The Formation of a Halogenocarbenoid of Zinc. A Novel Synthetic Route to Halogenocyclopropane Derivatives

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Summary 7-Fluoro-, 7-chloro-, 7-bromo-, or 7-iodonorcarane were obtained by the reaction of di-iodofluoromethane, dichloroiodomethane, dibromoiodomethane, or iodoform, respectively, with diethylzinc and cyclohexene.

We have studied the formation and reaction of zinc carbenoids *via* the reaction of dialkylzinc and polyhalogenoalkane,[1] which seemed to provide a more versatile route than the Simmons–Smith method.[2] We report here the formation of 7-halogenonorcarane by the reaction of ZnEt$_2$ and polyhalogenomethane with cyclohexene. This is probably the first report on the chemistry of halogenocarbenoids of zinc, although Köbrich[3] mentioned briefly the chlorocarbenoid of zinc in relation to lithium carbenoid.

The procedure we used [reaction (1)] was similar to that reported previously.[1]

CHFI$_2$,[4] CHBrClI,[5] CHCl$_2$I,[5] CHClI$_2$,[5] CHBr$_2$I,[5] and CHBrI$_2$[5] were prepared by minor modifications of literature methods.

CHF$_2$I was the most useful for the preparation of fluorocyclopropane, CHCl$_2$I for the preparation of chlorocyclopropane, and CHBr$_2$I for the preparation of bromocyclopropane. 7-Iodonorcarane was obtained in 10% yield as follows. To a stirred mixture of cyclohexene (5 ml) and ZnEt$_2$ (0·05 mol, 5 ml) under reflux, iodoform (0·05 mol, 19·7 g) suspended in cyclohexene (15 ml) was added. The physical properties (n.m.r., i.r., and mass spectra) of the 7-halogenonorcaranes except 7-iodonorcarane correspond with published values. The results are summarized in the Table.

Table

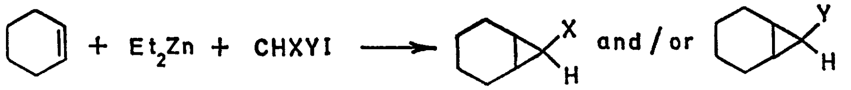
Yields and isomer ratios for 7-halogenonorcaranes in the reaction of diethylzinc and polyhalogenomethane with cyclohexene[a]

	7-Halogenonorcarane		
Halide	X	Yield[b] (%)	Isomer ratio (*endo*/*exo*)
CHFI$_2$	F	91	5·7
CHCl$_2$I	Cl	52	2·1
CHClBrI	Cl	45	3·1
	Br	Trace	2·1
	I	Trace	0·2
CHClI$_2$	Cl	17	11·0
	I	1	2·6
CHBr$_2$I	Br	53	1·3
CHBrI$_2$	Br	9	2·8
	I	13	1·8
CHI$_3$	I	Trace	0·5

[a] Reaction conditions: Cyclohexene (10 ml), light petroleum (20 ml), halide (0·05 mol), Et$_2$Zn (0·05 mol); reaction temp., 25—35 °C; time, 2 h.

[b] Based on the halide.

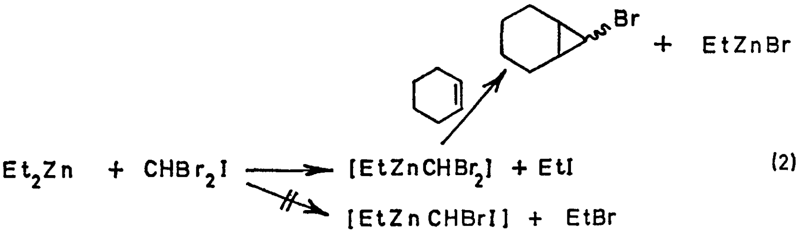
The reaction of cyclohexene (10 ml), ZnEt$_2$ (0·02 mole, 2 ml), and CHBr$_2$I (0·036 mole, 10·9 g) was carried out at 25—35 °C. After 2 h the mixture was treated with aqueous



(1)

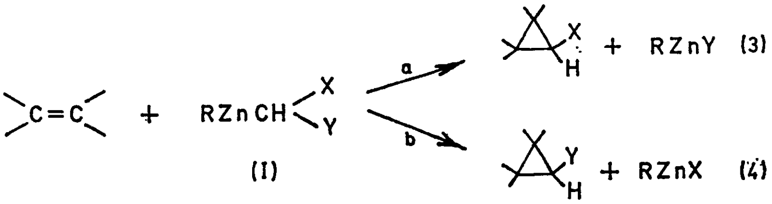
X, Y = F, Cl, Br, I.

NH_4Cl and analysed by g.l.c. EtBr was not detected, but EtI and 7-bromonorcarane were obtained in 75 and 53% yield respectively based on the halide, together with small amounts of unknown products. This result suggests that $ZnEt_2$ reacts mainly with iodine in a polyhalogenomethane to give an α-dihalogenozinc compound. This is supported by the fact that dihalogenomonoiodomethane afforded only small amounts of iodonorcarane.



(2)

$CHBrClI$, $CHClI_2$, or $CHBrI_2$ afforded two (or three) 7-halogenonorcaranes, indicating that two halogen-substituted bivalent carbon species are transferred to the olefin from the dihalogenomethylzinc compound (I) generated by the reaction of $ZnEt_2$ and each of these halides.



(3)

(4)

(I)

The yields of the 7-halogenonorcaranes suggest that halogen in the dihalogenomethylzinc compound undergoes α-elimination with the zinc moiety in the order: I, Br > Cl > F.

The stereoselectivity (Table) is also of interest. *endo*-Isomers of 7-fluoro-, 7-chloro-, and 7-bromo-norcarane were always formed predominantly over their *exo*-isomers. However, the selectivity of formation of 7-iodonorcarane depended upon the source of the iodocarbenoid. The *endo*-isomer was formed predominantly with $CHClI_2$ or $CHBrI_2$ (*syn*-selective formation); more *exo*-isomer formed with $CHBrClI$ or CHI_3 (*anti*-selective formation).

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