19. *ω-Nitrophenylglyoxalarylhydrazones.*

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ω-Nitroacetophenone couples readily with diazonium salts in solution in presence of sodium acetate, the corresponding *ω-nitrophenylglyoxalarylhydrazones* being formed:

$$\mathrm{R{\cdot}N_2Cl + Ph{\cdot}CO{\cdot}CH_2{\cdot}NO_2 \longrightarrow R{\cdot}NH{\cdot}N{:}C(NO_2){\cdot}COPh}$$

The action of bromine on these compounds is similar to that upon the corresponding arylazobenzoylacetones and arylazoacetoacetates (Chattaway and Lye, *Proc. Roy. Soc.*, 1932, *A*, **135**, 282; **137**, 489; J., 1933, 480) and causes the replacement of the nitro-group by bromine. For instance, bromine converts *ω-nitrophenylglyoxalphenylhydrazone* into *ω-nitrophenylglyoxal-*p*-bromophenylhydrazone*, and its further action first replaces the ω-nitro-group and then brings about substitution in one ortho-position:

$$\mathrm{C_6H_5{\cdot}NH{\cdot}N{:}C(NO_2){\cdot}COPh \longrightarrow (\mathit{p})C_6H_4Br{\cdot}NH{\cdot}N{:}C(NO_2){\cdot}COPh \longrightarrow}$$
$$\mathrm{(\mathit{p})C_6H_4Br{\cdot}NH{\cdot}N{:}CBr{\cdot}COPh \longrightarrow (2:4)C_6H_3Br_2{\cdot}NH{\cdot}N{:}CBr{\cdot}COPh}$$

Preparation of ω-Nitroacetophenone (compare Holleman, *Rec. trav. chim.*, 1914, **33**, 290).—A mixture of 80 g. of benzaldehyde and 48 g. of nitromethane was cooled, with stirring, to −10°, and 20 g. of anhydrous potassium carbonate added during 45 minutes, the temperature being kept below 10°. After 1 hour, 50 c.c. of acetic acid were added cautiously and then 1000 c.c. of water, the stirring being continued throughout. The heavy oily phenylnitromethylcarbinol obtained was washed with water and added to 120 g. of potassium dichromate and 60 c.c. of concentrated sulphuric acid in 1500 c.c. of water at 15°. The temperature was kept below 25° to prevent the formation of nitrostyrene. The mixture was then kept at room temperature for 14 days while ω-nitroacetophenone separated in leaflets, m. p. 105·5° after being washed with water and recrystallised from acetic acid; yield, 75 g.

Preparation of ω-Nitrophenylglyoxalphenylhydrazone.—A solution of 45 g. of ω-nitroacetophenone in 100 c.c. of boiling glacial acetic acid was poured with vigorous stirring into 300 c.c. of cold water, 200 g. of crystalline sodium acetate were added, the whole was cooled to 0°, and the diazonium solution obtained from 25 g. of aniline in 100 c.c. of concentrated hydrochloric acid was gradually added. After 1 hour's further stirring, the *ω-nitrophenylglyoxalphenylhydrazone* was collected and crystallised from alcohol, forming orange-yellow prisms with a blue reflex, m. p. 101°; yield, 60% (Found: N, 15·8. $C_{14}H_{11}O_3N_3$ requires N, 15·6%). The hydrazone is readily soluble in organic solvents, giving orange-red solutions, and in concentrated aqueous ammonia, giving a deep red solution; from the latter it is precipitated by hydrochloric acid, though not by water.

The following hydrazones were prepared similarly. *ω-Nitrophenylglyoxal-*p*-chlorophenylhydrazone*, long yellow needles from alcohol, m. p. 134° (Found: Cl, 11·7. $C_{14}H_{10}O_3N_3Cl$ requires Cl, 11·7%); 2 : 4-*dichlorophenylhydrazone*, pale yellow prisms from alcohol, m. p. 135·5° (Found: Cl, 21·15. $C_{14}H_9O_3N_3Cl_2$ requires Cl, 21·0%); 2 : 5-*dichlorophenylhydrazone*, pale yellow prisms from alcohol, m. p. 137° (Found: Cl, 21·1%); p-*bromophenylhydrazone*, small yellow needles from alcohol, m. p. 137° (Found: Br, 23·1. $C_{14}H_{10}O_3N_3Br$ requires Br, 23·0%); 2 : 4-*dibromophenylhydrazone*, yellow prisms from alcohol, m. p. 139° (Found: Br, 37·2. $C_{14}H_9O_3N_3Br_2$ requires Br, 37·5%); 2 : 4 : 6-*tribromophenylhydrazone*, yellow prisms from alcohol, m. p. 111° (Found : Br, 47·5. $C_{14}H_8O_3N_3Br_3$ requires Br, 47·4%); **3 : 4 : 5-*tribromophenylhydrazone***, small yellow needles from alcohol, m. p. 169° (Found : Br, 47·4%); o-***nitrophenylhydrazone***, yellow prisms from acetic acid, m. p. 118° (Found : N, 17·8. $C_{14}H_{10}O_5N_4$ requires N, 17·8%); *p*-nitrophenylhydrazone, bright yellow needles from acetic acid, m. p. 147° (Found : N, 17·8%) (compare Meyer and Weitheimer, *Ber.*, 1914, **47**, 2383).

Action of Bromine upon ω-*Nitrophenylglyoxalphenylhydrazone*.—(*a*) 5 G. of the hydrazone were dissolved in 15 c.c. of warm glacial acetic acid and treated with 3 g. (1 mol.) of bromine in 15 c.c. of acetic acid. After 24 hours, 100 c.c. of water were added; the precipitated ω-nitrophenylglyoxal-*p*-bromophenylhydrazone was, after crystallisation from alcohol, identical with that described above.

(*b*) 5 G. of ω-nitrophenylglyoxal-*p*-bromophenylhydrazone and 0·5 g. of crystalline sodium acetate were dissolved in 20 c.c. of acetic acid, 2·4 g. (1 mol.) of bromine in 10 c.c. of acetic acid added, and the whole kept for 24 hours. On addition of water (50 c.c.) ω-bromophenylglyoxal-*p*-bromophenylhydrazone separated; after crystallisation from alcohol, it was identical with a specimen prepared from *p*-bromophenylazobenzoylacetone (Chattaway and Lye, *loc. cit.*). The same product resulted from the action of 2 mols. of bromine upon ω-nitrophenylglyoxal-phenylhydrazone, the *p*-bromophenylhydrazone being first formed.

(*c*) 5 G. of ω-nitrophenylglyoxal-*p*-bromophenylhydrazone were refluxed with 4·8 g. of bromine in 20 c.c. of chloroform for 1 hour. On removal of the chloroform on a water-bath ω-bromophenylglyoxal-2 : 4-dibromophenylhydrazone remained as an amorphous mass. It was crystallised from acetic acid and shown to be identical with an authentic specimen obtained by the action of 1 mol. of bromine upon 2 : 4-dibromophenylazobenzoylacetone (*loc. cit.*). ω-Bromophenylglyoxal-2 : 4 : 6-tribromophenylhydrazone resulted similarly from the action of bromine upon ω-nitrophenylglyoxal-2 : 4 : 6-tribromophenylhydrazone, and was identical with a specimen prepared by the action of bromine upon 2 : 4 : 6-tribromophenylazobenzoyl-acetone (*loc. cit.*).

ω-*Aminophenylglyoxal*-2 : 4-*dibromophenylhydrazone*, obtained when 2 g. of ω-bromophenyl-glyoxal-2 : 4-dibromophenylhydrazone were heated under reflux for 30 minutes with 10 c.c. of alcoholic ammonia, crystallised from alcohol in yellow prisms, m. p. 134° (Found : Br, 39·8. $C_{14}H_{11}ON_3Br_2$ requires Br, 40·2%).

ω-*Anilinophenylglyoxal*-2 : 4-*dibromophenylhydrazone*, obtained similarly by the action of 0·5 g. of aniline in 5 c.c. of alcohol on 2 g. of ω-bromophenylglyoxal-2 : 4-dibromophenyl-hydrazone, crystallised from alcohol in yellow prisms, m. p. 137° (Found : Br, 33·6. $C_{20}H_{15}ON_3Br_2$ requires Br, 33·8%).

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