

SEQUENTIAL TRAPPING OF DICHLOROCARBENE
AND DICHLOROCARBONYL YLIDES

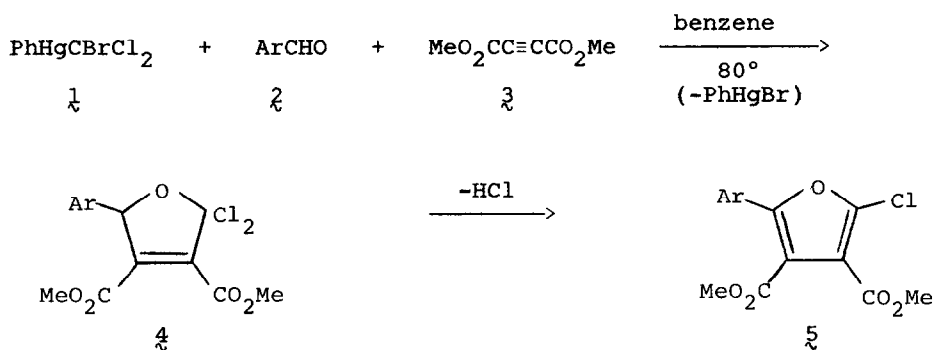
Harpal S. Gill and John A. Landgrebe

Department of Chemistry, University of Kansas, Lawrence, KS 66045

ABSTRACT. The thermal decomposition of phenyl(bromodichloromethyl)-mercury in the presence of aryl aldehydes and dimethyl acetylenedicarboxylate leads to the formation of dimethyl 2-halo-5-arylfuran-3,4-dicarboxylates by selective trapping of the intermediate dihalocarbonyl ylides.

Despite substantial interest in carbonyl ylides as an important new class of dipolar intermediates, most experimental efforts to study them have involved thermal and photochemical opening of oxiranes,¹ with comparatively few examples of the reaction of a carbene with a simple carbonyl derivative.² Our previous work has demonstrated that dichlorocarbene is involved in the thermal decomposition of phenyl(bromodichloromethyl)mercury (**1**) in the presence of an arylcarboxaldehyde (**2**), and that the mixture of products can be rationalized best in terms of an intermediate carbonyl ylide.^{2a,3}

We now report that dichlorocarbene generated by the thermal decomposition of mercurial **1** in the presence of aldehydes **2** and dimethyl acetylenedicarboxylate (**3**) undergoes selective attack on the aldehyde to give a carbonyl ylide which is captured by the electrophilic dipolarophile **3** in preference to intercession by aldehyde **2** which is observed in the absence of acetylenic trap.⁴ Spontaneous loss of hydrogen chloride from adduct **4** gave dimethyl 2-chloro-5-arylfuran-2,3-dicarboxylate (**5**), which was isolated by filtration of phenylmercuric bromide, evaporation of solvent, and flash chromatography on silica gel (Woelm, 32-63 μ m) with ethyl acetate/hexane.



The products summarized in Table I were identified by a combination of $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and mass spectrometry.⁶ Note that in several cases furan $\text{\textcircled{5}}$ was isolated mixed with varying amounts of the 2-bromo isomer believed to have been formed by an exchange reaction involving phenylmercuric bromide.^{2a}

Table I. Selected Data on the Reactions of PhHgCBrCl_2 with ArCHO and $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ in Benzene (80°C)^a

Ar	Reaction Time, h	Isolated Yield of $\text{\textcircled{5}}$, %	Mp ($^\circ\text{C}$)	2-Halogen (%) ^b
Ph	16	46	67.8-68.5	Cl(96), Br(4)
p-MeOPh	6	28	102.5-103.0	Cl(100)
p-MePh	17	29	101.5-102.5	Cl(92), Br(8)
	16	64 ^c		
3,5-Cl ₂ Ph		24	87-88	Cl(70), Br(30)
F ₅ Ph		13	oil	Cl(91), Br(9)

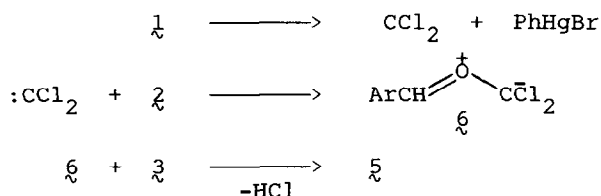
(a) Unless otherwise specified the ratio of mercurial to aldehyde to acetylenedicarboxylate = 1.1:3; the product is 2-halo-5-arylfuran-3,4-dicarboxylate.

(b) Mixtures were analyzed by GC and GC-MS (25 m, OV-101 capillary).

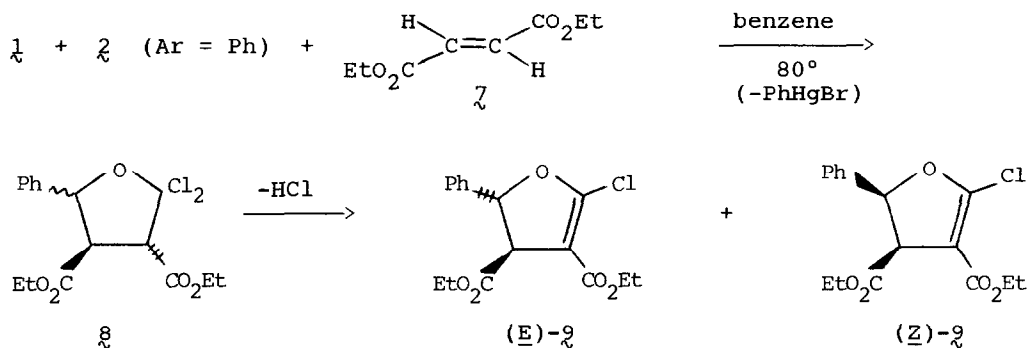
(c) Ratio of mercurial to aldehyde to acetylenedicarboxylate = 2 1.6.

These products reflect a novel sequential formation and reaction of electrophilic and nucleophilic reactive intermediates (the carbene and carbonyl ylide, respectively) as shown. Although no systematic efforts have

been made to optimize yields, it is apparent that increasing the ratio of mercurial and dipolarophile to aldehyde results in a substantial increase in the amount of furan **5** isolated (entry 4 in Table I) and makes these interesting structures readily available for further synthetic elaboration.



The replacement of acetylenedicarboxylate **3** with diethyl fumarate (**7**) resulted in the isolation of the (E)- and (Z)-isomers of dihydrofuran **9** in the approximate ratio of 70:30.



Stereochemical assignments for (E)-**9** and (Z)-**9** 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,^{7a} and the general observation that five-membered rings which cannot deviate appreciably from planarity exhibit coupling constants between vicinal hydrogens which correspond to $J_{\text{cis}} > J_{\text{trans}}$ ^{7b}

The use of tetracarboethoxyethylene, tetrachloroethylene, and perfluorocyclohexene failed to produce cycloaddition products for what may be steric reasons.

Acknowledgement We gratefully acknowledge generous support from the University of Kansas We are indebted to Dr. Charles Judson and Mr. Robert Drake for providing MS, GC-MS, and ^{13}C -NMR services.

REFERENCES AND NOTES

- (1) (a) Huisgen, R Angew. Chem. Int. Ed. Engl. 1977, 16, 572; (b) Griffin, G. W., Padwa, A In "Photochemistry of Heterocyclic Compounds"; Buchardt, O, Ed; Wiley· New York, 1976, Chapter 2, (c) Griffin, G. W., Bertoniere, N. R Carbenes 1973, 1, 305; (d) Griffin, G. W. Angew. Chem. Int. Ed. Engl. 1971, 10, 537 and references cited therein.
- (2) (a) Martin, C. W., Lund, P. R., Rapp, E.; Landgrebe, J. A. J. Org. Chem. 1978, 43, 1071, (b) Landgrebe, J. A., Iranmanesh, H Ibid. 1978, 43, 1244 and references cited therein.
- (3) (a) Martin, C. W., Landgrebe, J. A. J. Chem. Soc., Chem. Commun. 1971, 15, (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.
- (4) Whether or not the ylide intermediates would also be trapped by nucleophilic dipolarophiles as has been observed with carbonyl ylides generated from oxiranes,¹ is moot for the system under study because such a dipolarophile would selectively capture the carbene and circumvent ylide formation.^{2a,5}
- (5) Moss, R. A Carbenes 1973, 1, 153.
- (6) For example, structure 5 (Ar=Ph), $^1\text{H-NMR}(\text{CDCl}_3)$ δ 7.17-7.70 (m, 5H, Ph), 3.78 (s, 6H, OMe), $^{13}\text{C-NMR}(\text{CDCl}_3)$ 163.8 (s, C=O), 161.3 (s, C=O), 140.7 and 152.3 (s, C-Ph and C-Cl), 129.8 (d, Ph), 128.8 (d, Ph), 127.9 (s, Ph), 126.4 (d, Ph), 114.5 and 115.4 (s, C-CO₂Me), 52.2 and 52.7 (q, OMe), MS(70 eV) m/e (rel. intensity) 294.0269 (100; M⁺, calcd for C₁₄H₁₁O₅Cl, 294.0294).
- (7) (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.

(Received in USA 20 July 1982)