Journal of Organometallic Chemistry, 292 (1985) 75–80
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THALLATION OF CARBORANES *

V.I. BREGADZE *, A.YA. USIATINSKY and N.N. GODOVIKOV

A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Vavilov St, 28, Moscow (U.S.S.R.)

(Received November 19th, 1984)

Summary

The conditions of the preparation of boron–thallated 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes(12) (trivial names "*o*-, *m*- and *p*-carboranes") have been studied. It was shown that maximum yields of the products are attained when *o*- and *m*-carboranes are treated consecutively with equimolecular amounts of mercuric oxide and then thallium(III) trifluoroacetate or thallium(III) acetate sesquihydrate. Pure trifluoroacetic acid should be used as the solvent. The presence of water in the reaction mixture and overheating of the reaction mixture lead to a decrease in the yield of boron-thallated carboranes and an increase in the content of oxidized carboranes.

Introduction

In 1978 we were successful in carrying out the direct thallation of *o*- and *m*-carboranes, which led to the preparation of boron-thallated carboranes: derivatives of carboranes with a B–Tl σ-bond [1]. The thallation of carboranes was determined to be an electrophilic reaction [2] which takes place at position 9 of the carborane polyhedron. This was later confirmed by X-ray structure determination of (1,7-dimethyl-*m*-carboran-9-yl)thallium(α,α′-dipyridyl)bis(trifluoroacetate), the first derivative of carborane with a boron-non-transition metal σ-bond characterized by X-ray analysis [3]. The important preparative consequence of the synthesis of *B*-thallated carboranes was the possibility of using them to prepare different unknown carboranes substituted at the B(9) atom with B–F [4], B–SCN [5], B–Se, B–Te [6], and B–OCOCF$_3$ [7] bonds and bis-*B(9), B′(9)*-carboranyl [8]. Since *B*-thallated carboranes are so important, it was necessary to study the conditions of the carborane thallation reaction and to find convenient preparative methods of synthesizing *B*-thallated carboranes.

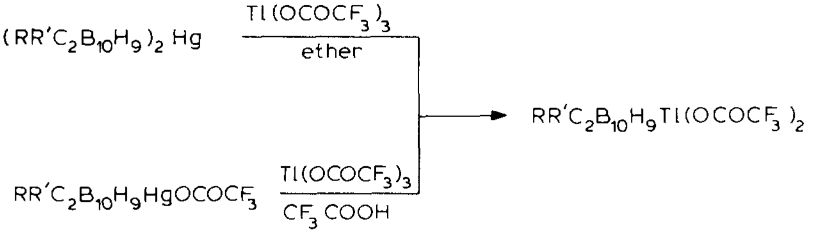
---

* Dedicated to Professor Oleg Reutov on the occasion of his 65th birthday on 5 September 1985.

0022-328X/85/$03.30

Results and discussion

We found that the direct thallation of unsubstituted *o*- and *m*-carboranes with thallium(III) trifluoroacetate in trifluoroacetic acid gives low yields (3–4%). In this reaction, satisfactory yields of thallated products were obtained only in the case of carborane activated by electron-donating substituents (see Table 1). Using *B*-mercurated carboranes as the initial compounds, we succeeded in obtaining *B*-thallated carboranes in good yields for all the carboranes studied:



$$(RR'C_2B_{10}H_9)_2Hg \xrightarrow[\text{ether}]{Tl(OCOCF_3)_3} RR'C_2B_{10}H_9Tl(OCOCF_3)_2 \xleftarrow[CF_3COOH]{Tl(OCOCF_3)_3} RR'C_2B_{10}H_9HgOCOCF_3 \qquad (1)$$

(R = R′ = H-*o*; R = R′ = H-*m*; R = R′ = H-*p*; R = Me, R′ = H-*o*; R = Ph, R′ = H-*o*; R = R′ = Me-*o*; R = R′ = Me-*m*)

However, the most convenient method of preparing *B*-thallated carboranes consists in the interaction of the initial carborane with mercuric oxide in trifluoroacetic acid, followed by treatment of the reaction mixture with thallium(III) trifluoroacetate:

$$RR'C_2B_{10}H_{10} \xrightarrow[\text{(b) Tl(OCOCF}_3)_3]{\text{(a) HgO, CF}_3\text{COOH}} RR'C_2B_{10}H_9Tl(OCOCF_3)_2 \qquad (2)$$

(R = R′ = H-*o*; R = R′ = H-*m*; R = R′ = H-*p*; R = Me, R′ = H-*o*; R = Ph, R′ = H-*o*; R = R′ = Me-*o*; R = R′ = Me-*m*)

Actually, this "one-pot" reaction combines two processes: the mercuration of carboranes according to ref. 9, and the transfer of the carboranyl group from the mercury atom to the thallium atom, as presented in eq. 1. However, in contrast to reaction a in eq. 2, this procedure allows the stage of isolation and purification of the intermediate *B*-mercurated carborane compound to be avoided without significant influence on the yields of the final products (see Table 1). *B*-Thallated carboranes prepared by procedure 2 precipitate from the reaction mixture and their purification is not practically required.

The yields of *B*-thallated carborane products increase to a certain degree in the presence of a catalytic amount of HgO in the reaction mixture containing thallium(III) trifluoroacetate, trifluoroacetic acid and carborane. For example, treatment of *o*-carborane with $Tl(OCOCF_3)_3$ in the presence of HgO (10 mol. %) leads to (*o*-carboran-9-yl)thallium bis(trifluoroacetate) in 18% yield instead of the 4% yield obtained in the case of direct thallation of *o*-carborane.

However, it is better to use equimolecular amounts of HgO rather than catalytic amounts since the yields of *B*-thallated carboranes are then much higher.

It was shown [10] that the rate constants of the thallation of aromatic substrates with thallium(III) acetate sesquihydrate ($Tl(OCOCH_3)_3 \cdot 1.5H_2O$) do not differ from these of the thallation of the same substrates with thallium(III) trifluoroacetate in

TABLE 1

(*B*-CARBORANYL)THALLIUM BIS(TRIFLUOROACETATES) $RR'C_2B_{10}H_9Tl(OCOCF_3)_2$

R	R′	Yield [a]				M.p. (°C)	Analysis (Found (calcd.) (%))				
		A	B	C	D		C	H	B	F	Tl
H	H-o	4	60	65	58	199-200	12.4 (12.6)	2.0 (1.9)	18.8 (18.8)	19.5 (19.9)	35.6 (35.6)
H	H-m	3	70	65	55	205-206	12.6 (12.6)	2.0 (1.9)	19.0 (18.8)	20.3 (19.9)	-
H	C_6H_5-o	5	70	70	-	160	22.0 (22.2)	2.4 (2.4)	16.8 (16.7)	16.6 (17.6)	31.8 (31.4)
H	CH_3-o	46	70	70	-	200	14.4 (14.2)	2.3 (2.1)	18.6 (18.6)	18.9 (19.3)	34.8 (34.9)
CH_3	CH_3-o	50	80	75	60	201	15.9 (15.9)	2.8 (2.5)	17.5 (17.3)	18.4 (18.9)	33.1 (34.0)
CH_3	CH_3-m	48	65	70	55	199	15.6 (15.9)	2.4 (2.5)	17.7 (17.3)	19.2 (18.9)	33.5 (34.0)
H	H-p	-	45	40	-	193	12.4 (12.6)	1.7 (1.9)	18.2 (18.8)	19.6 (19.9)	

[a] A: Yield of product prepared by direct thallation of carboranes. B: Yield of product prepared by interaction of $RR'C_2B_{10}H_9HgOCOCF_3$ with $Tl(OCOCF_3)_3$. C: Yield of product prepared by action of $Tl(OCOCF_3)_3$ on the reaction mixture containing the carboranylmercury intermediate. D: Yield of product prepared by action of $Tl(OCOCH_3)_3 \cdot 1.5\ H_2O$ on the reaction mixture containing the carboranylmercury intermediate.

trifluoroacetic acid. We found that thallation had taken place under treatment of dimethyl-*o*-carborane with thallium(III) acetate sesquihydrate in trifluoroacetic acid, but the yield of thallated product was essentially lower than that of the same product when thallium(III) trifluoroacetate in trifluoroacetic acid was used. In addition, considerable amounts of the product of carborane nucleus B–H bond oxidation, 9-oxycarborane, and unreacted dimethyl-*o*-carborane were found in the reaction mixture:

$$(CH_3)_2\text{-}o\text{-}C_2B_{10}H_{10} \xrightarrow[CF_3COOH]{Tl(OCOCH_3)_3\cdot 1.5H_2O} (CH_3)_2\text{-}o\text{-}C_2B_{10}H_9OH\ (20\%)$$
$$+ (CH_3)_2\text{-}o\text{-}C_2B_{10}H_9Tl(OCOCF_3)_2\ (8.5\%)$$

However, $Tl(OCOCH_3)_3 \cdot 1.5H_2O$ is a convenient thallating agent in the method of carborane thallation with equimolecular amounts of HgO. Sesquihydrate is even more convenient than trifluoroacetate in this method since it is readily prepared from Tl_2O_3 and aqueous acetic acid. There is practically no difference in the yield of *B*-thallated carboranes when thallium(III) acetate sesquihydrate is used instead of trifluoroacetate in this method:

$$R_2C_2B_{10}H_{10} \xrightarrow[(b)\ Tl(OCOCH_3)_3\cdot 1.5H_2O]{(a)\ HgO,\ CF_3COOH} R_2C_2B_{10}H_9Tl(OCOCF_3)_2$$

(R = H-*o*, H-*m*, Me-*o*, Me-*m*)

An attempt to thallate π-cyclopentadienyl-π-(3)-1,2-dicarbollyl complexes of iron(III) and cobalt(III) resulted in oxidation of the B–H bond at position 8 of the dicarbollyl ligand [11]. Unlike thallation of dicarbollyl ligands, the thallation of *closo*-carboranes results mainly in Tl–B bond formation. In our opinion, the oxidation of the B–H bond at position 9 of the carborane polyhedron is a side process. Thus, the reaction of 1,2-dimethyl-*o*-carborane with thallium(III) trifluoroacetate in trifluoroacetic acid for 12 h produces (1,2-dimethyl-*o*-carboran-9-yl)thallium bis(trifluoroacetate) as the main product (50%) *. The yield of 1,2-dimethyl-9-oxycarborane is only 7.4% in this reaction.

The presence of 9-oxycarborane in the reaction mixture, obtained by treatment of 1,2-dimethyl-*o*-carborane with thallium(III) acetate sesquihydrate in trifluoroacetic acid, allows us to suggest that the reason for B–H bond oxidation is the presence of a trace amount of water in the reaction mixture. Indeed, treatment of 1,2-dimethyl-*o*-carborane with thallium(III) trifluoroacetate in trifluoroacetic acid with water (10/1) resulted in inhibition of the thallation reaction and formation of oxidation products: boric acid and 1,2-dimethyl-9-oxy-*o*-carborane (40% yield). The presence of water probably increases the boiling point of the reaction mixture, which facilitates oxidation of the carborane nucleus B–H bond.

Experimental

1-Phenyl-*o*-carborane was purified by recrystallization from hexane. Other carboranes were purified by sublimation in vacuum. Trifluoroacetic acid was puri-

---

* The use of excess thallium(III) trifluoroacetate and GLC controls enables us to obtain higher yields of *B*-thallated products, but this method is not convenient. *B*-Trifluoroacetoxycarborane was found to be present in the reaction mixture too [2].

fied by shaking it with H_2SO_4, followed by distillation. Thallium(III) acetate sesquihydrate was obtained according to ref. 10.

Thallium(III) trifluoroacetate

20 g of Tl_2O_3 was dissolved in 100 ml of CF_3COOH, then the solution was evaporated. The solid residue was recrystallized from CF_3COOH.

A common method of the direct thallation of carboranes

Carborane (0.02 mol) was added to a solution of 10.8 g (0.02 mol) of $Tl(OCOCF_3)_3$ in 75 ml of CF_3COOH. The reaction mixture was stirred at 70°C for 15 h. After cooling, the precipitate obtained was filtered, washed with ether, and recrystallized from CF_3COOH. Yields and physical data of the *B*-thallated carboranes are listed in Table 1.

Preparation of B-thallated carboranes using HgO

(a) Carborane (0.05 mol) was added to a solution of 10.8 g (0.05 mol) of mercuric oxide in 150 ml of CF_3COOH *. The reaction mixture was stirred at 20°C until a homogeneous solution was formed. Then 27.2 g (0.05 mol) of $Tl(OCOCF_3)_3$ was added and the reaction mixture was boiled for 5 h. After cooling, the precipitate was filtered. The filtrate was evaporated to half its volume and after cooling a new portion of precipitate was obtained. Both portions of precipitates were combined, washed with ether, and dried over KOH.

(b) Carboranylthallium bis(trifluoroacetates) were obtained similarly using $Tl(OCOCH_3)_3 \cdot 1.5H_2O$ instead of $Tl(OCOCF_3)_3$. The reaction mixture was boiled for 10 h. Yields and physical data of the *B*-thallated carboranes are given in Table 1.

Thallation of o-carborane in the presence of catalytic amounts of HgO

To a solution of 10.8 g (0.02 mol) of $Tl(OCOCF_3)_3$ in 75 ml of CF_3COOH was added 0.4 g (0.002 mol) of HgO and then 2.9 g (0.02 mol) of *o*-carborane and the reaction mixture was boiled, under stirring, for 15 h. After the mixture had been cooled, the precipitate was filtered, washed with ether, and dried over KOH. 2.1 g (18%) of (*o*-carboran-9-yl)thalliumbis(trifluoroacetate) was obtained. The filtrate was poured into water and extracted with ether. 2.0 g of unreacted *o*-carborane was isolated from the extract.

Thallation of 1,2-dimethyl-o-carborane

(a) To a solution of 4.7 g (0.01 mol) of $Tl(OCOCH_3)_3 \cdot 1.5H_2O$ in 50 ml of CF_3COOH was added 1.7 g (0.01 mol) of 1,2-dimethyl-*o*-carborane and the reaction mixture was stirred under boiling for 20 h. After the mixture had been cooled, the precipitate was filtered, washed with ether, and dried to give 0.5 g (8.5%) of (1,2-dimethyl-*o*-carboran-9-yl)thalliumbis(trifluoroacetate). The filtrate was poured into water and extracted with ether. The ether extract was evaporated and the residue was recrystallized from a benzene/hexane mixture to give 0.38 g (20%) of 1,2-dimethyl-9-oxy-*o*-carborane, m.p. 287–288°C. Found: C, 25.2; H, 8.3; B, 57.2. $C_4H_{16}B_{10}O$ calcd.: C, 25.5; H, 8.5; B, 57.4% 1.2 g of unreacted 1,2-dimethyl-*o*-

---

* In the case of *p*-carborane, it is necessary to boil the solution.

carborane was isolated from the benzene/hexane filtrate by column chromatography on silica gel.

(b) To a solution of 10.8 g (0.02 mol) of $Tl(OCOCF_3)_3$ in 75 ml of CF_3COOH was added 3.4 g (0.02 mol) of 1,2-dimethyl-*o*-carborane and the reaction mixture was boiled, under vigorous stirring, for 15 h. After the mixture had been cooled, the precipitate was filtered, washed with ether, and dried to give 6.1 g (50%) of (1,2-dimethyl-*o*-carboran-9-yl)thallium bis(trifluoroacetate). The filtrate was poured into water and extracted with ether. The ether extract was washed with Na_2CO_3 and water, and then evaporated. The residue was recrystallized from benzene/hexane to give 0.28 g (7.4%) of 1,2-dimethyl-9-oxy-*o*-carborane, m.p. 287–288°C. 0.5 g of unreacted 1,2-dimethyl-*o*-carborane was isolated from the benzene/hexane filtrate by column chromatography.

Oxidation of 1,2-dimethyl-o-carborane

1.7 g (0.01 mol) of 1,2-dimethyl-*o*-carborane was added to a solution of 5.5 g of $Tl(OCOCF_3)_3$ in aqueous trifluoroacetic acid (90 ml of CF_3COOH and 10 ml of H_2O). The reaction mixture was boiled under vigorous stirring for 20 h and evaporated to one third of its volume. The precipitate was filtered and washed with ether. The insoluble residue (0.2 g), was boric acid (m.p. 184°C). The filtrate was poured into water and extracted with ether. Both protions of ether solution were combined, washed with Na_2CO_3 and water, and then evaporated. The residue was recrystallized from a benzene/hexane mixture to give 0.75 g (40%) of 1,2-dimethyl-9-oxy-*o*-carborane, m.p. 287–288°C. 0.65 g of unreacted 1,2-dimethyl-*o*-carborane was isolated from the benzene/hexane filtrate by column chromatography.

References

1 V.I. Bregadze, V.Ts. Kampel, A.Ya. Usiatinsky and N.N. Godovikov, J. Organomet. Chem., 154 (1978) C1.

2 A.Ya. Usiatinsky, V.I. Bregadze, T.M. Shcherbina and N.N. Godivikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1428.

3 A.I. Yanovsky, M.Yu. Antipin, Yu.T. Struchkov, V.I. Bregadze, A.Ya. Usiatinsky and N.N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 293.

4 V.I. Bregadze, A.Ya. Usiatinsky and N.N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2836.

5 V.I. Bregadze, A.Ya. Usiatinsky and N.N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 398.

6 V.I. Bregadze, V.Ts. Kampel, A.Ya. Usiatinsky, O.B. Ponomareva and N.N. Godovikov, J. Organomet. Chem., 233 (1982) C33.

7 V.I. Bregadze, A. Ya. Usiatinsky and N.N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 1876.

8 A.Ya. Usiatinsky, A.D. Ryabov, T.M. Shcherbina, V.I. Bregadze and N.N. Godovikov, Izv. Akad. Nauk SSSR, Ser., Khim., (1983) 1637.

9 V.I. Bregadze, V.Ts. Kampel and N.N. Godovikov, J. Organomet. Chem., 112 (1976) 249.

10 S.E.Al-Azzawi and R.M.G. Roberts, J. Chem. Soc., Perkin Trans. 2, (1982) 677.

11 L.I. Zakharkin, V.V. Kobak, A.I. Kovredov, N.G. Furmanova and Yu.T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 1097.