Usually, very high electron affinity is accompanied by great stability of the radical anion produced by electron acceptance. In such a case the fission of the radical anion becomes rate determining.

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(16) (a) The pK_a values of HCl, PhOH, and PhSH were taken from "Lange's Handbook of Chemistry", J. A. Dean, Ed., McGraw-Hill, New York, N.Y., 1973, section 5. (b) The pK_a of Ph_2PH was quoted by A. Tzschach, Abstracts of Papers, 1st European Conference on Organometallic Chemistry (Main Group), Warsaw, Poland, Sept 21–24, 1976, No. II.3.6.

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Halogenated Carbonyl Ylides in the Reactions of Mercurial Dihalocarbene Precursors with Substituted Benzaldehydes

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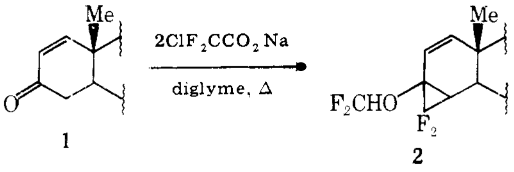
The reactions of phenyl(bromodichloromethyl)mercury (**12**) with several aromatic aldehydes (benzene, 80 °C; followed by treatment with methanol and pyridine at 0 °C) were investigated: [aldehyde (significant products)] **11a** (CO, **13a**, **14a**); **11b** (CO, **13b**, **14b**); **11c** (CO, **14c**, **15c**, **16c**); **11d** (CO, **14d**). Relative reactivities with respect to mercurial **12** (benzene, 80 °C) were 3-CF_3PhCHO (0.08), PhCHO (0.3), *n*-$BuCH{=}CH_2$ (0.3), 4-MeOPhCHO (0.9), c-C_6H_{10} (1.0), and $Me_2C{=}CMe_2$ (15.0). Complexation between the mercurial and benzaldehyde, which enhanced the rate of decomposition of the mercurial to produce :CCl_2 of the same reactivity as that from the mercurial alone, was observed. Evidence suggests the intermediacy of dichlorocarbonyl ylides.

Despite the availability of dihalocarbene precursors (which upon decomposition do not first produce the trihalomethyl anion), there are few examples of the reactions of such divalent intermediates with simple aldehydes and ketones.[1] Difluorocarbene from the apparently concerted decomposition of sodium chlorodifluoroacetate[3] reacts with steroidal enones such as **1** to produce, among other products, bis(difluorocarbene) adduct **2**,[4] with steroidal dienone **3** to form a small yield of rearranged aromatic fluoride **4**,[4c] and with methoxymethylene keto steroid **5** to form the product of a net 1,4 addition.[5]



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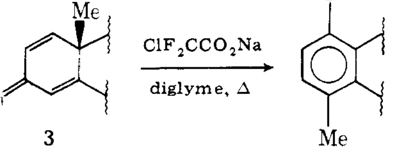

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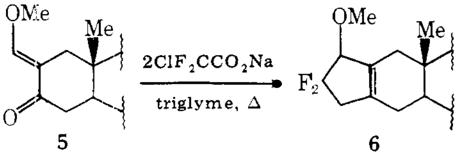

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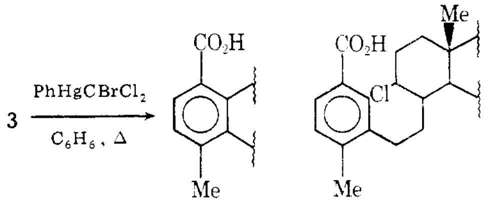
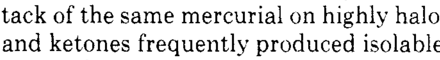


7 8

The attack of phenyl(bromodichloromethyl)mercury (with presumed intervention of dichlorocarbene)[6] on ketone **3** produced rearranged structures **7** and **8**.[7] Seyferth[8] has found that the attack of the same mercurial on highly halogenated aldehydes and ketones frequently produced isolable dichlorooxiranes. Merz[2d] has shown that dichlorocarbene can be used to convert aromatic aldehydes to the corresponding mandelic acids.



9 10

In preliminary communications[9,10] we have noted a variety of interesting and previously unobserved products from the reaction of phenyl(bromodichloromethyl)mercury (**12**) with benzaldehyde and benzophenone. We now report in more detail on the reactions of the mercurial with a series of substituted benzaldehydes.

Results and Discussion

Mercurial Decomposition. Although the addition of an equimolar amount of phenyl(bromodichloromethyl)mercury

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Table I. Carbonyl Complexes with Phenyl(bromodichloromethyl)mercury[a]

Compd	$\tilde{\nu}_{CO}$ (free)	$\tilde{\nu}_{CO}$ complexed)	$\Delta\tilde{\nu}_{CO}$	K_{eq}[b]	K_{eq}'[c]
PhCHO	1708.0	1696.0	12	0.57 ± 0.07	4.5 ± 0.5
Ph_2CO	1663.5	1647.5	16	0.56 ± 0.01	2.8 ± 0.1

[a] $\tilde{\nu}$ are given in cm^{-1} and were measured in degassed benzene under argon at ca. 25 °C. [b] For an assumed 1:1 complex. [c] For an assumed 1:2 (mercurial–ligand) complex.

Table II. Relative Reactivities of Selected Aldehydes and Olefins with Phenyl(bromodichloromethyl)mercury[a]

Compd	Registry no.	k_{rel}[b]	k_{rel}'[e]
$3\text{-}CF_3PhCHO$	454-89-7	0.08[c]	
PhCHO	100-52-7	0.3[c]	
4-MeOPhCHO	123-11-5	0.9[c]	
$n\text{-}BuCH{=}CH_2$	592-41-6	0.3[d]	0.3 (0.2)[f]
$c\text{-}C_6H_{10}$	110-83-8	1.0[d]	1.0 (1.0)[f]
$Me_2C{=}CMe_2$	563-79-1	15.0[d]	17.0 (16.0)[f]

[a] Benzene solvent, 48 h, 50 °C. [b] Precision ca. ± 15%. [c] Competition with equimolar amounts of aldehyde, cyclohexene, and mercurial 12. [d] Competition with equimolar amounts of benzaldehyde, cyclohexene, a second olefin, and mercurial 12. [e] Competition between olefins and mercurial 12 in the absence of aldehydes. [f] Data from C. M. Starks, *J. Am. Chem. Soc.*, **93**, 195 (1971), at 30–45 °C.

to a benzene solution of benzaldehyde produces a shift in the NMR position of the aldehyde hydrogen of only +0.01 ppm, a new carbonyl band can be seen in the IR spectrum sufficiently separated from the original bands that overlap at the maximum of the absorption corresponding to uncomplexed aldehyde is negligible. Some infrared data are summarized in Table I. The known formation of a 1:1 complex between mercuric bromide or chloride[11] with benzaldehyde as well as with other aromatic[11] and aliphatic[12] ketones suggests that the stoichiometry for complexation of phenyl(bromodichloromethyl)mercury with benzaldehyde and benzophenone is also 1:1. However, it is known that diphenylmercury and various perfluoroalkylmercurials form both 1:1 and 1:2 (mercurial to carbonyl) complexes with acetone.[13]

Of interest is the observation that the rate of decomposition of mercurial **12** is enhanced somewhat in the presence of an equimolar amount of benzaldehyde.[14] However, as indicated by the kinetic data of Table II, the relative reactivity of mercurial **12** toward several olefins remains essentially unchanged in the presence of a molar equivalent of benzaldehyde, and products derived from these olefins were only the anticipated dichlorocyclopropanes. The kinetic results imply that, once formed, the dichlorocarbene is as free from complexation with a metal-containing species as it is believed to be when no carbonyl compound is present.[17,18]

Aldehyde Reaction Products. The reactions of the aromatic aldehydes with mercurial **12** were carried out with at least a 1.7-fold excess of the aldehyde or ketone and at a temperature of 80 °C (inert atmosphere, usually in benzene; see Table I) for a period of time adequate to ensure complete decomposition of the mercurial.[19] The product mixtures from aldehydes **11** were then filtered and treated at 0 °C with excess methanol and pyridine prior to product analysis by NMR and VPC procedures. Yields are based on mercurial **12**. In every instance the stated products together with unreacted aldehyde or ketone account for essentially all of the starting aldehyde or ketone.

Shown in Table III are the major products observed in the reactions of several benzaldehydes with phenyl(bromodichloromethyl)mercury, while additional data on reaction conditions and product yields are summarized in Table IV.

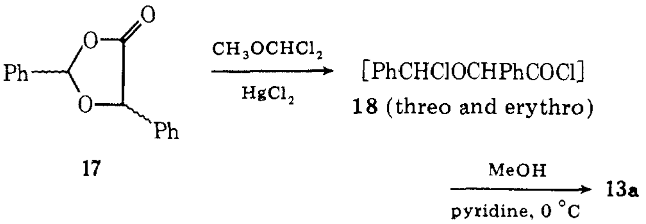
Table III

$$\underset{\mathbf{11}}{ArCHO} + \underset{\mathbf{12}}{PhHgCBrCl_2} \xrightarrow[80\ °C]{C_6H_6} PhHgBr + CO + \begin{bmatrix}\text{reaction}\\ \text{mixture}\end{bmatrix} \xrightarrow[\text{pyridine, 0 °C}]{\text{MeOH}}$$

Ar	Additional major products
Ph (**11a**)	$PhCH(OMe)OCHPhCO_2Me$[a] (**13a**) + $PhCHX_2$[b] (**14a**)
$3\text{-}CF_3Ph$ (**11b**)	$3\text{-}CF_3PhCH(OMe)OCH(3\text{-}CF_3Ph)CO_2Me$[c] (**13b**) + $3\text{-}CF_3PhCHCl_2$ (**14b**)
4-MeOPh (**11c**)	$4\text{-}MeOPhCHX_2$[d] (**14c**) + $4\text{-}MeOPhCH(OMe)_2$ (**15c**) + $4\text{-}MeOPhCHOHCO_2Me$ (**16c**)
$2,4,6\text{-}Me_3Ph$ (**11d**)	$2,4,6\text{-}Me_3PhCHX_2$ (**14d**)

[a] Diasteriomer ratio, 1.8:1. [b] Known to be a substantial mixture of benzal chloride and α-chloro-α-bromotoluene. [c] Diastereomer ratio, 1.2:1. [d] Presence or absence of bromine not determined.

Acetal esters **13a** and **13b** were found to be a mixture of diasteriomers, but spectral data did not allow threo and erythro stereochemistry to be assigned. Both **13a** and **13b** gave a satisfactory elemental analysis, and **13a**, when treated with aqueous acidic dioxane, was transformed to benzaldehyde and mandelic acid (1:1). In addition, **13a** was prepared by an independent synthesis (the first step of which was patterned after a reported preparation of 1-chlorodioxole)[20] as shown.



Use of a mercuric chloride catalyst[21] followed by the same workup procedure used in the study of the reaction of benzaldehyde with mercurial **12** resulted in the same 1.8:1 ratio of distereomeric acetal esters **13a**. Acid chlorides **18** are assumed to be the immediate precursors of the observed acetal esters.[22]

Minor products observed in the reaction of aldehyde **11a** with mercurial **12** include the dimethyl acetal of benzaldehyde (5–6%), methyl mandelate (3–4%), and methyl α-chlorophenylacetate (1–2%).

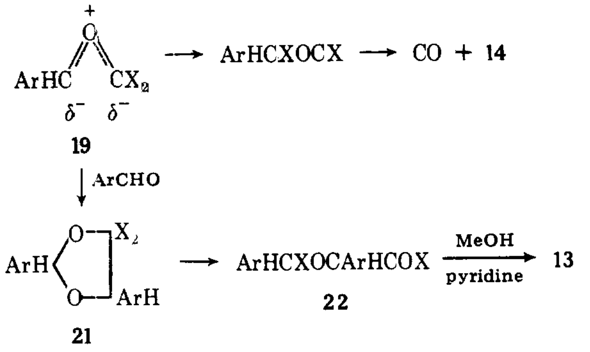
Reaction Pathways. A variety of observations suggest that carbonyl ylides are likely intermediates in the reactions of aromatic aldehydes with phenyl(bromodichloromethyl)mercury (Scheme I). Among the more convincing types of evidence is the fact that the independent synthesis of a sample of acetal esters **13a** from dioxolanone **17** resulted in exactly the same mixture of diastereomeric esters produced in the reaction of mercurial **12** with benzaldehyde (followed by treatment with methanol and pyridine). It is likely that the transformation **17** → **18** involves dioxolane **21** (Ar = Ph),[20] which would be expected as a product of the 1,3-dipolar ad-

Table IV. Summary of Selected Product Data for Reaction of Aromatic Aldehydes with Phenyl(trihalomethyl)mercury[a]

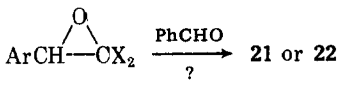
XPhCHO, X	$PhHgCBrY_2$, Y	Registry no.	$\frac{(ArCHO)_0}{(PhHgR)_0}$[b]	Solvent	CO,[c] %	13, %	No. of runs
H	Cl	3294-58-4	1.7	C_6H_6	39 ± 7	32 ± 19	13
			3.4	C_6H_6	36 ± 1	34 ± 7	5
			22.9	ArCHO	78 ± 1	0	2
H	Br	3294-60-8	1.8	C_6H_6	52 ± 18	0	7
			19.5	ArCHO	66	0	2
4-MeO	Cl		1.9	C_6H_6	57 ± 2	*d*	6
$3\text{-}CF_3$[e]	Cl		1.8	C_6H_6	11	60	1[f]
$2,4,6\text{-}Me_3$	Cl		1.7	C_6H_6	63 ± 3	0	6
$2,4,6\text{-}Me_3$	Cl		20.0	ArCHO	70	0	2

[a] Reactions done with 15 mmol of $PhHgCBrY_2$ in 30 mL of solvent for 3–3.5 h at 80 °C; yields based on starting mercurial. [b] ± 0.1. [c] An equimolar amount of $ArCHY_2$ in which $Y_2 = Br_2$, Cl_2, and BrCl was formed. [d] Unstable to reaction conditions; 25–42% yield of a mixture of **15c** and **16c** was observed. [e] A 23-mmol amount of $PhHgCBrCl_2$ in 35 mL of benzene. [f] Other runs made under somewhat different conditions gave comparable results.

Scheme I



dition of carbonyl ylide **19** (Ar = Ph) to benzaldehyde (Scheme I). Although the direct formation of either dioxolane **21** or acid chloride **22** from oxirane **23** cannot be formally excluded, it seems unlikely in view of the observations that 2,3-dicyano-



23

2,3-diphenyloxirane[23a] and 2-cyano-2,3-diphenyloxirane[23b] form adducts with dipolarophiles only under conditions where intermediate carbonyl ylides are formed and because the rate law for reaction of tetracyanoethylene oxide with olefins shows prior formation of a reactive intermediate (the carbonyl ylide) rather than direct reaction of the oxirane with olefin.[24] Stable 1,3-dioxolanes isolated in metal-catalyzed[25a–d] or photochemical[25e–g] decompositions of diazo esters,[25a–c] α-diazoacetophenone,[25d] and diazomethane[25e–g] with aromatic and aliphatic aldehydes and ketones (including benzaldehyde)[25b–d] and from the reaction of substituted epoxides with aromatic aldehydes[26] have been attributed to the 1,3 cycloaddition of an intermediate carbonyl ylide to a carbonyl group.

The initial formation of oxirane **23** (rather than carbonyl ylide **19**) requires that the conversion to ylide **19** (or dioxolane **21**) occurs to essentially the complete exclusion of rearrangement (by carbon–oxygen scission) to acid chloride **24**. This seems unreasonable in view of the known facility of the latter reaction[27] (except for dichlorooxiranes substituted with two very powerful electron-withdrawing groups).[8] Furthermore, evidence on carbon–carbon bond scission (analogous to that required to go from oxirane **23** to ylide **19**) in 2-phenyl-3-*p*-tolyloxirane,[28] 2-cyano-2,3-diphenyloxirane,[23b] 2,3-dicyano-2,3-diphenyloxirane,[23a] tetracyanoethylene oxide,[24,29] ethyl 2-methyl-3-phenylglycidate,[26a] and 2,2-dicyano-3-aryloxiranes[26b] indicates that these processes would be quite slow at 80 °C.

$$\mathbf{23} \rightarrow ArCHClCOCl$$

24

The formation of equimolar amounts of CO and *gem*-dihalide **14** coupled with the established ease with which alkoxyhalocarbenes break down with loss of CO[30] indicates the likely intermediacy of carbene **20**, which can arise by 1,3-halogen migration from ylide **19**. A transformation similar to **19** → **20** has been postulated in the sequence of steps used to explain the small yield of aryl fluoride **4**, which is produced from treatment of steroidal dienone **3** with sodium chlorodifluoroacetate.[4c]

Some additional observations are of considerable interest. Reference to the data in Table IV shows that a change in the substituent(s) on the aromatic ring of aldehyde **11** has a distinct effect on the distribution of products. For example, the yield of CO (and benzal halide **14**) increases in the order $3\text{-}CF_3PhCHO < PhCHO < 4\text{-}MeOPhCHO < 2,4,6\text{-}Me_3PhCHO$, the order of increasing electron density in the aromatic ring, a trend which would be consistent with the expected facilitation either of rearrangement of the ylide to carbene **20** and/or extrusion of CO from carbene **20**.[30]

The yield of acid chloride **22** (isolated as acetal ester **13**, Table III) decreases in the order $3\text{-}CF_3PhCHO > PhCHO > 2,4,6\text{-}Me_3PhCHO$. Although none of the acetal ester was detected from the reaction of anisaldehyde (**11c**) with mercurial **12**, significant yields of dimethyl acetal **15c** and hydroxy ester **16c** which were observed undoubtedly arose from the acid-catalyzed breakdown in methanol of an initially formed acetal ester. The lack of any acetal ester (or products from its acid-catalyzed methanolysis) from mesitaldehyde (**11d**) may reflect in part the operation of an unfavorable steric interaction in the formation of dioxolane **21**.

Control reactions (see Experimental Section) indicated that the significant amounts of benzal halide product containing both bromine and chlorine observed in the reactions of aldehydes **11a**, **11c**?, and **11d** with mercurial **12** did not arise from a simple exchange reaction of phenylmercuric bromide with the benzal chloride or from the initial production of: CBrCl. Therefore, the presence of an appropriately substituted α-bromo-α-chlorotoluene among the products of reaction of the more electron-rich aldehydes with mercurial **12** must be presumed to involve an exchange between phenylmercuric bromide and one or more of the reaction intermediates.

When benzaldehyde was treated with phenyl(tribromomethyl)mercury (followed by methanol and pyridine at 0 °C), the only observed products were CO and benzal bromide, which can can be rationalized as being due to a facilitation of the process **19** → **CO** + **14** (Scheme I) because of the smaller

C–X bond energy anticipated for bromine relative to chlorine.

$$\mathrm{PhCHO + PhHgCBr_3 \xrightarrow[80\ ^\circ C]{C_6H_6} \xrightarrow[pyridine]{MeOH} CO + PhCHBr_2}$$

Kinetic Considerations. Returning to the data of Table II, one notes that relative reactivities with respect to reaction with dichlorocarbene are 3-$CF_3PhCHO \ll PhCHO \sim n$-$BuCH{=}CH < 4$-$MeOPhCHO \sim c$-$C_6H_{10} \ll Me_2C{=}CMe_2$. Reactivity increases with increasing nucleophilicity of the carbonyl oxygen, consistent with the known electrophilic behavior of dichlorocarbene in addition reactions to olefins[18] and with the assumption of an early transition state for the attack rather than one which resembles the carbonyl ylide. The latter intermediate, which is isoelectronic with the allylic anion, should be stabilized by electron-withdrawing groups;[31] thus, a transition state resembling the ylide would lead to the opposite reactivity order among the aldehydes than that which was observed.[32]

Conclusions

The reactions of aromatic aldehydes and benzophenone with mercurial 12 in benzene are best described by initial breakdown of both mercurial 12 and a mercurial–carbonyl complex to give dichlorocarbene. The rate of carbene reaction with the carbonyl group was found to increase with increasing electron density in the aromatic ring. Although conclusions about some of the paths leading to observed products must remain tentative, a variety of evidence suggests that attack of dichlorocarbene on the aldehyde or ketone first forms a dichlorocarbonyl ylide. Once formed, the ylide can undergo halogen rearrangement and 1,3 cycloaddition to a second molecule of aldehyde. Similar halocarbonyl ylides have been suggested to explain the products resulting from the reaction of sodium chlorodifluoroacetate with steroidal ketones[4,5] and of mercurial 12 with steroidal ketones[7] and highly halogenated ketones.[8]

Experimental Section

Elemental analyses were performed by the Department of Medicinal Chemistry at the University of Kansas or by Chemalytics, Inc., Tempe, Ariz. Melting points are uncorrected. IR spectra were obtained on Beckman IR-8 and IR-10 instruments with a 1603-cm^{-1} polystyrene peak (vs. air) as reference. Proton NMR spectra were obtained on a Varian A-60 spectrometer. Quantitative analyses of the NMR spectra of mixtures were based on a known amount of added toluene. All chemical shifts are reported as τ values. An F and M Model 700 Chromatograph (thermal conductivity detector) was used for VPC analyses with the following columns: 10% OV-210 on 80–100 mesh Gas Chrom Q (6 ft × 1/8 in. glass), 10% OV-101 on 60–80 mesh Gas Chrom Q (5 ft × 1/8 in. aluminum), and 10% OV-1 on 60–80 mesh Gas Chrom Q (6 ft × 1/8 in., glass). Toluene served as an internal standard; areas (disc integrator) relative to that of toluene were corrected for detector sensitivity.

Reagent grade benzene, toluene, and pyridine were dried and distilled from calcium hydride and stored over Linde 4Å molecular sieves. Anhydrous methanol was dried over Linde 4Å sieves or distilled from magnesium prior to use. Tetrahydrofuran (reagent) was dried over Linde 4Å sieves and rendered peroxide free by passing it through basic alumina prior to use. Aldehydes were dried over Linde 4Å sieves and distilled from calcium hydride under purified dry nitrogen or argon immediately prior to use or stored for ≤24 h under nitrogen or argon. Diglyme was distilled and dried over Linde 4Å sieves. Mercurials were refrigerated and stored under nitrogen or argon.

Samples of 7,7-dichloronorcarane, 7-chloro-7-bromonorcarane, 1,1-dichloro-2,2,3,3-tetramethylcyclopropane, and 1,1-dichloro-2-butylcyclopropane were prepared from the corresponding olefin by treatment with the appropriate phenyl(trihalomethyl)mercurial.[6]

Phenyl(bromodichloromethyl)mercury was prepared in 74–80% yields (based on PhHgCl) by a modification of the procedure of Seyferth[33] in which the bromodichloromethane (freshly distilled) was added dropwise (30 min) to a cold (−25 °C) solution of phenylmercuric chloride, potassium *tert*-butoxide, and *tert*-butyl alcohol in dry tetrahydrofuran, followed by stirring for 30 min prior to workup. Mp 108–110 °C dec (lit.[33] mp 108–110 °C dec).

Mesital chloride was prepared from mesitaldehyde and thionyl chloride. Mp 34–36 °C (lit.[34] mp 35–36 °C).

α-Bromo-α-chlorotoluene was prepared by the addition of bromine to benzyl chloride at 150 °C under the influence of ultraviolet light.[35] The NMR spectrum (CCl_4) showed a multiplet at τ 2.40–2.82 (5 H) and singlets at τ 3.39 and 3.44 (1 H total), with the latter signal corresponding to benzal bromide impurity.[36]

Dimethyl acetals of benzaldehyde, anisaldehyde, and mesitaldehyde were prepared by treating the aldehyde with an excess of methanol in the presence of *p*-toluenesulfonic acid and removing water with Linde 3Å molecular sieves in a Soxhlet extractor. The distilled product from benzaldehyde had bp 87–88 °C (18 Torr) [lit.[37] bp 88 °C (18 Torr)]; NMR spectrum (CCl_4), multiplet at τ 2.50–2.82 (5 H), singlet at τ 4.63 (1 H), 6.79 (6 H). The product from anisaldehyde had bp 125 °C (13 Torr) [lit.[38] bp 249–250 °C (760 Torr)]; NMR spectrum (CCl_4), A_2B_2 multiplet at τ 2.62, 2.76, 3.13, 3.27 (4 H), singlets at τ 4.68 (1 H), 6.24 (3 H), 6.80 (6 H). The product from mesitaldehyde had bp 116–118 °C (10 Torr) [lit.[39] bp 242–243 °C (741 Torr)]; NMR spectrum (CCl_4), singlets at τ 3.32 (2 H), 4.63 (1 H), 6.75 (6 H), 7.68 (6 H), 7.82 (3 H).

Methyl α-Chlorophenylacetate. α-Chlorophenylacetyl chloride (6.1 g, 0.032 mol) was added slowly (30 min) to a stirred solution of methanol (1.1 g, 0.034 mol) and pyridine (2.6 g, 0.033 mol) in benzene (20 mL). After 4 h the reaction mixture was worked up in the usual manner to give the ester (2.73 g, 0.0148 mol, 46%): bp 121–123 °C (12 Torr) [lit.[40] bp 124 °C (8 Torr)]; NMR spectrum (CCl_4), multiplet at τ 2.50–2.85 (5 H), singlets at τ 4.75 (1 H), 6.40 (3 H); IR spectrum (CCl_4), carbonyl at 1760 cm^{-1}.

Methyl α-bromophenylacetate was prepared from phenylacetic acid,[41] bp 82–83 °C (1 Torr) [lit.[41] bp 122–146 °C (20 Torr)]; NMR spectrum (CCl_4), multiplet at τ 2.60–2.90 (5 H), singlets at τ 4.70 (1 H), 6.50 (3 H).

Methyl *p*-methoxymandelate was prepared from anisaldehyde by the general method of Knorr.[42] Distillation at 5 Torr followed by recrystallization from water produced a white product, mp 39–40 °C; NMR spectrum (CCl_4), A_2B_2 pattern at τ 3.03 (4 H), singlets at τ 5.01 (1 H), 5.93 (1 H), 6.38 (3 H), 6.45 (3 H); IR spectrum (CCl_4), 3450, 2960, 2840, 1735, 1614, 1515, 1442, 1245, 1177, 1080, 1030, 833, 797 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.09; H, 6.28.

Methyl Mesitylglycolate. Mesitylene was first converted to 2,4,6-trimethylacetophenone[43] followed by selenium dioxide oxidation, hydration, and rearrangement to the glycolic acid.[44] Esterification with diazomethane[45] resulted in a white crystalline product, mp 88–90 °C (lit.[44] mp 90–91 °C); NMR spectrum (CCl_4), singlets at τ 3.15 (2 H), 4.43 (1 H), 6.25 (3 H), 6.80 (1 H, broad), 7.68 (6 H), 7.74 (3 H); IR spectrum (CCl_4), 3520, 2960, 2860, 1740, 1610, 1440, 1370, 1230, 1140, 1070, 1030, 970, 850 cm^{-1}.

Methyl α-methoxyphenylacetate was prepared from α-chlorophenylacetyl chloride by treatment with excess sodium methoxide in methanol at reflux for 4 h. The crude product was purified by distillation, bp 123–124 °C (11 Torr) [lit.[46] bp 118–119 °C (8 Torr)]; NMR spectrum (CCl_4), multipet at τ 2.62–2.88 (5 H), singlets at τ 5.37 (1 H), 6.44 (3 H), 6.70 (3 H); IR spectrum (CCl_4), carbonyl at 1745 cm^{-1}.

Treatment of Aldehydes and Ketones with Phenyl(trihalomethyl)mercury. General Procedure. Glassware was cleaned in aqueous ethanolic NaOH solution, thoroughly rinsed, dried for ≥ 6 h at 110 °C, assembled while warm, and purged with argon or nitrogen (dried with Drierite and Linde 4Å molecular sieves). The entire reaction and workup was carried out in a dry, inert atmosphere; liquid transfers were made with oven-dried syringes. The apparatus consisted of a 100-mL four-necked flask (one male joint, capped during the initial reaction) equipped with an inert gas inlet, thermometer, magnetic stirrer, and a condenser attached to a gas burette, manometer, and storage balloon.

After a mixture of phenyl(bromodichloromethyl)mercury (6.61 g, 15 mmol) in benzene (30 mL) was stirred for a few min, benzaldehyde (2.71 g, 25.6 mmol) was added, the manometer was balanced, and initial readings of gas volume, room temperature, and atmospheric pressure were recorded. The reaction mixture was stirred, heated slowly (oil bath) to ca. 80 °C, maintained at that temperature until gas evolution ceased (3–4 h), and cooled to the starting temperature to allow final readings of gas volume to be made; IR of gas, 2120 and 2170 cm^{-1} (carbon monoxide). It was noted that the yield of CO was affected by the heating rate.

After the condenser had been replaced with a stopper, the contents of the flask were cooled (ice bath) and filtered (inert atmosphere) by connecting the male joint to a sintered glass funnel attached to a small, dry three-necked flask equipped with two stopcocks to control vacuum and inert gas. The precipitate was washed (3 × 20 mL of cold benzene), dried, weighed, and identified as phenylmercuric bromide (90–97% based on a starting mercurial), mp (crude product) 274–276 °C (when mixed with pure authentic phenylmercuric bromide mp 266–280 °C). This material may contain some phenylmercuric chloride.

The filtrate was kept cold (ice bath) while a cold solution of methanol (4 mL, 98.8 mmol) and pyridine (4 mL, 49.7 mmol) in benzene (30 mL) was added. After being stirred for 3–4 h at 0 °C, the reaction mixture was filtered, concentrated at reduced pressure, diluted with ca. 40 mL of benzene–cyclohexane (1:1), filtered, and concentrated at reduced pressure. The products were analyzed by VPC and NMR with a weighed sample of toluene (ca. 15% of the weight of the residue) added as an internal standard. (Nitromethane was added as an internal NMR standard for reactions involving mesitaldehyde.) As a further aid to the identification of products, a portion of the liquid product mixture (after treatment with methanol and pyridine) was sometimes subjected to simple distillation and/or column chromatography on Florisil (dried at 130 °C) with cyclohexane, benzene, and benzene–ether mixtures as eluents.

Variations in the reaction procedures described include changes in the ratio of aldehyde to mercurial, in the reaction time and temperature, in the nature and amount of solvent, and in the details of the workup procedure.

The amount of benzal halides and of acetal ester **13** was determined directly from NMR absorptions for the α-hydrogen of the former and the acetal hydrogen (from each diastereomer) of the latter. Methyl mandelate was determined directly from the tertiary hydrogen. Benzaldehyde dimethyl acetal was determined from the OCH_3 peak by subtracting the contribution to that peak from one OCH_3 group of acetal ester **13**. Corrections for differences in thermal conductivity detector sensitivity for the various compounds were made.

Treatment of Benzaldehyde with α-Chlorophenylacetyl Chloride, Phenylmercuric Bromide, and Benzal Chloride. A mixture of α-chlorophenylacetyl chloride (1.7 g, 9 mmol, freshly distilled), benzal chloride (0.80 g, 5 mmol), phenylmercuric bromide (6.1 g, 17 mmol), benzaldehyde (3.7 g, 35 mmol), and benzene (22 mL) was heated at 77–80 °C for 3.5 h in the same apparatus used for the reactions of benzaldehyde with phenyl(trihalomethyl)mercury. Total gas volume change was 1.0 mL.

The solution was filtered under argon to give phenylmercuric bromide (5.6 g, 97% recovery; mp 278–280 °C). The filtrate was treated with methanol (1.0 g, 31 mmol) and pyridine (1.2 g, 15 mmol) in benzene (15 mL) for 4 h. After workup, NMR analysis showed only methyl α-chlorophenylacetate, benzaldehyde, and benzal chloride. A small singlet at τ 4.43 was not positively identified but may be attributed to the tertiary hydrogen of phenyldimethoxymethane. VPC analysis (10% OV-1, 5 ft, 105 °C) showed only a trace of α-bromo-α-chlorotoluene, which also appeared to be present in the starting benzal chloride.

Treatment of Benzaldehyde with α-Chlorophenylacetyl Chloride and Phenylmercuric Bromide. A mixture of α-chlorophenylacetyl chloride (2.5 g, 13 mmol), benzaldehyde (4.4 g, 42 mmol), and phenylmercuric bromide (10.8 g, 30.2 mmol) in benzene (60 mL) was heated at 75–80 °C for 3.3 h in the same apparatus used for the reactions of benzaldehyde with phenyl(trihalomethyl)mercury. Total gas volume change was 1.6 mL. VPC analysis (6 ft glass, OV-1, 138 °C) showed benzaldehyde, α-chloroacetyl chloride, and a trace of benzal chloride.

Phenylmercuric bromide (10.5 g, 97%; mp 267–273 °C was recovered by filtration, and a portion (17.8%) of the filtrate was added to a solution of methanol (1.2 g, 37 mmol) and pyridine (2.4 g, 30 mmol) and allowed to stand (drying tube with $CaSO_4$) for 3.25 h. After being worked up in the usual manner, the solution was analyzed by NMR, which showed only absorptions for methyl α-chlorophenylacetate and benzaldehyde.

Treatment of Benzaldehyde and Benzal Bromide with Phenylmercuric Bromide, Methanol, and Pyridine. Each of the mentioned compounds (10 mL of each liquid and 10 g of each solid) was dissolved in benzene (30 mL) in the presence of hydrogen bromide gas. The reaction mixture was kept at reflux for 3 h. No benzaldehyde dimethyl acetal was observed by NMR analysis.

2,5-Diphenyl-1,3-dioxolan-4-one was prepared from mandelic acid and benzaldehyde by the general procedure of Salomaa and Sallinen.[47] Recrystallization of the crude product from carbon tetrachloride resulted in white crystalline material, mp 100.5–101.5 °C (lit.[48] mp 104–105 °C); IR spectrum (CCl_4), carbonyl singlet at 1800 cm^{-1}; NMR spectrum (CCl_4), multiplet at τ 2.58 (10 H), doublet at τ 3.53 (1 *H*, J = 1 Hz), doublet at τ 4.79 (1 H, *J* = 1 Hz).

Methyl 2,4-Diphenyl-3,5-dioxahexanoate. Dry benzene (13 mL), 2,5-diphenyl-1,3-dioxolan-4-one (6.9 g, 0.029 mol), methyl dichloromethyl ether (5.0 g, 0.044 mol, freshly distilled under argon), and dry mercury(II) chloride (0.03 g) were heated with an oil bath at 105–115 °C (argon atmosphere) for 1–2 days or until an NMR spectrum of a sample of the crude reaction mixture showed none of the starting dioxolanone. The reaction mixture was cooled (ice bath), diluted with benzene (10 mL), and filtered through a fritted glass funnel into a cold, stirred solution of methanol (4.8 g, 0.15 mol) and pyridine (7.9 g, 0.10 mol) in dry benzene (20 mL). After 12 h the reaction mixture was filtered, and the filtrate was washed with saturated sodium bicarbonate solution and saturated sodium chloride solution. Aqueous extracts were washed with benzene, and the combined benzene solutions were dried (K_2CO_3) and concentrated at reduced pressure (2 mm) to give 6.52 g of yellow oil, a portion of which (6 g) was further purified by molecular distillation (10^{-5} Torr; bath, 75 °C) to give an initial fraction (1.7 g) containing impurities and the desired product (3.47 g, 0.0121 mol, 41.8%) as a mixture of diasterioisomers; NMR spectrum (CCl_4), multiplet at τ 2.43–2.85 (10 H, Ph), singlets at τ 4.32 and 4.52 (1 H total, CHOMe), 4.87 and 4.89 (1 H total, $CHCO_2Me$), 6.44 and 6.47 (3 H total, $\mathbf{CH_3}OCHPh$), 6.83 and 6.85 (3 H total, CO_2CH_3); IR spectrum (CCl_4), 3130, 2850, 1760, 1740, 1540, 1490, 1460, 1440, 1355, 1270, 1250, 1205, 1190, 1170, 1110, 1100, 1075, 1055, 1023 cm^{-1}. The ratio of isomers based on NMR signals at τ 4.32 and 4.52 was 1.8:1, respectively.

Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.44; H, 6.22.

A portion of the product (1.23 g, 4 mmol) was hydrolyzed in a 0.6 N hydrochloric acid solution in 50% aqueous dioxane at 90 °C for 1 h under argon. The solution was cooled, made basic with 1 N sodium hydroxide solution (11 mL), and extracted with methylene chloride. The dried ($MgSO_4$) concentrated extract was shown by NMR to contain only benzaldehyde and dioxane. The acidified aqueous phase was extracted with ether, from which mandelic acid (0.62 g, 4 mmol) was isolated, mp 118–120 °C (from benzene). The identity was confirmed by IR and mixture melting point comparisons with an authentic sample.

The title compound was also isolated by molecular distillation (10^{-5} Torr) of the high-boiling product from a reaction of phenyl(bromodichloromethyl)mercury with benzaldehyde, carried out as described previously.

Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31: H, 6.34. Found: C, 71.62; H, 6.27.

Methyl 2,4-bis(*m*-trifluoromethylphenyl)-3,5-dioxahexanoate was isolated by preparative VPC of the reaction mixture from the treatment of *m*-trifluoromethylbenzaldehyde with phenyl(bromodichloromethyl)mercury in benzene. The product (a mixture of diastereomers) was purified by molecular distillation (10^{-5} Torr); NMR spectrum (CCl_4), multiplet at τ 2.2–2.7 (8 H), singlets at τ 4.20 and 4.37 (1 H total), 4.78 and 4.82 (1 H total), 6.28 and 6.39 (3 H total), 6.67 and 6.73 (3 H total); IR spectrum (CCl_4), 2980, 2860, 1745 d, 1445 d, 1330, 1175, 1135, 1075, 918, 701 cm^{-1}. The ratio of isomers based on NMR signals at τ 4.20 and 4.37 was 1.2:1, respectively.

Anal. Calcd for $C_{19}H_{16}O_4F_6$: C, 54.03; H, 3.82. Found: C, 53.97; H, 3.88.

Complexation of Phenyl(bromodichloromethyl)mercury with Benzophenone and Benzaldehyde. Measurements were obtained on a Perkin-Elmer Model 421 grating spectrophotometer with CaF_2 matched cells. Benzophenone was recrystallized (cyclohexane) and dried in a desiccator ($CaSO_4$), mp 48–49 °C (lit.[49] mp 48.1 °C). Benzaldehyde was freshly distilled under argon. The mercurial was recrystallized (3:1, hexane–chloroform) at 25 °C, mp 110–111 °C (lit.[50] mp 110–111 °C).

A benzene solution of the mercurial (0.251 M) and benzophenone (0.225 M) balanced against 0.200 M benzophenone (in benzene) in the reference call exhibited a carbonyl absorption at 1647.5 cm^{-1}, distinctly different from the absorption at 1663.5 cm^{-1} for a dilute benzene solution of benzophenone (vs. benzene). Similarly a benzene solution of the mercurial (0.350 M) and benzaldehyde (0.280 M) balanced against 0.240 M benzaldehyde (in benzene) exhibited a carbonyl absorption at 1696 cm^{-1}, compared to the normal carbonyl absorption of benzaldehyde at 1708 cm^{-1}.

A series of benzene solutions of benzophenone and benzaldehyde of known concentrations was used to establish a calibration curve which would allow the determination of the amount of free carbonyl in solutions containing both free and complexed carbonyl at ca. 25 °C. Measurements on benzaldehyde were carried out under argon with deoxygenated benzene and were completed in a few minutes, during which time no detectable decomposition of the mercurial occurred. Results are summarized in Table I.

Relative Reactivities. Approximate relative rates of reaction of mercurial **12** with aldehydes and olefins were determined at 50 °C (48 h) in benzene with equimolar mixtures of **11a**, **12**, and cyclohexene; **11a**, **12**, cyclohexene, and 2,3-dimethyl-2-butene; **11a**, **12**, cyclohexene, and 1-hexene; **11b**, **12**, and cyclohexene; and **11c**, **12**, and cyclohexene. Product mixtures were then treated with excess methanol and pyridine at 0 °C for 4 h, followed by addition of an internal toluene standard and analysis by NMR and VPC. Relative rates were calculated from a quantitative comparison of the dichlorocyclopropane products from the olefins with the combined yield of CO plus all ester and acetal products from the aldehydes.

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Registry No.—**11d**, 487-68-3; *erythro*-**13a**, 64761-19-9; *threo*-**13a**, 64761-21-3; *erythro*-**13b**, 64761-23-5; *threo*-**13b**, 64761-24-6; **16c**, 13305-14-1; **17**, 56535-98-9; benzophenone, 119-61-9; α-bromo-α-chlorotoluene, 22332-89-4; benzyl chloride, 100-44-7; benzaldehyde dimethyl acetal, 1125-88-8; anisaldehyde dimethyl acetal, 2186-92-7; mesitaldehyde dimethyl acetal, 64761-29-1; methyl α-chlorophenylacetate, 7476-66-6; α-chlorophenylacetyl chloride, 2912-62-1; methyl α-bromophenylacetate, 3042081-7; methyl mesitylglycolate, 63809-19-8; methyl α-methoxyphenylacetate, 3558-61-0; phenylmercuric bromide, 1192-89-8; carbon monoxide, 630-08-0; benzal chloride, 98-87-3; methanol, 67-56-1; sodium methoxide, 124-41-4.

References and Notes

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