Oxidative dimerization of vinylbornylacetylenes under the action of mercuric acetate

N. S. Vostrikov, A. V. Abutkov, and M. S. Miftakhov*

Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066. E-mail: chemorg@anrb.ru

Vinylbornylacetylenes and their trimethylsilyl derivatives undergo oxidative dimerization in the presence of an $Hg(OAc)_2$—HgO system in MeOH to give the corresponding diacetylenes.

Key words: bornylacetylenes, mercuric acetate, conjugated diynes.

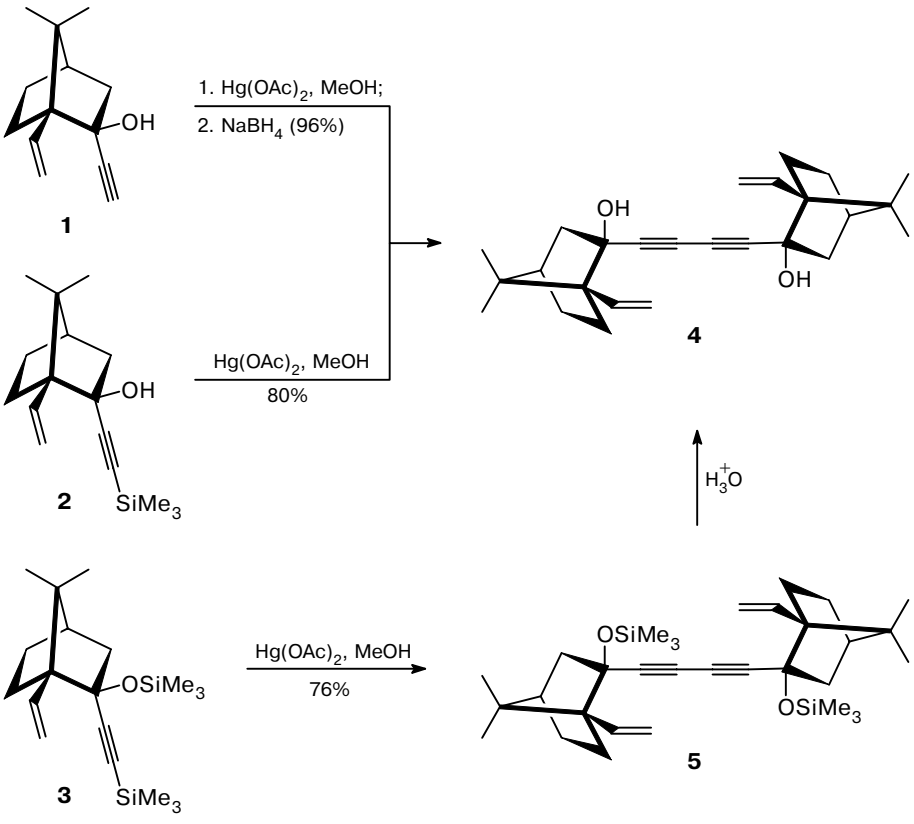
Under the conditions of reductive methoxy(acetoxy)mercuration,[1] ethynyl(vinyl)bicyclo[2.2.1]heptan-2-ol (**1**) and its trimethylsilyl (TMS) derivatives (**2** and **3**) might undergo Hg^{2+}-induced intramolecular cyclization because of the spatial proximity of the vinyl and ethynyl groups. However, it turned out that the reactions of these compounds with an $Hg(OAc)_2$—HgO system in MeOH yield the oxidative dimerization products, namely, diacetylenes **4** and **5** (Scheme 1).

Results and Discussion

Unlike compound **1**, TMS derivatives **2** and **3** were smoothly converted into dimers **4** and **5**, respectively, in the stage of methoxy(acetoxy)mercuration (without addition of $NaBH_4$). When treated with an acid, product **5** undergoes desilylation.

Compounds **1**—**3** were prepared by the condensation of the known oxo olefin **6** [2] with potassium acetylenide

Scheme 1

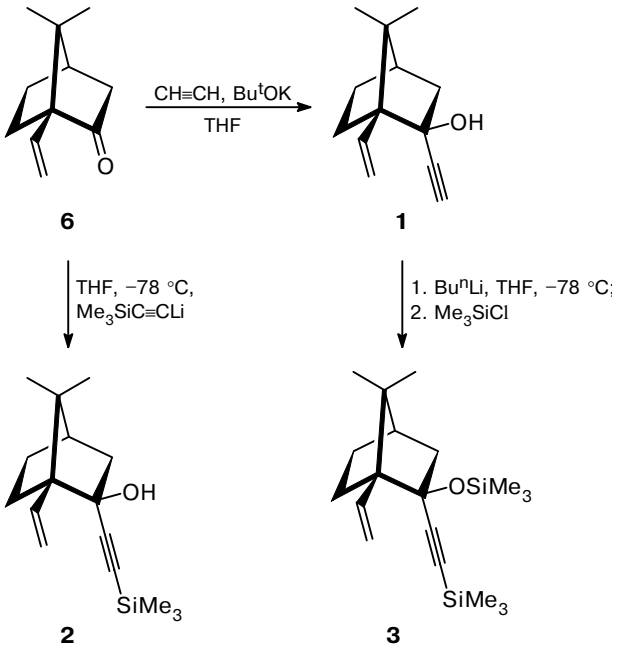


Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1181—1184, July, 2001.

1066-5285/01/5007-1238 $25.00

in THF, with lithium trimethylsilylacetylenide in THF, and by exhaustive silylation of acetylenic alcohol **1** deprotonated with butyllithium, respectively (Scheme 2).

Scheme 2

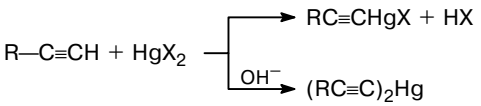


The exclusive formation of *exo*-alcohols **1** and **2** in the condensation of ketone **6** with the aforementioned acetylenides is due to the steric effect of the *syn*-C(7)-methyl group, which blocks the nucleophilic attack from the *exo*-side. A similar effect was discussed earlier[3,4] with relation to the condensation of vinyllithium reagents with ketone **6**; the same stereochemical outcome is also characteristic of the reactions of ketopinaldehyde and camphor with lithium acetylenide and other C-nucleophiles.[5—7]

The formation of diynes **4** and **5** is rather unusual, since such transformations induced by mercuric acetate have not probably been exemplified hitherto.

In aprotic media, terminal alkynes react[8,9] with HgX_2 to give the corresponding alkynylmercury halides and HX, which is bound by HgO added. Under the alkaline conditions of mercuration, terminal alkynes afford dialkynylmercury in good yields[10] (Scheme 3).

Scheme 3



In neutral or acidic media, Hg^{2+} salts add to the triple bonds to form vinylmercury derivatives.[9] In particular, mercuric acetate reacts with terminal alkynes in MeOH according to a common mechanism of oxymercuration; hydrolysis of the reaction products yields methyl ketones.[11]

Acetylene derivatives of Hg^{II} were also obtained[12] by the substitution reaction from HgX_2 and a series of organometallic compounds (Scheme 4).

Scheme 4

$$RM + HgX_2 \xrightarrow[-MX]{} RHgX \xrightarrow[-MX]{RM} R_2Hg,$$

M = Li, 1/2 Mg, 1/3 B, 1/3 Al, 1/3 Ti, 1/4 Si, 1/2 Zn, 1/4 Pb etc.

Dimerization of alkynylmercury halides has not been reported in the literature, although vinyl- and arylmercury derivatives are well known to dimerize under photolysis, catalysis by transition metal complexes, and heating.[9,13] Terminal alkynes easily undergo oxidative dimerization in the presence of Cu^+ ions and O_2 (the Glaser,[14] Eglinton,[15] and Cadiot—Chodkiewicz[16] reactions).

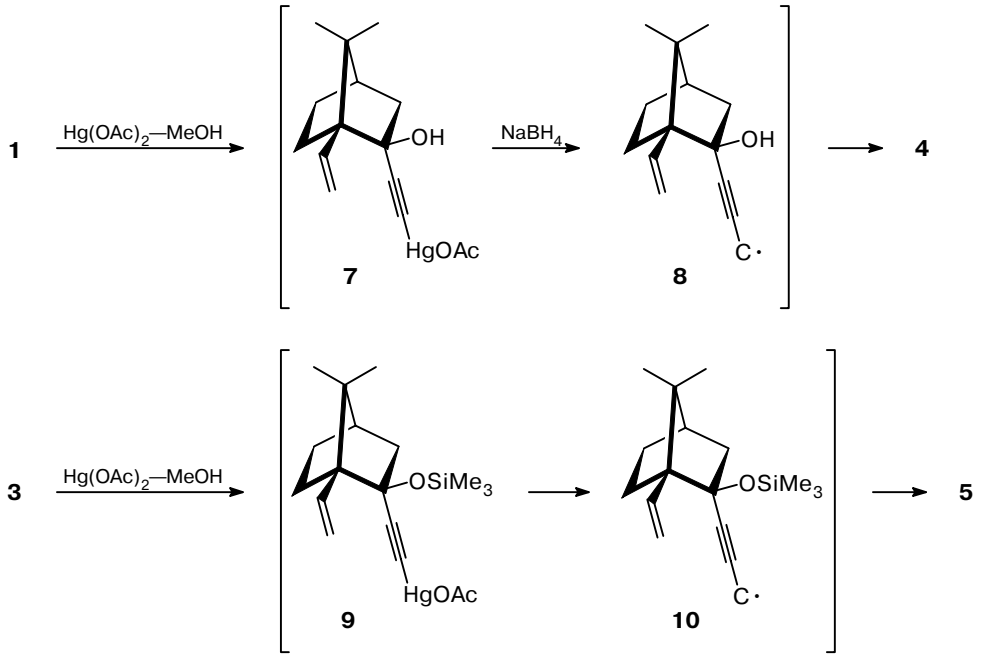
Based on the above literature data, one can interpret our results as follows (Scheme 5). Obviously, the mobile acetylenic H atom in alkyne **1** is replaced by HgOAc to give intermediate **7**. When treated with $NaBH_4$, it generates alkyne radicals **8**, which then dimerize. An analogous transformation for *C*-TMS-alkynes **2** and **3** must be preceded by a direct replacement of the C-bound Me_3Si group by Hg(OAc). The resulting alkynylmercury acetates **7** and **9** gradually decompose in the light to radicals **8** and **10** as the precursors of dimers **4** and **5**. The structure of compound **4** was confirmed by an independent synthesis from compound **1** by the Glaser reaction.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer (thin film or suspension in Vaseline oil). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75.47 MHz, respectively) in $CDCl_3$ with Me_4Si as the internal standard. Column chromatography was carried out on silica gel L 100/160 (Lachema). TLC was carried out on Silufol plates. Optical rotation was determined on a Perkin—Elmer 241 MC polarimeter. Mass spectra were recorded on an MKh-1320 instrument (EI, 70 eV, ionizing chamber temperature 80—90 °C).

(−)-(1*S*,2*S*,4*R*)-2-Ethynyl-7,7-dimethyl-1-vinylbicyclo[2.2.1]heptan-2-ol (1). Purified acetylene[17] was passed at ~20 °C into a solution of Bu^tOK (410 mg, 3.65 mmol) in 30 mL of THF. After 10 min, the solution became noticeably turbid, and a solution of enone **6** (200 mg, 1.22 mmol) in 5 mL of THF was added dropwise over 20 min. The reaction mixture was quenched with a saturated solution of NH_4Cl. The organic layer was separated, and the products were extracted from the aqueous layer with EtOAc (3×50 mL). The combined extracts were dried with Na_2SO_4, filtered, and concentrated. The residue was chromatographed on SiO_2 in hexane—ethyl

Scheme 5



acetate (10 : 1) to give oily compound **1** (210 mg, 90%), R_f = 0.57 (hexane—EtOAc, 10 : 1), $[\alpha]_D^{20}$ −50 (*c* 10, $CDCl_3$). Found (%): C, 82.15; H, 9.45. $C_{13}H_{18}O$. Calculated (%): C, 82.06; H, 9.53. IR, ν/cm^{-1}: 667 (≡C—H); 1640 (C=CH_2); 3320 (≡C—H); 3500 (—OH). ^{1}H NMR, δ: 0.85 (s, 3 H, Me); 0.90 (m, 1 H); 1.20—1.40 (m, 2 H); 1.20 (s, 3 H, Me); 1.70—2.45 (m, 4 H); 2.50 (s, 1 H, C≡C<u>H</u>); 5.30 (dd, 1 H, =CH_2, *J* = 17.5, 1.5 Hz); 5.40 (dd, 1 H, =CH_2, *J* = 11.0, 1.5 Hz); 6.05 (dd, 1 H, =CH, *J* = 17.5, 11.0 Hz). ^{13}C NMR, δ: 23.2, 23.4 (both Me); 28.7 (C(6)); 30.7 (C(5)); 47.9 (C(3)); 50.2 (C(4)); 51.2 (C(7)); 61.3 (C(1)); 74.0 (C≡<u>C</u>H); 80.4 (C(2)); 89.8 (—<u>C</u>≡C); 120.6 (=CH_2); 136.8 (—CH=).

(+)-(1*S*,2*R*,4*R*)-7,7-Dimethyl-2-(trimethylsilylethynyl)-1-vinylbicyclo[2.2.1]heptan-2-ol (2). A 1.5 *M* solution of BuLi (1.2 mL) in hexane was added at −78 °C to a solution of $Me_3SiC{\equiv}CH$ (180 mg, 1.83 mmol) in 30 mL of THF. Then a solution of enone **6** (200 mg, 1.22 mmol) in 5 mL of THF was added dropwise over 20 min. The reaction mixture was stirred for 3 h while the temperature raised to ~20 °C and worked up as described above. The yield of oily compound **2** was 240 mg (75%), R_f = 0.51 (hexane—EtOAc, 10 : 1), $[\alpha]_D^{20}$ +23 (*c* 10, $CDCl_3$). Found (%): C, 72.93; H, 9.75. $C_{16}H_{26}OSi$. Calculated (%): C, 73.22; H, 9.98. IR, ν/cm^{-1}: 840, 755 ($SiMe_3$); 1640 (C=CH_2); 3500 (OH). ^{1}H NMR, δ: 0.15 (s, 9 H, $SiMe_3$); 0.85 (s, 3 H, Me); 1.17 (s, 3 H, Me); 1.65—2.55 (m, 7 H, C(3), C(4), C(5), C(6)); 2.80 (s, 1 H, OH); 5.35 (dd, 1 H, =CH_2, *J* = 17.8, 1.8 Hz); 5.42 (dd, 1 H, =CH_2, *J* = 11.1, 1.8 Hz); 6.00 (dd, 1 H, =CH, *J* = 17.7, 11.1 Hz). ^{13}C NMR, δ: −0.06 ($SiMe_3$); 21.2, 21.3 (both Me); 26.6 (C(6)); 28.7 (C(5)); 45.7 (C(4)); 48.2 (C(3)); 48.9 (C(7)); 59.2 (C(1)); 78.6 (C(2)); 87.7 (—<u>C</u>≡C); 109.6 (≡<u>C</u>—$SiMe_3$); 118.2 (=CH_2); 134.9 (—CH=).

(+)-(1*S*,2*R*,4*R*)-7,7-Dimethyl-2-(trimethylsilylethynyl)-2-trimethylsilyloxy-1-vinylbicyclo[2.2.1]heptane (3). A 1.5 *M* solution of BuLi (1.1 mL) in hexane was added at −78 °C to a solution of compound **1** (100 mg, 0.53 mmol) in 30 mL of THF. Then a solution of Me_3SiCl (171 mg, 1.58 mmol) in 5 mL of THF was added dropwise. The reaction mixture was stirred for 3 h while the temperature raised to ~20 °C and worked up as described above. The yield of oily compound **3** was 146 mg (83%), R_f = 0.65 (hexane—EtOAc, 10 : 1), $[\alpha]_D^{20}$ +28 (*c* 10, $CDCl_3$). Found (%): C, 68.01; H, 10.12. $C_{19}H_{34}OSi_2$. Calculated (%): C, 68.19; H, 10.24. IR, ν/cm^{-1}: 840, 755 (—$SiMe_3$); 1065 (Si—O); 1650 (C=CH_2); 2185 (—C≡C—). ^{1}H NMR, δ: 0.17 (s, 18 H, $SiMe_3$); 0.82, 1.13 (both s, each 3 H, Me); 1.70—2.00 (m, 5 H, C(4), C(5), C(6)); 2.25—2.35 (m, 2 H, C(3)); 5.08 (dd, 1 H, =CH_2, *J* = 17.7, 1.9 Hz); 5.22 (dd, 1 H, =CH_2, *J* = 11.0, 1.9 Hz); 6.05 (dd, 1 H, =CH, *J* = 17.7, 11.0 Hz). ^{13}C NMR, δ: −0.3 ($SiMe_3$); 1.9 ($OSiMe_3$); 21.3, 21.6 (both Me_3); 25.8 (C(6)); 27.0 (C(5)); 46.2 (C(4)); 49.8 (C(3)); 52.0 (C(7)); 59.7 (C(1)); 79.6 (C(2)); 88.7 (C≡<u>C</u>—Si); 109.9 (—<u>C</u>≡C); 116.1 (=CH_2); 136.1 (—CH=).

1,4-Bis[(1*S*,2*S*,4*R*)-2-hydroxy-7,7-dimethyl-1-vinylbicyclo[2.2.1]heptan-2-yl]buta-1,3-diyne (4). ***A.*** Mercuric oxide (114 mg, 0.53 mmol) was added to a solution of compound **1** (200 mg, 1.05 mmol) and $Hg(OAc)_2$ (335 mg, 1.05 mmol) in 10 mL of MeOH. The resulting suspension was stirred at 20 °C for 1 h to give an orange-red solution. Then CH_2Cl_2 (20 mL), 1 *M* NaOH (0.5 mL), and $NaBH_4$ (68 mg, 1.78 mmol) were added at 0 °C, and the reaction mixture was stirred for 1 h. The excess of $NaBH_4$ was decomposed by adding water (5 mL), and the products were extracted from the aqueous phase with CH_2Cl_2 (3×10 mL). The combined extracts were washed with brine, dried with Na_2SO_4, filtered, and concentrated. The residue was purified on SiO_2 in hexane—EtOAc (10 : 1) to give diol **4** (207 mg, 96%), R_f = 0.29 (hexane—EtOAc, 7 : 3), $[\alpha]_D^{20}$ +6 (*c* 1, $CHCl_3$). Found (%): C, 82.32; H, 8.96. $C_{26}H_{34}O_2$. Calculated (%): C, 82.49; H, 9.05. IR, ν/cm^{-1}: 1643 (C=C); 3550 (OH). ^{1}H NMR, δ: 0.79, 1.13 (both s, each 6 H, C(7)Me_2, C(7′)Me_2); 1.70—2.05 (m, 10 H, C(4), C(4′), C(5), C(5′), C(6), C(6′)); 2.25—2.35 (m, 4 H, C(3), C(3′)); 2.80 (br.s, 2 H, OH); 5.22 (dd, 2 H, =CH_2, *J* = 17.6, 2.0 Hz), 5.35 (dd, 2 H, =CH_2, *J* = 11.0, 2.0 Hz); 6.06 (dd, 2 H, =CH, *J* = 17.6, 11.0 Hz). ^{13}C NMR, δ: 21.2, 21.4

(both Me); 26.6 (C(6)); 28.2 (C(5)); 45.8 (C(4)); 48.8 (C(3)); 49.3 (C(7)); 59.6 (C(1)); 78.7 (C(2)); 112.35 (—C≡C—COH—); 114.05 (—C≡C—COH—); 118.4 (=CH_2); 136.0 (—CH=). MS (EI), m/z (I_{rel} (%)): 378 $[M]^+$ (10), 360 $[M - H_2O]^+$ (8), 189 $[1/2\ M]^{\cdot +}$ (100).

B. Mercuric oxide (82 mg, 0.38 mmol) was added to a solution of *C*-silyl derivative **2** (200 mg, 0.76 mmol) and $Hg(OAc)_2$ (241 mg, 0.76 mmol) in 10 mL of MeOH. The resulting orange-red solution was stirred at 20 °C for 3 h. Then CH_2Cl_2 (20 mL) and brine (10 mL) were added and stirred. The organic layer was separated, and the extract was dried with Na_2SO_4, filtered, and concentrated. The residue was purified on SiO_2 in hexane—EtOAc (10 : 1) to give diol **4** (119 mg, 80%).

C. A solution of alkyne **1** (200 mg, 1.05 mmol), CuCl (10 mg, 0.11 mmol), and NH_4Cl (85 mg, 1.56 mmol) in aqueous MeOH (1 : 1) was stirred at ~20 °C for 6 h; methanol was removed, and the products were extracted from the aqueous phase with CH_2Cl_2 (3×10 mL). The combined extracts were washed with brine, dried with Na_2SO_4, filtered, and concentrated. The residue was purified on SiO_2 in hexane—EtOAc (10 : 1) to give diol **4** (126 mg, 85%).

All procedures (***A***, ***B***, and ***C***) afford the same compound **4** (IR, ^1H and ^{13}C NMR, and TLC data).

1,4-Bis[(1*S*,2*S*,4*R*)-7,7-dimethyl-2-trimethylsilyloxy-1-vinylbicyclo[2.2.1]heptan-2-yl]buta-1,3-diyne (5). Mercuric oxide (65 mg, 0.30 mmol) was added to a solution of *C*,*O*-silyl derivative **3** (200 mg, 0.60 mmol) and $Hg(OAc)_2$ (190 mg, 0.60 mmol) in 10 mL of MeOH. The resulting orange-red solution was stirred at 20 °C for 3 h. The reaction mixture was worked up as described above (see procedure ***B***) to give ether **5** (119 mg, 76%), R_f = 0.64 (hexane—EtOAc, 7 : 3), $[\alpha]_D^{20}$ +17 (*c* 5, $CHCl_3$). Found (%): C, 73.42; H, 9.55. $C_{32}H_{50}O_2Si_2$. Calculated (%): C, 73.50; H, 9.64. IR, ν/cm^{-1}: 755, 840, 1100. ^1H NMR, δ: 0.19 (s, 18 H, $OSiMe_3$); 0.70, 1.12 (both s, each 6 H, C(7)Me_2, C(7′)Me_2); 1.75—2.00 (m, 10 H, C(4), C(4′), C(5), C(5′), C(6), C(6′)); 2.25—2.35 (m, 4 H, C(3), C(3′)); 5.09 (dd, 2 H, =CH_2, J = 17.8, 2.0 Hz); 5.24 (dd, 2 H, =CH_2, J = 11.0, 2.0 Hz); 6.08 (dd, 2 H, =CH, J = 17.6, 11.0 Hz). ^{13}C NMR, δ: 2.0 ($OSiMe_3$); 21.2, 21.6 (both Me); 26.5 (C(6)); 26.9 (C(5)); 46.2 (C(4)); 49.8 (C(3)); 52.2 (C(7)); 59.9 (C(1)); 79.4 (C(2)); 109.6 (—C≡C—COSi—); 115.2 (—C≡C—COSi—); 115.9 (=CH_2); 136.1 (—CH=).

Acid hydrolysis of ether 5. A solution of *O*-TMS derivative **5** (50 mg) in 5 mL of THF—3% HCl (3 : 1) was stirred at 20 °C for 30 min to give diacetylene **4** (93%). The product was found to be identical with an authentic sample (IR, ^1H and ^{13}C NMR, and TLC data).

References

1. B. Giese, K. Heuck, H. Lenhardt, and U. Lüning, *Chem. Ber.*, 1984, **117**, 2132.
2. N. Fischer and G. Opitz, *Org. Synthesis*; J. Wiley, New York, 1973, Collect. Vol. **5**, 877.
3. L. A. Paquette, D. T. De Russy, T. Vandenheste, and R. D. Rogers, *J. Am. Chem. Soc.,* 1990, **112**, 5562.
4. L. A. Paquette, N. A. Pegg, D. Toops, G. D. Mainard, and R. D. Rogers, *J. Am. Chem. Soc.,* 1990, **112**, 227.
5. R. N. Saičić, *Tetrahedron Lett.*, 1997, **38**, 295.
6. V. Dimitrov, S. Bratovanov, S. Simova, and K. Kostova, *Tetrahedron Lett.,* 1994, **35**, 6713.
7. C. Palomo, A. Gonzales, J. M. Garcia, C. Landa, M. Oiarbide, S. Rodrigues, and A. Linden, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 180.
8. *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, **2**.
9. R. C. Larock, *Tetrahedron,* 1982, **38**, 1713.
10. J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.,* 1926, **48**, 469.
11. *Comprehensive Organic Chemistry*, Eds. D. Barton and W. D. Ollis, Pergamon Press, Oxford, 1983, **5**.
12. Houben-Weyl, *Methoden der Organischen Chemie*, 4. Aufl., *Metalloorganische Verbindungen Hg*, **13/2b**, J. Thieme Verlag, Stuttgart, 1974.
13. J. Barluenga and M. Yus, *Chem. Rev.*, 1988, **88**, 487.
14. C. Glaser, *Ann.*, 1870, **154**, 137.
15. G. Eglinton and A. Galbreith, *Chem. Ind.*, 1956, 737.
16. W. Chodkiewicz and W. Cadiot, *C. R. Acad. Sci.,* 1955, **241**, 1055.
17. F. M. Rapoport and A. A. Il′inskaya, *Laboratornye metody polucheniya chistykh gazov* [*Laboratory Methods for the Preparation of Pure Gases*], Goskhimizdat, Moscow, 1963, p. 362 (in Russian).

Received March 7, 2001;
in revised form May 17, 2001