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HALOMETHYL-METAL COMPOUNDS

LXXVII*. AN ORGANOMERCURY ROUTE TO TETRAFLUOROETHYLIDENE

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Summary

Phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury has been prepared by reaction of phenylmercuric chloride and 1-bromo-1,2,2,2-tetrafluoroethane with sodium methoxide in THF at −35°. This mercurial readily transferred CF_3CF to carbenophiles at 155°. With olefins good yields of *gem*-fluoro(trifluoromethyl)cyclopropanes were obtained and with triethylsilane Si—H insertion gave $Et_3SiCHFCF_3$. On reaction with thiobenzophenone, the intermediate thiirane underwent loss of sulfur to give $Ph_2C{=}CFCF_3$. A similar observation was made in the reactions of $PhHgCFBrCO_2Et$ with thiobenzophenone and thiofluorenone. Phenyl(1-bromo-1,2,2-trifluoro-2-ethoxyethyl)mercury also was prepared, but this compound did not exhibit divalent carbon transfer reactivity.

Introduction

Much work has been devoted to the synthesis of reagents which can be used in the generation of fluorinated carbenes and to the reaction chemistry of fluorinated carbenes [2, 3]. The chemistry of difluorocarbene is well developed, bis(trifluoromethyl)carbene has received much attention and an organosilicon precursor to trifluoroethylidene, CHF_2CF, is available [4]. However, no useful route to tetrafluoroethylidene, CF_3CF, had been developed.

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* For part LXXVI see ref. 1.

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Pentafluoroethyltrifluorosilane had been found to decompose at 180°, giving silicon tetrafluoride and a mixture of *cis-* and *trans-*2-perfluorobutene. An α-elimination process appeared to be involved since decompositions carried out in the presence of hydrogen bromide and trimethylsilane gave CF_3CHFBr and $Me_3SiCHFCF_3$, respectively [5]. Yields of these insertion products were not given. In any case, until a better synthesis of this silicon compound is available, $C_2F_5SiF_3$ cannot be considered a pratical CF_3CF source. Evidence has been presented that pentafluoroethyltetrafluorophosphorane decomposes at 240° to form PF_5 and tetrafluoroethylidene [6], but this temperature is too high to permit useful application of this compound in synthesis.

Several organomercury compounds which are potential sources of tetrafluoroethylidene had been reported previously but none had been examined for divalent carbon transfer reactivity. Most were prepared by mercuric fluoride addition to polyfluoroolefins in liquid HF or AsF_3, e.g., $(CF_3CFBr)_2Hg$ [7], $(CF_3CFCl)_2Hg$ [8], $CF_3CFClHgCl$ [9], and $(CF_3CF_2)_2Hg$ [8]. While nothing appeared to be known concerning the behavior of the first three on being heated, it had been shown [10] that bis(pentafluoroethyl)mercury decomposed at 250° to give metallic mercury and perfluoro-n-butane, an obviously homolytic process.

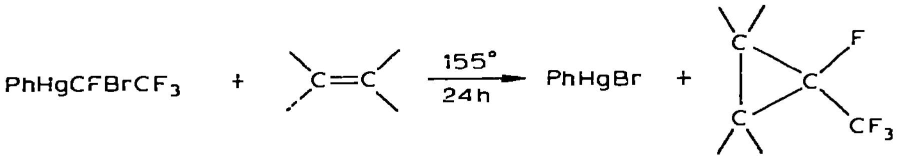
In a previous study we had developed $PhHgCClBrCF_3$ as a useful CF_3CCl source [11], and we felt that CF_3CFCl- and especially CF_3CFBr-substituted mercury compounds merited investigation as possible tetrafluoroethylidene sources. In view of the statement by Aldrich et al. [12] that the lower bis(polyfluoroalkyl)mercurials are volatile and their vapors toxic, we chose to direct our studies to mercurials of type $PhHgCFXCF_3$. These would have the advantage of being non-volatile. Furthermore, their decomposition by α-elimination would give the insoluble and easy-to-remove phenylmercuric chloride or bromide. Reactions of mercuric fluoride carried out in liquid hydrogen fluoride or arsenic trifluoride are not without their potential hazards. For this reason we felt that an alternate synthesis of such CF_3CFX-substituted mercurials would be desirable.

Results and discussion

Phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury was prepared in generally good (≈65%) yields by a variation [13] of our standard procedure [14] for the preparation of phenyl(trihalomethyl)mercury compounds (eqn. 1). This nicely crystalline compound, m.p. 121-122°, proved to be an excellent source of tetra-

$$PhHgCl + CF_3CHFBr + NaOCH_3\ (in\ CH_3OH) \xrightarrow{THF,\ -35^\circ} PhHgCFBrCF_3 + NaCl + CH_3OH \qquad (1)$$

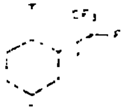
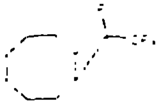
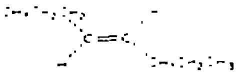
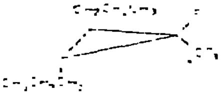
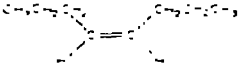
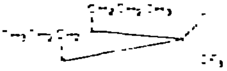
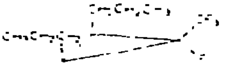
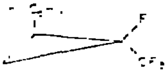
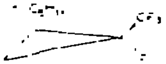
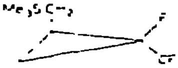
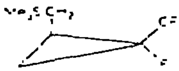
fluoroethylidene, as indicated by its reactions with several olefins (eqn. 2) and with triethylsilane (eqn. 3). The results are summarized in Table 1.



(2)

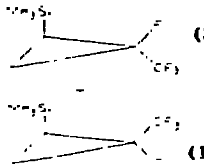
TABLE 1

REACTIONS OF $PhHgCFBrCF_3$ WITH OLEFINS ^{a}

Olefin	Yield of PhHgBr (%)	Cyclopropane product ^{b}	Yield (%)	n_D^{25}	Analysis found (calcd.) (%)	
					Carbon	Hydrogen
	[illegible]		(3.5 parts) 87	1.3820	52.89 (52.75)	5.62 (5.53)
		+ 	(1 part)	1.3893		
	[illegible]		(3.4 parts) 98	1.4052	57.19 (57.13)	6.83 (6.71)
		+ 	(1 part)	1.4110		
	[illegible]		80	1.3726	56.46 (56.59)	7.66 (7.60)
	[illegible]		(5.6 parts) 77	1.3736	56.59 (56.59)	7.68 (7.60)
		+ 	(1 part)	1.3781		
$n\text{-}C_4H_9CH{=}CH_2$	80		(1.6 parts) 70	1.3599	54.62 (54.54)	7.26 (7.12)
		+ 	(1 part)	1.3663		
$Me_3SiCH_2CH{=}CH_2$	99		(1.8 parts) 93	1.3702	44.80 (44.84)	6.62 (6.58)
		+ 	(1 part)	1.3744		

(continued)

TABLE 1 (continued)

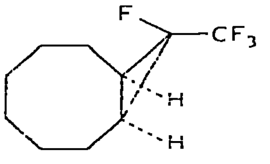
Olefin	Yield of PhHgBr (%)	Cyclopropane product [b]		Yield (%)	n_D^{25}	Analysis found (calcd.) (%) Carbon	Analysis found (calcd.) (%) Hydrogen
$Me_3SiCH{=}CH_2$	60		(3.1 part) (1 part)	16	1.3621 1.3690	41.94 (41.98)	6.18 (6.04)

[a] Reactions at 155° for 24 h in a sealed tube, olefin to mercurial ratio 3/1, benzene diluent, unless otherwise noted. [b] Isomer assignments are tentative except in the case of the cyclooctene reaction product [c] 72 h reaction time. [d] Olefin (10 ml) used as solvent. [e] 48 h reaction time.

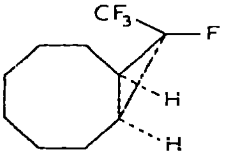
$$PhHgCFBrCF_3 + Et_3SiH \xrightarrow[24\ h]{155^\circ} PhHgBr + Et_3SiCHFCF_3 \qquad (3)$$

Phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury was more reactive as a CF_3CF source than was the CF_3CCl source, phenyl(1-bromo-1-chloro-2,2,2-trifluoroethyl)mercury, whose transfer reactions required reaction times of about 5 days at 140° [11]. However, the 80° reaction temperatures which sufficed in the carbene extrusion of the $PhHgCCl_nBr_{3-n}$ [15] and of $PhHgCCl_2F$ [13] were insufficient in the case of $PhHgCFBrCF_3$, and it was found convenient to carry out its reactions in sealed tubes at 155° for about 24 h.

In those reactions with olefins where addition of CF_3CF could result in formation of two cyclopropane isomers, both were formed, with one predominating. It would appear that the isomer which is preferred is the one with the trifluoromethyl group in the less hindered *anti* position. Thus, in the case of 9-fluoro-9-trifluoromethylbicyclo[6.1.0]nonane, obtained by reaction of $PhHgCFBrCF_3$ with cyclooctene, compound I was the major and II the minor isomer formed. These assignments are based on the ^{19}F NMR spectra of the



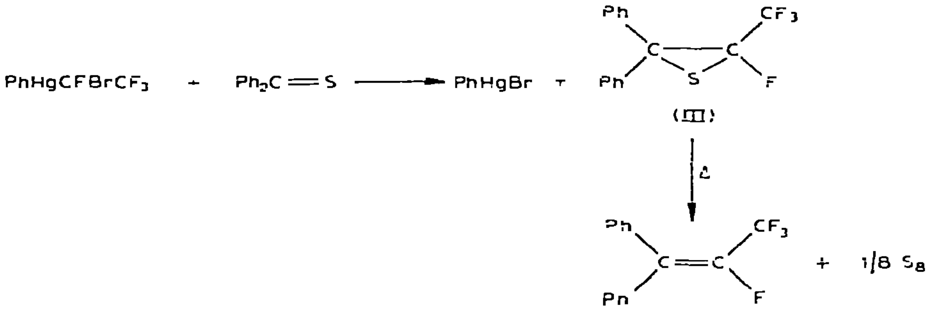
(I)



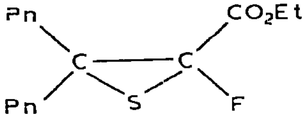
(II)

isomers. In the spectrum of the more abundant isomer, I, the CF_3 resonance was a sharply defined doublet (J(FF) 8 Hz) at −84.1 ppm relative to hexafluorobenzene. The *syn* fluorine substituent signal was not resolvable into the theoretical triplet of quartets, but rather appeared as a rounded multiplet at 67.8 ppm. Measuring the width of the multiplet at 1/6th height (34 Hz) and equating this to the sum of three times the quartet coupling plus two times the triplet coupling constant led to an approximate value for the triplet coupling constant of 5 Hz ($J(HF)_{trans}$). Similarly, the spectrum of the less abundant isomer, II, showed the CF_3 resonance as a sharp doublet with $J(FF)$ 8 Hz at −92.5 ppm. The *anti* fluorine resonance appeared as a broad symmetrical signal centered at 23.2 ppm (70 Hz width at 1/6th height) instead of as a resolved triplet of quartets. Using the same calculation gave an approximate $J(HF)_{cis}$ of 23 Hz. It is well known that in fluorocyclopropanes $J(HF)_{cis} > J(HF)_{trans}$ [16], and these calculated coupling constants are of the expected order to substantiate the postulated isomer assignments. We note also that the addition of CF_3CF to olefins is stereospecific. Thus, the reaction of *trans*-4-octene with $PhHgCFBrCF_3$ gave a single product, while the reaction of *cis*-4-octene with this reagent gave a 5.8/1 mixture of two isomers.

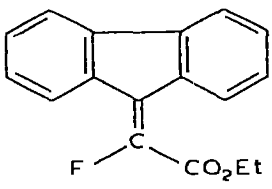
A reaction of $PhHgCFBrCF_3$ with thiobenzophenone was carried out with the expectation that a thiirane, III, would result. However, this was not the product obtained; instead $Ph_2C{=}CFCF_3$ was isolated in high yield. Presumably the thiirane was formed but underwent sulfur atom extrusion at the somewhat high reaction temperatures (eqn. 4). Sulfur extrusion of this type has been observed in the reaction of $PhHgCCl_2F$ with thiobenzophenone [13]. The reaction of $PhHgCCl_2Br$ with thiobenzophenone resulted in formation of stable 2,2-dichloro-3,3-diphenylthiirane whose thermolysis at 200° gave 1,1-dichloro-2,2-diphenylethylene and elemental sulfur [17]. That the general type of reaction depicted in eqn. 5 can be useful in the synthesis of novel fluoroolefins was shown by a reaction carried out between thiobenzophenone and $PhHgCFBrCO_2Et$ [18] at 125° in a sealed tube. Here again the intermediate thiirane (IV) was not stable under the reaction conditions and $Ph_2C{=}CFCO_2Et$ was obtained in 50% yield. A similar reaction carried out with thiofluorenone gave V in low yield.



(4)



(IV)



(V)

That the extrusion of a fluorocarbene from an organomercury precursor is faster than the extrusion of the corresponding chlorocarbene has already been demonstrated for a number of cases: CBrF vs. CBrCl [19], CClF vs. CCl_2

[13], $FCCO_2Me$ vs. $ClCCO_2Me$ [18], and the most likely reasons for this have been discussed [19]. In the present instance we have another example: CF_3CF vs. CF_3CCl and we reiterate our belief that it is the stabilizing effect of the fluorine substituent on the incipient carbene which is the decisive factor leading to this enhanced reactivity.

In conclusion, we report the preparation of phenyl(1-bromo-1,2,2-trifluoro-2-ethoxyethyl)mercury by our standard procedure (eqn. 5). Although about one-half of this mercurial had decomposed, giving phenylmercuric bromide, after

$$PhHgCl + CHBrFCF_2OC_2H_5 + Me_3COKMe_3COH \rightarrow KCl + 2\ Me_3COH + PhHgCFBrCF_2OC_2H_5 \qquad (5)$$

it had been heated in cyclooctene for 18 h at 145°, no product from the reaction of cyclooctene with $FCCF_2OC_2H_5$ was formed. It is likely that the carbene rearranged to $CF_2{=}CFOC_2H_5$ instead. This system was not examined further since no preparative applicability was apparent.

Experimental

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen. Gas—liquid chromatography (GLC) was used to examine reaction mixtures, isolate samples for product characterization and for yield determination (internal standard method). Commercial Hewlett—Packard F & M Model 700, 720, 5754 and 776 gas chromatographs were used.

^1H NMR spectra were recorded using a Varian Associates T60 spectrometer, ^{19}F NMR spectra with a Hitachi—Perkin—Elmer R20-B spectrometer at 56.446 MHz. Proton chemical shifts are recorded in δ units downfield from internal tetramethylsilane, ^{19}F chemical shifts in ppm relative to internal hexafluorobenzene*. Infrared spectra were determined using a Perkin—Elmer 457A spectrophotometer.

Preparation of 1-bromo-1,2,2,2-tetrafluoroethane

The procedure used by Miller et al. [20] for the preparation of 1-chloro-1,2,2,2-tetrafluoroethane was adapted to the preparation of this compound. A 450 ml stainless steel cylinder, fitted with a hoke valve and cap, was charged with 104 g (0.64 mol) of bromotrifluoroethylene, 200 ml of 92% formamide, 64 g of powdered anhydrous potassium fluoride and 5 steel balls for agitation. The cyclinder was warmed with continuous stirring in an oil bath at 70-75° for 2 days. Volatiles were then distilled into a 100 ml 3 neck flask fitted with a dropping funnel and a dry-ice condenser topped by a nitrogen inlet. The excess bromotrifluoroethylene was brominated by the addition of 3 ml of bromine and irradiation of the reaction mixture with a 275 Watt photoflood lamp for 30 min. The excess bromine was destroyed by the addition of 60 ml of saturated aqueous sodium sulfite. Volatiles were then distilled onto anhydrous sodium

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* δ values are positive for shifts to low field.

sulfate to dry and then into a steel cylinder for storage. Total yield of 1-bromo-1,2,2,2-tetrafluoroethane was 76.3 g (65%). The NMR spectral data for this compound agreed with those reported by Sharp and Coyle [5].

Preparation of phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury

A flame-dried, nitrogen-filled, two-liter three-necked flask, equipped with a mechanical stirring assembly, constant pressure addition funnel and Claisen adapter fitted with a low temperature thermometer and a dry-ice condenser, topped by a nitrogen inlet was charged with 75.0 g (0.24 mol) of phenylmercuric chloride, 96 g (0.53 mol) of 1-bromo-1,2,2,2-tetrafluoroethane and 850 ml of of tetrahydrofuran (freshly distilled from sodium benzophenone). The reaction mixture was cooled, with stirring, to −35°. At this point a solution of sodium methoxide, prepared by dissolving 6.1 g (0.26 mol) of sodium metal in 50 ml of absolute methanol and diluting with 150 ml of dry tetrahydrofuran, was added over a ten minute period. After the addition was complete, the reaction mixture was allowed to warm to room temperature over one hour. The contents of the flask were then transferred to a three liter single-neck flask, and the volatiles were stripped off under reduced pressure. The residue was taken up in 1200 ml of benzene and 100 ml of water, transferred to two quart bottles and centrifuged. The two liquid layers were filtered, the organic layer was separated, dried over anhydrous sodium sulfate, filtered and benzene removed by rotary evaporation under reduced pressure to yield 74.0 g of white crystalline solid, m.p. 110-114°. The material was dissolved in a solution of 70/30 wt.% hexane—methylene chloride, filtered through a 2 inch bed of silicic acid, solvent stripped under reduced pressure to give 70.5 g of product, m.p. 120-122°.

Recrystallization from 400 ml of hexane yielded in two crops 69.8 g (64%) of pure phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury, m.p. 121-122°, as dense colorless prisms up to 4 cm in length. Anal. found: C, 20.95; H, 1.21; Br, 17.61. $C_8H_5BrF_4Hg$ calcd.: C, 20.99; H, 1.10; Br, 17.46%.

IR(CCl_4): 3180m, 3170m, 3140(sh), 3000w, 1968w, 1950w, 1891w, 1871w, 1810w, 1575w, 1482m, 1433s, 1343(sh), 1335w, 1302(sh), 1271vs, 1242w, 1194vs, 1167vs, 1084w, 1047s, 1028m, 1002m, 905s, 728m, 700s cm^{-1}.

^1H NMR ($CDCl_3$) δ 7.1-7.6 ppm, complex multiplet, (aryl protons), downfield from TMS.

^{19}F NMR ($CDCl_3$): $PhHgC\underline{F}BrCF_3$ (t of q, 1F), 22.64 ppm downfield from hexafluorobenzene, $J(F-F)$ 15 Hz, $J(Hg-F_\alpha)$ 515 Hz; $PhHgCFBrC\underline{F}_3$ (t of d, 3F) 85.98 ppm downfield from hexafluorobenzene, $J(F-F)$ 15 Hz, $J(Hg-F_\beta)$ 71 Hz.

Reactions of phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury with olefins

A typical example, the reaction of this mercurial with cyclooctene, is described below to illustrate the procedure used. All reactions listed in Table 1 were carried out under these conditions, with variations in reaction time noted in the footnotes. In all cases where possible we noted the formation of both *syn* and *anti* isomers which were resolvable by GLC and have been separately characterized.

A 70 ml flame-dried, nitrogen-filled Pyrex bomb tube was charged with 6.98 g (15.3 mmol) of the mercurial, 5.8 ml (45 mmol) of cyclooctene and

7 ml of dry benzene, immersed in liquid nitrogen, evacuated to 0.2 mm Hg, degassed by one freeze-thaw cycle and sealed. When it reached room temperature, the mixture became homogeneous. The sealed tube was heated in a tube furnace at 155° for 24 h. The bomb was cooled, opened and the white crystalline solid which had formed was filtered and washed with hexane to give 5.26 g (96%) of phenylmercuric bromide, m.p. 276-278°, and traces of elemental mercury. The filtrate was trap-to-trap distilled (50° at 0.2 mm) and the lower boiling components were removed at atmospheric pressure by distillation through a Widmer column. The residue was examined by GLC (20% SE-30, 158°) and found to contain the desired 9-fluoro-9-trifluoromethylbicyclo[6.1.0]-nonane in 98% yield, with an isomer ratio of 3.4/1 in order of increasing retention time. Samples of both isomers were isolated by GLC (15 ft Apiezon L, 150°).

Major isomer: 9-*syn*-fluoro-9-*anti*-trifluoromethylbicyclo[6.1.0]nonane, (I) n_D^{25} 1.4052, eluted first on Apiezon L and SE-30.

Minor isomer: 9-*anti*-fluoro-9-*syn*-trifluoromethylbicyclo[6.1.0]nonane, (II) n_D^{25} 1.4110, eluted second on Apiezon L and SE-30.

The ^{19}F NMR spectra of each isomer are given in the discussion section. The ^{1}H NMR and the IR spectra were not especially informative. The combined isomers were analyzed: found: C, 57.19; H, 6.83. $C_{10}H_{14}F_4$ calcd.: C, 57.13; H, 6.71%.

Reaction of phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury with triethylsilane

Essentially the same procedure was used in the sealed tube reaction (24 h at 155°) between 7.02 g (15.3 mmol) of the mercury reagent and 9.7 ml (60 mmol) of triethylsilane (PCR, Inc.) in 5 ml of dry benzene. The tube was cooled and opened and hexane was added. Filtration removed 3.33 g (61%) of phenylmercuric bromide. Trap-to-trap distillation of the filtrate (100° at 0.15 mm) was followed by GLC (20% SE-30, 158°) examination of the distillate. The desired product was present in 53% yield, triethylbromosilane in about 4% yield. $Et_3SiCHCFCF_3$, n_D^{25} 1.3840; ^{1}H NMR (in CCl_4): δ 1.30-0.45 (m, 15H, Et_3Si) and 4.62 ppm (d of q, 1H, $J(HF_\alpha)$ 45.0 Hz, $J(HF_\beta)$ 11.0 Hz, $C\underline{H}CF_3$). Found: C, 44.41; H, 7.54. $C_8H_{16}F_4Si$ calcd.: C, 44.42; H, 7.46%.

Reaction of phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury with thiobenzophenone

The same procedure was used in the sealed tube reaction (40 h at 155°) of 7.08 g (15.5 mmol) of the mercurial and 3.13 g (15.9 mmol) of thiobenzophenone [21] in 15 ml of dry benzene. The blue color of the thioketone was discharged during the course of the reaction and a dark brown reaction mixture containing suspended solids, including elemental sulfur, was formed. The tube was cooled and opened and the mixture was filtered. The solid was washed with hexane to leave 4.73 g of PhHgBr (85%) contaminated with traces of elemental sulfur. The filtrate was chromatographed (12 inch alumina column, hexane eluant); the dark brown impurities and elemental sulfur were retained on the column. The hexane solution was concentrated and examined by GLC (UC W98, 175°). The product, identified as $Ph_2C{=}CFCF_3$, was present in 31% yield. It had n_D^{26} 1.5221. ^{19}F NMR (in CCl_4): δ 97.9 (d, J 9 Hz, 3F, CF_3) and 34.1 ppm (q, J 9 Hz, 1F, =C—F). This product is a known compound, n_D^{30} 1.5180 [22].

Reaction of phenyl(bromofluorocarboethoxymethyl)mercury with thiobenzophenone

A sealed tube reaction was carried out (24 h at 125°) between 2.76 g (6.0 mmol) of the mercury compound and 1.0 g (5.0 mmol) of thiobenzophenone in 6 ml of benzene. The bright blue solution became yellow in color during the heating period, and on cooling solid precipitated. Filtration gave 1.71 g (89%) of PhHgBr, m.p. 276-278°. The filtrate was chromatographed (6 inch silicic acid column, benzene eluant) to give 55 mg (34%) of elemental sulfur and an oil whose NMR spectrum showed the presence of an ethyl group. Crystallization from ligroin resulted in white crystals (0.67 g, 50%, m.p. 37-38°) of $Ph_2C{=}CFCO_2Et$. Another recrystallization from ligroin raised the m.p. to 37-38.5°. (Found: C, 75.21; H, 5.59. $C_{17}H_{15}O_2F$ calcd.: C, 75.54; H, 5.59%). IR(in CCl_4): ν(C=O) 1728 cm^{-1}. ^{1}H NMR (in CCl_4): δ 1.0 (t, J 7 Hz, 3H, CH_3), 3.65 (q, J 7 Hz, 2H, CH_2) and 7.25 ppm (m, 10H, Ph).

A similar reaction between 10 mmol of the mercurial and 10 mmol of thiofluorenone in 10 ml of dry benzene was carried out. The initially deep-green solution became deep-green-brown and inhomogeneous during the heating period of 24 h at 130°. Filtration gave 2.09 g of gray solid with m.p. > 340°. The organic materials were dissolved in 70/30 hexane—dichloromethane and chromatographed (10 inch silicic acid column). The first material to elute was the desired product, V (0.271 g, 10%). Recrystallization from methanol gave product with m.p. 77-79°. (Found: C, 75.98; H, 4.88. $C_{17}H_{13}O_2F$ calcd.: C, 76.11; H, 4.88%.) ^{1}H NMR (in CCl_4): δ 1.37 (t, J 7 Hz, 3H, CH_3), 4.18 (q, J 7 Hz, 2H, CH_2) and 7.05-8.70 ppm (m, 8H).

Preparation of phenyl(1-bromo-1,2,2-trifluoro-2-ethoxyethyl)mercury

A 500 ml, three-necked flask equipped with a mechanical stirrer, an addition funnel, a thermometer and a nitrogen inlet tube was charged with 15.65 g (50 mmol) of phenylmercuric chloride, 13.45 g (65 mmol) of $CHBrFCF_2OC_2H_5$ [23] and 150 ml of dry THF. To this mixture was added, with stirring, a slurry of 7.27 g (65 mmol) of Me_3COK (MSA Corp.) and 4.82 g (65 mmol) of Me_3COH in 50 ml of THF at 0° over a period of 10 min. The reaction mixture was stirred briefly at 0° and then was evaporated at reduced pressure. The residual sludge was taken up in a mixture of 500 ml of benzene and 1000 ml of water. The resulting emulsion was broken by adding diethyl ether. The organic layer was separated, filtered, dried and evaporated. The residue was dissolved in dichloromethane—hexane, filtered and the filtrate was slowly evaporated to obtain, in two crops, 6.00 g (25%) of white solid, m.p. 78-82°; m.p. 84-86° after recrystallization from hexane. Analysis and spectra were in agreement with its formulation as $PhHgCFBrCF_2OC_2H_5$. (Found: C, 24.76; H, 2.13; Br, 17.08. $C_{10}H_{10}BrF_3O$ calcd.: C, 24.83; H, 2.08; Br, 16.52%.) ^{1}H NMR (in $CCl_4/CDCl_3$): δ 1.37 (t, J 7.0 Hz, 3H, CH_3), 4.12 (q, J 7.0 Hz, 2H, CH_2) and 7.32 ppm (m, 5H, Ph). IR (in CCl_4): 3062w, 2995m, 2920w, 1485w, 1436w, 1377w, 1273vs, 1200s, 1162w, 1086(sh), 1051s (br), 1031(sh), 1004(sh), 915w, 855w, 730w and 700m cm^{-1}.

A reaction of this mercurial (4.84 g, 10 mmol) with 15 ml of cyclooctene was attempted. After this mixture had been heated at 145° for 18 h, the resulting pale-brown reaction mixture was filtered to remove 1.70 g (48%) of phenylmercuric bromide, m.p. 274-276°. GLC examination of the filtrate showed that no high boiling products were present. The filtrate was trap-to-trap distilled. An NMR spectrum of the 2.4 g pot residue showed starting organomercury compound to be present.

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