Journal of Organometallic Chemistry, 71 (1974) 335–346

HALOMETHYL—METAL COMPOUNDS

LXIX*. PREPARATION OF SOME FUNCTIONAL HALOMETHYL—MERCURY COMPOUNDS

DIETMAR SEYFERTH and ROBERT A. WOODRUFF

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received November 20th, 1973)

Summary

The organomercury reagents $PhHgCCl_2SO_2Ph$, $PhHgCBr_2SO_2Ph$, $PhHgCClICO_2Me$, cyclo-$C_6H_{11}HgCCl_2CO_2Me$, $PhCH_2CH_2HgCCl_2CO_2Me$, $PhHgCHClCO_2Et$ and $PhHgCCl_2CONMe_2$ have been prepared and their application as divalent carbon transfer reagents has been examined.

Introduction

In previous papers of this series we have reported concerning the preparation and the divalent carbon transfer chemistry of various functional halomethyl—mercurials, including $PhHgCCl_2CO_2Me$, $PhHgCClBrCO_2Me$ and $PhHgCBr_2CO_2Me$ [2], $PhHgCFXCO_2Et$ (X = Cl, Br) [3], $PhHgCXBrCF_3$ (X = Cl [4] and F [5]), $Hg(CX_2SiMe_3)_2$ (X = Cl, Br) [6], $PhHgCCl_2P(O)(OMe)_2$ [7] and $PhHgCCl_2CR(OR')_2$ [8]. We have continued our studies in this area with the aim of developing new functional divalent carbon transfer reagents of this type and of improving existing reagent systems.

Results and discussion

Sulfonyl-substituted mercurials

The report by Dutch workers [9] of convenient, high-yield preparations of phenyl(dichloromethyl)- and phenyl(dibromomethyl)sulfone suggested to us their application in the preparation of $PhHgCX_2SO_2Ph$ (X = Cl, Br), possible reagents for the generation of phenylsulfonyl-chloro- and -bromocarbene**.

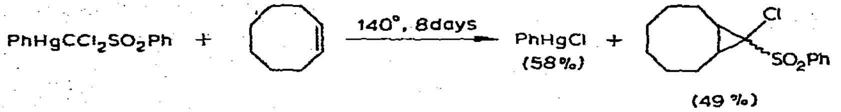
---

* For Part LXVIII see ref. 1.

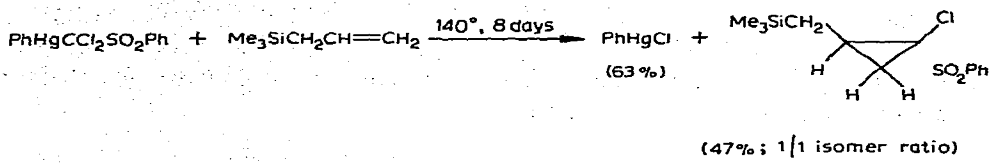
** Prior to this work, phenylsulfonylcarbene [10] and bis(phenylsulfonyl)carbene [11] had been generated from the respective diazoalkane.

When these phenyl(dihalomethyl)sulfones were treated with potassium tert-butoxide in the presence of phenylmercuric chloride, the expected organomercurials were formed in good yield (eqn. 1). Phenyl(phenylsulfonyldichloromethyl)mercury is a white, crystalline solid which is unaffected by air and water and is thermally very stable. It was found to be a $PhSO_2CCl$ transfer agent, but high temperatures and long reaction times in sealed tubes were required to effect such reactions (eqn. 2 and 3). However, such decomposition of $PhHgCCl_2SO_2Ph$ via α-elimination was not the only process which occurred. The formation in substantial yields of $PhSO_2CCl_2H$, metallic mercury and diphenylmercury indicated that a competing homolytic decomposition must be taking place as well (eqns. 4—6), with allylic hydrogen abstraction being involved in reaction 6.

$$PhSO_2CX_2H + Me_3COK + PhHgCl \xrightarrow{THF,\ -60^\circ} PhHgCX_2SO_2Ph + Me_3COH + KX \qquad (X = Cl, Br) \qquad (1)$$



(2)



(3)

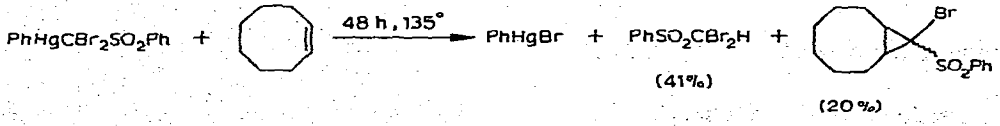
$$PhHgCCl_2SO_2Ph \rightarrow PhHg^{\bullet} + {}^{\bullet}CCl_2SO_2Ph \qquad (4)$$

$$2\,PhHg^{\bullet} \rightarrow Ph_2Hg + Hg \qquad (5)$$

$$PhSO_2CCl_2{}^{\bullet} + R\text{-}H \rightarrow PhSO_2CCl_2H + R^{\bullet} \qquad (6)$$

Such a competing homolytic process had been noticed previously in the high temperature chemistry of $Hg(CCl_2SiMe_3)_2$ [6].

Similar results were obtained when $PhHgCBr_2SO_2Ph$ was heated in chlorobenzene solution in the presence of cyclooctene (eqn. 7), but the olefin cycloaddition product yield was much lower.

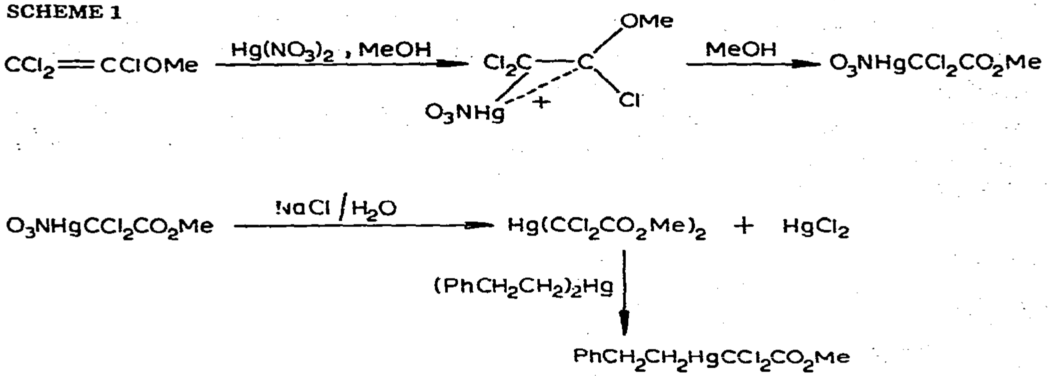


(7)

Carboalkoxy-substituted mercurials

We had prepared various phenyl(dihalocarboalkoxymethyl)mercury compounds, $PhHgCXX'CO_2R$ [2, 3], but had found these to be much less reactive as divalent carbon transfer reagents than the phenyl(trihalomethyl)mercurials. Our work with trihalomethyl—mercury systems of type $RHgCCl_2X$ had shown that increased CCl_2 transfer reactivity was obtained as X was varied from Cl to Br to I [12] and R from phenyl to cyclohexyl [13]. Such changes were investigated using $PhHgCCl_2CO_2CH_3$ as the starting point. Phenyl(iodochlorocarbomethoxymethyl)mercury was prepared by reaction of methyl iodochloroacetate with potassium tert-butoxide in the presence of phenylmercuric chloride at −60° in THF. This mercurial indeed was much less stable than $PhHgCCl_2CO_2Me$ or $PhHgCClBrCO_2Me$, decomposing in the presence of cyclooctene in benzene solution at reflux to give phenylmercuric iodide in 79% yield within only 8 h. However, the yield of the $ClCCO_2Me$ cycloaddition product, 9-chloro-9-carbomethoxybicyclo[6.1.0]nonane, was only 10%. In addition, a number of other products (which were not identified) were formed. A similar decomposition carried out in cyclooctene/chlorobenzene at 135° occurred even more rapidly, within 4 h, giving phenylmercuric iodide in 79% yield. Here also the yield of 9-chloro-9-carbomethoxybicyclo[6.1.0]nonane formed was low (10%) and other products were present as well. It is possible that at these temperatures free radical reactions of the carbon—iodine bond intrude. In view of the poor success of this approach, the effect of using an alkyl(dichlorocarbomethoxymethyl)mercury compound in place of $PhHgCCl_2CO_2Me$ was examined. Cyclohexyl(dichlorocarbomethoxymethyl)mercury was prepared by the method used in the synthesis of $PhHgCCl_2CO_2Me$. β-Phenylethyl(dichlorocarbomethoxymethyl)mercury also was prepared by this procedure, as well as by a different route patterned after the synthesis of $PhHgCClFCO_2Et$ [3] (Scheme 1).

SCHEME 1



Of these two mercurials, the cyclohexyl derivative proved to be the better $ClCCO_2Me$ transfer agent. It reacted with cyclooctene in refluxing chlorobenzene solution to give a mixture of the 9-chloro-9-carbomethoxybicyclo[6.1.0]-nonane isomers in 78% yield within a 57 h reaction time and with allyltrimethylsilane to give the expected 1-chloro-1-carbomethoxy-2-(trimethylsilylmethyl)-cyclopropane in 48% yield within 48 h. In comparison, divalent carbon transfer from $PhHgCCl_2CO_2Me$ to cyclooctene at 130° occurred in 59% yield within 72 h and to allyltrimethylsilane under similar conditions in 71% yield within 47 h. Thus the use of cyclo-$C_6H_{11}HgCCl_2CO_2Me$ does not appear to offer any outstanding advantage. β-Phenylethyl(dichlorocarbomethoxymethyl)mercury also was allowed to react with cyclooctene. After 44 h at ca. 140°, $PhCH_2CH_2HgCl$ had been formed in 75% yield, but the 9-chloro-9-carbomethoxybicyclo-[6.1.0]nonane yield was only 26%.

We conclude that as far as $ClCCO_2Me$ transfer reagents are concerned, $PhHgCCl_2CO_2Me$ is the most useful. Its ease of preparation from commercially available methyl dichloroacetate and phenylmercuric chloride outweighs its somewhat diminished reactivity compared to $PhHgCClBrCO_2Me$ and cyclo-$C_6H_{11}HgCCl_2CO_2Me$.

As expected, $PhHgCHClCO_2Et$, prepared according to Scheme 2, is much more stable than $PhHgCCl_2CO_2Me$. When it had been heated in cyclooctene solution in a sealed tube at 155—160° for 3 days, phenylmercuric chloride was formed in only 20% yield, and a 70% recovery of the starting material was effected. The yield of the divalent carbon transfer product, 9-carboethoxybicyclo[6.1.0]nonane, was 33%, based on unrecovered starting material. An equally low conversion of 7-carboethoxybicyclo[4.1.0]heptane was realized when $PhHgCHClCO_2Et$ was heated in cyclohexene (155° for 6.5 days).

SCHEME 2

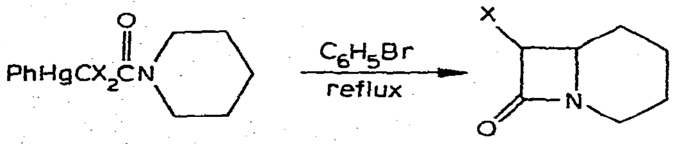
$$CHCl{=}CClOEt \xrightarrow{Hg(OAc)_2/EtOH} AcOHgCHClCO_2Et \xrightarrow{NaCl/H_2O} ClHgCHClCO_2Et$$

$$\xrightarrow{Ph_2Hg} PhHgCHClCO_2Et + PhHgCl$$

An amide-substituted mercurial

The reaction of *N,N*-dimethyl dichloroacetamide with potassium tert-butoxide in the presence of phenylmercuric chloride in THF at —60° gave $PhHgCCl_2C(O)NMe_2$ in 35% yield. The yield of this product very likely could be improved. However, its decomposition in the presence of cyclooctene at 148° gave little or none of the expected cycloaddition product and so further studies of this mercurial were not carried out.

We note, however, that Johansson [14] has prepared different amide-substituted mercurials, (I), which show carbene reactivity in a novel intramolecular C—H insertion reaction (eqn. 8).



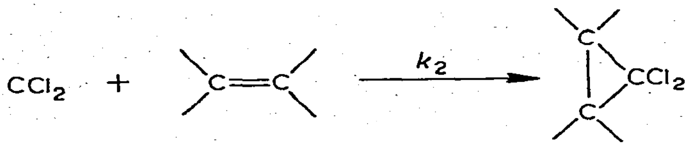
(8)

(I) (X = Cl, Br)

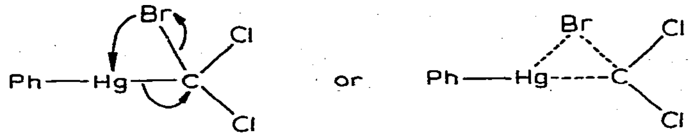
(both isomers)

In conclusion, some comment concerning the relatively poor reactivity of many of the functional $PhHgCX_2Z$ compounds which we have studied [X = Cl or Br; Z = CO_2R, SO_2Ph, $SiMe_3$, CF_3, $CONMe_2$, CH_3, $CR(OR')_2$ and H] compared with that of phenyl(trihalomethyl)mercury compounds [15], is appropriate. Our kinetic studies [16, 17] have shown that in the case of $PhHgCCl_2Br$ the mechanism shown in eqns. 9 and 10 is operative. A concerted extrusion of the carbene [transition state (II)] was suggested. Further work showed that the presence of fluorine substituents on the methyl carbon invariably resulted in an increase in the rate of carbene extrusion. The following reactivity sequences may be noted: $PhHgCFBr_2 \rightarrow CFBr > PhHgCBr_3 \rightarrow CBr_2$ [16]; $PhHgCFCl_2 \rightarrow CFCl > PhHgCCl_3 \rightarrow CCl_2$ [17]; $PhHgCFClCO_2Me \rightarrow FCCO_2Me > PhHgCCl_2CO_2Me \rightarrow ClCCO_2Me$ [3]; $PhHgCFBrCF_3 \rightarrow FCCF_3 > PhHgCClBrCF_3 \rightarrow ClCCF_3$ [5].

$$\mathrm{PhHgCCl_2Br} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PhHgBr} + \mathrm{CCl_2} \qquad (9)$$



(10)



(II)

A phenyl substituent on the methyl carbon also was found to lead to enhanced reactivity, $\mathrm{PhHgCCl_2Ph \rightarrow ClCPh > PhHgCCl_3 \rightarrow CCl_2}$ [18]. This suggested to us that the rate of divalent carbon extrusion process is determined largely by the stabilization available to the incipient carbene. Such stabilization is thought to be provided by donation of electron density to the vacant carbon *p* orbital of the singlet state carbene by substituents on the carbon atom via $p_\pi - p_\pi$ dative bonding. The substituents Z in $\mathrm{PhHgCX_2Z}$ compounds which result in more stable and less reactive divalent carbon transfer systems for the most part are ones which generally stabilize an adjacent anionic center, *not* an electron-deficient center, which is in agreement with the ideas mentioned. In further development of functional mercurials, one would expect those of type $\mathrm{PhHgCX_2OR}$, $\mathrm{PhHgCX_2SR}$ and $\mathrm{PhHgCX_2CH{=}CH_2}$ to be especially reactive on the basis of these considerations.

While there is no doubt that the ester, amide, sulfone, trimethylsilyl and trifluoromethyl-substituted mercurials are considerably more stable than the corresponding phenyl(trihalomethyl)mercury compounds, it is by no means certain that the long reaction times which appear to be required in their reactions with olefins are entirely due to this higher stability. The reaction times will be affected not only by the appropriate k_1 for each mercurial (e.g., eqn. 9) (assuming a carbene mechanism for each, which may not necessarily be correct), but also by the ratio k_1/k_2. If this ratio is large, then longer reaction times will result. Also of importance is the effective concentration of phenylmercuric halide during the progress of the reaction. In the $\mathrm{PhHgCX_3}$/olefin reactions, which are carried out at 80° or below, the phenylmercuric halide is largely insoluble. However, in the reactions under discussion, which are carried out at higher temperatures (130–150°), the phenylmercuric halide formed remains largely in solution and so is able to compete more ffectively with the olefin. The interception of $\mathrm{ClCCO_2Me}$ by phenylmercuric halide was demonstrated in an experiment in which $\mathrm{PhHgCClBrCO_2Me}$ was heated in chlorobenzene at 135° in the presence of an equimolar quantity of phenylmercuric chloride. In a reaction time of 7 h, $\mathrm{PhHgCCl_2CO_2Me}$ was formed in 72% yield, presumably via the process shown in eqns. 11 and 12.

$$PhHgCClBrCO_2Me \rightleftharpoons PhHgBr + ClCCO_2Me \quad (11)$$

$$PhHgCl + ClCCO_2Me \rightleftharpoons PhHgCCl_2CO_2Me \quad (12)$$

The observed product is more stable than the starting mercurial and thus accumulates in the reaction mixture. This reaction time should be compared with that required to effect $ClCCO_2Me$ transfer to cyclooctene in chlorobenzene solution at 128° in 67% yield, 24 h. In the case of $PhHgCFBrCO_2Et$ [3], it also was found that $FCCO_2Et$ transfer to phenylmercuric chloride (giving the more stable $PhHgCFClCO_2Et$) at ca. 135° occurred more rapidly than $FCCO_2Et$ transfer to cyclooctene [3]. In these reactions $XCCO_2R$ insertion into the Hg—Cl bond has been demonstrated; such insertion into the Hg—Br bond of phenylmercuric bromide should occur even more readily. Thus it seems quite probable that the long reaction times observed for $PhHgCX_2CO_2R$/olefin reactions are not indicative of the magnitude of the respective rate constant k_1.

Experimental

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. Carefully dried solvents were used in all reactions. NMR spectra were recorded using a Varian A60 or T60 spectrometer. Chemical shifts are given in δ units, ppm downfield from internal tetramethylsilane. Infrared spectra were recorded using a Perkin—Elmer Model 457A grating IR spectrophotometer. Gas liquid chromatography (GLC) was used for analysis of reaction mixtures, yield determinations and collection of samples. Commercial stainless steel columns were used in either an F&M (Hewlett—Packard) Model 700, 720 or 575 gas chromatograph. Yields were determined using the internal standard procedure.

Phenylmercuric chloride was prepared by reaction of tetraphenyltin with mercuric chloride [19]. Potassium tert-butoxide (unsolvated) was purchased from the MSA Research Corp. Cyclohexylmercuric chloride was obtained by reaction of dicyclohexylmercury (Grignard preparation) with mercuric chloride.

Preparation of starting materials

β-Phenylethylmercuric chloride. The Grignard reagent prepared from 1 g atom of magnesium turnings and 1.05 mol of β-phenylethyl bromide in 450 ml of THF was treated with 0.5 mol of mercuric chloride. The reaction mixture was hydrolyzed with dilute HCl and extracted with dichloromethane. The organic layer was dried and evaporated at reduced pressure to leave 164 g (ca. 80%) of a viscous oil that could not be crystallized. The NMR spectrum indicated the presence of bis(β-phenylethyl)mercury; δ 1.23 (t, J 7.5 Hz, 4H, CH_2Hg), 3.0 (t, J 7.5 Hz, 4H, $PhCH_2$) and 7.15 ppm (m, 10H, Ph) (in CCl_4). This compound has been reported as a nondistillable, noncrystallizable oil [20]. Others [21, 22] have reported m.p. —44° and b.p. 165—170°/0.003 mm.

To a solution of 10.3 g (25 mmol) of bis(β-phenylethyl)mercury in 20 ml of benzene in an Erlenmeyer flask was added a solution of 6.8 g (25 mmol) of mercuric chloride in hot chloroform. An immediate precipitate resulted. The mixture was heated on the steam bath and then was cooled to 0° and filtered to give 13.65 g (80%) of β-phenylethylmercuric chloride, m.p. 170—172°. (Bass [21] reports m.p. 164°).

Methyl iodochloroacetate. A 300 ml round-bottomed flask equipped with a reflux condenser and a drying tube was charged with 0.15 mol of methyl dichloroacetate, 0.30 mol of potassium iodide and 125 ml of anhydrous acetone. The mixture was stirred and heated at reflux for 5.5 days. During this time, the color gradually darkened to a deep red. The progress of the reaction was followed by periodically withdrawing a 5 ml aliquot of the solution, washing this with water and sodium thiosulfate solution and then observing the disappearance of starting material and formation of product by NMR. Heating was discontinued when aliquots withdrawn 24 h apart showed little difference in the relative concentrations of starting material and product. The acetone solution was washed with water (back extracted with carbon tetrachloride), then with sodium thiosulfate, giving ultimately a pale yellow solution. The latter was concentrated at reduced pressure and the residue was distilled to give 14 g of liquid with b.p. 65°/0.4 mm. Redistillation gave 12.1 g (34%) of a pale yellow oil which NMR showed to contain 3—4% of an impurity. The product decomposed when collection by GLC was attempted. NMR (in CCl_4): δ 3.90 (s, 3H, OCH_3) and 6.03 ppm (s, 1H, CHClI). IR: ν(C=O) 1750, 1735 (sh). The product rapidly became pink, then red, in daylight at room temperature but could be stored in the dark at low temperature if a small quantity of diphenylamine was added.

Methyl trichlorovinyl ether. To 0.69 mol of cold, absolute methanol was added 0.68 mol of chloral. The resulting crystalline chloral methyl hemiacetal was dissolved in 50 ml of benzene and added dropwise, with cooling as necessary, to 0.67 mol of thionyl chloride in 54 g of pyridine. The resulting mixture was stirred and cooled until pyridine hydrochloride had crystallized out. Filtration was followed by a water wash of the filtrate. The dried filtrate was distilled to give 87 g (0.44 mol) of methyl 1,2,2,2-tetrachloroethyl ether, b.p. 75—77°/23 mm; lit. [23] b.p. 76—78°/23 mm. NMR (CCl_4): δ 3.73 (s, 3H, OCH_3) and 5.69 ppm (s, 1H, CCl_3CHClO).

A solution of 0.44 mol of NaOH in 20 ml of water and 140 ml of ethanol was added, with stirring and cooling, to 84.5 g (0.43 mol) of $CH_3OCHClCCl_3$. The mixture was stirred at room temperature for 30 min and then was treated with 200 ml of water; a dense organic layer separated. The water/alcohol layer was extracted with dichloromethane. The organic layer and extracts were washed with cold water, dried and distilled. Methyl trichlorovinyl ether, 34.1 g (0.21 mol), b.p. 139—145°, was thus obtained; lit. [23] b.p. 135—140°. NMR (in CCl_4): δ 3.77 ppm (s, 3H).

Preparation of organomercury compounds

Phenyl(phenylsulfonyldichloromethyl)mercury. A 500 ml three-necked flask equipped with a paddle stirrer, an addition funnel and a Claisen adapter bearing a nitrogen inlet tube and a low temperature (pentane) thermometer was charged with 8.93 g (39.7 mmol) of phenyl(dichloromethyl)sulfone [9], 9.4 g (30 mmol) of phenylmercuric chloride and 150 ml of THF. In the addition funnel was prepared a solution of 4.5 g (40 mmol) of potassium tert-butoxide in 75 ml of THF. The alcoholate, t-BuOK·t-BuOH, was precipitated by addition of 3.75 ml of tert-butanol. The reaction vessel was cooled to —70° and the tert-butoxide slurry was added slowly, keeping the temperature below —60° at all times. Upon completion of the addition, the mixture was transferred to a round-bottomed flask and the solvent was removed at reduced pressure. The brown residue was dissolved in 600 ml of benzene and extracted with 100 ml of water. The benzene solution was evaporated at reduced pressure and the resulting pale brown residue was crystallized from chloroform/hexane to give 9.8 g (65%) of the title mercurial. Two recrystallizations from chloroform/hexane gave material with constant m.p. 175.5—177°. (Found: C, 30.92; H, 2.09; Cl, 14.28. $C_{13}H_{10}O_2Cl_2SHg$ calcd.: C, 31.12; H, 2.01; Cl, 14.13%.) NMR (CH_2Cl_2): δ 7.35 (broad s, 5H, Ph—Hg) and 7.5—8.1 ppm (m, 5H, PhS). IR(CCl_4): 3080 w, 1480 w, 1451 m, 1435 m, 1335 s, 1319 m, 1165 vs, 1085 s and 701 s, cm^{-1}. (The bands at 1335 and 1165 cm^{-1} are indicative of the SO_2 function).

Phenyl(phenylsulfonyldibromomethyl)mercury. Essentially the same procedure was used in the reaction of 30 mmol of $PhSO_2CBr_2H$ [9], 25 mmol of PhHgCl and 33 mmol of t-BuOK·t-BuOH in 175 ml of THF at —60°. The first crystallization from hot 5/1 CCl_4/$CHCl_3$ gave two crops with m.p. 190—195° and 180—189°, a total yield of 63%. Two further recrystallizations from 1/1 chloroform/hexane gave white needles, m.p. 193—195°. (Found: C, 26.14; H, 1.78 $C_{13}H_{10}O_2Br_2SHg$ calcd.: C, 26.43; H, 1.71%.) NMR ($CHCl_3$): δ 7.35 (broad s, 5H, Ph—Hg) and 7.5—8.3 (m, 5H, Ph—S).

Phenyl(iodochlorocarbomethoxymethyl)mercury. The same procedure was used in the reaction of 50 mmol of methyl iodochloroacetate, 40 mmol of PhHgCl and 50 mmol of t-BuOK·t-BuOH in 175 ml of THF at —60°. The amorphous yellow solid obtained initially was crystallized from chloroform/pentane to give 11.0 g (54%) of yellow powder, m.p. 142—146°, which underwent total decomposition at 180°. (Found: C, 21.14; H, 1.69. $C_9H_8O_2ClIHg$ calcd.: C, 21.15; H, 1.58%.) NMR ($CDCl_3$): δ 3.86 (s, 3H, OCH_3) and 7.36 ppm (m, 5H, Ph). IR ($CHCl_3$): ν(C=O) 1741 cm^{-1}.

Cyclohexyl(dichlorocarbomethoxymethyl)mercury. The same procedure was used in the reaction of 100 mmol of methyl dichloroacetate, 70 mmol of cyclohexylmercuric chloride and 90 mmol of t-BuOK·t-BuOH in 300 ml of THF at —65°. The product was obtained initially as a pale yellow oil which was recrystallized from 200 ml of hot hexane to give 16.9 g (57%) of cyclo-$C_6H_{11}HgCCl_2CO_2Me$, m.p. 65—70°. A pure sample, m.p. 73—76°, was obtained by recrystallization from petroleum ether. (Found: C, 25.37; H, 3.31; Cl, 16.41. $C_9H_{14}O_2Cl_2Hg$ calcd.: C, 25.39; H, 3.31; Cl, 16.66%.) NMR ($CDCl_3$): δ 3.93 (s, 3H, OCH_3), 2.55—3.05 (m, 1H, CHHg) and 1.2—2.1 ppm (m, 10H, cycloalkyl). IR (CCl_4): ν(C=O) 1735, 1721 cm^{-1}.

β-Phenylethyl(dichlorocarbomethoxymethyl)mercury. (a) Base-induced procedure. The same procedure was used in the reaction of 25 mmol of methyl dichloroacetate, 20 mmol of $PhCH_2CH_2HgCl$ and 25 mmol of t-BuOK·t-BuOH in 100 ml of THF at —65°. The product, obtained initially as an oil, was crystallized from hexane to give 6.36 g (71%) of pure material, m.p. 52—57°. (Found: C, 29.64; H, 2.70; Cl, 15.73. $C_{11}H_{12}O_2Cl_2Hg$ calcd.: C, 29.51; H, 2.70; Cl, 15.84%.) NMR (CCl_4): δ 2.10 (t, J 7 Hz, 2H, CH_2Hg), 3.03 (t, J 7 Hz, 2H, CH_2Ph), 3.81 (s, 3H, OCH_3) and 7.31 ppm (m, 5H, Ph). IR (CCl_4): ν(C=O) 1745, 1720 cm^{-1}. *(b) Via mercuration of methyl trichlorovinyl ether.* A 250 ml three-necked flask equipped with a paddle stirrer and an addition funnel was charged with 16.23 g (50 mmol) of mercuric acetate and 50 ml of absolute methanol. To this slurry was added, with stirring and cooling, 8.88 g (55 mmol) of methyl trichlorovinyl ether. The resulting homogeneous solution was stirred for 30 min and then treated with 50 mmol of sodium chloride in 100 ml of water. The white precipitate which formed was filtered and recrystallized from carbon tetrachloride to give 12.0 g (91%) of $Hg(CCl_2CO_2Me)_2$, m.p. 117—119°. (Found: C, 15.07; H, 1.30; Cl, 29.10. $C_6H_6O_4Cl_4Hg$ calcd.: C, 14.87; H, 1.25; Cl, 29.27%.) NMR ($CDCl_3$): δ 3.93 ppm (s, 6H, OCH_3). IR ($CHCl_3$): ν(C=O) 1750, 1725 cm^{-1}. The formation of this compound rather than $ClHgCCl_2CO_2$-Me is surprising. It may be that $ClHgCCl_2CO_2Me$ is unstable with respect to disproportionation to the symmetrical species or that in the equilibrium mixture involving all three species $Hg(CCl_2CO_2CH_3)_2$ is the least soluble component.

Phenyl(N,N,-dimethylamidodichloromethyl)mercury. A solution of unsolvated t-BuOK (70 mmol) in 100 ml of THF was added with stirring and under nitrogen to a mixture of 75 mmol of *N,N*-dimethyl dichloroacetamide and 50 mmol of phenylmercuric chloride in 200 ml of THF at —60°. The reaction mixture was stirred for 15 min, warmed to —30° and poured into a solution of 60 mmol of acetic acid in water. Extraction with dichloromethane was followed by washing of the organic layer with water. The dried organic layer was evaporated at reduced pressure. The residue was extracted with dichloromethane and these extracts were evaporated to dryness. The residue was extracted with carbon tetrachloride and these extracts were evaporated at reduced pressure. The solid which remained was precipitated from hexane solution by addition of diethyl ether, giving 7.5 g (35%) of white powder. Several recrystallizations from hexane gave material with m.p. 100—102°. (Found: C, 27.54; H, 2.72; N, 3.10. $C_{10}H_{11}ONCl_2Hg$ calcd.: C, 27.75; H, 2.56; N, 3.24%.) NMR (CCl_4): δ 3.18 (broad unresolved d, 6H, NCH_3) and 7.24 ppm (m, 5H, Ph). IR (CCl_4): ν(C=O) 1610 (broad).

Phenyl(chlorocarboethoxymethyl)mercury. Carboethoxychloromethylmercuric chloride was prepared by reaction of ethyl 1,2-dichlorovinyl ether with mercuric acetate in 66% yield [23]. A 2.90 g (8.1 mmol) portion of this material in 40 ml of chloroform in an Erlenmeyer flask was treated with 2.86 g (8.1 mmol) of diphenylmercury in 40 ml of benzene. Mixing resulted in immediate precipitation of phenylmercuric chloride (85%). The mixture was filtered and the filtrate was diluted with pentane and refrigerated to precipitate 2.55 g (79%) of white powder, m.p. 55—57°. Recrystallization from hot 1/100 chloroform/hexane gave needles with constant m.p. 71—72°. (Found: C, 29.79; H, 2.84. $C_{10}H_{11}O_2ClHg$ calcd.: C, 30.08; H, 2.78%.) NMR (CCl_4): δ 1.26 (t, *J* 7 Hz, 3H, $OCH_2\underline{CH_3}$), 4.02 (s, 1H, Hg—CHCl, with satellites, $J(^{199}Hg-^1H)$ 123 Hz), 4.06 ppm (q, *J* 7 Hz, OCH_2) and 7.05 ppm (m, 5H, Ph). IR (CCl_4): ν(C=O) 1738, 1718 cm^{-1}.

Reactions of $PhHgCCl_2SO_2Ph$

(a) With cyclooctene. A dry, heavy-walled Pyrex tube was flushed with nitrogen and charged with 10 mmol of the mercurial, 50 mmol of cyclooctene and 10 ml of benzene. The contents were degassed by three freeze-thaw cycles

under vacuum and the tube was sealed. The tube was heated in an oven at 140 ± 3° for 8 days. When the tube was cooled, a flaky white solid formed, in addition to the small pool of mercury already present. Filtration removed phenylmercuric chloride (58%) and metallic mercury (13%). Examination of the filtrate by TLC (Eastman Chromagram Sheet 6060, UV indicator) showed that adequate separation of the multicomponent mixture could be achieved using 70/30 v/v hexane/dichloromethane as eluent. The benzene solution was evaporated at reduced pressure and the residue separated by column chromatography (6″ X 1.5″ silicic acid column) using 70/30 hexane/dichloromethane as eluent. Nine fractions were collected and their composition examined by NMR spectroscopy. The first component to elute was a white crystlaline solid, m.p. 119—123°, and was identified as diphenylmercury (0.29 g, 8%). A recrystallized sample had m.p. 122—123°. The second component to elute was 9-chloro-9-phenylsulfonylbicyclo[6.1.0]nonane (49%), m.p. 130—135°. Four recrystallizations from 95% ethanol gave white needles, m.p. 146.5—147.5°. (Found: C, 60.19; H, 6.45; Cl, 11.89. $C_{15}H_{19}O_2SCl$ calcd.: C, 60.29; H, 6.41; Cl, 11.87%.) NMR (CCl_4): δ 1.07—2.07 (m, 14H, alicyclic H) and 7.45—8.0 ppm (m, 5H, Ph). IR (CCl_4): characteristic strong sulfonyl bands at 1343 and 1160 cm^{-1}. It seems likely that the purified material represents only one isomer, probably 9-*endo*-chloro-9-*exo*-phenylsulfonylbicyclo[6.1.0]nonane. The NMR spectra of the crude material and the purified material showed no significant differences.

The second component was followed closely by a third, which was identified as phenyl(dichloromethyl)sulfone (56%).

(b) With allyltrimethylsilane. The same procedure was used in the reaction of 10 mmol of the mercurial with 50 mmol of the olefin in 10 ml of benzene at 140° for 8 days. Filtration of the reaction mixture removed PhHgCl (63%) and metallic mercury (10%). Column chromatography as before separated diphenylmercury (5%) and a mixture of the two isomers of 1-chloro-1-phenylsulfonyl-2-(trimethylsilylmethyl)cyclopropane (47%). (Found: C, 51.61; H, 6.32; Cl, 11.61. $C_{13}H_{19}O_2SClSi$ calcd.: C, 51.54; H, 6.32; Cl, 11.71%.) GLC (F&M 5750, 4 ft. UCW 98 at 180°) showed the isomers to be present in about 1/1 ratio, and GLC was used to separate them. Their 60 MHz NMR spectra did not allow structural assignments. Their IR spectra (liquid film) showed characteristic sulfone bands (1327 and 1160; 1327 and 1163 cm^{-1}) and Me_3Si bands (1251 and 844; 1250 and 840 cm^{-1}).

Reaction of $PhHgCBr_2SO_2Ph$ with cyclooctene

The same procedure was used in the reaction of 10 mmol of the mercurial with 50 mmol of cyclooctene in 15 ml of chlorobenzene for 2 days at 135—140°. Filtration of the black reaction mixture removed 2.79 g of dense black powder, m.p. > 300°. Column chromatography (4″ silicic acid, benzene eluent) gave a rapidly eluted fraction which crystallized on standing. Sublimation, followed by recrystallization from methanol, gave white needles, m.p. 138—139°, of 9-bromo-9-phenylsulfonylbicyclo[6.1.0]nonane (20%). A second fraction was eluted and identified as phenyl(dibromomethyl)sulfone (42%) and a third fraction as unconverted starting mercurial (5%). (9-Bromo-9-phenylsulfonylbicyclo[6.1.0]nonane: found: C, 53.09; H, 5.79; Br, 23.54. $C_{15}H_{19}O_2SBr$ calcd.: C, 52.48; H, 5.58%.) IR (CCl_4): sulfonyl bands at 1330 and 1155 cm^{-1}.

Reactions of $RHgCCl_2CO_2Me$ compounds with olefins

A 50 ml three-necked flask equipped with a thermometer, a magnetic stirring unit and a Claisen head with a reflux condenser and a septum for aliquot withdrawals was charged with 5.0 mmol of cyclo-$C_6H_{11}HgCCl_2CO_2Me$, 38 mmol of cyclooctene, 5.0 ml of chlorobenzene and 2.0 mmol of tridecane (internal standard for GLC analysis). The mixture was heated to reflux and aliquots were withdrawn by syringe periodically for GLC analysis. After 57 h at 140°, a maximum yield of the two isomers of 9-chloro-9-carbomethoxybicyclo[6.1.0]-nonane [2] of 78% was achieved. Heating for an additional 16 h resulted in no increase in yield. Filtration gave cyclohexylmercuric chloride in 64% yield, m.p. 153—155°. The product isomer ratio, in order of elution on GLC (SE-30) was 1/2.74.

Other reactions with this mercurial and with $PhCH_2CH_2HgCCl_2CO_2Me$ were carried out in similar manner. The reaction mixtures from similar reactions of $PhHgCClICO_2Me$ with cyclooctene in benzene at reflux and in chlorobenzene at 135° were filtered to remove phenylmercuric iodide (ca. 80% yield, m.p. 256—258°) and the filtrates were trap-to-trap distilled at reduced pressure. The distillates were examined by GLC. In addition to the two isomers of 9-chloro-9-carbomethoxybicyclo[6.1.0]nonane there was present a third product in about the same yield (by GLC) which NMR spectroscopy indicated to be a mixture. The NMR spectrum of the pot residue showed nine distinct OCH_3 resonances.

Reaction of $PhHgCHClCO_2Et$ with cyclooctene

A heavy-walled Pyrex tube was charged with 5.0 mmol of the mercurial and 5.0 ml of cyclooctene, degassed, evacuated, sealed and heated for 48 h in a tube oven for 72 h at 155—160°. Filtration of the reaction mixture gave PhHgCl (0.31 g, 20%). The filtrate was trap-to-trap distilled at 0.03 mm; two fractions were collected, at 25° and to 120° pot temperature. The latter contained (by GLC) two major and six minor components. The major components were separated by preparative GLC (F&M 700, 6 ft. Carbowax 20M, at 140°) and identified by comparison of their NMR and IR spectra as a mixture (ca. 10% yield) of *exo-* and *endo*-carboethoxybicyclo[6.1.0]nonane. The isomer ratio was 1/4.5 in order of increasing GLC retention time. An authentic sample of such an isomer mixture, prepared by copper-catalyzed reaction of ethyl diazoacetate with cyclooctene [25] was available.

Crystallization of the pot residue from the distillation gave 1.4 g (70%) of unconverted starting mercurial.

A similar procedure was followed in the reaction of this mercurial with cyclohexene (6.5 days in a sealed tube at 155°) to give phenylmercuric chloride (35%), elemental mercury (14%), several unidentified volatile products and 7-*exo*-carboethoxybicyclo[4.1.0]heptane (10%). The latter, n_D^{25} 1.4651, was identified by comparison of its IR and NMR spectra with those of authentic material [25]. (Found: C, 70.91; H, 9.44. $C_{10}H_{16}O_2$ calcd.: C, 71.39; H, 9.59%.) NMR (CCl_4): δ 1.27 (t, J 7 Hz, 3H, CH_3), 0.9—2.1 (m, 11H, cycloalkyl) and 4.05 ppm (q, J 7 Hz, 2H, OCH_2).

Reaction of phenyl(bromochlorocarbomethoxymethyl)mercury with phenylmercuric chloride

A 100 ml three-necked flask equipped with a reflux condenser, a magnetic stirring unit, a nitrogen inlet tube and a thermometer was charged with 2.32 g (5.0 mmol) of $PhHgCClBrCO_2Me$ [2], 1.56 g (5 mmol) of phenylmercuric chloride and 20 ml of dry chlorobenzene. The mixture was stirred and heated at reflux for 7 h. The reaction mixture was homogeneous at 135° at first, but after 2h it was pale yellow and some precipitate had formed. The reaction mixture was cooled and filtered to remove 2.00 g of solid, m.p. 270—275° (mainly PhHgBr). The filtrate was diluted with hexane and refrigerated. The solid which precipitated (1.5 g, 72%), m.p. 140—144°, was identified (superimposable IR spectrum; m.p.) as $PhHgCCl_2CO_2Me$ [2].

Acknowledgement

The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this research (Grant AF-AFOSR-72-2204).

References

1 D. Seyferth and Y.M. Cheng, Synth., in press.
2 D. Seyferth, R.A. Woodruff, D.C. Mueller and R.L. Lambert, Jr., J. Organometal. Chem., 43 (1972) 55.
3 D. Seyferth and R.A. Woodruff, J. Org. Chem., 38 (1973) 4031.
4 D. Seyferth and D.C. Mueller, J. Amer. Chem. Soc., 93 (1971) 3714.
5 D. Seyferth and G.J. Murphy, J. Organometal. Chem., 52 (1973) C1.
6 D. Seyferth and E.M. Hanson, J. Organometal. Chem., 27 (1973) 19.
7 D. Seyferth, J.Y.-P. Mui and G. Singh, J. Organometal. Chem., 5 (1966) 185.
8 D.C. Mueller and D. Seyferth, J. Amer. Chem. Soc., 91 (1969) 1754.
9 W. Middlebos, J. Strating and B. Zwanenburg, Tetrahedron Lett., (1971) 351.
10 A.M. van Leusen, R.J. Mulder and J. Strating, Tetrahedron Lett., (1964) 543.
11 H. Nozaki, T. Sakai, H. Takaya and R. Noyori, Kogyo Kagaku Zasshi, 72 (1969) 280.
12 D. Seyferth and C.K. Haas, J. Organometal. Chem., 30 (1971) C38.
13 D. Seyferth and C.K. Haas, J. Organometal. Chem., 46 (1972) C33.
14 (a) N.G. Johansson and B. Akermark, Acta Chem. Scand., 25 (1971) 1927; (b) N.G. Johansson, Acta Chem. Scand., 27 (1973) 1417.
15 D. Seyferth, J.M. Burlitch, R.J. Minasz, J.Y.-P. Mui, H.D. Simmons, Jr., A.J.-H. Treiber and S.R. Dowd, J. Amer. Chem. Soc., 87 (1965) 4259.
16 D. Seyferth, J.Y.-P. Mui and J.M. Burlitch, J. Amer. Chem. Soc., 89 (1967) 4953.
17 D. Seyferth, J.Y.-P. Mui and R. Damrauer, J. Amer. Chem. Soc., 90 (1968) 6182.
18 D. Seyferth and D.C. Mueller, J. Organometal. Chem., 25 (1970) 293.
19 D. Seyferth and J.M. Burlitch, J. Organometal. Chem., 4 (1965) 127.
20 R. Criegee, P. Dimroth and R. Schempf, Chem. Ber., 90 (1957) 1337.
21 K.C. Bass, Nature, 205 (1965) 169.
22 F. Nerdel and S. Makower, Naturwissenschaften, 45 (1958) 490.
23 C.B. Miller and C. Woolf, U.S. Pat. 2803665; Chem. Abstr., 52 (1958) 2047f.
24 D. Seyferth, J.E. Hallgren, R.J. Spohn, G.H. Williams, M.O. Nestle and P.L.K. Hung, J. Organometal. Chem., in press.
25 S. Akiyoshi and T. Matsuda, J. Amer. Chem. Soc., 77 (1955) 2476.