CHLORINATION

1. Chlorination of Ethyl-β-anilino crotonate:

(α-chloro-β-anilino crotonic ester, hydrochloride)

Ethyl-β-anilino crotonate (10.25 g.) was dissolved in chloroform (30 c.c.) and an excess dry chlorine was passed into it. On account of the sparing solubility of the free chloro derivative, most of it fell out of the solution almost immediately. The solution was allowed to stand for thirty minutes. The product was collected. The mother liquor on evaporation gave more of the same product. Total yield: 8.2 g. (59.2 %).

The product was washed with ether (30 c.c.). It was crystallised from alcohol, m.p. 196°. The product can be precipitated from the alcoholic mother liquor by dilution with ether. (Found: Cl, 25.5 %; C₁₂H₁₅NO₂Cl₂ requires: Cl, 25.7 %). It has the following properties:

1. It is very soluble in water, soluble in alcohol, but insoluble in ether, benzene etc.
2. Its aqueous solution is strongly acidic to litmus.

3. Its aqueous solution when treated with silver nitrate gives precipitates of silver bromide. The same thing happens in its alcoholic solution.

**Estimation of chlorine (Volhard method):**

The chloro compound (0.2 g.) was dissolved in distilled water. Silver nitrate (0.4 g.) in distilled water was added to it, when precipitates of silver chloride were obtained, which were filtered off and the filtrate titrated back against N/20 ammonium sulphocyanide, using ferric indicator. (Found: Cl, 25.6 %; C_{12}H_{15}NO_{2}Cl_{2} requires: Cl, 25.7 %).

This proves that there are two chlorine atoms in the side-chain which are ionizable or rather accurately speaking, which are susceptible to the attack of silver nitrate and therefore easily removable, that is to say which become ionizable during treatment with silver nitrate.

4. On treatment with sodium hydroxide, an oil separates.
which on acetylation gave acetonilide, m.p. 113 C. It was therefore concluded that chlorine did not enter the nucleus and further that both the chlorine atoms were present in the side-chain of the compound.

5. The chloro compound also decomposes with one equivalent of either sodium hydroxide or silver nitrate, liberating aniline. Further, half the amount of the chloro compound remained unchanged.

6. It gave a deep purple colour with chlorine water. The above properties do not warrant an \( \alpha \)-dichloride structure which might have been formed as an unstable intermediate product. Further, it appears that the hydrochloride salt alone is stable and not the \( \alpha \)-chloro free unsaturated anilino crotonic ester.

2. Chlorination of ethyl-\( \alpha \)-(o-toluidino) crotonate:

\( \alpha \)-chloro-\( \alpha \)-(o-toluidino) crotonic ester, hydrochloride

Ethyl-\( \alpha \)-(o-toluidino) crotonate (10.95 g.)
was dissolved in chloroform (30 c.c.) and excess dry chlorine was passed into it. The product was worked up as before. Yield: 7.3 g. (50.6%). It was crystallised from alcohol, m.p. 207-2°C. (Found: Cl, 24.3%)

\[ C_{15}H_{17}NO_2Cl_2 \text{ requires: } Cl, \ 24.4\% \] Its properties are similar to those of the previous compound.

On treatment with sodium hydroxide, it gave o-toluidine which on acetylation gave aceto-o-toluidide, m.p. 110°C. Mixed m.p. with an authentic specimen was undepressed. It was therefore concluded that chlorine did not enter the nucleus.

It gave purple colouration with chlorine water.

3. Chlorination of ethyl-\( \beta \)-(m-toluidino) crotonate:

( \( \alpha \)-chloro-\( \beta \)-(m-toluidino) crotonic ester, hydrochloride )

Ethyl-\( \beta \)-(m-toluidino) crotonate (10.95 g.) was dissolved in chloroform (30 c.c.) and excess dry chlorine was passed into it. The product was worked up as before. Yield: 6.5 g. (44.8%). (Found: Cl,
24.1 %; \( C_{13}H_{17}NO_2Cl_2 \) requires: Cl, 24.4 %). It was crystallised from alcohol, m.p. 214 °C. Its properties are similar to those of the previous compound.

On treatment with sodium hydroxide, it gave m-toluidine, which on acetylation gave aceto-m-toluidide, m.p. 63 °C. Mixed m.p. with an authentic specimen was undepressed. It was therefore concluded that chlorine did not enter the nucleus.

It gave pinkish blue colouration with chlorine water.

4. Chlorination of ethyl-\( \beta-\) (p-toluidino) crotonate:

\( \beta-\) (\( \alpha-\) chloro-\( \beta-\) (p-toluidino) crotonic ester, hydrochloride)

Ethyl-\( \beta-\) (p-toluidino) crotonate (10.95 g.) was dissolved in chloroform (30 c.c.) and excess dry chlorine was passed into it. The product was worked up as before. Yield: 7.9 g. (54.7 %). It was crystallised from alcohol, m.p. 228-30 °C. (Found: Cl, 24.6 %)
were similar to those of the previous compound. 

Untreatment with sodium hydroxide, it gave p-toluidine, m.p. 45° C, which on acetylation gave aceto-p-toluidide, m.p. 148° C. Mixed m.p. with an authentic specimen was undepressed. It was therefore concluded that chlorine did not enter the nucleus.

It gave pink colouration with chlorine water.

5. Chlorination of ethyl-β-(o-chloroanilino) crotonate:

(α-chloro-β-(o-chloroanilino) crotonic ester, hydrochloride)

Ethyl-β-(o-chloroanilino) crotonate (11.37 g.) was dissolved in chloroform (30 c.c.) and excess dry chlorine was passed into it. The product was worked up as before. Yield: 8.7 g. (56.2 %). It was crystallised from alcohol, m.p. 222-24° (sublimation). (Found: Cl, 22.7 %; C_{12}H_{14}NO_{2}Cl \_3 requires: Cl, 22.9 %). Its properties were similar to those of the previous compound.
On treatment with sodium hydroxide, it gave o-chloroaniline which on acetylation gave o-chloro-acetanilide, m.p. 87°C. Mixed m.p. with an authentic specimen was undepressed. It was therefore concluded that chlorine did not enter the nucleus.

It gave orange colouration with chlorine water.

6. Chlorination of ethyl-\( p\)-(m-chloroanilino) crotonate:

( \( \alpha\)-chloro-\( p\)-(m-chloroanilino) crotonic ester, hydrochloride)

Ethyl-\( p\)-(m-chloroanilino) crotonate (11.97 g.) was dissolved in chloroform (30 c.c.) and excess dry chlorine was passed into it. The product was worked up as before. Yield: 7.9 g. (50.8%). It was crystallised from alcohol, m.p. 222°C. (Found: Cl, 22.6%)

\( \text{C}_1\text{H}_4\text{Cl}_7\text{NO}_2\text{Cl}_3 \) requires: Cl, 22.9%). Its properties were similar to those of the previous compound.

On treatment with sodium hydroxide, it gave m-chloroaniline which on acetylation gave m-chloro-acetanilide, m.p. 72°C. Mixed m.p. with an authentic
specimen was undepressed. It was therefore concluded that chlorine did not enter the nucleus.

It gave brick red colouration with chlorine water.

7. Chlorination of ethyl-$\beta$-(p-chloroanilino) crotonate:

( $\alpha$-chloro-$\beta$-(p-chloroanilino) crotonic ester hydrochloride )

ethyl-$\beta$-(p-chloroanilino) crotonate (11.97 g.) was dissolved in chloroform (30 c.c.) and excess dry chlorine was passed into it. The product was worked up as before. Yield: 7.3 g. (47.2%). It was crystallised from alcohol, m.p. 244-48°C (sublimation). ( Found: Cl, 23.0%; C$_{12}$H$_{14}$NO$_2$Cl$_3$ requires: Cl, 22.9% ). Its properties were similar to those of the previous compound.

On treatment with sodium hydroxide, it gave p-chloroaniline, m.p. 70°C, which on acetylation gave p-chloroacetanilide, m.p. 179°C. Mixed m.p. with an authentic specimen was undepressed. It was therefore concluded that chlorine did not enter the nucleus.

It gave chocolate red colouration with chlorine
water.

8. Chlorination of Ethyl-β-(o-anisidino) crotonate:

( α-chloro-β-(o-anisidino) crotonic ester, hydrochloride)

Ethyl-β-(o-anisidino) crotonate (12.4 g.) was dissolved in chloroform (30 c.c.) and excess dry chlorine was passed into it. The product was worked up as before. Yield: 8.6 g. (56.2 %). It was crystallised from alcohol, m.p. 224° C. (Found: Cl, 23.0 %; C_{13}H_{17}NO_{3}Cl_{2} requires: Cl, 23.2 %). Its properties were similar to those of the previous compound.

On treatment with sodium hydroxide, it gave o-anisidine, which on acetylation gave aceto-o-anisidine, m.p. 84° C. Mixed m.p. with an authentic specimen was undepressed. It was therefore concluded that chlorine did not enter the nucleus.

It gave blood red colouration with chlorine water.

9. Chlorination of Ethyl-β-(p-anisidino) crotonate:
(α-chloro-β-(p-anisidino) crotonic ester hydrochloride)

Ethyl-β-(p-anisidino) crotonate (12.4 g.)

was dissolved in chloroform (30 c.c.) and excess dry chlorine was passed into it. The product was worked up as before. Yield: 7.9 g. (51.5%). It was crystallised from alcohol, m.p. 215-12° C. (Found: Cl, 23.4%)

C_{13}H_{17}NO_{3}Cl_{2} requires: Cl, 23.2%). Its properties are similar to those of the previous compound.

On treatment with sodium hydroxide, it gave p-anisidine, m.p. 57° C, which on acetylation gave aceto-p-anisidine, m.p. 127° C. Mixed m.p. with an authentic specimen was undepressed. It was therefore concluded that chlorine did not enter the nucleus.

It gave purple colouration with chlorine water.

10. Chlorination of ethyl-β-(o-phenetidino) crotonate:

(α-chloro-β-(o-phenetidino) crotonic ester, hydrochloride)
Ethyl-β-(o-phenetidino) crotonate (13 g.) was dissolved in chloroform (30 c.c.) and excess dry chlorine was passed into it. The product was worked up as before. Yield: 8.8 g. (54.8%). It was crystallised from alcohol, m.p. 201-2 °C. (Found: Cl, 21.9%)

\[ C_{14}H_{19}NO_3Cl_2 \text{ requires: Cl, 22.2%} \]. Its properties were similar to those of the previous compound.

On treatment with sodium hydroxide, it gave o-phenetidino, which on acetylation gave aceto-o-phenetidido, m.p. 79 °C. Mixed m.p. with an authentic specimen was undepressed. It was therefore concluded that chlorine did not enter the nucleus.

It gave blood red colouration with chlorine water.