Low-temperature dehalogenation of benzyl halides with atomic magnesium in the ³P state

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Low-temperature reactions of benzyl halides with magnesium in the ³P state proceed according to the radical mechanism accompanied by abstraction of the halogen atom by the biradical magnesium atom.

Key words: magnesium, benzyl halides, dehalogenation, mechanism; ESR spectra.

Organic halides react with atomic magnesium at low temperature under conditions of cocondensation from the gaseous phase on the cooled surface.¹ The chemical properties of atomic magnesium prepared by different procedures differ substantially and depend on the electronic structure of Mg atoms.² The reactions of atomic magnesium in the ground state (¹S) with organic halides under conditions of cryosynthesis afforded Grignard reagents, while cocondensation of alkyl halides with atomic magnesium in the ³P state gave only products of recombination and disproportionation of alkyl radicals.^{1,2} The mechanism of the reactions of atomic magnesium in the ³P state with organic halides, which are characterized by low energies of the cleavage of the carbon halogen bond, remains poorly studied.

In this work, we studied the mechanism of the lowtemperature reactions of atomic magnesium in the ³P state with benzyl halides in detail. Cocondensation of a $Mg(^{3}P)$ vapor with benzyl halides, which were precipitated in the molecular beam mode on the surface cooled with liquid N₂, afforded white films. This films are stable at 77 K for no less than 24 h. At the melting temperatures of the samples, these films were decolorized. The melts obtained contained small amounts of solid white inclusions. The compositions of the cocondensates and the yields of the reaction products obtained after thawing and decomposition of the samples with water, deuterated water, and ethanol are given in Table 1.

After thawing and decomposition of the samples with water, 4,4'-ditolyl (2%), toluene ($\leq 0.2\%$), and 2,2'-ditolyl (<0.1%) were detected in the Mg(³P)—PhCH₂X systems (X = Cl, Br, or I) along with 1,2-diphenylethane (97–98%). The formation of 1,2-diphenylethane and 4,4'-ditolyl and the absence of 4-benzyl-1-methylbenzene among the reaction products indicate that the reaction proceeds according to the

radical mechanism. In this case, isomerization of benzyl radicals occurs only in the radical pair.³

The paramagnetic particles that formed in the reactions of Mg(³P) with PhCH₂X (X = Cl, Br, or I) were studied by ESR spectroscopy. The ESR spectrum of the cocondensate of magnesium with PhCH₂Br at 77 K has a triplet of quartets with a total width of about 50 G and the g factor of ~2.002. The ESR spectra of the cocondensates of Mg with PhCH₂X (X = Cl or I) are analogous to that of the cocondensate of Mg with PhCH₂Br. However, the former are more poorly resolved. A com-

Table 1. Yields of the products of the reactions of $Mg(^{3}P)$ with benzyl halides at 77 K after decomposition of the reaction mixture with $H_{2}O$, $D_{2}O$, or EtOH ^a

PhCH ₂ X	Yields of reaction products (mol.%)					
	PhMe ^b	PhCH ₂ CH ₂ Ph	MeC ₆ H ₄ -C ₆ H ₄ Me ^c	H ₂		
	After hydro	lysis or deuterol	ysis (at 298 K)			
PhCH ₂ Cl	0.2 (0.2)	97 (96)	2 (1.5)	0.02		
PhCH ₂ Br	0.1 (0.1)	97 (95)	2 (2)	0.02		
PhCH ₂ I		98 (96)	2(2)			
-	Afte	r ethanolysis (al	160 K)			
PhCH ₂ Cl	4	94	2	0.03		
PhCH ₂ Br	2	96	2	0.02		
PhCH ₂ I	l	97	2	—		

^a The molar ratio $PhCH_2X : Mg = 100 : 1$; the duration of cocondensation was 4 h. The yields were determined by GC (for H₂) and GLC.

^b Treatment of the samples with D_2O (99.8 at.% D) afforded PhCH₂D containing PhMe (0.2%).

^e The product isolated contained an admixture of 2,2'-ditolyl (<0.5%).

 \hat{d} The yields of the reaction products isolated by preparative liquid chromatography are given in parentheses.

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Table 2. Parameters of the ESR spectra (a/G) of the benzyl radical in solid matrices

8	a _{CH2} ^H	a, ^H	a _m H	a _p ^H	Reference
2.002±0.001	16.4±0.5	5.5±0.5	—	5.5±0.5	•
	16.5	6		6	4
	16.5±1	5.5±0.5		5.5±0.5	5
2.0026	16.34	5.13	1.77	6.17	6

* Data of this work.

parison of the parameters of the typical ESR spectrum obtained in this work with those of the benzyl radical in solid matrices⁴⁻⁶ allows the assignment of the signals of this spectrum to the benzyl radical (Table 2).

Examination of the ESR spectra recorded at different temperatures provides data on the stability and conversions of reaction intermediates. The intensity of the ESR signal gradually decreases as the cocondensates of Mg with benzyl halides are heated to 100 K. At temperatures higher than 130–150 K, the resolution of the ESR spectra is substantially impaired, apparently due to the overlap of the signals of the benzyl and 4-tolyl radicals as well as of the signals of the corresponding radical pairs. The ESR signal in the Mg—PhCH₂Cl system disappears at ~170 K. In PhCH₂Br and PhCH₂I, the ESR signal disappears at 185 and 210 K, respectively.

The facts that only the benzyl radical was detected at 77 K and the intensity of its signal gradually decreases as the temperature increases indicate that the formation of the radical pairs $PhCH_2 \cdot CH_2Ph$ occurs at T > 77 K, while their recombination and isomerization occur at T > 130-150 K. Otherwise, the ESR signals of the PhCH₂' and MeC₆H₄' radicals and of their radical pairs

would overlap at 77 K.

In the case of the reaction of Mg(${}^{3}P$) with PhCH₂X (X = Cl or Br), molecular hydrogen (<0.02%) was detected in the gaseous phase after thawing and treatment of the resulting samples with water. This may be a consequence either of the interaction of unconsumed Mg with H₂O or of hydrolysis of benzylpolymagnesium halides and benzylpolymagnesium hydrides formed according to the following scheme:^{7,8}



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However, the formation of organopolymagnesium halides and organopolymagnesium hydrides was observed in the reactions of Mg(¹S) with organic halides, which are characterized by high energies of the cleavage of the carbon—halogen bond,⁸ while these products were not detected in the reactions of Mg(¹S) with benzyl halides.⁷ The appearance of H₂ in small amounts indicates that benzylpolymagnesium halides and/or benzylpolymagnesium hydrides are absent in the reaction mixture or present in insignificant amounts. Consequently, Mg_rX (n > 1) radicals do not form in the reactions of Mg(³P) with benzyl halides.

The formation of a white matrix upon cocondensation of $Mg(^{3}P)$ with benzyl halides at 77 K suggests that charge-transfer complexes² virtually do not form on the magnesium surface as well.

Analysis of solid white inclusions, which were detected upon thawing of samples, demonstrated that the samples contained Mg^{2+} cations and halide anions whose ratio corresponded to the formula MgX_2 (X = Cl, Br, or I).

Based on the results obtained, it can be concluded that Mg atoms in the ³P state, whose energy is higher than that of Mg atoms in the ground state (¹S),² react with PhCH₂X on the surface even at 77 K.

$$PhCH_2X + Mg \longrightarrow PhCH_2 + MgX$$

X = Cl, Br, I

The formation of the radicals occurs in the solid PhCH₂X cage (PhCH₂X : Mg = 100 : 1). Therefore, at 77 K the high-energy 'MgX radical reacts with PhCH₂X via abstraction of the halogen atom. In this case, disproportionation of the 'MgX radical is highly improbable.

Recombination and isomerization of the $PhCH_2$ radicals proceed at T > 77 K according to the following scheme:



However, after thawing and hydrolysis of the resulting samples, Mg(OH)X (<0.2%) and toluene ($\leq 0.2\%$) were detected in the Mg(³P)—PhCH₂X systems (X = Cl

or Br). The formation of toluene in the reaction mixtures obtained after thawing and hydrolysis can occur either due to decomposition of PhCH₂MgX (X = Cl or Br) with water or according to the following reaction:

$$PhCH_2 + PhCH_2X \longrightarrow PhCH_3 + PhCHX$$

X = CL Br

However, products of recombination of the PhCHX[•] radical (X = Cl or Br) were not detected in the reaction mixtures. Deuterolysis of the samples, which were obtained after thawing, under the action of D_2O afforded PhCH₂D (see Table 1).

Consequently, the presence of toluene in the reaction mixtures, which were obtained after thawing and decomposition of the samples with water, allows the conclusion that the reaction of PhCH₂X (X = Cl, Br, or l) with atomic Mg, which was prepared by evaporating the metal with the use of a low-voltage electric arc, afforded the Grignard reagent along with other products.

In our experiments, evaporation of Mg using a lowvoltage electric arc afforded metal atoms in the excited ³P state in only 65–75% yields.² The remaining atoms were obtained in the ground state (¹S). The Mg atoms in the ¹S state react with PhCH₂X (X = Cl, Br, or I) at temperatures lower than the transition points of the matrices to form the radical pairs $PhCH_2 \cdot MgX$. Only at the transition temperatures or the melting temperatures of the matrices do these pairs recombine rapidly to give Grignard reagents according to the following scheme:⁷

$$PhCH_{2}X + Mg \longrightarrow PhCH_{2} + MgX \longrightarrow$$
$$PhCH_{2} \cdots MgX \longrightarrow PhCH_{2}MgX$$
$$X = CL Br. 1$$

On this basis, it can be suggested that the concentration of the Grignard reagent at the instant of phase transition of the matrix is higher than the concentration of toluene isolated after thawing and hydrolysis of the resulting sample. The decrease in the concentration of the Grignard reagent is associated with its interaction with free radicals⁹ and/or benzyl halides.¹⁰ To confirm this suggestion, we carried out a series of experiments on detection of PhCH₂MgX (X = Cl, Br, or I) at 160 K and on its reactions with benzyl halides and with intermediates of the reactions of PhCH₂X with Mg(³P).

Ethanolysis of the cocondensates of $Mg(^{3}P)$ with PhCH₂X (X = Cl, Br, or I) taken in a Mg : PhCH₂X ratio of 1 : 100 at 160 K afforded toluene in higher yields (4, 2, and 1%, respectively; see Table 1) compared to those obtained in the case of hydrolysis of these cocondensates at 298 K.

It is known that benzyl Grignard reagents do not react with PhCH₂Cl in solutions at 273 K.¹⁰ However, in the solid phase the situation can be different. To examine the possibility of this reaction, a twofold excess of PhCH₂X (X = Cl, Br, or I) was condensed at 77 K on the surface of the PhCH₂X—PhCH₂MgX systems (X = Cl, Br, or I) obtained by the reactions of Mg(¹S) with PhCH₂X.⁷ After thawing and hydrolysis, toluene was detected (by GLC) in an amount identical to that obtained upon hydrolysis of the initial PhCH₂X— PhCH₂MgX systems. The condensates under study do not give ESR signals. The results obtained indicate that PhCH₂X (X = Cl, Br, or I) does not react with PhCH₂MgX in the solid phase in the temperature range of 77—298 K.

Cocondensation of a Mg(³P) vapor with benzyl halides precipitated in the molecular beam mode at 77 K on the surface of the PhCH₂X—PhCH₂MgX systems (X = Cl, Br, or I), which were prepared by the reactions of Mg(¹S) with PhCH₂X (1 : 10),⁷ afforded white films. The ESR spectra of all the cocondensates at 77 K have a triplet of quartets with a total width of ~50 G and the g factor of ~2.002. This triplet was assigned to the benzyl radical. The intensities of the ESR signals obtained in these experiments at 77 K increase in the series Cl < Br < I by 5, 9, and 15%, respectively, compared to the intensities of the signals in the Mg(³P)—PhCH₂X cocondensates. Studies of the products of the reactions of the Mg(³P)—PhCH₂X cocondensates (1 : 50) with the

Table 3. Yields of the products of the reactions of the $PhCH_2X-PhCH_2MgX$ systems with $PhCH_2X$ or with the $Mg(^{3}P)-PhCH_2X$ cocondensates (1 : 50) at 77 K after hydrolysis of the reaction mixtures (at 298 K)

System	Reagent	Duration of	Yields of products (mol.%)	
		/h	PhMe ^a	PhCH ₂ CH ₂ Ph ^b
PhCH ₃ Cl-PhCH ₂ MgCl	PhCH ₂ Cl	0.5	95 (95)°	5 (5)
PhCH ₂ Br—PhCH ₂ MgBr	PhCH ₂ Br	0.5	93 (93)	$\frac{7}{7}$ (7)
PhCH ₂ I-PhCH ₂ MgI	PhCH ₂ I	0.5	86 (86)	14 (14)
PhCH ₂ Cl-PhCH ₂ MgCl	Mg—PhCH ₂ Cl	1.0	88 (93)	12 (7)
PhCH ₂ Br-PhCH ₂ MgBr	Mg-PhCH ₂ Br	1.0	83 (91)	17 (9)
PhCH ₂ I-PhCH ₂ Mgl	Mg-PhCH ₂ I	1.0	75 (88)	25 (12)

^a Treatment of the samples with D₂O (99.8% D) afforded PhCH₂D containing PhMe (0.2%).

^b The product contained admixtures of 4,4'-ditolyl ((1.5%) and 2,2'-ditolyl ((0.007%)). ^c The yields of the products of hydrolysis of the initial systems are given in parentheses. PhCH₂X--PhCH₂MgX systems (X = Cl, Br, or I) by GLC demonstrated that the yields of toluene (Table 3) decrease in the series Cl > Br > I by 5, 8, and 13%, respectively, compared to those obtained after hydrolysis of the systems.

Consequently, the decrease in the concentration of the Grignard reagent at the instant of phase transition of the matrix is associated with its reactions with free radicals, apparently, according to the following scheme:

$$PhCH_{2}MgX + PhCH_{2} \longrightarrow PhCH_{2}-CH_{2}Ph + MgX$$

$$PhCH_{2}MgX + MgX \longrightarrow PhCH_{2} + MgX_{2} + Mg$$

$$PhCH_{2} + PhCH_{2} \longrightarrow PhCH_{2}-CH_{2}Ph$$

$$MgX + MgX \longrightarrow Mg + MgX_{2}$$

$$X = CI, Br, I.$$

The results obtained allow the conclusion that the reactions of magnesium in the ³P state with benzyl halides at low temperature proceed in organic halide cages according to the radical mechanism via abstraction of the halogen atom by the Mg(³P) atom followed by the reaction of the resulting radical 'MgX (X = Cl, Br, or I) with a new molecule of benzyl halide.

Experimental

The ¹H NMR spectra were obtained on a Jeol FX-90Q spectrometer using 25-30% solutions of samples in CDCl₃. The accuracy of determination of chemical shifts was ± 0.01 ppm.

The ESR spectra were recorded on a Rubin radiospectrometer in films of cocondensates of magnesium and a 100-fold excess of benzyl halides at 77 K according to a known procedure.¹ Magnesium was evaporated using a low-voltage electric arc (12 V, 20 A) obtained between two Mg electrodes.

The reaction products were analyzed by gas (GC), gasliquid (GLC), preparative liquid, and ion chromatography.

The GLC analysis was performed on a Tsvet-162 chromatograph equipped with a heated flame ionization detector and a combined column (l = 2.5 m, d = 0.3 cm); a column (1.25 m) with Apiezon L (18%) on Chromaton N-AW as the stationary phase and a column (1.25 m) with PEG-20M (10%) on Chromaton N-AW as the stationary phase. The column temperature was 50-225 °C. The rate of heating was 30 K min⁻¹. Dodecane was used as the internal standard and N₂ was used as the carrier gas.

The reaction products in the gaseous phase were analyzed by gas chromatography on a Tsvet-162 chromatograph equipped with a thermal conductivity detector and a steel column (l = 2 m, d = 0.3 cm) filled with 4 Å molecular sieves (0.25-mm fraction). The column temperature was 50 °C; Ar was used as the carrier gas (the flow rate was 100 mL min⁻¹).

White solid inclusions were analyzed by ion chromatography on a Tsvet-3006 chromatograph equipped with a conductometric detector. The anions were analyzed on a steel column (l =200 nm, d = 4 mm). KhIKS-1 (Institute of Chemistry of the Academy of Sciences of Estonia; particle size 15 μ m) was used as the sorbent. A 0.03 M Na₂CO₃ solution in water was used as the eluent (flow rate was 2 mL min⁻¹). The volume of the sample was 10 μ L. The cations were analyzed on a Diacat-3 column (Elsiko, Moscow; l = 50 mm; d = 3 mm). The ethylenediamine-tartaric acid-citric acid system (molar ratio was 1.5 : 3.5 : 3.5) was used as the mobile phase. The flow rate was 1.5 mL min⁻¹.

The reaction products were isolated by preparative liquid chromatography on a Tsvet-304 chromatograph equipped with a UV detector ($\lambda = 254$ nm) using steel columns (l = 250 mm, d = 4 mm); Silasorb 600 (Chemapol, Czech Republic; particle sizes 15-25 µm) was used as the sorbent; a 5 : 1 hexane-ether mixture was used as the eluent.

Magnesium (Khlorvinil, Ukraine) was purified by a sevenfold sublimation *in vacuo* $(10^{-3}$ Torr) at 860–870 K according to a known procedure.¹¹ Admixtures of Fe, Al, Si, and heavy metals were not detected spectrometrically. Magnesium electrodes were prepared by remelting purified magnesium in Al₂O₃ molds under an Ar atmosphere at 300 Torr followed by treatment of the surface using a corundum instrument.

Benzyl chloride was dried with fused CaCl₂ and distilled; b.p. 63.5-64 °C (12 Torr), n_D^{25} 1.5386 (published data:¹² b.p. 63-64 °C (12 Torr), n_D^{25} 1.5386).

Benzyl bromide was dried with fused CaCl, and distilled; b.p. 83.5-84 °C (13 Torr) (published data:¹² b.p. 84 °C (13 Torr)).

Benzyl iodide was prepared according to a known procedure, ¹³ the yield was 90%; b.p. $61-62 \, ^{\circ}C \, (0.3 \, \text{Torr}) \, (\text{published data}; ^{13} \text{ b.p. } 60-62 \, ^{\circ}C \, (0.3 \, \text{Torr})).$ ¹H NMR (CCl₄), δ : 4.19 (s, 2 H, CH₂); 7.03 (m, 5 H, Ph).

Studies of the reactions of atomic $Mg({}^{3}P)$ with $PhCH_{2}X$ (X = Cl, Br, or I) were carried out in a vacuum apparatus analogous to that reported previously!⁴ in which an additional device for evaporation of metals with the use of a low-voltage electric arc was placed.¹⁵ The reagents were evaporated in an evacuated (10⁻⁴ Torr) reactor (V = 10 L) and condensed on the surface cooled with liquid N₂. Atomic Mg in the ³P state was prepared by evaporating the purified metal using a low-voltage electric arc (15 V, 32 A) obtained between two Mg electrodes. The rate of evaporation of Mg was 0.2 mmol min⁻¹. Benzyl halide was evaporated at 273–308 K (PhCH₂X : Mg = 100 : 1). The duration of cocondensation was 2–4 h.

Decomposition of samples with water or deuterated water. After completion of cocondensation, evacuation was terminated and the reactor was filled with dry pure Ar (p =760 Torr). The samples were heated to 298 K. At this temperature, the films melted and decolorized. The reaction mixtures were filtered in order to remove a small admixture of MgX₂ and a possible admixture of aggregated Mg. The filtrates were treated with H₂O or D₂O at 298 K under an atmosphere of pure dry Ar. The gas and liquid phases were analyzed by GC and GLC, respectively. The reaction products were isolated by preparative liquid chromatography. The results are given in Table 1.

Decomposition of samples with ethanol. After completion of cocondensation, the samples were heated to 160 K, kept at this temperature for 20 min, and then cooled to 77 K. EtOH (100 g) was condensed on their surfaces. After completion of condensation of EtOH, evacuation was terminated, the reactor was filled with dry pure Ar to p = 760 Torr, and the samples were heated to 160 K (at this temperature the films melted and were decolorized). The reaction mixtures were heated to 298 K and the compositions of the reaction products in the gas and liquid phases were analyzed by GC and GLC, respectively. The results are given in Table 1.

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Cryosynthesis of the PhCH₂X—PhCH₂MgX systems and their interactions with PhCH₂X or with the Mg(^{3}P)—PhCH₂X cocondensates (X = Cl, Br, or I) were carried out using the apparatus described above.

Atomic Mg in the ground state (¹S) was prepared by evaporating the purified metal from a quartz crucible at 640– 670 K.^{1,7} The rate of evaporation of Mg was 0.2 mmol min⁻¹. PhCH₂X (X = CI, Br, or I) was evaporated at 273–308 K (PhCH₂X : Mg = 10 : 1). The duration of cocondensation of the reagents was 1 h. After completion of cocondensation, the samples were heated to 170 K (X = Cl), 185 K (X = Br), or 210 K (X = I), kept at these temperatures for 30 min (as a result, the nut brown films decolorized). The colorless PhCH₂X-PhCH₂MgX films that formed were either (after evacuation was terminated and the reactor was filled with dry Ar) heated to 298 K, treated with H₂O, and analyzed by GLC or used in the reactions with PhCH₂X or with the Mg(³P)– PhCH₃X cocondensates (X = Cl, Br, or I).

To carry out reactions with $PhCH_2X$ (X = Cl, Br, or I), the $PhCH_2X-PhCH_2MgX$ samples were cooled to 77 K, the corresponding benzyl halide (240 mmol) was condensed on their surface, and the system was kept at 77 K for 30 min. After evacuation was terminated and the reactor was filled with dry Ar, the samples were heated to 298 K. The reaction mixtures were treated with H₂O and analyzed by GLC.

The reactions with the $\tilde{Mg}({}^{3}P)$ —PhCH₂X cocondensates were carried out as follows. The samples of the systems were cooled to 77 K and then a vapor of $Mg({}^{3}P)$ and benzyl halides, which were prepared as described above, taken in the ratio of 1 : 50 were condensed on the surface of the samples. The duration of cocondensation was 1 h. After completion of cocondensation, the samples were kept at 77 K for 30 min. Then evacuation was terminated and the reactor was filled with dry Ar to p = 760 Torr and heated to 298 K. The reaction mixtures were treated with H₂O and analyzed by GLC. The results are given in Table 3.

After thawing and decomposition of the resulting samples with H_2O or D_2O (99.8 at.% D), PhMe or PhCH₂D, which contained 0.02% PhMe, was isolated along with the following compounds: **1,2-Diphenylethane**, m.p. 51–52 °C (published data:¹⁶ m.p. 51–52 °C). ¹H NMR (CDCl₃), δ : 2.82 (s, 4 H, 2 CH₂); 7.02 (m, 10 H, 2 Ph). **4,4'-Ditolyl**, m.p. 120–122 °C (published data:¹⁷ m.p. 121–122 °C). ¹H NMR (CDCl₃), δ : 2.34 (s, 6 H, 2 CH₃); 7.18 (d, 4 H, H arom., J = 7.6 Hz); 7.44 (d, 4 H, H arom., J = 7.6 Hz).

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References

- 1. G. B. Sergeev, V. V. Smirnov, and V. V. Zagorsky, J. Organomet. Chem., 1980, 201, 9.
- 2. M. Moskovits and G. A. Ozin, Cryochemistry, Wiley, Chichester, 1976.
- 3. H. Gilman and R. E. Fortytrgiel, J. Am. Chem. Soc., 1928, 50, 3334.
- N. Ya. Buben, V. A. Tolkachev, and I. I. Chkheidze, *Kinet. Katal.*, 1963, 4, 683 [*Kinet. Catal.*, 1963, 4 (Engl. Transl.)].
- V. A. Tolkachev, I. I. Chkheidze, and N. Ya. Buben, Dokl. Akad. Nauk SSSR, 1962, 147, 643 [Dokl. Chem., 1962 (Engl. Transl.)].
- 6. P. Neta and R. H. Shuler, J. Phys. Chem., 1973, 77, 1368.
- 7. A. M. Egorov and A. V. Anisimov, Appl. Organomet. Chem., 1995, 9, 285.
- S. V. Kombarova, L. A. Tyurina, and V. V. Smirnov, Metalloorg. Khim., 1992, 5, 1038 [Organomet. Chem. USSR, 1992, 5 (Engl. Transl.)].
- 9. A. Tuulmets, M. Khyrak, K. Sarv, and E. Aaresil'd, Reakts. Sposob. Org. Soed. [Reactivity Org. Compd.], 1985, 22, 330 (in Russian).
- M. S. Malinovskii and A. A. Yavorskii, Zh. Obshch. Khim., 1955, 25, 2209 [J. Gen. Chem. USSR, 1955, 25 (Engl. Transl.)].
- 11. G. Brauer, Handbuch der Praeparativen Anorganischen Chemie, Enke Verlag, Stuttgart, Bd. 3, 1981.
- 12. T. Yokoyama, G. R. Wiley, and S. I. Miller, J. Org. Chem., 1969, 34, 1859.
- J. M. Aizpurua, B. Lecca, and C. Palomo, Can. J. Chem., 1986, 64, 2342.
- 14. P. L. Timms, J. Chem. Educ., 1972, 49, 782.
- J. E. Dobson, P. M. Tucker, F. G. A. Stone, and R. Shaeffer, J. Chem. Soc. (A), 1969, 1882.
- 16. P. Caubere and J. Moreau, Tetrahedron, 1969, 25, 2469.
- 17. J. Bergman, Tetrahedron, 1972, 28, 3323.

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