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HALOMETHYL–METAL COMPOUNDS

LV.* THE SYNTHESIS OF PHENYL(TRIFLUOROMETHYL)MERCURY BY FLUORINATION OF PHENYL(TRIBROMOMETHYL)MERCURY

DIETMAR SEYFERTH and STEVEN P. HOPPER

Department of Chemistry of the Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 *(U.S.A.)*

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SUMMARY

The reaction of phenylmercuric hydroxide with aqueous hydrofluoric acid gives a material which appears to be an HF adduct of phenylmercuric fluoride ("PhHgF · HF"). This material has been found to fluorinate phenyl(tribromomethyl)-mercury in benzene or toluene medium at room temperature to give phenyl(tri-fluoromethyl)mercury in yields averaging 60–65% when the reaction is carried out in the presence of 48% HF. Phenyl(trichloromethyl)mercury can be fluorinated to $PhHgCF_3$ in this manner, but a reaction temperature of 90° is required. Partial fluorination in good yield of phenyl(bromodichloromethyl)mercury to phenyl-(fluorodichloromethyl)mercury could be achieved at room temperature, but attempted partial fluorination of $PhHgCBr_3$, $PhHgCClBr_2$ and $PhHgCFBr_2$ was unsuccessful, $PhHgCF_3$ being the major product obtained. The possible mechanism of this novel fluorination process is discussed.

INTRODUCTION

Our previous work has shown phenyl(trihalomethyl)mercury compounds to be excellent sources of dihalocarbenes, and such reagents have been used to develop a preparatively useful chemistry of CCl_2, CClBr, CBr_2, CClF and CBrF[2]. A useful route to CF_2 by way of an organotin precursor, $(CH_3)_3SnCF_3$, already was available[3,4], but we felt that an organomercury route to difluorocarbene merited careful attention.

At the outset of this work, several (trifluoromethyl)mercury compounds had been known for some 20 years: CF_3HgX (X = Cl, Br, I)[5] and $(CF_3)_2Hg$[6]. Their preparation was accomplished as shown in eqns. (1)–(3). The yields obtained in these reactions were good, but a synthesis not based on the gaseous and expensive**

* For Part LIV see ref. 1.
** The current price of CF_3I is $65/100 g.

$$CF_3I + Hg \xrightarrow{\text{Sealed tube, UV}} CF_3HgI \quad (1)$$

$$CF_3HgI \xrightarrow{OH^-} CF_3HgOH \xrightarrow{HX} CF_3HgX \quad (X = Cl, Br) \quad (2)$$

$$CF_3HgI + Cd/Hg \xrightarrow[24\ h]{\text{Sealed tube, room temp.}} (CF_3)_2Hg \quad (3)$$

iodotrifluoromethane and on metallic mercury seemed a worthwhile objective. Accordingly, we commenced a study devoted to the synthesis of phenyl(trifluoromethyl)mercury. We report here concerning the preparation of this compound by fluorination of phenyl(tribromomethyl)mercury, a procedure which is not the most practical of those presently available, but which involves some very novel and interesting organomercury chemistry.

During a previous study, we had found that phenyl(bromodichloromethyl)-mercury reacts with phenylmercuric fluoride in refluxing benzene to give a mixture of $PhHgCCl_2F$ and $PhHgCCl_3$[7]. Two possible reaction courses could be responsible for formation of the former: (1) insertion of $PhHgCCl_2Br$-derived dichlorocarbene into the Hg–F linkage of phenylmercuric fluoride, and (2) direct fluorination of $PhHgCCl_2Br$ by phenylmercuric fluoride (*i.e.*, bromine–fluorine exchange). Preliminary evidence favored the latter mode of reaction[7]. The formation of $PhHgCCl_3$ was explicable in terms of the following sequence:

$$PhHgCCl_2F \xrightarrow{80^\circ} PhHgCl + CClF \quad (4)$$

$$PhHgCl + CCl_2 \text{ (from } PhHgCCl_2Br) \rightarrow PhHgCCl_3 \quad (5)$$

Chlorofluorocarbene extrusion from phenyl(fluorodichloromethyl)mercury is well documented[8], as is the insertion of CCl_2 into the Hg–Cl bond[9].

This novel fluorination reaction seemed worthy of further study, and in particular, its possible application to the synthesis of phenyl(trifluoromethyl)-mercury seemed an intriguing possibility.

RESULTS AND DISCUSSION

Phenylmercuric fluoride had been prepared by Wright by reaction of phenylmercuric chloride with silver fluoride in aqueous medium[10]. A product with m.p. 170° was claimed. This procedure is not very practical for large-scale application, and for this reason we examined the reaction of phenylmercuric hydroxide with hydrofluoric acid as a possible route to phenylmercuric fluoride. The action of an excess of 48% hydrofluoric acid on an ethanol slurry of phenylmercuric hydroxide gave a product which further work showed not to be PhHgF. This material, isolated as a white powder, decomposed at 165–170° with melting and bubbling to give a new solid whose melting point was above 360°. The infrared spectrum of the initial product (Nujol mull) showed a band at 3605 cm^{-1} and this product consumed about one equivalent of aqueous NaOH to give a new solid with m.p. above 300°. The infrared spectrum of the latter no longer showed a band around 3600 cm^{-1}. Analyses of these two materials suggested that the intial reaction product was an HF adduct approximating to the composition $PhHgF \cdot HF$ and that the product obtained when

this material was treated with base had the composition PhHgF. The HF contained in the original product appeared to be only loosely bound since prolonged standing at room temperature gave a solid which analyzed correctly for PhHgF, as did recrystallization from chloroform. The base-treated material (in contrast to the others discussed) was inactive as a fluorinating agent. Further work is required to define more closely the constitution of these materials and to establish their structure. One might expect phenylmercuric fluoride to be polymeric with Hg–F–Hg bridging, in analogy with other organometallic fluorides (*e.g.*, R_2AlF, R_3SnF, etc.). It may be speculated that the HF in the initial product is weakly hydrogen-bonded to the fluorine of PhHgF, thus preventing such polymerization, and that base treatment of the HF adduct leads to more extensive polymerization than do the other treatments which also serve to remove HF. However, as far as the present investigation is concerned, we have found it sufficient to define our reagent in terms of the procedure used in its synthesis, and in the fluorination reactions described below we have used either the crude, freshly prepared product ("PhHgF · HF") or the material which results on its storage at room temperature (compositions from "PhHgF · HF" through "PhHgF").

The intrusion of reactions 4 and 5 in the synthesis of $PhHgCCl_2F$ via the $PhHgCCl_2Br$/PhHgF reaction was, of course, undesirable. Since $PhHgCCl_2F$ was found to be stable in solution at room temperature, a lowering of the reaction temperature from 80° [where reaction (4) is moderately rapid and reaction (5) is quite rapid] to room temperature was an obvious response to the formation of the by-product $PhHgCCl_3$. Accordingly, in the present study aimed at the synthesis of $PhHgCF_3$ we worked at lower temperatures from the outset.

The initial results indicated that the desired reaction (eqn. 6) did indeed occur at room temperature, but the reaction in practice proved to be highly erratic. In

$$PhHgCBr_3 + 3\ PhHgF \rightarrow PhHgCF_3 + 3\ PhHgBr \qquad (6)$$

some cases, an immediate exothermic (but controllable) reaction would occur, but at other times variable induction periods often followed by vigorous, uncontrollable reactions were encountered. However, a readily controllable reaction which proceeded in a reproducible manner was obtained by the addition of 48% aqueous hydrofluoric acid to the reaction mixture (about 1 ml per 10 mmol of "PhHgF · HF"). In the presence of hydrofluoric acid there is no induction period. The reaction is fairly exothermic and therefore must be carried out in relatively dilute solution and with good temperature control. The fluorination reaction does not occur at temperatures substantially below 0°, proceeds only slowly at 0° and is rapid at room temperature. If it is carried out above 40°, the yield of $PhHgCF_3$ is markedly decreased. The solvents of choice are benzene or toluene, in which $PhHgCF_3$ is soluble. The insoluble solids formed in the fluorination reaction contain phenylmercuric bromide, which can be isolated as the pure solid by Soxhlet extraction. However, it is to be noted that the filtered solids from this reaction smell strongly of hydrogen halide. Such reactions give $PhHgCF_3$ in yields of 60–65%* and this material is obtained in the form of dense, glistening white needles upon crystallization from hexane.

* In calculating yields of $PhHgCF_3$, we have for simplicity's sake assumed the fluorinating agent to be PhHgF · HF in all cases.

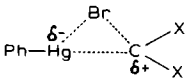
Phenyl(trichloromethyl)mercury was examined as a possible starting material, but was found to be inert to "PhHgF · HF" at room temperature. However, such a reaction carried out at 90° in the presence of 48% HF gave $PhHgCF_3$ in 55% yield. In view of this lesser reactivity of the C–Cl bond, as compared with that of the C–Br bond, it was no surprise to find that $PhHgCCl_2Br$ could be converted to $PhHgCCl_2F$ in good yield by room temperature fluorination with "PhHgF · HF"/48% HF.

Further, it might have been expected that similar selective fluorination of $PhHgCClBr_2$ would give $PhHgCF_2Cl$, a compound which we expected to be an excellent CF_2 source. Such, however, was not the case. The major product formed in the room temperature reaction of phenyl(dibromochloromethyl)mercury with 2 molar equivalents of "PhHgF · HF" was $PhHgCF_3$. Examination of the benzene-soluble solids obtained from a 2/1 "PhHgF · HF"/$PhHgCClBr_2$ reaction by means of their reaction (at 80°) with cyclooctene suggested the presence of $PhHgCF_2Cl$ (formation of 9,9-difluorobicyclo[6.1.0]nonane; $PhHgCF_3$ is unreactive at 80°) and of PhHgCFClBr (formation of 9-chloro-9-fluorobicyclo[6.1.0]nonane) in low yield. In addition, the presence of substantial amounts of unconverted $PhHgCClBr_2$ was indicated by formation of 9-bromo-9-chlorobicyclo[6.1.0]nonane. Also, $PhHgCF_3$ was isolated in substance. In another such experiment carried out in similar fashion with the object of quantitative isolation of $PhHgCF_3$, the yield of this mercurial was 55%, *i.e.*, almost equal to that obtained when $PhHgCBr_3$ was used as starting material. The problem with this reaction is not a matter of the instability of the assumed PhHgCFClBr intermediate and of the desired $PhHgCF_2Cl$ product toward α-elimination of phenylmercuric halide since none of the possible dihalonorcaranes were formed when such a "PhHgF · HF"/$PhHgCClBr_2$ reaction was carried out in the presence of cyclohexene. It would appear that PhHgCFClBr and $PhHgCF_2Cl$ are more reactive toward the fluorinating agent than is the $PhHgCClBr_2$ starting material. Attempted partial fluorination of $PhHgCBr_3$ also was unsuccessful, as was attempted conversion of $PhHgCFBr_2$[11] to $PhHgCF_2Br$. Here again, the only fluorination product which could be isolated was $PhHgCF_3$.

The fluorination of phenyl(trihalomethyl)mercury compounds by "PhHgF · HF" is a remarkable and surprising reaction. Phenylmercuric fluoride is not a conventional fluorinating agent. Although it has been reported to convert acid chlorides to acid fluorides[10], we have found it to be without effect on organic halides such as carbon tetrabromide, bromoform, bromodichloromethane and 7,7-dibromonorcarane. Furthermore, we were unable to fluorinate PhHgCHClBr or $PhHgCHBr_2$ at room temperature or at 70°. Mercuric fluoride is known to be a fluorinating agent[12], but it did not serve in the conversion of $PhHgCBr_3$ to $PhHgCF_3$, its main effect apparently being the cleavage of phenyl groups from mercury.

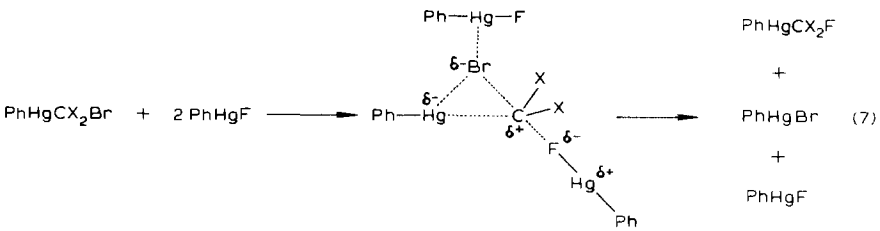
These fluorination reactions take place under conditions which usually do not result in a rapid extrusion of dihalocarbene from $PhHgCCl_2Br$ or $PhHgCBr_3$. The essentially quantitative release of CCl_2 from the former and of CBr_2 from the latter requires 15–18 days at room temperature in the presence of olefins[13]. Thus it is very unlikely that the conversion of these mercurials to $PhHgCCl_2F$ and $PhHgCF_3$, respectively, is a free carbene process. We suggest that the unique "PhHgF · HF" fluorination of phenyl(trihalomethyl)mercurials can best be understood in terms of a mercury-activated nucleophilic substitution at carbon. Evidence obtained in previous studies[14–16] suggests that the transition state for halocarbene extrusion

from (halomethyl)mercury compounds resembles (I). The loosening of the C–Br bond and the generation of a partial positive charge at the methyl carbon atom should



(I)

facilitate attack by phenylmercuric fluoride at carbon, perhaps with assistance from a second molecule of phenylmercuric fluoride. We note that nucleophilic displacement



of chloride ion in $RHgCH_2Cl$ compounds by iodide ion is an extremely facile process which has, in fact, been explained in terms of a transition state in which halide bridging from carbon to mercury plays an important role[17]. Especially suggestive is the reactivity sequence for the fluorination reaction, $PhHgCF_2Br \geqslant PhHgCFBr_2 > PhHgCBr_3 > PhHgCCl_3 > PhHgCHBr_2$ and PhHgCHClBr, which follows exactly the reactivity sequence for these mercury compounds with respect to halocarbene extrusion[11,18] at 80°, excluding of course the as yet unisolated $PhHgCF_2Br$ which must be an intermediate in the fluorination of $PhHgCBr_3$ and $PhHgCFBr_2$.

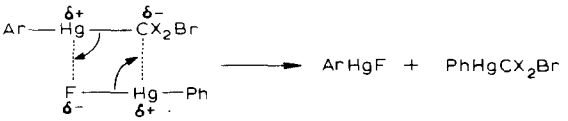
Although it seemed unlikely that fluorinated phenyl(trihalomethyl)mercury compounds were formed by dihalocarbene insertion into the Hg–F bond of phenylmercuric fluoride, an attempt was made to investigate this possibility experimentally. The 1/1 reaction of *p*-tolyl(bromodichloromethyl)mercury with "PhHgF·HF" should give *p*-$MeC_6H_4HgCCl_2F$ (benzene-soluble) and PhHgBr (benzene-insoluble) if a fluorination reaction of the type shown in eqn. (7) is involved, but *p*-MeC_6H_4HgBr (benzene-insoluble) and $PhHgCCl_2F$ (benzene-soluble) if CCl_2 insertion into the Hg–F bond is occurring. When this reaction was carried out in benzene at room temperature, the insoluble arylmercuric halides were found to contain both phenyl and *p*-tolyl groups (via their brominolysis), and the same was true for the benzene-soluble aryl(trihalomethyl)mercury compounds in the reaction mixture. This result is ambiguous in terms of the information sought and, in our opinion, is best explained in terms of the fluorination mechanism indicated in eqn. (7) complicated by substituent exchange between the mercurials present in the system [eqns. (8) and (9)]. Such exchange would represent a competitive but undamaging process in the

$$p\text{-}MeC_6H_4HgCCl_2Br + PhHgF \rightarrow p\text{-}MeC_6H_4HgF + PhHgCCl_2Br \quad (8)$$

$$p\text{-}MeC_6H_4HgCCl_2F + PhHgF \rightarrow p\text{-}MeC_6H_4HgF + PhHgCCl_2F \quad (9)$$

$PhHgCCl_2Br/PhHgF$ system. An exchange of this type, very possibly occurring via a four-center process (II), is not surprising since nucleophilic attack by fluorine as

shown should compete effectively with attack at carbon as indicated in eqn. (7). In support of this suggestion, we note that nucleophilic displacement of CX_3^- from $PhHgCX_3$ compounds is easily effected by charged nucleophiles such as iodide and thiocyanate ion[19].



(II)

The role which the 48% hydrofluoric acid plays in moderating the fluorination reaction is not understood at all. A control experiment established, in any case, that no reaction occurs when $PhHgCBr_3$ and 48% HF in benzene medium are stirred at room temperature in the absence of phenylmercuric fluoride. A better knowledge of the constitution and structure of "PhHgF · HF" might bring an explanation of the beneficial effect of added hydrofluoric acid.

In the meantime, better routes to $PhHgCF_3$ have been developed[20,21], but the fluorination of phenyl(trihalomethyl)mercury compounds with phenylmercuric fluoride represents an intriguing reaction which merits further mechanistic study. Also, the extension of this novel fluorination process to other halomethylmetal compounds is of interest and is under investigation.

EXPERIMENTAL

Preparation of phenylmercuric hydroxide

To a one-liter, three-necked Morton flask equipped with a mechanical stirrer was added 33.6 g (100 mmol) of phenylmercuric acetate (prepared by reaction of Ph_2Hg with $Hg(OAc)_2$ or obtained from Ventron Corp.), 8.0 g (200 mmol) of sodium hydroxide, 200 ml of benzene and 200 ml of distilled water. The reaction mixture was stirred *vigorously* for 90 min at room temperature and then was filtered through a Buchner funnel. The solid thus obtained was washed with 200 ml of benzene, filtered and dried *in vacuo* without application of heat to give 26.6 g (91%) of phenylmercuric hydroxide, m.p. 210–214°. The IR spectrum of this material was identical with that given by Bloodworth for PhHgOH[22]. To be noted are the presence of a strong, broad band near 3250 cm^{-1} and the absence of the intense band at 675 cm^{-1} due to the dehydration product, $Ph_2HgOHgPh_2$.

Preparation of "PhHgF · HF"

Phenylmercuric hydroxide prepared from 0.352 mol of PhHgOAc and 0.68 mol of NaOH was slurried in 350 ml of ethanol in a 600 ml Nalgene beaker and then 30 g of 48% hydrofluoric acid (0.72 mol of HF) was added in one portion. Upon addition of the acid the supernatant layer became opaque and most of the solid at the bottom of the beaker went into solution. The beaker was covered with a watch glass and the contents were stirred magnetically at room temperature for 5½ h. During this time the reaction mixture again became a white slurry. It was stored overnight at 5° and then filtered to yield 66.5 g of product. The filtrate was concentrated at reduced

pressure at room temperature to about 150 ml. This solution was cooled overnight at 5° and filtered to give another 16.5 g of product. The combined yield was 83 g (74%, as PhHgF · HF). On being heated, this material softens, froths and decomposes at 165–170°. (Found: C, 23.00; H, 1.99. $C_6H_6F_2Hg$ calcd.: C, 22.75; H, 1.91%) IR (cm^{-1}, Nujol mull): 3605 m, 3070 w, 3050 w, 1640 m (broad), 1590 w (broad), 1480 s, 1430 s, 1330 w, 1310 m, 1265 w, 1210 s, 1170 w, 1065 m, 1025 m, 1000 m, 915 m, 735 s, 705 s.

A 25.0 mmol sample of this material was slurried in 100 ml of 50% aq. ethanol and titrated to a phenolphthalein endpoint with 0.795 *N* NaOH. The endpoint was taken when the pink color was not discharged after 5 min of thorough agitation. Six such titrations gave an average value of 25.2 mmol of NaOH per 25.0 mmol of sample, with only little scatter. A sample of "PhHgF · HF" (16 mmol) was treated with 33 mmol of NaOH in 50% aq. ethanol for 1 h and then was filtered and air-dried. Its IR spectrum (Nujol mull) showed the absence of the bands at 3605 and 1210 cm^{-1}, but otherwise the spectrum was almost identical with that of "PhHgF · HF". The IR spectrum definitely indicated that this material was not PhHgOH. The base-treated product did not melt below 300°, and its analysis indicated the composition PhHgF. (Found: C, 24.27; H, 1.87; F, 6.23; Hg, 67.19; C_6H_5FHg calcd.: C, 24.29; H, 1.70; F, 6.40; Hg, 67.61%.) In another series of experiments, 25.0 mmol samples of "PhHgF · HF" in 100 ml of 50% aq. ethanol were treated with 50 ml of 0.780 *N* NaOH. The resulting mixture was stirred for 1 h and then treated with 50 ml of 0.680 *N* nitric acid, stirred and filtered. The filtered solid was washed carefully with 95% ethanol. The fluoride ion content of the combined filtrate and washings then was determined by the method of Allen and Furman[23]. For several samples, an average of 27.9 mmol of fluoride ion per mmol of "PhHgF · HF" was determined, with wider scatter (22.3 to 31.0 mmol F^-/25.0 mmol "PhHgF · HF") than in the case of the H^+ ion determinations. This, however, most likely reflects the cumbersome analytical procedure involved.

Another sample of "PhHgF · HF" was recrystallized from chloroform. The resulting solid also analyzed correctly for PhHgF. (Found: C, 24.38; H, 1.96; F, 6.15; Hg, 67.25%.) About 2.4 g of "PhHgF · HF" dissolved in 400 ml of boiling chloroform.

Reaction of phenyl(tribromomethyl)mercury with "PhHgF · HF": the preparation of phenyl(trifluoromethyl)mercury

A three-liter, three-necked Morton (creased) flask equipped with a mechanical stirrer, a gas exit tube and a stopper was charged with 105 g (0.33 mol) of "PhHgF · HF", 1 liter of benzene and a solution of 52.9 g (0.10 mol) of phenyl(tribromomethyl)-mercury[24] in 1 liter of benzene. This mixture was stirred *vigorously* and a mixture of 40 ml of toluene and 10 ml of 48% aqueous hydrofluoric acid, chilled to 0°, was added rapidly. The reaction mixture was stirred at room temperature for 30 min. During this time a gas appeared to be evolved. Filtration through a coarse fritted glass funnel gave 94 g of white solid (caution: hydrogen halide fumes). The latter was washed with 300 ml of benzene. The combined filtrate and washings were dried over anhydrous $MgSO_4$ and evaporated at reduced pressure. The residue was crystallized from hot hexane (ca. 25 ml per g) to give a first crop of 20.4 g, m.p. 141–143°, and a second crop, 2.0 g, m.p. 135–140°. The total yield, 22.4 g, represented a

65% yield, based on $PhHgCBr_3$. Another such reaction carried out on the same scale gave $PhHgCF_3$ in 64% yield.

Two further recrystallizations from hexane did not raise the m.p. from 141–143°. (Found: C, 24.27; H, 1.46; F, 16.25; Hg, 58.28. $C_7H_5F_3Hg$ calcd.: C, 24.35; H, 1.45; F, 16.44; Hg, 57.86%.) IR (cm^{-1}, KBr pellet): 3060 s, 3050 s, 3020 m, 2990 w, 2270 w, 2160 w, 2050 w, 2030 w, 1960 w, 1950 m, 1890 w, 1840 w, 1810 m, 1760 w, 1650 m, 1590 m, 1580 m, 1570 m, 1485 s, 1435 s, 1370 w, 1335 m, 1305 m, 1225 m, 1195 s, 1160 vs, 1150–1140 vs, 1110 s, 1080 vs, 1060–1000 vs, 915 s, 860 w, 750 s, 700 s. NMR: ^1H (Varian A60, in CCl_4): δ 7.20 ppm (s); ^{19}F (Hitachi Perkin Elmer R-20B at 56.446 MHz, in acetone solution): 79.0 ppm downfield from internal 1,1,2,2-tetrafluoro-3,3,4,4-tetrachlorocyclobutane [s, J(Hg–F) 1027 Hz].

In another reaction carried out with 60 mmol of $PhHgCBr_3$, the benzene-insoluble solids (64.0 g *vs.* 64.5 g expected PhHgBr) were examined. On being heated, a sample softened and turned tan at 270–280° but did not melt completely up to 300°. A 10 g sample was Soxhlet extracted with benzene to give 7.0 g of slightly impure PhHgBr, m.p. 275–280° with residue. The $PhHgCF_3$ yield in this reaction was 72%, m.p. 140–143°.

Reaction of phenyl(trichloromethyl)mercury and "PhHgF · HF"

A procedure identical to that described above was used, with the exception that the reaction mixture was heated slowly over the course of 30 min to 90° and stirred at that temperature for another 60 min. The same work-up procedure was used. In this manner, a reaction between 7.9 g (20 mmol) of $PhHgCCl_3$[24] in 80 ml of toluene, 18.4 g (58 mmol) of "PhHgF · HF" in 50 ml of toluene and 1 ml of 48% HF yielded 3.65 g (55%) of $PhHgCF_3$, m.p. 139–143°.

Another reaction was carried out on the same scale at room temperature. Filtration from 19.1 g of solid was followed by evaporation of the filtrate at reduced pressure. The residue was crystallized from hexane to give 5.80 g (72% recovery) of $PhHgCCl_3$, m.p. 111–113°.

Reaction of phenyl(bromodichloromethyl)mercury with "PhHgF · HF"

The procedure described for the reaction with $PhHgCBr_3$ was used in the reaction of 41.3 g (130 mmol) of "PhHgF · HF" in 220 ml of benzene, 44.0 g (100 mmol) of phenyl(bromodichloromethyl)mercury[24] in 500 ml of benzene and 3.3 ml of 48% HF in 15 ml of toluene. The same work-up procedure was used. Crystallization of the benzene-soluble solid from 800 ml of hot hexane gave 16.5 g of white, crystalline solid, m.p. 91–94°, as a first crop, and further crops of 5.7 g (m.p. 91–94°) and 1.6 g (m.p. 90–94°), for a combined yield of 22.8 g (60%) of $PhHgCCl_2F$. The reported[8] m.p. is 98–100°. The IR spectrum of the product was identical to that of an authentic sample of $PhHgCCl_2F$.

The $PhHgCCl_2F$ prepared in this manner reacted with sodium iodide (1/1 molar ratio) in 1,2-dimethoxyethane in the presence of cyclohexene (1 h at room temperature, 3 h at reflux) to give 7-fluoro-7-chloronorcarane in 89% yield. The procedure used is described in ref. 8.

Reaction of phenyl(dibromochloromethyl)mercury with "PhHgF · HF" (1/2 molar ratio)

The usual fluorination procedure was followed in the reaction of 31.7 g

(0.1 mol) of "PhHgF · HF" and 24.2 g (50 mmol) of phenyl(dibromochloromethyl)-mercury[24] in 800 ml of benzene in the presence of 26.5 g (0.25 mmol) of cyclooctene and 10 ml of 48% HF in 40 ml of toluene, at room temperature for 3 h. Filtration gave 40 g of benzene-insoluble solids whose subsequent brominolysis gave 106.1 mmol of bromobenzene (by GLC). The filtrate was trap-to-trap distilled at 0.05 mm Hg (pot temperature to 25°). The solid residue was charged into a 100 ml, three-necked flask equipped with a magnetic stirring unit and a reflux condenser topped with a nitrogen inlet tube together with 15.7 g (0.15 mol) of cyclooctene and 50 ml of dry benzene. The reaction mixture was stirred and heated for 10 h at reflux. Filtration was followed by brominolysis of the 7.6 g of white solid thus removed. Bromobenzene, 23.3 mmol by GLC yield determination, was obtained, indicating the presence of 23.3 mmol of phenylmercuric halide. The filtrate from this reaction was trap-to-trap distilled at 0.05 mm Hg, leaving as a residue 3.5 g of crude $PhHgCF_3$, m.p. 139–144°, which TLC showed to be free of other soluble mercury compounds. Brominolysis of this sample gave 9.5 mmol of bromobenzene. The accounting of initially charged phenyl groups thus is 138.8 mmol (92%). The trap-to-trap distillates from the fluorination reaction and from the reaction just described were combined and concentrated by distillation at atmospheric pressure. The liquid which remained was trap-to-trap distilled at 0.05 mm Hg (pot temperature to 80°) and the distillate was examined by GLC (F & M 700, 6 ft. Dow Corning DC–200 silicone oil, at 140°). Four 9,9-dihalobicyclo[6.1.0]nonanes were present: the difluoro, chlorofluoro, bromofluoro and bromochloro compounds. GLC yield determination indicated the presence of 4.5 mmol of the chlorofluoro and 3.2 mmol of the difluoro compounds; the bromofluoro compound was present in only trace amount and the bromochloro compound was present in larger quantity (10.5 mmol). The presence of the products implies the presence during the course of the fluorination reaction of PhHgCFClBr, $PhHgCFBr_2$, $PhHgCF_2X$ (X = Cl or Br) in addition to the isolated $PhHgCF_3$ and unreacted $PhHgCClBr_2$.

In another reaction carried out with 20 mmol of $PhHgCClBr_2$ and 60 mmol of "PhHgF · HF" in 50 ml of benzene in the presence of 1 ml of 48% HF at room temperature for $1\frac{1}{4}$ h phenyl(trifluoromethyl)mercury, m.p. 141–144°, was obtained in 55% yield.

Reaction of phenyl(dibromofluoromethyl)mercury with "PhHgF · HF"

The usual fluorination conditions were used in the reaction of 4.64 g (10 mmol) of $PhHgCFBr_2$[11] and 3.5 g (11 mmol) of "PhHgF · HF" in 150 ml of benzene in the presence of 1 ml of 48% HF and 50 ml of 1-heptene. The olefin was added because $PhHgCFBr_2$ releases its CFBr at room temperature[11] and it was desirable to monitor this competing process. The reaction was carried out at room temperature and was allowed to proceed for three days. Filtration removed 7.1 g of solid which were Soxhlet extracted with benzene to give 5.6 g of PhHgBr, m.p. 280–284°. The filtrate was trap-to-trap distilled at room temperature and 0.05 mm Hg. Extraction of the residue and subsequent evaporation of the extracts gave white solid which was crystallized from hexane. Phenyl(trifluoromethyl)mercury, 0.6 g (35% based on $PhHgCFBr_2$), m.p. 140–144°, thus was obtained. The distillate was examined by GLC (F & M 700, 6 ft. DC–200, at 90°, conditions which cleanly separate 1,1-difluoro- and 1-bromo-1-fluoro-pentylcyclopropane) showed the presence only of 1-bromo-1-fluoro-pentylcyclopropane[11] in 23% yield.

Reaction of p-tolyl(bromodichloromethyl)mercury with "PhHgF · HF"

p-Tolyl(bromodichloromethyl)mercury was prepared by our improved procedure for aryl(trihalomethyl)mercurials[24]. The product obtained in 81% yield (0.1 mol scale reaction) had m.p. 126–127° (dec.). (Found: C, 20.83; H, 1.31. $C_8H_7BrCl_2Hg$ calcd.: C, 21.14; H, 1.55%.) NMR (CS_2; Varian A60): 7.10 (s, 4 H, aryl) and 2.33 ppm (s, 3 H, CH_3). This compound had been prepared previously by the original phenyl(trihalomethyl)mercurial procedure and a m.p. of 116–117° (dec.) had been reported[25].

The usual fluorination procedure was used in the reaction of 6.55 g (20.8 mmol) of "PhHgF · HF" and 9.1 g (20 mmol) of *p*-tolyl(bromodichloromethyl)-mercury in 125 ml of toluene in the presence of 1 ml of 48% HF at room temperature for 2 h. The reaction mixture was filtered to give 8.6 g of white solid. Brominolysis showed this to contain 12.1 mmol of phenyl groups and 9.55 mmol of *p*-tolyl groups. The filtrate was evaporated and the residual solids also were brominated. The yields of bromobenzene and *p*-bromotoluene obtained indicated the presence of 6.83 mmol of phenyl groups and 7.87 mmol of *p*-tolyl groups in the benzene solubles.

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