Russian Journal of Organic Chemistry, Vol. 37, No. 8, 2001, pp. 1107–1110. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 8, 2001, pp. 1167–1169.

Synthesis and Certain Reactions of Primary Carboranyl Acetates and Tosylates

A. V. Kazantsev, V. V. Butyaikin, I. E. Gaas, E. A. Otrashchenkov, and M. M. Aksartov

Buketov Karaganda State University, Karaganda, 470074 Kasakhstan

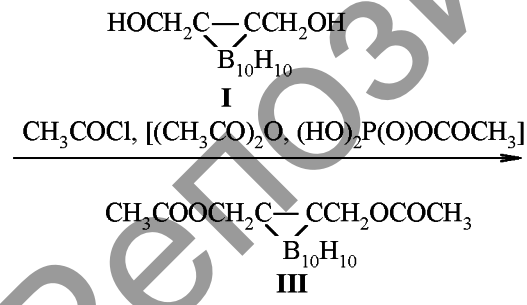
Received March 9, 2000

Abstract—Acetates and tosylates of primary carboranyl alcohols were prepared, and their reactions with nucleophilic reagents were investigated. Some specific features of these processes were revealed, and preparative procedures for previously unknown carboranyl amines were developed.

Until the present time no investigations have been conducted on reactions of carboranyl alcohols with nucleophilic reagents [1, 2]. In this connection we carried out acylation and tosylation of primary carboranyl alcohols and their alcoholates, and we studied the reactions of the acetates and tosylates obtained with some nucleophilic reagents.

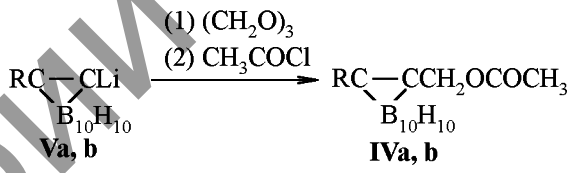
We applied as acylating reagents acetyl chloride, acetic anhydride, and acetoxyphosphoric anhydride, as tosylating agents *p*-toluenesulfonyl chloride.

The experiments showed that treatment of diol **I** with acetyl chloride and acetic anhydride afforded the target diacetate **III** in an yield no higher than 55–60%. The reaction with acetoxyphosphoric anhydride proceeded much faster and afforded the diacetate in quantitative yield.



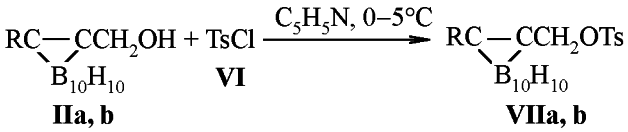
Similar results were obtained at acylation of alcohols **IIa, b.**

The successive treatment of lithium-*o*-carborane **Va, b** with dry paraformaldehyde at 60°C and then with acetyl chloride at 0–10°C provided acetates **IVa, b** in 75–80% yield.



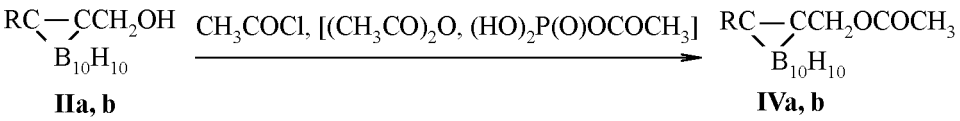
V, R = C_6H_5 (**a**), *iso*-C_3H_7 (**b**).

The reaction of *p*-toluenesulfonyl chloride (**VI**) with alcohols **IIa, b** under commonly applied conditions afforded the desired tosylates **VIIa, b** in yields no more than 45–50%.



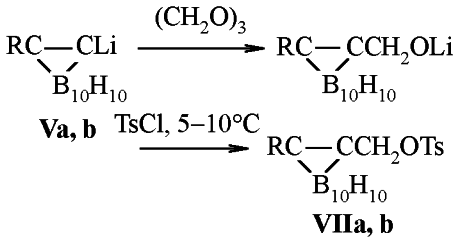
VII, R = C_6H_5 (**a**), *iso*-C_3H_7 (**b**).

At the treatment with *p*-tolyenesulfonyl chloride of lithium alcoholates of alcohols **IIa, b** the yields of tosylates **VIIa, b** amounted respectively to 95 and 83%.



II, IV, R = C_6H_5 (**a**), *iso*-C_3H_7 (**b**).

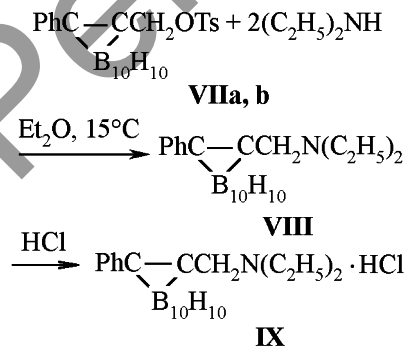
1070-4280/01/3708-1107$25.00 © 2001 MAIK "Nauka/Interperiodica"



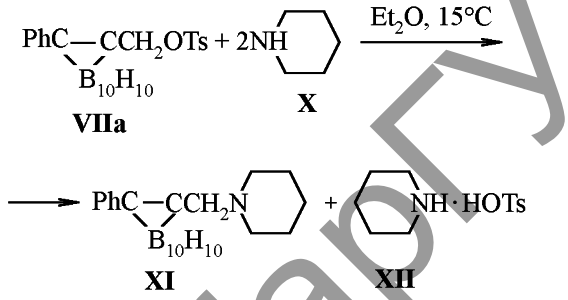
For the study of nucleophilic substitution in the acetates and tosylates obtained we selected as reagents KSCN, HCl, and amines of different basicity and nucleophilicity.

It turned out that carboranyl acetates **III** and **IVa, b** are not inclined to nucleophilic substitution: treatment with gaseous ammonia, diethylamine and piperidine in ether solution, and aqueous methylamine at moderate cooling provided complicated mixtures of products mostly originating from degradation of the carborane core, derivatives of dicarbaundecaborate. The target products formed in no more than 10% yield indicating low mobility of the acyloxy group in carboranyl acetates of **III** and **IV** type and unsuitability of these compounds for preparative syntheses.

Carboranyl tosylates **VIIa, b** are more fit to nucleophilic substitution but are sensitive to the nucleophile character. They do not give substitution products with KSCN in methanol, HCl in ether, with monoethanolamine and aniline characterized by low nucleophilicity, and reaction with excess aqueous methylamine or ammonia solution in ether at 20°C results mainly in cleavage of the carborane core to afford derivatives of dicarbaundecaborate. Yet the treatment of tosylate **VIIa** with the double excess of methylamine provided as a rule normal substitution products. The reaction of tosylate **VIIa** with a two-fold excess of diethylamine that is a stronger base than methylamine actually takes a single path and results in carboranylamine **VIII** and its hydrochloride **IX** in 85% overall yield.



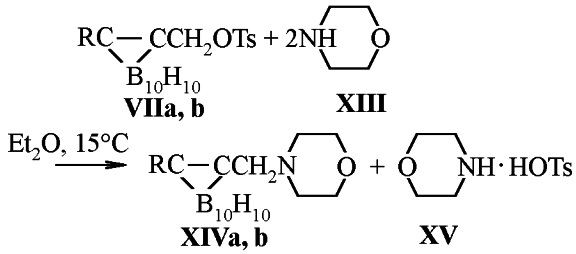
In reaction of tosylate **VIIa** with equimolar amount of piperidine (**X**) in ether also did not arise the dicarbaundecaborate derivatives; however the yield of carboranylamine **XI** did not exceed 40%. At the double excess of piperidine the yield of amine **XI** increased to 80%.



At greater excess of piperidine the yield of amine is reduced, and appear the dicarbaundecaborate derivatives.

The large difference in the amine yields at reagent ratio 1 : 1 and 1 : 2 is apparently due to considerably different rates of substitution and formation of salt **XII**.

The reactions between tosylates and less basic morpholine (**XIII**) proceed without side processes and afford the substitution products **XIVa, b** in virtually quantitative yield.



XIV, R = C_6H_5 (**a**), *iso*-C_3H_7 (**b**).

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from KBr pellets. The reactions with lithium-*o*-carboranes were carried out under nitrogen atmosphere.

1,2-Bis(acetoxymethyl)-*o*-carborane (III). (a) A mixture of 5.1 g (0.025 mol) of 1,2-bis(hydroxymethyl)-*o*-carborane (**I**) and 6.75 g (0.075 mol) of acetic anhydride was stirred for 3 h at 85°C. The excess anhydride was distilled off, the residue was recrystallized from hexane. We obtained 3.6 g (51%) of diacetate **III**, mp 145–147°C (from hexane).

(b) A mixture of 5.1 g (0.025 mol) of 1,2-bis-(hydroxymethyl)-*o*-carborane (**I**) and 10.2 g (0.075 mol) of acetoxyphosphoric anhydride was stirred for 0.5–1 h at 85°C, then was treated with ice water, and the products were extracted into ethyl ether. The extract was dried with Na_2SO_4 and evaporated. The residue was recrystallized from hexane. We obtained 6.92 g (96%) of diacetate **III**, mp 145–147°C (from hexane). IR spectrum (ν, cm^{-1}): 2600 (B–H), 1720 (C=O). Found, %: C 33.50; H 7.01; B 38.14. $C_8H_{20}B_{10}O_4$. Calculated, %: C 33.92; H 6.94; B 37.52.

2-Acetoxymethyl-1-phenyl-*o*-carborane (IVa). (a) In the same way as described above under *b* from 2.5 g (0.01 mol) of alcohol **IIa** and 3.4 g (0.025 mol) of acetoxyphosphoric anhydride we obtained 2.83 g (97%) of acetate **IVa**, bp 182–184°C (1 mm Hg). IR spectrum (ν, cm^{-1}): 2600 (B–H), 1720 (C=O). Found, %: C 44.83; H 7.21; B 36.67. $C_{11}H_{20}B_{10}O_2$. Calculated, %: C 45.21; H 6.85; B 36.99.

(b) To a benzene solution of 0.03 mol of 2-lithium-1-phenyl-*o*-carborane (**Va**) obtained from 6.6 g (0.03 mol) of phenyl-*o*-carborane and 0.036 mol of BuLi was added at 60°C 1.5 g (0.05 mol) of dry paraformaldehyde. The reaction mixture was stirred for 1 h at 60–70°C, cooled to 10°C, and 2.8 g (0.036 mol) of acetyl chloride was added. The mixture was left standing for 12 h, then it was treated with diluted HCl and extracted with ether. Extract was dried with Na_2SO_4 and evaporated. We obtained 6.7 g (76%) of acetate IVa, bp 182–184°C (1 mm Hg).

2-Tosyloxymethyl-1-phenyl-*o*-carborane (VIIa). To a benzene solution of 0.05 mol of 2-lithium-1-phenyl-*o*-carborane (**Va**) was added at 60°C 2.25 g (0.075 mol) of dry paraformaldehyde. The reaction mixture was stirred for 1 h at 60–70°C, cooled to 10°C, and 9.5 g (0.05 mol) of *p*-toluenesulfonyl chloride in benzene was added thereto. The mixture was left standing for 14 h, then treated with diluted HCl and extracted with ether.The extract was dried with $Na2SO4 and evaporated. The residue was re-crystallized. We obtained 19.2 g (95%) of tosylate **VIIa**, mp 113– 114°C (benzene–hexane). IR spectrum (ν, cm^{-1}): 2595 (B–H), 1600 (C_6H_5), 1360 and 1160 (SO_2). Found, %: C 47.92; H 6.04. $C_{16}H_{24}B_{10}O_3S$. Calculated, %: C 47.52; H 5.94.

1-Isopropyl-2-tosyloxymethyl-*o*-carborane (VIIb). Likewise from 0.05 mol of lithiumcarborane **Vb** and 0.05 mol of *p*-toluenesulfonyl chloride (**VI**) we obtained 15.4 g (83.2%) of tosylate **VIIb**, mp 76–77°C (heptane). IR spectrum (ν, cm^{-1}): 2600 (B–H), 1370 and 1170 (SO_2). Found, %: C 42.46; H 7.74. $C_{13}H_{26}B_{10}O_3S$. Calculated, %: C 42.16; H 7.02.

Treatment of tosylate VIIa with methylamine. To a solution of 1g (0.0025 mol) of tosylate **VIIa** in ether was added at room temperature 2 ml of 25% water solution of methylamine, and the mixture was left for 12 h with intermittent shaking. After treating the mixture with cold water, extraction with ether, and evaporation of solvents we obtained 0.5 g of dicarbaundecaborate derivative, mp 220–222°C. IR spectrum (ν, cm^{-1}): 2555 (B–H).

2-Diethylaminomethyl-1-phenyl-*o*-carborane hydrochloride (IX). To an ether solution of 1 g 90.0025 mol) of tosylate **VIIa** was added at room temperature while stirring 0.44 g (0.006 mol) of diethylamine. The reaction mixture was left for 12 h with intermittent shaking, the separated salt was filtered off, the ether layer was washed with cold water and dried with Na_2SO_4. Then through the ether solution was passed a flow of dry HCl gas. We obtained 0.75 g (85%) of hydrochloride **IX**, mp 185–186°C. IR spectrum (ν, cm^{-1}): 2950 (C–H), 2600 (B–H), 2500–2250 (N^+–H). Found, %: C 45.22; H 8.46; B 31.50; Cl 10.15; N 4.21. $C_{13}H_{28}B_{10}ClN$. Calculated, %: C 45.68; H 8.20; B 31.63; Cl 10.39; N 4.10.

2-Piperidinomethyl-1-phenyl-*o*-carborane (XI). (a) To an ether solution of 0.2 g (0.005 mol) of tosylate **VIIa** was added at 15°C 0.87 g (0.012 mol) of piperidine (**X**), and the mixture was kept for 15 h with intermittent shaking. The separated salt **XII** was filtered off, the ether layer was washed with cold water, dried with Na_2SO_4, and evaporated. The residue was recrystallized from hexane. We obtained 1.26 g (80%) of amine **XI**, mp 35–37°C.

(b) Likewise from 2 g (0.005 mol) of tosylate **VIIa** and 0.43 g (0.006 mol) of piperidine **X** was obtained 0.62 g (49%) of amine **XI**, mp 35–37°C. The product was identified as hydrochloride, mp 179–180°C. IR spectrum (ν, cm^{-1}): 2980, 2900 (C–H); 2600 (B–H); 2480, 2380 (N^+–H). Found, %: C 47.92; H 8.24; B 30.90. $C_{14}H_{28}B_{10}ClN$. Calculated, %: C 47.52; H 7.92; B 30.55.

2-Morpholinomethyl-1-phenyl-*o*-carborane (XIVa). Similarly to procedure *a* from 0.8 g (0.002 mol) of tosylate **VIIa** and 0.38 g (0.0044 mol) of morpholine (**XIII**) we obtained 0.55 g (87%) of amine **XIVa**, mp 124–125°C (hexane). IR spectrum (ν, cm^{-1}): 2980, 2880, 2800 (C–H); 2600 (B–H); 1250, 1150 (C–N); 1115 (C–O–C). Found, %: C 48.69; H 8.08; B 33.56; N 3.99. $C_{13}H_{25}B_{10}NO$. Calculated, %: C 48.90; H 7.84; B 33.86; N 4.39.

1-Isopropyl-2-morpholinomethyl-*o*-carborane (XIVb). Similarly from 0.74 g (0.002 mol) of tosylate **VIIb** and 0.4 g (0.005 mol) of morpholine (**XIII**) we obtained 0.5 g (87%) of amine **XIVb**, mp 92–93°C (hexane). IR spectrum (ν, cm^{-1}): 2980, 2880, 2800 (C–H); 2600 (B–H); 1250, 1150 (C–N); 1115 (C–O–C). Found, %: C 42.27; H 9.32; B 37.97; N 5.29. $C_{10}H_{27}B_{10}NO$. Calculated, %: C 42.10; H 9.47; B 37.89; N 44.91.

REFERENCES

1. Fein, M.M., Grafstein, D., Paustian, J.E., Bobinski, J., Lichstein, B.M., Mayes, N., Schwartz, N.N., and Cohen, M.S., *Inorg. Chem.*, 1963, no. 2, pp. 1115–1119.
2. Kazantsev, A.V., Meiramov, M.G., Kovredov, A.I., and Zakharkin, L.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, no. 7, pp. 1603–1605.