Halomethyl Metal Compounds. XLVI. Reaction of Phenyl(bromodichloromethyl)mercury with Heteroatom Cumulenes[1,2]

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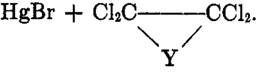
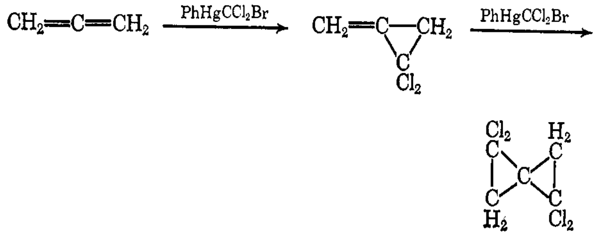
The reactions of phenyl(bromodichloromethyl)mercury with diisopropyl- and dicyclohexylcarbodiimide, phenyl and isopropyl isothiocyanate, phenyl isocyanate, and *trans*-1,2-diisocyanatoethylene, and with carbon disulfide have been studied. The products of the reaction with the carbodiimides are the dichloroimine, $RN{=}CCl_2$, and the isonitrile, $RN{\equiv}C$. With the isothiocyanates the major isolated product is perchlorothiirane, and this compound also is the major product in the reaction with carbon disulfide. *trans*-1,2-Diisocyanatoethylene reacts to give the expected dichlorocyclopropane in 84% yield, but the isocyanate function can react with the mercurial. Thus, reaction of $PhHgCCl_2Br$ with phenyl isocyanate gives *N*-phenyl-*C*-tetrachloroaziridine in 15% yield. These reactions can be generalized in terms of the overall process: $Y{=}C{=}Z + PhHgCCl_2Br \rightarrow PhHgBr + Cl_2C{=}Y + C{\equiv}Z$; $Cl_2C{=}Y + PhHgCCl_2Br \rightarrow PhHgBr + Cl_2C{-}CCl_2$ (with Y bridging).



$$Cl_2C{=}Y + PhHgCCl_2Br \rightarrow PhHgBr + \underset{\diagdown\ Y\ \diagup}{Cl_2C\text{———}CCl_2}$$

The addition of phenyl(trihalomethyl)mercury-derived dihalocarbenes to olefinic C=C bonds to give *gem*-dihalocyclopropanes[6] is by now a well-known reaction and is finding increasing application in organic synthesis.[7] More recently we have reported successful CX_2 transfer *via* phenyl(trihalomethyl)mercurials to compounds containing the C=N,[8] C=S,[9] and C=O[10] bonds. Among the olefins which were converted to *gem*-dichlorocyclopropanes *via* $PhHgCCl_2Br$ was allene (eq 1).[6] In view of this successful, stepwise CCl_2 transfer to the simplest all-carbon cumulene, it was of interest to examine the reactions of phenyl(bromodichloromethyl)mercury with heteroatom cumulenes of type Y=C=Y and Y=C=Z. Among the systems chosen for study were carbodiimides, carbon disulfide, isothiocyanates, and isocyanates.



(1)

Results

Successful CX_2 transfer to a C=N bond *via* $PhHgCX_3$ reagents to give an aziridine is possible when the nucleophilic character of the nitrogen atom has been significantly decreased.[8] Thus, compounds of type $RN{=}CCl_2$ could be converted to *C*-perchloroaziridines in good yield by reaction with phenyl(bromodichloromethyl)mercury, but imines of type $RN{=}CHR'$ and $RN{=}CR'_2$ appeared to react with these mercury reagents in other ways to give complex product mixtures. In view of this, one might expect to find that phenyl(bromodichloromethyl)mercury transfers CCl_2 to C=N bonds of carbodiimides. It is known that the nitrogen atoms of carbodiimides have a very low basicity and very little nucleophilic reactivity.[11]

When phenyl(bromodichloromethyl)mercury and diisopropylcarbodiimide were allowed to react in 1:1 molar ratio in benzene at reflux, phenylmercuric bromide precipitation was complete within 20 min. One major and five minor products were present. The major product, formed in 63% yield (based on eq 2), was *N*-isopropyldichloroimine, $Me_2CHN{=}CCl_2$. One of the minor products was isolated in an amount sufficient for spectroscopic characterization as isopropylisonitrile. The other minor products were shown (in an independent experiment) to arise from the complex reaction of phenyl(bromodichloromethyl)mercury with isopropylisonitrile and were not identified.[12] The reaction which occurs between phenyl(bromodichloromethyl)mercury and the carbodiimide thus appears to be that shown in eq 2.

$$Me_2CHN{=}C{=}NCHMe_2 + PhHgCCl_2Br \longrightarrow Me_2CHN{=}CCl_2 + Me_2CHN{\equiv}C + PhHgBr \quad (2)$$

Attempts to increase the isopropylisonitrile yield by increasing the ratio of carbodiimide to $PhHgCCl_2Br$ used to 10 failed. It would appear that the isonitrile is far more reactive toward the mercury reagent than is the carbodiimide. When the $Me_2CHN{=}C{=}NCHMe_2$–$PhHgCCl_2Br$ ratio was decreased to 1:2, the yield of *N*-isopropyldichloroimine was increased to 92%. Phenyl(bromodichloromethyl)mercury reacted in similar fashion with dicyclohexylcarbodiimide to give *N*-cyclohexyldichloroimine as major product.

As we discovered later,[8] *N*-organodichloroimines also react with phenyl(bromodichloromethyl)mercury, giving *N*-organo-*C*-tetrachloroaziridines. The present

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[1] Part XLV: D. Seyferth and D. C. Mueller, in press.

[2] Preliminary communication: D. Seyferth and R. Damrauer, *Tetrahedron Lett.*, 189 (1966).

[3] National Institutes of Health Predoctoral Fellow, 1964–1967.

[4] Postdoctoral Research Associate, 1968–1969.

[5] National Institutes of Health Postdoctoral Fellow, 1969–1970.

[6] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

[7] Complete listings of new examples of $PhHgCX_3$ reactions can be found in *Organometal. Chem. Rev., Sect. B.*

[8] D. Seyferth and W. Tronich, *J. Organometal. Chem.*, **21**, P3 (1970).

[9] D. Seyferth and W. Tronich, *J. Amer. Chem. Soc.*, **91**, 2138 (1969).

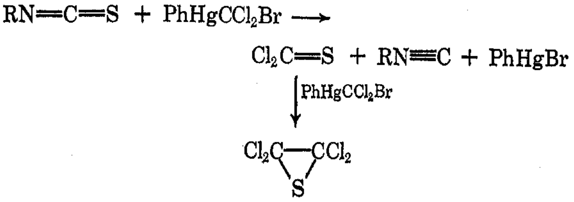
[10] D. Seyferth and W. Tronich, *J. Organometal. Chem.*, **18**, P8 (1969).

[11] (a) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 1, W. A. Benjamin, New York, N. Y., 1965; (b) I. T. Millar and H. D. Spingall, "Sidgwick's Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1966.

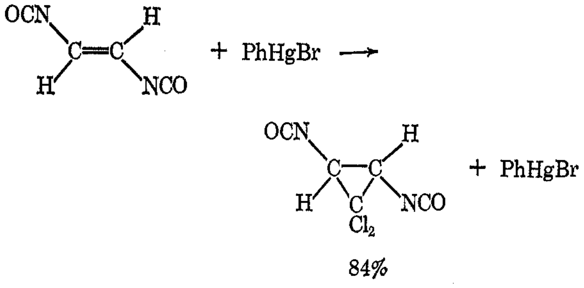
[12] A. Halleux, *Angew. Chem.*, **76**, 889 (1964), has reported that cyclohexylisonitrile reacts with dichlorocarbene (generated by the reaction of potassium alkoxide with chloroform or ethyl trichloroacetate) to give $C_6H_{11}N{=}C(OR)CCl_2H$. This observation, however, may not be relevant to the present case since the reaction of $PhHgCCl_2Br$ with the nucleophilic isonitrile very likely does not proceed *via* a free CCl_2 intermediate.

results indicate that the carbodiimides are rather more reactive toward this organomercury reagent than are the $RN{=}CCl_2$ products of the $PhHgCCl_2Br$-$RN{=}C{=}NR$ reaction.

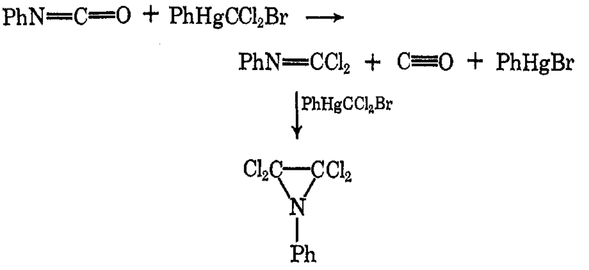
The reaction of phenyl(bromodichloromethyl)mercury with a slight excess of phenyl isothiocyanate at 70–75° resulted in formation of phenylmercuric bromide and only one major volatile product, identified as perchlorothiirane (59%), which is the product of the reaction of phenyl(bromodichloromethyl)mercury with thiophosgene.[9] The yield of perchlorothiirane could be improved to 74% (based on eq 3) by using a procedure in which the organomercury reagent (2 molar equiv) was added to the phenyl isothiocyanate (1 molar equiv) solution in two portions rather than all at once. Attempts to find $PhN{=}CCl_2$ among the products were unsuccessful. The reaction of phenyl(bromodichloromethyl)mercury with isopropyl isothiocyanate also gave perchlorothiirane as the major product. The expected isonitriles were not isolated, and it is assumed that they were almost totally consumed in reaction with the mercurial. The reaction occurring between phenyl(bromodichloromethyl)mercury and isothiocyanates thus would appear to be that shown in eq 3.


(3)

Phenyl(bromodichloromethyl)mercury reacts with allyl isocyanate to give 2,2-dichlorocyclopropylcarbinyl isocyanate in 60% yield,[6] and we have found that *trans*-1,2-diisocyanatoethylene is converted to the cyclopropane in high yield by this mercurial (eq 4). Thus, the NCO function is very much less reactive toward $PhHgCCl_2Br$ than is the olefinic double bond, but the N=C bond of the NCO group does enjoy a small measure of reactivity toward this mercury reagent. When a reaction was carried out at 80° in benzene solution between phenyl(bromodichloromethyl)mercury and a fivefold excess of phenyl isocyanate, one major high-boiling product (9% yield, based on eq 5), 1-phenyl-2,2,3,3-tetrachloroaziridine, was formed. No *N*-phenyldichloroimine was present, within the limits of glc detection. When this reaction was carried out at 90° in the absence of benzene diluent, the yield of the aziridine was raised to 15%. The reactions which appear to be occurring are those shown in eq 5.


(4)

The reaction of phenyl(bromodichloromethyl)mercury in twofold excess with carbon disulfide in benzene solution at 70–75° resulted in precipitation of phenylmercuric bromide. Perchlorothiirane was the major volatile product formed, but the yield was low, averaging 25–30% in several reactions. Increasing the mercurial to CS_2 ratio did not serve to raise the perchlorothiirane yield nor did a lower reaction temperature. Equation 6 summarizes the reactions which would appear to be responsible for the formation of perchlorothiirane.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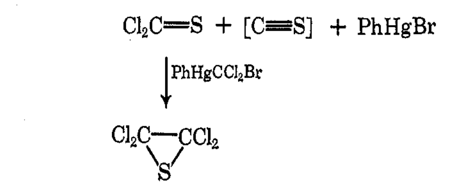
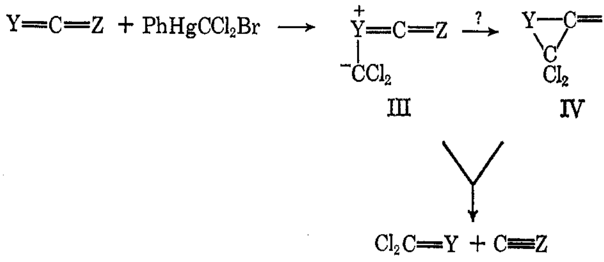

(6)

Discussion

Under the reaction conditions employed, all of the identifiable reactions of phenyl(bromodichloromethyl)mercury with the heteroatom cumulenes which we have investigated appear to take a common course (eq 7).


(7)

Further reaction of $Cl_2C{=}Y$ with phenyl(bromodichloromethyl)mercury occurs when this product is more reactive toward this mercurial than are $Y{=}C{=}Z$ and $C{\equiv}Z$ or when the mercurial is used in excess. We know nothing concerning the actual mechanism of these reactions. However, it should be pointed out that in the cases of the carbodiimides, isothiocyanates, isocyanates, and carbon disulfide we are dealing with substrates with available lone electron pairs. As we have shown previously, reactions of tertiary phosphines[13] and tertiary amines[14] with $PhHgCX_3$ compounds appear to proceed *via* direct attack of the nucleophile on the mercury reagent without the usually observed extrusion of CX_2. There is a possibility, as we have pointed out, that such also is the case when phenyl(trihalomethyl)mercurials react with compounds containing the $C{=}N$[2,3] and $C{=}S$[9] bonds. We indicate both structures III and IV as possibilities since there is

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(13) D. Seyferth, J. K. Heeren, G. Singh, S. O. Grim, and W. B. Hughes, *J. Organometal. Chem.*, **5**, 267 (1966).

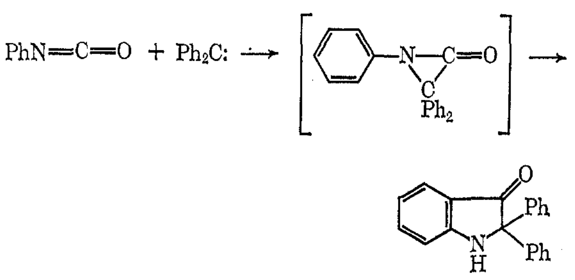
(14) D. Seyferth, M. E. Gordon, and R. Damrauer, *J. Org. Chem.*, **32**, 469 (1967).

no evidence that ring closure takes place in these systems. In the case of compounds containing isolated C=N and C=S bonds, the three-membered heterocyclic rings are formed by $PhHgCCl_2Br$ attack and are stable,[8,9] but in the present cases, in view of the fragmentation processes observed, ring closure is not a necessity.

In the case of phenyl isocyanate, we are dealing with a compound which really is very unreactive toward $PhHgCCl_2Br$. In one experiment in which these compounds were allowed to react, the PhNCO recovery was determined and found to be very high. However, in the case of the other substrates used during this study, the possibility of other reactions proceeding by alternate pathways exists (*e.g.*, *via* the dipolar reagent III which could act as a 1,3 dipole, $^{-}CCl_2-\ddot{Y}-\overset{+}{C}=Z$). To date, however, we have not isolated products other than those mentioned.

These reactions of phenyl(bromodichloromethyl)mercury cannot be considered to be well understood. However, they appear to have no useful application in synthesis and for this reason we have chosen to discontinue our studies of these systems at this time.

Reactions of three-atom cumulenes with other carbene reagents have been reported, but in these examples the reactions proceeded quite differently. The photochemical reaction of diphenyldiazomethane (believed to proceed *via* diphenylcarbene) took the course shown in eq 8,[15] while the reaction of $(CF_3)_2C$ (*via* the diazoalkane or the diazirine) with carbon disulfide at 150–175° gave cyclic polysulfides.[16]



(8)

Experimental Section

General Comments.—All reactions with $PhHgCCl_2Br$ were carried out in an atmosphere of prepurified nitrogen or argon in flame-dried glassware using rigorously dried solvents. Nmr spectra were recorded using a Varian Associates A-60 or T-60 spectrometer. Infrared spectra were recorded using a Perkin-Elmer 237B, 337, or 257 grating infrared spectrometer. Gas–liquid partition chromatography (glc) was used routinely for yield determinations and for collections of samples. Commercial stainless steel columns were employed with either an F & M Model 700, 720, or 5754 gas chromatograph. Yields were determined by the internal standard procedure. The standard apparatus used for the reactions of $PhHgCCl_2Br$ with the heteroatom cumulenes consisted of a three-necked flask of appropriate volume equipped with a reflux condenser topped with a gas inlet tube, a thermometer, and a magnetic stirring assembly. Phenyl(bromodichloromethyl)mercury was prepared as described in earlier papers of this series.[17,18] The progress of the reactions involving this reagent was followed using thin layer chromatography.[6]

Reaction of Phenyl(bromodichloromethyl)mercury with Diisopropylcarbodiimide.—The standard apparatus was charged with 3.15 g (25 mmol) of freshly distilled diisopropylcarbodiimide (Eastman), 22.03 g (50 mmol) of the mercurial, and 250 ml of dry chlorobenzene and stirred and heated at 80° for 20 min. A deep yellow mixture resulted. Filtration gave phenylmercuric bromide in 95% yield. Trap-to-trap distillation of the filtrate at 0.1 mm was followed by another distillation at reduced pressure using a small Vigreux column. Each fraction collected (7 total) contained much chlorobenzene, but the later fractions were rich in another major component. This was collected by glc (25% SE-30 silicone rubber gum at 62°) and was identified as *N*-isopropyldichloroimine, $Me_2CHN=CCl_2$. The ir spectrum (in CCl_4) showed bands at 2975 s, 2930 m, 2900 m, 2865 m, 1760 (broad) m, 1660 s, 1645 s, 1470 m, 1460 m, 1380 m, 1370 m, 1340 m, 1290 w, 1175 m, 1130 s, 1035 w, 990 w, 940 w, 880 s, 615 s, and 570 cm^{-1} m; nmr (in CCl_4) δ 1.8 (d, J = 7 Hz, 6, Me_2C) and 3.55–4.05 ppm (m, 1, Me_2CH).

Anal. Calcd for $C_4H_7Cl_2N$: C, 34.32; H, 5.04; N, 10.00; Cl, 50.64. Found: C, 34.15; H, 5.14; N, 10.09; Cl, 50.54.

An authentic sample of this compound, bp 110–114°, $n^{27}D$ 1.4460, was prepared by chlorination (using an excess of chlorine) of isopropyl isothiocyanate in carbon tetrachloride using the procedure of Bly, *et al.*[19] The material obtained was better than 99% pure by glc and its ir spectrum and glc retention time were identical with those of our reaction product.

The earlier fractions of the Vigreux column distillation above contained (by glc) $Me_2CHN=CCl_2$ as major component (in addition to solvent), as well as three minor components. One of these had a glc retention time identical with that of authentic isopropylisonitrile, and a collected sample of the three minor components (preparative glc separation was not feasible) had an ir spectrum which contained all the bands observed in the ir spectrum of $Me_2CHN\equiv C$. The low yield of this product precluded further characterization or yield determination. In further support for the presence of an isonitrile was the unusually pungent odor, characteristic of this class of compounds, which the reaction mixture had.

An authentic sample of isopropylisonitrile was prepared by the method of Ugi, *et al.*:[20] ir (in CCl_4) 2960 s, 2900 s, 2840 m, 2400 w, 2130 s, 2100 m, 2030 w, 1630 w, 1475 s, 1410 s, 1380 s, 1350 s, 1165 s, 1120 (broad) s, 930 w, and 910 cm^{-1} s.

Four reactions between $PhHgCCl_2Br$ and diisopropylcarbodiimide were carried out in C_6H_5Cl solution using the procedure described above, on a small scale and with variations in reagent ratio. Assuming the reaction shown in eq 2, the $Me_2CHN=CCl_2$ yields (by glc) for the following reagent ratios are given.

mmol of $Me_2CHN=C=NCHMe_2$	mmol of $PhHgCCl_2Br$	% yield of $Me_2CHN=CCl_2$
1.00	1.00	66
1.13	1.13	63
1.02	2.04	92
0.95	1.90	92

A reaction carried out using 10 mmol of the carbodiimide and 1 mmol of the mercurial in the hope of increasing the yield of isopropylisonitrile did not achieve the desired result. Again the yield of the latter was very small, and it would appear that the the isonitrile is much more reactive toward the mercurial than is the carbodiimide.

Reaction of Phenyl(bromodichloromethyl)mercury with Dicyclohexylcarbodiimide.—The carbodiimide (0.21 g, 1.0 mmol, Upjohn Co.) and 1 mmol of the mercury reagent in 10 ml of benzene were heated at 73° for 15 min. Filtration gave phenylmercuric bromide in 72% yield. The filtrate was trap-to-trap distilled at 0.05 mm (pot temperature to 80°) and the distillate was analyzed by glc (25% SE-30, 140°). One major component was present. Its infrared spectrum agreed well with that of an authentic sample of cyclo-$C_6H_{11}N=CCl_2$. The latter was prepared by chlorination of cyclohexyl isothiocyanate in 41% yield. Its infrared spectrum (neat liquid) showed bands at 2950 s, 2925 sh, 2865 s, 1780 m, 1725 m, 1660 s, 1650 sh, 1450 m, 1370 m, 1265 w, 1255 w, 1145 w, 1100 (broad) m, 1055 w, 1025 w, 955 m, 905 s, 890 s, 860 s, 790 s, 680 w and 625 cm^{-1} s.

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[15] J. C. Sheehan and I. Lengyel, *J. Org. Chem.*, **28**, 3252 (1963).

[16] M. S. Raasch, *ibid.*, **35**, 3470 (1970).

[17] D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

[18] D. Seyferth and R. L. Lambert, Jr., *ibid.*, **16**, 21 (1969).

[19] R. S. Bly, G. A. Perkins, and W. L. Lewis, *J. Amer. Chem. Soc.*, **44**, 2896 (1922).

[20] I. Ugi, R. Mayr, M. Lipinski, F. Bodesheim, and F. Rosendahl, *Org. Syn.*, **41**, 13 (1961).

Anal. Calcd for $C_7H_{11}NCl_2$: C, 46.69; H, 6.16. Found: C, 46.57; H, 6.67.

Further work with dicyclohexylcarbodiimide was discontinued when the second author (R. D.) became highly sensitized to the $PhHgCCl_2Br$–dicyclohexylcarbodiimide reaction mixtures. The resulting skin irritations were severe and believed due to the carbodiimide.

Reaction of Phenyl(bromodichloromethyl)mercury with Phenyl Isothiocyanate.—A mixture of 0.70 g (5.0 mmol) of phenyl isothiocyanate and 3.0 g (6.8 mmol) of the mercurial in 10 ml of dry benzene was stirred and heated at 70–75° for 30 min. (*n*-Decane, 1.47 mmol, was present as a glc internal standard.) The reaction mixture was cooled and an aliquot was analyzed by glc (20% DC-200, 135°); the yield of perchlorothiirane was 32%, based on eq 3. Another 6.8 mmol of $PhHgCCl_2Br$ was added to the reaction mixture and heating was continued for another 2 hr. Glc analysis at this time showed that perchlorothiirane was present in 74% yield.

In another experiment, 18.0 mmol of the mercury reagent and 5.0 mmol of phenyl isothiocyanate were mixed all at once in 22 ml of benzene and stirred and heated at 70–75° for 4 hr. The deep brown reaction mixture was filtered to remove 6.3 g of brown, impure phenylmercuric bromide (98%), mp 265–270°. Trap-to-trap distillation of the filtrate at 0.05 mm (pot temperature below 80° for 4 hr, and to 130° for 5 min) was followed by glc analysis of the distillate. Perchlorothiirane was present in 49% yield. This product was identified by comparison of its infrared spectrum and glc retention time with that of an authentic sample obtained by reaction of thiophosgene with $PhHgCCl_2Br$.[9]

When 20.0 mmol of the mercurial and 25.0 mmol of phenyl isothiocyanate in 25 ml of benzene were heated at 70–75° for 4 hr, the usual work-up of the red-brown reaction mixture gave crude phenylmercuric bromide in 96% yield and perchlorothiirane in 59% yield, together with tetrachloroethylene in 2% yield. The latter appears to result from thermolysis of perchlorothiirane; its determined "yield" varied with analysis conditions, being larger when higher column and injection port temperatures were used. Because of the thermal instability of perchlorothiirane, work-up and analysis under the lowest possible temperature conditions is recommended.[21]

N-Phenyldichloroimine was not detected in the glc analyses of these reaction mixtures and in another reaction carried out using 2.25 mmol of $PhHgCCl_2Br$, 0.5 ml of phenyl isothiocyanate, and 3 ml of benzene (3 hr at 81°) a search for higher boiling products (4 ft × 0.25 in., 10% UC W98 at 175°) failed to detect the presence of 1-phenyl-2,2,3,3-tetrachloroaziridine.

Reaction of Phenyl(bromodichloromethyl)mercury with Isopropyl Isothiocyanate.—The mercurial (4.4 g, 10.0 mmol) and the isothiocyanate (1.0 g, 10.0 mmol) in 50 ml of benzene were kept at 30° for 168 hr (with stirring). The reaction mixture turned brown and a brown solid was deposited. The latter, 2.9 g, was mostly phenylmercuric bromide, mp 278–282°. The filtrate was distilled at 0.02 mm (pot temperature to 40°). Analysis of the yellow distillate by glc showed the presence of solvent, a small quantity of tetrachloroethylene, unconverted isopropyl isothiocyanate, and perchlorothiirane (25% yield). *N*-Isopropyldichloroimine was not present.

Reaction of Phenyl(bromodichloromethyl)mercury with Phenyl Isocyanate.—The mercurial (1.0 g, 2.25 mmol) and phenyl isocyanate (3.0 g, 25 mmol) were stirred and heated at 90° for 3 hr. The resulting brown mixture was filtered from 0.75 g (94%) of crude phenylmercuric bromide. Glc analysis (4 ft × 0.25 in., 10% UC W98 on Chromosorb W, 135°) of the trap-to-trap distilled (at 0.02 mm, pot temperature to 100°) filtrate showed the presence of 1-phenyl-2,2,3,3-tetrachloroaziridine in 15% yield. Also present were several minor high-boiling products. The major product was identified by comparison of its infrared spectrum and glc retention time with that of an authentic sample prepared by reaction of $PhHgCCl_2Br$ with $PhN{=}CCl_2$.[8]

A reaction carried out between 5.0 mmol of the mercurial and 25 mmol of phenyl isocyanate in 8 ml of dry benzene at reflux for 3 hr gave the aziridine in 9.2% yield. The yield of crude phenylmercuric bromide was 84%.

A third reaction was carried out in which 10 mmol of $PhHgCCl_2Br$ and 3 ml of phenyl isocyanate were stirred and heated at 85° for 3 hr. The nitrogen sweep gas was passed into a trap containing 30% aqueous ammonia to convert any phosgene that might result from mercurial attack at the C=O bond into urea. Upon completion of the reaction the trap contents were boiled to expel ammonia. An aliquot was concentrated to 0.3 ml and treated with concentrated HNO_3; no precipitate formed. It is concluded that no phosgene had been formed and that the C=O bond of phenyl isocyanate is not involved in the reaction with phenyl(bromodichloromethyl)mercury.

Reaction of Phenyl(bromodichloromethyl)mercury with *trans*-1,2-Diisocyanatoethylene.—The mercurial (7.05 g, 16 mmol) and 1.60 g (14.5 mmol) of *trans*-1,2-diisocyanatoethylene (Aerojet General Corp., mp 67–69°) in 30 ml of dry benzene were stirred and heated at reflux for 2 hr. The light yellow reaction mixture was filtered from 5.34 g (94%) of phenylmercuric bromide, mp 283–286°. Glc analysis of the filtrate (4 ft × 0.25 in., 20% SE-30 at 120°) showed the presence of *trans*-1,2-diisocyanato-3,3-dichlorocyclopropane in 84% yield. A sample was isolated by glc, $n^{25}D$ 1.5138. The nmr spectrum (in CCl_4) showed a singlet at 3.18 ppm. The infrared spectrum (pure liquid) showed bands at 3030 w, 2900 w, 2260 vs, 1760 w, 1475 w, 1370 w, 1300 w, 1190 w, 1062 w, 980 w, 939 w, 903 w and 805 cm^{-1} m.

Anal. Calcd for $C_5H_2Cl_2N_2O_2$: C, 31.11; H, 1.04; Cl, 36.74. Found: C, 31.08; H, 1.22; Cl, 36.20.

Reaction of Phenyl(bromodichloromethyl)mercury with Carbon Disulfide.—A mixture of 0.76 g (10.0 mmol) of carbon disulfide and 11.0 g (25.0 mmol) of the mercurial in 30 ml of benzene was heated at 70–75° for 1 hr. The mixture was filtered from 6.5 g (77%) of phenylmercuric bromide. The red-brown filtrate was trap-to-trap distilled at 0.03 mm (pot temperature below 80°) using 4 g of dodecane as "chaser." Glc analysis (20% DC-200, 135°) showed the presence of perchlorothiirane in 30% yield, based on eq 6.

A second experiment in which 5.0 mmol of carbon disulfide and 27 mmol of the mercurial in 15 ml of benzene were allowed to react at 75–80° for 2 hr gave perchlorothiirane in 27% yield, in addition to a large amount of tetrachloroethylene resulting mostly from the thermolysis of the excess mercurial. The distillation residue in these experiments was a black, benzene- and acetone-soluble tar.

Registry No.—Phenyl(bromodichloromethyl)mercury, 3294-58-4; diisopropylcarbodiimide, 693-13-0; dicyclohexylcarbodiimide, 538-75-0; phenyl isothiocyanate, 103-72-0; isopropyl isothiocyanate, 2253-73-8; phenyl isocyanate, 103-71-9; *trans*-1,2-diisocyanatoethylene, 1441-73-2; carbon disulfide, 75-15-0; *N*-isopropyldichloroimine, 29119-58-2; cyclo-$C_6H_{11}N{=}CCl_2$, 2666-80-0; *trans*-1,2-diisocyanato-3,3-dichlorocyclopropane, 29119-60-6.

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(21) It should be noted that our reported[9] yield of perchlorothiirane as obtained in the $PhHgCCl_2Br$–Cl_2CS reaction, 36% yield, is too low because care was not taken to keep the temperature as low as possible during work-up and analysis. When this was done (W. E. Smith, unpublished), the yield of perchlorothiirane was 96%.