1,3-ELIMINATION IN γ-HALOGEN- AND γ-AMMONIUM-1-BORAADAMANTANE ATE-COMPLEXES

M. E. Gurskii, T. V. Potapova, K. L. Cherkasova, and Yu. N. Bubnov

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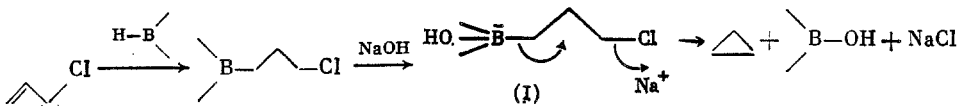
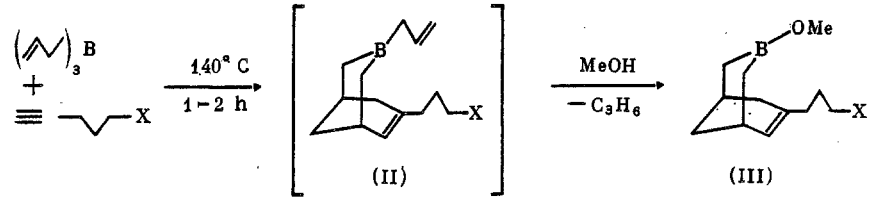
Alkylboron derivatives containing electronegative groups in the γ-position (halogens or OR) undergo 1,3-elimination reactions upon treatment with bases to form cyclopropane or its derivatives [1-4]. This reaction is the key step in the following two-step synthesis of cyclopropanes from allyl halides:



Cyclization is promoted by coordination of the base with the boron atom, which leads to the formation of an ate-complex (I).

This reaction has been used by us for the preparation of bi- and tricyclic boron derivatives (IX), (XII), and (XV), as well as of diols (X) and (XVI), from two types of γ-halo-1-boraadamantane derivatives (VI) and (XIII). The required 1-boraadamantane starting materials (VI) were prepared from bicyclic boron derivatives (III), which, in turn, were synthesized by condensation of triallylborane with the necessary acetylenic compounds (the allylboron–acetylene condensation [4]).

Heating triallylborane with 5-chloro- or 5-bromo-1-pentyne results in the formation of the corresponding 7-(3-halopropyl)-3-allyl-3-borabicyclo[3.3.1]non-6-enes (II), which undergo cleavage of the boron–allyl group bond treatment with MeOH, resulting in the formation of the methyl esters (III) in ~80% yield relative to triallylborane.



X = Cl, Br.

It has previously been demonstrated that hydroboration of 7-alkyl- [5], 7-alkylidene- [5], 7-trimethylsilylethyl- [6], and 7-(2-thienyl)methyl-3-methoxy-3-borabicyclo[3.3.1]non-6-enes [7] with the $H_3B \cdot THF$ complex, followed by heating at 60°C, leads to the formation of THF complexes of the corresponding 2-substituted 1-boraadamantane derivatives. We have used this method to prepare THF complexes of 2-(2-chloroethyl)- (VI, X = Cl) and 2-(2-bromoethyl)-1-boraadamantane (VI, X = Br) from the bicyclic precursors (III) (ratio of (III):BH_3 ≈ 2:1) (see scheme top of following page).

In the case of diboron compounds (IV), boron migration from the C^6 ring to the side chain [isomerization of (IV) to (V)] in the presence of compounds containing B–H bonds is complete within 2-3 h upon reflux in THF; essentially pure complexes (VI) are obtained after vacuum distillation. It should be emphasized at this point that almost all other organoboranes, including cycloalkylboranes (such as, for instance, the methyl- and ethylcyclohexene hydroboration products), isomerize only at temperatures ≥150°C [4].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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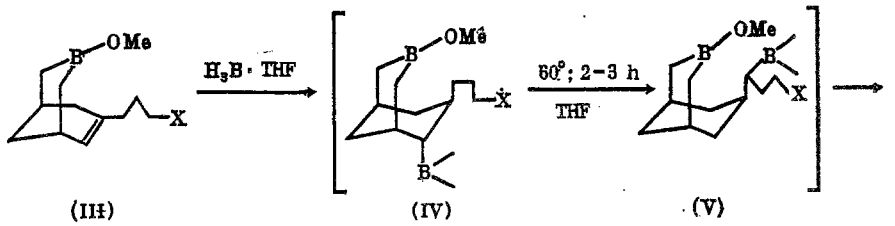
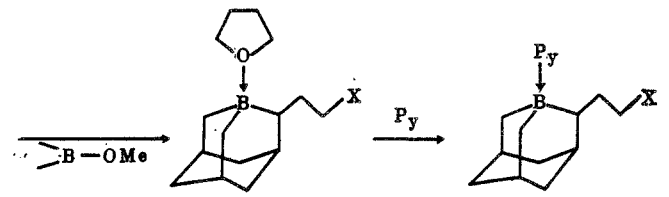
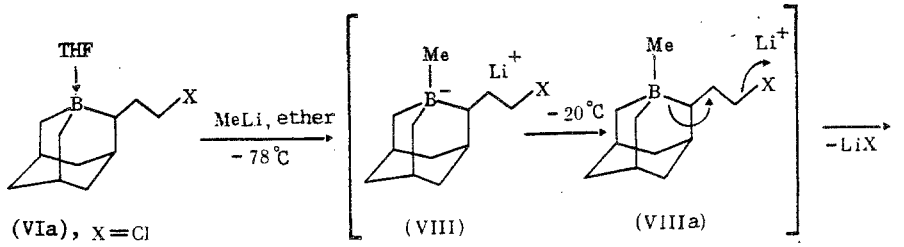


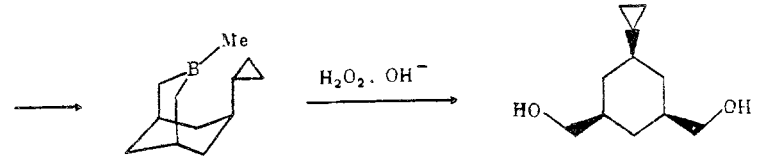


X = Cl, Br.

The THF-complexes (VI) are stable only in a dry inert gas atmosphere. Treatment of these complexes with pyridine results in the formation of pyridinate complexes (VII), which are stable in air. The ^{11}B-NMR chemical shifts of these compounds relative to BF_3 etherate are equal to −3.3 ppm (VIIc, X = Cl) and −3.1 ppm (VIIb, X = Br), respectively.

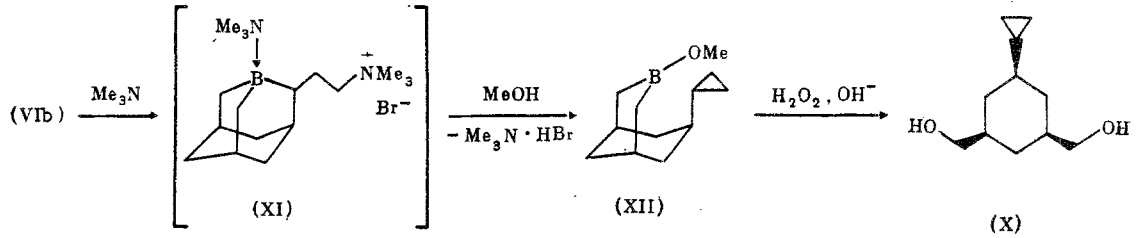
Treatment of complexes (VI) with methyllithium at −78°C leads to the formation of the corresponding ate-complexes (VIII), which undergo autodecomposition upon heating to ~20°C to give LiX and 7α-cyclopropyl-3-methyl-3-borabicyclo[3.3.1]nonane (IX).





Oxidation of borane (IX) with H_2O_2 in basic media gave diol (X), in which all three of the substituents occupy cis-positions relative to the cyclohexane ring.

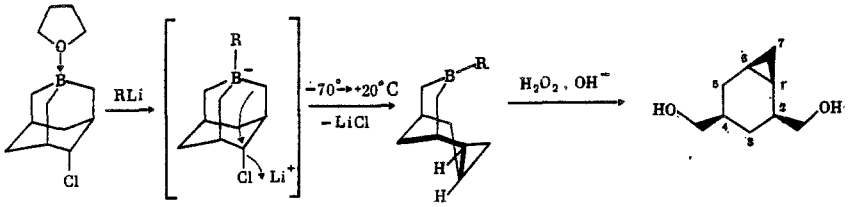
An analogous elimination reaction takes place in the case of complex (XI), in which the leaving group is an ammonium fragment. Compound (XI), which was prepared by reaction of the THF adduct (VIb) with excess Me_3N in benzene, decomposes upon treatment with alcohols to form the tricyclic boron ester (XII). Diol (X) was obtained in 92% yield upon oxidation of (XII).



The low-field chemical shift values observed for the C^9 and $C^{1,5}$ atoms in the ^{13}C NMR spectra of compounds (IX) and (XII) indicate [8] that these compounds exist predominantly in chair—chair conformations. The IR spectra of (IX) and (XII) contain intense bands at

3080 cm^{-1}, which are associated with the C–H stretching vibrations within the cyclopropane ring. The PMR spectra exhibit multiplets for the cyclopropane ring protons at 0.03 and 0.41 ppm (CH_2) in the case of compound (IX), and at –0.08 and 0.39 ppm in the case of compound (XII). The following signals in the ^{13}C NMR spectra are assigned to the three-membered ring (δ, ppm): 6.0 t, 18.8 d (IX), and 5.6 t, 18.7 d (XII).

Another system which contains a halogenoid group in the γ-position relative to boron is 4-chloro-1-boraadamantane (XIII) [9]. We have found that borate (XIV, R = Me), which was prepared via treatment of the THF-complex (XIII) with MeLi, undergoes auto-decomposition at –20°C, resulting in the formation of compound (XV, R = Me) and LiCl.



(XIII) (XIV) (XV) (XVI)

R = Me, MeO.

Borate (XIV, R = MeO), which was prepared from complex (XIII) and lithium methoxide at –78°C, also undergoes 1,3-elimination just as readily; in this case the decomposition product is the borate ester (XV, R = MeO), which can be oxidized to give the norcarane alcohol (XVI) with cis-oriented hydroxyl groups.

All three of the 1,3-elimination reactions described above apparently proceed in a synchronous manner: The B–C bond is cleaved simultaneously with halogen [or Me_3N^+ in the case of compound (XI)] dissociation, and a new C–C cyclopropane bond is formed. As has been shown recently [10], cyclization of linear γ-halogenoidpropylboranes takes place with inversion of the carbon atom attached to boron.

We have also demonstrated in the present paper that the 1,3-elimination process results in inversion of configuration at the carbon associated with the halogenoid leaving group as well. In this regard, complex (XIII) contains the chlorine atom in an axial position relative to the lower ring [9]. Ring closure to give a three-membered ring is possible only under conditions involving backside attack at the C^4 atom in (XIV) (trans-diaxial elimination).

It follows, therefore, that the formation of cyclopropane compounds from γ-halogenoidalkyl- and γ-halogenoidcycloalkylboranes occurs with inversion at both reaction sites. Inversion of configuration at both carbon atoms has been observed previously in a study of the fragmentation of hydroboration products derived from various hexahydronaphthalene-series mesylates [11].

EXPERIMENTAL

All operations with organoboron compounds were carried out under an atmosphere of dry Ar. PMR spectra were recorded on a Bruker WM-250 (250 MHz) spectrometer. ^{13}C and ^{11}B NMR spectra were obtained on a Bruker AM-300 (75.47 MHz for carbon and 96.3 MHz for boron) spectrometer. Signal assignments for the ^{13}C NMR spectra were made with the help of their off-resonance spectra, as well as by comparison of the chemical shift values within a series of related compounds.

5-Chloro- and 5-bromo-1-pentynes were synthesized from 1-pentyn-5-ol according to [12]. The 4-chloro-1-boraadamantane–THF complex was prepared according to [9]

3-Methoxy-7-(3-chloropropyl)-3-borabicyclo[3.3.1]non-6-ene (IIIa). To 5.88 g triallylborane at 130-140°C was added dropwise 4.5 g of 5-chloro-1-pentyne and the mixture was heated for 1.5 h at 140°C. The reaction mixture was then cooled to –10 to 0°C and 6 ml MeOH was added carefully; the mixture was then refluxed for 1 h. Yield 0.95 liter (98%) propylene. Distillation gave 8.13 g (82%) (IIIa), bp 93-95°C (1.5 mm Hg), n_D^{20} 1.5003. Found, %: C 62.89; H 8.72; B 5.27; Cl 15.80. $C_{12}H_{20}BClO$. Calculated, %: C 63.61; H 8.99; B 4.80; Cl 15.64. PMR spectrum (δ, ppm): 5.43 br d (1H, CH=C), 3.56 s (3H, OCH_3), 3.49 t (2H, CH_2Cl, J = 6.5 Hz).

3-Methoxy-7-(3-bromopropyl)-3-borabicyclo[3.3.1]non-6-ene (IIIb). To 12 g of triallylborane at 140-150°C was added over a 3 h period 11 g of 5-bromo-1-pentyne; the mixture was heated 3 h at 145°C, cooled to 0°C, and 11 ml MeOH was added and the mixture refluxed again for 1 h. Yield 1.9 liters (95%) of propylene. Distillation gave 19 g (79%) of (IIIb), bp 120-121°C (1 mm Hg), n_D^{20} 1.5170. Found, %: C 53.84; H 7.71; B 3.92; Br 28.39. $C_{12}H_{20}BBrO$. Calculated, %: C 53.18; H 7.44; B 3.99; Br 28.71. PMR spectrum (δ, ppm): 5.52 br d (1H, CH=D), 3.64 s (3H, OCH_3), 2.38 t (2H, CH_2Br, J = 6 Hz).

Complex of 2-(2-chloroethyl)-1-boraadamantane with THF (VIa). A solution of 1.63 g (IIIa) in 5 ml THF at 0°C was treated with 3.5 ml of a solution of BH_3·THF in THF (1.69 M), and refluxed for 3 h. After evaporation under vacuum 1.95 g (99%) of wet (VIa) was obtained as a colorless viscous liquid. PMR spectrum (δ, ppm): 3.94 m (2H, CH_2O), 3.7 m and 3.55 m (2H, CH_2Cl), 1.97 m (2H, CH_2THF), 0.65 d (2H, CH_2B).

Complex of 2-(2-Chloroethyl)-1-boraadamantane with Pyridine (VIIa). To a solution of 1.95 g (VIa) in THF (3 ml) was added 0.57 g Py, which resulted in heat evolution. After vacuum evaporation the residue was washed twice with cold pentane. Low-temperature crystallization from MeOH gave 1.7 g (85%) of (VIIa), mp 90.5-92°C (dec). Found, %: C 70.15; H 8.42; B 4.15; Cl 13.00. $C_{16}H_{23}BClN$. Calculated, %: C 69.72; H 8.41; B 3.93; Cl 12.86. PMR spectrum (δ, ppm): 8.5 m (2H, α-Py), 7.92 m (1H, γ-Py), 7.57 m (2H, β-Py), 3.5 m and 3.22 m (2H, CH_2Cl); δ ^{11}B −3.3 ppm.

Complex of 2-(2-Bromoethyl)-1-boraadamantane with Pyridine (VIIb). To a solution of 11 ml BH_3·THF (1.86 M) at 0°C was added dropwise 7.86 g (Vb) in 12 ml THF, and the solution was refluxed for 3 h. After vacuum distillation 9.07 g (100%) of wet (VIb) was obtained as a colorless oil. To a solution of 1.47 g (VIb) in 5 ml pentane was added 0.37 g Py. The resulting oil was washed twice with cold pentane. Low-temperature crystallization from MeOH gave 1.24 g (82.7%) (VIIb), mp 90-91°C. Found, %: C 60.25; H 7.40; B 3.41; Br 24.70; N 4.85. $C_{16}H_{23}BBrN$. Calculated, %: C 60.03; H 7.24; B 3.38; Br 24.97; N 4.48. PMR spectrum ($CDCl_3$, δ, ppm): 8.5 m (2H, α-Py), 7.93 m (1H, γ-Py), 7.56 (2H, β-Py), 3.45 ddd (1H, H_B, J_{BA} = 9.2, J_{BX} = 4.5, J_{BY} = 9.2 Hz), 3.15 dt (1H, H_A, J_{YA} = 7.0, $J_{AB} \approx J_{AX}$ = 9.2 Hz).

7-Cyclopropyl-3-methyl-3-borabicyclo[3.3.1]nonane (IX). To a solution of 3.23 g (VIa) in 15 ml ether at −70°C was added 6.3 ml of an ether solution of MeLi (1.66 M), and the solution was warmed to 20°C. After removal of the ether under vacuum the residue was washed with hexane (3 × 15 ml) and filtered. The solvent was evaporated and distillation gave 1.22 g (66%) of (IX), bp 59-60°C (2 mm Hg), n_D^{20} 1.4875. Found, %: C 81.56; H 11.86; B 5.94. $C_{12}H_{21}B$. Calculated, %: C 81.84; H 12.02; B 6.14. IR spectrum (ν, cm^{-1}): 3080 [cyclopropane ring (CPR) CH_2]. PMR spectrum ($CDCl_3$, δ, ppm): −0.03 m, 0.41 m (4H, CH_2 CPR), 0.61 s (3H, CH_3B). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 6.0 (CH_2 CPR), 18.8 (CH CPR), 27.2 (C^1, C^5), 35.5 (C^9), 37.2 (C^6, C^8), 38.2 (C^7).

3-Methoxy-7α-cyclopropyl-3-borabicyclo[3.3.1]nonane (XII). A mixture of 4 g (VIb), 9 g Me_3N, and 10 ml THF was sealed in an ampul. A white precipitate appeared upon standing. After 5 days the ampul was broken and 5 ml MeOH was added and the mixture evaporated under vacuum. The residue was washed with pentane and filtered to remove Me_3N·HBr (4.01 g). Distillation of the filtrate yielded 1.05 g (43%) of (XII), bp 61-63°C (1.5 mm Hg), n_D^{20} 1.4902. Found, %: C 74.88; H 11.01; B 5.65. $C_{12}H_{21}BO$. Calculated, %: C 75.02; H 11.02; B 5.63. PMR spectrum ($CDCl_3$, δ, ppm): 0.08 m and 0.39 m (4H, CH_2 CPR), 3.59 (3H, OCH_3). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 5.6 (CH_2 CPR), 18.7 (CH CPR), 27.3 (C^1, C^5), 35.2 (C^9), 37.4 (C^6, C^8), 37.8 (C^7).

cis-1,3-Dihydroxymethyl-5-cyclopropylcyclohexane (X). To a mixture of 0.4 g (XII) in 0.5 ml of 20% NaOH solution at 0°C was added 1 ml of 30% H_2O_2 and the mixture was allowed to stand overnight. The mixture was saturated with K_2CO_3 and extracted with ether (3 × 15 ml); the extract was dried over Na_2SO_4 and evaporated under vacuum. Recrystallization of the residue from ether gave 0.35 g (92%) of diol (X), mp 82-84°C. Found, %: C 71.23; H 10.81. $C_{11}H_{20}O_2$. Calculated, %: C 71.69; H 10.94. IR spectrum (ν, cm^{-1}): 3080 (CH_2 CPR), 3440 and 3630 (OH). PMR spectrum ($CDCl_3$, δ, ppm): 3.32 d (4H, CH_2O), 0.32 m and 0.01 m (4H, CH_2 CPR). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 3.55 (CH_2 CPR), 18.6 (CH CPR), 33.9 (C^2), 37.2 (C^4, C^6), 41.2 (C^1, C^3), 43.8 (C^5), 68.6 (CH_2O).

8-Methyl-8-boratricyclo[4.3.1.$0^{2,4}$]decane (XVa). To a suspension of 6.5 g of the 4-chloro-1-boraadamantane–THF complex (XIII) in 50 ml ether at −70°C was added 16.3 ml of an ether solution of MeLi (1.66 M); the mixture was stirred for 15 min at −70°C and then gradu-

ually warmed to ~20°C. At −60°C the precipitate which was present dissolved, and at −20°C LiCl began to separate out of solution. The mixture was stirred for 30 min at 20°C, the ether was evaporated under vacuum, and the residue was washed with pentane (3 × 30 ml), filtered, and the solvent evaporated. Distillation gave 2.94 g (XVa), bp 48-50°C (2.5 mm Hg), n_D^{20} 1.4935. Found, %: C 81.08; H 11.84; B 7.18. $C_{10}H_{17}B$. Calculated, %: C 81.12; H 11.57; B 7.31. IR spectrum (ν, cm^{-1}): 3050 (CH_2 CPR). PMR spectrum ($CDCl_3$, δ, ppm): −0.07 m, 0.39 m (2H, CH_2 CPR), 0.67 s (CH_3B), 1.17 m (1H, CH CPR). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 8.9 and 16.8 (C^2, C^4), 11.9 (C^3), 25.4 and 25.5 (C^1, C^6), 30.8 and 33.2 (C^5, C^{10}).

8-Methoxy-8-boratricyclo[4.3.1.$0^{2,4}$]decane (XVb). To a solution of 1.25 g MeOLi in 40 ml ether was added at −60°C 3.9 g (XIII) in 30 ml ether; the mixture was stirred for 15 min at −60°C, then warmed to 20°C. The ether was evaporated, the residue extracted with hexane. Subsequent distillation gave 2.96 g (55%) (XVb), bp 58.5-60°C (2.5 mm Hg). Found, %: C 73.68; H 10.79; B 6.30. $C_{10}H_{17}BO$. Calculated, %: C 73.20; H 10.44; B 6.69. PMR spectrum ($CDCl_3$, δ, ppm): 3.32 s (3H, CH_3O), 0.34 m and 0.27 m (2H, CH_2 CPR). ^{13}C NMR spectrum (δ, ppm): 8.5 and 17.1 (C^2, C^4), 9.9 (C^3), 24.7 and 26.1 (C^1, C^6), 31.7 and 33.6 (C^9, C^{10}), 52.6 (CH_3O).

cis-2,4-Dihydroxymethylbicyclo[4.3.0]heptane (XVI). To a solution of 1.71 g (XVb) in 15 ml ether was added 0.42 g NaOH in 5 ml H_2O; the mixture was cooled to 0°C and 1 ml of 30% H_2O_2 was added. The mixture was stirred 1 h at 20°C and 1 h at reflux. The mixture was extracted with ether (3 × 15 ml), and the extract was dried over Na_2SO_4. The solvent was evaporated and the residue purified by low-temperature crystallization from ether. Yield 1.3 g (80%) (XVI), mp 67.5-68.5°C. Found, %: C 69.13; H 10.34. $C_9H_{16}O_2$. Calculated, %: C 69.19; H 10.33. PMR spectrum ($CDCl_3$, δ, ppm): −0.02 m and 0.54 m (2H, CH_2 CPR), 4.6 m (4H, CH_2O). ^{13}C NMR spectrum (CD_3OD, δ, ppm): 8.7 (C^7), 9.3 and 14.4 (C^1, C^6), 27.0 and 28.0 (C^3, C^5), 38.1 and 38.6 (C^2, C^4), 68.2 and 68.6 (CH_2O).

CONCLUSIONS

1. Complexes of 2-(2-halogenoidethyl)-1-boraadamantanes with tetrahydrofuran and pyridine have been synthesized by the hydroboration–isomerization of 3-methoxy-7-(3-halogenoidpropyl)-3-borabicyclo[3.3.1]non-6-enes.

2. 4-Chloro-, and 2-(2-halogenoidethyl)-, and 2-(2-trimethylammoniumethyl)-1-boraadamantane ate-complexes undergo self-induced 1,3-elimination, resulting in the formation of substituted 3-borabicyclo[3.3.1]nonanes containing a cyclopropane fragment.

LITERATURE CITED

1. M. F. Hawthorne, J. Am. Chem. Soc., 82, 1886 (1960).
2. P. Binger and R. Köster, Tetrahedron Lett., 156 (1961).
3. R. Köster, Houben-Weyl Methoden der Organischen Chemie. Organobor-Verbindungen III, Vol. 13C, 275 (1984).
4. B. M. Mikhailov and Yu. N. Bubnov, Organoboron Compounds in Organic Synthesis [in Russian], Nauka, Moscow (1977), p. 427.
5. Yu. N. Bubnov, M. E. Gurskii, A. I. Grandberg, and D. G. Pershin, Tetrahedron, 42, 1079 (1986).
6. B. M. Mikhailov and M. Yu. Étinger, Izv. Akad. Nauk SSSR, Ser. Khim., 1197 (1984).
7. B. M. Mikhailov and K. L. Cherkasova, Izv. Akad. Nauk SSSR, Ser. Khim., 1837 (1984).
8. M. E. Gurskii, A. S. Shashkov, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 341 (1981).
9. B. M. Mikhailov and K. L. Cherkasova, J. Organomet. Chem., 246, 9 (1983).
10. H. L. Goering and S. L. Trenbeath, J. Am. Chem. Soc., 98, 5016 (1976).
11. J. A. Marshall, Synthesis, 229 (1971).
12. L. Brandsma, Preparative Acetylenic Chemistry, Elsevier Publishing Co., Amsterdam–London–New York (1979), p. 159.