

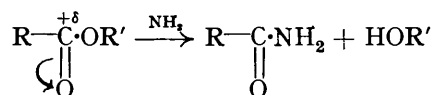
83. *The Action of Ammonia upon Esters.*

By F. D. CHATAWAY.

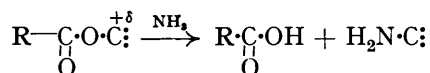
THE behaviour of esters under the action of ammonia affords a striking example of the influence of substituted atoms or groups upon the reactivity of the carbon atoms of an aliphatic chain.

When ammonia, an amine, or a hydrazine reacts with an ester, an amide or a hydrazide is usually formed together with the alcohol corresponding to the original ester. This type of reaction is so common that it has come to be regarded as the invariable way in which such reactions occur. It appears to be initiated by the greater attraction which

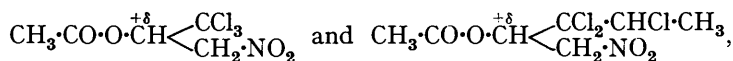
the donor molecule, ammonia, has for the kationoid carbon of the acyl group than for the electron-repelling alkyl group :



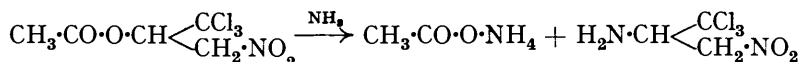
If this electronic state could be reversed by the introduction of a powerful kationoid centre in the alkyl group itself, then the donor molecule might attack not only the acyl group but to a greater or less extent the alkyl group, so that amines and hydrazines together with a salt of the ester acid would result :



Such a condition is realised in the acetic esters of the $\gamma\gamma\gamma$ - and $\gamma\gamma\delta$ -trichloro- α -nitro- β -hydroxy-paraffins (Chattaway and Witherington, J., 1935, 1178),



where in the highly substituted propyl and amyl groups both the CCl_3 and the $\text{CCl}_2\cdot\text{CHCl}\cdot\text{CH}_3$, and still more the $\text{CH}_2\cdot\text{NO}_2$ group are strongly electron-attracting. As a result, the carbon atom attached to these electron-attracting groups has become so kationoid that when the esters are acted upon by a donor molecule, such as ammonia, a primary amine, or a hydrazine, the carbon attached to the two kationoid groups and not the carbon atom of the carbonyl group becomes the point of attack and the resulting fission of the ester therefore yields a salt of acetic acid and an amine, an aniline, or a hydrazine. For example, when $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxypentane reacts with ammonia, $\gamma\gamma\gamma$ -trichloro- α -nitro- β -aminopropane and ammonium acetate are formed :



and similarly $\gamma\gamma\delta$ -trichloro- α -nitro- β -acetoxypentane yields ammonium acetate and $\gamma\gamma\delta$ -trichloro- α -nitro- β -aminopentane, $\text{CH}_3\cdot\text{CHCl}\cdot\text{CCl}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NO}_2$.

Precisely similar reactions occur when *p*-toluidine reacts with these esters, $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{NO}_2$ and $\text{CH}_3\cdot\text{CHCl}\cdot\text{CCl}_2\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{NO}_2$, being formed, and when they react with phenylhydrazine the corresponding hydrazines $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{NHPh})\cdot\text{CH}_2\cdot\text{NO}_2$ and $\text{CH}_3\cdot\text{CHCl}\cdot\text{CCl}_2\cdot\text{CH}(\text{NH}\cdot\text{NHPh})\cdot\text{CH}_2\cdot\text{NO}_2$ result.

The substituted amines and hydrazines thus formed show the usual behaviour of such compounds, forming, for example, stable well-characterised salts and acyl derivatives, the two *acetamido*-compounds crystallising especially well.

EXPERIMENTAL.

$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -aminopropane.—A solution of 25 g. of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxypentane (Chattaway and Witherington, J., 1935, 1179) in 30 c.c. of absolute alcohol (99.5%) was cooled in ice, saturated with dry ammonia, and kept at the ordinary temperature, protected from moisture, for 2 days. Most of the alcohol and any excess of ammonia were then evaporated on a water-bath, best under somewhat diminished pressure. A slight smell of acetamide was noticed during the evaporation. Excess of dilute hydrochloric acid was then added and the liquid was warmed with animal charcoal, filtered, and evaporated to dryness. The dry mixture of the hydrochlorides of ammonia and $\gamma\gamma\gamma$ -trichloro- α -nitro- β -aminopropane obtained was washed with a small quantity of an alcoholic solution of hydrogen chloride and dissolved in a little water. The solution was strongly cooled in a freezing mixture, and the $\gamma\gamma\gamma$ -trichloro- α -nitro- β -aminopropane liberated by cautious addition of a concentrated solution of potassium hydroxide. As the base dissolves readily in a strongly alkaline solution, any excess of alkali must be avoided. It separated as a liquid, which was best extracted by ether and obtained by distillation in a vacuum as a pale yellow liquid, b. p. $108^\circ/2$ mm. (Found: Cl, 57.1. $\text{C}_3\text{H}_5\text{O}_2\text{N}_2\text{Cl}_3$ requires Cl, 57.3%). The *hydrochloride* crystallised from dilute hydrochloric

acid in nodular aggregates of small, almost colourless prisms with a faint yellow tint (Found: Cl as HCl, 14.7; total Cl, 58.4. $C_3H_5O_2N_2Cl_3 \cdot HCl$ requires Cl as HCl, 14.6; total Cl, 58.2%).

When the base was warmed with a slight excess of acetic anhydride, it yielded $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetamidopropane, $CCl_3 \cdot CH(NHAc) \cdot CH_2 \cdot NO_2$, which crystallised from hot alcohol, in which it was readily soluble, in clusters of long transparent prisms, almost colourless with a very faint yellow tint, m. p. 137° (Found: Cl, 42.7. $C_5H_7O_3N_2Cl_3$ requires Cl, 42.7%).

$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -*p*-toluidinopropane.—25 G. (1 mol.) of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxyp propane and 22 g. (2 mols.) of *p*-toluidine were dissolved in 100 c.c. of 99.5% alcohol and heated to gentle boiling for 15–20 minutes until most of the alcohol had boiled away. The issuing vapour was distinctly acid from the liberation of acetic acid. The whole was poured into water and the viscous mass obtained was well washed with dilute acetic acid and finally with water and dissolved in hot alcohol. On cooling, $\gamma\gamma\gamma$ -trichloro- α -nitro- β -*p*-toluidinopropane separated in large yellow compact crystals, readily soluble in warm alcohol or light petroleum, from which it crystallised in aggregates of very pale yellow rhombs, m. p. 61° (Found: Cl, 35.6; N, 9.5. $C_{10}H_{11}O_2N_2Cl_3$ requires Cl, 35.8; N, 9.5%).

$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -phenylhydrazinopropane.—25 G. (1 mol.) of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxyp propane and 22 g. (1 mol.) of phenylhydrazine were dissolved in 50 c.c. of 99.5% alcohol and heated to gentle boiling for 10 minutes. $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -phenylhydrazinopropane, which separated on cooling, crystallised from boiling alcohol, in which it was moderately easily soluble, in very pale yellow, six-sided prisms with domed ends, m. p. about 120° (decomp.; rapid heating) (Found: C, 36.4; H, 3.2; N, 14.1; Cl, 35.7. $C_9H_{10}O_2N_3Cl_3$ requires C, 36.2; H, 3.0; N, 14.1; Cl, 35.6%). When heated with acetic anhydride, it formed $\gamma\gamma\gamma$ -trichloro- α -nitro- β -diacetylphenylhydrazinopropane, $CCl_3 \cdot CH(NAc \cdot NAcPh) \cdot CH_2 \cdot NO_2$. This crystallised from glacial acetic acid in colourless, six-sided, flattened prisms with domed ends, m. p. 199–200° (decomp.; rapid heating), but the exact m. p. depends on the rate of heating (Found: N, 11.1; Cl, 27.9. $C_{13}H_{14}O_4N_3Cl_3$ requires N, 11.0; Cl, 27.8%).

A number of other hydrazino-derivatives were similarly prepared: $\gamma\gamma\gamma$ -trichloro- α -nitro- β -*p*-tolylhydrazinopropane crystallised from alcohol in very pale yellow, six-sided prisms with domed ends, m. p. 115° (Found: Cl, 34.1. $C_{10}H_{12}O_2N_3Cl_3$ requires Cl, 34.1%), and its diacetyl derivative from acetic acid in thin, colourless, four-sided plates, m. p. 157–158° (Found: Cl, 27.2. $C_{14}H_{16}O_4N_3Cl_3$ requires Cl, 26.9%). $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -*p*-chlorophenylhydrazinopropane separated from alcohol in very pale yellow, stout, six-sided prisms with domed ends, m. p. 118° (Found: Cl, 42.7. $C_9H_9O_2N_3Cl_4$ requires Cl, 42.6%), and its diacetyl derivative from acetic acid, in which it was sparingly soluble, in clusters of small colourless plates, m. p. 152° (Found: Cl, 33.7. $C_{13}H_{13}O_4N_3Cl_4$ requires Cl, 33.6%). $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -2:4-dichlorophenylhydrazinopropane formed very pale yellow needles, m. p. 79°, from alcohol (Found: Cl, 47.7. $C_9H_8O_2N_3Cl_5$ requires Cl, 48.3%), and its diacetyl derivative, slender colourless prisms, m. p. 125°, from acetic acid (Found: N, 9.8; Cl, 40.1. $C_{13}H_{12}O_4N_3Cl_5$ requires N, 9.5; Cl, 39.3%). $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -*m*-nitrophenylhydrazinopropane crystallised from alcohol in bright yellow, rhombic plates, m. p. 112–113° (Found: N, 16.2; Cl, 31.2. $C_9H_9O_4N_4Cl_3$ requires N, 16.3; Cl, 31.0%).

$\gamma\gamma\delta$ -Trichloro- α -nitro- β -acetoxypentane reacts with ammonia, amines, and hydrazines in a similar manner to $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxyp propane.

$\gamma\gamma\delta$ -Trichloro- α -nitro- β -aminopentane was prepared by saturating a solution of $\gamma\gamma\delta$ -trichloro- α -nitro- β -acetoxypentane in absolute alcohol (99.5%) with dry ammonia, isolated as the hydrochloride, and liberated from its mixture with ammonium chloride much as previously described. It crystallised from alcohol in aggregates of colourless plates, m. p. 54–55° (Found: N, 11.7; Cl, 45.3. $C_5H_9O_2N_2Cl_3$ requires N, 11.9; Cl, 45.2%). The very easily soluble hydrochloride crystallised from dilute hydrochloric acid in small, colourless, short, six-sided prisms with domed ends (Found: Cl as HCl, 13.1; total Cl, 52.3. $C_5H_9O_2N_2Cl_3 \cdot HCl$ requires Cl as HCl, 13.1; total Cl, 52.2%). When heated with acetic anhydride, the base formed a well-crystallised monoacetyl derivative, which separated from acetic acid in thin, colourless, elongated, transparent plates, m. p. 104° (Found: Cl, 38.6. $C_7H_{11}O_3N_2Cl_3$ requires Cl, 38.4%).

$\gamma\gamma\delta$ -Trichloro- α -nitro- β -*p*-toluidinopentane.—28 G. (1 mol.) of $\gamma\gamma\delta$ -trichloro- α -nitro- β -acetoxypentane and 22 g. (2 mols.) of *p*-toluidine were dissolved in 200 c.c. of alcohol (99.5%) and heated to gentle boiling for about $\frac{1}{2}$ hour until the bulk was reduced to half; the mixture was then poured into excess of water. The product was well washed with dilute acetic acid and finally with water. This is necessary to remove the excess of toluidine and any small amount of unchanged ester, as, if these are not removed, subsequent crystallisation is difficult. The viscous mass thus obtained was dissolved in a little hot alcohol and cooled; $\gamma\gamma\delta$ -trichloro- α -

nitro-β-p-toluidinopentane then separated in short, compact, six-sided, yellow prisms, m. p. 110° (Found : N, 8·8; Cl, 32·4. $C_{12}H_{15}O_2N_2Cl_3$ requires N, 8·6; Cl, 32·7%).

γγδ-Trichloro-α-nitro-β-phenylhydrazinopentane, prepared similarly to the previous compound, crystallised from hot alcohol, in which it was moderately easily soluble, in aggregates of slender, flattened, six-sided prisms, almost colourless with a very faint yellow tint, m. p. 129° (Found : Cl, 32·6. $C_{11}H_{14}O_2N_2Cl_3$ requires Cl, 32·6%). Heated with excess of acetic anhydride, it formed a *monoacetyl* compound, which crystallised from alcohol in six-sided prisms, almost colourless with a very faint yellow tint, m. p. 111° (Found : N, 11·3; Cl, 29·1. $C_{13}H_{16}O_3N_3Cl_3$ requires N, 11·4; Cl, 28·9%). The action of acetic anhydride does not so easily carry the acetylation further, as with *γγγ-trichloro-α-nitro-β-phenylhydrazinopropane*, for when the monoacetyl compound was dissolved in hot acetic anhydride and cooled, it separated unchanged. When, however, it was heated with acetic anhydride in presence of a drop of concentrated sulphuric acid, the *diacetyl* compound was formed. It crystallised from acetic acid in colourless slender prisms, m. p. 158—159° (Found : Cl, 26·3. $C_{15}H_{18}O_4N_3Cl_3$ requires Cl, 25·9%).

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