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**Preliminary communication**

# New reactions of phenyl(trihalomethyl)mercurials. *C*-Perchloroaziridines and their thermally induced rearrangement

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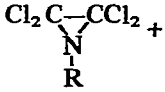
Our recent syntheses of perchlorothiirane[1] and polyhalooxiranes[2] by the addition of phenyl(trihalomethyl)mercury-derived dihalocarbenes to the appropriate C=S and C=O compounds suggested to us that a similar synthesis of the as yet unknown *C*-perhaloaziridines might be possible via reaction of $PhHgCX_3$ reagents with imines of type $RN{=}CX_2$ (*i.e.*, isonitrile dihalides). We report here concerning the preparation of *C*-perchloroaziridines (eq. 1) and their surprising thermal and hydrolytic stability.

$PhHgCCl_2Br + RN{=}CCl_2 \rightarrow$  $+ PhHgBr$ (1)

(I, R = Ph; II, R = cyclo-$C_6H_{11}$; III, R = i-Pr)

In a typical example, the reaction of $C_6H_5N{=}CCl_2$ (40 mmol) with 30 mmol of $PhHgCCl_2Br$ [3] in 70 ml of dry benzene was carried out with stirring under nitrogen at 60° for 12 h. Phenylmercuric bromide was filtered off in 84% yield and fractional distillation of the filtrate gave 1-phenyl-2,2,3,3-tetrachloroaziridine in 53% yield, b.p. 70–72° (0.02 mm); $n_D^{25}$ 1.5740. The liquid distillate crystallized on standing to give material of m.p. 38–40°. (*Anal.:* Found: C, 37.15; H, 1.99; Cl, 54.73; N, 5.70. $C_8H_5Cl_4N$ calcd.: C, 37.39; H, 1.96; Cl, 55.19; N, 5.46.) In similar fashion were prepared 1-cyclohexyl-2,2,3,3-tetrachloroaziridine (29%), b.p. 61–62° (0.02 mm), m.p. 48–50°, and 1-isopropyl-2,2,3,3-tetrachloroaziridine (43%), b.p. 60–62° (6.0 mm), $n_D^{25}$ 1.4810.

The addition of dichlorocarbene to imines of type ArN=CHAr' was reported some years ago, first by Fields and Sandri, who used the chloroform/$Me_3COK$ reagent[4], then by Kadaba and Edwards, who used the hexachloroacetone/NaOMe reagent for $CCl_2$ generation[5]. However, attempts to add dichlorocarbene to imines such as PhCH=NPh [6], PhCH=NMe [6] and $Me_2C{=}NPh$ via the phenyl(bromodichloromethyl)mercury route were unsuccessful. In all cases tarry reaction products rather than the expected aziridines were obtained. Another case, that of $Me_3CCH{=}NCMe_3$, has been recorded in which the $CHCl_3/Me_3COK$ reagent added $CCl_2$ to the C=N bond but in which attempted $CBr_2$ addition via $PhHgCBr_3$ did not succeed[7]. Qualitatively these reactions resembled those of tertiary amines with

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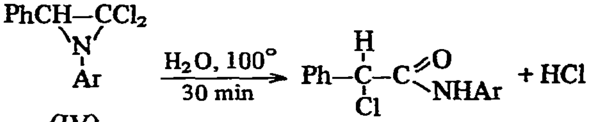
phenyl(bromodichloromethyl)mercury[8] and thus we believe that also in the case of these imines attack of the nucleophilic nitrogen center at mercury proceeds more rapidly than the extrusion of $CCl_2$ from the mercurial and that this causes the observed complications. In order for $CX_2$ addition to the $-N{=}C<$ bond via the mercurial route to be successful, the Lewis basicity of the nitrogen atom must be so diminished that nucleophilic attack at mercury no longer is a competing process to $CX_2$ extrusion from the $PhHgCX_3$ compound. On the basis of these considerations, the successful reactions of phenyl(bromodichloromethyl)mercury with isonitrile dichlorides are easily understood: the -I effect of the two chlorine substituents on the carbon atom serves to sufficiently decrease the nucleophilicity of the nitrogen atom as required*.

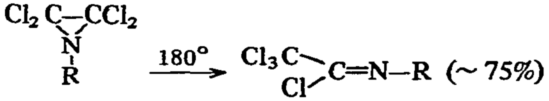
Aziridines of type IV are readily hydrolyzed (eq. 2). In contrast, our *N*-organo-*C*-perchloroaziridines survived 12 h of heating in water and in 2*N* hydrochloric acid. These



(IV)

(2)

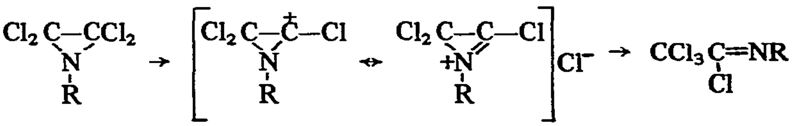
*N*-organo-*C*-perchloroaziridines are quite stable. The isopropyl compound III was recovered unchanged after being heated for 6 h at 180°. The phenyl and cyclohexyl derivatives (I and II), on the other hand, underwent rearrangement when heated for 3 h at 180° (eq. 3). The products were imines (V, b.p. 69–70° (0.02 mm), $n_D^{25}$ 1.5773, m.p. 35–37°; VI, b.p. 64–65° (0.02 mm), $n_D^{25}$ 1.5137), characterized by strong N=C absorption at ~ 1680 $cm^{-1}$



(3)

(V, R = Ph; VI, R = cyclo-$C_6H_{11}$)

in their infrared spectra. Hydrolysis of V in 2*N* HCl (2 h at 100°) gave the expected trichloroacetanilide in 95% yield. This isomerization of V and VI very likely proceeds as shown in eq. 4, the process being facilitated by carbonium–immonium resonance stabilization.



(4)

Mono- and dichloroaziridines, in contrast, are less stable. Monochloroaziridines must be stored at 0° to prevent their decomposition[10]. The hydrolysis of dichloroaziridines

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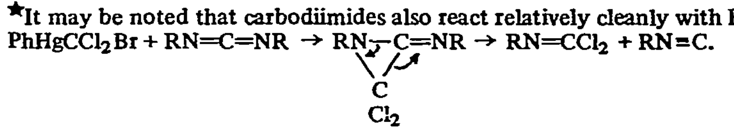
*It may be noted that carbodiimides also react relatively cleanly with $PhHgCCl_2Br$ [9]:

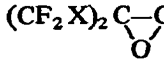


$PhHgCCl_2Br + RN{=}C{=}NR \rightarrow RN\underset{CCl_2}{-}C{=}NR \rightarrow RN{=}CCl_2 + RN{=}C.$

Here a similar explanation is applicable. In this case it is the -I effect of the RN= moiety which decreases the Lewis basicity of the other nitrogen atom in the RN=C=NR molecule.

of type IV is easily effected (3 h at 100° or 24 h at 25°)[4,5], and this hydrolytic rearrangement was suggested to proceed via carbonium–immonium ions of the type shown above. Thus very significant additional stability results when all carbon substituents are chlorine atoms.

Phenyl(dibromochloromethyl)mercury reacts with these isonitrile dichlorides in similar manner, but the resulting 1-organo-2-bromo-2,3,3-trichloroaziridines are much less stable than their *C*-perchloro analogs, undergoing partial rearrangement to the imines on distillation at 0.02 mm as shown by the presence of bands at ~ 1680 cm$^{-1}$ in the infrared spectra of the distillates. In none of these reactions could pure products be isolated. This decreased stability is readily understood in terms of the process shown in eq. 4.

This study, as well as our previous investigations, have shown that the phenyl(trihalomethyl)mercury reagents serve excellently in the synthesis of highly halogenated three-membered ring systems, not only hexahalocyclopropanes[11], but also perhalothiiranes[1] and oxiranes of type  $(\mathrm{CF_2X})_2\underbrace{\mathrm{C{-}C}}_{\mathrm{O}}\mathrm{Cl_2}$ (X = F and Cl)[2]. Such syntheses cannot be accomplished in a satisfactory manner with the more usual dihalocarbene reagents.

ACKNOWLEDGMENT

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