Reaction of Phenyl(trihalomethyl)mercury Compounds with Azodicarboxylate Esters. A New Route to Hydrazonodihalomethanes of Type $(RO_2C)_2NN{=}CX_2$[1,2]

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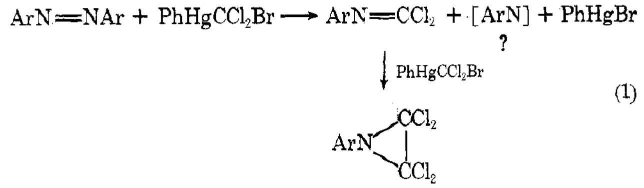
The reaction of phenyl(trihalomethyl)mercury compounds with azodicarboxylate esters in benzene at 80° gives hydrazonodihalomethanes of type $(RO_2C)_2NN{=}CX_2$ (X = Cl and/or Br). Sodium trichloroacetate reacts similarly, giving the same type of product (X = Cl). A study of this reaction (R = Me) as carried out at room temperature provided evidence for an intermediate in these reactions to which structure **10** was tentatively assigned on the basis of spectroscopic (^1H, ^{13}C, ir) evidence. In the case of the $PhHgCBr_3$-$MeO_2CN{=}NCO_2Me$ reaction the intermediate was isolated as a pure substance and a kinetic study of its thermal decomposition showed a first-order process to be operative with the following activation parameters: $\Delta H^* = -19.75$ kcal/mol; $\Delta S^* = -17.16$ eu.

In previous papers of this series we have reported concerning reactions of phenyl(trihalomethyl)mercury compounds in which CX_2 was added to C=N,[3] C=S,[4] and C=O[5] bonds. However, attempted addition of $PhHgCCl_2Br$-derived CCl_2 to the N=N bond of azoarenes was not successful, the only reaction observed being a fragmentation process (eq 1).[3] In spite of this observation

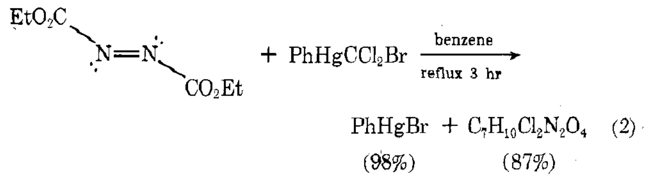


$$ArN{=}NAr + PhHgCCl_2Br \longrightarrow ArN{=}CCl_2 + [ArN] + PhHgBr \quad (1)$$

we extended our studies to include azodicarboxylate esters. In this work we have found the course of the $PhHgCX_3$-$RO_2CN{=}NCO_2R$ reactions to be completely different from that of the $PhHgCX_3$-$ArN{=}NAr$ reactions, and the chemistry which was uncovered has potential for synthetic applications.

Results and Discussion

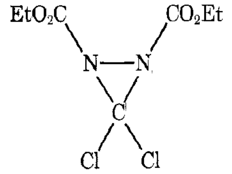
The $RO_2CN{=}NCO_2R$-$PhHgCX_3$ Reaction. The Final Product. The reaction of phenyl(bromodichloromethyl)mercury with diethyl azodicarboxylate proceeded as shown in eq 2. Analysis of the product, a distillable liquid, indicated the composition shown in eq 2. In its mass spec-



$$EtO_2CN{=}NCO_2Et + PhHgCCl_2Br \xrightarrow[\text{reflux 3 hr}]{\text{benzene}} \underset{(98\%)}{PhHgBr} + \underset{(87\%)}{C_7H_{10}Cl_2N_2O_4} \quad (2)$$

trum (70 eV) $[M - Cl]^+$ was the largest fragment observed. The ir spectrum showed, in addition to the ester carbonyl bands at 1805 (sh) and 1770 cm^{-1} (s), a medium band at 1590 cm^{-1}. The product absorbed in the uv region: λ_{max} (cyclohexane) 248 nm (ϵ 1655). A single ethoxy group resonance was observed in its proton nmr spectrum and its ^{13}C nmr spectrum confirmed the presence of apparently equivalent OEt groups. In addition, signals due to carbon atoms assignable to a C=O and a C=N moiety were observed.

Five structures (**1**–**5**) were given further consideration. Since the product obtained is very soluble in nonpolar solvents and is quite volatile at moderate temperature, the ionic structure **2** is excluded. If **1** and **2** were in equilibrium and the 1590-cm^{-1} band were due to the C=N vibration of **2**, then the solvent polarity should have a marked effect on the equilibrium and a solvent-dependent ir spectrum in the C=N region would be expected. In actual fact, there was no significant change in intensity of the ir band at 1590 cm^{-1} (C=N vibration) even when the spectrum was taken in a very polar medium such as acetonitrile. Further evidence against a mixture of **1** and **2** is that both the ^1H and ^{13}C nmr spectra showed only resonances which account for one structure rather than a mixture. The ir and uv spectral features of the product are not compatible with the diazirine structure of **1**.[6]



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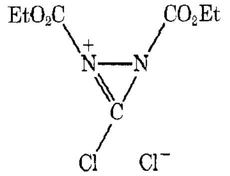

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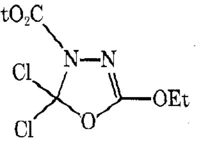

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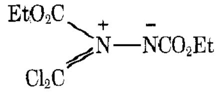

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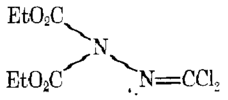

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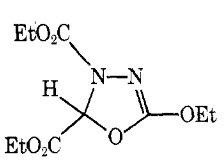
Structures **3** and **4** could be ruled out on the basis of the proton nmr spectrum of the product, which showed only a single resonance due to equivalent CO_2Et groups. In order to establish that it was a matter of equivalent CO_2Et groups, not of accidentally coincidental chemical shifts of nonequivalent ethoxy groups, two model compounds, **6** and **7**, were synthesized by the procedures of Fahr, *et al.*[7] Compound **6** displayed *three* different sets of OEt resonances in its nmr spectrum, while compound **7** showed only *two*, and thus it is likely we are dealing with equivalent CO_2Et groups in our product.[8]



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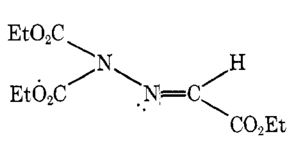

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Table I
Reactions of $PhHgCX_3$ with $RO_2CN{=}NCO_2R$ in Benzene at Reflux

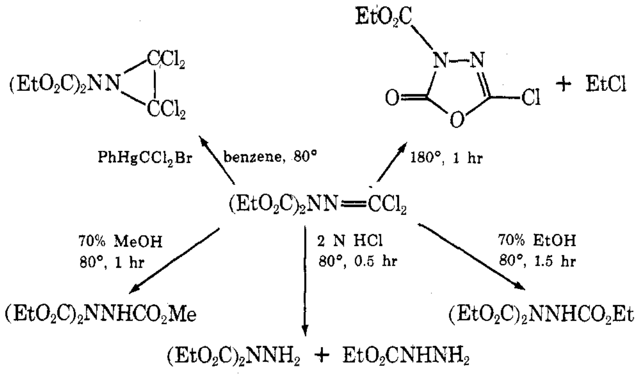
$RO_2CN{=}NCO_2R$ (registry no.)	Product (yield, %)[a] (registry no.)	Mp or bp, °C (mm)
	$PhHgCCl_2Br$ (3294-58-4)	
$MeO_2CN{=}NCO_2Me$ (2446-84-6)	$(MeO_2C)_2NN{=}CCl_2$ (61) (51381-23-8)	57–58
$EtO_2CN{=}NCO_2Et$ (1972-28-7)	$(EtO_2C)_2NN{=}CCl_2$ (87) (36133-63-8)	88 (0.24)
$Me_3CO_2CN{=}NCO_2CMe_3$ (870-50-8)	$(Me_3CO_2C)_2NN{=}CCl_2$ (38) (51381-24-9)	42–45
$PhCH_2O_2CN{=}NCO_2CH_2Ph$ (2449-05-0)	$(PhCH_2O_2C)_2NN{=}CCl_2$ (53) (51381-25-0)	*c*
$PhO_2CN{=}NCO_2Ph$ (2449-14-1)	$(PhO_2C)_2NN{=}CCl_3$ (34) (51381-26-1)	100–103[b]
	$PhHgCBr_3$ (3294-60-8)	
$MeO_2CN{=}NCO_2Me$	$(MeO_2C)_2NN{=}CBr_2$ (47) (51381-27-2)	82–84
$EtO_2CN{=}NCO_2Et$	$(EtO_2C)_2NN{=}CBr_2$ (59) (51381-28-3)	85–90 (0.02)[b]
$Me_3CO_2CN{=}NCO_2CMe_3$	$(Me_3CO_2C)_2NN{=}CBr_2$ (30) (51381-29-4)	108–109
$PhCH_2O_2CN{=}NCO_2CH_2Ph$	$(PhCH_2O_2C)_2NN{=}CBr_2$ (65) (51381-30-7)	*c*
$PhO_2CN{=}NCO_2Ph$	$(PhO_2C)_2NN{=}CBr_2$ (41) (51381-31-8)	138–140
	$PhHgCBr_2Cl$ (3294-59-5)	
$EtO_2CN{=}NCO_2Et$	$(EtO_2C)_2NN{=}CBrCl$ (55) (51381-32-9)	78–83 (0.02)[b]
$Me_3CO_2CN{=}NCO_2CMe_3$	$(Me_3CO_2C)_2NN{=}CBrCl$ (15) (51381-33-0)	77–79

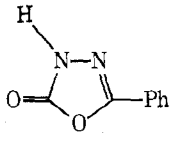
[a] Isolated yield. [b] Analytically pure sample was not obtained. [c] Vacuum distillation failed; crude oil product failed to crystallize.

Further evidence supports a phosgene hydrazone structure 5 as the structure of the isolated product of the $PhHgCCl_2Br$-$EtO_2CN{=}NCO_2Et$ reaction. The ir absorption of the C=N vibration for compounds of the type $RN{=}CCl_2$ normally appears at 1645-1660 cm^{-1} when R is an alkyl or aryl group,[9] but is seen at 1560-1610 cm^{-1} when R is a rather electronegative group, such as Cl, CH_3SO_2, $Cl_2C{=}N$, $N(CF_3)_2$, and $N(SiMe_3)_2$.[10] Our observation of $\nu_{C=N}$ at 1590 cm^{-1} falls within this latter range. The uv absorption of the product is also comparable to that of a carbonimidoyl dichloride. For instance, $Me_2CHN{=}CCl_2$[3] shows an uv absorption at λ_{max} (cyclohexane) 253 nm (ϵ 1040).

A brief chemical study of the product of the $PhHgCCl_2Br$-$EtO_2CN{=}NCO_2Et$ reaction summarized in Scheme I also supports structure 5 for the reaction product: Addition of CCl_2 to a C=N bond of $RN{=}CCl_2$ to give a tetrachloroaziridine is a known reaction.[3] The pyrolysis of 5 to give a 5-halo-1,3,4-oxadiazolin-2-one can be rationalized in terms of the known chemistry of the hydrazonoyl halides.[11] For instance, the thermolytic conversion of $EtO_2CNHN{=}C(Cl)Ph$ to 8 has been described.[12]

Scheme I





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The solvolysis reaction of a carbonimidoyl dichloride ($PhN{=}CCl_2$) with ethanol to give a N-substituted urethane ($PhNHCO_2Et$) was reported by Sell and Zierold.[13] In our case, the N substituent was a $N(CO_2Et)_2$ group, therefore a hydrazine derivative was obtained. Methanolysis and acid hydrolysis support that the CO_2Et groups in the compound in question are geminal rather than vicinal.

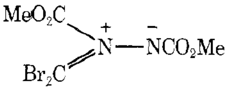
This study was extended to reactions of other phenyl(trihalomethyl)mercurials and other azodicarboxylate esters as well. The results are summarized in Table I. While the syntheses of a number of carbonyl halide hydrazones have been described,[10c,d,14-16] no carbonyl halide dicarboalkoxy or dicarbophenoxy hydrazones have been reported prior to our description of these phosgene dicarboalkoxy hydrazones prepared *via* the reactions of $PhHgCX_3$ compounds with azodicarboxylate esters.

The carbonyl halide dicarboalkoxy and dicarbophenoxy hydrazones are either colorless oils or solids. The compounds are characterized by their infrared absorption bands at 1770-1780 (very strong) and 1800-1825 cm^{-1} (shoulder) due to the $N(CO_2R)_2$ groups, 1570-1590 cm^{-1} (medium band) due to the C=N stretching vibration, and 960 (=CCl_2), 878-890 (=CBr_2), and 924-925 cm^{-1} (=CBrCl) (strong bands). Their ^1H and ^{13}C nmr spectra showed only one CO_2R signal. The ^{13}C nmr chemical shifts of the $=CCl_2$ carbon were observed at −17.5 (R = Me) and −18.6 ppm (R = Et) (*vs.* benzene).

The carbonyl halide hydrazones appeared to be rather stable to air, but the thermal stability of these hydrazones varied widely. For instance, $(MeO_2C)_2NN{=}CBr_2$, $(EtO_2C)_2NN{=}CBr_2$, and $(EtO_2C)_2NN{=}CBrCl$ have only marginal stability at room temperature, but $(PhO_2C)_2NN{=}CCl_2$ and $(PhO_2C)_2NN{=}CBr_2$ are stable at 160° for several hours. Generally speaking, phosgene hydrazones are more stable than either the carbonyl bromide or chloroformyl bromide hydrazones.

The Reaction Course. Detection and Isolation of an Intermediate. The carbonyl halide hydrazones isolated from reactions of $PhHgCX_3$ and azodicarboxylate esters cannot be the products formed initially, and to obtain further information concerning the reaction course, we followed the progress of the slow reaction at room temperature[17] of $PhHgCCl_2Br$ with dimethyl azodicarboxylate by means of ^1H and ir spectroscopy in carbon tetrachloride solution. Initially, a single methyl resonance at 4.0 ppm due to the starting ester was observed. After 1 day, two new singlets at 3.95 and 3.83 ppm were seen as well. These continued to increase in area, but another singlet at 3.80 ppm, which was due to the presence of $(MeO_2C)_2NN{=}CCl_2$, appeared and grew at the expense of the 3.95 and 3.83 ppm singlets.[18] Clearly, an intermediate with nonequivalent OCH_3 groups was formed initially and rearranged at room temperature to the final product. In an experiment where ir spectroscopy was applied, it was seen that the formation of the intermediate in the $MeO_2CN{=}NCO_2Me$-$PhHgCCl_2Br$ reaction correlated with the growth of a band at 1640 cm^{-1}.

Successful isolation of one such intermediate was realized in the reaction of $PhHgCBr_3$ and dimethyl azodicarboxylate at room temperature. After 6 days, about 50% of the starting azo compound had been consumed and the products formed contained the intermediate and the final product, $(MeO_2C)_2NN{=}CBr_2$, in about 2:1 ratio (by the nmr). The starting azo compound and the final product, as well as unreacted mercurial compound, could be removed from the reaction mixture by washing with 5% aqueous sodium sulfide solution, a treatment which the reaction intermediate survived. The crude intermediate was recrystallized from pentane, giving large crystals, mp 55-56.5°, which appeared to be air stable and could be stored in the refrigerator for weeks. Analysis indicated the composition $C_5H_6N_2Br_2O_4$. The product showed absorption in the ultraviolet region, λ_{max} (pentane) 224 nm (ϵ 1390). Its ^1H nmr spectrum indicated the presence of two nonequivalent OMe groups separated by 6.8 Hz. Both structure 9 and 10 are compatible with these spectral data. However, the CBr_2 of 9 (sp^2 carbon) and 10 (sp^3 carbon) might be expected to show very different chemical shifts in their ^{13}C nmr spectra, so distinction between the two structures might be possible if a model compound were available for comparison. Compound 11, the final reaction product, having a CBr_2 group very similar to that of 9, would be a reasonable model for this purpose. Both CBr_2 groups of 9 and 11 have sp^2-hybridized carbons, but an additional deshielding effect on the carbon nucleus due to the adjacent positive charge in 9 is expected. Thus the ^{13}C chemical shift of the CBr_2 group of 9 would be expected to appear further downfield than that of 11. On the other hand, the CBr_2 carbon of 10 which is sp^3 hybridized, is expected to show a resonance at substantially higher field than an sp^2 carbon CBr_2, as in 11. In actual fact, compound 11 showed its CBr_2 resonance at 9.15 ppm, while the CBr_2 resonance of the intermediate occurred at 31.93 ppm (*vs.* benzene), 22.78 ppm upfield from that of 11. Therefore, on the basis of the ^{13}C nmr results, the reaction intermediate would appear to have the 1,3,4-oxadiazoline structure 10. This structural question, however, cannot be considered as definitely settled at this time.



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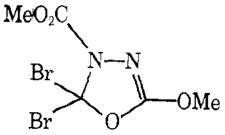
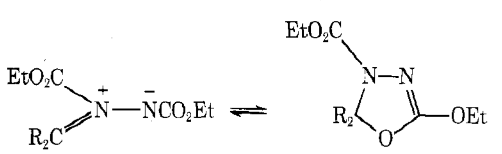


10

$(MeO_2C)_2NN{=}CBr_2$

11

Related ring-chain isomerization in solution, azomethinimine (12a) ⇄ oxadiazoline (12b), has been described,[19]



12a **12b**

but no decisive infrared assignments were reported. Nevertheless, it seems that the azomethinimine structure of 12a showed two distinguishable C=O stretching vibrations at 1783 and 1745 cm^{-1} and a C=N vibration at 1645 cm^{-1}. On the other hand, the same compound in the solid state, where 12b is believed to be the sole consituent, showed one C=O vibration at 1715, cm^{-1} and a C=N vibration at 1672 cm^{-1} in its ir spectrum (KBr pellet). A similar system was studied by Bettinetti and Capretti[20] with comparable results.

The infrared spectrum of our reaction intermediate, either in solution or as a Nujol mull, showed only one C=O band at 1790 cm^{-1} and a C=N vibration at 1640 cm^{-1}, in agreement with the proposed oxadiazoline structure 10. Although the intermediates in reactions of other azodicarboxylates with the various $PhHgCX_3$ were not isolated, spectroscopic studies of these reactions at room temperature indicated that similar 1,3,4-oxidiazoline intermediates were formed in all these reactions.

Kinetic Study of Thermal Rearrangement of the Intermediate. Thermal rearrangement of the 1,3,4-oxidiazoline intermediate to the final carbonyl halide hydrazone proceeded quantitatively on moderate heating in CCl_4 solution. In the case of the assumed 2-methoxy-4-carbomethoxy-5,5-dibromo-Δ^2-1,3,4-oxadiazoline (10), kinetic measurements of the reaction rate by means of ^1H nmr spectroscopy at various temperatures (73-99°) showed that the rearrangement was a first-order reaction. Plots of log (area)/(area)$_0$ *vs.* time allowed first-order rate constants (k) to be calculated from the slopes of the straight lines and the results are summarized in Table II. The following activation parameters were determined: $\Delta H^* = 19.75$ kcal/mol; $\Delta S^* = -17.16$ eu.

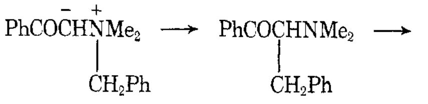
The rearrangement of 10 to 11 involves the migration of a carbomethoxy group from one nitrogen atom to another, and several mechanisms are possible for this kind of migration.[21]

The relatively large negative entropy of activation found in this reaction is of interest. The Stevens-type 1,2 shift involving cleavage-recombination *via* ionic or radical pair mechanisms does not seem likely to be involved in this rearrangement, since the activation parameters observed in a typical Stevens rearrangement (eq 3) ($\Delta H^* = 31.4$ kcal/mol and $\Delta S^* = -2.5$ eu) are quite different from those of our reaction.[22] However, our activation parame-

Table II
First-Order Reaction Rates of Thermal Rearrangement of 10 to 11 and Correlation of Log (Area) with t

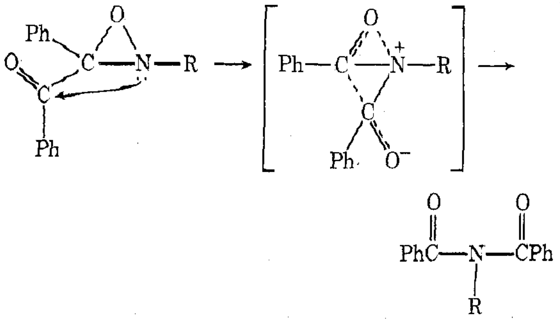
Temp, °C	k, sec^{-1}	S_E[a]
73.0	3.60×10^{-4}	0.0016
79.5	5.34×10^{-4}	0.0060
87.0	1.13×10^{-3}	0.0021
91.5	1.71×10^{-3}	0.0049
99.0	2.85×10^{-3}	0.0011

[a] Standard error of estimation, $S_E = [\Sigma d^2/(n - 1)]^{1/2}$ (where d = standard deviation). For details see C. L. Perrin, "Mathematics for Chemists," Wiley-Interscience, New York, N. Y., 1970, p 161, and E. L. Bauer, "A Statistical Manual for Chemists," 2nd ed, Academic Press, New York, N. Y., 1971.



$$\underset{\displaystyle CH_2Ph}{\mathrm{PhCO\overset{-}{C}H\overset{+}{N}Me_2}} \longrightarrow \underset{\displaystyle CH_2Ph}{\mathrm{PhCOCHNMe_2}} \longrightarrow \quad (3)$$

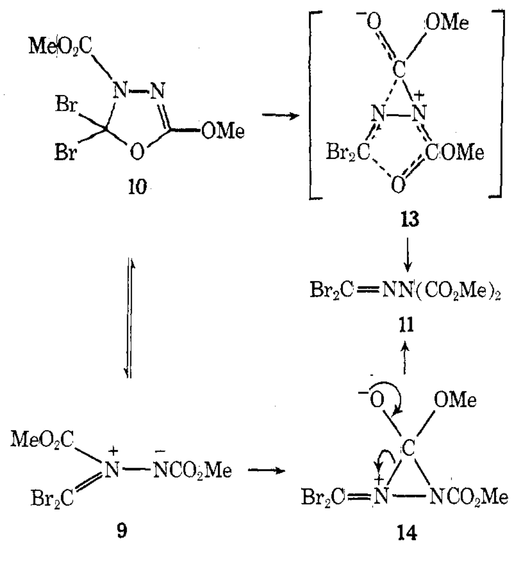
ters can be compared with those of the intramolecular rearrangement of an oxaziridine to a dibenzoylamine (eq 4) involving migration of a benzoyl group *via* a transition state as shown, where ΔH^* and ΔS^* were found to be 21.7 kcal/mol and −22.0 eu, respectively.[23]

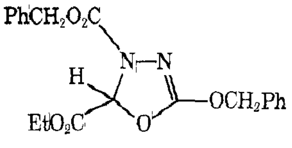


(4)

Although the exact mechanism of this rearrangement (10 to 11) cannot be assessed at this time, the observed large negative entropy of activation can be reasonably accommodated by a cyclic transition state such as 13 or 14 in an intramolecular reaction as shown in Scheme II. Attempts to trap the possible azomethinimine 9 with 1,3-dipolarophiles such as dimethyl acetylenedicarboxylate or phenyl isocyanate failed, but on the basis of these two experiments alone, 9 still cannot be excluded. The facile rearrangement of 10 to 11 finds precedent in the thermal isomerization of 15 to $(PhCH_2O_2C)_2NN{=}CHCO_2Et$.[7]

Scheme II





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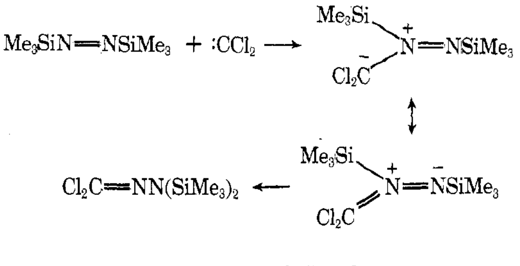
Reaction Mechanism. The reactive species which interacts with the azodicarboxylate esters in the case of $PhHgCCl_2Br$ could be either the mercurial itself or CCl_2 formed by decomposition of this mercurial. That it is the latter seems likely, since decarboxylation of CCl_3CO_2Na in the presence of $EtO_2CN{=}NCO_2Et$ in refluxing 1,2-dimethoxyethane also gives $(EtO_2C)_2NN{=}CCl_2$ in 69% yield. In terms of the final products obtained, there is a striking similarity between the reactions of azodicarboxylate esters with dihalocarbenes and with diazoalkanes.[19,24,25] However, very different reaction pathways are involved. In the case of the latter reagents, direct attack of the diazoalkanes as *carbon nucleophiles* at an azo ester nitrogen atom (rather than a carbene mechanism) was established by Fahr, *et al.*[7,26] A kinetic study showed that in the presence of azodicarboxylate esters, the diazoalkanes decomposed readily with evolution of nitrogen at 80°, but in the absence of the azodicarboxylate esters, no apparent decomposition of diazoalkanes occurred under the same reaction conditions.[26] Similar rate enhancement of the decomposition of dicyanodiazomethane in the presence of azodicarboxylate esters was noted by Ciganek.[25]

In the case of dihalocarbene reactions, we presumably are dealing with an initial *electrophilic* attack of the carbene at nitrogen to form a highly reactive nitrogen ylide intermediate which then undergoes further reaction. Formation of the 1,3,4-oxadiazoline intermediate in these reactions most likely involves the cyclization shown in Scheme III.

(Although none of our evidence speaks in favor of the formation of a diaziridine as a stable intermediate, it cannot be excluded as a transitory intermediate.)

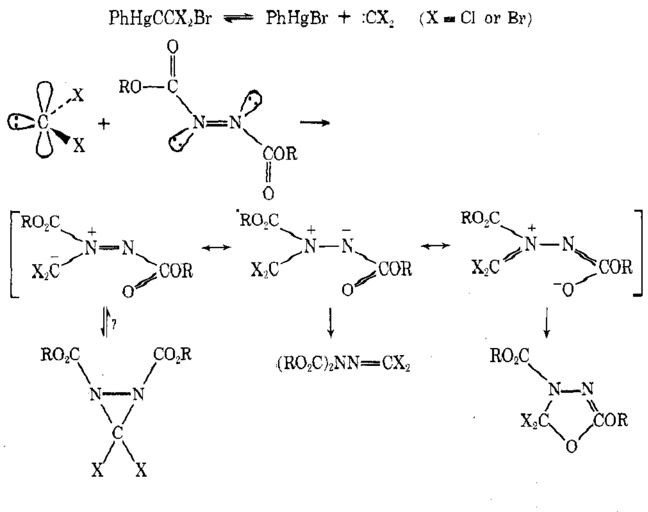
The mechanism shown in Scheme III finds support in the reaction of CCl_2 with $Me_3SiN{=}NSiMe_3$,[10d] where a phosgene hydrazone product was obtained. The product apparently is derived from the rearrangement of an ylide intermediate, as in the scheme shown below.



Experimental Section

General Comments. All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. Solvents were carefully dried. Infrared spectra were recorded using a Perkin-Elmer Model 457A, 257, or 337B grating infrared spectrophotometer, ultraviolet spectra using a Cary-14 spectrophotometer, and proton nuclear magnetic resonance spectra using a Varian Associates T-60 or a Hitachi Perkin-Elmer R-20B high-resolution nmr spectrometer. Chemical shifts are expressed in δ units, in parts per million downfield from tetramethylsilane. Carbon-13 nuclear magnetic resonance spectra were recorded using a Bruker HFX-90 nmr spectrometer interfaced with Digilab NMR/FTS-3 Fourier transform data system. The carbon-13 chemical shifts are expressed in parts per million with respect to internal benzene.

Scheme III



Mass spectra were recorded using a Hitachi Perkin-Elmer RMU-6 mass spectrometer. Gas-liquid partition chromatographs (glc) used were F & M Model 5750, 700, or 720 and MIT isothermal units. Thin layer chromatography (tlc) was used to examine high-boiling reaction mixtures; Eastman silica gel tlc sheets, type 6061, were used. The pretreated neutral alumina (activity III) (a product of M. Woelm, Germany) and Nylon tubing for dry-column chromatography[27] were obtained from Waters Associates Inc.

Phenyl(trihalomethyl)mercury compounds were prepared by our THF method.[28] Dimethyl azodicarboxylate was prepared by the oxidation of dimethyl *sym*-hydrazinedicarboxylate (Aldrich) with concentrated nitric acid.[29] Dibenzoyl azodicarboxylate was obtained from Lucidol Division, Pennwalt Corp., as a gift. Other azodicarboxylate esters were purchased from Aldrich Chemical Co.

Reaction of Diethyl Azodicarboxylate with Phenyl(bromodichloromethyl)mercury. A 50-ml three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube, a thermometer, and a magnetic stirbar (the "standard apparatus") was charged with diethyl azodicarboxylate (5.00 g, 26.0 mmol, obtained from Aldrich), $PhHgCCl_2Br$ (8.80 g, 20.0 mmol), and 30 ml of dry benzene. The reaction mixture was stirred and heated at reflux under nitrogen for 3 hr. The orange color of the solution gradually was discharged and PhHgBr precipitated. The reaction mixture was cooled to room temperature and filtered from 6.90 g (98%) of PhHgBr, mp 270–273° (lit.[30] mp 276°). Glc (4 ft × 0.25 in., 10% UC W-98, 110°) showed that a single product was present in 87% yield. The product, bp 88° (0.24 mm), $n^{25}D$ 1.4730, was isolated by vacuum distillation in 70% (3.60 g) yield: ir (neat) 2990 m, 2960 w, 2930 w, 1805 m, 1770 s, 1590 m, 1489 w, 1475 w, 1402 w, 1400 w, 1378 m, 1250 s, 1180 w, 1100 s, 1002 w, 970 m, 865 w, 760 cm^{-1} m; ^1H nmr (CCl_4) δ 1.38 (t, 6, *J* = 7.0 Hz, $OCH_2C\mathbf{H_3}$) and 4.40 ppm (q, 4, *J* = 7.0 Hz, $OC\mathbf{H_2}CH_3$); ^{13}C nmr ($CHCl_3$) δ −22.2 (C=O), −18.6 (C=N), 63.1 ($O\mathbf{C}H_2CH_3$), and 113.0 ppm ($OCH_2\mathbf{C}H_3$) *vs.* benzene; mass spectrum (70 eV) *m/e* (rel intensity) 221 (6), 184 (4), 148 (40), 138(19), 121 (77), 112 (35), 82 (27), 45 (38), and 29 (100). The molecular ion was not detected.

Anal. Calcd for $C_7H_{10}Cl_2N_2O_4$: C, 32.70; H, 3.90; N, 27.58; Cl, 10.90. Found: C, 32.47; H, 3.98; N, 27.48; Cl, 10.99.

A. Ethanolysis of the Product. A 0.50-g sample (1.95 mmol) was treated with 3.0 ml of 70% aqueous ethanol at 80° for 1.5 hr. The resulting reaction mixture was concentrated to *ca.* 1.0 ml and then was extracted with ether. The organic layer was separated, dried, and distilled. The colorless oil isolated by distillation (0.39 g, 80% yield) was identified as the 1,1,2-tricarboethoxyhydrazine $(EtO_2C)_2NNHCO_2Et$: bp 113° (0.10 mm); $n^{25}D$ 1.4490; ir (neat) 3340 m, 3000 m, 2960 w, 2930 w, 1800 m, 1750 s, 1520 w, 1480 w, 1378 m, 1270 s, 1181 w, 1110 s, 1070 m, 1020 w, 880 w, 785 cm^{-1} m; nmr ($CDCl_3$) δ 1.28 (t, 3, *J* = 7.0 Hz, $NHCO_2CH_2CH_3$), 1.32 [t, 6, *J* = 7.0 Hz, $N(CO_2CH_2CH_3)_2$], 4.42 (m, 6, CH_2), and 7.58 ppm (s, 1, NH).

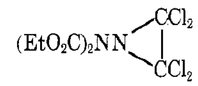
Anal. Calcd for $C_9H_{16}N_2O_6$: C, 43.54; H, 6.50; N, 11.29. Found: C, 43.46; H, 6.50; N, 11.66.

B. Methanolysis of the Product. To a 0.50-g sample (1.95 mmol) was added 3.0 ml of 70% aqueous methanol and the mixture was heated at 80° for 1 hr. The reaction mixture was worked up as described above. The product, a colorless oil, isolated by distillation and further purified by glc (6 ft × 0.25 in., 20% DC-200, 150°), was identified as 1-carbomethoxy-2,2-dicarboethoxyhydrazine, $MeO_2CNHN(CO_2Et)_2$: bp 89° (0.07 mm); $n^{25}D$ 1.4518; ir (neat) 3330 m, 3000 m, 1810 m, 1760 s, 1520 m, 1460 w, 1375 w, 1270 s, 1180 w, 1110 m, 1070 w, 1020 w, 920 w, 870 w, 775 cm^{-1} m; nmr (CCl_4) δ 1.30 (t, 6, *J* = 7.2 Hz, $OCH_2C\mathbf{H_3}$), 3.75 (s, 3, OCH_3), 4.28 (q, 4, *J* = 7.2 Hz, $OC\mathbf{H_2}CH_3$) and 7.81 ppm (broad, 1, NH).

Anal. Calcd for $C_8H_{14}N_2O_6$: C, 41.02; H, 6.02; N, 11.96. Found: C, 41.05; H, 6.16; N, 12.29.

C. Acid Hydrolysis of the Product. The sample (0.50 g, 1.95 mmol) was treated with 3.0 ml of 2 *N* HCl at 80° for 30 min. The solution was neutralized with aqueous sodium hydroxide and then was extracted with ether. The organic layer was separated, dried over sodium sulfate, and concentrated to *ca.* 1.0 ml. The products isolated by glc (4 ft × 0.25 in., 10% UC W-98, 130°) were ethyl hydrazinecarboxylate, EtO_2CNHNH_2, mp 46–47° (lit.[31] mp 45°), ir (CCl_4) 3460 and 1630 (NH_2), 3360 cm^{-1} (NH), nmr (CCl_4) δ 1.20 (t, 3, *J* = 7.0 Hz, $OCH_2C\mathbf{H_3}$), 4.02 (q, 2, *J* = 7.0 Hz, $OC\mathbf{H_2}CH_3$), 4.10 (broad, 2, NH_2), and 6.80 ppm (broad, 1, NH); diethyl 1,1-hydrazinedicarboxylate, $(EtO_2C)_2NNH_2$, mp 27–29° (lit.[31] mp 29°), ir (CCl_4) 3360 and 1630 cm^{-1} (NH_2), nmr (CCl_4) δ 1.22 (t, 6, *J* = 7.1 Hz, $OCH_2C\mathbf{H_3}$), 4.11 (q, 4, *J* = 7.1 Hz, $OC\mathbf{H_2}CH_3$), and 4.45 ppm (s, 2, NH_2); and a small amount of diethyl 1,2-hydrazinedicarboxylate, $EtO_2NHNHCO_2Et$, mp 135° (lit.[31] mp 135°), ir ($CHCl_3$) 3300 cm^{-1} (broad, NH), nmr ($CDCl_3$) δ 6.88 ppm (broad, 2, NH). The last compound was found to be a secondary product derived from the rearrangement of diethyl 1,1-hydrazinedicarboxylate on the glc column during the isolation of the products.

D. Reaction of the Product with $PhHgCCl_2Br$. The product (2.57 g, 10.0 mmol) and $PhHgCCl_2Br$ (4.40 g, 10.0 mmol) in 10.0 ml of benzene were stirred and heated at reflux under nitrogen for 3 hr. The reaction mixture was filtered from 3.50 g of PhHgBr (98%, mp 257–277°). After removal of the solvent using a rotary evaporator, the residue, which contained both an oil and a solid product, was filtered to collect the latter. The crude solid was purified by pentane extraction using a Soxhlet extractor. The colorless crystals were obtained in 25% yield (0.26 g) when the pentane extracts were cooled to room temperature. The product, mp 119–120°, was identified as a tetrachloroaziridine (i): ir ($CHCl_3$) 2980 w, 1800 m, 1765 s, 1460 w, 1395 w, 1370 m, 1245 s, 1100 s, 1002 w, 950 m, 880 s, and 660 cm^{-1} w; nmr ($CDCl_3$) δ 1.45 (t, 6, *J* = 7.2 Hz, OCH_2CH_3) and 4.39 ppm (q, 4, *J* = 7.2 Hz, $OC\mathbf{H_2}CH_3$).



i

Anal. Calcd for $C_8H_{10}Cl_4N_2O_4$: C, 28.26; H, 2.97; N, 8.24; Cl, 41.71. Found: C, 28.14; H, 2.93; N, 8.09; Cl, 41.33.

The oily product from the reaction was found to be thermally unstable. Attempted vacuum distillation at 0.02 mm (80°) gave impure products.

Reactions of Phenyl(bromodichloromethyl)mercury with Other Azodicarboxylate Esters. All these reactions were carried out as described for the $PhHgCCl_2Br + EtO_2CN{=}NCO_2Et$ reaction. Approximately equimolar quantities of the reactants in benzene solution (*ca.* 20 ml for 10 mmol of mercury reagent) were stirred and heated at reflux, under nitrogen, for 3 hr. After filtration of the phenylmercuric bromide formed (usually 95–98% yield), the filtrate was concentrated at reduced pressure to remove solvent. Further work-up is described for each individual case. In most cases, the reactions were carried out on a 10-mmol scale.

A. Dimethyl Azodicarboxylate. The residue was fractionally distilled to give 6.28 g (61%) of $(MeO_2C)_2NN{=}CCl_2$. The sample for analysis was further purified by glc (4 ft × 0.25 in., 10% UC W-98, 130°): bp 69–70° (0.04 mm); mp 57–58°; ir (CCl_4) 3000 w, 2950 m, 2890 w, 1802 m, 1760 s, 1579 m, 1432 s, 1340 w, 1260 s, 1190 w, 1115 s, 970 s, 940 w, 650 w, 630 cm^{-1} w; ^1H nmr (CCl_4) δ 3.81 ppm (s); ^{13}C nmr ($CHCl_3$) δ −21.0 (C=O), −17.5 ($N{=}CCl_2$) and 74.1 (OCH_3) *vs.* benzene.

Anal. Calcd for $C_5H_6Cl_2N_2O_4$: C, 26.22; H, 2.64; N, 12.23; Cl, 30.96. Found: C, 26.40; H, 2.76; N, 12.28; Cl, 30.88.

B. Di-*tert*-butyl Azodicarboxylate. The oily residue was crystallized from ether at −78° (0.85 g, 38% yield, mp 42–45°). Attempted recrystallization from acetone or ether at −78° failed to

Table III
Nmr and Ir Spectra of the Initial Product from the Reaction of $PhHgCCl_2Br$ with $RO_2CN{=}NCO_2R$ at Room Temperature

R	Me	Et	*t*-Bu	CH_2Ph	Ph
ν_{C-N}, cm^{-1}	1640	1640	1624	1638	1655
Nmr, ppm	3.82 (s)	1.22 (t)	1.42 (s)	5.19 (s)	
	3.93 (s)	1.28 (t)	1.51 (s)	5.31 (s)	7.32 (m)
		4.36 (q)[a]		7.36 (m)	

[a] Two resonances coincide.

give an analytically pure sample. However, the compound showed nmr and ir spectra consistent with the structure $(t\text{-}BuO_2C)_2NN{=}CCl_2$: nmr ($CCl_4$) δ 1.52 ppm (s); ir (CCl_4) 1800 w, 1760 s (CO_2CMe_3), 1570 m (C=N), and 960 cm^{-1} (CCl_2).

C. Diphenyl Azodicarboxylate. The crude product remaining after removal of solvent was twice recrystallized from methylene chloride at −78° to give white, solid product (1.20 g, 34% yield, mp 100–103°), $(PhO_2C)_2NN{=}CCl_2$: nmr (CCl_4) δ 7.20 ppm (m); ir (CCl_4) 1820 m, 1780 s (CO_2Ph), 1580 m (C=N), and 970 cm^{-1} m (CCl_2). An analytically pure sample was not obtained. The best analysis found follows.

Anal. Calcd for $C_{15}H_{10}N_2Cl_2O_4$: C, 51.01; H, 2.85; N, 7.93; Cl, 20.08. Found: C, 50.04; H, 3.03; N, 7.76; Cl, 19.25.

D. Dibenzyl Azodicarboxylate. The oily residue failed to crystallize from acetone or ether at −78°. However, the crude oil product (1.69 g, 53% yield) showed characteristic ir and nmr spectra indicative of the structure $(PhCH_2O_2C)_2NN{=}CCl_2$: nmr (CCl_4) δ 5.20 (s, 4, CH_2) and 7.20 ppm (m, 10, Ph); ir (CCl_4) 1800 w and 1760 s (CO_2CH_2Ph), 1580 m (C=N), and 960 cm^{-1} s (CCl_2).

Reactions of Phenyl(tribromomethyl)mercury with Azodicarboxylate Esters. Essentially the same procedure was used as is described in the $PhHgCCl_2Br$ experiments.

A. Dimethyl Azodicarboxylate (50-mmol scale). The oily residue was redissolved in CCl_4 and the solution then was washed quickly with 10 ml of cool, 5% aqueous sodium sulfide solution to remove most of the unconverted starting azo compound and the mercurial residue. The yellow precipitate formed during the washing was separated by centrifugation. The organic layer was dried and evaporated to dryness. The residue (8.30 g, mp 70–75°) was crystallized from acetone at −78° to give 7.40 g (47%) of white solid product, $(MeO_2C)_2NN{=}CBr_2$, mp 82–84°, which was found to be of only marginal stability at room temperature over prolonged times. A satisfactory combustion analysis could not be obtained: ir (CCl_4) 3000 w, 2985 w, 2840 w, 1805 m, 1770 s, 1565 m, 1432 s, 1330 w, 1260 s, 1190 w, 1105 s, 878 cm^{-1} s; ^1H nmr ($CDCl_3$) δ 3.82 ppm (s); ^{13}C nmr (CCl_4) δ −20.9 (C=O), 9.15 (CBr_2), and 77.8 ppm (CH_3) *vs.* benzene.

B. Diethyl Azodicarboxylate. Attempted isolation of the product by vacuum distillation at 0.02 mm (85–90°) or its glc isolation at 160° (4 ft × 0.25 in., 10% UC W-98) failed. The crude product also failed to crystallize from acetone or ether at −78°. However, the oily crude product (2.04 g, 59%) showed spectroscopic properties of the expected $(EtO_2C)_2NN{=}CBr_2$: nmr (CCl_4) δ 1.37 (t, 6, J = 7.0 Hz, CH_3) and 4.26 ppm (q, 4, J = 7.0 Hz, CH_2); ir (CCl_4) 1818 m, 1775 s (CO_2Et), 1582 m (C=N), and 885 cm^{-1} (CBr_2).

C. Di-*tert*-butyl Azodicarboxylate. The oily residue was redissolved in ether and the solution was filtered. Crystallization at −78° gave white solid product (2.20 g, 37% yield, mp 100–104°) which was further recrystallized from ether at room temperature to give 1.80 g (30%) of colorless crystals of $(t\text{-}BuO_2C)_2NN{=}CBr_2$: mp 108–109°; ir ($CCl_4$) 2982 m, 2940 w, 1801 m, 1760 s, 1573 m, 1476 w, 1453 w, 1392 w, 1371 m, 1298 w, 1240 s, 1160 s, 1115 w, 890 m, 872 m, 851 cm^{-1} m; nmr (CCl_4) δ 1.57 ppm (s, *t*-BuO).

Anal. Calcd for $C_{11}H_{18}Br_2N_2O_4$: C, 32.85; H, 4.51; N, 6.97; Br, 39.75. Found: C, 32.83; H, 4.61; N, 7.00 Br, 39.44.

D. Diphenyl Azodicarboxylate. The yellow solid (2.40 g, mp 115–120°) obtained after the filtrate had been evaporated to dryness was recrystallized from ether and then acetone at −78° to give colorless, solid product in 41% yield (1.80 g): mp 138–140°; ir ($CHCl_3$) 3060 w, 1825 m, 1780 s, 1570 m, 1492 m, 1265 s, 1180 s, 1162 s, 1070 w, 1045 w, 1002 w, 890 m, 690 cm^{-1} m; nmr ($CDCl_3$) δ 7.32 ppm (m, Ph).

Anal. Calcd for $C_{15}H_{10}Br_2N_2O_4$: C, 40.75; H, 2.28; N, 6.34. Found: C, 40.75; H, 2.31; N, 6.18.

E. Dibenzyl Azodicarboxylate. The oily residue was dissolved in CCl_4 and washed with 10 ml of 5% sodium sulfide solution. The organic layer was separated, dried, and evaporated to dryness. Attempted purification of the oily product (5.00 g, 65%) by crystallization from acetone or ether at −78° failed. However, the product was the expected $(PhCH_2O_2C)_2NN{=}CBr_2$, according to its spectra: nmr (CCl_4) δ 5.21 (s, 4, OCH_2Ph) and 7.33 (s, 10, Ph); ir (neat) 1805 w, 1760 s (CO_2CH_2Ph), 1570 m (C=N), and 880 cm^{-1} m (CBr_2).

Reactions of Phenyl(dibromochloromethyl)mercury with Azodicarboxylate Esters (Same Procedure). A. Diethyl Azodicarboxylate. Attempted purification of the product oil by vacuum distillation at 0.02 mm (100°) or by low-temperature crystallization failed. However, the product appeared to be $(EtO_2C)_2NN{=}CClBr$: bp 78–83° (0.02 mm); 1.67 g (55% yield); nmr (CCl_4) δ 1.32 (t, 6, J = 7.0 Hz) and 4.13 ppm (q, 4, J = 7.0 Hz); ir (neat) 1802 m, 1770 s (CO_2Et), 1572 m (C=N), and 925 cm^{-1} s (CBrCl).

B. Di-*tert*-butyl Azodicarboxylate. The ir spectrum of the yellow, oily residue indicated the presence of the expected $(t\text{-}BuO_2C)_2NN{=}CClBr$ [absorptions at 1580 (C=N) and 875 (CClBr) cm^{-1}], but the residue contained large portions of the unconverted starting azo compound, which made the product isolation by low-temperature fractional crystallization difficult. However, when the residue was subjected to dry-column chromatography (1.0 ft × 1.5 in., Nylon tubing packed with activity III neutral alumina, Woelm, Germany) developed with benzene, the starting azo compound decomposed (exothermally) and was absorbed on the column. Extraction of the alumina with ether was followed by chilling the extracts at −78° to give colorless, solid product in 23% yield (0.71 g), mp 55–60°. The crude product was further recrystallized from ether at 5° by slow evaporation of the solvent in the refrigerator. The crystals were collected by filtration and washed quickly with cold ether to give colorless needles in 15% yield (0.46 g): mp 77–79°; ir (CCl_4) 2980 m, 2930 w, 1996 w, 1752 s, 1580 m, 1470 w, 1450 w, 1390 w, 1367 s, 1295 w, 1265 s, 1240 s, 924 s, 850 cm^{-1} m; nmr (CCl_4) δ 1.55 ppm (s).

Anal. Calcd for $C_{11}H_{18}ClBrN_2O_4$: C, 36.94; H, 5.07; N, 7.83. Found: C, 36.72; H, 5.12; N, 7.68.

Detection of the Initially Formed Products of $PhHgCCl_2Br$–$RO_2CN{=}NCO_2R$ and $PhHgCBr_3$–$RO_2CN{=}NCO_2R$ Reactions by Proton Nmr. The organomercury reagent and the azodicarboxylate ester (1:1 molar ratio) were dissolved in carbon tetrachloride and the reaction was allowed to proceed at room temperature. After about 3 days the nmr spectral parameters given in Tables III and IV for the (assumed) cyclic intermediates were determined. Other samples were used to record the ir spectrum in each case.

Reaction of Diethyl Azodicarboxylate with Sodium Trichloroacetate. A 50-ml, three-necked flask equipped with a thermometer, a magnetic stirbar, and a condenser topped with a nitrogen inlet tube was charged with the azo compound (1.75 g, 10.0 mmol), sodium trichloroacetate (1.00 g, 5.40 mmol), and 15 ml of dry 1,2-dimethoxyethane (DME). The reaction mixture was stirred and heated at reflux under nitrogen for 8 hr. The resulting light brown solution was filtered from sodium chloride and the filtrate then was trap-to-trap distilled at 0.02 mm (pot temperature to 80°). Glc analysis of the distillate showed the major product (formed in 69% yield, 3.72 mmol) to be the phosgene hydrazone. The product isolated by glc (4 ft × 0.25 in., 10% UC W-98, 120°) has nmr and ir spectra as well as glc retention time identical with those of the authentic sample of $(EtO_2C)_2NN{=}CCl_2$ prepared *via* the mercurial route.

Isolation of the Initial Product of the Reaction of Dimethyl Azodicarboxylate with Phenyl(tribromomethyl)mercury. A 50-ml flask was charged with the azo compound (1.46 g, 10.0 mmol), $PhHgCBr_3$ (10.0 g, 19.0 mmol), and 30 ml of carbon tetrachloride. The reaction mixture was stirred at room temperature for 6 days. At this time, about 50% of the starting azo compound had been consumed and the products contained 65% of the initial

Table IV
Nmr and Ir Spectra of the Initial Product from the Reaction of $PhHgCBr_3$ with $RO_2CN{=}NCO_2R$ at Room Temperature

R	Me	Et	*t*-Bu	CH_2Ph	Ph
$\nu_{C=N}$, cm^{-1}	1640	1639	1624	1635	1650
Nmr, ppm	3.88 (s) 4.02 (s)	1.38 (t) 1.44 (t) 4.40 (q)[a]	1.50 (s) 1.61 (s)	5.20 (s) 5.32 (s) 7.41 (m)	7.33 (m)

[a] Two resonances coincide.

product and 35% of the rearranged final product, as indicated by the nmr spectrum of the mixture. After the reaction mixture was filtered from phenylmercuric bromide and the unconverted starting mercurial, the filtrate was washed thoroughly with 5% aqueous sodium sulfide solution until both the organic and aqueous layers no longer were colored. The organic layer was separated, dried over magnesium sulfate, and then distilled to remove the solvent (the pot temperature was kept below 15° to prevent thermal rearrangement of the initial product). The white solid residue from the distillation was extracted with pentane. The product crystallized from the pentane extracts at 0–5° as nice, colorless crystals which were collected by filtration in 30% (0.99 g) yield: mp 55–56.5°; uv λ_{max} (pentane) 224 nm (ϵ 1390); ir (CCl_4) 3002 w, 2960 w, 1811 w, 1790 s, 1643 s, 1450 w, 1440 m, 1335 m, 1222 s, 1190 s, 1112 w, 1005 w, 940 m, 845 w, 750 cm^{-1} m; ^1H nmr (CCl_4) δ 3.88 (s, OMe) and 4.02 ppm (s, OMe); ^{13}C nmr (CCl_4) −25.76 (C=O), −20.87 (C=N), 31.93 (CBr_2), 70.95 (OCH_3), and 71.99 ppm (OCH_3) *vs.* benzene.

Anal. Calcd for $C_5H_6Br_2N_2O_4$: C, 18.89; H, 1.90; N, 8.81; Br, 50.27. Found: C, 19.02; H, 1.99; N, 8.88; Br, 50.19.

Kinetic Study of the Rearrangement of the Initial Product of the Reaction of Dimethyl Azodicarboxylate with Phenyl(tribromomethyl)mercury. A sample of a 0.18 *M* carbon tetrachloride solution of the initial product obtained above was prepared and stored in the refrigerator. The reactions at various temperatures were carried out directly in a sealed nmr tube in the nmr probe of a Hitachi Perkin-Elmer R20 spectrometer with a R-202VT variable temperature accessory. The temperatures inside the probe were determined by measuring the differences of the chemical shifts ($\Delta\delta$) between the methylene and hydroxyl protons of ethylene glycol. A calibration chart of $\Delta\delta$ *vs.* temperature (°C) provided by the manufacturer of the spectrometer was used. The accuracy of the temperature control system was within ±0.1°.

The progress of the reaction was monitored by the integrated intensity of the less shielded OMe group of the initial product, **10**, at δ 4.02 ppm, using a 120-Hz sweep width and 100-sec sweep time.

Attempts to Trap an Azomethinimine Intermediate (9) in the Rearrangement of 10 to 11. The 1,3,4-oxadiazoline **10** (0.50 g, 1.58 mmol), dimethyl acetylenedicarboxylate (0.23 g, 1.60 mmol), and 0.5 ml of $CDCl_3$ were placed in an nmr tube. The reaction mixture was heated at 50° and the progress of the reaction was monitored by nmr. During the entire course of the rearrangement, no additional nmr resonances other than those of **10**, **11**, and dimethyl acetylenedicarboxylate were observed. No 1,3-dipolar adduct was detected by tlc. Even in reactions that were carried out using the dipolarophile (either dimethyl acetylenedicarboxylate or phenyl isocyanate) as a solvent at room temperature, no 1,3-dipolar adduct was detected.

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Registry No.—**10**, 51464-57-4; 1,1,2-tricarboethoxyhydrazine, 18283-23-3; 1-carbomethoxy-2,2-dicarboethoxyhydrazine, 36133-65-0; ethyl hydrazinecarboxylate, 4114-31-2; tetrachloroaziridine, 36271-58-6.

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