

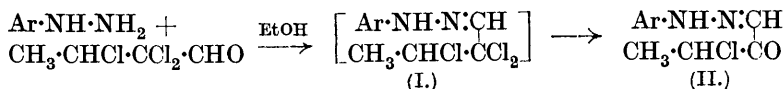
CI.—*The Condensation of Butyl Chloral Hydrate with Aryl Hydrazines.*

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It has recently been shown (Chattaway and Irving, J., 1930, 89) that when the 2:4-dihalogen-substituted phenylhydrazines react with butyl chloral in alcohol, the two α -chlorine atoms in the aldehyde nucleus of the initially formed hydrazone (I) are replaced by an atom of oxygen and the corresponding hydrazones of β -chloro- α -ketobutaldehyde (II) are produced.

The condensations of butyl chloral hydrate in alcohol with the monohalogen-substituted phenylhydrazines, with the three tolylhydrazines, and with phenylhydrazine itself have now been

examined and found to follow a similar course, the corresponding arylhydrazones of β -chloro- α -ketobutaldehyde (II) being formed.



These condensations do not proceed so smoothly as with the 2 : 4-dihalogen-substituted phenylhydrazines and may become violent unless carefully controlled : indeed, if carried out in water or acetic acid, only viscid black products result from which nothing crystalline or definite has been isolated.

The β -chloro- α -ketobutaldehyde arylhydrazones are all well-crystallised yellow substances which are insoluble in water but readily soluble in most organic solvents : they yield the corresponding anilines upon reduction.

EXPERIMENTAL.

The Interaction of Phenylhydrazine with Butyl Chloral Hydrate in Alcohol : Formation of β -Chloro- α -ketobutaldehydophenylhydrazone.—20 G. of butyl chloral hydrate (1 mol.), dissolved in 100 c.c. of ethyl alcohol, were cooled and added to a cooled solution of 11 g. of phenylhydrazine (1 mol.) in 50 c.c. of alcohol, the temperature being kept below 10°. The colour of the solution, originally very pale yellow, became orange, then red, and finally almost black. After 6—8 hours the liquid was poured into 1000 c.c. of water ; a viscid black mass then separated. This was dissolved in a little chloroform and, after drying over calcium chloride, the solvent was allowed to evaporate slowly. β -Chloro- α -ketobutaldehydophenylhydrazone, which separated, was washed free from viscous material with light petroleum and cold alcohol, and recrystallised repeatedly from boiling alcohol (animal charcoal). Yield, 3—4 g. It crystallised from boiling acetic acid, or methyl or ethyl alcohol, in which it was readily soluble, in pale yellow, flattened prisms, m. p. 144° (Found : C, 57.2 ; H, 5.2 ; N, 13.2 ; Cl, 16.75. $\text{C}_{10}\text{H}_{11}\text{ON}_2\text{Cl}$ requires C, 57.4 ; H, 5.3 ; N, 13.3 ; Cl, 16.8%).

The same compound was produced when the reaction was carried out in methyl alcohol.

If the reaction between phenylhydrazine and butyl chloral hydrate is carried out in solutions more concentrated than those above, or if the reaction is not at first retarded by cooling, or if at the beginning a little concentrated hydrochloric acid (which appears to act catalytically) is added, the ensuing reaction may become almost explosively violent, and nothing crystalline or definite can then be isolated from the black tar-like product.

The condensation of butyl chloral with *o*- or *m*-tolylhydrazine is almost as violent as, and closely resembles, the reaction with phenylhydrazine itself. The following compounds were prepared :

β -Chloro- α -ketobutaldehyde-*o*-tolylhydrazone separates from boiling alcohol, in which it is moderately easily soluble, in golden-yellow prisms, m. p. 118—120° (Found : Cl, 16.0. $C_{11}H_{13}ON_2Cl$ requires Cl, 15.8%).

β -Chloro- α -ketobutaldehyde-*m*-tolylhydrazone crystallises from boiling alcohol, in which it is readily soluble, in long, hair-like, yellow prisms, m. p. 157.5° (Found : Cl, 15.85%).

The condensation between butyl chloral and *p*-chloro-(or bromo)-phenylhydrazine or *p*-tolylhydrazine proceeds more smoothly than those described above, and it was found necessary to boil the alcoholic solution of the reactants for 5 minutes to complete the condensation. The arylhydrazones of β -chloro- α -ketobutaldehyde which slowly separated on cooling were crystallised from boiling alcohol (animal charcoal), in which they were readily soluble.

β -Chloro- α -ketobutaldehyde-*p*-tolylhydrazone, greenish-yellow, hair-like prisms, m. p. 145—146° (Found : Cl, 16.05%).

β -Chloro- α -ketobutaldehyde-*p*-chlorophenylhydrazone, six-sided, golden-yellow prisms, m. p. 156—157° (Found : Cl, 28.7. $C_{10}H_{10}ON_2Cl_2$ requires Cl, 29.0%).

β -Chloro- α -ketobutaldehyde-*p*-bromophenylhydrazone, deep golden-yellow, flattened prisms with a greenish tinge, m. p. 153° (Found : Cl + Br, 39.9. $C_{10}H_{10}ON_2ClBr$ requires Cl + Br, 39.9%).