

## Mechanochemical Reactions at High Pressure of the Gas Phase

VICTOR V. MOLCHANOV<sup>1</sup>, VASILY V. GOIDIN<sup>1</sup>, ROMAN A. BUYANOV<sup>1</sup>, ALEKSEY V. TKACHEV<sup>2</sup>  
and ANTON I. LUKASHEVICH<sup>1</sup>

<sup>1</sup>G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,  
Pr. Lavrentyeva 5, Novosibirsk 630090 (Russia)

E-mail: molchanov@catalysis.nsk.su

<sup>2</sup>N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,  
Pr. Lavrentyeva 9, Novosibirsk 630090 (Russia)

### Abstract

It is demonstrated with many examples that conducting mechanochemical reactions at increased pressure of the gas medium allows one to synthesize new compounds, to conduct catalytic reactions in solid, to find new more efficient routes for reactions, both in inorganic and in fine organic synthesis. At hydrogen pressure of 2–10 MPa, the hydrides of magnesium and intermetallic compounds are synthesized, including previously unknown hydride of the magnesium-copper intermetallide. At increased oxygen pressure, lower oxides of manganese are transformed into active manganese dioxide, which is efficient oxidizer for the processes of fine organic synthesis. Catalytic reactions are conducted under the conditions of mechanical activation at increased pressure of hydrogen, oxygen, and ammonia. Solid-phase hydrogenation of a series of organic compounds allows one to selectively reduce functional groups and unsaturated bonds. Hydro-dechlorination of toxic chlorinated aromatic compounds has been performed, including complete destruction of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin. At increased oxygen pressure, oxidative transformations of ursolic acid are performed. At increased ammonia pressure, the amide of ursolic acid is obtained. At increased temperature and increased hydrogen pressure, hydroalumination of heptene-1 and dihydromyrcene is performed, leading to the formation of the corresponding alumino derivatives  $R_3Al$ .

### INTRODUCTION

Extremal kinds of action on substances allow obtaining interesting results in the synthesis of various materials. Even more is expected when a combination of several kinds of extremal action is applied. An area being newly appearing and not investigated yet is the performance of mechanochemical reactions at high pressure of gas-phase reagents. We are aware of a limited number of works in which reactions of this type are described. For example, mechanical activation (MA) of metal titanium in the atmosphere of nitrogen at a pressure of 0.3–1.0 Pa leads to the formation of titanium nitride [1]. The formation of magnesium, zirconium and titanium hydrides  $MgH_2$ ,  $ZrH_{1.66}$ , and  $TiH_{1.9}$  occur under MA of these metals at increased pressure [2–5]. The formation of the hydrides of intermetallides was also observed

in the systems Zr – Ni [6] and Mg – Ni [7]. In all the cited works, gas pressure did not exceed 1.0 MPa.

### EXPERIMENTAL

Mechanical activation was carried out in AGO-2 planetary mill with steel balls 5–10 mm in diameter at the drum rotation frequency of 10–17 s<sup>−1</sup> and drum volume 150 cm<sup>3</sup>. The atmosphere in drums was created by a set-up allowing to achieve gas pressure up to 10 MPa.

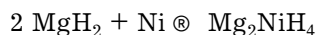
The analysis of inorganic products of reactions was carried out by means of X-ray phase analysis. X-ray diffraction patterns of the samples were obtained with HZG-4C diffractometer using  $CuK_\alpha$  radiation with graphite monochromator at the reflected beam. The analysis of organic products of reactions was carried out

by means of thin layer and gas-liquid chromatography, NMR spectroscopy and chromatomass spectroscopy. NMR spectrometers Bruker MSL-400 and Bruker DPX-250, and chromatomass spectrometer GC/MS were used.

## RESULTS AND DISCUSSION

### *Synthesis of the hydrides of intermetallic compounds*

Activation of magnesium-nickel alloy at the drum rotation frequency of  $10\text{ s}^{-1}$  for 30 min leads to the absorption of hydrogen in amount sufficient for the formation of magnesium hydride or the hydride of intermetallide  $\text{Mg}_2\text{NiH}_4$ . However, according to the data of X-ray diffraction, such a treatment causes amorphization of sample. Halos are observed in the regions where diffraction maxima of metal nickel should appear (Fig. 1). These data allow us to assume that activation at low drum rotation frequency leads to the formation of X-ray amorphous magnesium hydride and of metal nickel. An increase of the time of mechanical activation does not result in changes of phase composition. Similar results are obtained at the drum rotation frequency of  $17\text{ s}^{-1}$  and activation time of 5–10 min. Further treatment for 20–30 min leads to the formation of the hydride  $\text{Mg}_2\text{NiH}_4$ . It was assumed at first that the hydride was formed according to the reaction



A similar mechanism was proposed for the formation of hydride in the interaction of me-

chanical alloy with hydrogen at increased temperature and pressure [8].

Two interesting facts should be noted. They were discovered in obtaining hydrides by means of MA under high hydrogen pressure. When hydrogen is absorbed during MA, its pressure does not drop below 1.3 MPa; in case if initial hydrogen pressure is below this limit, no hydride of the intermetallide is formed. Using the dependence of the equilibrium hydrogen pressure on temperature obtained in [8]

$$\ln P = 14.711 - 7737T^{-1}$$

one can estimate the mobility of metal atoms conditioned by mechanical action. Calculation according to the above equation shows that the mobility of atoms corresponds to a temperature of 360 °C.

Another feature of the reaction under these conditions is the formation of high-temperature form of  $\text{Mg}_2\text{NiH}_4$  which is stable at room temperature. This is quite unusual because, according to literature data, the hydride of this composition exhibits a reversible phase transition at a temperature of 230 °C [9]. Measurement of the intensity of signal from the hydride protons in NMR spectra showed that the amount of hydrogen corresponded to the formula  $\text{Mg}_2\text{NiH}_6$  (sodium borohydride was used as a reference). Hydrogen content was determined by two more methods: by measuring the amount of hydrogen evolved during heating and during dissolution in hydrochloric acid. Both methods gave results confirming the NMR data. So, a likely reason of the stabilization of high-temperature modification of magnesium-nickel intermetallide is the formation of  $\text{Mg}_2\text{NiH}_6$  but not  $\text{Mg}_2\text{NiH}_4$ . It should be noted that the hydrides  $\text{Mg}_2\text{FeH}_6$  and  $\text{Mg}_2\text{CoH}_5$  have crystal structure which is isomorphous to the high-temperature modification of  $\text{Mg}_2\text{NiH}_4$ .

Besides magnesium-nickel alloy, we also investigated hydrogenation of other alloys under MA. For the Mg – Fe system, we did not succeed in obtaining the corresponding hydride; for the  $\text{LaNi}_5$  alloy, a known hydride of the composition  $\text{LaNi}_5\text{H}_7$  was obtained. An interesting result was obtained in hydrogenation of the mechanical Mg – Cu alloy. After MA at the initial hydrogen pressure of 80 atm, we detected a phase whose diffraction maxima

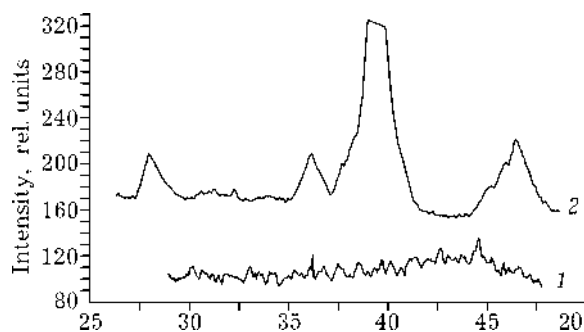


Fig. 1. X-ray diffraction patterns of mechanically activated samples of the 2Mg – Ni system. Rotation frequency,  $\text{s}^{-1}$ : 10 (1), 17 (2); MA time, min: 30 (1), 20 (2); hydrogen pressure: 50 atm.

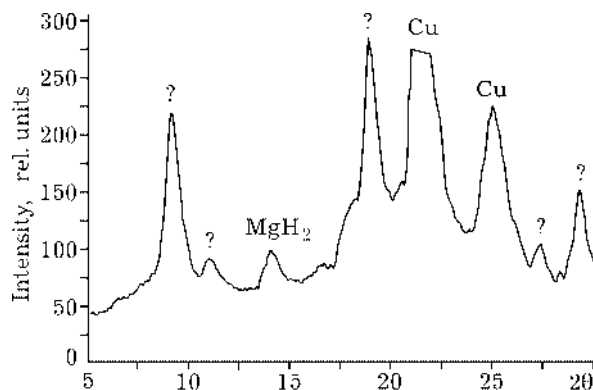


Fig. 2. X-ray diffraction patterns of the sample of 2Mg – Cu system after MA. Hydrogen pressure: 80 atm; rotation frequency:  $17\text{ s}^{-1}$ ; MA time: 30 min.

could not be attributed to known compounds in this system (Fig. 2). Taking into account the fact that MA is accompanied by hydrogen absorption, one can assume that a hydride of magnesium-copper intermetallide has been formed which has not yet been described in literature. It should be noted that attempts to synthesize such a hydride by traditional methods were unsuccessful, including the method involving the stage of mechanical alloying [10]. One can see in Fig. 2 that the system is multiphase; besides the unknown phase, the sample contains magnesium hydride, magnesium oxide, and metal copper. Because of this, it is rather difficult to evaluate chemical composition of the resulting hydride. Very approximate estimations of the content of different phases in the sample allow us assuming that the chemical composition of the new hydride is described by the formula  $\text{MgCuH}_2$ .

#### The $\text{MnO}_x - \text{O}_2$ system

Mechanical treatment of manganese oxides with oxidation degree  $\leq 4$  at increased hydrogen pressure leads to the formation of b- $\text{MnO}_2$ . This is confirmed by XPA (Fig. 3). The crystal structure of this modification is somewhat distorted since we observe redistribution of the intensities of maxima, in comparison with those available from the PC-PDF database (card 24-735). For example, the intensity of a maximum corresponding to the 110 planes, which should have relative intensity 100 %, is substantially decreased (see Fig. 3).

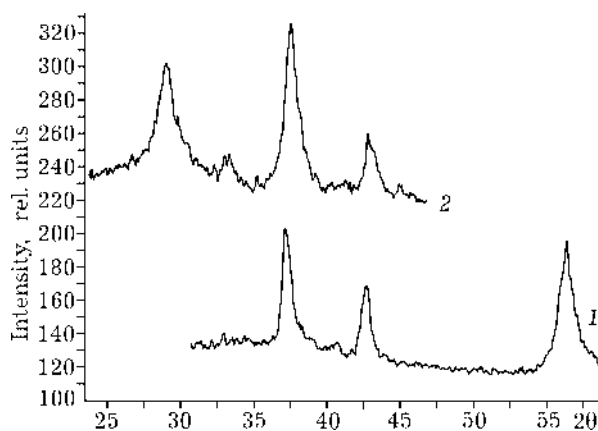


Fig. 3. X-ray diffraction patterns of manganese dioxide: initial sample (1), and sample after MA at  $\text{O}_2$  pressure of 60 atm (2). Rotation frequency:  $10\text{ s}^{-1}$ , MA time: 40 min.

If water is added to the system, the so-called active magnesium dioxide is formed, which is efficient oxidizer for fine organic synthesis. A traditional method to obtain active manganese dioxide is precipitation with alkalis, for example KOH, from a mixed solution of a salt of divalent manganese and potassium permanganate. This method results in large amount of waste water. The reagent obtained by precipitation should be used immediately after it is obtained, because it loses its activity during storage. One more shortcoming of the described method is the use of rather expensive potassium permanganate. The method involving MA is waste-free; manganese oxides cheaper than potassium permanganate are used. The reagent itself possesses a series of advantages over that obtained by precipitation: its activity in the oxidation of alcohols into aldehydes is several times higher (Table 1); it conserves its activity for a long time; mechanical treatment of the worked-out reagent, under the same conditions as those during obtaining it, allows recovering its activity.

#### Catalytic hydrogenation of organic compounds

These reactions have indisputable advantages over traditional methods. First of all, it does without the necessity to use organic solvents to perform hydrogenation, which as a rule is accompanied by the formation of by-products. Reactions go on at room tempera-

TABLE 1

Obtaining conditions and activity of manganese dioxide samples

MA time, min	Pressure of O <sub>2</sub> , MPa	H <sub>2</sub> O content, mass %	Conversion of benzyl alcohol, %
0*			70
10	50	4	72
1	50	10	12
30	50	10	75
60	50	10	70
30	50	20	72
30	100	10	75
30	2	10	55

\*A sample of active MnO<sub>2</sub> obtained by precipitation.

ture, which also allows one to limit the formation of by-products. High intensity of mixing allows eliminating the effect of mass transfer processes which manifest themselves during hydrogenation in solution and in melt.

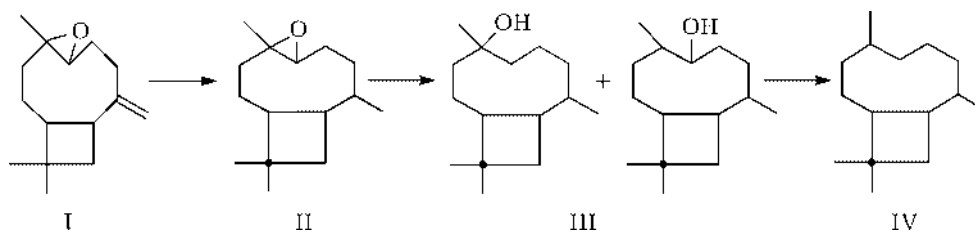
Experiments show that both unsaturated bonds and functional groups can be hydrogenated by this method. The most illustrative example is hydrogenation of caryophyllene-a-oxide. The analysis of products was carried out by means of thin layer chromatography and NMR spectroscopy. Activation of caryophyllene-a-oxide (I) for 10 min at the drum rotation frequency of 10 s<sup>-1</sup> in the presence of the hydride Mg<sub>2</sub>NiH<sub>4</sub> at hydrogen pressure of 5 atm leads to the hydrogenation of the double bond and to the quantitative transfor-

mation into dihydrocaryophyllene-a-oxide (II) (Scheme I). An increase of MA time to 90 min under the same conditions leads to the reduction of epoxy group to form hydroxyl group at a selectivity of 90 %; 14 isomers of alcohols (III) are formed. Finally, at drum rotation frequency of 17 s<sup>-1</sup>, complete removal of hydroxyl groups occurs within 20 min resulting in the formation of dihydrocaryophyllene (IV).

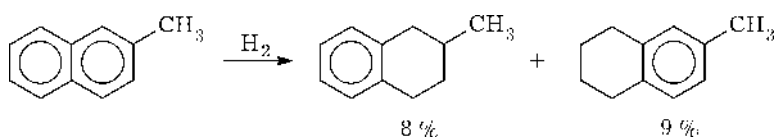
The use of other traditional hydrogenation catalysts, supported palladium and nickel, does not lead to any transformations; the same occurs with sodium borohydride used as a reducing agent. The Mg<sub>2</sub>NiH<sub>4</sub> hydride and caryophyllene-a-oxide were taken in amounts of 1.8 and 2.29 mmol, respectively. It is evident that the amount of hydrogen contained in hydride is insufficient for the above-described transformations. According to the data of X-ray phase analysis, no changes in the composition of hydride occur; hence, we may suppose that catalytic hydrogenation of caryophyllene-a-oxide occurs.

The MA of 2-methyl naphthalene for 30 min at hydrogen pressure of 20 atm (drum rotation frequency being 17 s<sup>-1</sup>) in the presence of the same hydride Mg<sub>2</sub>NiH<sub>4</sub> results in hydrogenation of one of benzene rings with the formation of a mixture of tetralines, as the data obtained by NMR on <sup>13</sup>C nuclei suggest (Scheme 2).

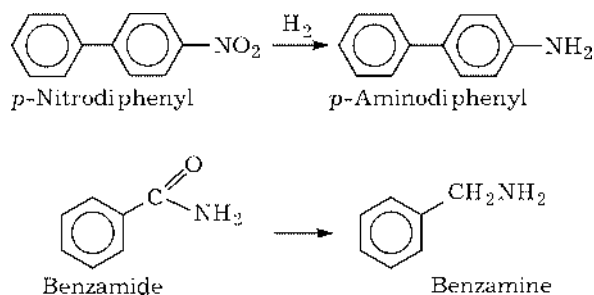
Quantitative transformations of *p*-nitrodiphenyl into *p*-aminodiphenyl and of benzamide into benzamine were also observed on



Scheme 1.



Scheme 2.



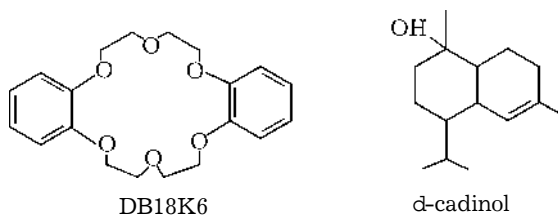
Scheme 3.

the  $Mg_2NiH_4$  hydride after MA for 30 min at drum rotation frequency of  $17\text{ s}^{-1}$  and hydrogen pressure of 15 atm (Scheme 3).

In all the listed examples, confirmations of catalytic hydrogenation similar to that described for caryophyllene- $\alpha$ -oxide were obtained.

Under the conditions described above, one cannot succeed in hydrogenating liquid organic compounds, which was demonstrated for  $\alpha$ -pinene, pinenoxime, and geraniol. Unsuccessful were attempts to hydrogenate a series of solid organic compounds: no hydrogenation of the benzene ring was observed in *p*-nitrodiphenyl, *p*-aminodiphenyl, benzamide, benzamine, double bonds in crown ether DB18K6 and *d*-cadinol (Scheme 4).

Consideration of the structural formulas of above-listed compounds shows that unsaturated bonds are within cycles and are likely to be sterically unavailable for the hydrogen of hydride catalyst. This is the reason of the absence of hydrogenation products. The described method can be applied in cases when it is necessary to perform selective hydrogenation of the end unsaturated bonds and functional groups without touching unsaturated bonds of the benzene ring and bonds lying inside cycles. Partial hydrogenation of 2-methylnaphthalene is explained by special properties of polyaromatic compounds, namely, by their acceptor properties towards hydrogen.



Scheme 4.

### Catalytic hydrodechlorination of chlorinated aromatic compounds

Working in this area we made an assumption that perchlorinated aromatic compounds, being most difficultly utilized toxic wastes, could be processed into less toxic, useful products by means of catalytic reactions under mechanical activation.

Catalysts based on hydrides of magnesium intermetallides, metal nickel and supported palladium were tested. Hydrides of magnesium intermetallides exhibit catalytic activity in hydrodechlorination of hexachlorobenzene; however, they are irreversibly deactivated by interacting with hydrogen sulphide which is reaction product. Bulk metal nickel does not exhibit activity, possibly because of low specific surface. The use of supported nickel catalysts is hindered by difficulties of procedure because nickel is usually present in them in its oxidized state and cannot be reduced under mechanical activation. Supported palladium catalysts (among them, IKT 3-30 and 7746 were tested) exhibited activity towards hexachlorobenzene under mechanical activation. The data obtained are shown in Table 2.

During the work, conditions were optimized for the catalytic hydrodechlorination of hexachlorobenzene during mechanical activation. Hydrides of magnesium intermetallides and supported palladium catalysts proved to be the most efficient ones in this process. The AGO-2 mill drum rotation frequency optimal for the process was  $17\text{ s}^{-1}$ , activation time was not

TABLE 2

Activity of different catalysts in hydrodechlorination reaction

Catalyst	Fraction of removed chloride ions per one hexachlorobenzene molecule
$Mg_2FeH_6$	0.74
$Mg_2NiH_4$	0.65
IKT 3-30(Pd/ $Al_2O_3$ )	0.4
7746(Pd-S/ $Al_2O_3$ )	0.17
Ni	0.06
GM-3(Ni/ $SiO_2$ )	0.1

more than 30 min, and sufficient oxygen pressure was 10–15 atm.

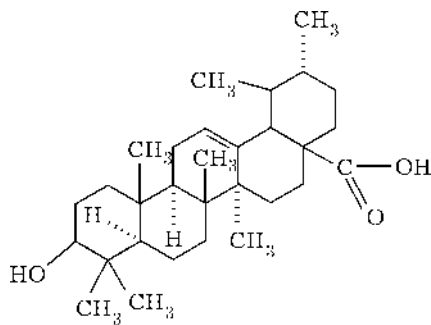
It was revealed that under mechanical activation without the use of solvents, only part of chlorine atoms could be removed from hexachlorobenzene. This allows one to hope for the directed selective synthesis of chlorine-containing compounds of the required structure starting from perchlorinated organic compounds, for example obtaining pentachlorophenol by hydroxylation of the formed pentachlorobenzene.

Results of experiments on catalytic dechlorination allowed assuming that chlorine atoms can be removed from dioxin molecules by a similar procedure. This could provide a substantial decrease of the toxicity of dioxins, since it is sufficient to remove only one chlorine atom from dioxin molecule to make it not so dangerous.

The application of the described procedure to dispose dioxins turned out unexpectedly to be efficient. We assumed that a part of chlorine atoms would be removed from molecule. However, the treatment resulted in complete destruction of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin. No dioxin was detected in reaction products at an accuracy of 0.0001 %. It was demonstrated that the use of the hydride of magnesium and nickel intermetallide as a catalyst causes complete destruction of dioxin molecule with the formation of tetrachloro- and pentachlorobenzene. These results give us grounds to think that this the most efficient and cheap method among the methods of dioxin disposal.

#### Catalytic transformations of ursolic acid

Ursolic acid (Scheme 5) is a triterpenic compound of  $\alpha$ -amyrin row. It is among most widespread triterpenic acids. Its structure allows synthesizing biologically active substances. Practically all the known derivatives of ursolic acid exhibit physiological activity. Possible syntheses are hindered because of the low reactivity of ursolic acid. Besides, it is practically insoluble in all the known solvents. Development of methods to involve ursolic acid into chemical processes will open way to new large-



Scheme 5.

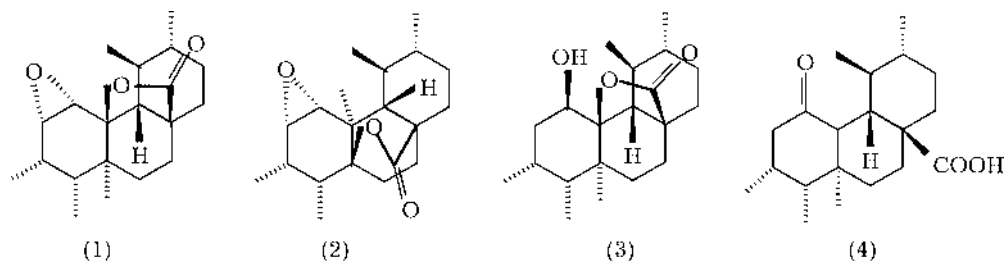
scale sources of raw materials for chemical industry because this acid is present in a series of plants in large amounts.

At the initial stage, the behaviour of ursolic acid is investigated under MA in the absence of reagents and catalysts. MA was carried out in a planetary centrifugal mill AGO-2 with steel balls 5 mm in diameter at drum rotation frequency of  $10\text{--}17\text{ s}^{-1}$ ; mass of balls was 0.2 kg, mass of sample to be activated was 0.5–5 g. Only initial ursolic acid was detected in the reaction mixture within the whole range of drum rotation frequencies at activation time till 30 min.

Investigation of the catalytic oxidation of ursolic acid was carried out under mechanochemical activation, increased oxygen pressure and the use of transition metal oxides as catalysts ( $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3$ ). It was discovered that the organic phase often got attached to the catalyst surface, which brought complications to isolation and identification of products. This fact made us develop criteria for the selection of catalysts to carry out transformations of insoluble and difficultly soluble organic compounds under MA. These criteria were used to develop methods of processing reaction mixture and isolating reaction products.

Using the developed methods we investigated catalytic oxidation of ursolic acid at increased oxygen pressure. For the reaction involving  $\text{WO}_3$  as catalyst, conditions were selected so that a single oxidation product was obtained, while the oxidation of ursolic acid by traditional methods gives a multicomponent mixture [11].

Under mechanochemical activation, the systems studied as oxidizers for ursolic acid included oxygen –  $\text{MnO}_2$ , and hydrogen pero-



Scheme 5.

xide in acetic acid. Reaction products were isolated and identified. Expected primary oxidation products (epoxides) were not detected since they underwent further transformations. Four compounds (1)–(4) are the major oxidation products. Fragments of the structural formula of ursolic acid that undergo transformations during oxidation are shown in Scheme 6.

The structure of products was stated by the researchers from the Novosibirsk Institute of Organic Chemistry (NIOCh), SB RAS, by means of the detailed analysis of IR spectra, numerical processing of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra using X-ray structural analysis.

Catalytic amination of ursolic acid was investigated under mechanochemical activation without solvents and in the presence of metals. Reaction products were isolated and identified. Copper salts were used as catalysts. For the process performed without solvents under MA in planetary mill under increased ammonia pressure, amide yield could not be obtained higher than 8–10 %. Amination at ammonia pressure of 15 atm and drum rotation frequency of  $17\text{ s}^{-1}$  with methanol as solvent allowed obtaining amide of ursolic acid at a yield of 65 %. By-products are practically absent. On the basis of these investigations, a laboratory procedure was developed for obtaining amide of ursolic acid. The structure of products was also investigated at the NIOCh, SB RAS, by means of detailed analysis of IR spectra, and numerical processing of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra using X-ray structural analysis.

A broad range of biological activity was revealed for ursolic acid itself. It exhibits antimicrobial, hypocholesterolic and antiatherosclerotic activity; it is assumed to be inhibitor of caries. As a rule, introduction of oxygen or nitrogen into such compounds gives biological-

ly active systems. The proposed approach allows one to involve insoluble and difficultly soluble compounds of plant origin into oxidation and amination reactions, which broadens the basis for chemistry and technology of the processing of renewable plant raw materials, opens way to the synthesis of new biologically active systems.

#### Hydroalumination reactions

We were the first to perform mechanochemical reactions at increased pressure and temperature. In order to carry out these reactions, we modified the AGO-2 planetary mill. Instead of water for cooling, silicon oil heated in a thermostat was fed to the mill. Temperature inside drums could be raised to  $150\text{ }^{\circ}\text{C}$ . Using the equipment described above, hydroalumination of heptene-1 and dihydromyrcene was carried out. Aluminium or its mechanical alloys, solutions of heptene-1 or dihydromyrcene in heptane, and triisobutyl aluminium in some cases, were loaded into drums with milling bodies. A drum was tightly closed; using the inlet system, hydrogen was pumped into the drum till the required pressure. Drums were heated to necessary temperature. Then mechanical activation was carried out. Reaction progress was monitored both by measuring the residual hydrogen pressure after MA and by determining the yield of primary alcohols after oxidation and hydrolysis of the formed aluminium-containing derivatives. Hydroalumination reaction turned out to proceed even on pure aluminium without adding other metals and triisobutylaluminium; the yield of heptanol-1 at the initial hydrogen pressure of 100 atm and temperature of  $120\text{ }^{\circ}\text{C}$  was 20 %. The use of mechanical alloys of aluminium with nickel, titanium or copper instead of pure

aluminium allows substantial increase of the efficiency of hydroalumination reaction. The yield of citronellol at the initial hydrogen pressure of 100 atm and 85 °C was 65 %, the yield of heptanol-1 under the same conditions was 60 %.

So, new methods are developed for the synthesis of organoaluminium compounds by hydroalumination reaction under mechanochemical activation at increased temperature and hydrogen pressure. It should be noted that mechanochemical reactions are likely to be carried out under these conditions for the first time.

## CONCLUSIONS

Mechanochemical reactions performed at increased gas-phase pressure allows synthesizing new, earlier unknown compounds. One of the examples can be the synthesis of hydrides of magnesium-copper intermetallide and of magnesium-nickel intermetallide  $Mg_2NiH_4$ . Reagents with increased reactivity and improved performance characteristics can be synthesized. Hydrides of intermetallic compounds find application as efficient reducing agents; active manganese dioxide obtained with the help of MA has some advantages over that obtained via traditional technology. It should be noted that the possibilities of the synthesis of earlier unknown compounds and of rendering unusual properties to the known ones are conditioned by obtaining conditions, namely, by combination of two types of action, and often are unique, *i. e.* they cannot be realized under any other conditions.

The possibility to perform catalytic transformations of organic compounds with high selectivity under MA at increased gas pressure

is demonstrated. The proposed technology allows one to perform reactions of compounds with very low reactivity and solubility. A bright example is amination and oxidation of ursolic acid, as well as reductive destruction of dioxin. Procedures are developed to conduct mechanochemical reactions at increased temperature and pressure of the gas medium. The listed examples are rather far from practical application yet. However, in our opinion, the development of the described direction will allow us to find new efficient ways in inorganic and fine organic synthesis.

## Acknowledgement

Authors thank Russian Foundation for Basic Research for financial support (Grants 00-15-97440 and 02-03-32327).

## REFERENCES

- 1 J. M. Criado, F. J. Gotor, C. Real, M. D. Alcala, Proc. 2nd Intern. Conf. on Mechanochemistry and Mechanical Activation, Novosibirsk, 1997, p. 37.
- 2 Y. Chen, J. S. Williams, Intern. Symp. on Metastable, Mechanically Alloyed and Nanocrystalline Materials (ISMANAM-95): Abstr., Quebec, July 24-28, 1995, P-A-7.2.
- 3 Y. Chen, J. S. Williams, *J. of Alloys and Comp.*, 217 (1995) 181.
- 4 Y. Chen, J. S. Williams, *Mater. Sci. Forum*, 225-227 (1996) 545.
- 5 Y. Chen, J. S. Williams, *Ibid.*, 225-227 (1996) 881.
- 6 S. Orimo, H. Fujii, T. Yoshino, *J. of Alloys and Comp.*, 217 (1995) 287.
- 7 S. Orimo, H. Fujii, *Ibid.*, 232 (1996) L16.
- 8 A. A. Stepanov, *Gidrirovaniye mekhanicheskikh splavov magniya*: Ph. D. Thesis, Novosibirsk, 1987.
- 9 J. J. Reilly, R. H. Wiswall, *Inorg. Chem.*, 7 (1968) 2254.
- 10 J. J. Reilly, R. H. Wiswall, *Ibid.*, 6 (1967) 2220.
- 11 A. V. Tkachev, *Khimiya vozobnovlyаемого растительного сырья: issledovaniye terpenoidov rasteniy Sibiri i Dal'nego Vostoka*: Dis. ...d-ra khim. nauk, Novosibirsk, 1996.