REACTIONS OF 3,3,3-TRICHLOROPROPENE AND 1,1,1,3- TETRACHLOROPROPANE WITH AROMATIC AMINES

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As we showed in a previous paper [1], in the reactions of 3,3,3-trichloropropene and of 1,1,3-trichloropropene with chlorobenzene, with bromobenzene, and with anisole in presence of aluminum chloride, smooth substitution of the group \( \text{CH}_2\text{CH} = \text{CCl}_2 \) occurs in the benzene ring, mainly in the para position:

\[
\begin{align*}
\text{XCH}_2\text{H}_5 + \text{CH}_2\text{Cl} & \rightarrow \text{XCH}_2\text{Cl} + \text{CH}_2 = \text{CCl}_2; \text{AlCl}_3 \rightarrow \text{p-XCH}_2\text{H}_4\text{CH}_2\text{CH} = \text{Cl} + \text{HCl},
\end{align*}
\]

in which \( X = \text{Cl, Br, CH}_3\text{O}. \)

With phenol, both in presence and in absence of aluminum chloride, a mixture of ortho and para derivatives is obtained on heating, but with alkaline aqueous sodium phenoxide, not only ortho and para C-alkylation occurs, but also O-oxidation with formation altogether of three substances:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{OH} + \text{CH}_2 = \text{CH} = \text{CCl}_2 & \rightarrow \text{p-HOC}_6\text{H}_4\text{CH}_2\text{CH} = \text{Cl} + \text{HCl}; \\
\text{CH}_2\text{Cl} = \text{CH} = \text{CCl}_2 & \rightarrow \text{O-HOC}_6\text{H}_4\text{CH}_2\text{CH} = \text{Cl} + \text{C}_6\text{H}_5\text{OCH}_2\text{CH} = \text{Cl}.
\end{align*}
\]

In the present investigation we studied the reactions of 3,3,3-trichloropropene with aniline, N-methylaniline, and N,N-dimethylaniline in absence of catalysts and also the reactions of the first two aromatic amines with 1,1,1,3-tetrachloropropane. On analogy with phenol [1] and diethylamine [2], in the reactions of aniline and N-methylaniline with 3,3,3-trichloropropene we might expect both N- and C-alkylation to occur. Actually, under the conditions studied only N-alkylation products were obtained. Thus, in the reaction of 3,3,3-trichloropropene with aniline a good yield was obtained of N-(3,3-dichloroallyl)aniline, the structure of which was proved by its conversion into the hydrochloride of N-phenyl-\( \beta \)-alanine ether ester and determination of the melting point of this in admixture with the hydrochloride obtained by reaction of aniline with ethyl 3-chloropropionate. A low yield was obtained also of a product containing two 3,3-dichloroallyl groups per molecule of aniline and probably having the tertiary amine structure \( \text{C}_6\text{H}_6\text{N}(\text{CH}_2\text{CH} = \text{CCl}_2)\). This structure is in accord with the fact that the substance cannot be acylated and can be prepared in high yield by heating the above mentioned N-(3,3-dichloroallyl)aniline with excess of 3,3,3- or 1,1,3-trichloropropane, the reaction being analogous with the reactions of the same trichloropropenes with N-methylaniline. N-methyl- and N,N-dimethyl-anilines gave the same substance, \( \text{C}_6\text{H}_5\text{N}(\text{CH}_2\text{CH} = \text{CCl}_2)\).

This structure is the only one possible, since in the case of alkylation of the aromatic ring two different substances would be obtained. Reaction with N,N-dimethylaniline was accompanied by elimination of methyl chloride, probably from the intermediately formed quaternary ammonium compound \( [\text{C}_6\text{H}_6\text{N}(\text{CH}_2\text{CH} = \text{CCl}_2)]\text{Cl}. \)
In all the cases studied, 1,1,3-trichloropropene (CH₂CH-CH = CCl₃) reacts with aromatic amines just like 3,3,3-trichloropropene. It has been noted on several occasions that 1,1,1,3-tetrachloropropane differs from higher α,α,α,ω-tetrachloroalkanes in that the lone chlorine cannot be replaced by other atoms or groups by the action of nucleophilic reagents [3, 4]. In the reactions of 1,1,3-tetrachloropropane with aniline and N-methylaniline, we succeeded in obtaining in low yield and identifying in the form of hydrochlorides two compounds of the following structures: C₆H₅NHCH₂CH₂CCl₃ and C₆H₅N(CH₃) CH₂CH₂CCl₃. The structure of the first of these was proved by the following transformations

\[
\begin{align*}
C₆H₅NHCH₂CH₂CCl₃ & \rightarrow C₆H₅N(COCH₃) CH₂CH₂CCl₃ \rightarrow C₆H₅N(COCH₃)CH₂CH = CCl₂ \rightarrow \nonumber \\
& \rightarrow C₆H₅N(COCH₃) CH₂CH₂COOH 
\end{align*}
\]

and determination of the melting point of a mixture of the final product with a known sample of N-acetyl-N-phenyl-β-alanine. The structure of the second compound was proved by its conversion with sodium ethoxide into C₆H₅N(CH₃) CH₂CH = CCl₂, conversion of this into its hydrochloride, and determination of the melting point of a mixture of the product and an authentic sample of the hydrochloride.

**EXPERIMENTAL**

Reaction of 3,3,3-Trichloropropene with Aniline. A mixture of 75 g of CCl₃ CH = CH₂ and 325 g of freshly distilled aniline was boiled for one hour, treated with saturated sodium carbonate solution, cooled, and extracted with ether. The ether extracts were dried over calcined sodium sulfate. After removal of solvent and excess of aniline (under reduced pressure), the residue was fractionated.

Fraction I, amounting to 81 g (77%), had b.p. 122-123°C (4 mm), nD²⁰ 1.5873; d₄¹° 1.2522. It was a colorless liquid which smelled like aniline. As will be shown below, it was N-(3,3-dichloroallyl) aniline C₆H₅NHCH₂CH = CCl₂.

Found %: C 53.74; 53.72; H 4.52; 4.57 C₆H₅Cl₂N. Calculated %: C 53.49; H 4.49

Its hydrochloride (from concentrated hydrochloric acid or alcohol-ether mixture) had m.p. 144-145°C.

Found %: C 45.32; 45.10; H 4.24; 4.25 C₁₃H₁₀Cl₂N. Calculated %: C 45.31; H 4.23

Fraction II, amounting to 5 g (5%), had b.p. 156-157°C (3.5 mm), nD²⁰ 1.5946; d₄¹° 1.3516.

Found %: C 46.61; 46.63; H 3.62; 3.67 C₁₂H₁₁Cl₂N. Calculated %: C 46.34; H 3.57

The chemical behavior of Fraction II corresponded to that of the tertiary base C₆H₅N(CH₃) CH₂CH = CCl₂, the hydrochloride of which has m.p. 139-140°C (from benzene). The same base was obtained in 65% yield by heating N-(3,3-dichloroallyl) aniline with excess of 1,1,3-trichloropropene. The identity of the two hydrochlorides was proved by a mixture melting point test.

Found %: Cl 51.07; 51.15 C₁₃H₁₃Cl₂N. Calculated %: Cl 51.02

N-Phenyl-β-alanine Ethyl Ester. A mixture of 30.3 g of C₆H₅NHCH₂CH = CCl₂, prepared as described above, and 120 g of 94% H₂SO₄ was heated with stirring for one hour at 120-145°C. After about 96% of the calculated amount of hydrogen chloride had been liberated, 60 ml of ethanol was added gradually to the hot reaction mixture, after which the solution was heated for a further 20 minutes at 80-90°C. The cooled reaction mixture was added carefully to a concentrated aqueous solution of sodium carbonate and extracted with ether or chloroform. Solvent was distilled off, and vacuum-distillation of the residue gave 23 g (80%) of N-phenyl-β-alanine ethyl ester, b.p. 146-147°C (6 mm), nD³₀ 1.5313; d₂³¹ 1.0679. The melting point of the hydrochloride was 98-99°C (from ethanol-ether). The literature [5] gives b.p. 185-186°C (30 mm), nD³₀ 1.5315; d₂³¹ 1.0709 for the free amino ester and m.p. 98-99°C for the hydrochloride. The hydrochloride obtained gave no depression of