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HALOMETHYL—METAL COMPOUNDS

LXVII*. THE APPLICATION OF PHENYL(TRIHALOMETHYL)MERCURY COMPOUNDS IN THE SYNTHESIS OF HIGHLY HALOGENATED OXIRANES

DIETMAR SEYFERTH, WOLFGANG TRONICH**, WILLIAM E. SMITH*** and STEVEN P. HOPPER
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (USA)

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Summary

Phenyl(trihalomethyl)mercury compounds react with highly halogenated ketones [$(CF_3)_2CO$, CF_3COCF_2Cl, $(CF_2Cl)_2CO$, $CF_2ClCOCFCl_2$], aldehydes (n-C_3F_7CHO, CCl_3CHO) and acid chlorides (CF_3COCl, CCl_3COCl) to add CX_2 to the C=O bond, giving oxiranes. In the case of hexachloroacetone and n-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$, ketones were obtained instead. In the reactions with the acid chlorides, ketones also were formed in addition to the oxiranes. Reaction of $PhHgCCl_2Br$ with oxalyl chloride produced the expected oxirane, 2,3,3-trichloro-2,3-epoxypropenoyl chloride, as well as trichloropyruvyl chloride, trichloroacetyl chloride and hexachlorobiacetyl. A reaction of this mercury reagent with benzil gave PhC(O)-CClPh-C(O)Cl, most likely via rearrangement of the initially formed oxirane.

Introduction

The addition of dihalocarbenes to the olefinic C=C bond is a well-known reaction, and dihalocarbene additions to the C=N bonds of imines [4] and carbonimidoyl dichlorides [1,5] and to the C=S bonds of thiophosgene and thiobenzophenone [6] also have been described. At the time we began these studies, only CF_2 addition to the C=O bond of perfluoroalkyl ketones had been reported (eqn. 1) [7]. Similar reactions of other dihalocarbenes were unknown. In view of the broadly applicable divalent carbon transfer activity of the phenyl(trihalomethyl)mercury compounds [8], we became interested in their possible application to the synthesis of halogenated oxiranes via their

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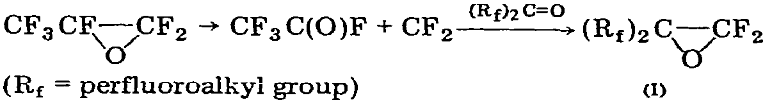
[*] For Preliminary Communications, see refs. 2 and 3; for part XLVI see ref. 1.
[**] Postdoctoral Research Associate, 1968—1969.
[***] National Institutes of Health Postdoctoral Fellow, 1969—1970.



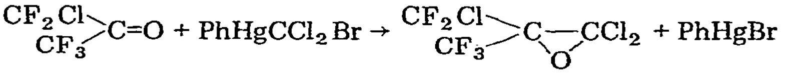
$$\underset{\mathrm{O}}{\mathrm{CF_3CF{-}CF_2}} \rightarrow \mathrm{CF_3C(O)F + CF_2} \xrightarrow{\mathrm{(R_f)_2C=O}} \underset{\mathrm{O}}{\mathrm{(R_f)_2C{-}CF_2}} \qquad (1)$$

(R_f = perfluoroalkyl group) (I)

reactions with the C=O bonds of aldehydes, ketones, acid halides, esters, etc. Early experiments showed that phenyl(bromodichloromethyl)mercury did not produce isolable *gem*-dichlorooxiranes upon reaction with benzophenone and 3-hexanone, although other workers [9] later showed that this mercury reagent does react with benzophenone to give carbon monoxide, diphenyldichloromethane and diphenylchloroacetyl chloride. (The latter very likely was produced by way of an unstable 2,2-dichloro-3,3-diphenyloxirane intermediate.) In view of the high thermal stability of perfluorooxiranes of type (I) and the fair thermal stability of tetrachlorooxirane [10], we directed our further efforts to reactions of phenyl(trihalomethyl)mercury compounds with highly halogenated carbonyl compounds. If these reactions did proceed as expected, it was hoped that the products would be sufficiently stable to permit their isolation and characterization.

Results and discussion

The reactions of phenyl(bromodichloromethyl)mercury with hexachloroacetone and *sym*-difluorotetrachloroacetone did not produce isolable oxiranes. In the case of the hexachloroacetone reaction, octachlorobutanone was produced in low yield. However, with more highly fluorinated ketones, $(CF_3)_2$-C=O, $CF_3C(O)CF_2Cl$, $(CF_2Cl)_2C{=}O$ and $CF_2ClC(O)CFCl_2$, addition of $PhHgCCl_2Br$-derived CCl_2 to the C=O bonds did give stable oxiranes, e.g., eqn. 2. Other phenyl(trihalomethyl)mercurials, $PhHgCClBr_2$ and $PhHgCBr_3$,



$$\mathrm{\underset{CF_3}{CF_2Cl}{>}C{=}O + PhHgCCl_2Br} \rightarrow \mathrm{\underset{CF_3}{CF_2Cl}{>}\underset{O}{C{-}CCl_2} + PhHgBr} \qquad (2)$$

were found to react in similar fashion. These were used to add CClBr and CBr_2 to the C=O bond of hexafluoroacetone and CClBr to the C=O bond of *sym*-tetrafluorodichloroacetone*.

These reactions usually were carried out in benzene solution at 60 - 80°. The yields of oxiranes as isolated by distillation varied from 25 - 74%; GLC yields were higher. The product yields very likely can be improved with further study of reaction variables, in particular in the case of those reactions with the gaseous hexafluoroacetone which were carried out in sealed tubes. These reactions, as well as others discussed below, are summarized in Table 1.

Hexafluorobutyraldehyde and trichloroacetaldehyde (chloral) reacted with phenyl(bromodichloromethyl)mercury to give stable oxiranes (eqn. 3). Trifluoro- and trichloroacetyl chloride also reacted with this mercurial, but in these cases two products were formed: the expected oxirane and an isomeric ketone (eqn. 4).

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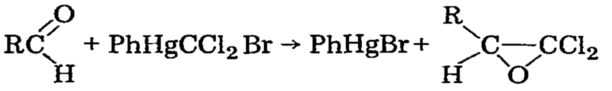
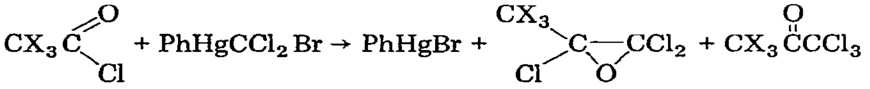
*More recently, $PhHgCFBr_2$ has been used to prepare $(CF_2Cl)_2\underset{O}{C{-}CFBr}$ by reaction with $(CF_2Cl)_2C{=}O$ [11].



(3)

(R = n-C_3F_7, 43%; CCl_3, 46%)



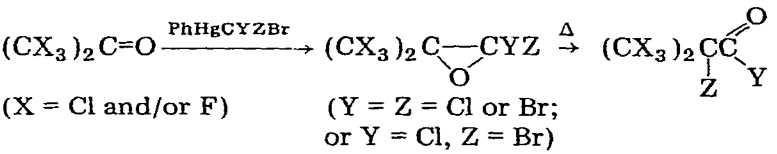
(4)

(X = F, 8%; Cl, 17%) (X = F, 26%; Cl, 33%)

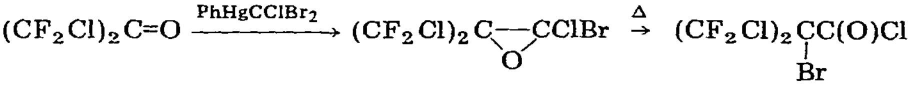
The possible addition of CCl_2 to the C=O bonds of two acid fluorides also was examined. Phenyl(bromodichloromethyl)mercury decomposed in the presence of pentafluorobenzoyl fluoride to give only tetrachloroethylene and hexachlorocyclopropane, the products obtained when this mercury reagent decomposes in the absence of a carbenophile [8]. The acid fluoride was recovered unchanged in 98% yield. On the other hand, a reaction of this mercurial with n-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ under the same conditions (in benzene at 80°) gave a CCl_2-derived product in 40% yield. This, however, was the ketone, n-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CCl_2F$, rather than the oxirane. A brief diversion into difluorocarbene chemistry showed similar results when trimethyl(trifluoromethyl)tin, a CF_2 source at 140 - 150° [12], was heated in the presence of these acid fluorides. No reaction occurred with pentafluorobenzoyl fluoride, either at 140° or at 200°, but reaction with n-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ gave the ketone n-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CF_3$ in 49% yield. The $PhHgCF_3/NaI$ reagent [13] also failed to react with $C_6F_5C(O)F$.

The oxiranes prepared were characterized by analysis and by their spectroscopic properties. Their IR spectra failed to show C=O absorptions (which in the case of perhaloacetones are found in the 1700—1800 cm^{-1} region), but showed a new, broad absorption in the 1350—1400 cm^{-1} region, which may represent the 1240—1260 cm^{-1} band usually found in nonhalogenated oxiranes [14]. The mass spectra of these oxiranes failed to show the expected molecular ions, even at a voltage of 9.8 eV. Characteristic fragments included $[M-Cl]^+$ (or $[M-Br]^+$ in the case of CClBr and CBr_2-derived products), CCl_2^+ (or $CClBr^+$ and CBr_2^+), $CF_nCCl_{3-n}^+$ and derived fragments, and $COCl^+$ (or $COBr^+$). An $[M—CO)^+$ fragment was seen only in the mass spectra of CClBr and CBr_2- (not of the CCl_2-) derived oxiranes.

Tetrachlorooxirane is known to undergo slow thermal rearrangement to trichloroacetyl chloride [10]. The oxiranes prepared in this study showed varying thermal stabilities. 2,2-Dichloro-3-n-heptafluoropropyloxirane was recovered unchanged after it had been heated at 230° for 1 h, while 2,2,3-trichloro-3-trifluoromethyloxirane survived heating for 1 h at 120°. Rearrangement of 2-bromo-2-chloro-3,3-bis(difluorochloromethyl)oxirane occurred when it was heated at 280° to give a product tentatively identified as $(CF_2Cl)_2CBrC(O)Cl$, and a heating period of 1 h at 150° served to convert 2,2,3-trichloro-3-trichloromethyloxirane to hexachloroacetone. However, systematic studies were not carried out to define more closely the thermal stabilities of the oxiranes prepared. The conversion sequence 5 could, in principle, provide a route to novel halogenated carboxylic acids, as the example shown in eqn. 6 suggests.



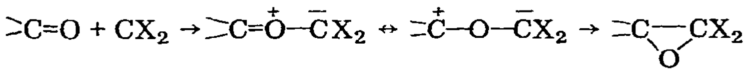
(5)



(6)

The $[M - CO]^+$ fragments seen in the mass spectra of the CClBr and CBr_2 oxiranes most likely arise from decarbonylation of a $(CX_3)_2CBrC(O)Y$ (Y = Cl or Br) intermediate. The fact that such fragments were not seen in the mass spectra of the CCl_2-derived oxiranes suggests that C—Br bond heterolysis occurs preferentially when oxiranes containing the CClBr ring member undergo thermal rearrangement.

We can only speculate concerning the mechanism of these CX_2 transfer reactions. It seems likely to us that we are dealing with reactions involving dihalocarbene intermediates, although even this is not wholly certain. If one does assume a carbene mechanism, then two possibilities for the formation of the oxirane can be considered. (*1*) A concerted CX_2 addition to the C=O bond may occur, similar to CX_2 addition to the C=C bond of olefins. (*2*) The initial interaction of CX_2 with the $\gtrdot C{=}O$ compound may lead to a carbonyl ylide which then cyclizes to the oxirane (eqn. 7). We note in this connection that

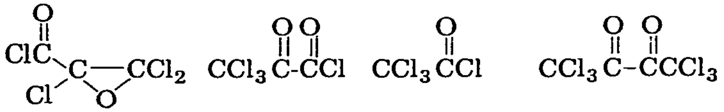


(7)

evidence by Bradley and Ledwith [15] has implicated such a species, $Me_2\overset{+}{C}{-}O{-}\overset{-}{C}H_2$, in the reaction of methylene (generated via photolysis of diazomethane) with acetone. Griffin et al. [16] have shown that a carbonyl ylide can cyclize to an oxirane. The possibility of a carbonyl ylide intermediate in the reaction of phenyl(bromodichloromethyl)mercury with benzophenone also has been discussed [9]. However, none of our experiments provide evidence concerning this question of mechanism.

The formation of ketones in addition to or to the exclusion of the expected oxiranes in the reactions of $PhHgCCl_2Br$ with acid halides requires comment. In the case of the trichloroacetyl chloride reaction, the formation of hexachloroacetone could in principle result by way of thermal rearrangement of 2,2,3-trichloro-3-trichloromethyloxirane, since thermal conversion of the latter to the ketone has been demonstrated. Such a route to $CF_3C(O)CCl_3$, however, is much less likely, since our control experiments showed that 2,2,3-trichloro-3-trifluoromethyloxirane does not undergo such rearrangement when heated at 120 ° for 1 h, either alone or in the presence of phenylmercuric bromide. Thus other routes to these ketones, possibly direct insertion of CCl_2 into the C—Cl or C—F bonds of the acid halides, must be considered. The formation of octachlorobutanone in the $PhHgCCl_2Br$/hexachloroacetone reaction is best explained in terms of thermal rearrangement of the intitally formed oxirane.

These studies were extended to reactions of phenyl(bromodichloromethyl)mercury with two α-dicarbonyl compounds. The reaction of this mercurial with oxalyl chloride in benzene for 18 h at 60 - 65° gave phenylmercuric bromide and a mixture of volatile products:



$CCl_3C(=O)C(=O)Cl$ $\quad CCl_3C(=O)Cl$ $\quad CCl_3C(=O)C(=O)CCl_3$

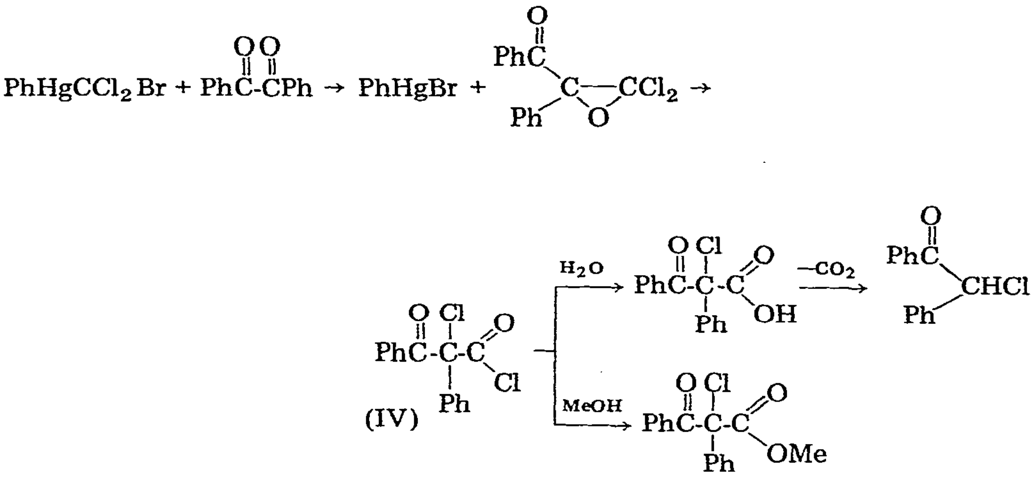
(II) (19%) (III) (40%) (7%) (5%)

Our initial assumption was that the trichloropyruvyl chloride (III) resulted from thermal rearrangement of the oxirane product, 2,3,3-trichloro-2,3-epoxypropenoyl chloride (II). If this were correct, then a shorter reaction time possibly should reduce the extent of such rearrangement. However, this was not the case. Such a change in reaction conditions suppressed formation of trichloroacetyl chloride but did not materially change the (III)/(II) ratio. Under harsher reaction conditions (3 h at 65 - 70°, 24 h at 120°, in chlorobenzene solution) trichloroacetyl chloride was the only product of the $PhHgCCl_2Br$/oxalyl chloride reaction.

The partial conversion of (II) to (III) and of the latter in part to trichloroacetyl chloride during the course of the reaction and during subsequent workup seems a reasonable possibility. Separate experiments showed that (II) undergoes partial decomposition to CCl_3COCl when it is heated at 120° in the presence or absence of phenylmercuric bromide and complete decomposition in this sense at 190°. Under these conditions no trichloropyruvyl chloride was observed but this may simply be due to the relative rates ($k_2 > k_1$) of the processes involved under these conditions: (II) $\xrightarrow{k1}$ (III) $\xrightarrow{k2}$ $CCl_3COCl + CO$. However, as with the CF_3COCl and CCl_3COCl reactions, the formation of the CCl_3 products in the present reaction could have resulted from CCl_2 insertion into the C—Cl bond of oxalyl chloride and of (III).

The reaction of phenyl(bromodichloromethyl)mercury with benzil resembled that of this mercurial with benzophenone [9] in that a stable oxirane was not produced. Instead, a solid product resulted which was found to be unstable toward atmospheric moisture and whose IR spectrum showed two strong carbonyl absorptions at 1678 and 1728 cm^{-1}. This solid reacted with methanol in the presence of pyridine to give α-methoxycarbonyl-α-phenylacetophenone and its hydrolysis in sodium acetate-buffered aqueous THF resulted in formation of α-benzoylbenzyl chloride. On the basis of this evidence, the $PhHgCCl_2Br$/benzil reaction product was identified as α-chloro-α-benzoyl-α-phenylacetyl chloride, (IV). The reaction course indicated below seems a likely route to these products.

In conclusion, we note then that dihalocarbene addition to C=O bonds of organic carbonyl compounds seems to be a potentially useful reaction. In some cases, the initially formed oxirane is stable and capable of isolation, but in others it is not. Furthermore, in other cases alternate reaction paths appear to be operative which do not involve an intermediate oxirane [9,17]. It is clear that reactions of dihalocarbenes with carbonyl compounds require further study so that the scope of possible synthetic applications can be established and the operating mechanisms defined.



Experimental

General comments

All reactions were carried out under an atmosphere of dry nitrogen using flame-dried glassware. 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 Perkin—Elmer 337, 257 and 457A infrared spectrophotometers. Gas liquid chromatography (GLC) was used for yield determinations and for collection of samples. Commercial stainless steel columns were employed in either an F&M (Hewlett—Packard) Model 700, 720 or 5754 gas chromatograph. Yields were determined using the internal standard procedure. Phenyl(bromodichloromethyl)mercury was prepared as described in a previous paper of this series [18]. The carbonyl compounds used in this study all were commercial samples (Peninsular Chemical Research, Aldrich Chemical Co.) and were redistilled before use.

Reactions of phenyl(trihalomethyl)mercurials with liquid substrates

A three-necked, round-bottomed flask of appropriate size equipped with a reflux condenser, a magnetic stirring unit, a thermometer and a nitrogen inlet tube was charged with the mercurial, the substrate and the solvent, if any was used. The resulting solution was heated at the reaction temperature, with stirring under nitrogen, for the stated time (Table 1). During this time, phenylmercuric bromide precipitated. Upon completion of the reaction, the latter was filtered and washed with benzene. The combined filtrate and benzene washings were distilled, first at atmospheric pressure to remove solvent and, if possible, starting material (Vigreux column), and then at reduced pressure to isolate product(s). Gas chromatography served in separation and purification of products; generally 20% Dow Corning Corp. DC-200 silicone oil columns were used. Alternatively, the filtrate was trap-to-trap distilled at reduced pressure and subsequent gas chromatographic analysis of the distillate served to determine the products formed.

The details of the reactions carried out are given in Table 1. Properties and analyses of all new products are given in Table 2.

Reactions of phenyl(trihalomethyl)mercurials with gaseous or low-boiling substrates in sealed tubes

A heavy walled Pyrex bomb tube (generally 15 - 18 cm long, 19 mm inside diameter) was well dried and flushed with nitrogen and charged with the mercurial, the substrate and the solvent, when one was used. The tube was cooled, evacuated and sealed and then was heated in a rocking furnace for the time indicated in Table 1. Alternatively, a magnetic stirring bar was added to the contents of the tube and then the sealed tube was heated (with external stirring) in an oil bath.

Upon completion of the reaction, the tube was opened and the phenylmercuric bromide filtered. The volatiles were distilled using a 20 cm Vigreux column and then were refractionated on a Teflon spinning band column. Analytical samples and samples for spectroscopic characterization were obtained by GLC. Tables 1 and 2 provide detailed information concerning reaction conditions and products formed.

In some examples, either the reaction conditions or the workup procedures used differed from those outlined above and these are described in more detail below.

Reaction of phenyl(bromodichloromethyl)mercury with oxalyl chloride

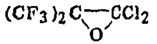
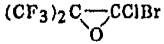
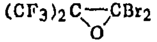
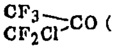
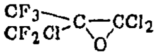
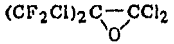
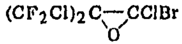
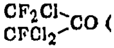
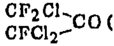
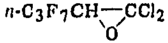
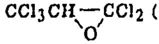
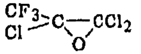
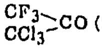
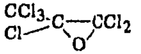
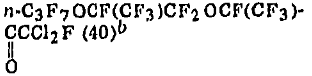
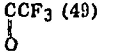
The standard apparatus was charged with 13.21 g (30 mmol) of the mercurial, 7.62 g (60 mmol) of oxalyl chloride and 50 ml of dry benzene. This mixture was stirred and heated at 60° under nitrogen for 18 h. Filtration under nitrogen served to remove 9.9 g (93%) of phenylmercuric bromide. The yellow-green filtrate was distilled using a 100 cm Vigreux column to remove the solvent and the residue was trap-to-trap distilled at reduced pressure to give 4.81 g of clear yellow liquid. GLC analysis (6 ft 10% Apiezon column at 75°, 40 ml helium per min, injection port and detector temperatures lowered to 110°) indicated the presence of 0.38 g (7%) of trichloroacetyl chloride (identified by IR comparison), 1.20 g (19%) of the oxirane 2,3,3-trichloro-2,3-epoxypropenoyl chloride and 2.54 g (40%) of trichloropyruvyl chloride. The latter two isomers were separated by GLC and characterized (Table 2).

IR: 2,3,3-Trichloro-2,3-epoxypropenoyl chloride: 1860w, 1790s (sharp), 1350m, 1323m, 1259w, 1095m, sh, 1082s, 1016w, 981m, 902m, 863s, 835s, 785s and 709w cm^{-1}. Trichloropyruvyl chloride: 1765s (br), 1256w, 1130m, 1057w, 1012w, 912s, 852s, 816s, 703m and 660s cm^{-1}. The structure assignments for these isomers are based on the location and relative broadness of the carbonyl absorption of the trichloropyruvyl chloride as well as its pale yellow color (characteristic of 1,2 dicarbonyl compounds).

In addition to these products, a slow-eluting component, apparently a diadduct mixture (hexachlorobiacetyl and possibly an oxirane) was present (ca. 0.2 g, 5%). Its characterization is described in the following experiment.

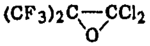
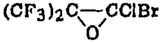
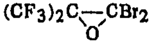
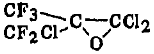
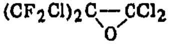
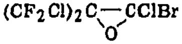
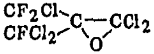
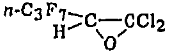
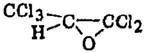
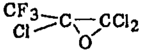
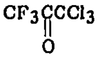
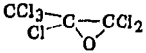
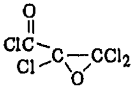
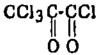
(continued on p. 350)

TABLE 1. REACTIONS OF PHENYL(TRIHALOMETHYL)MERCURIALS WITH CARBONYL COMPOUNDS

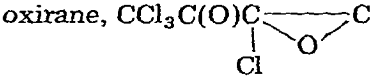
Mercurial (mmol)	Carbenophile (mmol)	Solvent (ml)	Reaction Conditions	PhHgBr (% yield)	Products (% yield)
$PhHgCCl_2Br$ (20)	$(CF_3)_2CO$ (22)	Benzene (50)	72 h at 60°, sealed tube	96	 (36)[a]
$PhHgCClBr_2$ (20)	$(CF_3)_2CO$ (22)	Benzene (50)	72 h at 60°, sealed tube	93	 (18)[a]
$PhHgCBr_3$ (20)	$(CF_3)_2CO$ (42)	PhCl (50)	12 h at 80°, sealed tube	98	 (26)[a]
$PhHgCCl_2Br$ (10)	 $CF_3(CF_2Cl)CO$ (20)	PhCl (15)	18 h at 60°, sealed tube	96	 (66)[b]
$PhHgCCl_2Br$ (10)	$(CF_2Cl)_2CO$ (20)	Benzene (50)	72 h at 60°	100	 (74)[a]
$PhHgCClBr_2$ (20)	$(CF_2Cl)_2CO$ (30)	Benzene (70)	72 h at 60°	97	 (48)[a]
$PhHgCCl_2Br$ (10)	 $CF_2Cl(CFCl_2)CO$ (15)	Benzene (40)	20 h at 60°	90	 $CF_2Cl(CFCl_2)CO$ (33)[a]
$PhHgCCl_2Br$ (10)	$n\text{-}C_3F_7CHO$ (53.5)[c]	Benzene (10)	1.5 h at 90°, sealed tube	85	 (43)[b]
$PhHgCCl_2Br$ (10)	CCl_3CHO (130)[d]	None	20 h at 70°	83	 (46)[b]
$PhHgCCl_2Br$ (20)	CF_3COCl (80)	PhCl (10)	18 h at 60 - 65°, sealed tube	91	 (8)[b, e] +  $CF_3(CCl_3)CO$ (26)[b, e]
$PhHgCCl_2Br$ (20)	CCl_3COCl (25 ml)	None	18 h at 70°	89	 (17)[b, f] + $(CCl_3)_2CO$ (33)[b, f]
$PhHgCCl_2Br$ (5)	$n\text{-}C_3F_7OCF(CF_3)$-$CF_2OCF(CF_3)COF$ (14.6)	Benzene (25)	3 h at 80°[g]	76	 $n\text{-}C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=O)CCl_2F$ (40)[b]
$PhHgCCl_2Br$ (10)	C_6F_5COF (34.4)	Benzene (30)	4.5 h at 80°	82	C_6F_5COF (98), C_2Cl_4 (36), cyclo-C_3Cl_6
Me_3SnCF_3 (5)	$n\text{-}C_3F_7OCF(CF_3)$-$CF_2OCF(CF_3)COF$ (18.5)	None	20 h at 140°, sealed tube	Me_3SnF (83)	 $n\text{-}C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=O)CF_3$ (49)
Me_3SnCF_3 (10)	C_6F_5COF (30)	None	24 h at 135°, sealed tube	Me_3SnF (98)	C_6F_5COF (100% recovery)
$PhHgCF_3$ (10) + NaI (30)	C_6F_5COF (30)	Benzene (40)	20 h at 80°		C_6F_5COF (97% recovery)

[a] Isolated (distillation) yield. [b] GLC yield. [c] Obtained by treating $n\text{-}C_3F_7CH(OH)(OEt)$ with polyphosphoric acid at 150 - 170°. [d] Obtained by treating chloral hydrate with conc. H_2SO_4 at 95 - 100°. [e] Separated using a 6 ft. 10% DC-200 silicone oil column. [f] Separated using a 6 ft. 20% DC-200 column at 120°. [g] Two liquid phases present in reaction mixture and in trap-to-trap distillate on workup. The upper layer contained only benzene.

TABLE 2. PRODUCTS OF $PhHgCX_3$ + CARBONYL COMPOUND REACTIONS

Compound	B.p. (°C/mm)	n_D^{25}	Analysis found (calcd.) (%) C	Halogen	F
	67 - 70 (760)	1.330	19.42 (19.28)	Cl: 28.94 (28.54)	46.41 (45.75)
	73 - 75 (760)	1.3550	16.92 (16.38)	Cl: 13.00 (12.06) Br: 27.66 (27.28)	36.70 (38.84)
	99 - 101 (760)	1.3820	14.82 (14.23)	Br: 47.33 (47.31)	
	100 (760)	1.3689	17.90 (18.10)	Cl: 40.20 (40.08)	37.69 (35.79)
	98 - 102 (125)	1.4048	17.17 (17.04)	Cl: 50.28 (50.32)	25.46 (26.97)
	114 - 116 (126)	1.4298	14.85 (14.72)	Br: 32.93 (32.60)	23.52 (23.29)
	130 - 132 (125)	1.4415	16.21 (16.10)	Cl: 59.56 (59.43)	19.21 (19.11)
	94 (760)	1.3361	21.52 (21.37)[b]	Cl: 25.10 (25.23)	
	175 (760)	1.4938	15.94 (15.65)[c]	Cl: 77.50 (76.97)	
	GLC isolated		16.70 (16.73)[d]	Cl: 49.20 (49.38)[d]	26.60 (26.46)[d]
 $CF_3C(O)CCl_3$	83.5 (760)	1.3824	Known compound[e]		
	GLC isolated		14.00 (13.61)	Cl: 81.01 (80.35)	
$n\text{-}C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CCl_2F$	GLC isolated	1.3110	19.99 (20.67)	Cl: 12.18 (12.20)	
$n\text{-}C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CF_3$	GLC isolated	<1.300	21.81 (21.92)		
	GLC isolated		17.35 (17.17)	Cl: 67.12 (67.58)	
 $CCl_3C(O)C(O)Cl$	GLC isolated		17.06 (17.17)	Cl: 67.21 (67.58)	

[a]The results of fluorine analyses for these compounds were erratic. The several analytical services used often differed by several per cent in fluorine analyses of samples taken from the same product batch. We must conclude that a "good" fluorine analysis is as meaningless as a "bad" one. [b]% H; found, 0.52; calcd., 0.36. [c]% H: found, 0.54; calcd., 0.44. [d]Analysis of a mixture of this oxirane and the isomeric CF_3COCCl_3. [e]Lit. b.p. 83.5 - 84.5°

A reaction of 20 mmol of $PhHgCCl_2Br$ and 40 mmol of oxalyl chloride in 25 ml of benzene was carried out under milder conditions: 3 h at 65°. The same workup procedure gave PhHgBr in 86% yield and a clear yellow trap-to-trap distillate. GLC analysis of the latter (at 75° column temperature) showed the presence of trichloroacetyl chloride (1.2%), 2,3,3-trichloro-2,3-epoxypropenoyl chloride (15%) and trichloropyruvyl chloride (46%). GLC isolation (6 ft. 20% DC-200 column at 120°) of the higher boiling products gave a bright yellow eluent, but the last portion to elute was colorless. IR: 1780s, 1625w, 1550w, 1350m, 1263w, 1185w, 1141s, 1122m, 1012w, 993m, 972m, 938w, 901s, 878s, 811s, 769m, 715s, 698m and 662s cm^{-1}. We suggest that hexachlorobiacetyl is the major component of the fraction, with possibly some of the isomeric oxirane,  $\mathrm{CCl_3C(O)\underset{Cl}{C}\underset{O}{\text{———}}CCl_2}$, also present.

A third reaction of $PhHgCCl_2Br$ (20 mmol) with 40 mmol of oxalyl chloride in 20 ml of dry chlorobenzene was carried out for 3 h at 65 - 70° and then for 24 h at 120°. In this case GLC analysis of the volatiles indicated the presence of trichloroacetyl chloride in 42% yield. PhHgBr (7g) was isolated.

Reaction of phenyl(bromodichloromethyl)mercury with benzil

The standard apparatus was charged with 13.21 g (30 mmol) of the mercury reagent, 6.32 g (30 mmol) of benzil and 60 ml of dry benzene. This mixture was stirred and heated at reflux for 6 h under nitrogen. Filtration removed 10.0 g (93%) of phenylmercuric bromide, m.p. 283 - 286°. The filtrate was evaporated, leaving 10.6 g of yellow-orange oil. Treatment of the latter with 75 ml of pentane afforded 2.35 g of yellow crystals, m.p. 90 - 93°, identified as benzil. Evaporation of this filtrate left 6.7 g of a brown oil which showed two carbonyl bands in its IR spectrum at 1678 and 1782 cm^{-1}. The oil was heated strongly in vacuo in a short path distillation apparatus to give 0.27 g of a gummy solid at 105 - 149° at 0.5 mm. The residue (4.7 g) was taken up in chloroform; upon addition of 30 ml of pentane to this solution, 0.3 g of gummy yellow solid was formed. After the latter had been separated, the solution was evaporated. The resulting oil was treated with warm methanol. An off-white, crystalline solid, mp. 103 - 106°, precipitated when this solution was chilled. Charcoal treatment and two recrystallizations from hexane gave pure α-chloro-α-methoxycarbonyl-α-phenylacetophenone, m.p. 110 - 111°, in 30% overall yield. (Found: C, 66.66; H, 4.66; Cl, 12.32. $C_{16}H_{13}O_3Cl$ calcd.: C, 66.56; H, 4.54; Cl, 12.28%.) IR (melt): ν(C=O) at 1680 and 1755 cm^{-1}. NMR (CCl_4): δ 3.75 (s, 3H) and 7.2 - 7.9 ppm (m, 10 H).

In another experiment carried out in the same manner and on the same scale, the pentane solution remaining after separation of the unconverted benzil was stored at —20° with gradual separation of pale yellow solid, three crops with melting ranges of 42 - 49°, 46 - 51° and 43 - 50°, 6.26 g (72% yield). Attempted purification of this solid was not successful. A 4.0 g sample (13.6 mmol) of this solid (which showed carbonyl absorptions at 1678 and 1782 cm^{-1}) was added to 25 ml of methanol containing 1.08 g (13.6 mmol) of pyridine. After the exothermic reaction had subsided, the reaction mixture was allowed to stand for 8 h and then was added to a mixture of 50 ml each of water, hexane and diethyl ether. The organic phase was evaporated, leaving 3.5 g (89%) of crude α-chloro-α-methoxycarbonyl-α-phenylacetophenone, m.p. 91 - 97°. Recrystallization from 8/1 hexane/chloroform gave pure material, m.p. 107 - 109°.

In a further experiment carried out in the same manner and on the same scale, the solution remaining after separation of unconverted benzil was evaporated. The 9.1 g of oil thus obtained was dissolved in 125 ml of 4/1 tetrahydrofuran/water, giving an acidic solution. This solution was treated with 10 g of sodium acetate and the resulting mixture was stirred at room temperature for 24 h. An ether extraction was followed by drying and evaporation of the ether extracts to leave 6.2 g of tacky solid. The latter was taken up in 100 ml of boiling hexane; a 0.60 g residue of PhHgBr was filtered. The hexane solution was chilled to —20° to afford 3.11 g (68%) of desyl chloride (α-benzoylbenzyl chloride), m.p. 54 - 59°, 64 - 65° after recrystallization; lit. [19] m.p. 66 - 67°. The IR and NMR spectra of this product were identical to those given in the Sadtler collections.

Reaction of phenyl(bromodichloromethyl)mercury with hexachloroacetone

Hexachloroacetone (20 ml) was stirred under nitrogen at 170° in the standard apparatus while 8.82 g (20 mmol) of the mercurial was added in small portions over the period of 1 h via a solids addition tube. The resulting yellow solution was cooled and filtered to remove 6.4 g (88%) of phenylmercuric bromide. The filtrate was trap-to-trap distilled in two fractions: (1) 29.8 g of colorless liquid containing no higher boiling materials and (2) 2.1 g of yellow liquid. The latter was shown by GLC to contain a higher boiling material in 6% yield. This was isolated and identified as octachlorobutanone, $CCl_3CCl_2C(O)CCl_3$, n_D^{25} 1.5390, m.p. 18 - 20°. (Found: C, 14.17; Cl, 81.32. C_4Cl_8O calcd.: C, 13.82; Cl, 81.58%.) IR: 1767s, 1171w, 1113m, 1014w, 971w, 925w, 877s, 851s, 811s, 766m and 654s cm^{-1}.

In another experiment in which the mercury reagent and the ketone were heated together for 1 h at 80 - 100°, no octachlorobutanone was detected.

Thermolysis of oxirane products

(a). 2-Bromo-2-chloro-3,3-bis(difluorochloromethyl)oxirane The oxirane (0.2 g, 1.27 mmol) was sealed in a thick-walled tube (20 cm long, 1 cm diameter) which then was heated for 100 h at 280°. The red-brown reaction mixture was trap-to-trap distilled at 0.05 mm and the distillate was analyzed by GLC (6 ft. DC 200 column). A small amount of undecomposed oxirane remained. There was one major product (60% yield) which was separated by GLC and identified as $(CF_2Cl)_2CBrC(O)Cl$. (Found: C, 15.01; Cl, 32.28; Br, 24.41. $C_4Cl_3BrF_4O$ calcd.: C, 14.72; Cl, 32.60; Br, 24.49%.) IR (liquid film): 1845w, 1795(sh), 1790(sh), 1780s, 1640w, 1580w, 1475w, 1260w, 1170s (br), 1050s, 1030s, 1015(sh), 985m, 965(sh), 920m, 900m, 860m, 830m, 815m, 800m, 775s, 735m, 715m and 685m cm^{-1}. The mass spectrum (at 80 eV) showed the following fragment ions (^{35}Cl and ^{79}Br), *m/e*(rel. intensity): 296(7.6), $C_3F_4Cl_3Br^+$, $[M - CO]^+$, 289(3.0), $C_4F_4Cl_2BrO^+$, $[M - Cl]^+$, 261(8.2), $C_3F_4Cl_2Br^+$, $[M - COCl]^+$, 249(0.8), $C_2F_4Cl_2Br^+$, 245(3.0), $C_4F_4Cl_3O^+$, $[M - Br]^+$, 217(15.0), $C_3F_4Cl_3{}^+$, 211(17.5), $C_2Cl_2F_2Br^+$, 176(58.0), $C_2F_2ClBr^+$,

163(6.8), $C_3F_4ClO^+$, 147(22.8), $C_3F_4Cl^+$, 132(15.0), $C_2F_2Cl_2^+$, 129(11.6), CF_2Br^+, 113(1.5), $C_2F_2Cl_2O^+$, 101(2.3), $CFCl_2^+$, 97(3.0), $C_2F_3O^+$, 91(1.5), CBr^+, 85(100.0), CF_2Cl^+, 82(3.8), CCl_2^+, 79(1.2) Br^+, 69(16.5), CF_3^+, 63(10.5), $COCl^+$, 50(1.5), CF_2^+, 47(4.5), CCl^+, 43(27.0), C_2F^+, 36(5.3), HCl^+, 35(1.5), Cl^+, 31(6.8), CF^+.

(b) 2,2,3-Trichloro-3-trichloromethyloxirane. In similar fashion, GLC-isolated samples of this oxirane were heated for 1 h at 150°. The liquid present after this heating period had an IR spectrum identical with that of hexachloroacetone.

(c). 2,3,3-Trichloro-2,3-epoxypropenoyl chloride. When a sample of this compound was sealed in a thick-walled tube and heated for 1 h at 120°, the pressure increase was apparent when the tube was opened. The IR spectrum of the liquid contents indicated the presence of undecomposed starting material (absorption at 1082 cm^{-1}) and of trichloroacetyl chloride (1018 cm^{-1}). Trichloropyruvyl chloride was not present. A heating period of 1 h at 190° resulted in complete conversion to trichloroacetyl chloride. Thermolysis of trichloropyruvyl chloride under these conditions caused complete decarbonylation, giving trichloroacetyl chloride.

Treatment of 2,3,3-trichloro-2,3-epoxypropenoyl chloride and also of trichloropyruvyl chloride with 4 weight per cent of aluminum chloride at room temperature resulted in spontaneous gas evolution. Within a few minutes, the liquid residue was composed solely of trichloroacetyl chloride (by IR).

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