11. *The Condensation of Chloral with Tolyl- and Nitrophenyl-ureas.*

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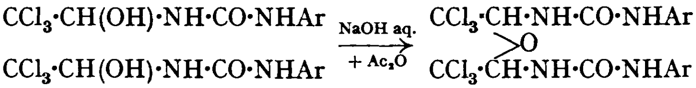
Chloral condenses readily with *o*- and *p*-tolylurea, and with *m*- and *p*-nitrophenylurea, at 100°, crystalline N-*aryl*-N′-βββ-*trichloro*-α-*hydroxyethylureas* being formed:

$$CCl_3\cdot CHO + H_2N\cdot CO\cdot NHAr \longrightarrow CCl_3\cdot CH(OH)\cdot NH\cdot CO\cdot NHAr.$$

The condensation products yield with acetic anhydride *diacetyl* derivatives, $CCl_3\cdot CH(OAc)\cdot NH\cdot CO\cdot NAcAr$. They dissolve in cold dilute sodium hydroxide, and separate unchanged if the solutions are immediately acidified. When such solutions are kept for any length of time, or are heated, the chloral condensation product is hydrolysed to chloroform, sodium formate, and the parent urea.

From well-cooled freshly-made alkaline solutions and acetic anhydride, ***anhydro-compounds*** of ether-like structure are formed,



$$\begin{matrix} CCl_3\cdot CH(OH)\cdot NH\cdot CO\cdot NHAr \\ CCl_3\cdot CH(OH)\cdot NH\cdot CO\cdot NHAr \end{matrix} \xrightarrow[+\,Ac_2O]{NaOH\ aq.} \begin{matrix} CCl_3\cdot CH\cdot NH\cdot CO\cdot NHAr \\ \quad >O \\ CCl_3\cdot CH\cdot NH\cdot CO\cdot NHAr \end{matrix}$$

which with acetic anhydride yield *diacetyl* derivatives, $[NAcAr\cdot CO\cdot NH\cdot CH(CCl_3)]_2O$.

When a solution of one of these ethers and a sodium alkoxide in the corresponding alcohol is kept for some time, fission occurs at the ether linkage and an N-*aryl*-N′-βββ-*trichloro-α-alkoxyethylurea*, $CCl_3\cdot CH(OR)\cdot NH\cdot CO\cdot NHAr$, is formed. These alkoxy-compounds can more conveniently be made directly from the chloral ureas without isolation of the anhydro-compound by adding slightly more than the equivalent of acetic anhydride to a well-cooled solution of the *N*-aryl-*N*′-βββ-trichloro-α-hydroxyethylurea in alcoholic potash.

EXPERIMENTAL.

N-o-*Tolyl*-N′-βββ-*trichloro-α-hydroxyethylurea*, obtained as a colourless viscid mass by heating 15 g. of *o*-tolylurea and 25 g. (1 mol. + excess) of chloral hydrate on a water-bath for 15 min., crystallised from aq. EtOH in long, slender, colourless prisms, m. p. 146° (decomp.) (Found : Cl, 35·5. $C_{10}H_{11}O_2N_2Cl_3$ requires Cl, 35·8%). Its *diacetyl* derivative crystallised from boiling AcOH in small, compact, colourless prisms, m. p. 114° (decomp.) (Found : Cl, 27·7. $C_{14}H_{15}O_4N_2Cl_3$ requires Cl, 27·9%).

Bis-(βββ-*trichloro*-α-N′-o-*tolylcarbamidoethyl*) *Ether*.—To a solution of 10 g. of *N*-*o*-tolyl-*N*′-βββ-trichloro-α-hydroxyethylurea in 100 c.c. of ice-cold *N*-NaOH, 5 g. of Ac_2O were added drop by drop at 0—5°. The *ether* separated as a colourless flocculent solid and crystallised from boiling aq. EtOH in long colourless prisms, m. p. 198° (decomp.) (Found : Cl, 36·9. $C_{20}H_{20}O_3N_4Cl_6$ requires Cl, 36·9%). Its *diacetyl* derivative crystallised from aq. EtOH in clusters of short colourless prisms, m. p. 166° (decomp.) (Found : Cl, 32·2. $C_{24}H_{24}O_5N_4Cl_6$ requires Cl, 32·2%).

N-o-*Tolyl*-N′-βββ-*trichloro-α-ethoxyethylurea*.—(1) To 5 g. of the preceding ether in 15 c.c. of EtOH, 0·2 g. of Na in 20 c.c. of EtOH was added. After 12 hr., during which time sodium formate separated, the liquid was poured into 200 c.c. of cold H_2O; N-o-*tolyl*-N′-βββ-*trichloro-α-ethoxyethylurea* then separated. It crystallised from boiling aq. EtOH in long colourless prisms, m. p. 136° (decomp.).

(2) 10 G. of *N*-*o*-tolyl-*N*′-βββ-trichloro-α-hydroxyethylurea were dissolved in an ice-cold solution of 4 g. of KOH in 100 c.c. of EtOH, 5 g. of Ac_2O added drop by drop, and, after standing at room temp. for ½ hr., the whole was poured into 300 c.c. of cold H_2O; *N*-*o*-tolyl-*N*′-βββ-trichloro-α-ethoxyethylurea then separated and was crystallised as before (Found : Cl, 32·6. $C_{12}H_{15}O_2N_2Cl_3$ requires Cl, 32·7%).

N-o-*Tolyl*-N′-βββ-*trichloro-α-methoxyethylurea*, prepared by similar methods, crystallised from boiling aq. EtOH in colourless lustrous plates, m. p. 157° (decomp.) (Found : Cl, 34·1. $C_{11}H_{13}O_2N_2Cl_3$ requires Cl, 34·2%).

By analogous reactions the following compounds were prepared from other ureas.

N-p-*Tolyl*-N′-βββ-*trichloro-α-hydroxyethylurea*, colourless compact bi-pyramids from aq. EtOH; m. p. 181° (decomp.) (Found : Cl, 35·6%). N-*Acetyl*-N-p-*tolyl*-N′-βββ-*trichloro-α-acetoxyethylurea*, colourless unctuous leaflets from aq. AcOH; m. p. 120° (decomp.) (Found : Cl, 27·8%). *Bis*-(βββ-*trichloro*-α-N′-p-*tolylcarbamidoethyl*) *ether*, long, colourless, irregular prisms from EtOH; m. p. 203° (decomp.) (Found : Cl, 36·3%). *Bis*-(βββ-*trichloro*-α-N′-*acetyl*-N′-p-*tolylcarbamidoethyl*) *ether*, compact colourless prisms from EtOH; m. p. 167° (decomp.) (Found : Cl, 32·1%). N-p-*Tolyl*-N′-βββ-*trichloro-α-methoxyethylurea*, colourless flattened prisms from aq. EtOH; m. p. 149° (decomp.) (Found : Cl, 33·8%). N-p-*Tolyl*-N′-βββ-*trichloro-α-ethoxyethylurea*, colourless flattened prisms from aq. EtOH; m. p. 136° (decomp.) (Found : Cl, 32·6%).

N-p-*Nitrophenyl*-N′-βββ-*trichloro-α-hydroxyethylurea*, obtained from *p*-nitrophenylurea prepared by Pierron's method (*Ann. Chem.*, 1908, **2**, 180), formed long, slender, pale yellow prisms from aq. EtOH; m. p. 196° (decomp.) (Found : Cl, 31·9. $C_9H_8O_4N_3Cl_3$ requires Cl, 32·4%). N-*Acetyl*-N-p-*nitrophenyl*-N′-βββ-*trichloro-α-acetoxyethylurea*, very pale yellow, irregular plates from aq. EtOH; m. p. 128° (decomp.) (Found : Cl, 25·2. $C_{13}H_{12}O_6N_3Cl_3$ requires Cl, 25·8%). *Bis*-(βββ-*trichloro*-α-N′-p-*nitrophenylcarbamidoethyl*) *ether*, pale yellow, six-sided tablets from

AcOH; m. p. 203° (decomp.) (Found : Cl, 32·9. $C_{18}H_{14}O_7N_6Cl_6$ requires Cl, 33·3%). *Bis*-(ββ*β*-*trichloro*-α-N′-*acetyl*-N′-p-*nitrophenylcarbamidoethyl*) *ether*, colourless flattened prisms from AcOH; m. p. 151° (decomp.) (Found : Cl, 29·1. $C_{22}H_{18}O_9N_6Cl_6$ requires Cl, 29·5%). N-p-*Nitrophenyl*-N′-βββ-*trichloro*-α-*methoxyethylurea*, short yellow prisms from AcOH; m. p. 192° (decomp.) (Found : Cl, 30·7. $C_{10}H_{10}O_4N_3Cl_3$ requires Cl, 31·1%). N-p-*Nitrophenyl*-N′-βββ-*trichloro*-α-*ethoxyethylurea*, short, pale yellow prisms from AcOH; m. p. 161° (decomp.) (Found : Cl, 30·6. $C_{11}H_{12}O_4N_3Cl_3$ requires Cl, 29·9%).

N-m-*Nitrophenyl*-N′-βββ-*trichloro*-α-*hydroxyethylurea*, lustrous, irregular, very pale yellow plates from EtOH; m. p. 173° (decomp.) (Found : Cl, 32·1%). N-*Acetyl*-N-m-*nitrophenyl*-N′-βββ-*trichloro*-α-*acetoxyethylurea*, colourless microcryst. powder from aq. EtOH; m. p. 126° (decomp.) (Found : Cl, 25·0%). *Bis*-(βββ-*trichloro*-α-N′-m-*nitrophenylcarbamidoethyl*) *ether*, pale yellow, flattened prisms from AcOH; m. p. 217° (decomp.) (Found : Cl, 33·2%). *Bis*-(βββ-*trichloro*-α-N′-*acetyl*-N′-m-*nitrophenylcarbamidoethyl*) *ether*, colourless microcryst. powder from aq. AcOH; m. p. 170° (decomp.) (Found : Cl, 29·0%). N-m-*Nitrophenyl*-N′-βββ-*trichloro*-α-*methoxyethylurea*, long colourless prisms from aq. EtOH; m. p. 170° (decomp.) (Found : Cl, 30·3%). N-m-*Nitrophenyl*-N′-βββ-*trichloro*-α-*ethoxyethylurea*, slender colourless prisms from aq. EtOH, m. p. 146° (decomp.) (Found : Cl, 29·3%).

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