V. Sysolyatin, A. A. Lobanova, Yu. T. Chernikova, and G. V. Sakovich, *Usp. Khim.*, 2005, **74**, 830 [*Russ. Chem. Rev.*, 2005, **74**, 757 (Engl. Transl.)].
- 2. J. Mathieu and H. Stucki, Chimia, 2004, 58, 383.
- R. L. Simpson, P. A. Urtiew, D. L. Ornellas, G. L. Moody, K. J. Scribner, and D. M. Hoffman, *Propell. Explos. Pyrot.*, 1997, 22, 249.
- 4. U. R. Nair, R. Sivablan, G. M. Gor, M. Giza, Sh. N. Astina, and H. Singh, *Fiz. Goren. Vzryva*, 2005, 4, 3 [Comb., *Explos., and Shock Waves*, 2005, 41, 121 (Engl. Transl.)].
- 5. US Pat. 5739325; Chem. Abstr., 1998, 127, 110983.
- 6. US Pat. 6147209; Chem. Abstr., 2000, 133, 352267.
- A. T. Nielsen, R. A. Nissan, D. J. Vanderah, C. L. Coon, R. D. Gilardi, C. F. George, and J. Flippen-Andersen, *J. Org. Chem.*, 1990, 55, 1459.
- M. R. Crampton, J. Hamid, R. Millar, and G. Ferguson, J. Chem. Soc., Perkin Trans., 1993, 2, 923.

- R. B. Wardle, J. C. Hinshaw, P. Brathwaite, M. Rose, G. Johnston, R. Jones, and K. Poush, in *Proc. 27th Intern. Ann. Conf. of ICT*, Karlsruhe, 1996, 27/1.
- A. P. Koskin and I. L. Simakova, Sb. dokl. I Vseros. nauchtekh. konf. "Perspektivy sozdaniya i primeneniya kondensirovannykh energeticheskikh materialov" [Proceedings of the I All-Russia Scientific Technical Conference "Prospects of Creation and Application of Condensed Energetic Materials"] (Biisk, September 27–29, 2006), Biisk, 2006, 42 (in Russian).
- A. T. Nielsen, A. P. Chafin, S. L. Christian, D. W. Moore, M. P. Nadler, R. A. Nissan, D. J. Vanderah, R. D. Gilardi, C. F. George, and J. Flippen-Andersen, *Tetrahedron*, 1998, 54, 11793.
- 12. A. J. Bellamy, Tetrahedron, 1995, 51, 4711.
- W. Han, Y. Ou, and B. Chen, J. Beijing Inst. Tech. (China), 2006, 15, 225; Chem. Abstr., 2000, 132, 78224.
- S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley, New York, 2001, p. 607.

Received June 7, 2007; in revised form November 15, 2007