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HALOMETHYL-METAL COMPOUNDS

LIV*. PHENYL(DIHALOCARBOMETHOXYMETHYL)MERCURY COMPOUNDS AS HALOCARBOMETHOXYCARBENE TRANSFER AGENTS

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SUMMARY

The phenyl(dihalocarboalkoxymethyl)mercury compounds $PhHgCCl_2CO_2CH_3$, $PhHgCClBrCO_2CH_3$, $PhHgCBr_2CO_2CH_3$, $PhHgCCl_2CO_2CH_2CH{=}CH_2$ and $PhHgCCl_2CO_2CMe_3$ have been prepared by the reaction of phenylmercuric chloride, the appropriate dihaloacetic acid ester and $Me_3COK \cdot Me_3COH$ in THF at $-50°$ to $-65°$. The first two mercurials were found to transfer $ClCCO_2CH_3$ to olefins and to triethylsilane, while the third proved to be a source of $BrCCO_2CH_3$. The rather high stability of these mercury compounds, however, limits their application in the synthesis of carbomethoxy-substituted cyclopropanes.

INTRODUCTION

Following our in-depth development of the chemistry of the versatile phenyl(trihalomethyl)mercury reagents[2], we began a study of organomercury compounds which would be potential sources of substituted carbenes or carbenoids. In previous papers we have reported concerning $PhHgCClXCF_3$ ($X{=}Cl, Br$)[3], $(Me_3SiCX_2)_2Hg$ ($X{=}Cl, Br$)[4], $PhHgCCl_2Ph$[5], $PhHgCCl_2CH_3$[6], $PhHgCCl_2CR$(ethylenedioxy) and $PhHgCCl_2CH(OEt)_2$[7] and $PhHgCCl_2P(O)(OMe)_2$[8]. Of these, the first three proved to be useful divalent carbon transfer agents. In the present report we describe the synthesis and divalent carbon transfer chemistry of phenyl(dihalocarbomethoxymethyl)mercury compounds (I), (II) and (III). In view of the possible further transformations of the CO_2CH_3 substituent after $XCCO_2CH_3$ transfer to the carbenophile,

$PhHgCCl_2CO_2CH_3$	$PhHgCClBrCO_2CH_3$	$PhHgCBr_2CO_2CH_3$
(I)	(II)	(III)

these compounds were of particular interest in terms of further development of synthetic chemistry.

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* For Part LIII see ref. 1.
** National Science Foundation Graduate Fellow, 1970–1972.
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RESULTS AND DISCUSSION

The three phenyl(dihalocarbomethoxymethyl)mercury compounds were prepared in good yield using the general procedure which served well in the preparation of the phenyl(trihalomethyl)mercury reagents (eqn. (1))[9]. All three were isolated as white, crystalline stable compounds which decomposed slowly at their melting

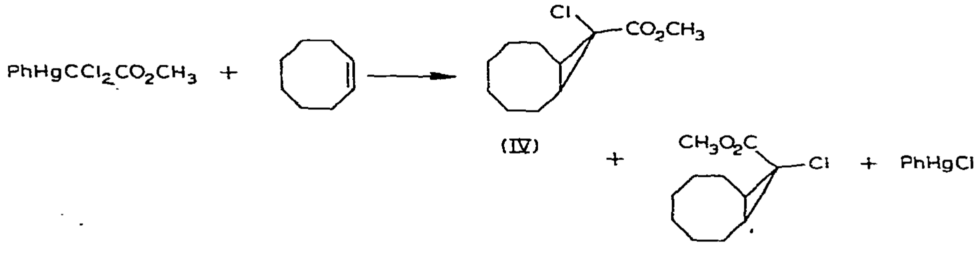
$$\mathrm{PhHgCl + HCXYCO_2CH_3 + Me_3COK \xrightarrow[-50^\circ]{THF} PhHgCXYCO_2CH_3 + KCl + Me_3COH}$$
$$(\mathrm{X, Y = Cl, Cl; Cl, Br; Br, Br}) \qquad (1)$$

points. This synthesis should be extendable to many other phenyl(dihalocarboalkoxymethyl)mercurials, and during the course of this research was used in the preparation of $PhHgCCl_2CO_2CH_2CH{=}CH_2$ from allyl dichloroacetate.

The three phenyl(dihalocarbomethoxymethyl)mercury compounds were found to undergo $XCCO_2CH_3$ transfer to olefins and to triethylsilane. However, in marked contrast to the phenyl(trihalomethyl)mercury reagents, whose CX_2 transfer chemistry is readily accessible at temperatures of 50–80°, these mercurials were much more stable, requiring reaction temperatures of ca. 120–140° for successful $XCCO_2CH_3$ transfer.

Phenyl(dichlorocarbomethoxymethyl)mercury

Of the three mercurials examined, $PhHgCCl_2CO_2CH_3$ was the most stable. No reaction occurred when it was heated in the presence of an excess of cyclohexene in benzene solution at reflux. Its reaction with cyclooctene (eqn. (2)) was carried out at 140°, and even at that temperature, the reaction progressed slowly. A reaction of 5 mmol of $PhHgCCl_2CO_2CH_3$ and 50 mmol of cyclooctene in 2.5 ml of chlorobenzene (to give a homogeneous mixture initially) containing 2.5 mmol of n-dodecane as internal GLC standard was carried out at 140° and the extent of reaction was followed by GLC analysis of aliquots withdrawn periodically. Figure 1 shows a plot of the yields of each isomer ((IV) and (V)) as a function of time. The optimum reaction time under these conditions is in the order of 3 days. After 5 days, the reaction mixture was worked up. Phenylmercuric chloride had been formed in 82% yield, and a total yield of (IV) and (V) of 73% was determined by GLC analysis of the filtrate. The isomer ratio was 1/3.2*. A similar study with allyltrimethylsilane (at 115–118°, since this



(IV)

(V)

(2)

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* In this paper, the "isomer ratio" is given in terms of the molar ratio of the isomer with the shorter GLC retention time on a SE-30 silicone rubber gum (General Electric Co.) GLC column to that of the isomer with the longer retention time.

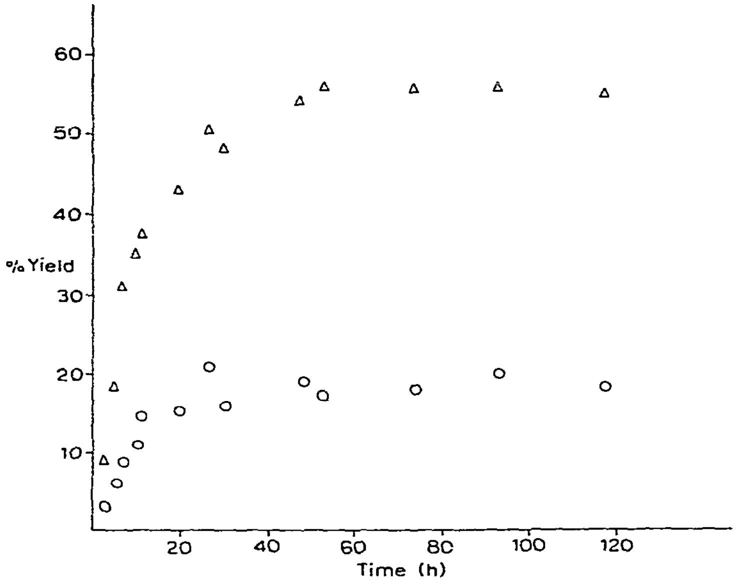
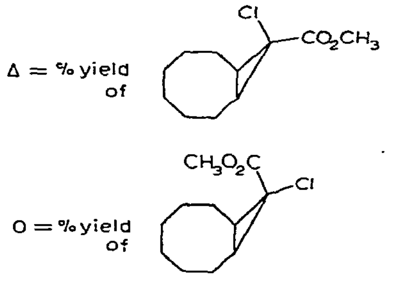
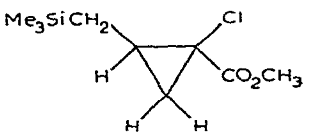


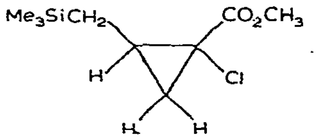
Fig. 1. Reaction of $PhHgCCl_2CO_2CH_3$ (5.0 mmol) with cyclooctene (50 mmol) in 5 ml of chlorobenzene at 140° as followed by gas chromatography (MIT isothermal unit, 4 ft. General Electric Co. SE–30 column, at 142°, n-dodecane internal standard).



olefin has a b.p. of 85°) demonstrated an optimum reaction time of about 4.5–5 days. After a 6 day reaction time, phenylmercuric chloride had been produced in 70% yield, and the two product isomers (VI) and (VII) in 60% yield. It should be emphasized that the "optimum time" thus determined is an empirical expression of the optimum cyclopropane product yield, not of the completeness of the decomposition of the mercury reagent. At these high temperatures and long reaction times there no doubt is an "optimum" balance between extent of mercurial decomposition and the rate of cyclopropane product decomposition which defines the "optimum reaction time" for a preparative reaction.



(VI)



(VII)

The reaction of $PhHgCCl_2CO_2CH_3$ with triethylsilane (in tenfold excess) at 118–119° was followed for only 72 h since no increase in product yield was noticed after 30 h. The desired reaction (eqn. (3)) was complicated by the reactivity of triethylsilane as a reducing agent, especially at higher temperatures. After the 72 h reaction

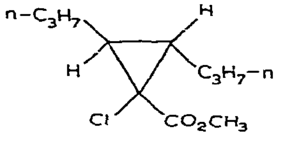
$$PhHgCCl_2CO_2CH_3 + Et_3SiH \rightarrow Et_3SiCHClCO_2CH_3 + PhHgCl \qquad (3)$$

time, the yield of $Et_3SiCHClCO_2CH_3$ was 47%, but PhHgCl was present in only 25% yield. However, metallic mercury was formed in 56% yield, most likely by the process shown in eqn. (4).

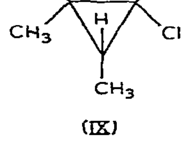
$$PhHgCl + Et_3SiH \rightarrow Et_3SiCl + [PhHgH] \rightarrow C_6H_6 + Hg \qquad (4)$$

Reactions of $PhHgCCl_2CO_2CH_3$ with other olefins were examined, but not in such detail, and the conditions used do not necessarily represent the optimum ones. For olefins with b.p. below 100°, reactions were carried out at 125–135° in sealed tubes. Thus the reaction of $PhHgCCl_2CO_2CH_3$ with an excess of cyclohexene in benzene solution at 120–135° in a sealed tube for 7 days gave a mixture of the two 7-chloro-7-carbomethoxynorcarane isomers in 42% yield (isomer ratio of 1/2.9). Phenylmercuric chloride and elemental mercury were present in yields of 76% and 8%, respectively. A similar sealed tube reaction at 124–125° in chlorobenzene solution between $PhHgCCl_2CO_2CH_3$ and allyltrimethylsilane (sevenfold excess) for 7 days gave a mixture of (VI) and (VII) in 73% yield (isomer ratio of 1/2.1).

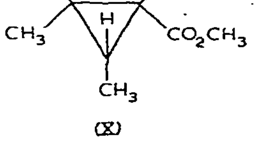
Much poorer yields of cyclopropane products were obtained with more highly alkylated olefins in sealed tube reactions carried out at 125° for 7 days (excess of olefin in chlorobenzene solution). Reaction of $PhHgCCl_2CO_2CH_3$ with *trans*-4-octene gave (VIII) in 20% yield, in addition to other high-boiling products which were not identified, but which showed NMR signals in the OCH_3 region. With $Me_2C{=}CHMe$, the expected isomer mixture ((IX) and (X)) was obtained in about 20% yield, but the cyclopropane derived from tetramethylethylene, (XI), was obtained in only 4% yield. In these three examples it is likely that decomposition of the cyclopropane products under the reaction conditions is severely limiting product yields.



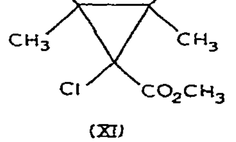
(VIII)



(IX)



(X)



(XI)

Phenyl(bromochlorocarbomethoxymethyl)mercury

The rate of CCl_2 extrusion from phenyl(dichlorohalomethyl)mercurials decreases in the order $PhHgCCl_2I > PhHgCCl_2Br > PhHgCCl_3$[2,10], and thus it was expected that $PhHgCClBrCO_2CH_3$ should be a more reactive source of $ClCCO_2CH_3$ than $PhHgCCl_2CO_2CH_3$. Such turned out to be the case, but for reasons not understood, the utility (in terms of product yields) of $PhHgCClBrCO_2CH_3$ varied from batch to batch. This mercurial could be brought into reaction in refluxing benzene solution, although better results were obtained at higher temperatures. Thus a reaction of $PhHgCClBrCO_2CH_3$ with an excess of cyclooctene in benzene at reflux for 6.5 h gave a mixture of (IV) and (V) (isomer ratio, as defined, = 1/2.7) in 27% yield. In comparison, a reaction of this mercurial with an excess of cyclooctene in chlorobenzene at reflux (ca. 135°) for 27 h resulted in a mixture of (IV) and (V) in 56% yield. Another set of experiments carried out in sealed tubes at 127–128° between the reactants in chlorobenzene for 24 h gave mixtures of (IV) and (V) in yields of 56–67%. A similar sealed tube reaction with allyltrimethylsilane (125° for 24 h) produced a mixture of (VI) and (VII) (isomer ratio, 1/2) in 64% yield, and another reaction of $PhHgCClBrCO_2CH_3$ with this olefin in mesitylene at 105–110°, monitored by GLC, was found to give the optimum product yield (41%) within 15 h (isomer ratio 1/2). Sealed tube reactions of $PhHgCClBrCO_2CH_3$ with $Me_2C{=}CHMe$ and with $Me_2C{=}CMe_2$ in chlorobenzene at 130–135° for 2–3 days gave the expected cyclopropanes, but the product yields were low, 19% and 9%, respectively.

Insertion of $PhHgCClBrCO_2CH_3$-derived $ClCCO_2CH_3$ into the Si–H bond of triethylsilane could be achieved in 40% yield (sealed tube, chlorobenzene solution, 24 h at 125°). Some elemental mercury was formed, but this side reaction was less important than in the case of the $PhHgCCl_2CO_2CH_3/Et_3SiH$ reaction.

Phenyl(dibromocarbomethoxymethyl)mercury

The reactivity of $PhHgCBr_2CO_2CH_3$ was quite similar to that of $PhHgCClBrCO_2CH_3$. Again, yields of *gem*-bromocarbomethoxycyclopropanes were variable. With cyclooctene and allyltrimethylsilane, product yields as high as 50–60% were obtained, but in other runs using these olefins, in which the PhHgBr yields were equally high, inexplicably much lower yields of the expected cyclopropanes resulted. Insertion of $BrCCO_2CH_3$ into the Si–H bond of triethylsilane, to give $Et_3SiCHBrCO_2CH_3$ in 35% yield, also was accomplished.

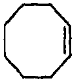
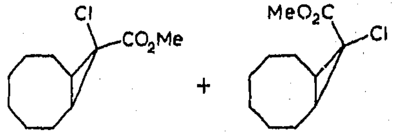
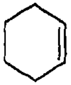
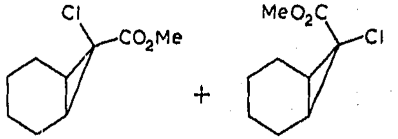
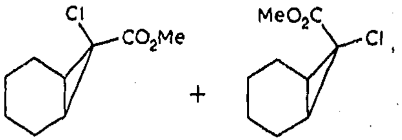
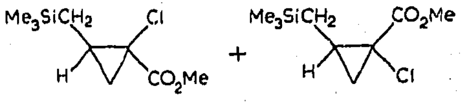
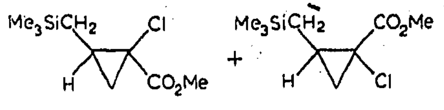
General considerations

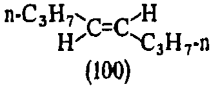
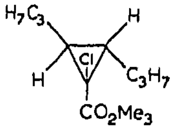
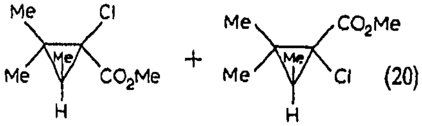
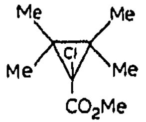
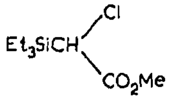
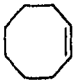
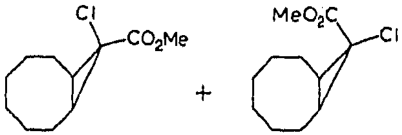
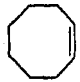
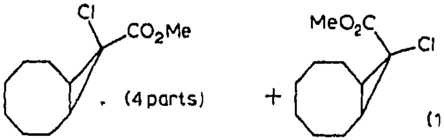
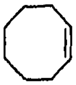
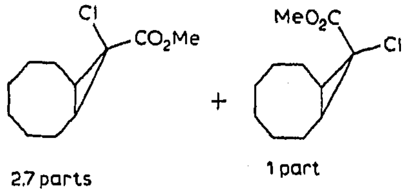
From the above discussion and from the results of all of our experiments with $PhHgCX_2CO_2CH_3$ compounds (Table 1), it is apparent that their utility in cyclopropane synthesis is somewhat limited. All three compounds, especially $PhHgCCl_2CO_2CH_3$, are too stable to be practical divalent carbon transfer reagents. Furthermore, during these reaction times at higher temperatures, undesirable side reactions intrude, as evidenced by the disparity between the phenylmercuric halide and the cyclopropane product yields. The former were always high, indicating complete or nearly complete consumption of the $PhHgCX_2CO_2CH_3$ reagent. No other major volatile products were found in the reaction mixtures and thus the nature of the counter-productive $XCCO_2CH_3$-consuming side reactions remains unknown.

(*continued on p.* 66)

TABLE 1

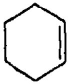
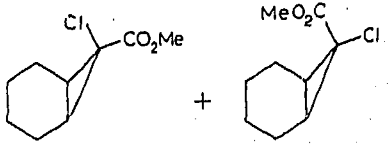
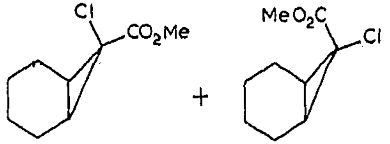
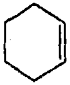
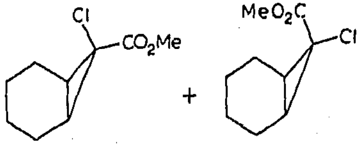
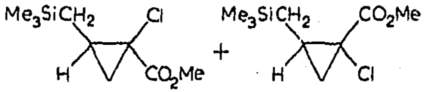
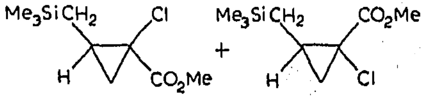
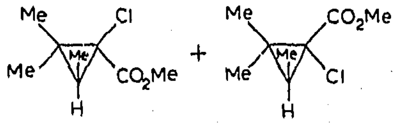
DIVALENT CARBON TRANSFER REACTIONS OF $PhHgCCl_2CO_2CH_3$, $PhHgCClBrCO_2CH_3$ AND $PhHgCBr_2CO_2CH_3$

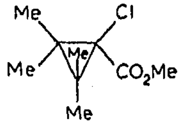
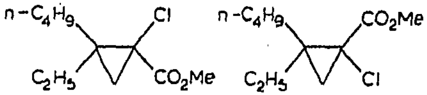
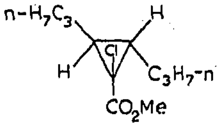
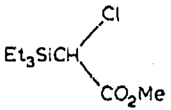
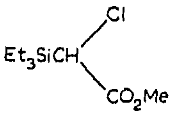
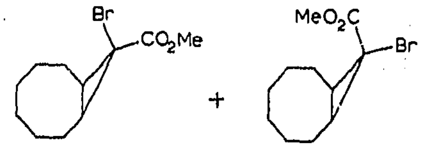
Substrate (mmol)	*mmol of mercurial*	*Solvent*	*Reaction temperature (°C)*	*Reaction time*	*Yield of PhHgX (%)*	*Products (% yield)*
Reactions of $PhHgCCl_2CO_2CH_3$						
 (38)	5	none	130°	3 days	86	 (59)
 (100)	18.4	C_6H_6 (5.0 ml)	110–135° (sealed tube)	7 days	76 (+8% Hg)	 (42)
 (100)	15	PhCl (5.0 ml)	124–125° (sealed tube)	7 days	74 (+9% Hg)	 (36)
$Me_3SiCH_2CH{=}CH_2$ (16.6)	10.15	PhCl (20 ml)	reflux	47 h	93	 (71)
$Me_3SiCH_2CH{=}CH_2$ (100)	15	PhCl (5 ml)	124–125° (sealed tube)	7 days	87 (+8% Hg)	 (73)

 $n\text{-}C_3H_7(H)C{=}C(H)C_3H_7\text{-}n$ (100)	15	PhCl (5 ml)	~125° (sealed tube)	7 days	67 (+8% Hg)	 (20)
$Me_2C{=}CHMe$ (103)	10	PhCl (28 ml)	~135° (sealed tube)	6 days	96 (+5% Hg)	 (20)
$Me_2C{=}CMe_2$ (22.6)	9.56	PhCl (10 ml)	~135° (sealed tube)	6 days	64 (+15% Hg)	 (~4%)
Et_3SiH (26.5)	20.1	PhCl (60 ml)	reflux	62 h	86 (+18% Hg)	 (42)
Reactions of $PhHgCClBrCO_2CH_3$						
 (15.6)	4.6	PhCl (20 ml)	reflux	27 h	90	 (56)
 (50)[a]	5	PhCl (2.5 ml)	127–128° (sealed tube)	24 h	92	 (4 parts) (1 part) (67)
 (38)	9.7	C_6H_6 (10 ml)	95°	6.5 h	74	 2.7 parts 1 part (27)

(continued)

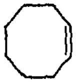
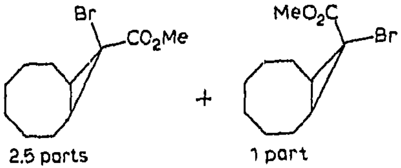
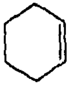
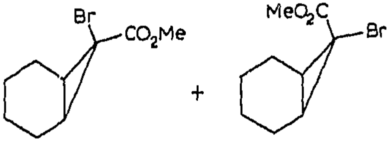
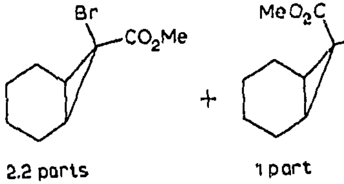
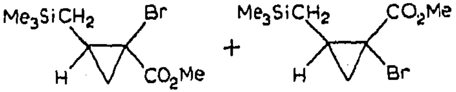
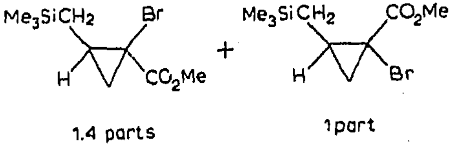
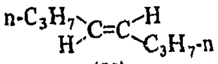
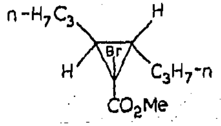
TABLE 1 (*continued*)

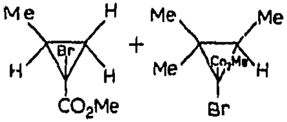
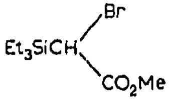
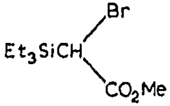
Substrate (mmol)	*mmol of mercurial*	*Solvent*	*Reaction temperature (°C)*	*Reaction time*	*Yield of PhHgX (%)*	*Products (% yield)*
 (22.8)	10	PhCl (25 ml)	reflux	25 h	90	 (32)
 (50)	5	PhCl (2.5 ml)	128° (sealed tube)	24 h	91	 (12) 3 parts 1 part
 (100)	10	PhCl (10 ml)	101°	8 h^b	67	 (44)
$Me_3SiCH_2CH{=}CH_2$ (12.3)	4.9	PhCl (5 ml)	reflux	22 h	95	 (48)
$Me_3SiCH_2CH{=}CH_2$ (50)	5	PhCl (2.5 ml)	125–126° (sealed tube)	24 h	98	 (64) 2 parts 1 part
$Me_2C{=}CHMe$ (21.2)	5	PhCl (10 ml)	~134° (sealed tube)	52 h	78	 (19)

$Me_2C{=}CMe_2$ (11.4)	7.45	PhCl (5 ml)	~130° (sealed tube)	69 h	85	 (9)
(18.5)	1.57	125 ml	reflux	44 h	53	(8)
$n\text{-}C_4H_9(C_2H_5)C{=}CH_2$ (33)	18.6	PhCl (20 ml)	120°	20 h	89	 (1.7 part) (1 part) (~30)
$n\text{-}C_3H_7(H)C{=}C(H)C_3H_7\text{-}n$ (50)	5	PhCl (2.5 ml)	125°	24 h	87	 (~6)
Et_3SiH (21.4)	9.5	PhCl (20 ml)	reflux	12 h	81	 (24)
Et_3SiH (50)	5	PhCl (5 ml)	125–126° (sealed tube)	24 h	66 (+26% Hg)	 (40)
Reactions of $PhHgCBr_2CO_2Me$						
 (38)	10	PhCl (20 ml)	reflux	43 h	87	 (50) 2.33 parts 1 part

(continued)

TABLE 1 (*continued*)

Substrate (*mmol*)	*mmol of mercurial*	*Solvent*	*Reaction temperature* (°C)	*Reaction time*	*Yield of PhHgX* (%)	*Products* (% *yield*)
 (50)	10	PhCl (5 ml)	130°	48 h	73	 (19)
 (22)	4.8	PhCl (20 ml)	reflux	4 h	78	 (11)
 (100)	10	PhCl (10 ml)	101°	24 h	84	 (12) [+22% $HCBr_2$–CO_2Me]
$Me_3SiCH_2CH{=}CH_2$ (13)	5.5	PhCl (20 ml)	reflux	21 h	95	 (62)
$Me_3SiCH_2CH{=}CH_2$ (100)	10	PhCl (10 ml)	100°	24 h	94	 (25)
 $n\text{-}C_3H_7(H)C{=}C(H)C_3H_7\text{-}n$ (50)	10	PhCl (5 ml)	125°	48 h	97	 (5)

$Me_2C{=}CHMe$ (12)	4	PhCl (10 ml)	130°	24 h	92		(9) [+9% $HCBr_2CO_2Me$]
Et_3SiH (21)	8.8	PhCl (20 ml)	reflux	12 h	89	 $Et_3SiCH(Br)CO_2Me$	(35)
Et_3SiH (100)	10	PhCl (10 ml)	118°	24 h	81	 $Et_3SiCH(Br)CO_2Me$	(8)

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[a] When 25 mmol of the olefin and 7.5 ml of PhCl were used, a 4.2/1 mixture of products was obtained in 56% yield. A reaction with 10 mmol of the olefin in 15 ml of PhCl gave a 3.7/1 isomer ratio in 63% yield.

[b] C_6Cl_6 internal standard monitored by GLC.

The presence of residual tar after trap-to-trap distillations of reaction mixtures implies polymer formation as a result of cyclopropane product decomposition.

The isomer ratios of the cyclopropane products (*e.g.*, in the case of cyclooctene; *cf.* Table 1) were somewhat variable, but usually one isomer predominated, at least by a factor of 2. NMR and IR spectroscopy did not appear to be of help in making structural assignments. Both steric and electronic factors operate to determine the stereoselectivity in additions of CXY carbenes to olefins[11], and in the case of carboalkoxycarbenes (or carbenoids) addition generally occurs to give the less hindered cyclopropane (CO_2R *exo* or *anti* to the greater number of alkyl substituents on the cyclopropane ring[11]). Thus UV-initiated reaction of N_2CHCO_2Et with cyclohexene gave 7-carboethoxynorcarane with an *exo/endo* ratio of 1.89; with thermally generated $HCCO_2Et$ (from the diazo compound), this ratio was 8.33, and for copper-catalyzed $HCCO_2Et$ transfer to cyclohexene[12] the *exo/endo* ratio was 10. In view of the larger steric bulk of the CO_2Me groups as compared with a chlorine atom, we suggest that the isomer produced in greater yield would be the one in which the Cl substituent is *syn* to the alkyl substituents of the cyclopropane ring formed, as shown in the structures in Table 1.

One might expect to obtain larger *exo/endo* ratios if the carboalkoxy group in the $PhHgCCl_2CO_2R$ compound were made bulkier. Accordingly, we prepared the new mercurial $PhHgCCl_2CO_2CMe_3$ and allowed it to react with allyltrimethylsilane and cyclohexene. The cyclopropane products did not appear to be very stable. In the case of the reaction with allyltrimethylsilane, carried out in t-butylbenzene at about 117° for 3 days, the yield of 1-chloro-1-carbo-t-butoxy-2-(trimethylsilylmethyl)cyclopropane was only 4%. The isomer ratio as defined above was 1/2.98, but in view of the low yield obtained, we hesitate to attach any significance to this number. The reaction of $PhHgCCl_2CO_2CMe_3$ with cyclohexene, carried out in a bomb tube, was unsuccessful and was accompanied by considerable build-up of pressure (formation of $Me_2C{=}CH_2$?).

In conclusion, we note that Schöllkopf and coworkers[13] have prepared the halocarboethoxydiazoalkanes, $XC(N_2)CO_2Et$ (X = Cl, Br, I) by halogen cleavage of $Hg[C(N_2)CO_2Et]_2$ and have found that photolysis of these diazoalkanes in the presence of olefins gives *gem*-halocarboethoxycyclopropanes in 30–50% yield. Because of the milder reaction conditions employed, this procedure has the advantage that it can be applied to the synthesis of a wider variety of *gem*-halocarboalkoxycyclopropanes than the procedure based on the organomercury reagents described in the present paper.

EXPERIMENTAL

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen. Infrared spectra were recorded using a Perkin–Elmer 337 or 257 grating infrared spectrophotometer, NMR spectra using a Varian Associates T60 spectrometer. Chemical shifts are given in δ units (ppm) downfield from internal TMS. Gas liquid partition chromatography (GLC) was used extensively to monitor progress of reactions, to determine yields and to isolate samples of products. The internal standard procedure was used in yield determination.

Preparation of methyl bromochloroacetate

Into a 500 ml, three-necked flask equipped with a reflux condenser, a magnetic stirring unit and a pressure equalizing dropping funnel with its delivery tube reaching to near the bottom of the flask was charged 14.1 g (0.1 mol) of EtOCCl=CHCl and 64 g (2.0 mol) of methanol. The solution was cooled in an ice bath and then 17.6 g (0.11 mol) of bromine in 20 ml of CCl_4 was added beneath the surface of the methanol solution via the dropping funnel. The resulting red solution was stirred for 1 h at 0° and then was treated with 300 ml of water. After phase separation, the aqueous layer was extracted with CCl_4. The combined organic layers were washed with aqueous sodium thiosulfate, dried and trap-to-trap distilled at 0.05 mmHg. GLC analysis of the distillate (F&M 5750, 4 ft. UCW–98, 110°) indicated that methyl bromochloroacetate had been formed in 84% yield, together with a small amount (4%) of the ethyl ester. Fractional distillation gave 13.1 g (70%) of $CHBrClCO_2CH_3$, b.p. 80–84°/45 mmHg which was contaminated with 3% of $CHBrClCO_2C_2H_5$. Material of greater than 99% purity was obtained by refluxing the distillate with an excess of methanol in the presence of a strong acid catalyst, washing and redistilling. NMR (CCl_4): δ 3.87 (s, 3H, OCH_3) and 5.90 ppm (s, 1H, CHBrCl). IR (liquid film): ν(C=O) 1762 cm^{-1}.

The procedure used represents a modification of the procedure of Crompton[14].

Preparation of phenyl(dihalocarboalkoxymethyl)mercury compounds

1. *$PhHgCCl_2CO_2CH_3$*. A slurry of 35.5 g (0.114 mol) of PhHgCl and 43 g (0.29 mol) of methyl dichloroacetate in 300 ml of dry tetrahydrofuran (THF) was prepared in a 1 l, three-necked flask equipped with a mechanical stirrer, a pentane thermometer and a nitrogen inlet tube. The mixture was cooled to −50° with a Dry Ice–acetone bath and 30 g of $Me_3COK \cdot Me_3COH$ (0.16 mol) was added as the solid through a solids addition tube over a period of 20 min. During the addition, color changes from colorless to yellow to red-brown were observed. The reaction mixture was stirred at −50° for 40 min and then was concentrated at reduced pressure to about 150 ml. Water (50 ml) and benzene (700 ml) were added. The organic layer was decanted through a filter, dried and evaporated. The yellow-orange solid residue was crystallized from low-boiling petroleum ether/dichloromethane to give 35.62 g (75%) of white, crystalline solid, m.p. 140–144° (slow dec.). (Found: C, 25.66; H, 1.72; Cl, 16.31. $C_9H_8O_2Cl_2Hg$ calcd.: C, 25.76; H, 1.92; Cl, 16.90). NMR ($CDCl_3$): δ 3.85 (s, 3H, OCH_3) and 7.24 ppm (m, 5H, Ph). IR (KBr): ν(C=O) 1725 cm^{-1}.

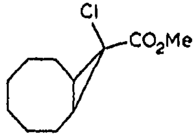
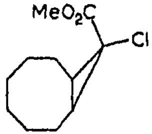
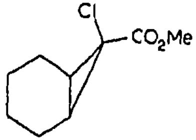
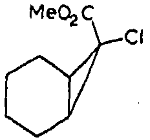
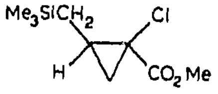
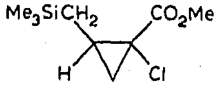
2. *$PhHgCBr_2CO_2CH_3$*. Using the procedure outlined in (1), 23 g (0.12 mol) of $Me_3COK \cdot Me_3COH$ was added over a period of 15 min to a slurry of 31.31 g (0.1 mol) of PhHgCl in 36.8 g (0.16 mol) of methyl dibromoacetate and 300 ml of THF at −60°. An orange color developed during the addition period. Work-up as in (1) gave an organic layer which was evaporated to leave a white, semicrystalline solid. Crystallization from 600 ml of 1/1 chloroform/hexane gave 27.55 g (55%) of white crystalline solid, m.p. 154–157° (partial dec.). A 2.34 g second crop, m.p. 149–152°, also was obtained. A recrystallized sample, m.p. 154–156° (dec.), was analyzed. (Found: C, 21.35; H, 1.56; Br, 31.11. $C_9H_8Br_2O_2Hg$ calcd.: C, 21.25; H, 1.58; Br, 31.40). NMR ($CDCl_3$): δ 3.84 (s, 3H, OCH_3) and 7.27 ppm (m, 5H, Ph). IR (KBr): ν(C=O) 1720 cm^{-1}. Using this procedure, yields as high as 68% were achieved in later experiments.

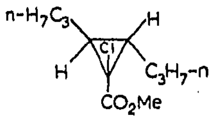
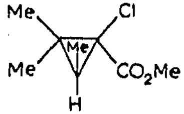
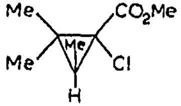
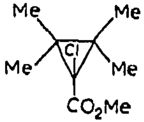
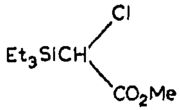
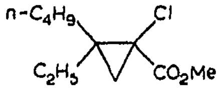
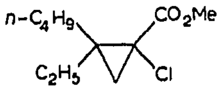
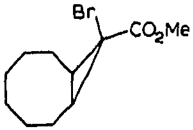
3. *$PhHgCClBrCO_2CH_3$*. The procedure outlined in (1) was used. The Me_3-

(*continued on p.* 72)

TABLE 2

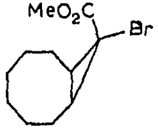
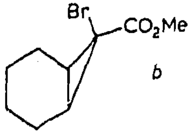
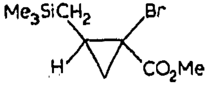
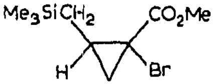
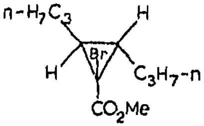
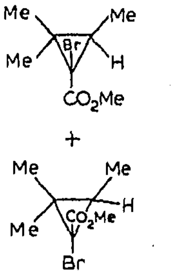
REACTION PRODUCTS

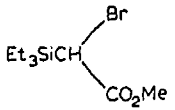
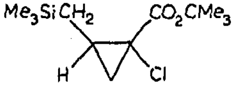
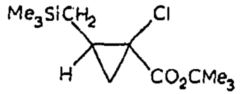
Compound	*B.p. (°C) (mmHg)*	n_D^{25}	*Analysis: found (calcd.) (%)*			*NMR, δ (ppm) (in CCl_4 unless otherwise stated)*	*IR (cm^{-1}) ν(C=O) (liquid film)*
			C	*H*	*Halogen*		
		1.4990	60.85 (60.96)	7.99 (7.91)	16.30 (16.36)	1.57 (m), 14H, ring C–H; 3.73 (s), 3H, OCH_3	1745, 1724
		1.4940	60.98 (60.96)	7.77 (7.91)	16.14 (16.36)	1.57 (m), 14H, ring C–H; 3.72 (s), 3H, OCH_3	1728
		1.4938	57.14 (57.30)	6.96 (6.94)	18.72^a (18.80)	0.92–1.93 (m), 10H, ring C–H; 3.68 (s), 3H, OCH_3	1740, 1718
		1.4849	57.34 (57.30)	6.86 (6.94)	18.72^a (18.80)	0.95–2.08 (m), 10H, ring C–H; 3.77 (s), 3H, OCH_3	1725
	80° (0.03)^a	1.4580	48.83^a (48.96)	7.63^a (7.76)	16.35^a (16.06)	(in $CHCl_3$) −0.08 (s), 9H, Me_3Si; 0.43–0.83 (m), 3H, ring C–H; 1.33–1.67 (m), 2H, $SiCH_2$–; 3.57 (s), 3H, OCH_3	1750, 1729
	80° (0.03)^a	1.4541				(in $CHCl_3$) −0.08 (s), 9H, Me_3Si; 0.43–0.75 (m), 3H, ring C–H; 1.18–1.45 (m), 2H, $SiCH_2$; 3.62 (s), 3H, OCH_3	1744, 1729

		1.4495	60.08 (60.40)	8.81 (8.76)	16.39 (16.21)	0.75–1.70 (m), 16H, ring and propyl C–H; 3.75 (s), 3H, OCH_3	1745, 1731
		1.4533	54.66[a] (54.39)	7.41[a] (7.42)	19.66[a] (20.07)	1.05 (d, $J = 6.0$ Hz), 3H, $C\underline{H}_3$–C–H; 1.14 (s), 6H, $(CH_3)_2C$; 1.74 (q, $J = 6.0$ Hz), 1H, CH_3–C–$\underline{H}$; 3.70 (s), 3H, OCH_3	1728
		1.4530				1.26 (d, $J = 6.0$ Hz), 3H, $C\underline{H}_3$–C–H; 1.28 (s), 3H, $C\underline{H}_3$–C–CH_3; 1.35 (s), 3H, CH_3–C–$C\underline{H}_3$; 1.75 (q, $J = 6.0$ Hz), 1H, CH_3–C–$\underline{H}$; 3.70 (s), 3H, OCH_3	1738
		1.4574	56.65 (56.69)	7.91 (7.93)		1.18 (s), 12H, $(CH_3)_2C$; 3.65 (s), 3H, OCH_3	1737
	87–91° (3.5)	1.4590	48.45 (48.52)	8.55 (8.60)		0.6–1.2 (m), 15H, Et_3–Si; 3.7 (s), 3H, OCH_3; 3.9 (s), 1H, $\mathrm{SiCH}\overset{\mathrm{Cl}}{<}$	1748, 1718
		1.4608	61.05[a] (60.60)	8.81[a] (8.76)	16.39[a] (16.21)	0.8–1.8 (m), 16H, ring and chain C–H; 3.73 (s), 3H, OCH_3	1750–1755 (v broad)
		1.4605				0.87–1.7 (m), 16H, ring and chain H; 3.71 (s), 3H, OCH_3	1745, 1731
	81–87° (0.1)[a] 75–76° (0.03)[a]		50.84[a] (50.58)	6.47[a] (6.56)		(in $CDCl_3$) 1.61 (m), 14H, ring C–H; 3.75 (s), 3H, OCH_3	1740, 1720

(continued)

TABLE 2 (*continued*)

Compound	*B.p. (°C) (mmHg)*	n_D^{25}	*Analysis: found (calcd.) (%)*			*NMR, δ (ppm) (in CCl_4 unless otherwise stated)*	*IR (cm^{-1}) ν(C=O) (liquid film)*
			C	*H*	*Halogen*		
	81–87° (0.1)[a] 75–76° (0.03)[a]					1.56 (m), 14H, ring C–H; 3.77 (s), 3H, OCH_3	1735, 1715
 b		1.5138	46.49 (46.37)	5.83 (5.62)		1.13–2.0 (m), 10H, ring C–H; 3.65 (s), 3H, OCH_3	1743, 1717
	~110° (0.05)[a]	1.4756	40.64[a] (40.75)	6.43[a] (6.46)	30.24[a] (30.13)	−0.03 (s), 9H, Me_3Si; 0.4–2.0 (m), 5H, ring C–H+Si–CH_2; 3.89 (s), 3H, OCH_3	1744, 1719
		1.4700				0.01 (s), 9H, Me_3Si; 0.57–1.17 (m), 3H, ring C–H; 1.37–1.67 (m), 2H, Si–CH_2; 3.95 (s), 3H, OCH_3	1742, 1723
		1.4654	50.28 (50.20)	7.19 (7.20)		0.60–1.68 (m), 16H, ring and propyl C–H; 3.70 (s), 3H, OCH_3	1740
		1.4723[a]	43.42[a] (43.46)	5.92[a] (5.92)		1.08 (d, *J* = 5.5 Hz), 3H, H–C–C$\underline{H}_3$; 1.12 (s), 3H, C$\underline{H}_3$–C–CH_3; 1.17 (s), 3H, CH_3–C–C$\underline{H}_3$; 1.3–1.7 (m), 1H, $\underline{H}$–C–CH_3; 3.68 (s), 3H, OCH_3	1728[a] (broad)

		1.4766	40.44 (40.44)	7.15 (7.16)		0.23–1.00 (m), 15H, Et_3–Si; 3.45 (s), 3H, OCH_3; 3.50 (s), 1H, SiCHBr	1742, 1714
	44–45° (0.04)[a]	1.4474	54.83[a] (54.83)	8.89[a] (8.82)	13.54[a] (13.49)	0.03 (s), 9H, Me_3Si; 0.5–1.2 (m), 3H, cyclopropyl H; 1.40 (m), 2H, $SiCH_2$; 1.48 (s), 9H, CMe_3	1730 (sh), 1724
		1.4480				0.01 (s), 9H, Me_3Si; 0.5–1.1 (m), 3H, cyclopropyl H; 1.40 (m), 2H, $SiCH_2$; 1.43 (s), 9H, CMe_3	1735, 1712

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[a] Data for mixture of isomers as obtained in reaction.

[b] Other isomer could not be separated as a pure compound by GLC.

$COK \cdot Me_3COH$ used was prepared by mixing 0.07 mol each of unsolvated Me_3COK (MSA Research) and dry Me_3COH in 100 ml of THF. The resulting slurry was added to 0.05 mol of PhHgCl and 0.07 mol of $CHBrClCO_2CH_3$ in 150 ml of THF at −64°. Similar work-up gave white solid product which was recrystallized from 800 ml of 1/1 chloroform/hexane to give, in three crops, 19.82 g (85%), m.p. 148–154° (dec.). (Found: C, 23.33; H, 1.77; Hg, 43.53. $C_9H_8O_2ClBrHg$ calcd.: C, 23.29; H, 1.74; Hg, 43.22). NMR ($CDCl_3$): δ 3.87 (s, 3H, OCH_3) and 7.27 ppm (m, 5H, Ph). IR ($CHCl_3$): ν(C=O) 1735 cm^{-1}.

4. *$PhHgCCl_2CO_2CH_2CH{=}CH_2$.* The procedure outlined in (1) was used in the reaction of 0.112 mol of $Me_3COK \cdot Me_3COH$ with 0.10 mol of PhHgCl and 0.153 mol of allyl dichloroacetate[15] (n_D^{25} 1.4560; ν(C=O) 1764, 1748 cm^{-1}; b.p. 98–102°/62 mmHg) in 300 ml of THF at −45°. The crude solid product was precipitated from a methanol solution by cooling to −78° to give 27.3 g (61%) of white solid, m.p. 57–59°. An analytical sample, m.p. 59–60°, was obtained by recrystallization from hexane. (Found: C, 29.73; H, 2.27; Cl, 15.91; Hg, 45.06. $C_{11}H_{10}O_2Cl_2Hg$ calcd.: C, 29.64; H, 2.26; Cl, 15.91; Hg, 45.01). NMR ($CDCl_3$): δ 4.65 (d, 2H, OCH_2–), 5.00–5.53 (m, 2H, =CH_2), 5.60–6.27 (m, 1H, –CH=) and 7.23 ppm (m, 5H, Ph). IR (film): ν(C=O) 1728 cm^{-1}.

5. *$PhHgCCl_2CO_2CMe_3$.* Essentially the same procedure was used in the reaction of 0.065 mol of $Me_3COK \cdot Me_3COH$ with 0.05 mol of PhHgCl and 0.065 mol of t-butyl dichloroacetate in 200 ml of THF at −60°. Similar work-up gave 14.7 g (64%) of crude product, m.p. 115–122°. Recrystallization from hexane resulted in white cubic crystals, m.p. 120–124°. (Found: C, 31.15; H, 3.11. $C_{12}H_{14}O_2Cl_2Hg$ calcd.: C, 31.21; H, 3.06). NMR ($CDCl_3$): δ 1.51 (s, 9H, t-Bu) and 7.32 ppm (m, 5H, Ph). IR (CCl_4): ν(C=O) 1747 cm^{-1}.

Reactions of phenyl(dihalocarbomethoxymethyl)mercury compounds with olefins

1. *Reactions at atmospheric pressure.* A three-necked flask of appropriate size equipped with a reflux condenser, a magnetic stirring assembly, a thermometer and a nitrogen inlet tube was charged with the mercurial, the olefin and the solvent (if any) in the amounts given in Table 1. The reaction mixture was stirred and heated at the given temperature for the stated length of time. In some cases, the progress of the reaction was followed by GLC analysis of periodically withdrawn aliquots (*e.g.*, Fig. 1). Upon completion of the heating period, the reaction mixture was filtered to remove phenylmercuric halide. The filtrate was either analyzed directly by GLC or was trap-to-trap distilled prior to GLC analysis. Samples for analysis and for spectral measurements were isolated by GLC. The reactions are summarized in Table 1. Table 2 provides information concerning the products obtained. In most cases, GLC analysis and isolation was performed using UCW–98 silicone columns. The procedure used in reactions with triethylsilane was the same as that described above.

9-Bromo-9-carbomethoxybicyclo[6.1.0]nonane (isomer mixture) decomposed in part during GLC analysis and isolation. An analytical sample of the mixed isomers was obtained by careful distillation using a short path distillation apparatus.

2. *Sealed tube reactions.* The mercurial, the olefin and the solvent (if any) were charged into a dry, heavy-walled Pyrex tube of appropriate size which had been well flushed with nitrogen. The tube was cooled to −78° or below, evacuated to about

0.5 mmHg and sealed. The tube then was heated in a tube oven for the appropriate length of time at the temperature indicated in Table 1. There was no provision for continuous agitation, but the oven was shaken occasionally during the heating period. After the tube had been opened, further work-up followed the procedure outlined in (1). In the case of $PhHgCCl_2CO_2CH_3$, phenylmercuric chloride did not precipitate in substantial amount until the tube was cooled to room temperature. With $PhHgCClBrCO_2CH_3$, phenylmercuric bromide precipitated in large quantity during the heating period.

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