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HALOMETHYL-METAL COMPOUNDS

LVII. A CONVENIENT SYNTHESIS OF ARYL(TRIFLUOROMETHYL)MERCURY COMPOUNDS*

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SUMMARY

Phenyl(trifluoromethyl)mercury, a useful difluorocarbene precursor, is conveniently prepared by the sequence: $HgO \rightarrow Hg(O_2CCF_3)_2 \rightarrow CF_3HgO_2CCF_3 \rightarrow CF_3HgBr \rightarrow PhHgCF_3$. The last step involves a substituent exchange reaction between CF_3HgBr and diphenylmercury. Similar substituent exchanges between CF_3HgI, CF_3HgCl and $CF_3HgO_2CCF_3$ and diphenylmercury are described. A recent report (*J. Organometal. Chem.*, 36 (1972) 227) that fluorophenyl(trifluoromethyl)mercury compounds can be prepared by decarboxylation of the respective fluorophenylmercuric trifluoroacetates in 1,2-dimethoxyethane at 60–70° is shown to be incorrect by comparison of the claimed products with authentic *m*- and *p*-$FC_6H_4HgCF_3$ and $FC_6H_4HgO_2CCF_3$. ^{19}F NMR data for a number of CF_3–Hg compounds are reported.

INTRODUCTION

Our investigations have shown phenyl(trifluoromethyl)mercury to be an excellent difluorocarbene precursor[3]. We have reported the preparation of this mercury reagent in good yield by the fluorination of phenyl(tribromomethyl)mercury with PhHgF/HF[3,4]. This procedure, however, suffers from the fact that neither of the organomercury starting materials is available commercially, and furthermore, phenylmercuric hydroxide first must be prepared in good purity for the phenylmercuric fluoride preparation. In order for phenyl(trifluoromethyl)mercury to be a really useful CF_2 reagent, a simpler and cheaper synthesis was required. In this paper we address ourselves to this question.

Trifluoromethylmercury compounds, notably CF_3HgI and $(CF_3)_2Hg$, had been prepared as early as 1948[5,6]. These preparations, however, are based on sealed tube reactions of elemental mercury with the gaseous (and expensive) iodotrifluoromethane and for this reason were not very attractive for larger scale application.

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* For part LVI see ref. 1; Preliminary communication see ref. 2.

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Another preparation of bis(trifluoromethyl)mercury was even less practical, using the reaction of $(CF_3)_3P$ with mercuric oxide[7].

A third published route to trifluoromethylmercury derivatives seemed more promising. The decarboxylation of mercuric salts of carboxylic acids is a well-known route to compounds with a C–Hg bond[8]. When R in $(RCO_2)_2Hg$ is an alkyl or a simple aryl group, the decarboxylation process requires radical initiation[9], but there are many examples in which R is an electronegative organic substituent where decarboxylation can be effected thermally, neat or in an appropriate solvent[8]. An example of recent interest is the thermal decarboxylation in refluxing pyridine solution of various mercury(II) derivatives of pentafluorobenzoic acid to give C_6F_5–Hg compounds[10]. The 1,10-phenanthroline and 2,2′-bipyridine complexes of mercuric trifluoroacetate have been shown to undergo decarboxylation to give $(CF_3)_2Hg \cdot L$ complexes when heated at temperatures around 200°[11]. However, of greater potential interest for our purposes was a du Pont patent[12] which described the high temperature conversion of $(CF_3CO_2)_2Hg$ to $CF_3HgO_2CCF_3$. It is this reaction which is the first step of the improved synthesis of $PhHgCF_3$ which we report here.

RESULTS AND DISCUSSION

The procedure outlined in the Aldrich patent[12] serves well in the synthesis of $CF_3HgO_2CCF_3$ when carried out with due care. The product, obtained (in 50–60% yield), which melts over the range 93–100°, is sufficiently pure for further use. A sample recrystallized from chloroform melted at 116–117.5° and was obtained in analytical purity as white, hygroscopic needles. Attempted decarboxylation of $CF_3HgO_2CCF_3$ to $(CF_3)_2Hg$ was not successful. Phenylmercuric trifluoroacetate also did not undergo thermal decarboxylation; at 300° it refluxed vigorously but did not evolve carbon dioxide.

Trifluoromethylmercuric trifluoroacetate did not serve as a useful source of CF_2 when our sodium iodide displacement procedure[3,13,14] was applied[15], and for this reason its conversion to $PhHgCF_3$, a compound of proven utility, was investigated.

An oft-encountered reaction in organomercury chemistry which, depending on the circumstances, can either be very useful or a nuisance, is that of substituent exchange (redistribution, disproportionation, symmetrization)[16]. A redistribution reaction between $CF_3HgO_2CCF_3$ and diphenylmercury was readily effected (eqn. 1). However, the yields of phenyl(trifluoromethyl)mercury were only 50–60% and

$$Ph_2Hg + CF_3HgO_2CCF_3 \xrightarrow{\text{hexane, } 80^\circ} PhHgCF_3 + PhHgO_2CCF_3 \tag{1}$$

column chromatography was required in order to obtain pure material. A cleaner separation and higher yields were expected in reactions in which the trifluoromethylmercuric halides were used as starting materials since the phenylmercuric halides are poorly soluble in common organic solvents at moderate temperatures (eqn. 2). Accordingly, the conversion of $CF_3HgO_2CCF_3$ to the chloride, bromide and iodide

$$Ph_2Hg + CF_3HgX \longrightarrow PhHgCF_3 + PhHgX \tag{2}$$

derivatives was carried out as shown in eqns. 3 and 4. Each of the three halides was then heated with an equimolar quantity of diphenylmercury to give $PhHgCF_3$ and

$$CF_3HgO_2CCF_3 \xrightarrow{NaOH,\ H_2O} [CF_3HgOH] \xrightarrow[(X=Cl,\ Br)]{conc.\ HX} CF_3HgX \quad (3)$$

$$CF_3HgO_2CCF_3 \xrightarrow[Et_2O]{NaI \cdot 2H_2O \text{ in DME}} CF_3HgI \quad (4)$$

the respective phenylmercuric halide. The reaction with CF_3HgBr gave consistently higher yields of $PhHgCF_3$ (>75%) than the reactions with CF_3HgCl and CF_3HgI.

The preferred route to $PhHgCF_3$ thus is summarized by eqns. 5–8.

$$2\ CF_3CO_2H + HgO \longrightarrow Hg(O_2CCF_3)_2 \qquad \text{(ref. 12, or better, ref. 17)} \quad (5)$$

$$Hg(O_2CCF_3)_2 \xrightarrow{300^\circ} CF_3HgO_2CCF_3 + CO_2 \quad (6)$$

$$CF_3HgO_2CCF_3 \xrightarrow{NaOH,\ H_2O} \xrightarrow{conc.\ HBr} CF_3HgBr \quad (7)$$

$$Ph_2Hg + CF_3HgBr \longrightarrow PhHgCF_3 + PhHgBr \quad (8)$$

This route has the advantage that relatively cheap and readily available starting materials are used* and that these reactions all are easily effected and can all be carried out on a fairly large scale. Phenyl(trifluoromethyl)mercury thus can be obtained in large amounts in good purity as a crystalline, nonvolatile solid which is very stable thermally. It is not affected by light and atmospheric oxygen or moisture and thus can be stored indefinitely under ambient conditions. It is well soluble in common organic solvents and serves excellently as a source of CF_2 on treatment with anhydrous sodium iodide in benzene medium[3,15].

Subsequent research[15] showed that CF_3HgI (but not CF_3HgCl or CF_3HgBr) is a good CF_2 precursor (via the NaI procedure). However, CF_3HgI does not represent the ideal organomercury CF_2 reagent: it is volatile, hence organomercury toxicity can be a problem; it is decomposed by exposure to light (formation of red mercuric iodide) and in general has a poor shelf life. Phenyl(trifluoromethyl)mercury definitely is the reagent of choice.

EPILOGUE

Upon completion of the work described above[18], Kravtsov *et al.*[19] reported a study of the ^{19}F NMR spectra of some *m*- and *p*-fluorophenylmercurials, including the new compounds *m*-$FC_6H_4HgCF_3$ and *p*-$FC_6H_4HgCF_3$. As described, the preparation of these compounds was extremely simple in concept and in practice, involving merely the reaction sequence shown in eqns. 9 and 10. The 1,2-dimethoxyethane (DME) solutions of the two arylmercuric trifluoroacetates simply were heated

$$ArHgOH + CF_3CO_2H \xrightarrow{EtOH} ArHgO_2CCF_3 + H_2O \quad (9)$$

$$ArHgO_2CCF_3 \xrightarrow[60-70^\circ]{MeOCH_2CH_2OMe} CO_2 + ArHgCF_3 \quad (10)$$

"until the evolution of CO_2 ceased", the solvent was removed in vacuo and the solid residue was treated with water, dried and crystallized from cyclohexane. Melting

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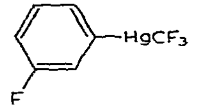
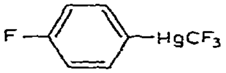
* Diphenylmercury is readily prepared by symmetrization of commercially available (Ventron Corp.) phenylmercuric acetate or chloride.

points, C, H, analyses and the chemical shifts of the fluorine atoms on the aryl ring were the only characterizing data provided:



m.p. 93–94°. (Found: C, 23.68; H, 1.34. Calcd.: C, 23.05; H, 1.10%).



m.p. 100–101°. (Found: C, 23.02; H, 1.39. Calcd.: C, 23.05; H, 1.10%).

In particular, no infrared spectra, fluorine or mercury analyses and ^{19}F chemical shifts for the CF_3 groups (and their expected ^{199}Hg–^{19}F spin–spin coupling constants) were given.

This simple procedure has obvious advantages over our route to $PhHgCF_3$ as outlined in eqns. 5–8, but this report[19], in our opinion, lacked credibility in that the reactions reported seemed to us inconsistent with the previously demonstrated high thermal stability of mercury(II) trifluoroacetates[11,12,20]. In view of these reservations concerning the chemistry reported, we undertook to repeat the preparations of these two fluorophenylmercurials.

In our hands, the reaction of *m*-fluorophenylmercuric hydroxide with trifluoroacetic acid in ethanol gave *m*-$FC_6H_4HgO_2CCF_3$, m.p. 93–95° (crude material), 96–97.5° (after recrystallization from cyclohexane). All attempts to decarboxylate this compound by heating its solution in DME at reflux for times ranging from several hours to several days were unsuccessful. No carbon dioxide was evolved (test with $Ba(OH)_2$ solution) and the trifluoroacetate was recovered in essentially quantitative yield. Similarly, *p*-fluorophenylmercuric trifluoroacetate, m.p. 101–103° (crude material), 102–103.5° (after recrystallization from CCl_4), was stable to decarboxylation under these conditions. There is no doubt of the identity of these compounds. In their infrared spectra in CCl_4 very strong bands at 1684 and 1686 cm^{-1}, respectively, assignable to the C=O stretching frequency, were apparent and no ^{199}Hg–^{19}F spin–spin coupling involving the CF_3 groups was observed in their ^{19}F NMR spectra. In this connection, we note that C and H analyses are of dubious value to the problem in hand: $FC_6H_4HgO_2CCF_3$ calcd.: C, 23.51; H, 0.99%, while $FC_6H_4HgCF_3$ calcd.: C, 23.05; H, 1.10%. Analyses for mercury or fluorine would be more decisive in distinguishing between these two compounds.

To resolve this question without doubt, we prepared *m*- and *p*-fluorophenyl(trifluoromethyl)mercury by the reaction of the respective diarylmercurial with trifluoromethylmercuric bromide. Such a reaction between $(m\text{-}FC_6H_4)_2Hg$ and CF_3HgBr gave *m*-$FC_6H_4HgCF_3$ in 68% yield. This product had a m.p. of 127–128° after purification by sublimation. Its ^{19}F NMR spectrum showed the CF_3 group as a singlet with mercury satellites, $J(^{199}Hg\text{–}^{19}F) = 1046$ Hz. A similar reaction using $(p\text{-}FC_6H_4)_2Hg$ gave *p*-$FC_6H_4HgCF_3$ in 59% yield, m.p. 104–105° (from hexane). Its ^{19}F NMR spectrum also showed the CF_3 resonance with mercury satellites, $J(^{199}Hg\text{–}^{19}F) = 1030$ Hz. In the infrared spectrum of neither of these compounds was there a strong band in the expected C=O region. The mass spectra of both compounds showed the expected molecular ions, $FC_6H_4HgCF_3^+$, and the fragmentation patterns were those to be expected for such structures. As expected for trifluoromethylmercurials, both compounds reacted with sodium iodide in the presence of olefins to give *gem*-difluorocyclopropanes.

The results of these experiments indicate the Russian workers did, in fact, not obtain the $ArHgCF_3$ compounds claimed in their reactions, rather that they were dealing with the arylmercuric trifluoroacetates. The observations of previous workers concerning the high thermal stability of mercury(II) trifluoroacetates and the high temperatures required for their decarboxylation are thus without exception.

EXPERIMENTAL

General comments

Infrared spectra were obtained using Perkin–Elmer Model 257 and 457A grating infrared spectrophotometers, proton NMR spectra using a Varian Associates T60 spectrometer. Proton chemical shifts are given in δ units, ppm downfield from TMS. The ^{19}F NMR spectra were obtained using a Hitachi–Perkin–Elmer R-20B spectrometer at 56.446 MHz and are summarized in Table 1. Mass spectral data was obtained using a Hitachi–Perkin–Elmer RMU-6 mass spectrometer (70 eV source voltage). Only those ions involving $^{12}C^{19}F^{202}Hg$ isotope combinations are reported.

TABLE 1

^{19}F NMR SPECTRA OF SOME CF_3–Hg AND CF_3CO_2–Hg COMPOUNDS

Compound[a]	$\delta(CF_3)$ (ppm)[b]	$J(^{199}Hg-^{19}F)$ (Hz)[c]	$\delta(CF_3CO_2)$ (ppm)[b]	$\delta(FC_6H_4)$ (ppm)[b]
$PhHgCF_3$	124.7	1008		
m-$FC_6H_4HgCF_3$	124.5	1046		50.2
p-$FC_6H_4HgCF_3$	124.6	1031		53.6
$(CF_3)_2Hg$	126.0	1250		
CF_3HgCl	130.9	1920[c]		
CF_3HgBr	130.4	1800		
$CF_3HgO_2CCF_3$	132.4	2208	88.9	
m-$FC_6H_4HgO_2CCF_3$			88.1	51.5
p-$FC_6H_4HgO_2CCF_3$			88.4	53.0

[a] In $CHCl_3$ solution. [b] Downfield from internal hexafluorobenzene, ±0.1 ppm. [c] ±4 Hz.

In determining the relative abundances of the ions in the mass spectra, the summation of the abundances of all seven mercury isotopes was approximated by multiplying the abundances of the ^{202}Hg isotope-containing ions by the factor 100/29.8, a procedure shown by Bryant and Kinstle[21] to serve well in organomercury mass spectroscopy. The data given are ion *m/e* (rel. intensity in %). C and H analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, mercury and fluorine analyses by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, Germany.

Preparation of trifluoromethylmercuric trifluoroacetate[12]

Because the patent may not be generally available, we describe this preparation in detail.

To a stirred slurry of 43.4 g (0.20 mol) of mercuric oxide and 200 ml of distilled water in an evaporating dish was added 50 g (0.45 mol) of trifluoroacetic acid. The mixture became homogeneous with complete solution of the mercuric oxide. The dish was placed on the steam bath and most of the water was evaporated, leaving an opaque gel. The slightly damp gel was placed in a 100 ml Pyrex distillation flask equipped with a distillation head and take-off tube that were wrapped with Nichrome wire and heated by this means to about 100°. The take-off tube led into a three-necked receiving flask equipped with a condenser and immersed in ice. The distillation pot was heated with a Bunsen burner. After the solid had melted, the pot was heated cautiously while the decarboxylation began and the residual water passed over. The vigorous frothing caused by the decarboxylation was controlled by selective heating with the burner. When the vapor temperature had reached 220°, heating was discontinued and the water was removed from the receiver. (At this point it becomes important to ensure that path to the receiver is maintained at 100°: significantly lower temperatures will result in plugging of the path from pot to receiver with subsequent violent rupture of the apparatus.) During the initial heating, the pot contents turned yellow; on further heating, they became brown and finally yellow-green. Heating of the pot was resumed after the receiver had been changed. Product passed over with a vapor temperature of 270–280°. Once this distillation is in progress, it should not be interrupted. Distillation was stopped when the distillation pot contained a solid yellow-green mass. The product solidified in the ice-cooled receiver to give a white solid. Upon completion of the reaction, this solid was stored over sulfuric acid to remove any residual water. A total of 40 g (53%) of crude $CF_3HgO_2CCF_3$ was obtained in this manner. The white, crystalline solid is hygroscopic. It may be used (*i.e.*, eqn. 1, 3 or 4) without further purification and its behavior on being heated (softens at 85–93°, melts at 93–100° to an opaque liquid) agreed with that reported by Aldrich[12]. A small sample was recrystallized from chloroform to give white, hygroscopic needles with m.p. 116–117.5°. (Found: C, 9.68. $C_3O_2F_6Hg$ calcd.: C, 9.42%.) IR (Nujol mull): 1675s, 1210s, 1180s, 1140s, 1090s, 1040m, 880m, 860m, 825m, 805m, 745m and 740m cm^{-1}.

Preparation of trifluoromethylmercuric halides

(*a*) *Trifluoromethylmercuric iodide.* A 500 ml, three-necked flask equipped with a magnetic stirring unit, a reflux condenser and an addition funnel was charged with 15.3 g (40 mmol) of trifluoromethylmercuric trifluoroacetate and 200 ml of diethyl ether. The solution was heated to reflux and 8.2 g (44 mmol) of $NaI \cdot 2H_2O$ dissolved in the minimum amount of DME (from a freshly opened bottle but not distilled) was added dropwise with stirring over a 1 h period. The reaction mixture was heated at reflux for 30 min, cooled to room temperature and treated with 40 ml of 1*M* HCl with vigorous stirring. The organic layer was separated and extracted with 50 ml of water. The aqueous phase was extracted with three 50 ml portions of ether. The combined ether solution was dried and evaporated to dryness in vacuo. The residue was redissolved in ether and separated from a small amount of red HgI_2. After the ether solution had been evaporated, the residue was sublimed at 90° (0.1 mm) to give 12.3 g (78%) of CF_3HgI, m.p. 105–106.5°. Three further sublimations gave pure material, m.p. 112–114°; lit.[5] m.p. 112.5°. IR (CCl_4): 1125s, 1105s, 1015m and 975m cm^{-1}.

(*b*) *Trifluoromethylmercuric chloride.* Trifluoromethylmercuric trifluoroacetate, 38.2 g (0.10 mol) was dissolved in 50 ml of water in a 250 ml beaker and 6.0 g (0.15 mol) of NaOH in 15 ml of water was added. The mixture was stirred for 5 min to give a dark green-gray slurry with a pH of 13. This solution was treated with 20 ml of conc. HCl. The gray slurry which was obtained (pH 3) was filtered from 0.2 g of gray solid. The filtrate was evaporated to dryness at room temperature. The white solid residue was extracted with three 100 ml portions of boiling ether. The extracts were evaporated at room temperature to 50 ml and then heated to boiling after the addition of 150 ml of hexane. Cooling to 10° gave a white solid; several further crops were obtained by this procedure, to give 24.1 g (79%) of CF_3HgCl, m.p. 75–76° (sealed tube); lit.[6a] m.p. 76°. Sublimation at 90° (1 atm) did not raise the m.p. IR (CCl_4): 1550m, 1250w, 1220w, 1130s, 1110s, 1010w, 980w and 725w cm^{-1}.

(*c*) *Trifluoromethylmercuric bromide.* Using the procedure described in (b), 38.2 g (0.10 mol) of $CF_3HgO_2CCF_3$ in 25 ml of water and 6.0 g (0.15 mol) of NaOH in 15 ml of water were mixed and the resulting slurry was treated with 35 ml of 48% HBr (to pH 3). Similar work-up and crystallization procedures gave 27.6 g (86%) of CF_3HgBr, m.p. 87.5–90° (sealed tube). A sublimation at 120° (1 atm) raised the m.p. to 88.5–90° (sealed tube). (Found: C, 3.50; Br, 22.96. CF_3BrHg calcd.: C, 3.44; Br, 22.86%.) IR (CCl_4): 1550m, 1250w, 1230w, 1130s, 1100s, 1005w, 980w and 720m cm^{-1}.

Reactions of diphenylmercury with CF_3HgX compounds

(*a*) *Trifluoromethylmercuric iodide.* A 100 ml three-necked flask equipped with a reflux condenser, a magnetic stirring unit and a nitrogen inlet tube was charged with 6.15 g (15.5 mmol) of CF_3HgI, 5.31 g (15 mmol) of diphenylmercury and 50 ml of dry benzene. The mixture was stirred at reflux for 3 h, cooled and filtered to remove 5.5 g (88%) of phenylmercuric iodide, m.p. 272–275°. The filtrate was evaporated at reduced pressure and the residue was crystallized from hexane to give 3.9 g (75%) of phenyl(trifluoromethyl)mercury, m.p. 141–143°, identical in all respects with authentic material prepared by fluorination of phenyl(tribromomethyl)mercury[3,4]. During the isolation of $PhHgCF_3$, another 0.3 g of PhHgI was collected, for a total yield of 95%.

(*b*) *Trifluoromethylmercuric chloride.* The reaction between 3.34 g (11 mmol) of CF_3HgCl and 3.80 g (11 mmol) of diphenylmercury in 30 ml of benzene was carried out as in (a). Filtration gave 3.45 g (100%) of phenylmercuric chloride, m.p. 258–261°. Work-up of the filtrate resulted in isolation of 2.3 g (62%) of $PhHgCF_3$, m.p. 140–143°.

(*c*) *Trifluoromethylmercuric bromide.* The reaction between 3.84 g (10.8 mmol) of CF_3HgBr and 3.80 g (11 mmol) of diphenylmercury in 30 ml of benzene, carried out as in (a) above, gave 3.80 g (97%) of phenylmercuric bromide, m.p. 280–283°, and 2.81 g (77%) of $PhHgCF_3$.

(*d*) *Trifluoromethylmercuric trifluoroacetate.* A mixture of 8.4 g (22 mmol) of $CF_3HgO_2CCF_3$ and 7.1 g (20 mmol) of diphenylmercury in 50 ml of hexane was heated at reflux for 5 h. The hot reaction mixture was composed of two layers at the end of this time. The lower layer was an oil composed mostly of phenylmercuric trifluoroacetate, while the upper layer was a hexane solution of mostly $PhHgCF_3$. The hot layers were separated by decantation. Rinsing the bottom layer with several portions of boiling hexane was followed by evaporation of the combined hexane solutions. The crude solid was chromatographed on a 10 in. × 45 mm column of silicic acid using dichloromethane as eluent. The appearance of $PhHgCF_3$ in the eluate was detected by TLC[22]. The yield of pure $PhHgCF_3$, m.p. 141–143°, was 3.7 g (54%).

The bottom layer of the reaction mixture was extracted with three 100 ml portions of hot benzene. The benzene extracts were evaporated to leave a solid residue which was crystallized from benzene/hexane to give 4.8 g (62%) of $PhHgO_2CCF_3$, m.p. 119–121.5°. Two crystalline modifications of this compound have been reported: needles, with m.p. 115.5–116.5°, and cubes, with m.p. 127–128°, and these forms are readily interchangeable[23]. The material isolated in this experiment showed a m.p. of 125–127° upon a second heating in the m.p. capillary. The IR spectrum was identical with that of an authentic sample.

Preparation of arylmercuric trifluoroacetates

(*a*) *m-Fluorophenylmercuric trifluoroacetate.* To a solution of 4.61 g (14.7 mmol) of crude *m*-fluorophenylmercuric hydroxide[19] in 45 ml of ethanol was added 2.04 g (17.9 mmol) of trifluoroacetic acid in 5 ml of ethanol. The reaction mixture was stirred for 10 min, filtered through Celite, and the solvent was removed at reduced pressure to leave the crude product, m.p. 93–95°. Recrystallization of this material from 30 ml of cyclohexane gave 3.64 g (61%) of pure *m*-$FC_6H_4HgO_2CCF_3$, m.p. 96–97.5°. (Found: C, 23.57; H, 1.04; F, 18.32; Hg, 49.44. $C_8H_4O_2F_4Hg$ calcd.: C, 23.51; H, 0.99; F, 18.59; Hg, 49.08%). IR (in CCl_4): 3060w, 1684s, 1585m, 1576m, 1560sh, 1473m, 1459(sh), 1417m, 1402(sh), 1264w, 1214s, 1182s, 1166s, 1002w, 854m, 752w and 682m cm^{-1}.

Attempts to decarboxylate this material were unsuccessful. In a typical experiment, a dry, 100 ml flask equipped with a reflux condenser topped with a nitrogen inlet and a magnetic stirring assembly was charged with 2.75 g of *m*-$FC_6H_4HgO_2CCF_3$ and 30 ml of dry 1,2-dimethoxyethane. The reaction mixture was heated for 24 h at reflux. Passage of the exit gases into $Ba(OH)_2$ solution did not cause precipitation of barium carbonate at any time. Removal of the solvent at reduced pressure gave at first a glassy residue which changed to a white crystalline solid (2.72 g, m.p. 96–98°). The infrared spectrum of this material was identical with that of the starting material.

(*b*) *p-Fluorophenylmercuric trifluoroacetate.* The same procedure was used in the reaction of 5.70 g (18.2 mmol) of crude *p*-fluorophenylmercuric hydroxide[19] and 2.12 g (18.6 mmol) of trifluoroacetic acid in 40 ml of ethanol. Two recrystallizations from cyclohexane gave 2.08 g of material, m.p. 101–103°. An additional recrystallization from CCl_4 gave pure product, m.p. 102–103.5° (1.93 g). (Found: C, 23.44; H, 1.00; F, 18.78; Hg, 49.79. $C_8H_4O_2F_4Hg$ calcd.: C, 23.51; H, 0.99; F, 18.59; Hg, 49.08%). IR (in CCl_4): 3080w, 1890w, 1795w, 1686s, 1585m, 1570(sh), 1495s, 1415m, 1397(sh), 1240s, 1216s, 1185s, 1169s, 1081w, 1065w, 1024w, 860m, 738s, 620w, 585w cm^{-1}.

Attempts to decarboxylate this compound in refluxing DME solution were unsuccessful. Only starting material was recovered.

Preparation of the fluorophenyl(trifluoromethyl)mercurials

(*a*) *m-Fluorophenyl(trifluoromethyl)mercury.* A solution of 6.47 g of (*m*-$FC_6H_4)_2Hg$ and 6.07 g (17.4 mmol) of CF_3HgBr in 60 ml of benzene was heated at reflux for 3 h, cooled and filtered to remove 6.03 g (97%) of *m*-FC_6H_4HgBr, m.p. 235–239° (lit.[24] m.p. 243–245°). The filtrate was evaporated under reduced pressure and the residue was recrystallized from cyclohexane to give 4.05 g (68%) of *m*-$FC_6H_4HgCF_3$, m.p. 122–125°. Sublimation at 90° (0.1 mm) gave an analytical sample, m.p. 127–128°.

(Found: C, 22.97; H, 1.17; F, 21.08; Hg, 55.57. $C_7H_4F_4Hg$ calcd.: C, 23.05; H, 1.10; F, 20.84; Hg 55.01%). IR (in CCl_4): 3065w, 3030(sh), 1945w, 1864w, 1765w, 1593(sh), 1575m, 1475m, 1414s, 1263w, 1221s, 1166m, 1144s, 1096m, 1065s, 1002w, 901w, 873w, 860m, 737m, 690m cm^{-1}. Mass spectrum, m/e (rel. intensity, %): 366(13.6) (M^+, calcd.: 366); 347(2.58), $(M-F)^+$; 328(1.81), $(M-2F)^+$; 297(31.1), $FC_6H_4Hg^+$; 202(5.67), Hg^+; 95(100), $C_6H_4F^+$; 75(38.5), $C_6H_3^+$; 69(18.9), CF_3^+.

(*b*) *p-Fluorophenyl(trifluoromethyl)mercury.* A reaction between 7.18 g (18.4 mmol) of $(p\text{-}FC_6H_4)_2Hg$ and 6.76 g (19.4 mmol) of CF_3HgBr in 50 ml of benzene was carried out as in (a). The yield of $p\text{-}FC_6H_4HgBr$, m.p. 306–308° (sealed tube) (lit.[25] m.p. 303–305°) was 98%. *p*-Fluorophenyl(trifluoromethyl)mercury, m.p. 104–105°, was obtained in 59% yield (3.94 g) after recrystallization of the crude benzene-soluble product from hexane. (Found: C, 23.05; H, 1.18; F, 20.85; Hg, 55.40. $C_7H_4F_4Hg$ calcd.: C, 23.05; H, 1.10; F, 20.84; Hg, 55.01%). IR (in CCl_4): 3090w, 3065w, 3042w, 1890w, 1770w, 1635w, 1585s, 1495s, 1390w, 1306w, 1238s, 1170m, 1147s, 1114w, 1090m, 1066s, 939w, 740m, 715w cm^{-1}. Mass spectrum (M^+ calcd. 366): 366(12.6), 347(2.38), 328(1.64), 297(32.3), 202(5.67), 95(100), 75(37.6), 69(18.1).

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