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HALOMETHYL–METAL COMPOUNDS

LXI*. PHENYL(FLUORODIBROMOMETHYL)MERCURY, A FLUOROBROMOCARBENE PRECURSOR

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SUMMARY

Phenyl(fluorodibromomethyl)mercury has been prepared by reaction of fluorodibromomethane, phenylmercuric chloride and sodium methoxide or potassium tert-butoxide in THF at low temperature. This organomercury reagent is an excellent source of fluorobromocarbene, releasing CFBr within 20 min at 80° or within 4 days at room temperature. The addition of $PhHgCFBr_2$-derived CFBr to the C=C bond of 10 olefins and to the C=O bond of $(CF_2Cl)_2CO$ and the insertion of CFBr into the Si–H bond of triethylsilane are described. Reduction of $Et_3SiCHFBr$ with tri-n-butyltin hydride gave Et_3SiCH_2F.

INTRODUCTION

In previous papers of this series we have reported new organomercury reagents which serve in the generation of difluorocarbene[1], fluorochlorocarbene[2,3] and (trifluoromethyl)chloro- and (trifluoromethyl)bromocarbene[4]. Our continued interest in the chemistry of fluorinated carbenes prompted the present investigation of the synthesis and chemistry of phenyl(fluorobromomethyl)mercury, a compound which would be expected to be a CFBr precursor.

The generation of fluorobromocarbene by the Doering–Hoffmann route, in the presence of olefins to give *gem*-fluorobromocyclopropanes, already has been reported by several groups[5–10]. But, as in the case of other dihalocarbenes, development of the alternate organomercury-based preparation of the divalent carbon species not involving basic reaction conditions and not fraught with nonproductive side reactions seemed a worthwhile objective**. In the absence of a synthetically useful direct route to monofluorocarbene***, such further development of alternate routes to

* For Part LX see Ref. 1.

** For a discussion of the advantages of the organomercury route in dihalocarbene generation and a general review of this area, see ref. 11.

*** Schlosser and Heinz[9] have reported the direct generation of CHF (or the respective carbenoid) by reaction of an organolithium reagent with $CHFBr_2$, but when CHF was generated in this manner in the presence of olefins, the fluorocyclopropane yields were quite low.

CFBr was of special interest, since reduction of the C–Br bond in the CFBr-derived product can be effected easily and in excellent yield[5,7–9].

RESULTS AND DISCUSSION

The general procedure for the synthesis of phenyl(trihalomethyl)mercury compounds involves the reaction of the appropriate haloform with potassium tert-butoxide (usually as the mono-tert-butanol solvate) in the presence of phenylmercuric chloride in THF medium at −25°[12]. Application of these exact conditions to the reaction with fluorodibromomethane did not give $PhHgCFBr_2$. Experiments in which the temperature, solvent system and base were varied led to two procedures which gave this organomercury reagent in reproducible and acceptable yields, eqns. (1) and (2).

$$PhHgCl + Me_3COK + CHFBr_2 \xrightarrow{THF,\ -65^\circ} PhHgCFBr_2 \quad (35\text{–}40\%) \qquad (1)$$
(2 equiv.)

$$PhHgCl + NaOMe + CHFBr_2 \xrightarrow{THF,\ -25^\circ} PhHgCFBr_2 \quad (50\text{–}55\%) \qquad (2)$$
(2 equiv.)

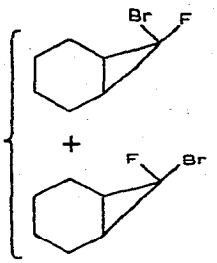
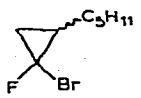
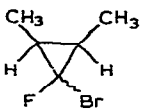
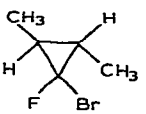
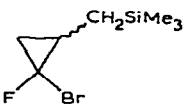
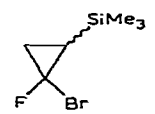
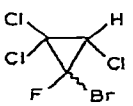
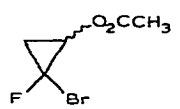
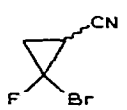
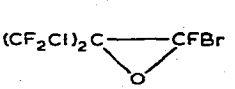
Phenyl(fluorodibromomethyl)mercury was isolated as a crystalline solid which melted at 85–88° (rapid heating) and decomposed at 94°. As the solid, it is stable for longer periods at 0° but decomposes slowly at room temperature. In solution, it is quite unstable. In particular, oxygenated solvents such as ketones, ethers and alcohols can induce its spontaneous, exothermic decomposition. For instance, sudden, exothermic decomposition occurred (reproducibly) when a sample of $PhHgCFBr_2$ was placed in a flask which had been washed out with acetone but not completely dried. The marginal solution stability of this mercurial requires that all operations during its synthesis, isolation and purification be carried out with maximum dispatch.

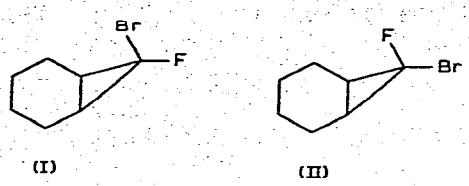
Our previous work has shown that the rate of phenylmercuric halide (PhHgX) elimination from a phenyl(halodichloromethyl)mercury compound ($PhHgCCl_2X$) increases as the halogen, X, is changed: F < Cl < Br < I[11,13]. Thus it was to be expected that $PhHgCFBr_2$ would be a more reactive dihalocarbene source than $PhHgCFCl_2$. Such was the case, and, in fact, this mercurial was found to be the most reactive of all the halomethylmercurials whose divalent carbon transfer reaction involves elimination of phenylmercuric bromide which we have examined thus far. For example, $PhHgCBr_3$ and $PhHgCClBr_2$ transfer CBr_2 and CClBr, respectively, to olefins at 80°, and about two hours are required for complete reaction[14]. Such transfer could also be effected at room temperature with these mercurials, but correspondingly longer reaction times, about 15–16 days, were necessary[15]. In contrast, with $PhHgCFBr_2$, CFBr transfer to olefins is complete within 20 min at 80° in benzene solution and within four days at room temperature. *gem*-Fluorobromocyclopropane yields were good to excellent. The reactions of this mercurial with olefins are summarized in Table 1.

As expected, reaction of CFBr with terminal monosubstituted olefins, with *cis*-1,2-disubstituted olefins and with cyclic olefins resulted in formation of two isomers. In the case of cyclohexene, the two isomers were formed in a ratio of 1.9/1, with preference for that isomer with the bromine atom *syn* to the tetramethylene bridge [(I)/(II) 1.9]. The (I)/(II) ratio was 1.7 when CFBr was generated by the $CHFBr_2/Me_3$-

TABLE 1

REACTIONS OF PHENYL(FLUORODIBROMOMETHYL)MERCURY

Carbenophile	*Product*	*Yield (%)*		*Isomer ratio*
		4 days at room temp.	*20 min at 80°*	
Cyclohexene		58 32	58 30	
n-$C_5H_{11}CH{=}CH_2$		78	72	
cis-$CH_3CH{=}CHCH_3$		99		1.70
trans-$CH_3CH{=}CHCH_3$		98		
$Me_3SiCH_2CH{=}CH_2$		60	70	
$Me_3SiCH{=}CH_2$		55		2.5
$CCl_2{=}CHCl$			58	1.95
$CH_3CO_2CH{=}CH_2$			95	1.5
$CH_2{=}CHCN$		33	24	1.9
			57	
$(CF_2Cl)_2C{=}O$		74		
Et_3SiH	$Et_3SiCHFBr$	87	68	



(I) (II)

COK route[5,9]. (1.8 in our hands). The isomer assignment was confirmed by treatment of the (I)/(II) mixture produced in a $PhHgCFBr_2$/cyclohexene reaction with quinoline at 200° [5]. Only one isomer survived, and on the basis of halocyclopropane stabilities[16], this would be expected to be the one with the *anti* bromine substituent, (II). The addition of CFBr to olefins occurs stereospecifically, as shown by the results obtained with *cis*- and *trans*-2-butene. A single 1-fluoro-1-bromo-2,3-dimethylcyclopropane isomer was obtained from the *trans* olefin, while reaction with the *cis* olefin gave two such isomers which were different from the *trans*-2-butene-derived product.

Noteworthy among the reactions listed in Table 1 are those with trichloroethylene, vinyltrimethylsilane, acrylonitrile and vinyl acetate. The first two are olefins which are only poorly reactive toward dihalocarbenes[14,17], while acrylonitrile and vinyl acetate are base-sensitive and, furthermore, trap the trihalomethyl anion intermediate when the dihalocarbene is generated by the haloform/base procedure. While the CFBr adduct yields of the first three of these olefins obtained with $PhHgCFBr_2$ are only moderate, the fact that these reactions are observed at all speaks strongly for the special advantages of this organomercury reagent.

Phenyl(fluorodibromomethyl)mercury-derived CFBr was found to insert into the Si–H bond [eqn. (3)], a reaction which opens a useful route to monofluorosilanes [eqn. (4)]. [Analogous chemistry has been developed with the $PhHgCCl_nBr_{3-n}$ ($n=0$–2) reagents[18].]

$$PhHgCFBr_2 + Et_3SiH \xrightarrow{25°,\ 4\ days} Et_3SiCHFBr + PhHgBr \quad (3)$$

(87%)

(68% after 20 min at 80°)

$$Et_3SiCHFBr + n\text{-}Bu_3SnH \rightarrow Et_3SiCH_2F + n\text{-}Bu_3SnBr \quad (4)$$

(74%, based on $PhHgCFBr_2$)

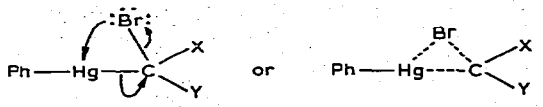
Another dihalocarbene reaction developed with our phenyl(trihalomethyl)-mercury reagents is the synthesis of oxiranes from highly halogenated carbonyl compounds[19,20]. Phenyl(fluorodibromomethyl)mercury also was found to add CFBr to the C=O linkage [eqn. (5)].

$$(CF_2Cl)_2C{=}O + PhHgCFBr_2 \xrightarrow{25°,\ 4\ days} (CF_2Cl)_2C\!\!<\!\!\begin{matrix}O\\ \diagup\\ \diagdown\end{matrix}\!\!CFBr + PhHgBr \quad (5)$$

(74%)

The unexpectedly high reactivity of $PhHgCFBr_2$ as a CFBr transfer agent merits further discussion. In previous work, we had prepared and studied the CFCl transfer chemistry of $PhHgCFCl_2$[2]. Initially, on the basis of reactions with olefins whose rate was followed by thin layer chromatography, its reactivity had been estimated as being comparable to that of $PhHgCCl_3$, but later work[3] showed $PhHgCFCl_2$

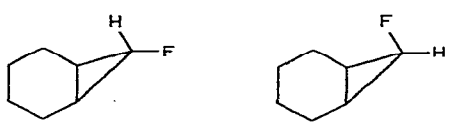
to be about four times more reactive than $PhHgCCl_3$. From these results it would appear that the presence of a fluorine substituent on the incipient carbene carbon atom favors the α-elimination process in phenyl(trihalomethyl)mercury compounds. This observation finds ready accommodation in our views of the nature of the α-elimination process as developed thus far. On the basis of evidence from rate studies[21,22], transition state (III) was suggested for the carbene extrusion reaction. Fur-



(III)

ther studies of the reactivity of $PhHgCCl_2Ph$ (which was highly reactive)[23] and compounds such as $PhHgCCl_2CO_2CH_3$[24] and $PhHgCClBrCF_3$[4] (which were rather unreactive as divalent carbon transfer agents) led to the proposal[25] that the rate of the divalent carbon extrusion process is determined in large part by the stabilization available to the incipient carbene. The stability of singlet state carbenes is a function of the substituents on the carbon atom, with substituents which can donate electron density to the vacant carbon *p* orbital via p_π–p_π dative bonding providing special stabilization[26]. For halogen substituents, such stabilization increases in the order I < Br < Cl < F, and these ideas then serve to explain the "enhanced" reactivity of $PhHgCFCl_2$ and $PhHgCFBr_2$.

As mentioned above, the reduction of *gem*-fluorobromo- (and fluorochloro-)[5,7,27] cyclopropanes serves as the most useful route to monofluorocyclopropanes. A previous report by Japanese workers[5] claimed that the reduction of the *syn* and *anti* isomers of 7-fluoro-7-bromonorcarane [(I) and (II)] with tri-n-butyltin hydride



(IV) (V)

(58°, 30 min, no solvent, no catalyst) occurred stereospecifically. A 1.7/1 (I)/(II) mixture was reported to give a 1.8/1 mixture of (IV) and (V), respectively, and reduction of pure (II) with tri-n-butyltin hydride was claimed to give *only* (V). In our hands, tri-n-butyltin hydride reductions of 7-fluoro-7-bromonorcarane were highly stereoselective but not stereospecific (Table 2).

TABLE 2

REDUCTION OF 7-FLUORO-7-BROMONORCARANE WITH TRI-n-BUTYLTIN HYDRIDE

7-Fluoro-7-bromonorcarane isomer	*7-Fluoronorcarane produced*
(I) + (II) (1.8 (I)/(II) ratio)	(IV) + (V) [1.43 (IV)/(V) ratio]
(I) (99% pure, by GLC)	(IV) + (V) [9/1 (IV)/(V) ratio]
(II) (99% pure, by GLC)	(IV) + (V) [1/7.3 (IV)/(V) ratio]

EXPERIMENTAL

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. Solvents and liquid starting materials were carefully dried, usually by distillation from an active hydride or benzophenone ketyl. Infrared spectra were obtained using Perkin–Elmer 237B, 257 or 457A grating infrared spectrophotometers. ^{1}H NMR spectra using a Varian Associates T60 spectrometer. Chemical shifts are given in δ units, ppm downfield from internal TMS. ^{19}F NMR spectra were obtained using a Perkin–Elmer R20B spectrometer operating at 56.446 MHz. GLC was used extensively in this work to analyze reaction mixtures, determine product yields and isolate pure samples of products.

Preparation of fluorodibromomethane[28]

A 500 ml three-necked flask, equipped with a mechanical stirrer and a Claisen head fitted with a thermometer and a West condenser leading to a receiving flask, was charged with 1 kg (3.96 mol) of bromoform and 256 g (1.50 mol) of antimony trifluoride. The reaction flask was immersed in an oil bath at 120°, the mixture was stirred for 5 min and then 10 ml of bromine was added. After a short while, the dark red reaction mixture became homogeneous and a mixture of the fluorodibromomethane and bromine began to distil into the receiving flask. The initial exotherm resulted in a head temperature of 100°, but most of the distillate came over at 60–80°. A small amount of water was pipetted away from the distillate (650 g) which then was treated cautiously with 1-decene to remove the bromine. The product was obtained by careful distillation through a Widmer column. The yield was 479 g (62%); b.p. 64–65°, n_D^{25} 1.4680; lit.[28,29] b.p. 64.9°, n_D^{20} 1.4685.

Preparation of phenyl(fluorodibromomethyl)mercury

(*a*). *Sodium methoxide procedure.* A 500 ml three-necked flask equipped with a mechanical stirrer, a nitrogen inlet tube, a low temperature thermometer and a pressure-equalizing addition funnel was charged with 37.5 g (0.12 mol) of phenylmercuric chloride, 39.0 g (0.20 mol) of fluorodibromomethane and 100 ml of dry THF. This mixture was cooled to −25°. The addition funnel was charged with sodium methoxide solution [from 3.0 g (0.13 g-atom) in 50 ml of methanol] and this solution was added dropwise with stirring over a period of 20 min while the temperature was maintained at −22° to −25°. The reaction mixture was stirred for another 5 min and the resulting gray, opalescent mixture was evaporated at reduced pressure to semi-dryness. This residue was shaken vigorously first with 300 ml of benzene and then 150 ml of dilute HCl was added and the mixture was shaken vigorously again. After phase separation, the benzene layer was dried over anhydrous magnesium sulfate. The aqueous phase was washed with benzene and the combined benzene extracts were then evaporated to dryness. The white residue was extracted with 300 ml of hexane. After the extracts had been evaporated to about 75 ml, filtration gave 31 g (55%) of $PhHgCFBr_2$. It must be emphasized that the instability of the product in solution necessitates that all steps of this procedure be carried out as rapidly as possible and that the preparation of $PhHgCFBr_2$, once started, be continued without interruption. Temperatures above 25° must be avoided.

Phenyl(fluorodibromomethyl)mercury was isolated as a white, crystalline solid. Its melting point is dependent on the rate of heating. Slow heating simply results in slow decomposition. With rapid heating (ca. 10°/min) and placing the sample in the melting point apparatus about 10° below its melting point, a clear melt was observed at 85–88°. At 94° the sample decomposed rapidly, turning black and evolving a gas. (Found: C, 17.39; H, 1.21; Br, 34.83; F, 3.92. $C_7H_5Br_2FHg$ calcd.: C, 17.04; H, 1.08; Br, 34.11; F, 4.15%.) IR (Nujol mull, cm^{-1}): 3050 w, 3030 w, 1435 m, 1010 s, 840 s, 800 s.

(*b*). *Potassium tert-butoxide procedure.* A flask equipped as described in (*a*) was charged with 0.10 mol of phenylmercuric chloride and 150 ml of dry THF. The mixture was cooled to about −25° and 14.5 g (0.13 mol) of unsolvated potassium tert-butoxide (M.S.A. Corp.) was added with stirring from a solids addition funnel (100 ml THF rinse). The mixture was stirred for 15 min at −25° to give a green-gray suspension. The latter was cooled to −55° and 39.0 g (0.2 mol) of fluorodibromomethane was added rapidly. The resulting mixture was stirred under nitrogen at −55° for 5 min and then was evaporated to dryness under reduced pressure. The solid residue was extracted with 200 ml of dichloromethane and 300 ml of hexane. Evaporation of the combined extracts gave 23 g of gray solid which was extracted again with 200 ml of dichloromethane and 300 ml of hexane. Evaporation of the extracts to 100 ml, addition of another 200 ml of hexane and subsequent evaporation to 50 ml was followed by filtration to give 15.5 g (35%) of $PhHgCFBr_2$.

Reaction of phenyl(fluorodibromomethyl)mercury with olefins

The room temperature and 80° reactions with cyclohexene are described in detail to illustrate the procedure used.

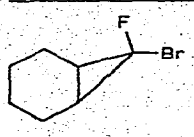
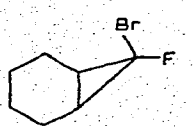
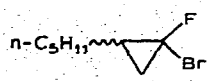
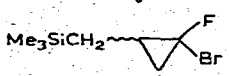
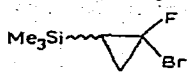
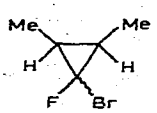
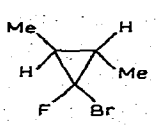
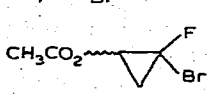
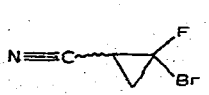
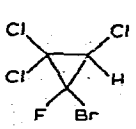
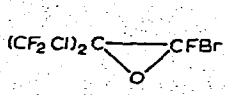
A 50 ml three-necked flask equipped with a magnetic stirring unit and a nitrogen inlet tube was charged with 2.34 g (5 mmol) of the mercurial, 2.5 g (30 mmol) of cyclohexene and 10 ml of dry benzene. The reaction mixture was stirred at room temperature for 3 days, at which time thin layer chromatography[14] indicated that the mercury reagent had been consumed. Filtration of 1.55 g (87%) of phenylmercuric bromide, m.p. 286–288°, was followed by trap-to-trap distillation of the filtrate at 0.05 mmHg (pot temperature to 25°). GLC analysis (8.5 ft. 20% General Electric Co. SE-30 column at 120°) indicated the presence of two products in yields of 32 and 58%, respectively, in order of increasing GLC retention time. The products were collected using preparative GLC (12 ft. 10% Carbowax 20M column at 150°) and identified as (II) and (I) respectively; *cf.* Table 3.

In the 80° reaction, the same reaction apparatus was charged with 4.05 mmol of the mercurial, 30 mmol of cyclohexene and 10 ml of dry benzene. The flask was placed in a preheated oil bath (85–90°) and the reaction mixture was heated to reflux with stirring under nitrogen, over a period of 5 min. Even before the reflux temperature was reached, the initially homogeneous reaction mixture became heavily clouded with phenylmercuric bromide. The reaction mixture was heated at reflux for 20 min. A work-up identical to that used for the room temperature reaction gave 1.35 g (94%) of phenylmercuric bromide and (II) and (I) in yields of 30% and 50%, respectively, a (I)/(II) isomer ratio of 1.75.

The reactions with other olefins (Tables 1 and 3) were carried out in a similar manner using 5–10 mmol of mercurial and 30–60 mmol of olefin. In those cases where two isomers were expected, GLC did not separate them using the columns available

TABLE 3

COMPOUNDS PREPARED VIA $PhHgCFBr_2$

Compound	*Isomer ratio*	n_D^{25}	*Analysis found (calcd.) (%)*		
			C	*H*	*Br*
		1.4870	43.57 (43.54)	5.29 (5.22)	41.26[a] (41.39)
		1.4876	44.24 (43.54)	5.29 (5.22)	40.55 (41.39)
	Not determined	1.4418	46.10 (45.95)	6.84 (6.75)	38.31 (38.22)
	Not determined	1.4430	37.50 (37.33)	6.67 (6.27)	35.88 (35.47)
	2.5	1.4440	34.37 (34.14)	5.75 (5.72)	38.15 (37.84)
	1.7	1.4372	36.01 (35.95)	4.86 (4.83)	47.55 (47.85)
		1.4305	36.06 (35.95)	4.78 (4.83)	47.45 (47.85)
	1.5	1.4398	30.47 (30.48)	3.18 (3.07)	
	1.9	1.4645	29.23 (29.29)	2.07 (1.84)	
	1.95	1.5016	14.98 (14.87)	0.57 (0.42)	
		1.4826	33.21 (33.17)	3.43 (3.34)	44.29 (44.15)
		1.3885	15.59 (15.50)		25.30 (25.79)
$(C_2H_5)_3SiCHFBr$		1.4557	36.96 (37.00)	7.32 (7.10)	34.85 (35.17)

[a] Fluorine: found, 9.30; calcd., 9.84%.

to us. However, in some cases (*cf.* Table 1) the presence of two isomers was established using ^{19}F NMR spectroscopy. In the case of acrylonitrile the reaction mixtures in both the room temperature and 80° reactions became dark brown and polyacrylonitrile was formed.

The ^{19}F NMR spectra (obtained in CCl_4 solution) follow. Chemical shifts are given in ppm upfield from internal fluorobenzene).

1-Fluoro-2,2,3-trichloro-1-bromocyclopropane: 16.0 (d, $J(HF_{cis})$ 20.2 Hz, rel. area 1.95) and 27.6 ppm (s, rel. area 1).

1-Fluoro-1-bromo-2-acetoxycyclopropane: 24.8 (m, rel. area 1) and 42.5 ppm (t, $J(HF_{cis})$ 14.1 Hz, rel. area 1.5).

1-Fluoro-1-bromo-2-cyanocyclopropane: 20.8 (t, $J(HF_{cis})$ 14.1 Hz, rel. area 1.9) and 26.4 ppm (m, rel. area 1).

1-Fluoro-1-bromo-*cis*-2,3-dimethylcyclopropane: 7.5 (t, $J(HF_{cis})$ 20 Hz, rel. area 1.7) and 48.2 ppm (s, rel. area 1).

1-Fluoro-1-bromo-*trans*-2,3-dimethylcyclopropane: 28.5 ppm (d, $J(HF_{cis})$ 21.2 Hz).

Reaction of phenyl(fluorodibromomethyl)mercury with sym-tetrafluorodichloroacetone

Using the procedure described above, a reaction of 4.70 g (10 mmol) of the mercurial and 12 g (60 mmol) of the acetone derivative in 10 ml of benzene was carried out at room temperature for 4 days. Phenylmercuric bromide was obtained in quantitative yield. The expected oxirane (*cf.* Table 3) was obtained in 74% yield. IR (liquid film): 1410 s, 1235 vs, 1185 vs, 1140 s, 1070 s, 1000 vs, 880 vs, 850 vs, 830 m, 755 w, 725 m, 700 w, 690 m, 660 m, 645 m, 625 m and 600 m cm^{-1}. ^{19}F NMR (in CCl_4): multiplets at 28.1 (CF_2Cl) and 15.1 ppm downfield from fluorobenzene (cyclopropyl F).

Reaction of phenyl(fluorodibromomethyl)mercury with triethylsilane

Using the procedure described above, 4.7 g (10 mmol) of the mercurial and 7.0 g (65 mmol) of triethylsilane (PCR Inc.) in 15 ml of benzene were allowed to react for four days at room temperature. Phenylmercuric bromide was isolated in 98% yield. The yield of $Et_3SiCHFBr$ (*cf.* Table 3) was 87%. IR (liquid film): 2940 s, 2920 s, 2880 s, 1460 m, 1415 m, 1380 w, 1300 m, 1240 m, 1140 w, 1105 vs, 765 s(sh), 735 s and 680 m cm^{-1}. ^1H NMR (in CCl_4): δ 0.79 (m, 15H, Et_3Si) and 6.45 ppm (d, 1H, J(H–F) 46 Hz, CHFBr).

A similar reaction carried out at 80° for 30 min gave phenylmercuric bromide in 88% and $Et_3SiCHFBr$ in 68% yield.

Reduction of triethyl(fluorobromomethyl)silane

The distillate from the reaction of 10 mmol of $PhHgCFBr_2$ and 60 mmol of triethylsilane in 15 ml of benzene was charged into a 50 ml three-necked flask equipped with a reflux condenser, a magnetic stirring unit, a pressure equalizing addition funnel and a nitrogen inlet tube. Tri-n-butyltin hydride (3.2 g, 11 mmol) was added dropwise with stirring during 1 h and the reaction mixture subsequently was stirred at room temperature overnight. Trap-to-trap distillation (0.05 mmHg and 25°) followed. The liquid residue was distilled to give 3.4 g (92%) of tri-n-butyltin bromide, b.p. 86–88°/0.07 mmHg, n_D^{25} 1.4980. The trap-to-trap distillate contained triethyl(fluoromethyl)-silane and the yield was determined (GLC) to be 74%. A sample of the product was

isolated by preparative GLC; n_D^{25} 1.4142. (Found: C, 56.55; H, 11.47. $C_7H_{17}FSi$ calcd.: C, 56.69; H, 11.56%.) IR (liquid film): 2960 s, 2900 s, 2870 s, 1480 s, 1470 s, 1425 s, 1390 m, 1300 w, 1250 s, 1225 m, 1005 s, 980 s, 770 s and 725 s cm^{-1}. ^1H NMR (in CCl_4): δ 0.81 (m, 15H, Et_3Si) and 4.40 ppm (d, 2H J(H–F) 48 Hz, CH_2F).

Reduction of 7-fluoro-7-bromonorcarane with tri-n-butyltin hydride

A 10 ml flask equipped with a magnetic stirring unit and a constant pressure addition funnel topped with a nitrogen inlet tube was charged with 2.0 g (10.3 mmol) of 7-fluoro-7-bromonorcarane (1.8/1 mixture of (I) and (II), prepared by the Doering–Hoffmann procedure in 37% yield). The flask was immersed in an oil bath at 60° and 3.3 g (11.4 mmol) of tri-n-butyltin hydride was added dropwise with stirring during 15 min. The mixture was stirred at 60° for 30 min and then was trap-to-trap distilled at 0.05 mmHg (pot temp. to 50°). The pot residue was short-path distilled to give 2.9 g (78%) of n-Bu_3SnBr, b.p. 80–85°/0.05 mmHg, n_D^{25} 1.5010. The trap-to-trap distillate was analyzed by GLC (8 ft. 20% SE-30 column at 110°). The yield of the two 7-fluoronorcarane isomers was 97% and the isomer ratio [(IV)/(V)] was 1.43 (8 ft. 15% Carbowax 20M at 60°). Both isomers were collected. 7-*anti*-Fluoronorcarane, n_D^{25} 1.4353; 7-*syn*-fluoronorcarane, n_D^{25} 1.4390. The IR and ^1H NMR spectra agreed with those reported by Ando *et al.*[7].

The 7-fluoro-7-bromonorcarane isomers were separated using a 6 ft. 10% Carbowax 20M column at 150° and each was obtained in 99% isomeric purity. Each isomer was separately reduced with tri-n-butyltin hydride using the procedure described above. The results of these experiments are summarized in Table 2.

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