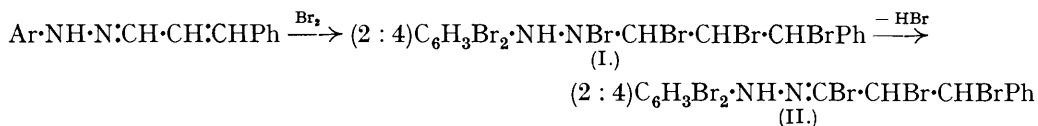


20. The Action of Halogens upon the Arylhydrazones of Unsaturated Aldehydes.

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THE action of halogens upon the arylhydrazones of unsaturated aldehydes in general resembles their action upon the corresponding saturated compounds (compare Chattaway and Walker, J., 1925, **127**, 975, 1687; Chattaway and Adamson, J., 1930, 157; 1931, 2787, 2792; Chattaway, Adair, and Deighton, J., 1931, 1925). The methine hydrogen atom of the aldehyde residue is replaced, the nucleus being in no case attacked, addition of halogen to the ethylenic linkage occurs, and the aryl nucleus of the hydrazine residue is substituted, the extent of this substitution being determined by the presence or absence of substituent atoms or groups.

When, for example, 4 mols. of bromine act upon cinnamaldehydephenylhydrazone dissolved in acetic acid at the ordinary temperature, $\omega\alpha\beta$ -tribromo- β -phenylpropaldehyde-2 : 4-dibromophenylhydrazone (II) is produced, and the same compound results from the action of 3 mols. of bromine upon cinnamaldehyde-*p*-bromophenylhydrazone, and from the action of 2 mols. of bromine upon cinnamaldehyde-2 : 4-dibromophenylhydrazone. Substitution in the methine group is apparently preceded by a loose addition of halogen at the nitrogen-methine linkage, since the action of excess of bromine upon any of the three original cinnamaldehyde-hydrazones causes the formation of an unstable yellow bromine addition compound, probably of the constitution (I), which on crystallisation from acetic acid readily loses hydrogen bromide and yields the brominated hydrazone (II). Thus :



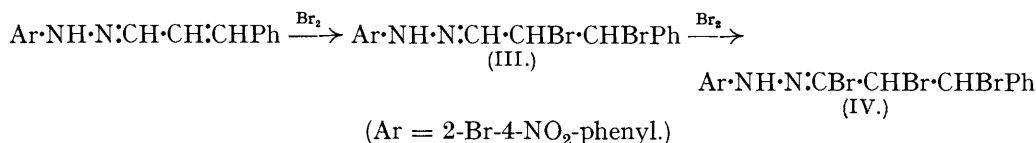
(Where Ar = phenyl, *p*-bromophenyl, and 2 : 4-dibromophenyl.)

This is supported by the fact that when cinnamaldehyde-2 : 4 : 6-tribromophenylhydrazone is acted upon by a large excess of bromine, a similar unstable yellow addition compound is formed which loses hydrogen bromide on crystallisation from acetic acid and yields the colourless $\omega\alpha\beta$ -tribromo- β -phenylpropaldehyde-2 : 4 : 6-tribromophenylhydrazone, $(2 : 4 : 6)\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NH}\cdot\text{N}\cdot\text{CBr}\cdot\text{CHBr}\cdot\text{CHBr}\text{Ph}$.

In the bromination of the cinnamaldehyde-arylhydrazones no definitely preferential attack can be recognised even when less than the theoretical amount of halogen is used, since only the final fully brominated product (II) can be isolated whilst a portion of the original hydrazone is left unaltered.

The presence of a *p*-nitro-group in the phenylhydrazine residue prevents any further substitution by bromine in the nucleus, the usual reactions occurring in the aldehyde side chain only with the formation of $\omega\alpha\beta$ -tribromo- β -phenylpropaldehyde-*p*-nitrophenylhydrazone (as II).

When, however, such a nitro-group is present, the reaction can sometimes be checked at an intermediate stage. Thus, when 1 mol. of bromine is added to a solution of cinnamaldehyde-2-bromo-4-nitrophenylhydrazone in acetic acid at the ordinary temperature, the bromine adds on to the ethylenic linkage, no hydrogen bromide is eliminated, and $\alpha\beta$ -dibromo- β -phenylpropaldehyde-2-bromo-4-nitrophenylhydrazone (III) is formed. This compound is entirely different in properties from its isomeride, $\omega\alpha\beta$ -tribromo- β -phenylpropaldehyde-*p*-nitrophenylhydrazone (above). The two hydrazones melt at 210° and 193° respectively, and whilst the latter cannot be further brominated, when 1 mol. of bromine is added to a suspension of the former (III) in acetic acid at the ordinary temperature, hydrogen bromide is evolved and $\omega\alpha\beta$ -tribromo- β -phenylpropaldehyde-2-bromo-4-nitrophenylhydrazone (IV) separates. Thus :



The action of chlorine upon the cinnamaldehyde-arylhydrazones resembles that of bromine, but in every case substitution in the phenyl nucleus of the hydrazine residue can be carried a stage further. Thus, when chlorine is passed through a cooled suspension in acetic acid of cinnamaldehydephenylhydrazone, of cinnamaldehyde-*p*-chlorophenylhydrazone, or of cinnamaldehyde-2 : 4-dichlorophenylhydrazone, chlorine adds on at the ethylenic linkage and substitutes in the ω -position in the aldehyde chain and in the *p*- and one *o*-position in the hydrazine nucleus (where these are not already occupied), $\omega\alpha\beta$ -trichloro- β -phenylpropaldehyde-2 : 4-dichlorophenylhydrazone (as II) being formed. Further chlorination of this compound in warm acetic acid causes substitution in the remaining *o*-position and $\omega\alpha\beta$ -trichloro- β -phenylpropaldehyde-2 : 4 : 6-trichlorophenylhydrazone, (2 : 4 : 6)C₆H₂Cl₃·NH·N:CCl·CHCl·CHClPh, is formed, identical with the compound produced by the action of chlorine upon cinnamaldehyde-2 : 4 : 6-trichlorophenylhydrazone.

The action of chlorine upon cinnamaldehyde-*p*-nitrophenylhydrazone is similar, the halogen adding on at the ethylenic linkage, and substituting the methine hydrogen, but only entering one *o*-position in the hydrazine residue. The compound formed, $\omega\alpha\beta$ -trichloro- β -phenylpropaldehyde-2-chloro-4-nitrophenylhydrazone (as IV), also results from the chlorination of cinnamaldehyde-2-chloro-4-nitrophenylhydrazone under similar conditions. Direct chlorination, even in hot acetic acid solution, does not effect the introduction of another atom of chlorine into the remaining unoccupied *o*-position in the hydrazine residue, the nitro-group here, as in bromination, hindering the substitution.

EXPERIMENTAL.

The Action of Excess of Bromine upon Cinnamaldehydephenylhydrazone.—16 G. (excess) of bromine were dissolved in 10 c.c. of acetic acid and added slowly to 4.4 g. of cinnamaldehydephenylhydrazone (1 mol.) suspended in 20 c.c. of glacial acetic acid at the ordinary temperature. Hydrogen bromide was evolved and a yellow bromine addition compound began to separate. After 30 minutes this was collected and crystallised from boiling acetic acid; $\omega\alpha\beta$ -tribromo- β -phenylpropaldehyde-2 : 4-dibromophenylhydrazone (II) then separated as small clusters of colourless prisms, m. p. 180° (Found : Br, 64.7. C₁₅H₁₁N₂Br₅ requires Br, 64.4%). On reduction with tin and hydrochloric acid in acetic acid solution it yielded 2 : 4-dibromoaniline, which was identified by means of its acetyl derivative.

Action of Bromine upon Cinnamaldehyde-2 : 4 : 6-tribromophenylhydrazone.—3.2 G. of bromine in 10 c.c. of acetic acid were added slowly to 4.6 g. of cinnamaldehyde-2 : 4 : 6-tribromophenylhydrazone suspended in 20 c.c. of acetic acid at the ordinary temperature. Hydrogen bromide was evolved and $\omega\alpha\beta$ -tribromo- β -phenylpropaldehyde-2 : 4 : 6-tribromophenylhydrazone separated almost at once. It crystallised from acetic acid in colourless minute needles, m. p. 173° (Found : Br, 68.7. C₁₅H₁₀N₂Br₆ requires Br, 68.8%).

$\omega\alpha\beta$ -Tribromo- β -phenylpropaldehyde-*p*-nitrophenylhydrazone, prepared similarly by the action of excess of bromine upon cinnamaldehyde-*p*-nitrophenylhydrazone, crystallised from acetic acid in yellow rectangular plates, m. p. 193° (Found : Br, 47.5. C₁₅H₁₂O₂N₃Br₃ requires Br, 47.4%).

Action of Bromine (1 Mol.) upon Cinnamaldehyde-2-bromo-4-nitrophenylhydrazone.—1.6 G. of bromine (1 mol.) in 5 c.c. of acetic acid were added to 3.5 g. (1 mol.) of cinnamaldehyde-2-bromo-4-nitrophenylhydrazone dissolved in 200 c.c. of cold acetic acid. The coloration due to the bromine disappeared almost at once, no hydrogen bromide being evolved. On careful addition of water to the resulting clear solution, $\alpha\beta$ -dibromo- β -phenylpropaldehyde-2-bromo-4-nitrophenylhydrazone (III) separated as a dark solid. It crystallised from alcohol in very dark yellow, minute prisms, m. p. 210°. This hydrazone was also synthesised directly from 3 g. of cinnamaldehyde dibromide (Zincke, *Ber.*, 1884, 17, 1814) and 2.4 g. of *o*-bromo-*p*-nitrophenylhydrazine in warm acetic acid.

Action of Bromine (2 Mols.) upon Cinnamaldehyde-2-bromo-4-nitrophenylhydrazone.—4.8 G. of bromine in 10 c.c. of acetic acid were added to 3.5 g. of cinnamaldehyde-2-bromo-4-nitro-

phenylhydrazine suspended in 20 c.c. of acetic acid at the ordinary temperature. Hydrogen bromide was evolved; after 30 minutes, when the clear solution obtained was cautiously diluted with water, $\omega\alpha\beta$ -tribromo- β -phenylpropaldehyde-2-bromo-4-nitrophenylhydrazone (IV) separated as a solid, which crystallised from acetic acid in pale yellow, flattened, rectangular plates, m. p. 199° (Found: Br, 54.8. $C_{15}H_{11}O_2N_3Br_4$ requires Br, 54.7%).

Action of Chlorine upon Cinnamaldehydephenylhydrazone in Cold Acetic Acid.—A slow stream of chlorine was passed into a suspension of 4.4 g. of cinnamaldehydephenylhydrazone in acetic acid for 15 minutes, care being taken that the temperature did not rise above 0°. On cautious dilution of the clear, deep yellow solution which resulted, $\omega\alpha\beta$ -trichloro- β -phenylpropaldehyde-2:4-dichlorophenylhydrazone (as II) separated as a viscous yellow solid. It crystallised from acetic acid in almost colourless, hair-like needles, m. p. 158° (Found: Cl, 44.5. $C_{15}H_{11}N_2Cl_5$ requires Cl, 44.8%). On reduction with tin and hydrochloric acid in acetic acid solution it yielded 2:4-dichloroaniline, which was characterised by its acetyl derivative.

Action of Chlorine upon Cinnamaldehydephenylhydrazone in Warm Acetic Acid.—A rapid stream of chlorine was passed into a suspension of 4.4 g. of cinnamaldehydephenylhydrazone in 20 c.c. of acetic acid for about 20 minutes. The temperature rose to about 60° and hydrogen chloride was freely evolved. On careful addition of water to the resulting clear solution, $\omega\alpha\beta$ -trichloro- β -phenylpropaldehyde-2:4:6-trichlorophenylhydrazone separated as a yellow solid, which crystallised from acetic acid in colourless, short, hair-like prisms, m. p. 111° (Found: Cl, 49.3. $C_{15}H_{10}N_2Cl_6$ requires Cl, 49.4%).

This hydrazone was also obtained by the chlorination under similar conditions of cinnamaldehyde-*p*-chloro-, -2:4-dichloro-, and -2:4:6-trichloro-phenylhydrazone, and of $\omega\alpha\beta$ -trichloro- β -phenylpropaldehyde-2:4-dichlorophenylhydrazone. On reduction it yielded 2:4:6-trichloroaniline.

*Action of Chlorine upon Cinnamaldehyde-*p*-nitrophenylhydrazone.*—Chlorine was passed for 20 minutes through a suspension of 5.4 g. of cinnamaldehyde-*p*-nitrophenylhydrazone in 20 c.c. of warm acetic acid. The temperature rose somewhat and hydrogen chloride was evolved. On addition of water to the resulting clear solution $\omega\alpha\beta$ -trichloro- β -phenylpropaldehyde-2-chloro-4-nitrophenylhydrazone separated as an orange viscous solid. It crystallised from acetic acid in deep yellow, flattened, rectangular prisms, m. p. 190°, identical with the product of chlorinating cinnamaldehyde-2-chloro-4-nitrophenylhydrazone under similar conditions (Found: Cl, 34.6. $C_{15}H_{11}O_2N_3Cl_4$ requires Cl, 34.9%).

Preparation of 2-Bromo-4-nitrophenylhydrazine.—The hydrobromide of 2-bromo-4-nitroaniline, prepared in quantitative yield by the addition of 16 g. of bromine to a solution of 14 g. of *p*-nitroaniline in 200 c.c. of warm acetic acid (compare Korner and Contardi, *Atti R. Accad. Lincei*, 1914, 5, 285), was made into a paste with 25 c.c. of concentrated hydrochloric acid and diazotised at 0–5° with 7 g. of sodium nitrate in 20 c.c. of water. The filtered diazonium solution was reduced with 56 c.c. of saturated ammonium sulphite and 12 c.c. of aqueous ammonia, and the yellow disulphonate which separated was digested on a water-bath with 30 c.c. of concentrated hydrochloric acid until no more sulphur dioxide was evolved (10–15 minutes). The hydrazine hydrochloride which separated on cooling was collected and dissolved in water, and the free base liberated by the addition of a concentrated aqueous solution of sodium acetate. 2-Bromo-4-nitrophenylhydrazine so obtained crystallised from alcohol in bright yellow needles, m. p. 142° (Found: Br, 34.65. $C_6H_6O_2N_3Br$ requires Br, 34.5%).

2-Chloro-4-nitrophenylhydrazine, prepared similarly, crystallised from alcohol in orange elongated plates, m. p. 140° (Found: Cl, 19.0. $C_6H_6O_2N_3Cl$ requires Cl, 18.9%).

The following hydrazones, prepared in the course of the research, have not previously been described: cinnamaldehyde-2:4-dibromophenylhydrazone, felted mass of fine yellow needles from alcohol (labile form), which changed to yellow rhombic plates (stable form), m. p. 164° (Found: Br, 42.3. $C_{15}H_{13}N_2Br_2$ requires Br, 42.0%); cinnamaldehyde-2:4:6-tribromophenylhydrazone, buff-coloured rectangular plates from alcohol, m. p. 125° (Found: Br, 52.0. $C_{15}H_{11}N_2Br_3$ requires Br, 52.3%); cinnamaldehyde-2-bromo-4-nitrophenylhydrazone, small, crimson, flattened prisms, m. p. 148° (Found: Br, 23.1. $C_{15}H_{12}O_2N_3Br$ requires Br, 23.1%); cinnamaldehyde-2-chloro-4-nitrophenylhydrazone, small, red, rectangular prisms, m. p. 157°, from alcohol (Found: Cl, 11.7. $C_{15}H_{12}O_2N_3Cl$ requires Cl, 11.8%).