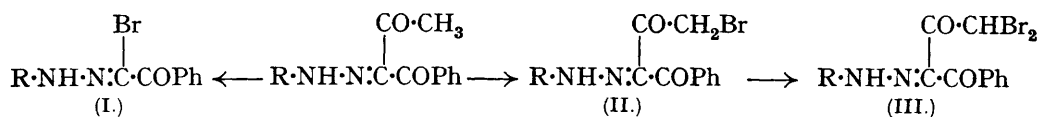


384. The Action of Halogens upon the Nitrophenylazobenzoylacetoncs.

By F. D. CHATTAWAY and D. R. ASHWORTH.

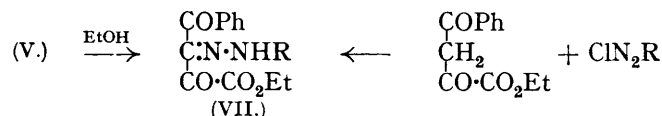
As in similar reactions (this vol., pp. 475, 1143), the action of chlorine or bromine upon the *nitrophenylazobenzoylacetoncs* alters with the medium in which the action occurs. In acetic acid in the presence of crystalline sodium acetate bromine replaces the acetyl group, yielding *ω-bromophenylglyoxalnitrophenylhydrazones* (I). In boiling glacial acetic acid or chloroform it substitutes in the acetyl group, yielding first *δ-bromo-*, then *δδ-dibromo-*



αβγ-triketo-α-phenylbutane-β-nitrophenylhydrazones (II and III), the halogen not entering the nucleus in either case.

$$\text{NO}_2\text{C}_6\text{H}_4\text{NH}\cdot\text{N}(\text{Cl})\text{COPh} \xleftarrow{\text{CHCl}_3} \text{NO}_2\text{C}_6\text{H}_4\text{NH}\cdot\text{N}(\text{CO}\cdot\text{CH}_3)\text{COPh} \xrightarrow{\text{HAc}} \text{NO}_2\text{C}_6\text{H}_4\text{NH}\cdot\text{N}(\text{Cl})\text{COPh}$$
$$\text{COPh}-\text{C} \begin{array}{l} \text{=N-NHR} \\ \text{CO-CH}_2\text{Br} \\ \text{(or CHBr}_2\text{)} \end{array} \longrightarrow \text{COPh}-\text{C} \begin{array}{l} \text{=N-NR} \\ \text{C(OH):CH} \\ \text{(or CBr)} \end{array} \quad (\text{IV.})$$
$$\begin{array}{c} \text{COPh} \cdot \text{C} \equiv \text{N} \\ | \\ \text{C}(\text{OH}) : \text{CH} \end{array} \text{NR} \rightleftharpoons \begin{array}{c} \text{COPh} \cdot \text{C} \equiv \text{N} \\ | \\ \text{CO} \cdot \text{CH}_2 \end{array} \text{NR} \longrightarrow \begin{array}{c} \text{COPh} \cdot \text{C} \equiv \text{N} \\ | \\ \text{CO} \cdot \text{CCl}_2 \end{array} \text{NR (V.)} \longrightarrow \begin{array}{c} \text{COPh} \cdot \text{C} \equiv \text{N} \\ | \\ \text{C}(\text{OH}) : \text{CCl} \end{array} \text{NR (VI.)}$$

When these 5:5-dichloro-4-pyrazolones are heated with alcohols, the ring opens with the formation of *hydrazones of $\alpha\beta\gamma$ -triketo- γ -phenylbutyric esters* (VII), identical with the compounds produced by coupling the appropriate diazonium salt with benzoylpyruvic ester (Beyer and Claisen, *Ber.*, 1887, **20**, 2187).



EXPERIMENTAL.

***ω*-Bromophenylglyoxal-*p*-nitrophenylhydrazone (I).**—1.2 G. of bromine in 5 c.c. of acetic acid were added to a solution of 2.25 g. of *p*-nitrophenylazobenzoylacetone and 2 g. of crystalline sodium acetate in 100 c.c. of acetic acid at 40°, and the whole left for an hour. On careful addition of water *ω*-bromophenylglyoxal-*p*-nitrophenylhydrazone separated. It crystallised from acetic acid in a felted mass of pale yellow, slender prisms, m. p. 247° (decomp.) (Found : Br, 23.3. $C_{14}H_{10}O_3N_3Br$ requires Br, 23.0%).

1626 *The Action of Halogens upon the Nitrophenylazobenzoylacetones.*

ω -Chlorophenylglyoxal-*p*-nitrophenylhydrazone, obtained when 1 g. of *p*-nitrophenylazobenzoylacetone was suspended in 15 c.c. of dry chloroform, chlorine passed for 15 minutes, and the chloroform removed, crystallised from acetic acid in pale yellow, hair-like prisms, m. p. 243° (Found : Cl, 11.9. $C_{14}H_{10}O_3N_3Cl$ requires Cl, 11.7%). The corresponding *o*-nitro-compound crystallised from alcohol in yellow, very long, slender prisms, m. p. 151° (Found : Cl, 11.8%).

ω -Chlorophenylglyoxal-2-chloro-4-nitrophenylhydrazone.—2 G. of *p*-nitrophenylazobenzoylacetone were dissolved in 50 c.c. of acetic acid at 40°, and chlorine passed for $\frac{1}{2}$ hour. On careful addition of water ω -chlorophenylglyoxal-2-chloro-4-nitrophenylhydrazone separated. It crystallised from acetic acid as a labile form in pale yellow, hair-like prisms, which gradually redissolved whilst yellow rhombic plates of the stable form separated; m. p. 183° (Found : Cl, 21.3. $C_{14}H_8O_3N_3Cl_2$ requires Cl, 21.0%). The 4-chloro-2-nitrophenylhydrazone, similarly prepared, crystallised from alcohol as a labile form in pale yellow, hair-like prisms, which gradually redissolved whilst yellow rectangular prisms with domed ends, exhibiting dendritic twinning, of the stable form separated, m. p. 157° (Found : Cl, 21.2%).

δ -Bromo- $\alpha\beta\gamma$ -triketo- α -phenylbutane- β -*p*-nitrophenylhydrazone (II).—2.4 G. of bromine in 3 c.c. of acetic acid were added to a solution of 4.5 g. of *p*-nitrophenylazobenzoylacetone in 40 c.c. of boiling acetic acid. On cooling, the hydrazone (II) separated in quantitative yield. It crystallised from alcohol in yellow, long, hair-like needles, m. p. 172° (decomp.) (Found : Br, 20.2. $C_{16}H_{12}O_4N_3Br$ requires Br, 20.5%). The corresponding *o*-nitro-compound crystallised from acetic acid in yellow, long, slender prisms, m. p. 155° (decomp.) (Found : Br, 20.3%). Similarly, by using 2 mols. of bromine, was obtained $\delta\delta$ -dibromo- $\alpha\beta\gamma$ -triketo- α -phenylbutane- β -*p*-nitrophenylhydrazone, which crystallised from alcohol in yellow, long, slender, rectangular prisms, m. p. 190° (decomp.) (Found : Br, 33.7. $C_{16}H_{10}O_4N_3Br_2$ requires Br, 34.1%).

4-Hydroxy-3-benzoyl-1-*p*-nitrophenylpyrazole (IV).—1 G. of potassium acetate was added to 4 g. of δ -bromo- $\alpha\beta\gamma$ -triketo- α -phenylbutane- β -*p*-nitrophenylhydrazone suspended in 100 c.c. of boiling alcohol. A clear solution was obtained, from which 4-hydroxy-3-benzoyl-1-*p*-nitrophenylpyrazole separated almost at once. It crystallised from acetic acid as a labile form in felted masses of yellow hair-like prisms, which gradually redissolved whilst yellow, large, rectangular, flattened prisms of the stable form separated, m. p. 211.5° (Found : N, 13.4. $C_{16}H_{11}O_4N_3$ requires N, 13.6%). The corresponding *o*-nitro-compound crystallised from alcohol in yellow, large, compact, irregular prisms, m. p. 121° (Found : N, 13.6%). Similarly, from $\delta\delta$ -dibromo- $\alpha\beta\gamma$ -triketo- α -phenylbutane- β -*p*-nitrophenylhydrazone was obtained 5-bromo-4-hydroxy-3-benzoyl-1-*p*-nitrophenylpyrazole, which crystallised from acetic acid as a labile form in bright yellow, short, slender prisms, which gradually redissolved whilst yellow, fragile, rhombic plates of the stable form separated, m. p. 167° (Found : Br, 20.4. $C_{16}H_{10}O_4N_3Br$ requires Br, 20.6%).

5 : 5-Dichloro-3-benzoyl-1-*p*-nitrophenyl-4-pyrazolone (V).—2 G. of 4-hydroxy-3-benzoyl-1-*p*-nitrophenylpyrazole were suspended in 15 c.c. of chloroform, and chlorine passed for 15 minutes. On removal of the chloroform from the resulting orange solution, 5 : 5-dichloro-3-benzoyl-1-*p*-nitrophenyl-4-pyrazolone remained. It crystallised from chloroform–light petroleum in orange, dense, rectangular prisms, m. p. 145° (Found : Cl, 18.6. $C_{16}H_8O_4N_3Cl_2$ requires Cl, 18.8%). The corresponding *o*-nitro-compound crystallised in yellow, compact, rectangular prisms, m. p. 166° (Found : Cl, 18.7%).

Formation of 5-Chloro-4-hydroxy-3-benzoyl-1-*p*-nitrophenylpyrazole.—2 G. of potassium iodide were dissolved in 10 c.c. of water and 5 c.c. of acetic acid and added to a solution of 1.5 g. of 5 : 5-dichloro-3-benzoyl-1-*p*-nitrophenyl-4-pyrazolone in 10 c.c. of acetic acid. On gentle warming, iodine was liberated and 5-chloro-4-hydroxy-3-benzoyl-1-*p*-nitrophenylpyrazole separated. It crystallised from alcohol in pale yellow, long, slender prisms, m. p. 177° (Found : Cl, 10.5. $C_{16}H_{10}O_4N_3Cl$ requires Cl, 10.3%). The corresponding *o*-nitro-compound crystallised from alcohol in pale yellow, large, fragile rhombic plates, m. p. 120° (Found : Cl, 10.3%).

Formation of Ethyl $\alpha\beta\gamma$ -Triketo- γ -phenyl-*n*-butyrate- β -*p*-nitrophenylhydrazone (VII).—(1) 1 G. of 5 : 5-dichloro-3-benzoyl-1-*p*-nitrophenyl-4-pyrazolone was boiled for 5 minutes with 10 c.c. of alcohol. On cooling, the ester (VII) separated. It crystallised from alcohol in yellow, long, slender prisms, m. p. 135° (Found : N, 11.5. $C_{18}H_{15}O_6N_3$ requires N, 11.4%).

(2) 2 G. of *p*-nitroaniline were diazotised and the diazonium solution was run into a cooled well-stirred mixture of 4 g. of ethyl sodiobenzoylpyruvate and 25 g. of crystalline sodium acetate in 150 c.c. of water. The yellow solid which separated at once was shown on crystallisation to be identical with the above.

By a similar method to (1) above have been prepared : ethyl $\alpha\beta\gamma$ -triketo- γ -phenyl-*n*-butyrate- β -*o*-nitrophenylhydrazone, yellow, somewhat flattened prisms from alcohol, m. p. 108° (Found : N, 11.3%), and methyl $\alpha\beta\gamma$ -triketo- γ -phenyl-*n*-butyrate- β -*o*-nitrophenylhydrazone, yellow, long,

slender, four-sided prisms from alcohol, m. p. 119° (Found : N, 11.9. $C_{17}H_{13}O_6N_3$ requires N, 11.8%).

$\alpha\beta\gamma$ -Triketo- γ -phenyl-n-butyric acid- β -p-nitrophenylhydrazine.—2 G. of finely powdered 5 : 5-dichloro-3-benzoyl-1-p-nitrophenyl-4-pyrazolone were shaken for 15 minutes with 2 g. of sodium hydroxide in 150 c.c. of water. Much decomposition occurred, but on acidification of the filtered solution with dilute hydrochloric acid the above acid was obtained in 10—15% yield. It crystallised from chloroform–light petroleum in yellow, short, flattened prisms, m. p. 154° (Found : N, 12.4. $C_{16}H_{11}O_6N_3$ requires N, 12.3%).

THE QUEEN'S COLLEGE LABORATORY, OXFORD.

[Received, November 6th, 1933.]
