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REACTION OF SECONDARY AMINES WITH PHENYL(TRICHLOROMETHYL)MERCURY

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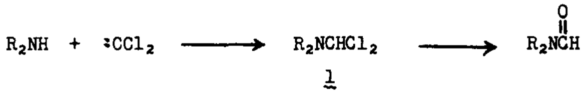
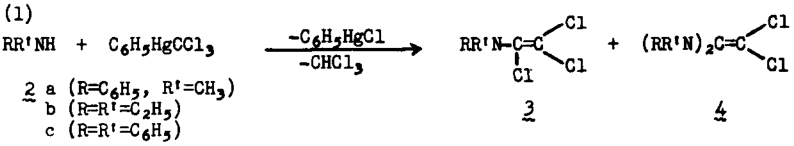
The reaction of secondary amines with chloroform and potassium t-butoxide is reported to give formamides as products, both when reaction mixtures are processed in the presence or absence of water.[1] It has been suggested[1] that the reactions proceed by attack of dichlorocarbene on the amine to give the expected dichloromethylamines 1, and that these intermediates proceed to the observed amides under the reaction conditions or workup.



$$R_2NH + :CCl_2 \longrightarrow \underset{1}{R_2NCHCl_2} \longrightarrow R_2N\overset{O}{\overset{\|}{C}}H$$

We have observed that the reaction of secondary amines with phenyl(trichloromethyl)mercury (the Seyferth[2] procedure for generating dichlorocarbene) proceeds in a different manner, and as summarized by equation 1.

(1)



2 a ($R=C_6H_5$, $R'=CH_3$)
b ($R=R'=C_2H_5$)
c ($R=R'=C_6H_5$)

3

4

Thus, the reaction of N-methylaniline (1 molar equivalent) with phenyl(trichloromethyl)mercury (2 molar equivalents) in benzene solution was

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carried out at 80° for 43 hours. Most of the benzene was removed by distillation and was found to contain chloroform (1 mole, 94% yield). The resulting mixture was treated with petroleum ether (b.p. 60–68°) and filtered to remove phenylmercuric chloride (2 moles, 98% yield). Concentration of the filtrate resulted, in some cases (with diethylamine), in the precipitation of a small amount of diphenylmercury which was removed by filtration before removal of all of the solvent. Distillation of the product gave **3a** as a pale yellow liquid (b.p. 75–90° at 0.01 mm., N_D^{25} 1.5847–1.5860, 14.5%; analytical sample had b.p. 70–71° at 0.02 mm., N_D^{25} 1.5850; found: C, 45.2; H, 3.4; $C_9H_8Cl_3N$ requires C, 45.7; H, 3.4). The pot residue solidified when cooled to give an 84% yield of crude **4a** (m.p. 69–77°), which was purified to m.p. 86–87° (found: C, 62.7; H, 5.2; Cl, 23.3; N, 9.3; $C_{16}H_{16}Cl_2N_2$ requires C, 62.6; H, 5.3; Cl, 23.1; N, 9.1) by recrystallization from petroleum ether (b.p. 60–68°) and from ethanol.

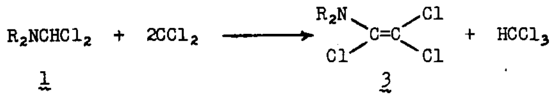
The reactions of diethylamine and diphenylamine with phenyl(trichloromethyl)mercury were carried out in the same manner with the following results: **3b** (collected at 65–95° at 5 mm., N_D^{25} 1.4825, 4% yield), **4b** (b.p. 54° at 0.5 mm., N_D^{25} 1.4927, 42% yield; found: C, 50.3; H, 8.6; Cl, 29.9; $C_{10}H_{20}Cl_2N_2$ requires C, 50.2; H, 8.4; Cl, 29.7), **3c** [isolated by chromatography of the crude product on alumina, using petroleum ether (b.p. 60–68°) as eluant, 45% yield, m.p. 44–48°; analytical sample, m.p. 48–50° from methanol; found: C, 56.4; H, 3.1; N, 4.8; $C_{14}H_{10}Cl_3N$ requires C, 56.3; H, 3.4; N, 4.7], **4c** (none observed).

The trichlorovinylamines **3b** and **3c** had properties and spectra essentially identical to those described by Speziale and Freeman.[3] The olefin **3a** is new and was further characterized by hydrolysis with 4% aqueous hydrochloric acid to the amide (m.p. and mixture m.p. 66–68°) derived from N-methylaniline and dichloroacetylchloride. The analytical sample of this amide had m.p. 68–70° (lit.,[4] m.p. 69.9°).

The _bis_-amines **4** are new; their structures were confirmed by composition, spectra (I.R. and N.M.R.) and by hydrolysis of **4a** to N-methylaniline (85% yield) and 2,2-dichloro-N-methylacetanilide (73% yield) by action of 4% aqueous hydrochloric acid.

The mechanism of this new reaction is unknown; however, the products do not appear anomalous if one assumes that the initially formed dichloromethylamine (**1**) can react with two equivalents of dichlorocarbene or its

$$R_2NH + CCl_2 \longrightarrow \underset{\mathbf{1}}{R_2NCHCl_2}$$

(2) 

$$(3)\quad \mathbf{1} + R_2NH \longrightarrow \underset{\mathbf{5}}{(R_2N)_2CHCl\cdot HCl}$$

$$(4)\quad \mathbf{5} + 3CCl_2 \longrightarrow \underset{\mathbf{4}}{(R_2N)_2C{=}CCl_2} + 2CHCl_3$$

precursor to give **3** (equation 2)* or, alternatively, with a second equivalent

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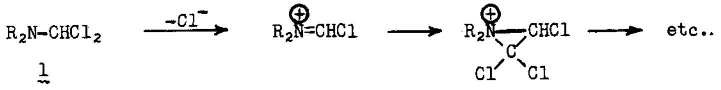
*The dichloromethylamine (**1**) could react with dichlorocarbene, or its precursor, by direct insertion, by prior loss of chloride ion (equation 5), or by prior loss of hydrogen chloride to give a carbonoid intermediate (equation 6); consequently a variety of detailed reaction

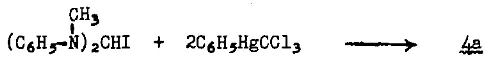
(5) 

$$(6)\quad \mathbf{1} \xrightarrow{-HCl} R_2N\text{-}\ddot{C}Cl \longrightarrow \text{etc.}$$

paths can be formulated for equation 2. Similar considerations obtain for equations 3 and 4.

of amine to give **5** (equation 3) which subsequently reacts with three equivalents of dichlorocarbene or its precursor, to give **4** (equation 4).

The fact that diphenylamine gives **3c**, but no detectable amount of **4c** is not surprising in view of the weak nucleophilic character of this amine. Two additional observations are consistent with the scheme proposed above: (1) the trichlorovinylamine **3a** does not react with N-methylaniline in boiling benzene; consequently, **3a** is not an intermediate in the formation of **4**, and (2) the reaction of **6** (1 equivalent), prepared as described by



$$(C_6H_5\overset{CH_3}{\overset{|}{-N}})_2CHI \quad + \quad 2C_6H_5HgCCl_3 \quad \longrightarrow \quad \mathbf{4a}$$

6

Clemens, Shropshire and Emmons,[5] and phenyl(trichloromethyl)mercury (2 equivalents) gave **4a** (85%, m.p. 51-74°; 33%, m.p. 85-87°, from ethanol).

When the reaction of N-methylaniline with phenyl(trichloromethyl)-mercury was carried out as described above, but in the presence of t-butyl alcohol (2 equivalents), the products were: recovered starting amine (10.7%), **3a** (4%), **4a** (70%, m.p. 47-74°; 47%, m.p. 85-87°) and N-methyl-formanilide (13%).*

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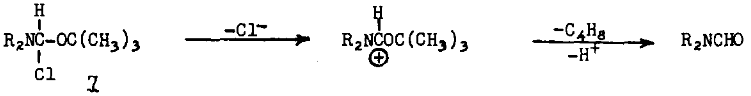
*The formation of formamide when oxygen containing bases are present may occur as summarized by the following equation.



$$R_2N\overset{H}{\underset{Cl}{C}}-OC(CH_3)_3 \xrightarrow{-Cl^-} R_2N\overset{H}{\underset{\oplus}{C}}OC(CH_3)_3 \xrightarrow[-H^+]{-C_4H_8} R_2NCHO$$

7

The proposed intermediate **7** is the expected reaction product of the cation or carbene, described in equation 5 and 6, with t-butyl alcohol or t-butoxide ion.

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