Halomethyl Metal Compounds. LXVI. Preparation of *C*-Tetrachloroaziridines by Reaction of Carbonimidoyl Dichlorides with Phenyl(bromodichloromethyl)mercury. Fragmentation of Azo- and Azoxyarenes upon Reaction with Phenyl(bromodichloromethyl)mercury[1,2]

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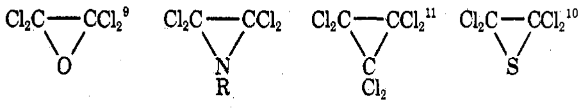
Phenyl(bromodichloromethyl)mercury has been found to transfer CCl_2 to alkyl- and arylcarbonimidoyl dichlorides to give 1-alkyl- and 1-aryl-2,2,3,3-tetrachloroaziridines in fair yield. These *C*-tetrachloroaziridines are much more stable thermally than monochloro- or *gem*-dichloroaziridines but do rearrange to give the $RN{=}C(Cl)CCl_3$ compound (R = Ph and c-C_6H_{11}, but not *i*-C_3H_7) when heated at 180° for 3 hr. Similar CCl_2 addition to the C=N bond of $PhN{=}C(Cl)Ph$ was observed. Azoarenes reacted with $PhHgCCl_2Br$ with cleavage of the N=N bond, giving $ArN{=}CCl_2$ when an excess of the azoarene is used and a 1-aryl-2,2,3,3-tetrachloroaziridine when an excess of the mercurial is used. Azoxyarenes react similarly after an initial deoxygenation by CCl_2 to give the azoarene.

The addition of a dihalocarbene to the C=N bond of imines of type $ArN{=}CHAr'$ to give 1,2-diaryl-3,3-dihaloaziridines was reported first by Fields and Sandri in 1959,[4] and this reaction was utilized subsequently by others.[5] In these reactions, the dihalocarbene was generated by the haloform-base or the hexachloroacetone-base procedures. However, all of our earlier attempts[2,6] to add dichlorocarbene to the N=C bond of imines of types $PhCH{=}NPh$,[2,6] $PhCH{=}NCH_3$,[6] and $Me_2C{=}NPh$[2] using $PhHgCCl_2Br$[7] as the potential CCl_2 source were unsuccessful. In all cases, tarry reaction products rather than the expected aziridines were obtained. Other workers have recorded a similar lack of success in the attempted reaction of $PhHgCBr_3$ with $Me_3CCH{=}NCMe_3$.[5c] In more recent studies, we have found that a reaction of $PhCH{=}NPh$ with a twofold excess of phenyl(bromodichloromethyl)mercury for 18 hr at 50° did indeed give the expected 1,2-diphenyl-3,3-dichloroaziridine, but only in low yield. Again, the major reaction which occurred in this system was one which produced much tar.

Tar formation of the type encountered in these $PhHgCCl_2Br$-imine reactions is characteristic of the reactions of such mercurials with tertiary amines.[8] It thus may be that in the case of these imines, as with trialkylamines, the main reaction involves initial attack by the nucleophilic nitrogen center at the electrophilic mercury atom of the $PhHgCX_3$ compound, with subsequent reactions producing the observed tarry products. Dihalocarbene extrusion from $PhHgCX_2Br$ (X = Cl and Br) would appear to be too slow to be competitive with this rapid nucleophilic substitution reaction.

In order to achieve successful CX_2 addition to the C=N bond of an imine *via* a phenyl(trihalomethyl)mercury reagent, one must, on the basis of the above considerations, decrease the nucleophilicity of the nitrogen atom.

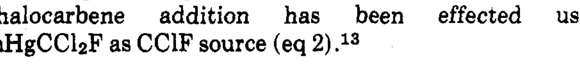
The carbonimidoyl dihalides (or isonitrile dihalides), $RN{=}CX_2$, are such a class of imines in which the nitrogen atom of the C=N bond should be decidedly less nucleophilic as a result of the electron-withdrawing effect of the two halogen substituents on the carbon atom of the C=N bond. This decrease in the availability of the lone electron pair on nitrogen might be sufficient to allow successful CX_2 extrusion from $PhHgCX_2Br$ and subsequent CX_2 addition to the C=N bond. Should such addition be successful, a new and interesting class of compounds, the *C*-tetrachloroaziridines, would be in hand, to add to the *C*-perhalo series of three-membered rings. The *C*-perchloro analogs are the following.



Accordingly, we have investigated reactions of *N*-alkyl- and *N*-arylcarbonimidoyl dichlorides, which are readily prepared from aryl isothiocyanates or *N*-arylformamides, with phenyl(bromodichloromethyl)mercury.

Results and Discussion

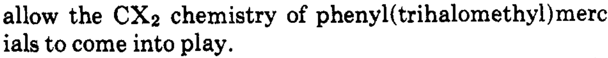
We have found that the carbonimidoyl dichlorides as a class react readily with phenyl(bromodichloromethyl)mercury in benzene at 70-80° as shown in eq 1. The isolated



$$\mathrm{RN{=}CCl_2 + PhHgCCl_2Br \longrightarrow PhHgBr + RN\left\langle \begin{matrix} CCl_2 \\ | \\ CCl_2 \end{matrix} \right.} \qquad (1)$$

I

yields of the 2,2,3,3-tetrachloroaziridines obtained ranged from about 30 to 55%, and glc yields tended to be higher. Prepared in this manner were compounds of type I with R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, c-C_6H_{11}, and *i*-C_3H_7 (Table I). In another study,[12] reaction of $(EtO_2C)_2NN{=}CCl_2$ with $PhHgCCl_2Br$ gave I with R = $(EtO_2C)_2N$. Also, such dihalocarbene addition has been effected using $PhHgCCl_2F$ as CClF source (eq 2).[13]

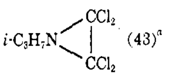
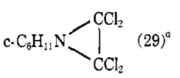
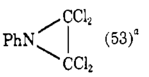
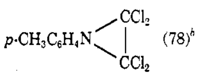
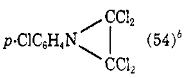


$$\mathrm{PhN{=}CCl_2 + PhHgCCl_2F \xrightarrow{80^\circ,\ 40\ hr} PhHgCl + \underset{74\%}{PhN\left\langle \begin{matrix} CCl_2 \\ | \\ CClF \end{matrix} \right.}} \qquad (2)$$

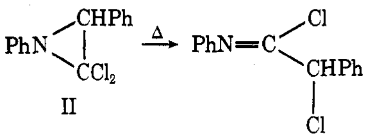
It thus appears that the chlorine substitution on carbon does indeed reduce the nucleophilicity of the nitrogen atom in $RN{=}CCl_2$ compounds to an extent sufficient to allow the CX_2 chemistry of phenyl(trihalomethyl)mercurials to come into play.

Compounds of type I are very stable and survive both distillation and glc at temperatures around 150°. They are significantly more stable than monochloroaziridines, which must be stored at 0° to prevent their decomposition,[14] and dichloroaziridines, *e.g.*, II, whose thermal rearrangement (eq 3) can be accomplished by heating its toluene solution at reflux for a few hours.[15,16] In the case of compounds of type I, the *N*-isopropyl derivative was recovered unchanged after it had been heated for 6 hr at 180°. The *N*-phenyl and *N*-cyclohexyl derivatives, on the

Table I
Reactions of Carbonimidoyl Dichlorides with Phenyl(bromodichloromethyl)mercury

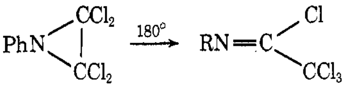
$RN{=}CCl_2$ (mmol)	Registry no.	$PhHgCCl_2Br$, mmol	C_6H_6, ml	Reaction conditions	Product (% yield)	Registry no.	PhHgBr, %
$i\text{-}C_3H_7N{=}CCl_2$ (50)	29119-58-2	50	80	3 hr, 80°	 (43)[a]	25252-60-2	80
$c\text{-}C_6H_{11}N{=}CCl_2$ (30)	2666-80-0	30	70	12 hr, 60°	 (29)[a]	25252-59-9	84
$PhN{=}CCl_2$ (40)	622-44-6	30	70	12 hr, 60°	 (53)[a]	25252-58-8	84
$p\text{-}CH_3C_6H_4N{=}CCl_2$ (16)	16001-28-8	10	15	3 hr, 80°	 (78)[b]	42880-62-6	90
$p\text{-}ClC_6H_4N{=}CCl_2$ (12)	2771-67-7	10	20	3 hr, 80°	 (54)[b]	42880-63-7	99

[a] Isolated (by distillation) yield. [b] Glc yield.


(3)

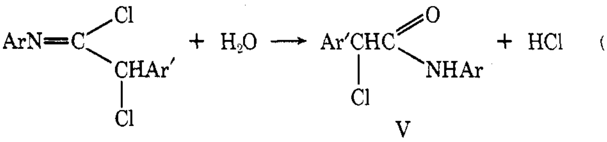
II III

other hand, underwent such rearrangement when they were heated at 180° for 3 hr (eq 4).


(4)

IV

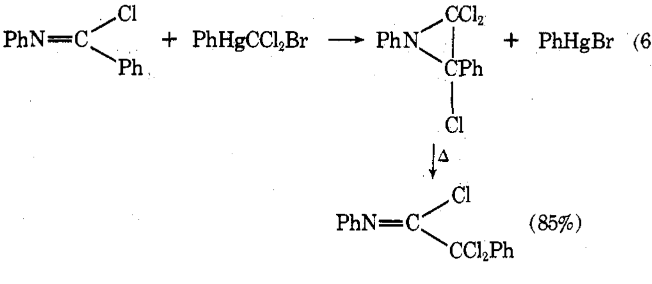
Compounds of type III are known to hydrolyze as shown in eq 5, and thus the hydrolysis product IV (R = Ph), tri-


(5)

V

chloroacetanilide, $CCl_3C(O)NHPh$, obtained in 95% yield, provided good confirmation of the structure of IV. The thermal rearrangement-hydrolysis sequence of 1,2-diaryl-3,3-dichloroaziridines (II) to give anilides (V) may be accomplished simply by heating them in boiling water for 30 min, but as a result of their greater thermal stability, C-tetrachloroaziridines are not affected when heated in 2 *N* hydrochloric acid for 12 hr at 100°.

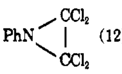
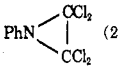
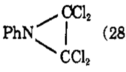
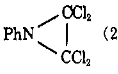
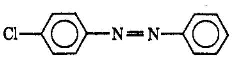
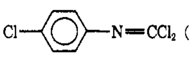
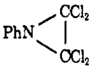
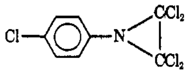
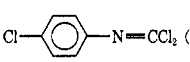
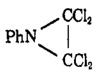
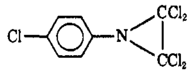
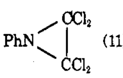
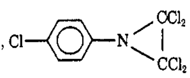
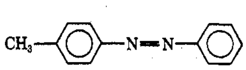
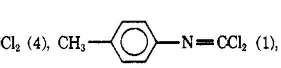
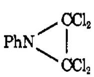
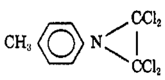
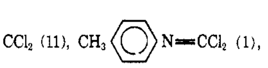
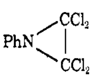
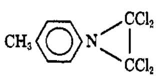
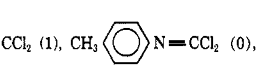
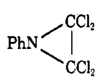
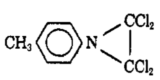
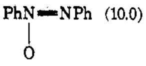
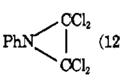
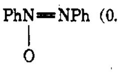
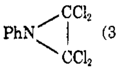
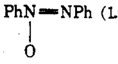
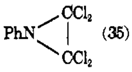
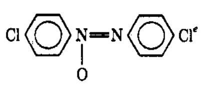
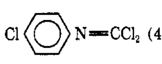
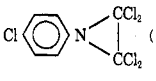
This study was extended to an investigation of possible CCl_2 addition to compounds of type $PhN{=}C(Cl)R$ (R = Ph, CCl_3). Phenylbenzimidoyl chloride did react with phenyl(bromodichloromethyl)mercury to give the expected aziridine, as shown by infrared spectroscopic examination of the reaction mixture, but attempted isolation of the aziridine by distillation resulted in its partial rearrangement (eq 6). On the other hand, $PhN{=}C(Cl)CCl_3$ did not react with phenyl(bromodichloromethyl)mercury, even under forcing conditions. Presumably, this lack of reactivity is a consequence of the steric bulk of the trichloromethyl substituent on carbon.


(6)

More complicated reactions of other organonitrogen compounds with phenyl(trihalomethyl)mercurials have been found to give *C*-tetrachloroaziridines, in all cases *via* intermediate carbonimidoyl dichlorides. We have reported previously[17] that phenyl isocyanate reacts with $PhHgCCl_2Br$ to give 1-phenyl-2,2,3,3-tetrachloroaziridine in low yield. The reaction of carbodiimides with this mercurial was found to result in formation of $RN{=}CCl_2$ compounds,[17] and, given sufficient starting mercurial, these could be converted *in situ* to the *C*-tetrachloroaziridine. Gibson, *et al.*,[18] reported the reaction of phenyl(trichloromethyl)mercury with phenyl azide in 1,2-dimethoxyethane at 80°, which gives first phenylcarbonimidoyl dichloride and then 1-phenyl-2,2,3,3-tetrachloroaziridine. Their rate studies indicated that dichlorocarbene was an intermediate in both steps. Other classes of compounds which react with phenyl(bromodichloromethyl)mercury to give first $ArN{=}CCl_2$ and then 1-aryl-2,2,3,3-tetrachloroaziridines are, as we have found, the azoarenes and azoxyarenes.

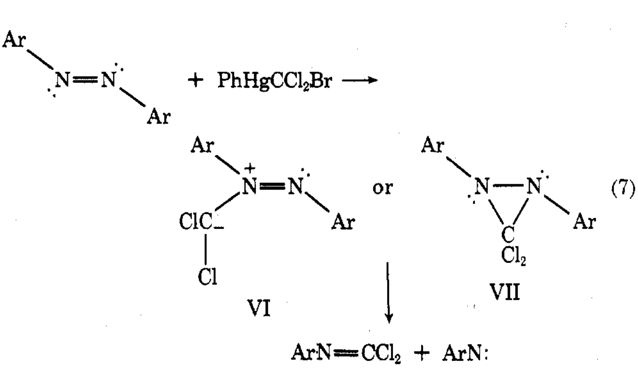
Depending on the reactant stoichiometry, the major product of the azoarene–$PhHgCCl_2Br$ reactions is either the arylcarbonimidoyl dichloride (azoarene in excess) or the *C*-tetrachloroaziridine (mercurial in excess). Such reactions, however, do not proceed without complications, and product yields did not exceed 40–50% and often were lower (Table II). Information concerning these reactions was sought by allowing $PhHgCCl_2Br$ to react with two unsymmetrically substituted azoarenes. In the case of 4-chloroazobenzene there appeared to be no significant difference in the effect of the substituted and the unsubstituted benzene rings, as far as product yields indicated (Table II). With 4-methylazobenzene, products containing the unsubstituted phenyl group appeared to be favored. However, in view of the poor product yields and material balances in these experiments, we hesitate to read any great significance into these results. These systems, unfortunately, do not appear to be amenable to mechanistic

Table II
Reactions of Azo- and Azoxybenzenes with Phenyl(bromodichloromethyl)mercury

Azoarene (mmol)	Registry no.	$PhHgCCl_2Br$, mmol	Products (% yield)
PhN=NPh (2.00)[a]	103-33-3	10.00	 (12)
PhN=NPh (0.48)[b]		4.50	 (28)
PhN=NPh (0.46)[c]		4.50	 (28)
PhN=NPh (10.0)[a]		5.0	$PhN=CCl_2$ (12),  (2)
 (5.0)[c]	4340-77-6	5.0	$PhN=CCl_2$ (19),  (19),  (9),  (5)
(5.0)[a]		2.3	$PhN=CCl_2$ (25),  (22),  (6),  (0)
(0.46)[a]		4.5	 (11),  (9)
 (5.0)[e]	949-87-1	5.0	$PhN=CCl_2$ (4),  (1),  (1.3),  (0)
(5.0)[a]		2.3	$PhN=CCl_2$ (11),  (1),  (1.2),  (0)
(2.3)[a]		5.0	$PhN=CCl_2$ (1),  (0),  (8),  (4)
 PhN=NPh(O) (10.0)	495-48-7	10.0	$PhN=CCl_2$ (3),  (12), PhN=NPh (6)
 PhN=NPh(O) (0.46)[d]		4.50	 (34)
 PhN=NPh(O) (1.06)[b]		5.00	 (35)
 (3.0)	614-26-6	11.0	 (4),  (15)

[a] In 10 ml of benzene at 80° for 3 hr. [b] In 3 ml of benzene at 80° for 3 hr; mercurial added in portions. [c] In 3 ml of benzene at room temperature for 9 days. [d] In 10 ml of benzene at room temperature for 15 days. [e] In 10 ml of benzene at 50° for 12 hr.

study. The formation of the initial product, the carbonimidoyl dichloride, may be pictured as occurring *via* an open (VI) or a cyclic (VII) intermediate, which then decomposes to give the observed $ArN=CCl_2$ and an arylnitrene.



The latter, in principle, could react with $PhHgCCl_2Br$ or with CCl_2 derived from it to give more $ArN=CCl_2$.[19] However, further speculation is not justified in view of the limited information available.

The reaction of phenyl(bromodichloromethyl)mercury with *1* molar equiv of azoxybenzene in benzene solution at 80° for 3 hr gave three products: azobenzene, 6% yield; phenylcarbonimidoyl dichloride, 3% yield; and 1-phenyl-2,2,3,3-tetrachloroaziridine, 12% yield. The use of an excess of the mercurial in such a reaction increased the yield of the aziridine to 35%, and in such reactions no $PhN=CCl_2$ was obtained. A similar reaction occurred with 4,4′-dichloroazoxybenzene. The course of these reactions is the same as those of azobenzene after an initial deoxygenation of the azoxyarene by $PhHgCCl_2Br$ to give the corresponding azoarene. Such an initial step is made plausible by a report[21] that $PhHgCCl_3$-derived dichlorocarbene can deoxygenate pyridine *N*-oxide. In view of the generally poor product yields in these reactions of phenyl(bromodichloromethyl)mercury with azo- and azoxyarenes, further investigation of their scope and mechanism was not worthwhile.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry nitrogen using flame-dried glassware. Carefully dried solvents were used in all reactions. Nmr spectra were recorded using a Varian A60 or T60 spectrometer. Chemical shifts are given in δ units, parts per million downfield from internal tetramethylsilane. Unless otherwise specified, the solvent used was carbon tetrachloride. Infrared spectra were recorded using Perkin-Elmer 337, 257, or 457A infrared spectrophotometers. Gas–liquid chromatography (glc) was used for yield determinations and for collection of liquid samples. Commercial stainless steel columns were employed with an F & M (Hewlett-Packard) Model 700, 720, or 5754 gas chromatograph. Yields were determined using the internal standard procedure. The standard apparatus used in these reactions of phenyl(bromodichloromethyl)mercury consisted of a three-necked flask of appropriate size 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 a previous paper of this series.[22] The progress of the reactions involving this mercurial was followed using thin layer chromatography.[11]

Preparation of Organonitrogen Starting Materials. The carbonimidoyl dichlorides used in this study are all known compounds and were prepared by standard literature procedures.[23] Isopropyl- and cyclohexylcarbonimidoyl dichlorides, in particular, have been characterized in a previous paper of this series.[11] Phenylbenzimidoyl chloride was prepared using the method of von Braun and Pinkernelle.[24]

The reaction of nitrosobenzene with the respective 4-substituted aniline in glacial acetic acid was used to prepare 4-methyl- and 4-chloroazobenzene. Both are known compounds.[25,26]

Reactions of Phenyl(bromodichloromethyl)mercury with Carbonimidoyl Dichlorides. The reaction of phenylcarbonimidoyl dichloride with $PhHgCCl_2Br$ is described in detail. The other reactions are summarized in Table I. Table III presents physical and spectroscopic properties for the *C*-tetrachloroaziridines prepared.

A solution of 13.2 g (30 mmol) of the mercurial and 7.0 g (40 mmol) of $PhN{=}CCl_2$ in 70 ml of dry benzene was prepared in the standard apparatus under nitrogen and was stirred and heated at 60° for 12 hr. The reaction mixture was filtered to remove 9.0 g (84%) of crude phenylmercuric bromide, mp 265–268°. The filtrate was concentrated at 50° (rotary evaporator) to leave a red-brown, liquid residue. Distillation of the latter gave, after initial fractions containing benzene and $PhN{=}CCl_2$, 4.1 g (53% yield, based on the mercurial) of 1-phenyl-2,2,3,3-tetrachloroaziridine, bp 70–72° (0.02 mm), as a colorless liquid which crystallized on standing to give large crystals, mp 38–40°.

In some other reactions, *e.g.*, that of $PhHgCCl_2Br$ with *p*-tolylcarbonimidoyl dichloride, the reaction mixture was heated at 80° for 3 hr. The yield of 1-*p*-tolyl-2,2,3,3-tetrachloroaziridine was determined by glc (4 ft × 0.25 in. 10% UC W-98 silicone column at 140°) and analytical and spectroscopic samples also were isolated by glc.

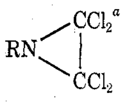
Reaction of Phenyl(bromodichloromethyl)mercury with Phenylbenzimidoyl Chloride. The imidoyl chloride (2.16 g, 10.0 mmol), $PhHgCCl_2Br$ (5.00 g, 11.2 mmol), and 10 ml of benzene were stirred and heated at 80° for 3 hr. The reaction mixture was filtered from 3.60 g (98%) of PhHgBr, mp 265–267°. Evaporation of the solvent *in vacuo* gave an oily residue (2.56 g, 86%). The ir spectrum of the residue showed the presence of the expected 1,3-diphenyl-2,2,3-trichloroaziridine by strong bands at 1370 and 835 cm^{-1}. Attempted purification of the product by distillation at 120° (0.01 mm) resulted in partial rearrangement of the initial product to the imidoyl chloride as indicated by a new ir band at 1670 cm^{-1}.

When the crude product (1.0 g, 3.36 mmol) was distilled at 160° (1.0 mm), pure rearranged product, $PhN{=}C(CCl_2Ph)Cl$, was obtained in 85% yield (0.85 g): $n^{25}D$ 1.6088; ir (neat) 3060 m, 3030 w, 1940 w, 1880 w, 1670 s, 1590 s, 1520 w, 1480 s, 1443 s, 1380 w, 1310 w, 1280 w, 1210 m, 1180 m, 1070 w, 1050 s, 1025 w, 1000 w, 870 m, 830 w, 800 s, 755 s, 710 s, 690 s, 660 w, 600 cm^{-1} w, nmr (CCl_4) δ 7.30 ppm (m, aromatic protons).

Anal. Calcd for $C_{14}H_{10}NCl_3$: C, 56.31; H, 3.38; N, 4.69; Cl, 35.62. Found: C, 56.09; H, 3.43; N, 4.71; Cl, 35.06.

Reaction of $PhHgCCl_2Br$ with Phenyltrichloroacetimidoyl Chloride. The imidoyl chloride (2.56 g, 10.0 mmol), $PhHgCCl_2Br$ (8.80 g, 20.0 mmol), and 20 ml of benzene were stirred and heated at 80° for 4 hr. The reaction mixture was filtered from 7.0 g (97%) of PhHgBr, mp 250–256°. The solvent was evaporated with a rotary evaporator. The high-boiling residue (2.49 g) showed an identical ir spectrum with that of the starting material. No ir band at 1370 cm^{-1}, a characteristic band for the aziridine ring, was observed. Glc (4 ft × 0.25 in., 10% UC W-98, 130–180°) and tlc showed no sign of the expected aziridine product.

Table III
C-Tetrachloroaziridines[c]



R	Bp, °C (mm)	Mp, °C	$n^{25}D$
i-C_3H_7	60–62 (6.0)		1.4810
c-C_6H_{11}	61–62 (0.02)	47–50[b]	1.5130
C_6H_5	70–72 (0.02)	38–40[b]	1.5740
p-$CH_3C_6H_4$			1.5698
p-ClC_6H_4			1.5870

[a] The ir and nmr spectra of these compounds were in agreement with the presence of the groups on nitrogen indicated. [b] The oily product crystallized upon prolonged standing. [c] Satisfactory analytical data were reported for all compounds listed in the table.

Another experiment was carried out in the absence of solvent. The mercurial (2.20 g, 5.0 mmol) was dropped into preheated (100°) phenyltrichloroacetimidoyl chloride (2.53 g, 10.0 mmol) by portions. After the reaction mixture was heated at 100° for 2 hr, it was worked up as in the previous experiment. The imidoyl chloride was recovered quantitatively.

Reaction of Phenyl(bromodichloromethyl)mercury with *N*-Benzylideneaniline. The mercurial (9.0 g, 20 mmol) and $PhN{=}CHPh$ (1.80 g, 10 mmol) in 15 ml of carbon tetrachloride were stirred and heated at 50° under nitrogen for 18 hr. The resulting red-brown solution was filtered from crude (brown) phenylmercuric bromide (6.40 g, 90%, mp 257–265°). The nmr spectrum of the filtrate showed a singlet at 3.58 ppm and the ir spectrum showed bands at 1400 and 760 cm^{-1}, which indicated the presence of the expected 1,2-diphenyl-3,3-dichloroaziridine. An authentic sample of the latter had been prepared by reaction of *N*-benzylideneaniline with 50% aqueous $NaOH{-}CHCl_3$ in the presence of a catalytic amount of benzyltriethylammonium chloride, and it was found to have identical spectroscopic properties.

Attempted isolation of the aziridine product from the reaction mixture by distillation (to 130° at 0.35 mm) gave only a trace amount of this product (identified by its nmr spectrum) and left a tarry residue.

Thermal Rearrangement of the *C*-Tetrachloroaziridines. 1-Phenyl-2,2,3,3-tetrachloroaziridine (3.7 g, 14 mmol) was sealed under nitrogen in a heavy-walled tube and heated for 3.5 hr at 180°. The tube contents quickly turned dark brown. The disappearance of the aziridine is indicated by the disappearance of a strong, broad absorption in the ir spectrum characteristic of these aziridines and by the appearance of a new, strong band at around 1680 cm^{-1} (ν C=N). The oily reaction mixture was distilled at reduced pressure to give 2.6 g (76%) of phenyltrichloroacetimidoyl chloride [$PhN{=}C(Cl)CCl_3$], bp 69–70° (0.02 mm), $n^{25}D$ 1.5773, as a colorless oil which crystallized after prolonged standing to give a solid with mp 35–37°.

Anal. Calcd for $C_8H_5NCl_4$: C, 37.39; H, 1.96; N, 5.46; Cl, 55.19. Found: C, 37.72; H, 2.15; N, 5.52; Cl, 54.86.

Ir (neat liquid) 3105 w, 3095 w, 3080 m, 3040 m, 3030 w, 1965 w, 1945 w, 1870 w, 1790 w, 1740 w, 1690 s (broad), 1670 s, 1600 s, 1585 s, 1495 s, 1455 s, 1360 w, 1290 w, 1260 w, 1235 sh, 1215 s, 1175 m, 1160 w, 1105 w, 1080 s, 1060 s, 1030 m, 1005 m, 910 m, 880 s, 810 s, 780 s, 770 s, 730 s, 710 s, 640 cm^{-1} m.

Similar treatment of 6.7 mmol of 1-cyclohexyl-2,2,3,3-tetrachloroaziridine gave cyclohexyltrichloroacetimidoyl chloride c-$C_6H_{11}N{=}C(Cl)CCl_3$ (75%), bp 64–65° (0.02 mm), $n^{25}D$ 1.5137.

Anal. Calcd for $C_8H_{11}NCl_4$: C, 36.52; H, 4.22; Cl, 53.94. Found: C, 36.93; H, 4.15; Cl, 53.77.

In the ir spectrum (liquid film) strong bands at 1690, 1685, and 1670 cm^{-1} were present.

Similar heating of 1-isopropyl-2,2,3,3-tetrachloroaziridine failed to cause any change.

An 0.8-g (31 mmol) sample of $PhN{=}C(Cl)CCl_3$ and 5 ml of 2 *N*

HCl were charged into a 25-ml round-bottomed flask equipped with a reflux condenser and a magnetic stirring unit. The mixture was stirred and heated at 100° for 2 hr. The bottom organic layer crystallized after the two-phase mixture had cooled to give 0.7 g (95%) of trichloroacetanilide, mp 93–94° after two recrystallizations from ethanol (lit.[27] mp 94–95°).

1-Phenyl-2,2,3,3-tetrachloroaziridine was not hydrolyzed under these conditions and was recovered unchanged.

Reactions of Phenyl(bromodichloromethyl)mercury with Azobenzene and Azoxybenzene. A 50-ml flask equipped with a thermometer, magnetic stir bar, and a condenser topped with a nitrogen inlet tube was charged with the azobenzene or azoxybenzene and the mercurial. The reaction was carried out either at room temperature in benzene solution or in refluxing benzene solution. The resulting reaction mixture was dark red-brown in color. The crude PhHgBr, obtained as a brown solid in 80–90% yield, decomposed at 230° to give a black tar. The filtrate was directly analyzed with an MIT isothermal unit or was trap-to-trap distilled at 0.02 mm (pot temperature to 100°). The distillate was examined by glc (F & M Model 700 gas chromatograph using a 4 ft × 0.25 in. column, 10% UC W-98 at 130–150°, *n*-hexadecane as internal standard). Products were isolated by glc and identified by the comparison of their ir spectrum and glc retention time with those of the authentic samples synthesized independently. The results are summarized in Table II.

Acknowledgments. The authors are grateful to the U. S. Air Force Office of Scientific Research (NC)-AFSC (Grant AF-AFOSR-72-2204) for generous support of this work and to M & T Chemicals, Inc., for gifts of chemicals.

Registry No. Phenyl(bromodichloromethyl)mercury, 3294-58-4; phenylbenzimidoyl chloride, 4903-36-0; 1,3-diphenyl-2,2,3-trichloroaziridine, 42880-67-1; diphenyldichloroacetimidoyl chloride, 42880-68-2; phenyltrichloroacetimidoyl chloride, 25252-86-2; *N*-benzylideneaniline, 538-51-2; 1,2-diphenyl-3,3-dichloroaziridine, 3543-98-4; cyclohexyltrichloroacetimidoyl chloride, 25252-87-3.

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Aziridines. 27. The Synthesis and Reactions of 4-Aroyltetrahydro-2*H*-1,2,4-oxadiazines

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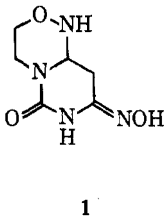
2-Aryl- or 2-alkyl-4-aroyltetrahydro-2*H*-1,2,4-oxadiazines have been prepared by heating 1-aroylaziridines and nitrones in toluene or *m*-xylene. In hot acetic acid 2-(*p*-tolyl)-3-phenyl-4-(3,5-dinitrobenzoyl)tetrahydro-2*H*-1,2,4-oxadiazine (**6**) is converted into a mixture of *p*-azotoluene, *p*-azoxytoluene, benzaldehyde and *N*-(β-hydroxyethyl)-3,5-dinitrobenzamide. **6** reacts with *p*-nitrotoluene in concentrated sulfuric acid to give 2-methyl-5-nitro-4′-aminodiphenylmethane, *N*-(β-hydroxyethyl)-3,5-dinitrobenzamide, and benzaldehyde. In hot basic solution 2-(*p*-tolyl)-3-phenyl-4-(*p*-nitrobenzoyl)tetrahydro-2*H*-1,2,4-oxadiazine (**5**) isomerizes into *N*-(*p*-tolyl)-β-(*p*-nitrobenzamido)ethylbenzimidate (**17**). Reduction of **6** leads to *N*-benzyl-*p*-toluidine and thermolysis of **6** at 200° causes vigorous decomposition and formation of *N*-benzal-*p*-toluidine.

Only a limited number of saturated 1,2,4-oxadiazines are known. Those that have been reported include the dihydrocytosine derivative **1**[1] and the 1,2,4-oxadiazinium salts **2**. The salts **2** were prepared by treating aziridinium perchlorates with cyclic nitrones.[2,3] In view of this reaction and the known ring-opening reactions of 1-carbethoxy- and 1-aroylaziridines by dipolar species such as enamines,[4] phosphonium and arsonium ylides,[5,6] and dimethyl sulfoxide,[7] it seemed likely that nitrones would interact with 1-aroylaziridines to produce 4-aroyltetrahydro-2*H*-1,2,4-oxadiazines (**3**). The purpose of this paper is to describe the synthesis of **3** and to delineate the reactions of **3** with glacial acetic acid, sulfuric acid, reducing reagents, and potassium hydroxide in dimethylformamide (DMF).



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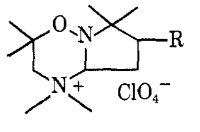

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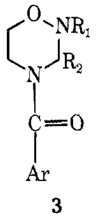

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