very low amine concentration),[4] introduces another path that requires two molecules of amine and about one molecule of salt (Figure 4).

The inhibiting effect of Bu_4NCl on the reaction of **3** with 1,4-db indicates the formation of a complex **3**–Cl (ion paired with Bu_4N^+). The chloride ion is in fact a strong hydrogen-bond acceptor. We may assume that the complex **3**–Cl^- is also the reactive species in the reaction of **3** with *n*-$BuNH_2$ when Bu_4NCl is added. Thus, we can calculate the reactivity of the complex with Cl^- from the intercept of Figure 4. Its value (4.2×10^{-3}), only slightly lower than that in the absence of salt (5.8×10^{-3}),[2] indicates that this adduct has a reactivity similar to that of the complex **3**–NH_2Bu, which is therefore more likely a hydrogen-bonded species than the previously suggested ion pair.

Conclusions

Hydroxyl groups in the appropriate position relative to the reacting center in aminolysis reactions can stabilize the transition state. The free hydroxyl group is capable of acid catalysis as a hydrogen-bond donor as in the case of the aminolysis of phenyl salicylate, **1**.[1] On the other hand, the free hydroxyl group is not capable by itself of providing significant catalysis as a hydrogen-bond acceptor, but it becomes very efficient when hydrogen bonded to bases such as amines or other hydrogen-bond-accepting species such as HMPT or chloride ion as in the aminolysis of *o*-hydroxyphenyl benzoate, **3**. The *o*-hydroxyl group therefore functions as a relay for the action of reagents in solution that do not perform significant intermolecular catalysis but that thus become involved in very efficient intramolecular catalysis.

Experimental Section

Materials. Acetonitrile,[17] *n*-butylamine,[13] 1,2-diaminoethane,[13] 1,3-diaminopropane,[13] 1,4-diaminobutane,[13] hexamethylphosphoric triamide,[13] and tetra-*n*-butylammonium perchlorate[2] were purified according to reported procedures. Tetra-*n*-butylammonium chloride was prepared from the corresponding perchlorate with an ion-exchange resin (Dowex 1, X8 20–50 mesh) in the chloride form because the commercial chloride could not be purified by simple crystallization. After evaporation of the chloride solution in a rotor evaporator, the residual water was eliminated by azeotropic distillation with benzene. After several crystallizations from dry benzene, the solid was desiccated under vacuum.

o-Hydroxyphenyl benzoate and *o*-methoxyphenyl benzoate were those used in previous work.[2]

N-(4-Aminobutyl)benzamide hydrochloride was prepared by mixing benzoyl chloride and 1,4-diaminobutane in diethyl ether in a 1:2 molar ratio. The precipitate was washed with water to separate the hydrochlorides from the disubstituted amine. The hydrochloride of the monosubstitued derivative was separated from the hydrochloride of the unreacted amine by chloroform extraction of the aqueous solution saturated with sodium chloride. After evaporation of chloroform, crystallization from ethanol–ethyl ether yielded white crystals, mp 170 °C (lit.[18] mp 169–170 °C).

Kinetics. All reactions were followed at 25 °C in a thermostated cell compartment of a UV–vis spectrophotometer at 270–280 nm.

Good linear first-order plots were obtained in all cases. All solutions were prepared and kept under a nitrogen atmosphere. The reacting solution was prepared in a cuvette by adding 50 μL of substrate solution to a thermostated cuvette containing 3 mL of a solution containing the nucleophile and if necessary other additives. The final substrate concentration was about 10^{-4} M.

The experimental and mock-infinity values for the reaction of *o*-hydroxyphenyl benzoate with 1,4-diaminobutane agreed within experimental error. The mock-infinity value was prepared with the hydrochloride of the amide because HCl does not absorb in the spectral region used for the experiments.

All kinetics performed with the diamines reacting with **3** gave isosbestic points at 287 and 257 nm, indicating that only a single reaction occurred after a fast preequilibrium.

Acknowledgment. This work was supported by CNR, Rome.

Registry No. **3**, 5876-92-6; **4**, 1523-19-9; 1,2-diaminoethane, 107-15-3; 1,3-diaminopropane, 109-76-2; 1,4-diaminobutane, 110-60-1; hexamethylphosphoric triamide, 680-31-9; tetrabutylammonium perchlorate, 1923-70-2; tetrabutylammonium chloride, 1112-67-0; butylamine, 109-73-9.

(17) Deacon, T.; Steltner, A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1778.

(18) Kanewskaja, S. *J. Russ. Phys. Chem. Ges.* **1927**, *59*, 639.

Selective Formation and Trapping of Dihalocarbonyl Ylides Derived from Dihalocarbenes and Substituted Benzaldehydes

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The thermal decompositions of several phenyl(trihalomethyl)mercury compounds in the presence of substituted benzaldehydes **1** and dimethyl acetylenedicarboxylate (**7**) in dry benzene at 80 °C resulted in 2-halo-5-arylfuran-3,4-dicarboxylates **9** in isolated yields (not optimized) that ranged from 13% to 64%. These products appear to be the result of selective attack by dihalocarbene on the aldehyde followed by preferential capture of the resulting carbonyl ylide by the acetylenic dipolarophile and loss of hydrogen halide. The substitution of diethyl fumarate (**12**) for acetylene **7** produced a mixture of the *E* and *Z* isomers of dihydrofuran **14** in a ratio of 70:30. Tetrasubstituted dipolarophiles failed to give comparable products. The intermediate dihalocarbonyl ylides were shown to undergo halogen exchange.

Previous experimental work[1] has provided a body of evidence that the thermal decomposition of phenyl(trihalomethyl)mercury in the presence of various aromatic aldehydes **1** involves initial generation of dihalocarbene

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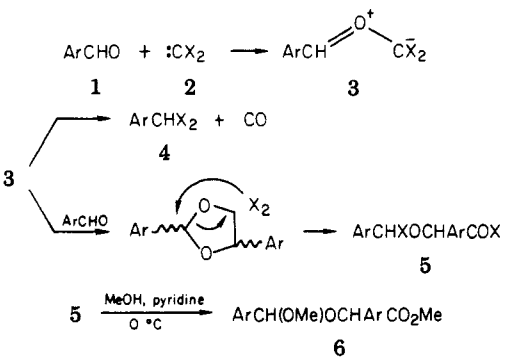
Table I. Reaction of $PhHgCX_3$ with ArCHO and Electrophilic Dipolarophiles[a]

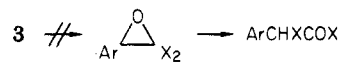
entry	$PhHgCX_3$ (M)	ArCHO (A)	dipolarophile (D)[b]	molar ratio M:A:D	rctn time, h	isolated yield,[c] %	2-halogen (%)[c]
1	$BrCl_2$	Ph	DMAD	1:1:3	16	46	Cl (96), Br (4)
2	Br_3	Ph	DMAD	1:1:3	16	38	Br (100)
3	$BrCl_2$	*p*-MeOPh	DMAD	1:1:3	6	28	Cl (100)
4	Cl_3	*p*-MeOPh	DMAD	1:1:3	66	30	Cl (100)
5	$BrCl_2$	*p*-MePh	DMAD	1:1:3	17	29[d]	Cl (92), Br (8)
6	$BrCl_2$	*p*-MePh	DMAD	2:1:6	16	64[e]	
7	$BrCl_2$	3,5-Cl_2Ph	DMAD	1:1:3	24	24	Cl (70), Br (30)
8	$BrCl_2$	F_5Ph	DMAD	1:1:3	24	13	Cl (91), Br (9)
9	$BrCl_2$	Ph	DEF	1:1:3	6	30[f]	
10	$BrCl_2$	Ph	DEF	2:3:16[g]	21	18[f]	
11	$BrCl_2$	Ph	DEF	1:148:3[h]	12	0	
12	$BrCl_2$	Ph	TEET	1:1:3	17	0	
13	$BrCl_2$	Ph	TCE	1:1:22[i]	36	0	
14	$BrCl_2$	Ph	DFC	1:1:3	114	0	

[a] Solvent is benzene at 80 °C unless otherwise specified. [b] DMAD = dimethyl acetylenedicarboxylate, DEF = diethyl fumarate, TEET = tetraethyl ethylenetetracarboxylate, TCE = tetrachloroethylene, DFC = decafluorocyclohexene. [c] Ylide trapped by D; products are dimethyl 2-halo-5-arylfuran-3,4-dicarboxylates when D = DMAD and diethyl (*Z*)- and (*E*)-2-chloro-5-phenyl-4,5-dihydrofuran-3,4-dicarboxylate when D = DEF; yields have not been optimized. [d] Conversion = 56%. [e] Conversion ≅ 100%. [f] 70% *E*, 30% *Z*. [g] Solvent is DEF at 82–84 °C. [h] Solvent is PhCHO at 82–84 °C. [i] Solvent is TCE at 82–84 °C.

2[2] followed by the production of dihalocarbonyl ylide **3**. The latter intermediate undergoes either a unimolecular decomposition to dihalide **4** and carbon monoxide or a bimolecular reaction with starting aldehyde, which culminates in the formation of acid halide **5** (isolated as a mixture of the diastereiomers of ester **6**). Products that



might have been expected from electrocyclic ring closure of **3** to the dihalooxirane followed by the known facile rearrangement of such oxiranes to an α-halo acid halide[3] were not observed, although this process may dominate in the reaction of dihalocarbenes with benzophenone.[4]



We now report on the reactions of various phenyl(trihalomethyl)mercury compounds with substituted benzaldehydes in the presence of highly electrophilic dipolarophiles that can selectively trap the intermediate carbonyl ylide but remain unreactive to attack by the initially formed dihalocarbene.[5]

Table II. Selected Data on Dimethyl 2-Halo-5-arylfuran-3,4-dicarboxylates

aryl	halogen	mp, °C	analysis[a] calcd *m/e*	analysis[a] obsd *m/e*
Ph	Cl	67.8–68.5[b]	294.029	294.027
Ph	Br	93.0–93.8[c]	337.979	337.979
p-MeOPh	Cl	102.5–103	324.040	324.040
p-MePh	Cl	101.5–102.5[d]	308.045	308.044
p-MePh	Br	*e*	351.995	351.995
3,5-Cl_2Ph	Cl	87.0–88.0[f]	361.951	361.953
3,5-Cl_2Ph	Br	*e*	405.901	405.902
F_5Ph	Cl	oil[g]	383.982	383.980
F_5Ph	Br	*e*	427.932	427.930

[a] Precise *m/e* values were determined by peak matching on a Varian MAT CH-5 mass spectrometer; two-seven determinations were within ±0.003 mass unit of calculated values. [b] Contains ca. 4% of the 2-bromo isomer. [c] Recrystallized from hexane. [d] Contains ca. 8% of the 2-bromo isomer. [e] Not isolated. [f] Recrystallized from cyclohexane; contains ca. 30% of the 2-bromo isomer. [g] Contains ca. 9% of the 2-bromo isomer.

Results and Discussion

Dimethyl Acetylenedicarboxylate. The thermal decompositions of several phenyl(trihalomethyl)mercury compounds were carried out in the presence of substituted benzaldehydes and dimethyl acetylenedicarboxylate (**7**) in dry benzene at 80 °C. Appropriate data are summarized in Table I (entries 1–8). Filtration of phenylmercuric halide, evaporation of solvent, and flash chromatography on silica gel with ethyl acetate/hexane led to the isolation of 2-halo-5-arylfuran-3,4-dicarboxylates **9**, which were identified by a combination of ^1H NMR, ^{13}C NMR, MS, and an elemental analysis determined by precise *m/e* values on the parent ion. Data on these new compounds are recorded in Table II and in the Experimental Section. Although no systematic efforts were made to optimize yields, it is apparent from entry 6 (Table I) that increasing the ratio of mercurial and dipolarophile to aldehyde has a dramatic effect. Furthermore, except for longer reaction times, the use of phenyl(trichloromethyl)mercury rather than the more difficult to prepare phenyl(bromodichloromethyl)mercury gave a comparable yield of furan **9** (compare entries 4 and 3). No furans were produced

(1) (a) Martin, C. W.; Lund, P. R.; Rapp, E.; Landgrebe, J. A. *J. Org. Chem.* **1978**, *43*, 1071. (b) Martin, C. W.; Landgrebe, J. A.; Rapp, E. *J. Chem. Soc., Chem. Commun.* **1971**, 1438. (c) Martin, C. W.; Landgrebe, J. A.; Rapp, E. *Angew. Chem.* **1972**, *84*, 307.

(2) Although relative reactivity measurements indicate that the same dichlorocarbene intermediate is produced from phenyl(bromodichloromethyl)mercury in the presence of benzaldehyde as in its absence, an aldehyde–mercurial complex is known to form and decomposes to the carbene more rapidly at a given temperature than the mercurial alone.[1a]

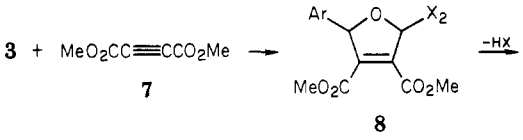
(3) McDonald, R. N. *Mech. Mol. Migr.* **1971**, *3*, 67.

(4) (a) Martin, C. W.; Landgrebe, J. A. *J. Chem. Soc., Chem. Commun.* **1971**, 15. (b) No products are observed which correspond to the breakdown of the ylide to phosgene and an arylcarbene.

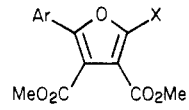
(5) Gill, H. S.; Landgrebe, J. A. *Tetrahedron Lett.* **1982**, 5099.

when benzaldehyde was heated in benzene with acetylene 7 and phenylmercuric bromide.

The results are consistent with selective attack by dihalocarbene 2 on aldehyde 1 followed by preferential capture of the resulting carbonyl ylide 3 by acetylene 7 and loss of hydrogen halide to give furan 9. Previous exper-



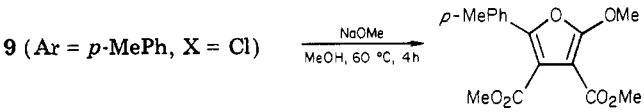
7 8



9

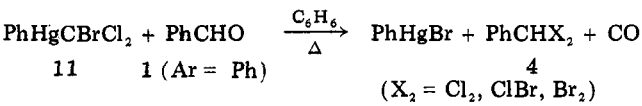
imental work has established similar reactivity toward dichlorocarbene attack by benzaldehyde and 1-hexene and by *p*-anisaldehyde and cyclohexene.[1a] Thus, it is not surprising that no evidence was found for dihalocarbene addition to the highly electron deficient acetylene 7 in competition with the aldehyde. This same electron deficiency is responsible for the effectiveness with which the acetylene traps the ylide and circumvents the formation of products 4 and 5. Although other reports indicate that electron-rich as well as electron-deficient dipolarophiles are effective traps for nonhalogenated carbonyl ylides,[6] the use of electron-rich dipolarophiles in this study is precluded by their high reactivity toward dihalocarbene addition.[7]

The treatment of furan 9 (Ar = *p*-MePh, X = Cl) with sodium methoxide in methanol resulted in the quantitative replacement of Cl with OMe.



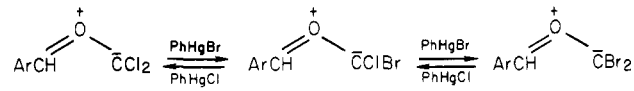
10

Some additional observations are of special interest. Data in the last column of Table I indicate that with the use of phenyl(bromodichloromethyl)mercury (11; entries 1, 3, 5, 7, 8), 2-bromofuran 9 (X = Br) was present in amounts that varied from 0% to 30% of the total amount of 9. It has been found that in the reaction of this mercurial with benzaldehyde, benzal halide 4 was actually a substantial mixture of the dichloro and bromochloro compounds with smaller amounts of the dibromo compound.[1a]



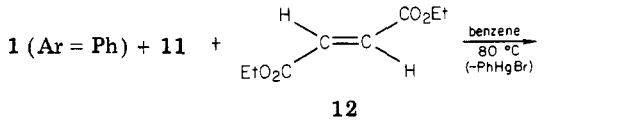
11 1 (Ar = Ph) 4 (X_2 = Cl_2, ClBr, Br_2)

Suitable control reactions showed that brominated 4 did not arise by exchange of benzal chloride with phenylmercuric bromide or by initial production of :CBrCl. In the current study, treatment of dimethyl 2-chloro-5-phenylfuran-3,4-dicarboxylate (9, Ar = Ph, X = Cl) with phenylmercuric bromide in benzene at 80 °C did not result in any detectable halogen exchange. Thus, observation of 2-bromofurans indicates the presence of brominated ylides that must arise by an exchange with phenylmercuric bromide.

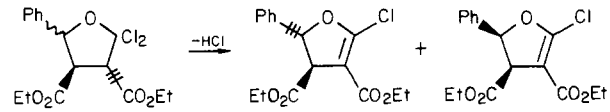


3 (X_2 = Cl_2) 3 (X_2 = ClBr) 3 (X_2 = Br_2)

Other Dipolarophiles. Although acetylenedicarboxylate 7 was the most effective of the dipolarophiles tried, the use of diethyl fumarate (12) with benzaldehyde (1, Ar = Ph) and mercurial 11 resulted in the isolation of the *E* and *Z* isomers of dihydrofuran 14 in the approximate ratio of 70:30 (entry 9, Table I).[8] None of the dichlorocarbene adduct to 12 was observed.



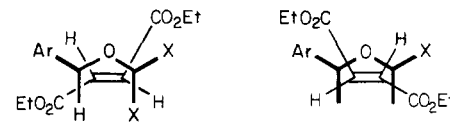
12



13 (*E*)-14 (*Z*)-14

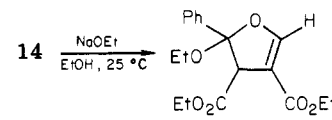
Stereochemical assignments for 14 were based on a comparison of the values of $J_{4,5}$ (7 and 11 Hz, respectively) with similar values reported for the cis and trans isomers of dimethyl 1,3-diphenyl-Δ^2-pyrazoline-4,5-dicarboxylate[9a] and the general observation that five-membered rings that cannot deviate appreciably from planarity always exhibits coupling constants between vicinal hydrogens that correspond to $J_{cis} > J_{trans}$.[9b]

The *E* stereochemistry of the dominant isomer is consistent with the expected parallel approach of a planar carbonyl ylide 3 to fumarate 11 in which the ethoxycarbonyl groups are oriented so as to minimize steric interactions as shown in structure 15.[10] The less sterically



15 16

favored orientation shown in structure 16, in which the ethoxycarbonyl group now experiences a torsional interaction with both halogens, would lead to the minor product. It is of interest that the treatment of dihydrofuran (*E*)-14 with sodium ethoxide in ethanol resulted in the formation of dihydrofuran 17 by double-bond migration and elimination of hydrogen chloride followed by conjugate addition of ethoxide. The stereochemistry of 17 was not determined.



17

Tetraethyl ethylenetetracarboxylate, tetrachloroethylene, and decafluorocyclohexene (entries 12–14, Table

(6) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572 and references cited therein. (b) deMarch, P.; Huisgen, *J. Am. Chem. Soc.* **1982**, *104*, 4952, 4953.

(7) Moss, R. A. In "Carbenes"; Jones, M., Jr.; Moss, R. A., Eds.; Wiley-Interscience: New York, 1973; Vol. 1, Chapter 2.

(8) Although small amounts of the corresponding bromodihydrofurans may have been present as two peaks in the GC trace of the reaction mixture (≤2% each of the major products and with slightly longer retention times), no definite identification was attempted.

(9) (a) Sustmann, R.; Huisgen, R.; Huber, H. *Chem. Ber.* **1967**, *100*, 1802. (b) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon: Oxford, 1969; pp 286–288.

(10) Houk, K. N.; Rondan, N. G.; Santiago, C.; Gallo, C. J.; Gandour, R. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 1504.

I) failed to trap the intermediate ylide. Reference to structure **15** and **16** suggests that with these tetrasubstituted dipolarophiles severe steric interactions cannot be avoided in the orientations required for concerted cycloaddition.

Summary and Conclusions

It is evident that electron-deficient dipolarophiles such as acetylenedicarboxylate **7** and fumarate **12** can compete effectively with aromatic aldehydes to capture and dihalocarbonyl ylide **3** produced in the reaction of phenyl(trihalomethyl)mercury with these same aldehydes. Rapid loss of hydrogen halide from the resulting cycloadduct **8** gave reasonable isolated yields of 2-halo-5-arylfuran-3,4-dicarboxylate **9** and makes these unusual substituted furans available for further synthetic transformations. Tetrasubstituted dipolarophiles fail to capture the ylide for what appears to be steric reasons. In addition, it was shown that the halogens of these dihalocarbonyl ylides are easily exchanged.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{13}C NMR spectra were determined with a Bruker WP80-FT instrument, while ^1H NMR were obtained with either a Varian EM-360 or A-60 spectrometer. Precise m/e values were determined by peak matching with a Varian MAT CH-5 mass spectrometer interfaced with a PDP-8A computer. Other mass spectral data including GC/MS with a 25-m OV-101 capillary column were determined with a Riber R10-10 quadrupole mass spectrometer interfaced with a PDP-8A computer. Infrared data were recorded with a Beckman IR-8 spectrophotometer. A Perkin-Elmer Sigma 3B chromatograph equipped with a 25-m OV-101 capillary column and a flame-ionization detector and attached to a Hewlett-Packard 3390A recording integrator was used for GC analyses. Thin-layer chromatograms were run on plastic sheets coated with silica gel 60F-254 (E. Merck). Flash chromatography was done with 32–63-μm silica gel (Woelm). All glassware and syringe needles were assembled hot and cooled under dry argon.

Reagent grade benzene was dried with calcium hydride, distilled, and stored over 5-Å molecular sieves. Benzaldehyde, *p*-tolualdehyde, and *p*-anisaldehyde were stored under argon prior to use. 3,5-Dichlorobenzaldehyde and pentafluorobenzaldehyde (Aldrich) were used without further purification. Diethyl fumarate was dried over molecular sieves, distilled under argon, and stored over fresh sieves. Dimethyl acetylenedicarboxylate (Aldrich) was distilled in vacuo and stored under argon. Tetrachloroethylene was distilled from calcium hydride and perfluorocyclohexene (Chemalog) was dried over phosphorous pentoxide and passed through a column of silica gel (neutral). Tetraethyl ethylenetetracarboxylate was dried in vacuo over phosphorus pentoxide, mp 56.5–57 °C (lit.[11] mp 57–58 °C).

Phenyl(bromodichloromethyl)mercury was prepared by the method of Seyferth and Lambert[12] in 65–70% yield, mp 109–110 °C dec (lit.[12] mp 108–111 °C dec).

Phenyl(tribromomethyl)mercury was prepared by the method of Fedoryński and Makosza.[13] The combined bromoform extracts were diluted with a small amount of hexane followed by filtration of the resulting phenylmercuric bromide, further dilution with hexane, and refrigeration to give product in 46% yield, mp 122 °C (lit.[12] mp 119–120 °C).

Phenyl(trichloromethyl)mercury was prepared in 50% yield by the method of Fedoryński and Makosza,[13] mp 110–111 °C (lit.[14] mp 111–112 °C).

***p*-Methoxybenzal chloride** was prepared from anisaldehyde by the general procedure of Vitullo and Wilgis[15] to give product in 93% yield, bp 79 °C (0.1 torr) (lit.[15] bp 130–132 °C (13 torr)). The ^1H NMR ($CDCl_3$) was entirely consistent with the structure and with the spectrum published in CCl_4[15] with chemical shift values slightly shifted because of the difference in solvent.

α,α-Dibromotoluene and α-bromo-α-chlorotoluene were prepared as a mixture by the treatment of benzyl chloride with bromine according to the method of Heble et al.[16] The product mixture (distilled through a 15-cm Vigreux column exhibited singlets in the ^1H NMR spectrum at δ 3.42 (CHBrCl) and 3.50 ($CHBr_2$) consistent with previous assignments.[1a]

Diethyl *trans*-3,3-dichlorocyclopropane-1,2-dicarboxylate, the dichlorocarbene adduct to **12**, was prepared by a modification of the method of Seyferth and Shih,[17] in which the reaction was carried out at reflux in benzene for 22 h to give product (32% yield): bp 84 °C (0.2 torr); ^1H NMR ($CDCl_3$) δ 4.37 (q, 4 H), 3.1 (s, 2 H), 1.38 (t, 6 H); ^{13}C NMR ($CDCl_3$) 165.1 (s, C=O), 62.3 (t, CH_2), 58.2 (s, CCl_2), 37.4 (d, CH), 14.2 (q, CH_3) ppm; MS (CI), m/e 255, 257, 259 ($M^+ + 1$); MS (EI, 70 eV), m/e (relative intensity) 181, 183, 185 (3.2, 2.2, 0.4, $M^+ - CO_2Et$), 84, 86, 88 (100, 64.9, 10.4, $CH_2Cl_2^+$).

Treatment of Aldehydes with Phenyl(trihalomethyl)mercury in the Presence of Dipolarophiles. General Procedure. A mixture of phenyl(trihalomethyl)mercury (5.0 g, 11.4 mmol), aromatic aldehyde, dipolarophile trapping agent, and dry benzene (25 mL) was heated at 80 °C under argon for a specified period of time. (See Table I for other experimental details.) The progress of the reaction was monitored by TLC (ethyl acetate/hexane, 1:19) and GC (25-m OV-101 capillary). Samples of dimethyl acetylenedicarboxylate on silica gel 60F-254 (E. Merck) turn blue-grey when heated for a few minutes at ca. 140 °C. Identification of thin-layer spots containing mercury compounds is facilitated by exposing the plate to hydrogen sulfide vapor over an aqueous solution for a few minutes followed by brief heating to ca. 140 °C. A brown to black color results before or after heating. The reaction mixture was filtered through sintered glass (positive argon pressure) and the collected phenylmercuric bromide was washed with benzene. The benzene washings and filtrate were combined, mixed with silica gel (15 g, 32–63 μm), and evaporated followed by application of the residue to the top of a flash chromatography column (15 cm × 5 cm o.d.) filled with the same adsorbent and elution with mixtures of hexane and ethyl acetate (typically 19:1, 9:1, and 4:1). Fractions were combined on the basis of TLC results with the same solvent mixture used on the column and evaporated to give products.

Dimethyl 2-halo-5-arylfuran-3,4-dicarboxylates (9) were prepared by the general procedure and eluted from the flash chromatography column with ethyl acetate/cyclohexane (1:19) for the 2-chloro-5-phenyl compound; ethyl acetate/hexane (1:19) for the 2-bromo-5-phenyl, 2-chloro-5-*p*-anisyl, and 2-chloro-5-(3,5-dichlorophenyl) compounds; and ethyl acetate/hexane (1:39) for the 2-chloro-5-*p*-tolyl and 2-chloro-5-pentafluorophenyl compounds. The general order of elution was benzal halides, mercury compounds, unreacted aldehyde, dimethyl acetylenedicarboxylate, and product. After elution of the acetylenic diester, the solvent system was changed in several of the experiments as follows: for 2-bromo-5-phenyl and 2-chloro-5-pentafluorphenyl, ethyl acetate/hexane (1:4); for 2-chloro-5-*p*-tolyl, ethyl acetate/hexane (3:7); for 2-chloro-5-(3,5-dichlorophenyl), ethyl acetate/hexane (1:5).

Melting points and analytical data by precise mass measurements are summarized in Table II.

Dimethyl 2-chloro-5-phenylfuran-3,4-dicarboxylate: ^1H NMR ($CDCl_3$) δ 7.17–7.70 (m, 5 H, Ph), 3.78 (s, 6 H, CH_3O); ^{13}C NMR ($CDCl_3$) δ 163.8, 161.3 (s, C=O), 152.3 (s, CCl), 140.7 (s, CPh), 129.8, 128.8, 127.9, 126.4 (Ph), 115.4, 114.5 (s, CCO_2Me), 52.7, 52.2 (q, CH_3O); GC/MS (70 eV), m/e (relative intensity), 294 (M^+, 100), 263 (39.6), 259 (20.3), 231 (30.8), 207 (33.0), 203 (26.4), 179 (15.4), 149 (17.4); 129 (26.4), 113 (30.0), 105 (25.8).

Dimethyl 2-bromo-5-phenylfuran-3,4-dicarboxylate: ^1H NMR ($CDCl_3$) δ 7.22–7.84 (m, 5 H, Ph), 3.88 (s, 6 H, CH_3O); ^{13}C NMR ($CDCl_3$) δ 163.7, 161.4 (s, C=O), 154.9 (s, CCl), 129.8 (s, CPh), 128.7, 127.9, 127.8, 126.5 (Ph), 118.7, 115.7 (s, CCO_2Me),

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52.7, 52.2 (q, CH_3O); MS (70 eV), m/e (relative intensity) 338 (M^+, 98.9), 307 (39.6), 259 (18.4), 251 (31.9), 231 (100), 203 (94.8), 129 (67.6), 113 (53.9).

Dimethyl-2-chloro-5-*p*-anisylfuran-3,4-dicarboxylate: ^1H NMR ($CDCl_3$) δ 6.77–7.69 (A_2B_2, 4 H, Ar), 3.86 (s, 6 H, CH_3O_2C), 3.77 (s, 3 H, CH_3OPh); ^{13}C NMR ($CDCl_3$) δ 163.7, 161.4 (s, C=O), 153.1 (s, CCl), 139.8 (s, CAr), 160.9, 128.3, 120.5, 114.5 (Ar), 114.2, 113.9 (s, CCO_2Me), 55.3 (q, CH_3OPh), 52.5, 52.1, (q, CH_3O_2C); MS (70 eV), m/e (relative intensity) 324 (M^+, 100), 309 (4.62), 293 (15.4), 289 (24.2), 281 (14.8), 264 (19.8), 261 (49.7), 249 (15.6), 237 (22.0), 233 (25.8), 179 (14.8), 159 (19.8), 135 (79.1).

Dimethyl 2-chloro-5-*p*-tolylfuran-3,4-dicarboxylate: ^1H NMR ($CDCl_3$) δ 7.10–7.64 (A_2B_2, 4 H, Ar), 3.85 (s, 6 H, CH_3O), 2.30 (s, 3 H, CH_3Ph); ^{13}C NMR ($CDCl_3$) δ 163.8, 161.2 (s, C=O), 152.6 (s, CCl), 140.2 (s, CAr), 140.0, 129.4, 126.3, 125.0 (Ar), 114.7, 114.3 (s, CCO_2Me), 52.5, 52.1 (q, CH_3O_2C), 21.2 (q, CH_3Ph); MS (70 eV), m/e (relative intensity), 308 (M^+, 100), 277 (20.3), 273 (17.6), 245 (31.3), 221 (28.6), 217 (26.4), 193 (13.2), 163 (15.9), 143 (31.7), 127 (30.6), 119 (29.7), 91 (16.5), 89 (8.79).

Dimethyl 2-bromo-5-*p*-tolylfuran-3,4-dicarboxylate (not isolated): GC/MS (70 eV), m/e (relative intensity), 352 (M^+, 100), 321 (18.7), 289 (8.8), 273 (18.1), 265 (14.1), 241 (19.8), 217 (64.8), 143 (18.7), 127 (61.5), 119 (20.9), 111 (11.0), 89 (14.3).

Dimethyl 2-chloro-5-(3,5-dichlorophenyl)furan-3,4-dicarboxylate: ^1H NMR ($CDCl_3$) δ 7.55 (d, 2 H, J = 2 Hz, Ar), 7.30 (t, 1 H, J = 2 Hz, Ar), 3.90, 3.88 (s, 6 H, CH_3O); GC/MS (70 eV), m/e (relative intensity), 362 (M^+, 91.2), 331 (80.0), 299 (15.4), 275 (41.2), 247 (20.6), 217 (12.6), 197 (19.8), 181 (32.4), 173 (18.5), 145 (19.2), 109 (17.6), 59 (100).

Dimethyl 2-bromo-5-(3,5-dichlorophenyl)furan-3,4-dicarboxylate (not isolated): GC/MS (70 eV), m/e (relative intensity), 406 (M^+, 45.1), 375 (36.3), 319 (12.1), 299 (30.0), 271 (31.8), 197 (36.6), 181 (35.2), 173 (22.0), 145 (24.7), 111 (31.3), 59 (100).

Dimethyl 2-chloro-5-(pentafluorophenyl)furan-3,4-dicarboxylate: ^1H NMR ($CDCl_3$) δ 3.94, 3.85 (s, CH_3O); GC/MS (70 eV), m/e (relative intensity), 384 (M^+, 100), 353 (41.2), 312 (15.6), 297 (32.4), 293 (15.4), 269 (29.7), 239 (24.7), 219 (40.1), 203 (39.6), 195 (12.1), 167 (23.1), 153 (7.7), 141 (11.0), 134 (7.7), 117 (9.3), 93 (18.1), 59 (80.0).

Dimethyl 2-bromo-5-(pentafluorophenyl)furan-3,4-dicarboxylate (not isolated): GC/MS (70 eV), m/e (relative intensity) 428 (M^+, 19.0), 397 (13.3), 349 (11.1), 341 7.73), 321 (14.4), 313 (7.73), 293 (18.2), 231 (17.7), 219 (37.4), 203 (42.5), 195 (22.1), 167 (14.9), 153 (8.3), 141 (11.1), 117 (12.2), 59 (100).

Treatment of Benzaldehyde with Diethyl Fumarate and Phenylmercuric Bromide. Benzaldehyde (1.20 g, 11.3 mmol), diethyl fumarate (1.95 g, 11.3 mmol), and phenylmercuric bromide (4.1 g, 11.5 mmol) in benzene (20 mL) were kept at at reflux overnight. TLC analysis showed only unreacted starting materials.

Treatment of Benzaldehyde with Dimethyl Acetylenedicarboxylate and Phenylmercuric Bromide. Benzaldehyde (0.14 g, 1.3 mmol) and dimethyl acetylenedicarboxylate (0.53 g, 3.1 mmol) were heated at reflux in benzene (2.4 mL). After 27 h, TLC analysis revealed only unreacted staring materials. Phenylmercuric bromide (0.48 g, 1.3 mmol) was added, and after an additional 14 h at reflux, TLC analysis again revealed only starting materials. Addition of phenyl(bromodichloromethyl)-mercury (0.60 g, 1.4 mmol) followed by 3 h at reflux resulted in the production of dimethyl 2-chloro-5-phenyl-3,4-furandicarboxylate detected by TLC in the deep reddish-orange solution.

Treatment of Dimethyl 2-Chloro-5-phenyl-4,5-dihydrofuran-3,4-dicarboxylate (9; Ar = Ph, X = Cl) with Phenylmercuric Bromide. The furan (43.2 mg, 0.15 mmol) and phenylmercuric bromide (52.6 mg, 0.15 mmol) were kept at reflux in dry benzene (5 mL, argon) for 14 h followed by GC analysis (25-m OV-101 capillary), which showed no apparent halogen exchange.

Diethyl 2-Chloro-5-phenyl-4,5-dihydrofuran-3,4-dicarboxylate (14). A mixture of the E and Z isomer was prepared by the general procedure and eluted from the flash chromatography column with ethyl acetate/cyclohexane (1:19) in the following order: benzal halide, benzaldehyde and diethyl fumarate, mercurials, E product, Z product. The latter compounds were oils that each exhibited single spots by TLC analysis.

***E* isomer**: ^1H NMR (CCl_4) δ 7.32 (s, 5 H, Ph), 5.69 (d, 1 H, J = 7 Hz, CHO), 4.20, 4.13 (q, 4 H, J = 7 Hz, CH_2O), 3.96 (d, 1 H, J = 7 Hz, $CHCO_2Et$), 1.26, 1.23, (t, 6 H, J = 7 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 171.6, 162.9 (s, C=O), 154.2 (s, =CCl), 138.7, 129.2, 125.4 (CPh), 101.5 (s, $=CCO_2Et$), 87.3 (d, CHPh), 61.8, 60.5 (t, CH_2O), 56.0 (d, $CHCO_2Et$), 14.2 (q, CH_3); MS (70 eV), m/e (relative intensity) 324 (M^+, 2.9, confirmed by CI), 289 (46.1), 261 (12.5), 251 (43.1), 215 (19.9), 205 (24.1), 199 (91.1), 187 (60.6), 171 (75.4), 170 (57.3), 159 (27.9), 143 (88.1), 131 (24.1), 115 (100); precise m/e calcd for $C_{16}H_{17}O_5Cl$ 324.076, found 324.073 ± 0.001.

***Z* isomer**: ^1H NMR ($CDCl_3$) δ 7.30 (s, Ph), 5.95 (d, 1 H, J = 11 Hz, CHO), 4.27 (d, 1 H, J = 11 Hz, $CHCO_2Et$), 4.16, 3.63 (q, 4 H, J = 7 Hz, CH_2O), 1.21, 0.77 (t, 6 H, J = 7 Hz, CH_3); MS (70 eV), m/e (relative intensity) 324 (M^+, 0.3, confirmed by CI), 289 (7.9), 261 (4.6), 251 (10.5), 243 (2.9), 215 (6.8), 205 (7.5), 199 (31.5), 187 (37.6), 171 (43.4), 170 (47.0), 159 (26.7), 149 (14.5), 143 (49.4), 131 (19.6), 115 (100); precise m/e calcd for $C_{16}H_{17}O_5Cl$ 324.076, found 324.074 ● 0.001.

Dimethyl 2-Methoxy-5-*p*-tolylfuran-3,4-dicarboxylate (10). Dimethyl 2-chloro-5-*p*-tolylfuran-3,4,-dicarboxylate that contained ca. 8% of the 2-bromo isomer (0.30 g, *ca* 0.96 mmol) was treated with 3.35 mL of 0.43 M sodium methoxide (1.44 mmol) in methanol. After 1 h at 25 °C, the stirred reaction mixture was heated at 60–62 °C for 4 h at which time TLC (ethyl acetate/hexane, 1:19) showed a product spot and no starting material. Water (10 mL) was added and the resulting mixture was extracted with diethyl ether (3 × 15 mL), which was dried (Na_2SO_4) and evaporated to give the white solid product (0.21 g, 0.69 mmol, 71.9%): mp 109–110 °C; ^1H NMR ($CDCl_3$) δ 7.07–7.54 (m, 4 H, A_2B_2), 4.15 (s, 3 H, CH_3O), 3.88 (s, 3 H, CH_3O), 3.79 (s, 3 H, CH_3O), 2.33 (s, 3 H, CH_3Ph); MS (70 eV), m/e (relative intensity) 304 (M^+, 35.9), 2.89 (20.6), 273 (5.8), 245 (3.1), 217 (6.4), 119 (100); precise m/e calcd for $C_{16}H_{16}O_6$ 304.095, found 304.094 ± 0.001.

Diethyl 5-Ethoxy-5-phenyl-4,5-dihydrofuran-3,4-dicarboxylate (17). Diethyl (*E*)-2-chloro-5-phenyl-4,5-dihydrofuran-3,4-dicarboxylate (0.337 g, 1.04 mmol) was treated with 45 mL of 0.43 *M* sodium ethoxide (1.94 mmol) in ethanol. The reaction was followed by TLC (ethyl acetate/cyclohexane, 1:4). After 1 h at ca. 25 °C, the excess ethanol was evaporated from the deep-yellow solution, and the residue was mixed with ethyl acetate/cyclohexane (15:85) applied to a flash chromatography column (15 cm × 3 cm) and eluted with ethyl acetate/cyclohexane (1:4) to give the product (0.16 g, 0.48 mmol, 46%): ^1H NMR ($CDCl_3$) δ 7.96 (s, 1 H, C=CHO), 7.40 (s, 5 H, Ph), 4.70 (s, 1 H, HCC=O) 4.27 (q, 2 H, CH_2O), 4.19 (q, 4 H, CH_2O), 1.30 (t, 3 H, CH_3), 1.23 (t, 6 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 167.6, (s, C=O), 166.6 (s, C=O), 142.9 (d, =CHO), 134.6, 129.2, 128.8 (Ph), 127 (s, C=), 61.7 (t, 2 CH_2O), 61.3 (t, CH_2O), 50.9 (d, CH), 14.0 (q, 3 CH_3) (C_5 not observed); MS (70 eV), m/e (relative intensity) 334 (M^+, 15.2), 289 (14.2), 261 (97.1), 216 (31.4), 215 (20.9), 188 (77.1), 187 (51.4), 160 (34.2), 159 (41.9), 143 (76.1), 131 (20.9), 115 (100); precise m/e calcd for $C_{18}H_{22}O_6$ 334.142, found 334.140 ± 0.001. ^1H NMR suggested that the product was a single stereoisomer.

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Registry No. 1 (Ar = Ph), 100-52-7; 1 (Ar = *p*-$MeOC_6H_4$), 123-11-5; 1 (Ar = *p*-MeC_6H_4), 104-87-0; 1 (Ar = 3,5-$Cl_2C_6H_3$), 10203-08-4; 1 (Ar = C_6F_5), 653-37-2; 4 (Ar = *p*-$MeOC_6H_4$, X = Cl), 21185-25-1; 4 (Ar = Ph; X = Br), 618-31-5; 7, 762-42-5; 9 (Ar = Ph; X = Cl), 84681-08-3; 9 (Ar = Ph; X = Br), 84681-09-4; 9 (Ar = *p*-$MeOC_6H_4$; X = Cl), 84681-10-7; 9 (Ar = *p*-MeC_6H_4; X = Cl), 84681-11-8; 9 (Ar = *p*-MeC_6H_4; X = Br), 82577-52-4; 9 (Ar = 3,5-$Cl_2C_6H_3$; X = Cl), 84681-12-9; 9 (Ar = 3,5-$Cl_2C_6H_3$; X = Br), 84681-13-0; 9 (Ar = C_6F_5; X = Cl, 84681-14-1; 9 (Ar = C_6F_5; X = Br), 84693-97-0; 10, 84681-15-2; 11, 3294-58-4; 12, 623-91-6; (*E*)-14, 84681-16-3; (*Z*)-14, 84681-17-4; 17, 84681-18-5; $PhHgCBr_3$, 3294-60-8; $PhHgCCl_3$, 3294-57-3; TEET, 6174-95-4; TCE, 127-18-4; DFC, 355-75-9; α-bromo-α-chlorotoluene, 22332-89-4; diethyl *trans*-3,3-dichlorocyclopropane-1,2-dicarboxylate, 51806-31-6.