

Carboranyl derivatives of mercury and thallium as synthons for boron-substituted carboranes

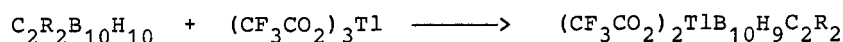
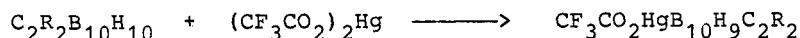
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Abstract - Carboranyl derivatives of mercury and thallium have been obtained by mercuriation and thallation of carboranes(12) in the 9 position of the carborane cage. The substitution of metal atom in boron-mercurated and boron-thallated carboranes allowed a great variety of B(9)-substituted carboranes to be prepared. The previously unknown carboran-9-yl derivatives of nontransition metals, 9-fluoro-, 9-thiocyano-, 9-trifluoroacetoxy-carboranes, bis(carboran-9-yl)diselenides and bis(carboran 9-yl)tellurides as well as the known 9-hydroxy-, 9-mercapto- and 9-iodocarboranes were synthesized. In many cases, the reactions occur under radical conditions (photolysis, pyrolysis) to give B(9)-centered radicals which undergo further transformation.

INTRODUCTION

In 1976-78 we have discovered the direct mercuriation and thallation of 1,2-, 1,7- and 1,12-dicarba-closo-dodecaboranes(12) (the trivial names are o-, m- and p-carboranes, respectively) (ref. 1,2).



The metallation of unsubstituted and C,C'- substituted o- and m-carboranes occurs mainly (85-99%) in the 9 position of the carborane nucleus (ref. 3,4), i.e. it provides the better selectivity than many other carborane substitution reactions. The metallation reaction enabled us to prepare the different types of carboranyl derivatives of mercury and thallium with Hg-B and Tl-B σ-bond. We have previously published the detailed description of the carborane metallation and the properties of boron-mercurated and boron-thallated carboranes (ref. 5,6).

The most important feature of boron-mercurated and boron-thallated carboranes is their possibility to take part in the reactions which are typical of organometallic compounds, Hg-B and Tl-B bonds acting as Hg-C and Tl-C bonds, respectively.

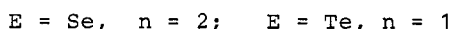
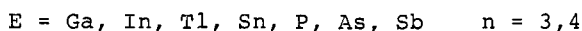
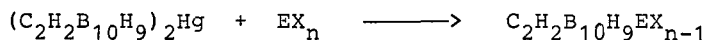
Organomercury and organothallium compounds are known to be widely used for preparation of organic (ref. 7) and organometallic compounds (ref. 8). Taking it into account we tried to use carboranyl derivatives of mercury and thallium as synthons for boron-substituted carboranes.

The high selectivity of the mercuriation and thallation of o- and m-carboranes as well as the possibility of substituting metal atom in boron-mercurated and boron-thallated carboranes allowed us to prepare a great variety of B(9)-substituted carboranes. These, for the most part, were not previously known, some of the reported compounds were not prepared selectively.

PREPARATION OF BORON-SUBSTITUTED CARBORANES

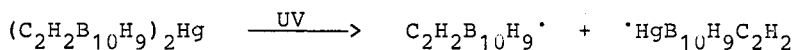
(a) From boron-carboranyl derivatives of mercury

We found that mercury in the B(9)-carboranylmercuric salts or symmetrical B(9)-carboranyl derivatives of mercury can be substituted by main groups III-V elements or non-metals of group VI to give the B(9)-carboranyl derivatives of groups III-VI elements (ref. 9).

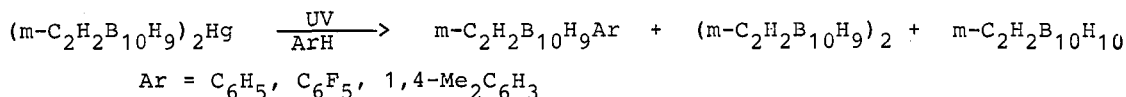


Zakharkin and Pisareva have prepared stable derivatives of carboranes with B-Pt σ -bond by the interaction of o(m)-carboran-9-yl mercury chlorides with $Pt(Ph_3P)_3$ (ref. 10).

We found that the formation of the B-carboranyl radicals occurs under the photodecomposition of bis(B-carboranyl)mercury compounds in solution. It has been proved by the EPR method for o-carboran-9-yl, m-carboran-9-yl and p-carboran-2-yl derivatives. Depending on the type of a trap used, spectra of adducts derived from either B-centered radicals with 4-methyl-2,4,6-tri-tert-butyl-cyclohexa-2,5-diene-1-one or Hg-centered radicals with 3,6-di-tert-butyl-o-benzoquinone have been recorded (ref. 11).

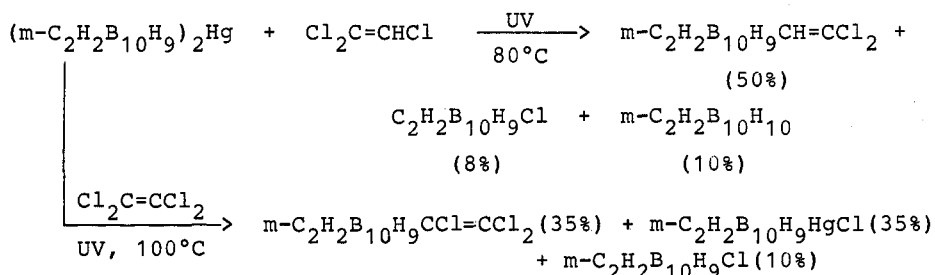


The formation of the B-centered carboranyl radicals from boron-metallated carboranes is more selective than their formation in the decomposition of tert-butyl peroxide in the presence of o-, m- and p-carboranes described previously by Tumansky, Valetsky *et al.* (ref. 12). Reactions of B-o-carboranyl radicals prepared by the peroxide method with arenes lead to the mixture of isomers containing the substituent on boron atoms in the 8(10), 9(12) and 3(6) positions of the carborane nucleus in a molar ratio 4:2:1 (ref. 13). The photodecomposition of bis(m-carboran-9-yl)mercury in the arene medium proceeds more selectively to give aryl-m-carboranes (more than 50% yield) containing mainly (90%) the substituent in the 9 position of the carborane nucleus (ref. 14). The reaction mixture also includes bis(m-carboran-9-yl) and m-carborane.

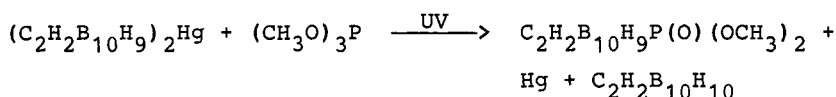


Zakharkin and Pisareva (ref. 15) have shown that the thermolysis of bis(carboran-9-yl)mercuric derivatives in sealed glass ampoules above 300°C gives mercury, carboranes, oligocarboranes and small amount of dicarboranyl which apparently are formed by recombination of the free carboranyl radicals. An increased yield of a dicarboranyl was obtained in the decomposition of bis(m-carboran-9-yl)mercury in HMPA at 100°C in the presence of the catalyst, $(Ph_3P)_3RhCl$.

The reactions of bis(m-carboran-9-yl)mercury with trichloroethylene and tetrachloroethylene are suggested to proceed via the formation of B-centered and Hg-centered radicals (ref. 16).



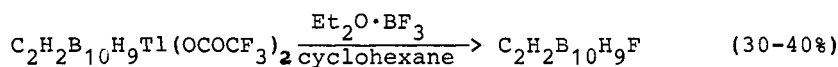
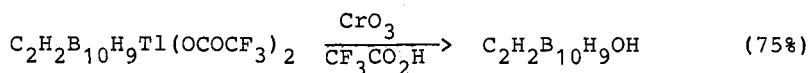
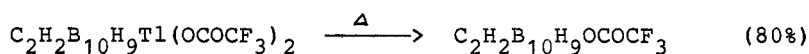
Photolysis of bis(m-carboran-9-yl)mercury and bis(p-carboran-2-yl)mercury in trimethylphosphite results in the formation of dimethyl esters of (m-carboran-9-yl)- and (p-carboran-2-yl)phosphonic acids (ref. 17).



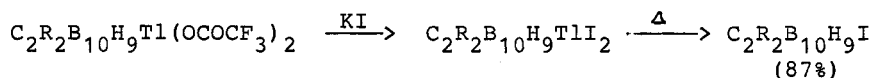
The course of the reaction is affected by the nature of the carboranyl group. The yield of the m-carborane derivative is 5% and of the p-isomer is 60% while in the case of bis(o-carboran-9-yl)mercury the phosphonate does not form. Since steric factors in o-, m- and p-carboranyl radicals are similar, the different yields were ascribed to the inductive effects of B-carboranyl groups.

(b) From boron-carboranyl derivatives of thallium

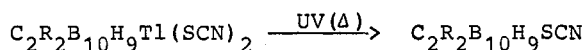
One of the most important features of organothallium compounds is their use for the selective preparation of arene derivatives. We have obtained carboranes with substituents in the 9 position of the icosahedron by substitution of thallium atom in boron-thallated carboranes (ref. 9,18).



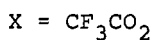
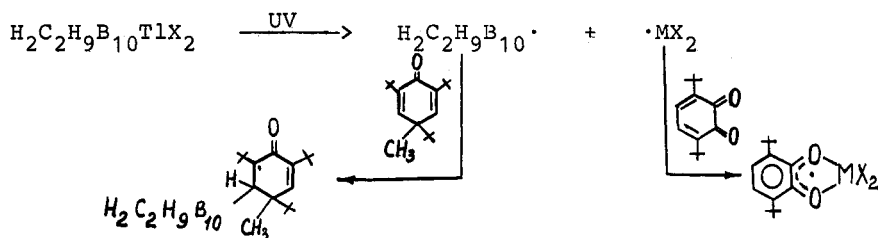
We found that contrary to the arylthallium salts which easily form aryl iodide under the action of KI boron-thallated carboranes react with KI to give stable in boiling trifluoroacetic acid or water boron-carboranylthallium diiodides. It is possible to break the B-Tl bond in these compounds by pyrolysis (ref. 18).



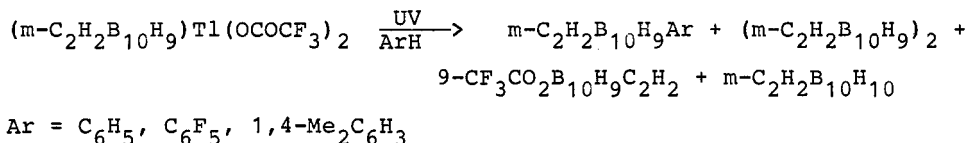
9-Thiocyano-o(m)-carboranes were synthesized under photolysis or pyrolysis of the corresponding carboranylthalliumdithiocyanates with 50-60% yield.



It has been suggested that these processes are due to the ability of the B-Tl bond to undergo homolytic decomposition. When toluene solution of (p-carboran-2-yl)thallium bis(trifluoroacetate) is photoirradiated or heated above 120°C in the presence of 3,6-di-tert-butyl-o-benzoquinone, the EPR spectra of the adduct of Tl-centered radical with o-benzoquinone indicate unambiguously homolysis of the Tl-B bond. B-centered radical does not give rise to spin adduct with o-benzoquinone. Its formation has been demonstrated in the presence of 4-methyl-2,4,6-tri-tert-butyl-cyclohexa-2,5-dien-1-one (ref. 19).



The photodecomposition of (m-carboran-9-yl)thallium bis(trifluoroacetate) in the presence of benzene, pentafluorobenzene or xylene leads to the formation of 9-aryl-m-carborane, 9-trifluoroacetoxy-m-carborane, bis(m-carboran-9-yl) and m-carborane (ref. 14).



We have also studied the possibility of carboranylation of olefins and of the formation of dicarboranyls using combinations of boron-thallated carboranes (or carboranes and thallium salts) with catalytic quantities of palladium(II) salts. (o-Carboran-9-yl)styrene, o-carborane, metallic palladium and thallium salts were identified in products of the reaction of (o-carboran-9-yl)thallium bis(trifluoroacetate) with Pd(OAc)₂ in the presence of styrene (ref. 20). The interaction of 1,2-dimethyl-o-carborane with thallium(III) trifluoroacetate in the presence of palladium(II) acetate gives bis(1,2-dimethyl-o-carboran-9-yl) in 35% yield (ref. 21).

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