

Halomethyl Metal Compounds. XXXI. Phenyl(fluorodichloromethyl)mercury. A Useful Source of Fluorochlorocarbene¹

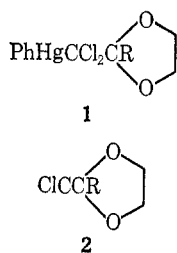
DIETMAR SEYFERTH AND KIRK V. DARRAGH²

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Phenyl(fluorodichloromethyl)mercury, PhHgCCl₂F, can be prepared in moderate yield by the reaction of phenylmercuric chloride, fluorodichloromethane, and potassium *t*-butoxide in diethyl ether at -25° with high-speed stirring. Diphenylmercury is an unavoidable and inseparable contaminant (*ca.* 20%) but does not interfere in the CFCl transfer reactions of PhHgCCl₂F. A number of *gem*-fluorochlorocyclopropanes have been prepared in high yield by the thermolysis of PhHgCCl₂F in the presence of the appropriate olefin in benzene solution at 80° for 48 hr (Table I). The olefins thus successfully converted include base-sensitive acrylonitrile and vinyl acetate and the poorly nucleophilic vinyltrimethylsilane. Insertion of PhHgCCl₂F-derived CFCl into the C-H bond of 2,5-dihydrofuran, the Si-H bond of triethylsilane, and the Sn-Sn bond of hexamethylditin also have been observed. An alternate and also preparatively useful method for releasing CFCl from PhHgCCl₂F involves treating this mercurial with sodium iodide in DME in the presence of the olefin. This procedure proceeds rapidly (within 5 hr at 80–85°, within 48 hr at room temperature) and gives good yields of *gem*-fluorochlorocyclopropanes.

We have developed a number of organomercury compounds which serve as effective divalent carbon transfer agents: PhHgCCl₂Br and PhHgCCl₃ (CCl₂ sources);³ PhHgCClBr₂ (a CClBr source);³ PhHgCBr₃ (a CBr₂ source);³ PhHgCCLXH (X = Cl or Br)^{4,5} and PhHgCBr₂H,⁵ which transfer CHCl and CHBr, respectively; Hg(CH₂Br)₂ and ICH₂HgI,^{1,6} both CH₂ transfer agents; PhHgCCl₂CO₂Me and PhHgCBr₂CO₂Me, sources of ClCCO₂Me and BrCCO₂Me, respectively;⁷ PhHgCClBrCF₃ (a source of ClCCF₃);⁷ (Me₃SiCCl₂)₂Hg, which transfers Me₃SiCCl;⁸ and 1 (R = H,

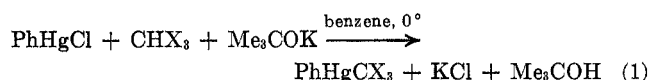


Me, Ph), sources of carbenes⁹ of type 2. Notably absent from this list is a fluorocarbene of type FCX. Current studies are devoted to providing organometallic precursors for fluorocarbenes. We have recently reported concerning a new CF₂-generating system, the Me₃SnCF₃ + NaI reagent,¹⁰ and in the present report we describe the preparation and some reactions of phenyl(fluorodichloromethyl)mercury, PhHgCCl₂F, a precursor for fluorochlorocarbene.

All of the previously known methods for the generation of fluorochlorocarbene utilize either the action of strong base on a CCl₂F⁻ anion source or the high-

temperature reaction of fluorodichloromethane with ethylene oxide in the presence of a catalytic quantity of tetraethylammonium bromide.¹¹ Among the precursors, the treatment of which with base generated CFCl, were fluorodichloromethane,^{12–16} methyl fluorodichloroacetate,^{17,18} and *sym*-difluorotetrachloroacetone.^{17,19–23} A further procedure for CFCl generation which is as yet not well developed is based on the photolysis of fluorochlorodiazirine.²⁴ Clearly, a CFCl precursor which releases this carbene in neutral medium under mild temperature conditions would be a useful reagent.

Preliminary experiments showed that direct adaptation of the Reutov–Lovtsova procedure^{25,26} for phenyl(trihalomethyl)mercury preparation (eq 1) to the



synthesis of PhHgCCl₂F was not possible. This mercurial was obtained in trace yields at best when fluorodichloromethane was used in the reaction described by eq 1. The finding that diethyl ether could replace benzene as solvent in reaction 1^{27,28} permitted the preparation of phenyl(fluorodichloromethyl)mercury in moderate yield. The reaction of phenylmercuric

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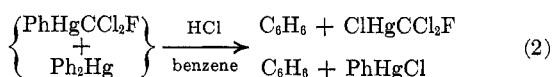
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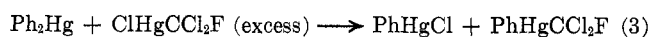
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chloride (or bromide) with fluorodichloromethane and potassium *t*-butoxide-*t*-butyl alcohol monosolvate in 1:6.5:2 molar ratio in anhydrous diethyl ether at -25° with high-speed stirring gave this mercurial in $\sim 35\%$ yield. This marked effect of solvent on reaction 1 when CHCl_2F is the haloform used may be rationalized in terms of more effective solvation (hence stabilization) of the intermediate CCl_2F^- anion in diethyl ether and somewhat greater solubility of phenylmercuric chloride in ether.

Closer examination of the product obtained in the $\text{PhHgX}-\text{CHCl}_2\text{F}-\text{Me}_3\text{COK}$ reaction showed it to be contaminated with diphenylmercury. Using the conditions specified above, the product was shown by means of exhaustive brominolysis to contain *ca.* 20% diphenylmercury. No change in reaction conditions prevented formation of this contaminant, and the best product purity to be achieved was 85%. Neither fractional crystallization nor chromatographic techniques could effect separation of diphenylmercury from phenyl(fluorodichloromethyl)mercury and, indeed, such separation was not required for the synthetic utilization of this reagent. A pure sample of $\text{PhHgCCl}_2\text{F}$ was obtained by treating the $\text{PhHgCCl}_2\text{F}-\text{Ph}_2\text{Hg}$ mixture with gaseous hydrogen chloride (eq 2). Fluorodi-

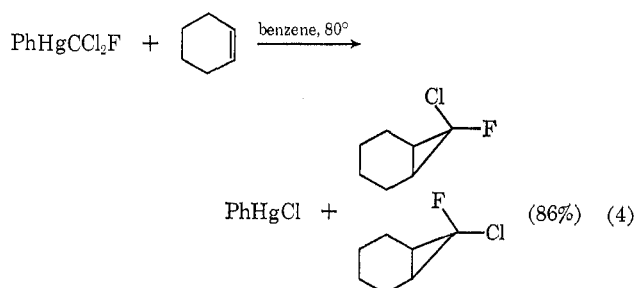


chloromethylmercuric chloride was recovered in 88% yield after column chromatographic separation from phenylmercuric chloride and subsequently was allowed to undergo substituent redistribution with diphenylmercury (eq 3). Pure $\text{PhHgCCl}_2\text{F}$ was isolated in 45% yield.



In all of the reactions of $\text{PhHgCCl}_2\text{F}$ which were studied, mercurial starting material containing *ca.* 20% diphenylmercury was used. The latter did not interfere in any way, being an inert diluent as far as the reactions studied were concerned. Analytical brominolysis served to determine the amount of this impurity in each batch of mercurial used.

Our studies have shown phenyl(fluorodichloromethyl)mercury to be an excellent source of fluorochlorocarbene. For example, when this mercurial was heated at reflux with 3 molar equiv of cyclohexene in benzene diluent for 48 hr, 7-fluoro-7-chloronorcarane was obtained in 86% yield as a mixture of the *syn* and *anti* isomers (eq 4). No 7,7-dichloronorcarane, the



product which would be obtained if elimination of phenylmercuric fluoride were a competing process, was obtained. The *syn* and *anti* isomers were partially resolved by gas-liquid partition chromatography (glpc),

but no attempt was made to separate them. The progress of the reaction was monitored by thin layer chromatographic analysis²⁶ for starting mercurial.

In terms of our current ideas concerning dihalocarbene extrusion from phenyl(trihalomethyl)mercury compounds,²⁸ the exclusive formation of CFCl and phenylmercuric chloride in phenyl(fluorodichloromethyl)mercury thermolysis is not surprising. The greater nucleophilicity of Cl (*vs.* F), the weaker $\text{C}-\text{Cl}$ bond (*vs.* $\text{C}-\text{F}$), and the greater stabilization by internal π bonding of CFCl (*vs.* CCl_2) all would operate to favor the extrusion process observed. Since in $\text{PhHgCCl}_2\text{F}$ it is phenylmercuric chloride which is eliminated, it is not surprising that its stability (hence its effective CFCl transfer reaction rate) is close to that of phenyl(trichloromethyl)mercury.³




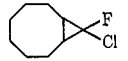
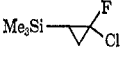
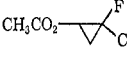
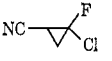
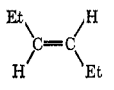
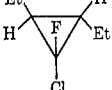
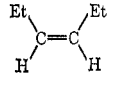
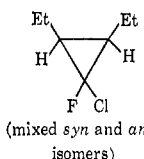

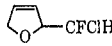

Other olefins were converted into fluorochlorocyclopropanes using $\text{PhHgCCl}_2\text{F}$, and in most cases excellent product yields were obtained. In all reactions studied, a mixture of the two possible geometric isomers was formed. Table I shows the results which were obtained. All of these reactions were carried out in benzene solution at 80° for 48 hr. Trimethylvinylsilane is an olefin which is very unreactive toward dihalocarbenes generated by the haloform-base method;²⁹ yet it gave the expected fluorochlorocyclopropyltrimethylsilane in nearly quantitative yield on reaction with $\text{PhHgCCl}_2\text{F}$. Vinyl acetate and acrylonitrile are both base sensitive, hence not suited to cyclopropanation reactions in which basic reagents are used; in the present study they were converted into the fluorochlorocyclopropanes in good yield.

The reactions with *trans*- and *cis*-3-hexene provide information concerning the stereochemistry of the $\text{PhHgCCl}_2\text{F}$ -olefin reaction. The formation of only one isomer in the case of *trans*-3-hexene and of two isomers with *cis*-3-hexene is exactly what would be expected if the reactions are stereospecific with respect to the configuration of substituents at the $\text{C}=\text{C}$ bond. Also of interest was the stereoselectivity, *i.e.*, the *syn/anti* ratio in the case of *cis*-3-hexene. (Here "*syn*" denotes that structure in which the Cl substituent on the cyclopropane ring is in *syn* relationship to the two ethyl groups.) In this connection, the previous work of Moss and Gerstl²² on the addition of CFCl to *cis*- and *trans*-2-butene is helpful. In making their structural assignments on the basis of ^{19}F nmr spectral data, these authors made the following points. (1) Since *cis* vicinal $\text{H}-\text{F}$ coupling usually is observed to be greater than *trans* vicinal $\text{H}-\text{F}$ coupling,³⁰ the isomer with the Cl *anti* with respect to the alkyl groups (*e.g.*, the *anti* isomer above) should have a fluorine resonance in its ^{19}F nmr spectrum that should be less broadened than those of the other two isomers (*i.e.*, of the *syn* isomer and of the isomer in which the alkyl groups are *trans* to one another) because of the absence of *cis* vicinal $\text{H}-\text{F}$ coupling. Support for this argument was provided by Japanese workers,¹⁸ who reported the vicinal $\text{H}-\text{F}$ coupling in 7-fluoronorcarane to be larger when *cis* (18.0 Hz) than when *trans* (9.0 Hz). They also assigned the structures of the two isomers of 7-chloro-7-fluoronorcarane on this basis,

(29) D. Seyferth and H. Dertouzos, *J. Organometal. Chem.*, **11**, 263 (1968), and references cited therein.

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TABLE I
 PRODUCTS DERIVED FROM CFCl REACTIONS

Substrate	Product ^a	Yield, ^b %	n_D^{20} ^c	Found (calcd), %			
				Carbon	Hydrogen	Chlorine	Fluorine
		85	1.4591 (lit. ¹¹ n_D^{20} 1.4603)				
		91	1.4707 (lit. ¹¹ n_D^{20} 1.4712)	61.04 (61.17)	8.20 (7.99)	20.19 (20.08)	10.64 (10.76)
Me ₃ SiCH=CH ₂		95	1.4194	43.33 (43.21)	7.58 (7.26)		
CH ₃ CO ₂ CH=CH ₂		86	1.4113	39.69 (39.44)	3.95 (3.97)	23.28 (23.25)	12.70 (12.46)
CH ₂ =CHCN		40	1.4276	40.33 (40.14)	2.78 (2.53)		
		97	1.4071	55.83 (55.80)	8.10 (8.04)		
	 (mixed <i>syn</i> and <i>anti</i> isomers)	86	1.4129	55.59 (55.80)	8.07 (8.04)		
		8.4		43.96 (43.96)	4.59 (4.43)		
		75	1.4483	43.76 (43.96)	4.36 (4.43)		
Et ₃ SiH	Et ₃ SiCFClH	83	1.4351	45.59 (45.97)	8.65 (8.83)		
Me ₃ SnSnMe ₃	Me ₃ SnCFClSnMe ₃	36	1.5253	21.72 (21.32)	4.77 (4.60)	8.88 (9.00)	

^a Mixed *syn-anti* isomers which were not separated. ^b In a reaction carried out in refluxing benzene for 48 hr. ^c Refractive indices of mixed *syn-anti* isomers for all olefins except *trans*-3-hexene.

with $J_{H-F}^{cis} = 19.0$ Hz and $J_{H-F}^{trans} = 5.0$ Hz. In Table II are given ¹⁹F nmr data for the fluorochlorocyclopropanes derived from the *cis* and *trans* isomers of 2-butene and 3-hexene. It is apparent that the fluorine resonance of one isomer was indeed less broadened than those of the other two in the case of the products from each pair of olefin isomers. (2) Since cyclopropyl protons were known to be shielded by *cis* methyl groups and deshielded by *trans* methyl groups,³¹ a similar shielding effect on the fluorine resonance of fluorocyclopropanes was expected; however, a more pronounced difference in these differential shielding effects was expected in the ¹⁹F nmr spectra.³² Thus the addition of a *cis* alkyl group and/or removal of a *trans* alkyl group should result in an upfield shift of the fluorine resonance. The data in Table II support this argument. On this basis then, we make the structural assignments for the isomers obtained from *cis*-3-hexene. The *syn/anti* ratio of the fluorochlorocyclopropanes from *cis*-3-hexene thus would be 1.2, and so, as in other cases of CFCl addition to olefins,^{18,22} formation of the isomer in which the Cl is *syn* to the greater number of alkyl groups is preferred. In the case of *cis*-2-butene the *syn/anti* ratio in the product was *ca.* 3.1;²² however, a significant steric effect must be introduced when the two methyl groups of *cis*-2-butene are replaced by two

ethyl groups, and thus a decrease in this ratio on going to *cis*-3-hexene is not surprising.

In the case of the 2,5-dihydrofuran-PhHgCCl₂F reaction the C=C addition/C—H insertion ratio observed was about 9. For the 2,5-dihydrofuran-PhHgCCl₂Br reaction this ratio was 0.85,³ and in the 2,5-dihydrofuran-CF₂ reaction¹⁰ the C=C addition product, 3-oxa-6,6-difluorobicyclo[3.1.0]hexane, was the only product formed. These results are as expected, since the selectivity of the dihalocarbenes in question decreases in the order CF₂ > CFCl > CCl₂ (ref 23 and references cited therein).

The long reaction time required in these PhHgCCl₂F-olefin reactions was a major disadvantage. In a previous study³³ we had shown that dichlorocarbene release from phenyl(trichloromethyl)mercury, which was equally slow in benzene at 80°, could be greatly accelerated by carrying out the olefin-mercurial reaction in 1,2-dimethoxyethane (DME) at reflux in the presence of 1 molar equiv of anhydrous sodium iodide. This "activation" proceeded *via* a change in mechanism: the iodide ion displaced the CCl₃⁻ ion from mercury in a fairly rapid reaction, and the latter then gave dichlorocarbene. Reaction times could be shortened from 48 hr to *ca.* 3 hr at 80–85°, and the *gem*-dichlorocyclopropane yields were, in general, quite good. This sodium

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TABLE II
¹⁹F NMR SPECTRA OF SOME *gem*-FLUOROCHLOROCYCLOPROPANES

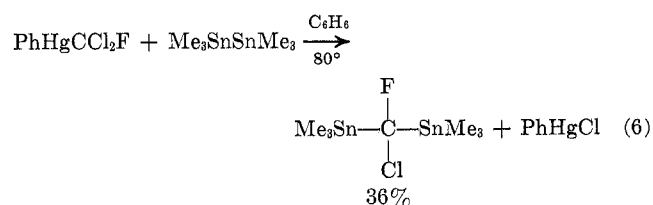
Compd	Registry no.	Obsd resonance	$W_{1/2}$, ^a Hz	W_B , ^a Hz	Chemical shift, Hz ^b
	23359-72-0	Broad multiplet	38		4313 ^c
	23348-94-9	Broad envelope	18		5506 ^c
	23348-95-0	Broad envelope	41		3206 ^c
	23348-96-1	Multiplet		42	8265 ^d
	23359-73-1	Envelope	7	16	9334 ^d
	23348-97-2	Triplet of multiplets		50	7164 ^d

^a $W_{1/2}$ = width at half height; W_B = width at base. ^b Chemical shift in hertz upfield from internal standard CCl_3F at 56.4 MHz solvent, CCl_4 . ^c Frequency response = 5 Hz. ^d Frequency response = 1–2 Hz; data from ref 22.

iodide procedure had been applied to the generation of CF_2 from trimethyl(trifluoromethyl)tin with good advantage,¹⁰ and we have found that it also is very useful in the generation of CFCl . When phenyl(fluoro-dichloromethyl)mercury and 1 equiv of sodium iodide were allowed to react in DME solution in the presence of an excess of cyclohexene at 85° for 5 hr, 7-fluoro-7-chloronorcarane (mixture of isomers) was obtained in 79% yield. An analogous reaction, carried out at room temperature for 48 hr, gave this product in 85% yield.

In the case of the $\text{PhHgCCl}_2\text{F}-\text{NaI}$ reagent, the intermediate CCl_3^- ion could be intercepted with vinyl acetate and acrylonitrile.³³ However, reaction of these olefins with the $\text{PhHgCCl}_2\text{F}-\text{NaI}$ reagent in DME at 85° gave only the CFCl adducts, 2-chloro-2-fluorocyclopropyl acetate (70%) and 1-chloro-1-fluoro-2-cyanocyclopropane (33%), respectively. No CCl_2F^- adducts could be detected. These results are interpreted not as evidence against the intermediacy of CCl_2F^- in these reactions, but rather as confirmatory evidence relating to the lesser stability of this anion, relative to CCl_3^- . As Hine and coworkers³⁴ have pointed out, fluorine substitution tends to make the trihalomethyl anion less stable and to increase the stability of the dihalocarbene. Thus, of the two competing processes, CCl_2F^- addition to the $\text{C}=\text{C}$ bonds or CCl_2F^- decomposition to $\text{CFCl} + \text{Cl}^-$, the latter seems to proceed at a significantly faster rate.

Other possible single-bond insertion reactions of CFCl were examined, and the results were in general indicative of a much diminished reactivity on going from CCl_2 to CFCl . Thus dichlorocarbene inserts into the C–H bond α to the oxygen of tetrahydrofuran in 67% yield.³ In contrast, decomposition of $\text{PhHgCCl}_2\text{F}$ in the presence of tetrahydrofuran gave no isolable product. In similar fashion, $\text{PhHgCCl}_2\text{F}$ -derived CFCl was inert toward isobutyltrimethylsilane, a compound into whose C–H bond β to the silicon atom CCl_2 inserts in high yield.³⁵ Successful insertions of CFCl into single bonds was accomplished in the case of triethylsilane and hexamethylditin (eq 5 and 6). Previous work had



shown that dichlorocarbene inserts readily into silicon-hydrogen bonds³⁶ and into the Sn–Sn bond of hexa-

(34) (a) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Amer. Chem. Soc.*, **79**, 1406 (1957); (b) J. Hine and S. J. Ehrenson, *ibid.*, **80**, 824 (1958).

(35) S. S. Washburne, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1968.

(36) D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organometal. Chem.*, **7**, 405 (1967).

methyliditin.³⁷ These reactions of CFCl with 2,5-dihydrofuran, triethylsilane, and hexamethylditin are the first examples of CFCl insertion into single bonds.

In summary, the thermolysis of phenyl(fluorodichloromethyl)mercury gives clearly superior yields of fluorochlorocyclopropanes compared with any other method of generating CFCl, and complications arising from basic reaction conditions, higher temperatures, and major competing side reactions are avoided. Phenylmercuric chloride is recovered from these reactions in nearly quantitative yield and good purity and may easily be recycled to preparation of more PhHgCCl₂F. Although the thermal reaction in benzene gives excellent yields of CFCl transfer products, the reaction time is rather long, and the PhHgCCl₂F-NaI reagent system is an attractive alternative, giving good yields in relatively short reaction times. This work has demonstrated the utility of phenyl(fluorodichloromethyl)mercury as a CFCl transfer agent and has shown that the mercurial route allows the development of hitherto inaccessible CFCl chemistry. The one drawback of this new procedure lies in the difficulty with which PhHgCCl₂F is prepared even in modest yields, and current research is aimed at improving this procedure or at developing a better, alternate route.^{37a}

Experimental Section

General Comments.—All reactions involving the preparation or the reactions of the mercurial reagent were carried out under an atmosphere of prepurified nitrogen. Infrared spectra were recorded on a Perkin-Elmer Infracord 337 or 237B grating spectrophotometer. Nmr spectra were obtained on a Varian Associates high-resolution spectrometer (¹H) or a Varian HA-60 instrument (¹H and ¹⁹F). Proton chemical shifts are given in δ units downfield from internal tetramethylsilane and were measured in carbon tetrachloride solution unless otherwise specified. Thin layer chromatography (tlc) was performed on Eastman silica gel tlc sheet (K301R); the eluent was 20% benzene in cyclohexane. Development was accomplished by staining with iodine vapor followed by spraying with 10% Na₂S in 50% aqueous ethanol.

The following columns were used in gas chromatographic analysis and isolation: column 1, 8 ft \times 12 mm glass packed with 20% General Electric Co. SE-30 silicone rubber gum on 80-100 mesh Johns Manville Chromosorb W; MIT isothermal glpc instrument; column 2, 7 ft \times 8 mm glass column, otherwise same as column 1; column 3, 3 ft \times 12 mm glass column, otherwise same as column 1; column 4, 12 ft \times 0.25 in. aluminum column, same packing as column 1, F & M model 5754 gas chromatograph; column 5, 4 ft \times 0.25 in. stainless steel column packed with 10% UC98W silicone rubber on Chromosorb W, F & M 5754. Thermal conductivity detectors were used in all cases.

Preparation of Phenyl(fluorodichloromethyl)mercury.—A 1-l., three-necked, creased flask equipped with a high-speed stirring assembly ("Stir-O-Vac," Labline Catalog No. 1280) and a nitrogen inlet tube was charged with 117 g (0.375 mol) of phenylmercuric chloride and ca. 1200 ml of dry diethyl ether. The mixture was cooled to -25° and then 250 g (2.43 mol) of fluorodichloromethane (Matheson Co.) was added. The latter had been dried by passing it as the gas mixed with nitrogen through a drying tower filled with 20% P₂O₅ on anhydrous calcium chloride and was condensed into a trap cooled to -30° . While the temperature was maintained at -25° ($\pm 5^\circ$), high-speed stirring was started; ~ 0.75 mol of potassium *t*-butoxide in the form of its *t*-butyl alcohol monosolvate³⁸ was added over a 20-min period.

Stirring was continued at -20° for 45 min and then the mixture was poured slowly into 600 ml of distilled water. Filtration afforded impure PhHgCl (27.6 g, 24%). The organic phase was dried with anhydrous MgSO₄, filtered, and evaporated to dryness. Recrystallization of the crude solids thus obtained from 1:2 chloroform-hexane gave 60.7 g of solid, mp 111-115° (softening at ca. 108°). This material was shown by bromine cleavage (see below) to contain PhHgCCl₂F together with ca. 20% diphenylmercury as an impurity. Thus the yield of PhHgCCl₂F was 35%. No conditions for recrystallization, column chromatography, or tlc could be found which would make possible the efficient separation of these two components.

This reaction was carried out several times with slight variations to attempt to improve upon the results described above. No substantial improvement resulted; the best PhHgCCl₂F purity to be achieved was 85%.

Analysis of the PhHgCCl₂F-Ph₂Hg Mixture by Brominolysis.—A 50-ml, three-necked flask equipped with a magnetic stirring assembly, a 60-ml pressure-equalizing dropping funnel, and a Dry Ice-acetone cold finger topped with a nitrogen inlet tube was charged with 1.89 g of the mixture and 10 ml of dry benzene. Bromine, 12 ml of a 1 M solution in carbon tetrachloride, was added dropwise to the stirred solution over a 35-min period. The mixture was stirred for another hour and then 1.5 g of anhydrous MgSO₄ and 2.5 g of finely powdered Na₂S₂O₈ · 5H₂O were added. Stirring was continued until the bromine color had been discharged. The filtered organic layer was trap-to-trap distilled (0.1 mm, pot temperature to 100°). Glpc analysis of the distillate (column 2, 96°, 15 psi of helium, external standard method) showed the presence of 3.9 mmol of CCl₂FBr and 6.0 mmol of bromobenzene. If the PhHgCCl₂F were 100% pure, a 1.89-g sample would be 5 mmol and bromination should give 5 mmol each of the two cleavage products. Thus R in PhHgR was as follows.

$$100 \left(\frac{3.9 \text{ mmol}}{[3.9 + (6.0 - 5.0)] \text{ mmol}} \right) = 80\% \text{ CCl}_2\text{F}$$

$$100 \left(\frac{[6.0 - 5.0] \text{ mmol}}{[3.9 + (6.0 - 5.0)] \text{ mmol}} \right) = 20\% \text{ C}_6\text{H}_5$$

Thus the mixture was 80% PhHgCCl₂F and 20% Ph₂Hg.

Preparation of a Pure Sample of Phenyl(fluorodichloromethyl)mercury.—A 200-ml, three-necked flask equipped with a magnetic stirring assembly, a gas inlet tube, and a gas exit tube was charged with 28.4 g of 4:1 PhHgCCl₂F-Ph₂Hg mixture (60 mmol of PhHgCCl₂F) and 140 ml of dry benzene. Anhydrous HCl (Matheson Co.) was bubbled into the solution with vigorous stirring for 1 hr; a white solid precipitated immediately. The unconverted HCl in the mixture was purged with nitrogen. The precipitate (2.27 g), mp 230-270° dec (partial), was filtered and the filtrate was evaporated to dryness. The crude, benzene-soluble solids were chromatographed on a 27 \times 3.5 cm silica gel column using 1:1 benzene-hexane as eluent. The white solid obtained was recrystallized from chloroform-hexane to give 17.7 g of white, silky needles, mp 146-149°. Another recrystallization gave an analytical sample, mp 149.5-151°, of fluorodichloromethylmercuric chloride, CFCl₂HgCl.

Anal. Calcd for CCl₂FHg: C, 3.55; Cl, 31.47; F, 5.62. Found: C, 3.79; Cl, 31.14; F, 5.23.

The CFCl₂HgCl thus obtained (1.35 g, 4.0 mmol) was heated at reflux with 1.06 g (3.0 mmol) of diphenylmercury in 12 ml of dry benzene. Filtration removed 1.11 g of white solid, mp 255-260° (partial). Evaporation of the filtrate gave 1.4 g of white solid, the recrystallization of which from 1:2 chloroform-hexane (three times) yielded 0.51 g of PhHgCCl₂F: mp 98-100°; *ir* (Nujol) 1582 (w), 1026 (w), 1007 (m), 1002 (m), 794 (m), 748 (m), 735 (ms), 724 (m) and 696 cm⁻¹ (m).

Anal. Calcd for C₇H₅Cl₂FHg: C, 22.15; H, 1.33; Cl, 18.68; F, 5.00. Found: C, 22.05; H, 1.23; Cl, 18.70; F, 4.48.

Reaction of Phenyl(fluorodichloromethyl)mercury with Cyclooctene.—To a 50-ml three-necked flask equipped with a magnetic stirring assembly and a reflux condenser topped with a nitrogen inlet tube were added 2.48 g of PhHgCCl₂F-Ph₂Hg mixture containing 5.2 mmol of PhHgCCl₂F, 1.66 g (15 mmol) of cyclooctene, and 10 ml of dry benzene. The reaction mixture was stirred and heated at reflux; the progress of the reaction was monitored by tlc. During the 48-hr reaction period phenylmercuric chloride

(37) D. Seyferth, F. M. Armbrecht, Jr., and B. Schneider, *J. Amer. Chem. Soc.*, **91**, 1954 (1969).

(37a) NOTE ADDED IN PROOF.—An improved procedure, the fluorination of PhHgCCl₂Br with phenylmercuric fluoride, has been developed for the synthesis of PhHgCCl₂F in the meantime: D. Seyferth, S. P. Hopper, and K. V. Darragh, *ibid.*, **91**, 6536 (1969).

(38) A. J. Speziale and K. W. Ratts, *ibid.*, **84**, 854 (1962).

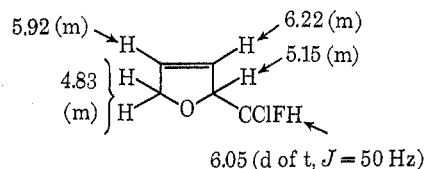
precipitated and after the completion of the reaction was filtered off in quantitative yield (1.63 g), mp 254–256°. The filtrate was trap-to-trap distilled at 0.1 mm (pot temperature to 60°). Glpc analysis of the distillate (column 2, 154°, 15 psi helium) showed the presence of 9-fluoro-9-chlorobicyclo[6.1.0]nonane in 91% yield. Overlapping peaks in the gas chromatogram indicated the presence of both the *syn* and the *anti* isomer. Pure samples of the mixed isomers were isolated by preparative glpc.

This procedure served in the reactions of $\text{PhHgCCl}_2\text{F}$ with the other olefins (*cf.* Table I), cyclohexene, vinyltrimethylsilane, vinyl acetate, acrylonitrile and the isomeric heptenes. In no cases were the individual *syn* and *anti* isomers separated. Their peaks in the gas chromatograms always overlapped. In all cases the isomer with the longer glpc retention time on a silicone oil column was present in slightly greater amount, *ca.* 1.1–1.2:1.

Reaction of $\text{PhHgCCl}_2\text{F}$ with 2,5-Dihydrofuran.—The procedure described above was used in the reaction of 11.85 g of $\text{PhHgCCl}_2\text{F}$ - Ph_2Hg mixture containing 25 mmol of $\text{PhHgCCl}_2\text{F}$ with 74 mmol of 2,5-dihydrofuran in 50 ml of benzene at reflux for 48 hr. Filtration from phenylmercuric chloride and trap-to-trap distillation of the filtrate at 0.1 mm was followed by glpc analysis (column 2, 90°, 15 psi helium) of the distillate. Two higher boiling products were present. The product of shorter glpc retention time (I) was identified as 2-fluoro-2-chloromethyl-2,5-dihydrofuran (8.4% yield), and the other product was identified as the mixed *syn* and *anti* isomers (overlapping peaks) of 3-oxa-6-fluoro-6-chlorobicyclo[3.1.0]hexane (II, 75% yield). Pure samples were isolated by preparative glpc.

Product I gave the following data: ir (CCl_4) 3090 (w), 2980 (sh), 2944 (m), 2900 (sh), 2870 (vs), 2690 (vw), 1620 (w), 1480 (w), 1468 (w), 1368 (m), 1365 (m), 1325 (m), 1300 (w), 1278 (w), 1229 (m), 1185 (w), 1135 (sh), 1122 (s), 1085 (vs), 1041 (s), 1022 (sh), 963 (w), 950 (m), 918 (m), and 873 cm^{-1} (m); mass spectrum *m/e* (rel intensity) parent peak 69, mass ion 136 (ratio 136:138 = 3), 138 (<1), 136 (2), 107 (*ca.* 1), 99 (2), 81 (2), 79 (2.5), 78 (21), 77 (4.3), 73 (10), 70 (5.5), 69 (100, M - CClFH), 53 (9), 51 (10), 44 (9), 41 (25), 39 (18), 29 (5.5), and 27 (6.5).

The nmr spectrum is shown below.



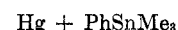
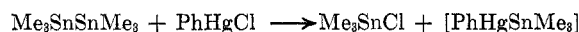
Product II gave the following data: ir (liquid film) 3065 (w), 2965 (s), 2935 (s), 2880 (vs), 1975 (w), 1481 (m), 1471 (m), 1424 (s), 1400 (s), 1342 (vs), 1281 (s), 1235 (s), 1195 (vs), 1125 (vs), 1042 (vs), 990 (s), 954 (m), 896 (vs), 867 (vs), 825 (m), 804 (m), 738 (vs), and 719 cm^{-1} (s).

Reaction of Phenyl(fluorodichloromethyl)mercury with Triethylsilane.—The reaction was carried out at 80° for 48 hr using the procedure described above with 2.48 g of $\text{PhHgCCl}_2\text{F}$ - Ph_2Hg mixture containing 5.2 mmol of $\text{PhHgCCl}_2\text{F}$ and 1.59 g (14 mmol) of triethylsilane (Peninsular ChemResearch) in 10 ml of dry benzene. Phenylmercuric chloride was obtained in quantitative yield. Trap-to-trap distillation of the filtrate at 0.1 mm (pot temperature to 60°) was followed by glpc analysis (column 2, 145°, 15 psi of helium) of the distillate, which showed that triethyl(fluoro-chloromethyl)silane had been formed in 83% yield: ir (liquid film) 2965 (s), 2920 (s), 2885 (s), 1470 (sh), 1460 (m), 1415 (m), 1380 (w), 1303 (w), 1242 (m), 1005 (s, broad), 975 (sh), 782 (s), 735 (s, broad), 695 (s), and 607 cm^{-1} (m); nmr δ 0.94 (m, 15 H, Et_3Si) and 6.13 (d, 1 H, $J = 45.5$ Hz, CClFH).

Reaction of Phenyl(fluorodichloromethyl)mercury with Hexamethylditin.—The $\text{PhHgCCl}_2\text{F}$ - Ph_2Hg mixture (4.76 g, con-

taining 10 mmol of $\text{PhHgCCl}_2\text{F}$) and 6.42 g (20 mmol) of hexamethylditin (M & T Chemicals, Inc.) in 20 ml of dry benzene were heated at reflux under nitrogen for 48 hr. The precipitated solids (2.34 g, PhHgCl and metallic mercury) were filtered and the filtrate was trap-to-trap distilled at 0.0002 mm (pot temperature to 150°). Glpc analysis of the distillate (column 5, programmed at 60–170° at 4°/min) showed the following components to be present: bis(trimethyltin)fluoro-chloromethane (36%), bis(trimethyltin)dichloromethane (8%), unconverted hexamethylditin (10%), phenyltrimethyltin (4.5 mmol), trimethyltin chloride (3.9 mmol), and small amounts of other unidentified high-boiling compounds.

All by-products were identified by comparison of their glpc retention times and infrared spectra with those of authentic samples. The formation of phenyltrimethyltin and trimethyltin chloride could be explained by the process shown below.



Pure samples of $\text{Me}_3\text{SnCClF}_2\text{SnMe}_3$ were isolated by preparative glpc. This compound appeared to be somewhat unstable to the atmosphere and was best handled in an inert atmosphere: ir (CCl_4) 2980 (s), 2910 (s), 2355 (m), 2320 (sh), 1480 (sh), 1385 (m), 1192 (m), 923 (s) 714 (s), and 681 cm^{-1} (s); a liquid film spectrum showed bands also at 765 (s) and 740 cm^{-1} (sh).

Reaction of Phenyl(fluorodichloromethyl)mercury-Sodium Iodide with Cyclohexene.—A 50-ml, three-necked flask equipped with a magnetic stirring assembly, a 60-ml pressure-equalizing dropping funnel, and a reflux condenser topped with a nitrogen inlet tube was charged with 2.38 g of the $\text{PhHgCCl}_2\text{F}$ - Ph_2Hg mixture containing 5.0 mmol of $\text{PhHgCCl}_2\text{F}$, 1.23 g (15 mmol) of cyclohexene, and 10 ml of DME (freshly distilled under nitrogen from lithium aluminum hydride). The dropping funnel was charged with a solution of 0.91 g (6 mmol) of sodium iodide [dried at 150° (0.02 mm) for 12 hr] in 10 ml of DME. The mercurial solution was heated to reflux and then the sodium iodide solution was added dropwise with stirring over a 15-min period. White solid began to precipitate immediately. The reaction mixture was stirred and heated for 5 hr, cooled, and filtered. The filtrate was trap-to-trap distilled at 0.05 mm (pot temperature to 80°). Glpc analysis of the filtrate (column 2, 121°, 15 psi of helium) showed the presence of the mixed *syn* and *anti* isomers of 7-fluoro-7-chloronorcarane in 79% yield.

The same reaction carried out at room temperature (*ca.* 25°) for 48 hr gave this product in 85% yield.

The procedure described above (*i.e.*, a reaction carried out at reflux) was used in the reaction of the $\text{PhHgCCl}_2\text{F}$ - NaI reagent with vinyl acetate and acrylonitrile.

Registry No.—Phenyl(fluorodichloromethyl)mercury, 19326-35-3; fluorochlorocarbene, 1691-88-9; fluorodichloromethylmercuric chloride, 23348-91-6; 2-fluoro-chloromethyl-2,5-dihydrofuran, 23348-92-7; cyclo-octene, 931-88-4; 2,5-dihydrofuran, 1708-29-8; triethylsilane, 617-86-7; hexamethylditin, 661-69-8; cyclohexene, 110-83-8.

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