

THE ACTION OF LITHIUM ALUMINIUM HYDRIDE AND SODIUM BOROHYDRIDE ON C-METHYL-C'-FLUOROALKENYL-*o*- AND -*m*-CARBORANES

L. I. ZAKHARKIN AND V. N. LEBEDEV

Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

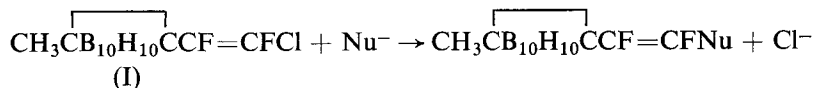
(Received July 19, 1972)

SUMMARY

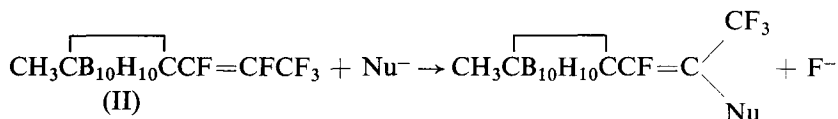
1-Methyl-2-(fluoroalkenyl)-*o*-carboranes react easily with LiAlH_4 and NaBH_4 in protic and aprotic media to give mixtures of 1-methyl-2-(hydrofluoroalkenyl)-*o*-carboranes. It has been shown that the reaction is not stereospecific in the case of *trans*-1-methyl-2-(α,β -difluoro- β -chlorovinyl)-*o*-carborane (I) but is stereospecific for *trans*-1-methyl-2-(α,β -difluoro- β -trifluoromethylvinyl)-*o*-carborane. The reaction of 1-methyl-7-(trifluorovinyl)-*m*-carborane with LiAlH_4 has been shown to be more selective giving 1-methyl-7-(α,β -difluorovinyl)-*m*-carborane. C-Methyl-C'-(α,β -difluorovinyl)-*o*- and -*m*-carboranes may be metallated with butyl-lithium to give C-methyl-C'-(α,β -difluoro- β -vinyl-lithium)-*o*- and -*m*-carboranes. A lithium derivative can also be obtained from 1-methyl-2-(α,β -difluoro- β -chloro)-*o*-carborane and butyl-lithium *via* chlorine-lithium exchange. The lithium derivatives are useful synthetic intermediates since the metal can be replaced by a variety of reagents.

INTRODUCTION

Vinylic halogen is usually inert towards nucleophilic substitution but reaction takes place when the olefin is activated by an electron-attractive group. We have shown earlier^{1,2} that fluoro-olefins of the type $\text{RCF}=\text{CFX}$ (where $\text{X} = \text{Cl}$ or CF_3 , and R is the 1-methyl-*o*-carboranyl group* exhibiting a strong inductive electron-attractive effect³) may readily enter nucleophilic substitution reactions:



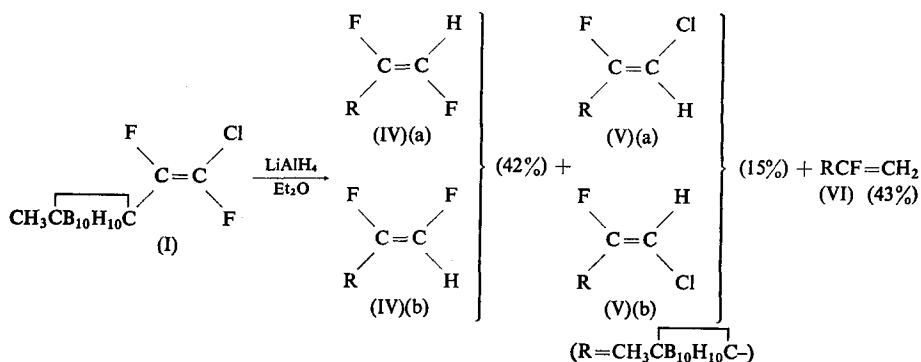
* *o*-Carborane = 1,2-dicarba-closo-dodecaborane(12).



where Nu^- is the nucleophilic reagent. Alcoholates, mercaptides and phenyllithium have been investigated as nucleophilic agents. Thus it was found that nucleophilic substitution of the halogen in compounds (I) and (II) occurs with more or less complete retention of configuration, the stereospecificity of the reaction depending partially upon the nature of the nucleophile. Thus *trans*-(I) on reacting with $\text{C}_2\text{H}_5\text{O}^-$ gives 90% of *trans*- and 10% of *cis*-vinyl ether whilst with $n\text{-C}_4\text{H}_9\text{S}^-$ it produces only *trans*-thioether. Recently, Burton and Krutzsch have shown⁴ that in reactions of chloro-olefins of the type $\text{ArC}(\text{R}_1)=\text{CFCl}$ with CH_3O^- , chlorine substitution by the CH_3O^- group is also highly stereospecific.

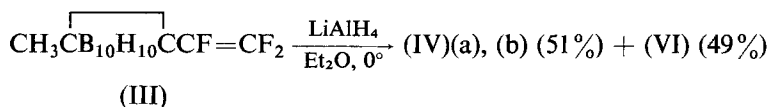
As a continuation of our earlier investigations, we report here on the action of such nucleophilic agents as lithium aluminium hydride and sodium borohydride upon (I), (II), 1-methyl-2-(trifluorovinyl)-*o*-carborane (III) and 1-methyl-7-(trifluorovinyl)-*m*-carborane (VII)*. As has been shown previously⁵⁻⁸, these complex hydrides react with acyclic fluoro-olefins, readily substituting the vinylic halogen by hydrogen. However, Burton *et al.*¹⁰ have found that in protic media the reaction with NaBH_4 leads to hydrogenation of the double bond.

Unlike the nucleophilic agents investigated earlier^{1,2}, the reaction of *trans*-(I) with LiAlH_4 and NaBH_4 is not specific; in addition to the substitution of chlorine by hydrogen, substitution of β -fluorine by hydrogen also occurs, and the reactions may proceed further, leading to replacement of both terminal halogens by hydrogen. Thus the reaction of LiAlH_4 in ether solution with *trans*-(I) at 0° gives a mixture consisting of 42% of *cis/trans*-1-methyl-(α,β -difluorovinyl)-*o*-carborane (IV), 15% of *cis/trans*-1-methyl-2-(α -fluoro- β -chlorovinyl)-*o*-carborane (V) and 43% of 1-methyl-2-(α -fluorovinyl)-*o*-carborane (VI):

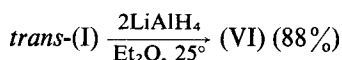


* *m*-Carborane = 1,7-dicarba-closo-dodecaborane(12).

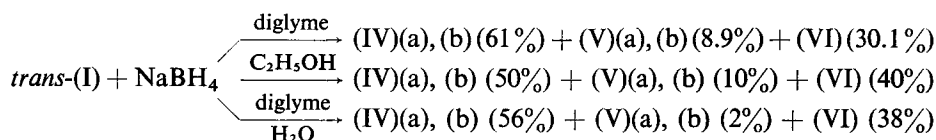
1-Methyl-2-(trifluorovinyl)-*o*-carborane (III) reacts with LiAlH_4 to give a similar mixture of hydrofluoroalkenyl-*o*-carboranes:



When *trans*-(I) and (III) react with an excess of LiAlH_4 , only (VI) is produced in high yield:



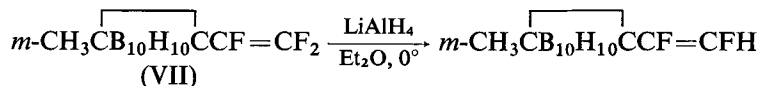
The reduction of *trans*-(I) with sodium borohydride in diglyme, ethanol or diglyme-water leads to the formation of a mixture of hydrofluoroalkenyl-*o*-carboranes according to the scheme



From the data presented, it can be seen that the action of NaBH_4 on *trans*-(I) in both the aprotic and protic media leads to the same results.

On reaction with NaBH_4 in ethanol, compound (III) forms a mixture consisting of (IV)(a), (b) (65%) and (VI) (35%). From a comparison of the reactions of LiAlH_4 and NaBH_4 with *trans*-(I), it follows that the latter hydride is a weaker nucleophile with respect to LiAlH_4 .

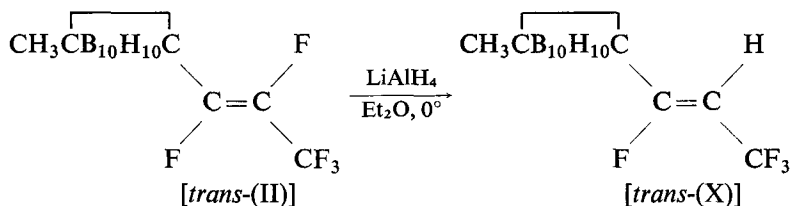
Unlike compound (III), the action of LiAlH_4 on 1-methyl-7-(trifluorovinyl)-*m*-carborane (VII) is more specific and results only in the substitution of one fluorine atom by hydrogen:



The resulting product corresponds to a 65% yield of *cis*-(IX)(a) and *trans*-(IX)(b) in a 1:1 ratio.

As is evident from the results obtained, the monohydrofluoroalkenyl derivatives (IV)(a), (b) and (IX)(a), (b), differing only in the structure of the carborane nucleus, display different reactivities towards LiAlH_4 . We assume that such a difference is generally due⁹ to the considerable $-\text{I}$ effect of *o*-carborane relative to *m*-carborane which results in a greater double-bond activation in (IV)(a), (b) than in (IX)(a), (b).

1-Methyl-2-(α,β -difluoro- β -trifluoromethylvinyl)-*o*-carborane [*trans*-(II)] in the presence of LiAlH_4 substitutes the fluorine in the β position for hydrogen. The reaction involves a complete retention of configuration:



The stereochemical results of the reactions of *trans*-(I) with NaBH_4 and LiAlH_4 , shown in Table 1, are rather interesting. For comparison, this table also

TABLE 1

THE STEREOCHEMICAL RESULTS OF THE REACTION OF 1-METHYL-2-(FLUOROALKENYL)-*o*-CARBORANES WITH VARIOUS NUCLEOPHILIC REAGENTS

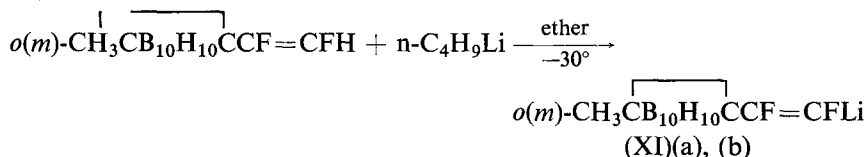
Carborane	Ratio of <i>cis/trans</i> substitution product	Nucleophile	Solvent
<i>Trans</i> - $\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CFCl}$	10/90	NaOC_2H_5	ethanol
<i>Trans</i> - $\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CFCl}$	0/100	NaSC_4H_9	ethanol
<i>Trans</i> - $\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CFCl}$	0/100	$\text{C}_6\text{H}_5\text{Li}$	ether
<i>Trans</i> - $\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CFCl}$	50/50	LiAlH_4	ether
<i>Trans</i> - $\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CFCl}$	74/26	NaBH_4	diglyme-water
<i>Trans</i> - $\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CFCl}$	70/30	NaBH_4	ethanol
<i>Trans</i> - $\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CFCl}$	76/24	NaBH_4	diglyme
$\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CF}_2$	50/50	LiAlH_4	ether
$\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CF}_2$	75/25	NaBH_4	ethanol
<i>m</i> - $\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{CCF}=\text{CF}_2$	52/48	LiAlH_4	ether

lists the data obtained previously on the stereochemistry of the reactions of *trans*-(I) with $\text{C}_2\text{H}_5\text{ONa}$, $n\text{-C}_4\text{H}_9\text{SNa}$ and $\text{C}_6\text{H}_5\text{Li}$. As seen from the table, the stereochemistry of the reactions of *trans*-(I) with LiAlH_4 and in particular with NaBH_4 differs considerably from that of the reactions of *trans*-(I) with $\text{C}_2\text{H}_5\text{ONa}$, $n\text{-C}_4\text{H}_9\text{SNa}$ and $\text{C}_6\text{H}_5\text{Li}$. The reactions with the latter nucleophiles occur with a higher stereospecificity towards retention of configuration. The reaction of *trans*-(I) with LiAlH_4 is non-stereospecific as it leads to the mixture of *cis/trans*-(IV) (1:1), while the reaction of *trans*-(I) with NaBH_4 involves an even greater inversion of

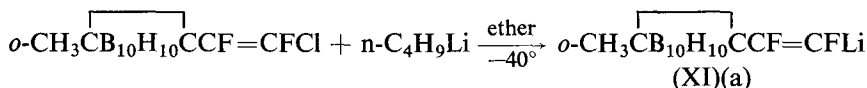
configuration, giving mixtures consisting of 70–76% of the *cis* isomer of (IV) and 24–30% of the *trans* isomer of (IV).

The nature and the stereochemistry of the reaction products indicate the formation of an intermediate carbanion resulting from the attack of the nucleophile at the double bond. The stereochemistry of the reaction of fluoroalkenyl-*o*- and -*m*-carboranes with LiAlH₄ and NaBH₄ appears to be defined mainly by a thermodynamic factor. Apparently the introduction of the hydrogen atom as a substituent decreases the rate of elimination of the halogen ion relative to such substituents as OR and SR, and this leads to an increase in the lifetime of the intermediate carbanion. This lifetime is quite sufficient to enable a change in the configuration in the carbanion to occur through rotation about the carbon–carbon bond.

We have found that the hydrogen atoms of the difluorovinyl groups in (IV)(a), (b) and (IX)(a), (b) are quite acidic so that under the action of butyllithium they are readily substituted by lithium, in a similar manner¹¹ to trifluoroethylene:

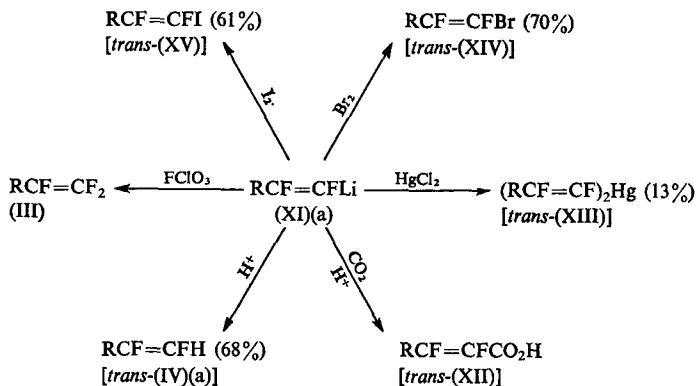


That 1-methyl-2-(α,β -difluoro- β -chlorovinyl)-*o*-carborane (I) enters an exchange reaction with *n*-C₄H₉Li, giving rise to the same 1-methyl-2-(α,β -difluoro-lithium vinyl)-*o*-carborane, was unexpected, however:



Such an exchange has not been observed previously in this fluoro-olefin series.

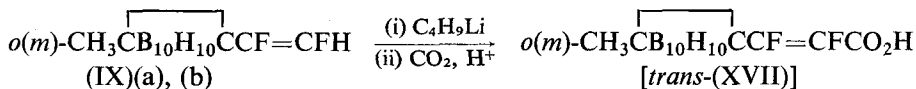
The following transformations of the lithio compound (XI)(a) to the respective derivatives have also been carried out:



where R = $\overline{\text{CH}_3\text{CB}_{10}\text{H}_{10}\text{C}}$ - in (XI)(a).

Products with the *trans* configuration were always formed from metallation of (IV)(a) and (b) with $n\text{-C}_4\text{H}_9\text{Li}$, or in the exchange of $n\text{-C}_4\text{H}_9\text{Li}$ with a mixture of *cis/trans*-(I), followed by the subsequent action of the above mentioned reagents. We assume that this is due to the fact that, under the reaction conditions, *trans*-(XI)(a) is stable while *cis*-(XI)(a) is unstable and decomposes. For this reason, products with the *trans* configuration are generated.

From the reaction of (IX)(a) and (b) with $n\text{-C}_4\text{H}_9\text{Li}$, after subsequent carbonation, *trans*- β -(1-methyl-*m*-carboranyl)- α,β -difluoroacrylic acid was isolated:



The formation of *trans*-(XVII) from the mixture of *cis/trans*-(IX)(a), (b) may be explained in the same fashion as in the case of the *o*-carborane compounds.

The structures of the compounds obtained were confirmed by IR and ¹⁹F NMR spectroscopic data (Table 2), the ratio of *cis* and *trans* isomers being determined from the basis of Andreades work¹⁴. The *cis*- and *trans*-(H-F) coupling constants obtained are in a good agreement with the data reported earlier^{12,13} for fluoro-olefins.

TABLE 2

THE ¹⁹F CHEMICAL SHIFTS* AND COUPLING CONSTANTS OF *trans*-C-METHYL-C'-
(β -SUBSTITUTED)FLUOROALKENYL-*o*- AND -*m*-CARBORANES

Compound	X	Y	Chemical shift (ppm)			Coupling constants (Hz)		
			δ_1	δ_2	δ_3	$J(1,2)$	$J(1,3)$	$J(2,3)$
(IV)(a)	F	H	65.0	72.0	—	138.0	3.0	68.0
(IV)(b)	H	F	43.0	—	67.0	14.5	6.5	68.0
(V)(a)	H	Cl	15.5	—	—	21.0	—	—
(V)(b)	Cl	H	11.6	—	—	—	2.0	—
(VI)	H	H	7.6	—	—	45.0	13.5	—
(IX)(a) [†]	F	H	65.6	89.6	—	135.0	2.0	72.0
(IX)(b) [†]	H	F	43.5	—	78.3	16.1	7.3	72.0
(X)	H	CF ₃	2.2	—	-19.8	32.2	17.0	2.3
(XII)	F	CO ₂ H	37.0	65.0	—	137.0	—	—
(XIII)	F	Hg	46.5	53.2	—	118.0	—	—
(XIV)	F	Br	21.4	42.5	—	145.0	—	—
(XV)	F	I	39.0	52.0	—	146.0	—	—
(XVI)	F	F	79.0	25.4	10.5	103.0	38.6	45.0
(XVII)	F	CO ₂	52.3	75.0	—	135.0	—	—

* The ¹⁹F chemical shifts were measured relative to CF₃COOH as an external standard.

[†] *m*-CH₃CB₁₀H₁₀C-

EXPERIMENTAL

The ^{19}F NMR spectra were measured on a Hitachi H-60 instrument at 56.4 MHz. The composition and ratio of the products formed in the reactions of C-methyl-C'-(fluoroalkenyl)-*o*- and -*m*-carboranes with LiAlH_4 and NaBH_4 were determined by GLC using a Tsvet 3 instrument, employing a column of length 3 m, packed with SE 301 and maintained at a temperature of 200° .

*Reactions of trans-1-methyl-2-(α,β -difluoro- β -chlorovinyl)-*o*-carborane (I) and 1-methyl-2-(trifluorovinyl)-*o*-carborane (III) with LiAlH_4*

(a) A solution consisting of 5.5 g of *trans*-(I) in 10 ml of absolute ether was gradually added dropwise with stirring at 0° under argon to a solution consisting of 0.82 g of LiAlH_4 in 60 ml of absolute ether. The mixture was kept for 1 h at this temperature and then decomposed by the addition of dilute hydrochloric acid. The ethereal layer was separated and dried over CaCl_2 . After removal of the ether, the residue was sublimed at $100^\circ/0.1$ mmHg to produce 4.1 g (86%) of a white crystalline substance which was a mixture of (IV)(a), (b) (42%), (V)(a), (b) (15%) and (VI) (43%). According to the ^{19}F NMR data, the mixtures of compounds (IV)(a), (b) and (V)(a), (b) each contained the *cis* and *trans* isomers in a 1:1 ratio. Compounds (IV)(a) and (VI) were identified by GLC and (IV)(b) and (V)(a), (b) by ^{19}F NMR spectroscopy (Table 2).

(b) Using the same procedure as that described in (a), the 1-methyl-2-trifluorovinyl compound (III) (1 g) gave a mixture of (IV)(a), (b) (51%) and (VI) (49%).

(c) A solution consisting of 1 g of LiAlH_4 in 20 ml of absolute ether was mixed with 1 g of (I) in 10 ml of absolute ether at 0° . The mixture was heated slowly for 1 h up to 25° and kept at this temperature for 10 h. After standard treatment (see previous run), sublimation of the reaction mixture at $80^\circ/0.1$ mmHg gave 0.7 (88%) of 1-methyl-2-(α -fluorovinyl)-*o*-carborane (VI) (nc), m.p. $124\text{--}125^\circ$ (from hexane). Analysis: Found: C, 29.56; H, 7.86; F, 9.16%. $\text{C}_5\text{H}_{15}\text{B}_{10}\text{F}$ requires C, 29.65; H, 7.43; F, 9.41%.

(d) In a similar manner to run (c), 0.5 g of compound (III) and 0.5 g of LiAlH_4 led to the formation of 0.3 g of (VI) (74%).

Reaction of trans-(I) with NaBH_4

(a) In diglyme solution

A solution consisting of 1.06 g of NaBH_4 in 20 ml of diglyme was added with stirring at 0° to a solution consisting of 7 g of *trans*-(I) in 10 ml of diglyme (distilled over LiAlH_4). The mixture was kept at 0° for 5 h when it was decomposed with dilute hydrochloric acid. The organic layer was separated and mixed with 50 ml of hexane. The hexane solution was washed with water until removal of diglyme was complete and then dried over P_2O_5 . The hexane was evaporated and sublimation of the residue gave 5 g (83%) of a mixture of (IV)(a), (b) (61%), (V)(a), (b) (9.0%) and (VI) (30.0%).

(b) In aqueous diglyme

In a similar manner to the previous run, 2 g of *trans*-(I) dissolved in a mixture of 5 ml of water, 10 ml of diglyme and 0.3 g of NaBH₄ led to the formation of a mixture of (IV)(a), (b) (56%), (V)(a), (b) (2%), (VI) (38%) and 4% of an unidentified product.

(c) In ethanol solution

A mixture consisting of 5.9 g of *trans*-(I) in 10 ml of ethanol and 0.84 g of NaBH₄ in 40 ml of ethanol was stored for 10 h. The reaction mixture was worked up in a similar manner to the previous run when 3 g (63%) of the following mixture was obtained: (IV)(a), (b) (50%), (V)(a), (b) (40%) and (VI) (40%). No product resulting from hydrogen addition to the double bond was apparently formed.

Trans-1-methyl-2-(α,β-difluorovinyl)-o-carborane (IV)(a)

A solution consisting of 7 ml of 1.54 mol l⁻¹ C₄H₉Li in benzene was added at -30° to a solution of 2.54 g of (I) in 10 ml of ether. After 5 min, the mixture was treated with 10 ml of HCl. The organic layer was separated and dried over CaCl₂. The solvents were removed *in vacuo*, the residue sublimed at 80°/0.1 mmHg when 1.5 g (68%) of *trans*-(IV)(a), (nc), was obtained, m.p. 83–84° (ethanol–water, 4:1). Analysis: Found: C, 27.35; H, 6.37; F, 16.91%. C₅H₁₄B₁₀F₂ requires C, 27.17; H, 6.36; F, 17.20%.

Cis/trans-1-methyl-7-(α,β-difluorovinyl)-m-carborane (IX)(a), (b)

A solution consisting of 2 g of (VII) in 5 ml of absolute ether was added to a solution of 0.38 g of LiAlH₄ in 10 ml of absolute ether. The mixture was stirred at 25° for 0.5 h then decomposed with dilute hydrochloric acid. Distillation *in vacuo* gave 1.2 g (65%) of (IX)(a), (b), (nc), b.p. 43–51°/0.1 mmHg. Analysis: Found: F, 16.86%. C₅H₁₄B₁₀F₂ requires F, 17.20%.

Trans-1-methyl-2-(α-fluoro-β-trifluoromethylvinyl)-o-carborane (X)

A solution consisting of 6.2 g of (II) in 15 ml of absolute ether was gradually added dropwise with stirring under pure argon at the boiling point of the ether to a solution of 0.82 g of LiAlH₄ in 20 ml of absolute ether. The mixture was kept at 25° for 3 h and then treated with dilute hydrochloric acid. The ethereal layer was separated and dried over P₂O₅. Distillation *in vacuo* gave 4 g (69%) of *trans*-(X), (nc), b.p. 59–61°/0.1 mmHg. Analysis: Found: C, 26.53; H, 5.21; F, 27.98%. C₆H₁₄B₁₀F₄ requires C, 26.61; H, 5.18; F, 28.10%. IR spectrum; ν(C=C), 1710 cm⁻¹.

Trans-1-methyl-2-(α,β-difluoro-β-carboxyvinyl)-o-carborane (XII)

A solution consisting of 7.5 ml of 1.91 mol l⁻¹ of C₄H₉Li in benzene was added at -40° under pure argon to a solution consisting of 3 g of (I) in 20 ml of absolute ether. After 1 min, solid carbon dioxide was carefully added to the solution and

subsequently the benzene and ether were evaporated *in vacuo* at 25°. The residue was dissolved in 30 ml of pentane and the lithium salt which precipitated was filtered off and dissolved in 15 ml of water. The aqueous layer was filtered, acidified with hydrochloric acid and extracted with ether when 1 g of a viscous oil was obtained after distillation at 100–105°/0.1 mmHg. After crystallization from CCl₄–pentane (2:3), 0.93 g (30%) of (XII) (nc) was obtained, m.p. 146–147°. Analysis: Found: C, 27.72; H, 5.67; F, 13.88%. C₆H₁₄B₁₀F₂O₂ requires C, 26.81; H, 5.21; F, 14.16%. IR spectrum; $\nu(\text{C}=\text{C})$, 1680 cm⁻¹, $\nu(\text{C}=\text{O})$, 1728 cm⁻¹, $\nu(\text{OH})$, 2900–3100 cm⁻¹.

*Trans-1-methyl-7-(α,β -difluoro- β -carboxyvinyl)-*m*-carborane (XVII)*

In a similar manner to the previous experiment, 1 g of (IX)(a), (b) led to 0.4 g (33%) of (XVII) (nc), b.p. 84–86°/0.1 mmHg. Analysis: Found: F, 13.27%. C₆H₁₄B₂₀F₂O₂ requires: F, 14.16%. IR spectrum; $\nu(\text{C}=\text{C})$, 1690 cm⁻¹, $\nu(\text{C}=\text{O})$, 1730 cm⁻¹, $\nu(\text{OH})$, 2900–3200 cm⁻¹.

*Bis[1-methyl-2-(α,β -difluorovinyl)-*o*-carboranyl]mercury (XIII)*

A solution of (XI)(a) was prepared from 1.14 g of (I) in 10 ml of absolute ether and 2.3 ml of a 1.91 mol l⁻¹ solution of butyl-lithium in benzene at -40°. Then 1.3 g of HgCl₂ was added under an argon stream and with vigorous stirring. The temperature was allowed to increase to 25° when 50 ml of heptane was added and the mixture filtered. The heptane was evaporated *in vacuo* from the filtrate and the residue crystallized from heptane when 0.7 g (13%) of (XIII) (nc) was obtained, m.p. 133–135°. Analysis: Found: F, 11.17%. C₁₀H₂₅B₂₀F₄Hg requires F, 11.89%.

*Trans-1-methyl-2-(α,β -difluoro- β -bromovinyl)-*o*-carborane (XIV)*

Br₂ (2 g) was added at -40° to a solution of (XI)(a) in 20 ml of ether (from 2.6 g of (I)* and 7.8 ml of 1.52 mol l⁻¹ solution of C₄H₉Li in benzene). The mixture was heated to 25° and poured into 30 ml of a saturated hyposulphate solution. The organic layer was dried over CaCl₂. Vacuum distillation gave 2.2 g (70%) of (XIV) (nc), m.p. 48–49° (ethanol–water, 4:1). Analysis: Found: C, 20.32; H, 4.54%. C₅H₁₃B₁₀BrF₂ requires C, 20.01; H, 4.35%.

*Trans-1-methyl-2-(α,β -difluoro- β -iodovinyl)-*o*-carborane (XV)*

I₂ (5 g) in 50 ml of ether was added with stirring at -40° to a solution of (XI)(a) in ether (from 4.82 g of (I)). After 5 min, the mixture was poured into dilute hydrochloric acid, extracted with pentane and the organic layer dried over CaCl₂. The solvent was removed *in vacuo*. The residue was distilled at 108°/0.1 mmHg to give 4 g (61%) of (XV) (nc), m.p. 74–75° (ethanol–water, 1:1). Analysis: Found: C, 17.34; H, 3.37; I, 36.58%. C₅H₁₃B₁₀IF₂ requires C, 17.31; H, 3.76; I, 36.61%.

* Consisting of a mixture of 20% *cis* and 80% *trans*.

1-Methyl-2-(trifluorovinyl)-o-carborane (III)

FCIO₃ (1.7 g) was bubbled for 0.5 h with vigorous stirring at -30° into a solution of (XI)(a) in 20 ml of ether (from 4.2 g of (I)). The mixture was heated to 10° for 1 h and washed with NaHCO₃ solution (four times using 50 ml portions). The organic layer was dried over CaCl₂ and the ether removed *in vacuo* when 1.5 g (38%) of (III) was obtained after distillation from the residue, b.p. 42-43°/0.1 mmHg. Analysis: Found: F, 23.16%. C₅H₁₃B₁₀F₃ requires F, 23.91%.

REFERENCES

- 1 L. I. ZAKHARKIN AND V. N. LEBEDEV, *Zhur. Obshchei Khim.*, **4** (1971) 817.
- 2 L. I. ZAKHARKIN AND V. N. LEBEDEV, *Zhur. Obshchei Khim.*, **3** (1972) 558.
- 3 M. F. HAWTHORNE, T. E. BERRY AND P. A. WEGNER, *J. Amer. Chem. Soc.*, **87** (1965) 4746.
- 4 D. J. BURTON AND H. G. KRUTZCH, *J. Org. Chem.*, **36** (1971) 2351.
- 5 F. J. METTILLE AND D. J. BURTON, *Fluorine Chem. Rev.*, **1** (1967) 315.
- 6 D. J. BURTON AND F. J. METTILLE, *Inorg. Nuclear Chem. Letters*, **4** (1968) 9.
- 7 D. J. BURTON, R. L. JONSON AND R. T. BOGAN, *Canad. J. Chem.*, **44** (1966) 635.
- 8 R. T. BOGAN AND D. J. BURTON, presented at the 152nd National Meeting of the American Society, New York, 1966, Abstract k029.
- 9 L. I. ZAKHARKIN, V. N. KALININ AND I. P. SHEPILOV, *Doklady Akad. Nauk S.S.S.R.*, **174** (1967) 606.
- 10 A. ANDERSON, R. T. BOGAN AND D. J. BURTON, *J. Fluorine Chem.*, **1** (1971/1972) 121.
- 11 F. G. DRAKESMITH, R. D. RICHARDSON, O. J. STEWART AND P. TARRANT, *J. Org. Chem.*, **33** (1968) 286.
- 12 C. A. REILLY, *J. Chem. Phys.*, **37** (1962) 456.
- 13 C. N. BANWELL AND N. SHEPARD, *Proc. Roy. Soc.*, **A263** (1961) 136.
- 14 S. ANDREADES, *J. Amer. Chem. Soc.*, **84** (1962) 864.