TABLE IV

REACTION CONDITIONS AND PRODUCT YIELDS[a]

CF_3COF, mmol	Alcohol (mmol)	Time, day	Ester (mmol)	Mol wt[b]
10.0	C_2H_5OH (4.0)	0.5	$CF_3CO_2C_2H_5$ (3.9)	142.8 (142.0)[c]
11.0	CF_3CH_2OH (4.0)	0.5	$CF_3CO_2CH_2CF_3$ (3.9)	195.6 (196.0)
7.0	$(CF_3)_2CHOH$ (4.0)	4.0	$CF_3CO_2C(CF_3)_2H$ (3.4)	263.1 (264.0)
6.0	$(CF_3)_2C(CH_3)OH$ (2.0)	4.0	$CF_3CO_2C(CF_3)_2CH_3$ (1.6)	279.3 (278.0)
5.0	$(CF_3)_3COH$ (1.1)	2.0	$CF_3CO_2C(CF_3)_3$ (1.1)	331.3 (332.0)
0.8	$(CF_3)_2C(C_2F_5)OH$ (0.6)	3.0	$CF_3CO_2C(CF_3)_2C_2F_5$ (0.6)	380.7 (382.0)

[a] All reactions were carried out in the presence of CsF at room temperature. [b] Vapor density determined assuming ideal gas behavior by Regnault's method. [c] Calculated value.

TABLE V

ELEMENTAL ANALYSIS AND THERMODYNAMIC DATA

	Elemental analysis, %			Bp,	ΔH_v,	ΔS_v,	Log $P_{mm} = a - b/T$	
Ester	C	H	F	°C	kcal/mol	eu	a	b
$CF_3CO_2C_2H_5$	33.8 (33.8)[a]	3.6 (3.5)	39.9 (40.1)	62	8.3	24.6	8.27	1809
$CF_3CO_2CH_2CF_3$	24.5 (24.5)	1.0 (1.0)	24.5 (24.5)	57	7.6	23.1	7.92	1663
$CF_3CO_2C(CF_3)_2H$	22.7 (22.7)	0.4 (0.4)	65.5 (64.8)	48	6.8	21.2	7.51	1487
$CF_3CO_2C(CF_3)_2CH_3$	25.9 (25.9)	1.1 (1.1)	62.0 (61.5)	65	8.0	23.6	8.04	1743
$CF_3CO_2C(CF_3)_3$	21.7 (21.7)		68.9 (68.7)	56	7.9	24.0	8.12	1724
$CF_3CO_2C(CF_3)_2C_2F_5$	21.9 (22.0)		69.7 (69.6)					

[a] Calculated value.

Preparative Procedure.—In a typical reaction a 2.5:1 excess of CF_3COF was condensed into a vessel which contained 4 mmol of the appropriate alcohol and about 5 g of activated CsF. The mixture was left at 25° until the band due to OH stretch (~3600 cm^{-1}) disappeared from the infrared spectrum of the mixture. The volatilities of all the esters prepared were much less than that of the trifluoroacetyl fluoride (CF_3COF), which facilitated the separation of the esters from the excess unreacted CF_3COF by fractional condensation. Except for hexafluoroisopropyl alcohol, $(CF_3)_2CHOH$, and hexafluoro-2-methylpropanol-2, $(CF_3)_2C(CH_3)OH$, reaction of CF_3COF with the other alcohols went to completion without any difficulty, giving pure esters. The cesium fluoride recovered from these reactions became increasingly more active. $(CF_3)_2CHOH$ and $(CF_3)_2C(CH_3)OH$ reacted more slowly. Some unreacted alcohol always remained in these latter cases and the complete separation from the ester was difficult. However, completion of the reaction could be achieved by condensing the impure ester onto fresh CsF in the presence of excess CF_3COF. The solid recovered from these latter reactions had a moist appearance and on heating at 100° evolved the parent alcohol. Reaction conditions and yields of products are given in Table IV. Elemental analyses and thermodynamic data are found in Table V.

Acknowledgment.—Fluorine research at the University of Idaho is supported by the National Science Foundation and the Office of Naval Research. We thank Mr. N. R. Zack for mass spectra and Mr. C. Srivanavit for nuclear magnetic resonance spectra. Dr. C. T. Ratcliffe provided samples of $(CF_3)_3COH$ and $(CF_3)_2(C_2F_5)COH$.

Halomethyl-Metal Compounds. LXV. Generation of Fluorocarboalkoxycarbenes *via* the Organomercury Route[1,2]

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Received June 29, 1973

The organomercurials $PhHgCFClCO_2R$ (R = CH_3 and C_2H_5) and $PhHgCFBrCO_2C_2H_5$ have been prepared by reaction of the respective alkyl dihaloacetate with potassium *tert*-butoxide and phenylmercuric chloride or by mercuration of the respective ethyl trihalovinyl ether with mercuric nitrate in ethanol, followed by redistribution of the mercuration product with diphenylmercury. These mercurials are $FCCO_2R$ transfer agents at temperatures above 125°, reacting with olefins to give *gem*-fluorocarboalkoxycyclopropanes and inserting $FCCO_2R$ into the Si–H bond of triethylsilane. Also described is $FCCO_2Et$ addition to the C=N bond of $PhN{=}CCl_2$.

In a previous investigation[3] we prepared $PhHgCCl_2CO_2CH_3$ and $PhHgCClBrCO_2CH_3$, both $ClCCO_2CH_3$ transfer agents, as well as $PhHgCBr_2CO_2CH_3$, a source of $BrCCO_2CH_3$. In view of our interest in organometallic routes to fluorinated carbenes,[4-9] we have extended these studies to mercury compounds of the type $PhHgCFXCO_2R$ (X = Cl, Br; R = CH_3 or C_2H_5). The divalent carbon transfer chemistry of the $PhHgCClXCO_2CH_3$ compounds and of $PhHgCBr_2CO_2CH_3$ required rather drastic conditions, but it was expected

(1) Part LXIV: D. Seyferth and Y. M. Cheng, *J. Amer. Chem. Soc.*, **95**, 6763 (1973). (This paper is labeled part XIII by error.)

(2) Preliminary communication: D. Seyferth and R. A. Woodruff, *J. Fluorine Chem.*, **2**, 214 (1972).

(3) D. Seyferth, R. A. Woodruff, D. C. Mueller, and R. L. Lambert, Jr., *J. Organometal. Chem.*, **43**, 55 (1972).

(4) D. Seyferth and S. P. Hopper, *J. Org. Chem.*, **37**, 4070 (1972).

(5) D. Seyferth, H. Dertouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, **32**, 2980 (1967).

(6) D. Seyferth and K. V. Darragh, *J. Org. Chem.*, **35**, 1297 (1970).

(7) D. Seyferth and G. J. Murphy, *J. Organometal. Chem.*, **49**, 117 (1973).

(8) D. Seyferth and S. P. Hopper, *J. Organometal. Chem.*, **51**, 77 (1973).

(9) D. Seyferth and G. J. Murphy, *J. Organometal. Chem.*, **52**, C1 (1973).

TABLE I

FLUOROCARBOALKOXYCARBENE TRANSFER REACTIONS OF $PhHgCFClCO_2R$

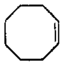
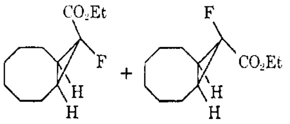
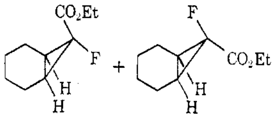
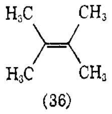
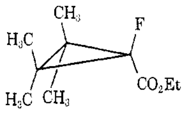
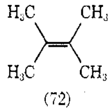
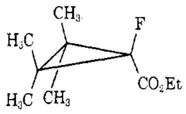
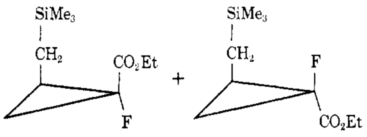
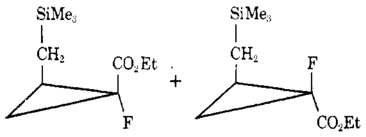
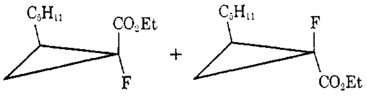
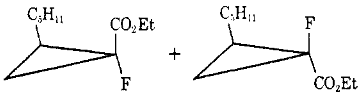
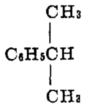
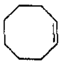
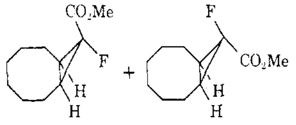
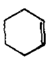
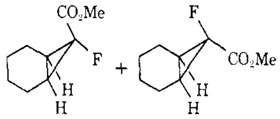
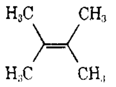
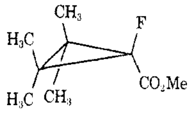
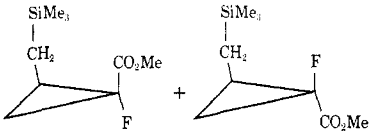
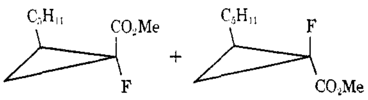
Substrate (mmol)	Mmol of mercurial	Solvent (ml)	Reaction temp, °C	Reaction time, hr	Yield PhHgCl, %	Recovered starting material, %	Products (% yield based on consumption of starting mercurial)
			Reactions of $PhHgCFClCO_2Et$				
 (neat)	12.0	Olefin (20)	144	36	96		 (1 part) (2.45 parts) (85%)
 (neat)	12.0	Olefin (20)	132 (sealed tube)	24	79	19	 (1 part) (2.39 parts) (69%)
 (36)	12.0	Benzene (12)	135 (sealed tube)	24	26	64	 (22%)
 (72)	12.0	Benzene (12)	155 (sealed tube)	72	72 +Hg^0 (21)		 (38%)
$Me_3SiCH_2CH{=}CH_2$ (neat)	12.0	Olefin (20)	129 (sealed tube)	36	66 +Hg^0 (19)		 (1 part) (1.85 parts) (24%)
$Me_3SiCH_2CH{=}CH_2$ (neat)	12.0	Olefin (20)	133 (sealed tube)	62	55 +Hg^0 (21)		 (1 part) (1.9 parts) (55%)
$CH_2{=}CHC_5H_{11}$-*n* (neat)	12.0	Olefin (20)	134 (sealed tube)	48	37 +Hg^0 (18)	9	 (1 part) (2.5 parts) (15%)
$CH_2{=}CHC_5H_{11}$-*n* (neat)	10.3	Olefin (12)	145 (sealed tube)	24	33 +Hg^0 (14)	18	 (1 part) (2.6 parts) (18%)
Et_3SiH (neat)	12.0	Et_3SiH (20)	108–110	50	25 +Hg^0 (54)		$Et_3SiCHFCO_2Et$ (71%)
 $C_6H_5CH(CH_3)_2$	24.0	Cumene (20)	155 (sealed tube)	72	23 +Hg^0 (11)	37+	None
 (neat)	12.0	THF (30)	155 (sealed tube)	48	0, + Hg^0 (54)		None

Table I

(*Continued*)

Substrate (mmol)	Mmol of mer-curial	Sol-vent (ml)	Reaction temp, °C	Reac-tion time, hr	Yield PhHgCl, Yield %	Recov-ered start-ing mate-rial, %	Products (% yield based on consumption of starting mercurial)
			Reactions of $PhHgCClFCO_2Me$				
 (22)	7.2	Benzene (7.0)	135 (sealed tube)	48	58	38	 (1 part) (1.8-1.9 parts) (85-88%)
 (24)	8.0	Benzene (8)	135 (sealed tube)	60	57		 (1 part) (1.9 parts) (47%)
 (60)	10.0	Benzene (10)	155 (sealed tube)	72	54 +Hg⁰ (29)		 (48%)
$Me_3SiCH_2CH{=}CH_2$ (24)	8.0	Benzene (8)	135 (sealed tube)	60	71	10	 (1 part) (1.4 parts) (61%)
$CH_2{=}CHC_5H_{11}$-*n*	8.0	Benzene (8)	135 (sealed tube)	60	47		 (1 part) (1.9 parts) (24%)
Et_3SiH (24)	8.0	Benzene (8)	135 (sealed tube)	60	63 +Hg⁰ (25)		$Et_3SiCHFCO_2Me$ (72%)

that the extrusion of $FCCO_2R$ from $PhHgCFXCO_2R$ compounds should occur more readily. Previous work in these laboratories had shown that thermolytic elimination of fluorocarbenes is much more favorable than elimination of the analogous chloro- or bromocarbenes.[7,8]

Results and Discussion

Mercurial Synthesis.—Phenyl(fluorochlorocarbomethoxymethyl)mercury could be prepared by a variation of our route to phenyl(trihalomethyl)mercury compounds[10] (eq 1). It was found essential to neutralize the reaction mixture at low temperature with dilute HCl. When this step was omitted, no product could be isolated. Application of this procedure to the reaction of phenylmercuric chloride, ethyl bromofluoroacetate, and potassium *tert*-butoxide gave the desired $PhHgCFBrCO_2C_2H_5$ in only 8% yield.

$$PhHgCl + HCClFCO_2CH_3 \xrightarrow[THF/-60°]{1.5\ t\text{-BuOK}} \xrightarrow{HCl-H_2O} PhHgCClFCO_2CH_3\ (44\%) + t\text{-BuOH} + KCl \quad (1)$$

A second route to such mercurials is based on some results of Knunyants and his coworkers,[11] who reported that halogenated vinyl ethers could be mercurated (eq 2) to give a mixture of products. We found that this mixture, isolated as a heavy oil, could be converted cleanly into the desired product, $PhHgCFClCO_2Et$, by a substituent redistribution reaction with diphenylmercury. After filtration of the phenylmercuric chloride which had formed, phenyl(fluorochlorocarbomethoxymethyl)mercury was isolated in good yield. A similar approach was used in the preparation of $PhHgCFBrCO_2Et$ (Scheme I).

All three of these mercurials are stable, crystalline solids and were found to transfer $FCCO_2R$ to appropriate carbenophiles.

Divalent Carbon Transfer Chemistry.—When a cyclooctene solution of $PhHgCFClCO_2Et$ was heated at

$$EtOCF{=}CFCl + Hg(NO_3)_2 \xrightarrow{EtOH} \xrightarrow{aq\ NaCl} Hg(CFClCO_2Et)_2 + ClHgCFClCO_2Et \quad (2)$$

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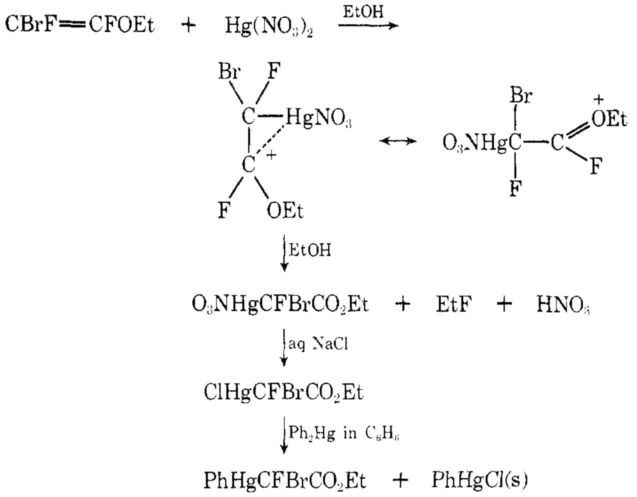
[10] D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).

[11] V. R. Polishchuk, L. S. German, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2024 (1971).

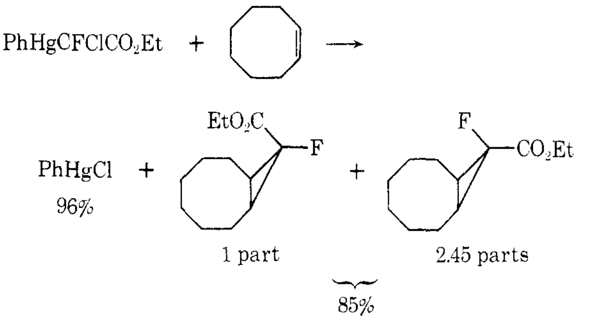
SCHEME I



144° under nitrogen for 36 hr, transfer of $FCCO_2Et$ to the olefin occurred in high yield (eq 3). Precipitation of phenylmercuric chloride did not occur until the reaction mixture was cooled. Further experiments with other olefins established the generality of this transfer reaction. Rather similar reactivity was exhibited by $PhHgCFClCO_2CH_3$. These reactions are summarized in Table I. Although better product yields were obtained when no diluent such as benzene was used, reactions in which benzene was present also gave reasonably good results. Both of these mercurials inserted their respective divalent carbon species into the Si–H bond of triethylsilane in good yield (eq 4), but attempted

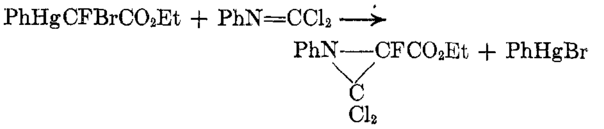
$$PhHgCFClCO_2R + Et_3SiH \longrightarrow Et_3SiCHFCO_2R + PhHgCl \quad (4)$$

$FCCO_2Et$ insertion into C–H bonds known to be quite reactive to CCl_2 (cumene and tetrahydrofuran)[12] was not successful.



(3)

The reaction conditions required for $FCCO_2R$ transfer from $PhHgCFClCO_2R$ compounds, 2–3 days at 135–145°, were rather severe. Since the elimination of PhHgX from $PhHgCCl_2X$ compounds becomes more facile as X is changed from Cl to Br to I,[13] it was expected and found that $FCCO_2Ft$ transfer proceeds more readily from $PhHgCFBrCO_2Et$ than from $PhHgCFClCO_2Et$. Thus a reaction of the former with cyclooctene (1:3 molar ratio) in benzene medium at 125° gave 9-fluoro-9-carboethoxybicyclo[6.1.0]nonane in 74% yield and phenylmercuric bromide in 83% yield after only 20 hr. Other reactions are summarized in Table II. Phenyl(fluorobromocarboethoxymethyl)mercury also reacted with triethylsilane to insert $FCCO_2Et$ into the Si–H bond, but no C–H insertions (*e.g.*, with cyclooctane and 2,5-dihydrofuran) were observed. Fluorocarboethoxycarbene addition to a C=N bond also was achieved (eq 5).



(5)

It would be of interest to know the nature of the transfer process involved in these reactions, *i.e.*, whether an $FCCO_2R$ carbene intermediate actually is involved, but the results in hand do not allow an answer to this question. Mechanistic implications cannot be derived from product yield comparisons between the various olefins, and, since many of the reactions were carried out in sealed tubes, even crude rate measurements were not possible. With unreactive substrates (*e.g.*, cumene and cyclooctane), starting mercurial recovery was high after heating times which in the case of reactions with olefins gave high phenylmercuric halide yields. However, this observation also does not help to distinguish between a direct transfer process and one involving a carbene intermediate. In the case of a carbene extrusion process, such starting material recovery can be explained in terms of continual regeneration of starting mercurial by insertion of $FCCO_2R$ into the Hg–X bond of the phenylmercuric halide formed in the extrusion step. Dichlorocarbene extrusion from $PhHgCCl_2Br$ is known to be a reversible process.[14] In the present instance, the reversibility of carbene extrusion was implied by the finding that, when the decomposition of $PhHgCFBrCO_2Et$ was carried out in the presence of 1 molar equiv of phenylmercuric chloride, $PhHgCFClCO_2Et$ was formed in 55% isolated yield, together with phenylmercuric bromide (eq 6). This observation is best rationalized

$$PhHgCFBrCO_2Et + PhHgCl \xrightarrow{PhCl,\ 133°} PhHgCFClCO_2Et + PhHgBr \quad (6)$$

in terms of $FCCO_2Et$ insertion into the Hg–Cl bond of phenylmercuric chloride. The organomercury compound formed, being more stable than the starting mercurial, thus accumulates in the reaction mixture.

The absence of C–H insertion reactions in the chemistry of these new mercurials also provides no mechanistic insight. Insertion reactions of bromocarboethoxycarbene occur in only low yield,[15] and the stabilizing effect of fluorine relative to bromine on a singlet state carbene center should increase the selectivity of the $FCCO_2R$ species sufficiently so as to preclude C–H insertion.

In any event, this limited investigation has shown the $PhHgCFXCO_2R$ reagents to be useful $FCCO_2R$ transfer agents, although the reaction conditions, *ca.* 1 day of heating at 125°, are still rather severe. Since they serve to introduce both a fluorine atom and a reactive functional substituent into the product, they may find useful synthetic applications.

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(12) D. Seyferth, J. M. Burlitch, K. Yamamoto, S. S. Washburne, and C. J. Attridge, *J. Org. Chem.*, **35**, 1989 (1970).

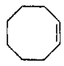
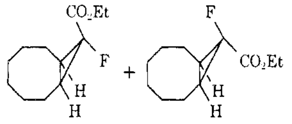
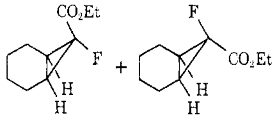
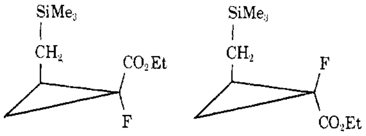
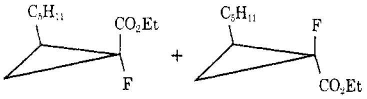
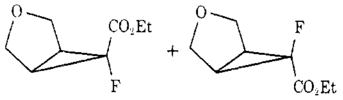
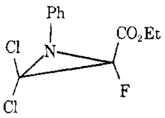
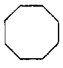
(13) D. Seyferth and C. K. Haas, *J. Organometal. Chem.*, **30**, C38 (1971).

(14) D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 4953 (1967).

(15) U. Schöllkopf and M. Reetz, *Tetrahedron Lett.*, 1541 (1969).

TABLE II

FLUOROCARBOETHOXYCARBENE TRANSFER REACTIONS OF $PhHgCBrFCO_2Et$

Substrate (mmol)	Mmol of mercurial	Solvent (ml)	Reaction temp, °C	Reaction time, hr	Yield PhHgBr, %	Recovered starting material, %	Products (% yield based on starting material consumed)
 (21)	7.0	Benzene (7)	125 (sealed tube)	20	83		 (1 part) (2.2 parts) (74%)
 (21)	7.0	Benzene (7)	125 (sealed tube)	20	80		 (1 part) (2.2 parts) (59%)
$Me_3SiCH_2CH{=}CH_2$ (18)	6.0	Benzene (6)	135 (sealed tube)	24	86		 (1 part) (1.6 parts) (72%)
$CH_2{=}CHC_5H_{11}$-*n* (18)	6.0	Benzene (6)	135 (sealed tube)	24	77		 (1 part) (2.9 parts) (19%)
Et_3SiH (21)	7.0	Benzene (7)	125 (sealed tube)	20	93		$Et_3SiCHFCO_2Et$ (74%)
 (neat)	6.0	Olefin (6)	125 (sealed tube)	24	Mixed with polymer and Hg^0		 (1 part) (1.3 parts) (*ca.* 15%)
$PhN{=}CCl_2$ (6.0)	6.0	Benzene (6)	125 (sealed tube)	24	38	36	 (40-55)
 (neat)	6.0	Hydrocarbon (6.0)	135 (sealed tube)	24	68		No volatile products

Experimental Section

General Comments.—All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. Solvents were dried before use. Sealed tube reactions were carried out using a tube oven which was thermostatically controlled to ±2°. Proton nmr spectra were recorded using a Varian Associates T60 or a Hitachi Perkin-Elmer R-20B spectrometer. Chemical shifts are recorded in δ units, parts per million downfield from internal tetramethylsilane. Chloroform or dichloromethane were used as alternative internal standards when necessary. Fluorine nmr spectra were recorded using the R-20B spectrometer with accessory ^{19}F FR generator (56.446 MHz). Fluorine chemical shifts are reported in parts per million upfield from internal hexafluorobenzene. Infrared spectra were obtained using a Perkin-Elmer Model 257 or 457A grating spectrophotometer. Reactions of the $PhHgCFXCO_2R$ compounds are summarized in Tables I and II. Characterization data for compounds prepared are found in Table III. Two examples of the general techniques used in these reactions are reported in detail. All other reactions followed these procedures, with the exception of those involving $PhN{=}CCl_2$ and PhHgCl as carbenophiles.

Preparation of the Organomercury Reagents. A. By the Base Procedure.—A 500-ml, three-necked flask equipped with an addition funnel, paddle stirrer, and Claisen adapter with low-temperature (pentane) thermometer and a nitrogen inlet was charged with 15.65 g (50 mmol) of phenylmercuric chloride, 8.86 g (70 mmol) of methyl fluorochloroacetate,[16] and 100 ml of THF. In the addition funnel was prepared a solution of 7.85 g (70 mmol) of potassium *tert*-butoxide (MSA Research) in 50 ml of THF, precipitated as the alcoholate by addition of 6.6 ml (*ca.* 70 mmol) of *tert*-butyl alcohol.

The reaction mixture was cooled to below −50° in a Dry Ice–

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[16] (a) E. R. Larsen, *J. Org. Chem.*, **28**, 1133 (1963). (b) R. S. Corley, J. Lal, and M. W. Kane, *J. Amer. Chem. Soc.*, **78**, 3489 (1956). (c) B. Englund, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, pp 184, 423.

TABLE III
REACTION PRODUCTS

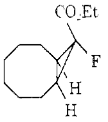
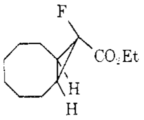
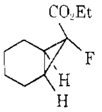
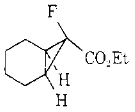
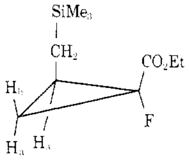
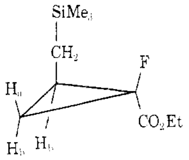
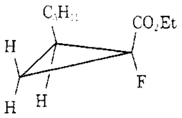
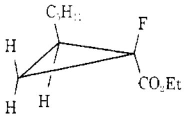
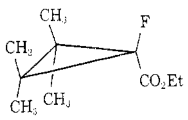
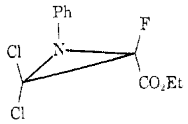
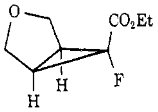
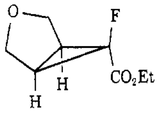
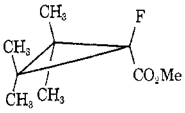
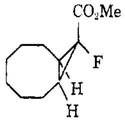
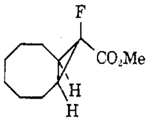
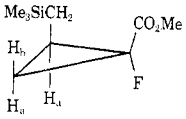
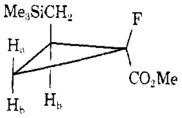
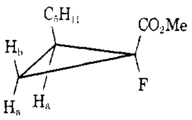
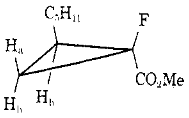
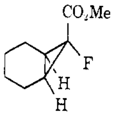
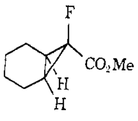
Registry no.	Structure[a]	$n^{25}D$	Ir (C=O), cm^{-1}	Nmr (CCl_4), δ, ppm	^{19}F nmr, ppm upfield from C_6F_6
38204-10-3		1.4652	1732	1.13 (t, J = 7 Hz, 3 H, OCH_2CH_3) 0.75–1.81 (m, 14 H, ring H) 4.06 (q, J = 7 Hz, 2 H, OCH_2CH_3)	11.3 (t, J = 23.6 Hz)
38204-09-0		1.4699	1746 1729	1.13 (t, J = 7 Hz, 3 H, OCH_2CH_3) 0.93–1.90 (m, 14 H, ring H) 4.06 (q, J = 7 Hz, 2 H, OCH_2CH_3)	57.0 (s, br)
38324-35-5		1.4559	1735	1.10 (t, J = 7 Hz, 3 H, OCH_2CH_3) 0.66–1.86 (m, 10 H, ring H) 4.03 (q, J = 7 Hz, 2 H, OCH_2CH_3)	10.5 (t, J = 21.5 Hz)
38204-11-4		1.4580	1744 1730	1.33 (t, J = 7 Hz, 3 H, OCH_2CH_3) 1.0–2.2 (m, 10 H, ring H) 4.22 (q, J = 7 Hz, 2 H, OCH_2CH_3)	53.2 (s, br)
38204-13-6		1.4299[b]	1734	0.10 (s, 9 H, Me_3Si) 0.6–1.8 (complex m, 5 H, $SiCH_2$) 1.37 (t, J = 7 Hz, 3 H, OCH_2CH_3) 4.19 (q, J = 7 Hz, 2 H, OCH_2CH_3)	14.6 (t of d, J_{F-H_a} = 18.7 Hz, J_{F-H_b} = 8.5 Hz)
38204-12-5		1.4302[b]	1749 1733	0.14 (s, 9 H, Me_3Si) 0.7–1.7 (complex m, 5 H, $SiCH_2$) 1.36 (t, J = 7 Hz, 3 H, OCH_2CH_3) 4.18 (q, J = 7 Hz, 2H, OCH_2CH_3)	45.0 (d of t, J_{F-H_a} = 15.2 Hz, J_{F-H_b} = 5.6 Hz)
42086-83-9		1.4267	1733	0.40–1.56 (m, 14 H, alkyl and ring H) 1.15 (t, J = 7 Hz, 3 H, OCH_2CH_3) 4.08 (q, J = 7 Hz, 2 H, OCH_2CH_3)	21.7 (complex m)
42086-84-0		1.4271	1751 1732	0.43–1.43 (m, 14 H, alkyl and ring H) 1.10 (t, J = 7 Hz, 3 H, OCH_2CH_3) 4.01 (q, J = 7 Hz, 2 H, OCH_2CH_3)	46.1 (complex m, approximates a doublet of triplets)
38204-14-7	$Et_3SiCHFCO_2Et$	1.4354	1752 1719	0.42–1.2 (m, 15 H, Et_3Si) 1.25 (t, J = 7 Hz, 3 H, OCH_2CH_3) 4.06 (q, J = 7 Hz, 2 H, OCH_2CH_3) 4.82 (d, J = 47.2 Hz, 1 H, $SiCHFCO_2$–)	64.0 (d, J = 48 Hz)
42117-05-5		1.4307	1731	1.16 (s, 6 H, Me_2) 1.21 (s, 6 H, Me_2) 1.33 (t, J = 7 Hz, 3 H, OCH_2CH_3) 4.18 (q, J = 7 Hz, 2 H, OCH_2CH_3)	
42117-06-6		1.5190	1761	1.35 (t, J = 7 Hz, 3 H, OCH_2CH_3) 4.34 (q, J = 7 Hz, 2 H, OCH_2CH_3) 6.7–7.5 (m, 5 H, Ph)	

TABLE III
(*Continued*)

Registry no.	Structure[a]	n^{25}_D	Ir (C=O), cm^{-1}	Nmr (CCl$_4$), δ, ppm	^{19}F nmr, ppm upfield from C$_6$F$_6$
42086-85-1		1.4408	1742	1.35 (t, J = 7 Hz, 3 H, OCH$_2$CH$_3$) 2.1 and 2.4 (d of m, J_{HF} = 18 Hz, 2 H, cyclopropyl H) 3.6–4.1 (m, 4 H, ring H) 4.24 (q, J = 7 Hz, 2 H, OCH$_2$CH$_3$)	24.9 (t, J_{HF} = 18 Hz)
42086-86-2		1.4492	1750 1736	1.37 (t, J = 7 Hz, 3 H, OCH$_2$CH$_3$) 2.25–2.45 (m, 2 H, cyclopropyl H) 4.10 (m, 4 H, ring H) 4.27 (q, J = 7 Hz, 2 H, OCH$_2$CH$_3$)	62.2 (t, J = 3.2 Hz)
42117-08-8		1.4315	1735	1.0–1.2 (m, 12 H, Me$_4$) 3.75 (s, 3 H, OCH$_3$)	36.5 (s, br, some fine splitting to Me)
42117-09-9	Et$_3$SiCHFCO$_2$Me	1.4362	1754 1727	0.44–1.22 (m, 15 H, Et$_3$Si) 3.62 (s, 3 H, OCH$_3$) 4.84 (d, J_{HF} = 47.5 Hz, 1 H, SiCHFCO$_2$–)	64.9 (d, J_{HF} = 47.9 Hz)
42086-87-3		1.4691	1737	0.93–1.93 (m, 14 H, ring) 3.75 (s, 3 H, OCH$_3$)	14.2 (t, J_{FH} = 21.1 Hz)
42086-88-4		1.4727	1751 1735	0.93–2.08 (m, 14 H, ring) 3.75 (s, 3 H, OCH$_3$)	60.0 (s, br) width at half height = 11 Hz
42086-89-5		1.4372	1753 (sh) 1738	0.05 (s, 9 H, Me$_3$Si) 0.56–1.70 (m, 5 H, SiCH$_2$-c-C$_3$H$_5$) 3.80 (s, 3 H, OCH$_3$)	25.4 (t of d, J_{FH_a} = 19, J_{FH_b} = 8.5–10 Hz)
42086-90-8		1.4330	1756 1738	0.08 (s, 9 H, Me$_3$Si) 0.41–1.61 (m, 5 H, SiCH$_2$-c-C$_3$H$_5$) 3.77 (s, 3 H, OCH$_3$)	48.0 (d of t, J_{FH_a} = 17, J_{FH_b} = 5.3 Hz)
42086-91-9		1.4242	1754 (sh) 1740	0.61–1.83 (m, 14 H, ring and chain H) 3.80 (s, 3 H, OCH$_3$)	25.3 (complex m, approximates a t of d, J_{FH_a} = 19, J_{FH_b} = 7 Hz)
42086-92-0		1.4262	1756 1739	0.66–1.66 (m, 14 H, ring and chain H) 3.78 (s, 3 H, OCH$_3$)	50.2 (complex m, approximates a d of t, J_{FH_a} = 18, J_{FH_b} = 5.3 Hz)
42086-93-1		1.4580	1738 1732 (sh)	1.0–2.1 (m, 10 H, ring H) 3.80 (s, 3 H, OCH$_3$)	10.9 (t, J_{FH} = 21.5 Hz)
42086-94-2		1.4604	1752 1748 1735	3.75 (s, 3 H, OCH$_3$)	54.2 (s, br, width at half height = 13 Hz)

[a] All compounds listed gave acceptable (±0.3%) carbon and hydrogen analyses. In those cases where two geometrical isomers were formed, the mixture of isomers was analyzed. [b] Refractive index of material *ca.* 95% pure, contaminated with its epimer.

acetone bath, and the solvated butoxide was added over a 15-min period, keeping the temperature below −50° at all times. The resulting clear solution was stirred at −50° for 30 min, then was poured into 500 ml of cold water containing 6 ml (70 mmol) of concentrated HCl, to give a milky white, two-phase system. The mixture was extracted with 500 ml of chloroform. The chloroform was removed on a rotary evaporator to give a white, crystalline residue, which was slurried in 100 ml of chloroform and filtered to remove phenylmercuric chloride. A 100-ml portion of hexane was added, precipitating a small additional amount of phenylmercuric chloride. The solution was placed in a freezer overnight. Filtration gave, in two crops, 8.9 g (22 mmol, 44%) of $PhHgCFClCO_2CH_3$. Material recrystallized twice from 1:1 chloroform–hexane gave a constant melting point of 115–117°.

The following analytical data support the assigned structure: nmr ($CDCl_3$) δ 7.41 (m, 5 H, C_6H_5) and 3.96 ppm (s, 3 H, OCH_3); ir (CCl_4) 3080 (w), 1965 (w), 1764 (vs), 1733 (vs), 1483 (w), 1434 (m), 1280 (vs), 1240 (sh), 1070 (m, br), 1028 (w), and 700 cm^{-1} (m).

Anal. Calcd for $C_9H_8ClFO_2Hg$: C, 26.81; H, 2.00. Found: C, 26.81; H, 2.05.

Essentially the same procedure was used in the reaction of 30 mmol of phenylmercuric chloride with 6.61 g (35.6 mmol) of ethyl bromofluoroacetate[17] and 35 mmol of *t*-BuOK-*t*-BuOH in 150 ml of THF at −50° for 1 hr. The same work-up procedure gave, upon crystallization from 1:1 chloroform–hexane, 1.10 g (8%) of $PhHgCFBrCO_2Et$: mp 111–114° (two further recrystallizations gave a constant melting point of 113–115°); nmr ($CDCl_3$) δ 1.35 (t, J = 7 Hz, 3 H, OCH_2CH_3), 4.26 (q, J = 7 Hz, 2 H, OCH_2–), and 7.15 ppm (m, 5 H, Ph); ^{19}F nmr (acetone) 36.9 ppm downfield from internal C_6F_6 (s, with Hg satellites, J_{F-Hg} = 565 Hz); ir (CCl_4) 3075 (w), 3060 (w), 2989 (m), 2960 (w), 1753 (s), 1722 (vs), 1487 (w), 1465 (w), 1432 (m), 1385 (w), 1368 (w), 1295 (m), 1265 (sh), 1246 (vs, br), 1170 (w), 1091 (m), 1070 (sh), 1058 (s), 1035 (sh), 1026 (sh), 1000 (w), 911 (w), 860 (w), 700 (s), 618 cm^{-1} (m).

Anal. Calcd for $C_{10}H_{10}BrFO_2Hg$: C, 26.01; H, 2.18; Br, 17.31. Found: C, 25.93; H, 2.18; Br, 17.57.

B. By the Olefin Mercuration Procedure. 1. Phenyl(fluorochlorocarboethoxymethyl)mercury.—A 250-ml three-necked flask equipped with an addition funnel and a magnetic stirring bar was charged with 32.5 g (0.10 mol) of mercuric nitrate (Merck, reagent) and 40 ml of absolute ethanol. From the addition funnel was added 15.0 g (0.118 mol) of ethyl 2-chloro-1,2-difluorovinyl ether.[18] The mercuric nitrate dissolved with heat evolution. The resulting solution was stirred for 1 hr and then was poured into a solution of 27.1 g (0.1 mol) of mercuric chloride in 600 ml of distilled water. A dense white oil separated. Extraction with chloroform followed by drying and removal of solvent gave 35.0 g of a dense, light yellow oil. The oil was diluted to 100.0 ml with benzene.

A solution of 3.54 g (10.0 mmol) of diphenylmercury in 40 ml of benzene in an erlenmeyer flask was "titrated" with the above solution until phenylmercuric chloride no longer precipitated. The end point was reached after addition of 15.0 ml of this solution. Filtration of the resulting mixture gave 3.16 g (10.0 mmol, 100%) of phenylmercuric chloride, mp 254–256°. Solvent was removed from the filtrate to give a white powder which was washed with hexane and suction filtered to give 3.77 g of material, mp 98–105°. Recrystallization two times from methylene chloride–hexane gave material of constant mp 101–105°, which was identified as phenyl(chlorofluorocarboethoxymethyl)mercury (9.05 mmol, 90%) on the basis of the following data: nmr ($CDCl_3$) δ 1.33 (t, J = 7 Hz, 3 H, OCH_2CH_3), 4.35 (q, J = 7 Hz, 2 H, OCH_2CH_3), and 7.13–7.47 ppm (m, 5 H, Ph); ^{19}F nmr (acetone) 39.9 ppm downfield from internal C_6F_6 (s, with Hg satellites, J_{F-Hg} = 578 Hz); ir (CCl_4) 3070 (w), 3060 (w), 2985 (m), 2905 (w), 1758 (vs), 1730 (vs), 1432 (w), 1371 (w), 1300 (sh), 1268 (vs), 1239 (s), 1070 (s, br), 1030 (m), 730 (s), 700 (m), 672 (w), and 679 cm^{-1} (w).

Anal. Calcd for $C_{10}H_{10}ClFO_2Hg$: C, 28.78; H, 2.42; Cl, 8.50. Found: C, 28.80; H, 2.55; Cl, 8.78.

Based upon the stoichiometry used, the overall yield of the title mercurial was 67 mmol (67%). The originally obtained mercuration product is thought to consist of a mixture of $ClHgCClFCO_2Et$ and $Hg(CClFCO_2Et)_2$, based upon its nmr spectrum, which showed two overlapping quartets assigned to the CH_2 resonance of the ethyl group.

2. Phenyl(fluorobromocarboethoxymethyl)mercury.—The required starting material, ethyl 2-bromo-1,2-difluorovinyl ether, was prepared in a two-step sequence from bromotrifluoroethylene.

A 250-ml three-necked flask equipped with a magnetic stirrer, a gas addition tube extending to the bottom of the flask, and a Dewar condenser was charged with 100 ml of absolute ethanol and 2.3 g (0.1 mol) of sodium. When the sodium had dissolved, the flask was cooled in an ice bath, and a total of 41.5 g (0.26 mol) of bromotrifluoroethylene was distilled into the stirred sodium ethoxide solution. When bromotrifluoroethylene no longer condensed on the cold finger, the reaction mixture was poured into 250 ml of cold water, separating a dense, yellow liquid. The aqueous layer was extracted with two 25-ml portions of methylene chloride, which were combined with the organic layer, washed with cold water, dried over anhydrous magnesium sulfate, and distilled. A fraction boiling at 102–107.5° (47.5 g, 0.25 mol, 96%) was collected (lit.[17] bp 108°) and identified as 2-bromo-1,1,2-trifluoroethyl ethyl ether: $n^{25}D$ 1.3707 (lit.[17] $n^{20}D$ 1.375); nmr (CCl_4) δ 1.35 (t, J = 7 Hz, 3 H, OCH_2CH_3), 4.07 (q, J = 7 Hz, 2 H, OCH_2CH_3), and 6.29 ppm (d of t, $J_{F-H_{gem}}$ = 48 Hz, $J_{F-H\alpha}$ = 5 Hz, 1 H, $CHFBrCF_2$–); ir (thin film) 3000 (m), 2949 (w), 2930 (w), 2884 (w), 1485 (w), 1448 (w), 1412 (sh), 1380 (s), 1361 (s), 1307 (s, br), 1276 (s), 1254 (w), 1217 (vs, br), 1195 (s, br), 1149 (w), 1085 (vs, br), 1051 (vs, br), 1025 (sh), 936 (w), 912 (sh), 900 (m), 830 (m), 755 (s), 737 (s), and 681 cm^{-1} (w).

A 250-ml three-necked flask equipped with a paddle stirrer and an addition funnel was charged with 13.4 g (120 mmol) of potassium *tert*-butoxide (MSA Research) and 30 ml of *n*-decane. From the addition funnel was added 20.7 g (100 mmol) of 2-bromo-1,1,2-trifluoroethyl ethyl ether over a 5-min period. A pale yellow color developed, and the mixture became somewhat viscous. The reaction was mildly exothermic. The addition funnel was immediately replaced with a 6-in. Vigreux column and stillhead, an additional 10 ml of *n*-decane was added to aid stirring, and the mixture was heated to distil out volatiles. Two low-boiling fractions (I, 81–83°, and II, 83–90°) were examined by glc and found to contain principally *tert*-butyl alcohol. A third fraction (91–101°) was virtually pure 1-bromo-1,2-difluorovinyl ethyl ether (7.82 g, 42 mmol, 42%), and a fourth fraction, 101–115°, was found to contain the 1-bromo-1,2-difluorovinyl ethyl ether and *n*-decane. Both of the higher boiling fractions were suitable for use in the preparation of bromofluorocarboethoxymethylmercuric chloride. The infrared spectrum of a portion of fraction III was identical with that of an authentic sample of the ether prepared previously and characterized on the basis of the following analytical data: nmr (CCl_4) (mixed cis and trans) δ 1.41 (t, J = 7 Hz, 3 H, OCH_2CH_3) and 4.03 and 4.05 ppm [2 t, J = 7 Hz, 2 H (combined), OCH_2CH_3]; ir (thin film) 3000 (m), 2919 (w), 1867 (vs), 1743 (s), 1480 (w), 1445 (w), 1395 (w), 1377 (m), 1275 (vs), 1251 (sh), 1196 (s), 1165 (vs), 1110 (m), 1070 (vs), 1048 (sh), 1027 (s), 996 (m), 985 (sh), 880 (s, br), and 690 cm^{-1} (m); $n^{25}D$ (mixture of isomers, as obtained) 1.3961.

Anal. Calcd for $C_4H_5BrF_2O$: C, 25.69; H, 2.70; Br, 42.74. Found (mixed isomers): C, 25.61; H, 2.73; Br, 42.93.

The preparation of the mercurial then was accomplished as follows.

A 250-ml three-necked flask equipped with an addition funnel and a paddle stirrer was charged with 13.0 g (40 mmol) of mercuric nitrate and 60 ml of absolute ethanol. From the addition funnel was added 7.8 g (42 mmol) of ethyl 2-bromodifluorovinyl ether over a 5-min period. The mixture became homogeneous, and a yellow color appeared. Cooling was required to moderate the reaction. The solution was stirred for 10 min at 0°, then 2.34 g (40 mmol) of NaCl in 50 ml of water was added. The mixture became cloudy. The mixture was poured into an additional 100 ml of water and extracted with two 200-ml portions of chloroform. Filtration removed a small amount of yellow powder, leaving a colorless, homogeneous solution. The solvent was removed on a rotary evaporator and the oily white residue was taken up in benzene and diluted to 50.0 ml. A 3.54-g (10.0 mmol) portion of diphenylmercury in 40 ml of benzene was "titrated" with the mercurial solution. After addition of 24 ml of the latter, a precipitate of phenylmercuric chloride no longer appeared on addition of 1 drop of the solution. The remaining 26 ml of solution was added to another 10 mmol of diphenylmercury, and the mercurial slurries were combined and filtered to give 6.20 g (19.8 mmol) of phenylmercuric chloride (99%), mp 256°. The filtrate was concentrated on a rotary evaporator, then precipitated by addition of cold hexane, giving 9.0 g (19.5 mmol) of the title mercurial, mp 113–115° (49% based on starting mercuric nitrate).

The spectroscopic properties of this product were identical with those of the material obtained by the base reaction (see above).

Reaction of Phenyl(fluorochlorocarboethoxymethyl)mercury with Cyclooctene.—A 100-ml three-necked flask equipped with a reflux condenser, a thermometer, and a magnetic stirring bar was charged with 5.0 g (12.0 mmol) of the mercurial and 20 ml (*ca.*

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[17] R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).

[18] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

150 mmol) of cyclooctene. The mixture was heated to reflux, becoming homogeneous at *ca.* 100°. Heating was continued at 143–145° for 36 hr. On cooling, the flask was filled with a precipitate of phenylmercuric chloride. The mixture was filtered to give 3.63 g (11.6 mmol, 96%) of phenylmercuric chloride, mp 255–261°. Glc examination of the filtrate indicated the presence of two products (MIT isothermal glc, 4 ft SE-30, 142°). A portion of the filtrate was saved for analysis and the remainder was distilled *in vacuo* in two fractions: I, 0.04 mm, to room temperature; II, 0.04 mm, 61–65°. Fraction II was analyzed by glc and found to contain two products: A, minor product, retention time 4.2 min; B, major product, retention time 5.5 min. They were separated by preparative glc (F & M 720, 6 ft DC-200, 180°) and identified as 9-*exo*-fluoro-9-*endo*-carboethoxybicyclo[6.1.0]nonane (A) and 9-*endo*-fluoro-9-*exo*-carboethoxybicyclo[6.1.0]nonane (B) on the basis of the analytical data shown in Table III.

Fraction II (2.07 g) contained no other products; thus the distilled yield of mixed isomers of 9-fluoro-9-carboethoxybicyclo-[6.1.0]nonane was 9.67 mmol (80%). Glc yield analysis indicated the overall yield to be 85%. The products were formed in a ratio of 1:2.45 in order of elution on glc.

The assignment of structure for the two isomers is based on the fact that in fluorocyclopropanes, J_{HF} (cis) > J_{HF} (trans).[19] Thus, the ^{19}F nmr spectrum of A appeared as a triplet, $J_{HF} = 23.6$ Hz, at 11.3 ppm upfield from internal hexafluorobenzene, while the corresponding fluorine signal of B appeared as a broadened singlet at 57.0 ppm, with a width at half height of 8.5 Hz.[20] The limit for J in this system thus becomes 4.25 Hz. Precedent for such assignments may be found, for example, in the case of 7-phenyl-7-fluoronorcarane.[21]

Reaction of Phenyl(chlorofluorocarboethoxymethyl)mercury with Cyclohexene.—A heavy-walled Pyrex tube (flame dried and flushed with nitrogen) was charged with 5.0 g (12.0 mmol) of the mercurial and 20 ml of cyclohexene. It was evacuated to *ca.* 0.5 mm and sealed. The sealed tube was heated in a tube oven at 133° for 24 hr with occasional agitation. When removed from the oven, the contents of the tube were homogeneous, but on cooling, the tube was filled with a precipitate. Filtration of the reaction mixture gave a white, crystalline solid, mp 255–258°, identified as phenylmercuric chloride (2.97 g, 9.5 mmol, 79%), and traces of elemental mercury. A portion of the filtrate was saved for yield analysis, and the remainder was distilled *in vacuo* in two fractions: I, 0.04 mm, to room temperature; II, 0.04 mm, 37–43°. Glc analysis of fraction II (F & M 5750, 4 ft UCW 98, 145°) showed six products. However, two of these accounted for *ca.* 88% of the fraction. These were separated by preparative glc (F & M 720, 6 ft DC-200, 155°) and identified as the two isomers of 7-fluoro-7-carboethoxybicyclo[4.1.0]heptane on the basis of the analytical data shown in Table III. Crystallization of the pot residue from distillation from hexane gave 0.95 g (*ca.* 19%) of starting mercurial. Glc yield analysis (MIT isothermal glc, SE-30, 142°) indicated the overall yield of 7-fluoro-7-carboethoxybicyclo[4.1.0]heptane to be 69%, based on starting mercurial consumed.

Reaction of Phenyl(fluorobromocarboethoxymethyl)mercury with *N*-Phenyliminophosgene.—A reaction of 6 mmol of the mercurial with 1.04 g (6 mmol) of $PhN{=}CCl_2$ in 6 ml of dry benzene was carried out in a sealed tube at 125° for 24 hr. After the tube had been opened, filtration removed 0.82 g (38%) of phenylmercuric bromide, mp 276–278°, from the light yellow solution. Glc examination of the filtrate showed the presence of $PhN{=}CCl_2$ (47%) and a higher boiling product. Vacuum distillation removed the solvent and the unconverted $PhN{=}CCl_2$. The pot residue was dissolved in ether and treated with a small amount of hexane to precipitate 0.6 g (22%) of starting mercurial. The remaining material was chromatographed on a small silicic acid column. The first fraction to elute (using 1:1 v/v hexane–dichloromethane) was a colorless oil which was purified by preparative glc (F & M 700, 6 ft UCW 98, 175°) and identified as 1-phenyl-2,2-dichloro-3-fluoro-3-carboethoxyaziridine (Table III). Its yield, estimated by glc, was *ca.* 50%. The second fraction to elute crystallized upon removal of solvent to give another 0.4 g of $PhHgCFBrCO_2Et$, making a total recovery of 36%.

Reaction of Phenyl(fluorobromocarboethoxymethyl)mercury with Phenylmercuric Chloride.—A 50-ml flask equipped with a magnetic stirring bar and a reflux condenser with a nitrogen inlet tube was charged with 2.13 g (4.6 mmol) of the mercurial, 1.45 g (4.6 mmol) of phenylmercuric chloride, and 10 ml of dry chlorobenzene. The mixture was stirred and heated at reflux for 4 hr. As the reflux temperature was reached, the reaction mixture became homogeneous, and as the heating period progressed, gradual precipitation of a flaky white solid was observed. The mixture was cooled and filtered to leave 1.87 g of white solid, mp 271–277°, assumed to be mostly PhHgBr containing some PhHgCl. The filtrate was evaporated. Addition of pentane to the residue and refrigeration produced 1.06 g of white solid, mp 99–101°, identified as $PhHgCFClCO_2Et$ (ir and nmr). The absence of significant amounts of $PhHgCFBrCO_2Et$ was indicated by the absence of the Br–C stretch at 618 cm^{-1}. Recrystallization raised the melting point to 101–105°.

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Registry No.—$PhHgCFClCO_2Et$, 38204-06-7; $PhHgCFClCO_2Me$, 42117-02-2; $PhHgCBrFCO_2Et$, 42117-03-3; phenylmercuric chloride, 100-56-1; methyl fluorochloroacetate, 433-52-3; ethyl bromofluoroacetate, 401-55-8; ethyl 2-chloro-1,2-difluorovinyl ether, 401-54-7; 2-bromo-1,1,2-trifluoroethyl ethyl ether, 380-78-9; cyclooctene, 931-88-4; cyclohexene, 110-83-8; 2,3-dimethyl-2-butene, 563-79-1; trimethylallylsilane, 762-72-1; 1-heptene, 592-76-7; triethylsilane, 617-86-7.

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[19] K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *J. Amer. Chem. Soc.*, **88**, 5678 (1966).

[20] The half-height width of a singlet may be taken as the limiting value approached by $2J$ for the same peak interpreted as a poorly resolved 1:2:1 triplet.

[21] T. Ando, Y. Kotoku, H. Yamanaka, and W. Funusaka, *Tetrahedron Lett.*, 2479 (1968).