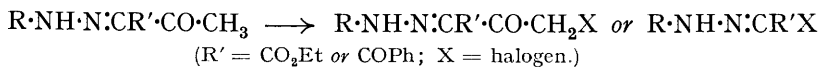


196. *The Action of Halogens upon the Arylazoacetylacetones.*

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

DURING the past few years several papers have been published describing the action of chlorine and bromine upon a series of compounds obtained by coupling diazonium salts with substances containing a methylene group activated by adjoining groups. In the compounds so far studied, the arylazoacetoacetates (Chattaway and Lye, *Proc. Roy. Soc.*, 1932, *A*, **135**, 282; Chattaway and Ashworth, *J.*, 1933, 475) and the arylazobenzoylacetones (*J.*, 1933, 481, 1624), the two groups attached to the linking methylene carbon atom have

been different and one of them an acetyl group which in every case was substituted or replaced by halogen.



The action of halogens upon the arylazoacetylacetones is of special interest, as in them the two groups attached to the linking carbon atom of the ketonic residue are identical and, since each is an acetyl group, equally susceptible to attack by the halogen. As with the compounds previously studied, the action is profoundly influenced by the conditions of reaction and by the substituents in the aryl nucleus.

When one mol. of bromine acts at the ordinary temperature upon phenylazoacetylacetone dissolved in acetic acid or chloroform, the phenyl nucleus is first attacked and *p*-bromophenylazoacetylacetone (I) chiefly formed, identical with the compound obtained by coupling *p*-bromobenzenediazonium chloride with acetylacetone :



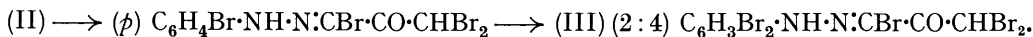
No other product can be definitely isolated, although an acetyl group is probably also substituted and replaced to a certain extent.

When two mols. of bromine react with phenylazoacetylacetone under similar conditions, a mixture results, from which no individual compound can be separated. When, however, three mols. of bromine are used in hot or cold acetic acid solution, bromine is substituted for hydrogen in the *p*-position in the phenyl nucleus and also in one acetyl group, the other acetyl group is replaced, and $\beta\omega$ -dibromo- α -ketopropaldehyde-*p*-bromophenylhydrazone (II) formed :

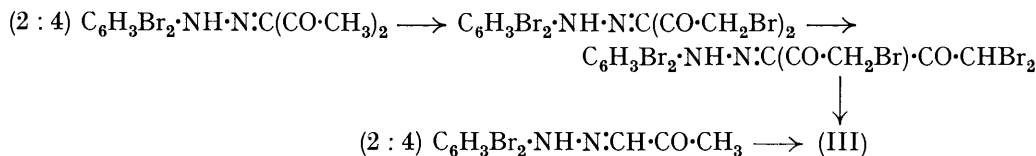


The same compound is obtained by the action of two mols. of bromine upon *p*-bromophenylazoacetylacetone or α -ketopropaldehyde-*p*-bromophenylhydrazone dissolved in hot glacial acetic acid.

The continued action of excess of bromine upon $\beta\omega$ -dibromo- α -ketopropaldehyde-*p*-bromophenylhydrazone, dissolved in boiling glacial acetic acid, produces first $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-*p*-bromophenylhydrazone, and then, more slowly, bromine enters the nucleus in an *o*-position, $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-2 : 4-dibromophenylhydrazone (III) being formed :

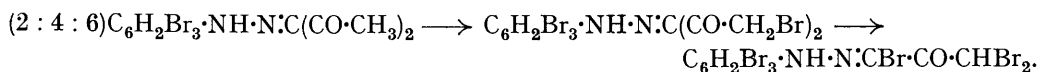


When two mols. of bromine react with 2 : 4-dibromophenylazoacetylacetone dissolved in boiling chloroform, both acetyl groups are substituted and 2 : 4-dibromophenylazo- $\gamma\gamma'$ -dibromoacetylacetone is formed in quantitative yield. The action of a third mol. of bromine upon this compound, dissolved in boiling glacial acetic acid, causes further substitution in one of the already substituted acetyl groups, 2 : 4-dibromophenylazo- $\gamma\gamma'$ -tribromoacetylacetone being formed. When excess of bromine is used and the action in acetic acid at 100° is prolonged, one of the substituted acetyl groups is replaced by bromine, $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-2 : 4-dibromophenylhydrazone (III) being formed, identical with the product obtained by the action of excess of bromine in boiling acetic acid upon α -ketopropaldehyde-2 : 4-dibromophenylhydrazone :



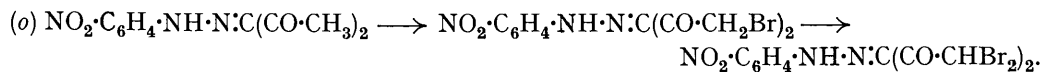
The action of bromine upon 2 : 4 : 6-tribromophenylazoacetylacetone is similar. When this is treated with two mols. of bromine in boiling chloroform solution, substitution in

each of the acetyl groups occurs and 2 : 4 : 6-*tribromophenylazo- $\gamma\gamma'$ -dibromoacetylacetone* is formed. The further action of bromine upon this compound, dissolved in boiling acetic acid, replaces one of the substituted acetyl groups and fully substitutes the other, $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-2 : 4 : 6-tribromophenylhydrazone being formed. It was not found possible to isolate 2 : 4 : 6-tribromophenylazo- $\gamma\gamma\gamma'$ -tribromoacetylacetone which may be formed as an intermediate stage.



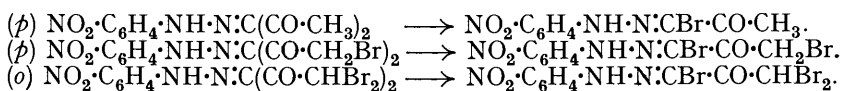
The behaviour of bromine with *p*-nitrophenylazoacetylacetone is similar; in boiling chloroform solution *p*-nitrophenylazo- $\gamma\gamma'$ -dibromoacetylacetone is formed, and the further action of bromine upon this compound results in the formation of $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-*p*-nitrophenylhydrazone.

The action of bromine upon *o*-nitrophenylazoacetylacetone, dissolved in chloroform, causes first substitution in each acetyl group, *o*-nitrophenylazo- $\gamma\gamma'$ -dibromoacetylacetone being formed. This compound on treatment with two mols. of bromine in boiling glacial acetic acid solution is substituted further in each acetyl group, and *o*-nitrophenylazo- $\gamma\gamma\gamma'\gamma'$ -tetrabromoacetylacetone formed in quantitative yield :



This is the only case in which a tetrabromoacetylacetone could be isolated. The effect of the nitro-group in an ortho-position in promoting this substitution in the acetyl group is lessened by the presence of bromine in the phenyl nucleus; for example, 4-bromo-2-nitro-, and 4 : 6-dibromo-2-nitro-phenylazoacetylacetones, whilst yielding $\gamma\gamma'$ -dibromo-derivatives, are not substituted further, the compounds breaking down when action is pressed.

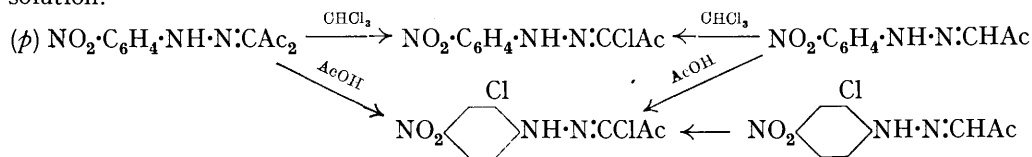
When any one of the arylazoacetylacetones or the arylazohalogenoacetylacetones is treated with one mol. of bromine in cold acetic acid solution containing crystalline sodium acetate, one acetyl group or substituted acetyl group is replaced by bromine, the corresponding ω -bromo- α -ketopropaldehydearylhydrazone being quantitatively formed. Thus *p*-nitrophenylazoacetylacetone yields ω -bromo- α -ketopropaldehyde-*p*-nitrophenylhydrazone, *p*-nitrophenylazo- $\gamma\gamma'$ -dibromoacetylacetone yields $\beta\omega$ -dibromo- α -ketopropaldehyde-*p*-nitrophenylhydrazone, and *o*-nitrophenylazo- $\gamma\gamma\gamma'\gamma'$ -tetrabromoacetylacetone yields $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-*o*-nitrophenylhydrazone. Identical compounds can be obtained by the action of bromine upon the corresponding α -ketopropaldehydearylhydrazone (J., *loc. cit.*) :



Action of Chlorine upon the Arylazoacetylacetones.—This action always causes the replacement of one acetyl group by chlorine, the remaining acetyl group never being substituted, ω -chloro- α -ketopropaldehydearylhydrazones resulting in every case; e.g., 2 : 4-dibromophenylazoacetylacetone on treatment with chlorine in chloroform or acetic acid solution, with or without addition of sodium acetate, yields ω -chloro- α -ketopropaldehyde-2 : 4-dibromophenylhydrazone.

Again, when chlorine is passed through a solution of either *o*- or *p*-nitrophenylazoacetylacetone or the *o*- or *p*-nitrophenylhydrazone of α -ketopropaldehyde in dry chloroform, the corresponding ω -chloro- α -ketopropaldehyde-nitrophenylhydrazone is formed, no substitution occurring in the nucleus. When, however, reaction takes place in acetic acid solution, it is more vigorous and chlorine, although not substituting in an acetyl group, enters the nucleus in the unoccupied *p*- or *o*-position. Thus *p*-nitrophenylazoacetylacetone or α -ketopropaldehyde-*p*-nitrophenylhydrazone in dry chloroform solution yields ω -chloro- α -ketopropaldehyde-*p*-nitrophenylhydrazone and in acetic acid solution ω -chloro- α -ketopropaldehyde-2-chloro-4-nitrophenylhydrazone, identical with the compound obtained by the action

of chlorine upon α -ketopropaldehyde-2-chloro-4-nitrophenylhydrazone in acetic acid solution.



The halogen atom in the ω -chloro- and ω -bromo- α -ketopropaldehydearylhyazones is very reactive and can easily be replaced by an amino- or anilino-group on treatment with alcoholic ammonia or aniline, the corresponding ω -amino- and ω -anilino-compounds being respectively formed.

When any one of the arylazo- $\gamma\gamma'$ -dibromoacetylacetones is warmed with an alcoholic solution of potassium acetate, pyridine, sodium ethoxide, ammonia, or potassium cyanide, reaction occurs and alkali bromide separates, but in no case is the action a clean one, viscous dark-coloured substances being formed, from which nothing definite or crystalline can be isolated.

EXPERIMENTAL.

Formation of p-Bromophenylazoacetylacetone.—9 G. of *p*-bromoaniline were diazotised in the usual manner and the filtered diazonium solution was run into a cooled well-stirred mixture of 50 g. of crystalline sodium acetate and 6 g. of acetylacetone in 50 c.c. of water. *p*-Bromophenylazoacetylacetone began to separate at once and was collected after 12 hours; it crystallised from acetic acid in yellow, large, flattened prisms, m. p. 142° (Found : Br, 35.7. $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3\text{Br}$ requires Br, 35.6%).

The following were similarly prepared : 2 : 4-Dibromophenylazoacetylacetone, yellow, short, flattened prisms from acetic acid, m. p. 186° (Found : Br, 44.4. $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2\text{Br}_2$ requires Br, 44.2%); 2 : 4 : 6-tribromophenylazoacetylacetone, yellow, very long, slender prisms from alcohol, m. p. 130° (Found : Br, 54.6. $\text{C}_{11}\text{H}_9\text{O}_2\text{N}_2\text{Br}_3$ requires Br, 54.4%); *p*-nitrophenylazoacetylacetone, yellow, long, four-sided prisms from acetic acid, m. p. 219° (Found : N, 17.0. $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}_3$ requires N, 16.9%); *o*-nitrophenylazoacetylacetone, yellow lustrous leaflets from acetic acid, m. p. 184° (Found : N, 16.8%); 4-bromo-2-nitrophenylazoacetylacetone, yellow, very long, slender prisms from acetic acid, m. p. 184° (Found : Br, 24.5. $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_3\text{Br}$ requires Br, 24.4%); 4 : 6-dibromo-2-nitrophenylazoacetylacetone, yellow, slender, flattened prisms from acetic acid, m. p. 174° (Found : Br, 39.3. $\text{C}_{11}\text{H}_9\text{O}_4\text{N}_3\text{Br}_2$ requires Br, 39.3%).

Action of Bromine upon Phenylazoacetylacetone.—(1) *Formation of p-bromophenylazoacetylacetone.* 1.5 G. of bromine in 3 c.c. of acetic acid were added to a solution of 2 g. of phenylazoacetylacetone in 20 c.c. of acetic acid. After $\frac{1}{2}$ hour, addition of water precipitated a viscous yellow solid, from which by repeated crystallisation was obtained *p*-bromophenylazoacetylacetone identical with the compound described above.

(2) *Formation of $\beta\omega$ -dibromo- α -ketopropaldehyde-*p*-bromophenylhydrazone.* 4.5 G. of bromine in 5 c.c. of acetic acid were added to a solution of 2 g. of phenylazoacetylacetone in 15 c.c. of boiling acetic acid. On cooling and dilution with water a viscous yellow solid was obtained from which on repeated crystallisation from alcohol was isolated $\beta\omega$ -dibromo- α -ketopropaldehyde-*p*-bromophenylhydrazone (0.5 g.) in pale yellow, long, hair-like needles, m. p. 175° (Found : Br, 60.4. $\text{C}_9\text{H}_7\text{ON}_2\text{Br}_3$ requires Br, 60.15%). This compound was also obtained when 1.2 g. of bromine were added to 1 g. of α -ketopropaldehyde-*p*-bromophenylhydrazone in 10 c.c. of boiling acetic acid and when 2.4 g. of bromine were added to 2.1 g. of *p*-bromophenylazoacetylacetone in 10 c.c. of boiling acetic acid.

(3) *Formation of $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-*p*-bromophenylhydrazone.* 8 G. of bromine in 5 c.c. of acetic acid were added to a solution of 2 g. of phenylazoacetylacetone in 10 c.c. of boiling acetic acid. On cooling, a yellow solid separated from which on repeated crystallisation was obtained the above compound in deep yellow, rhombic plates, m. p. 164° (Found : Br, 66.9. $\text{C}_9\text{H}_6\text{ON}_2\text{Br}_4$ requires Br, 66.8%).

Action of Bromine upon 2 : 4-Dibromophenylazoacetylacetone.—(1) *Formation of 2 : 4-dibromophenylazo- $\gamma\gamma'$ -dibromoacetylacetone.* 2.4 G. of bromine in 3 c.c. of acetic acid were added to 2.7 g. of 2 : 4-dibromophenylazoacetylacetone in 20 c.c. of boiling acetic acid. On cooling, the above compound separated; it crystallised from acetic acid in yellow, short, fragile, flattened prisms, m. p. 162° (Found : Br, 61.8. $\text{C}_{11}\text{H}_8\text{O}_2\text{N}_2\text{Br}_4$ requires Br, 61.5%).

(2) *Formation of 2:4-dibromophenylazo- $\gamma\gamma'$ -tribromoacetylacetone.* 1 G. of bromine in 3 c.c. of acetic acid was added to 2.4 g. of 2:4-dibromophenylazo- $\gamma\gamma'$ -dibromoacetylacetone in 15 c.c. of acetic acid, and the whole heated on a water-bath for $\frac{1}{2}$ hour. On cooling, the above compound separated; it crystallised from acetic acid in deep yellow, long, flattened prisms, m. p. 165° (Found : N, 4.4; Br, 67.0. $C_{11}H_7O_2N_2Br_5$ requires N, 4.7; Br, 66.8%).

Each of the above compounds, when heated with excess of bromine in acetic acid solution, yielded $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-2:4-dibromophenylhydrazone identical with an authentic specimen (*Proc. Roy. Soc.*, 1932, A, 137, 489).

Action of Bromine upon 2:4:6-Tribromophenylazoacetylacetone.—(1) *Formation of 2:4:6-tribromophenylazo- $\gamma\gamma'$ -dibromoacetylacetone.* 1.9 G. of bromine in 3 c.c. of acetic acid were added to a solution of 2.6 g. of 2:4:6-tribromophenylazoacetylacetone in 10 c.c. of boiling chloroform. On removal of the chloroform on a water-bath the above compound separated; it crystallised from chloroform–light petroleum in yellow, long, fragile, flattened prisms, m. p. 123° (Found : Br, 67.1. $C_{11}H_7O_2N_2Br_5$ requires Br, 66.8%).

(2) *Formation of $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-2:4:6-tribromophenylhydrazone.* 3.9 G. of bromine of 4 c.c. of acetic acid were added to 2.6 g. of 2:4:6-tribromophenylazoacetylacetone in 10 c.c. of boiling acetic acid. On addition of water the above compound separated as a viscous solid. After crystallisation from chloroform–light petroleum it was identical with an authentic specimen (*Proc. Roy. Soc.*, 1932, A, 135, 282).

In a similar fashion were obtained *p*-nitrophenylazo- $\gamma\gamma'$ -dibromoacetylacetone, yellow, long, very slender prisms from alcohol, m. p. 150° (Found : Br, 39.1. $C_{11}H_9O_4N_3Br_2$ requires Br, 39.3%), and $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-*p*-nitrophenylhydrazone (J., 1933, 475).

The following have been obtained in a similar fashion to (1) above : *o*-Nitrophenylazo- $\gamma\gamma'$ -dibromoacetylacetone, yellow, irregular, lustrous, flattened prisms, from acetic acid, m. p. 168° (Found : Br, 39.6%); 4-bromo-2-nitrophenylazo- $\gamma\gamma'$ -dibromoacetylacetone, orange, compact, rhombic tablets from acetic acid, m. p. 158° (Found : Br, 49.3. $C_{11}H_8O_4N_3Br_3$ requires Br, 49.4%); 4:6-dibromo-2-nitrophenylazo- $\gamma\gamma'$ -dibromoacetylacetone, yellow, long, flattened prisms from acetic acid, m. p. 165° (Found : Br, 56.7. $C_{11}H_7O_4N_3Br_4$ requires Br, 56.6%).

Formation of o-Nitrophenylazo- $\gamma\gamma\gamma'$ -tetrabromoacetylacetone.—6 G. of bromine in 3 c.c. of acetic acid were added to a solution of 2 g. of *o*-nitrophenylazoacetylacetone in 15 c.c. of boiling acetic acid. On cooling and careful addition of water the tetrabromo-compound separated. It crystallised from alcohol in yellow, long, slender, flattened prisms, m. p. 132° (Found : Br, 56.3; N, 7.4. $C_{11}H_7O_4N_3Br_4$ requires Br, 56.6; N, 7.4%).

Formation of ω -Chloro- α -ketopropaldehyde-2:4:6-tribromophenylhydrazone.—2 G. of 2:4:6-tribromophenylazoacetylacetone were dissolved in 10 c.c. of acetic acid and chlorine was passed for 10 minutes. On careful addition of water the above compound separated. It crystallised from alcohol in very pale yellow, long, slender, flattened prisms, m. p. 136° (Found : Br, 55.3; Cl, 8.2. $C_9H_6ON_2ClBr_3$ requires Br, 55.4; Cl, 8.2%).

ω -Chloro- α -ketopropaldehyde-2:4-dibromophenylhydrazone, clusters of colourless, short, hair-like prisms, m. p. 141° (Found : Cl, 9.8; Br, 44.8. $C_9H_7ON_2ClBr_2$ requires Cl, 10.0; Br, 45.1%), was obtained similarly. From *p*-nitrophenylazoacetylacetone, α -ketopropaldehyde-*p*-nitro- and -2-chloro-4-nitro-phenylhydrazone was obtained ω -chloro- α -ketopropaldehyde-2-chloro-4-nitrophenylhydrazone, clusters of pale yellow, minute prisms from alcohol, m. p. 148° (Found : Cl, 26.0. $C_9H_7O_3N_3Cl_2$ requires Cl, 25.7%). By similar methods was obtained ω -chloro- α -ketopropaldehyde-4-chloro-2-nitrophenylhydrazone, deep yellow, long, slender prisms from alcohol, m. p. 155° (Found : Cl, 25.9%).

ω -Chloro- β -bromo- α -ketopropaldehyde-2-chloro-4-nitrophenylhydrazone was prepared by the action of chlorine upon *p*-nitrophenylazo- $\gamma\gamma'$ -dibromoacetylacetone and by the action of 1 mol. of bromine upon ω -chloro- α -ketopropaldehyde-2-chloro-4-nitrophenylhydrazone; it crystallised from alcohol in pale yellow, short, flattened prisms, m. p. 178° (Found : Cl, 20.1; Br, 22.7. $C_9H_6O_3N_3Cl_2Br$ requires Cl, 20.0; Br, 22.5%).

*Formation of ω -Chloro- α -ketopropaldehyde-*p*-nitrophenylhydrazone.*—2 G. of *p*-nitrophenylazoacetylacetone or of α -ketopropaldehyde-*p*-nitrophenylhydrazone were suspended in 15 c.c. of dry chloroform, and a stream of dry chlorine passed in for 15 minutes. On removal of the chloroform the above compound remained. It crystallised from alcohol in pale yellow, slender prisms, m. p. 224° (Found : Cl, 14.9. $C_9H_8O_3N_3Cl$ requires Cl, 14.7%).

Similarly was obtained ω -chloro- α -ketopropaldehyde-*o*-nitrophenylhydrazone, yellow, long, flattened, rectangular prisms from alcohol, m. p. 173° (Found : Cl, 14.3%).

When ω -chloro- α -ketopropaldehyde-*p*-nitrophenylhydrazone was stirred into alcoholic ammonia, a quantitative yield of ω -amino- α -ketopropaldehyde-*p*-nitrophenylhydrazone was

obtained identical with an authentic specimen (J., *loc. cit.*). Similarly was obtained ω -amino- α -ketopropaldehyde-2-chloro-4-nitrophenylhydrazone, orange slender prisms from alcohol, m. p. 201° (Found : Cl, 14.0. $C_9H_8O_3N_4Cl$ requires Cl, 13.85%).

By the method previously given (J., *loc. cit.*), the following have been prepared : α -ketopropaldehyde-4-chloro-2-nitrophenylhydrazone, clusters of yellow minute prisms from alcohol, m. p. 170° (Found : Cl, 14.8. $C_9H_8O_3N_3Cl$ requires Cl, 14.7%); α -ketopropaldehyde-2-chloro-4-nitrophenylhydrazone, which separated from solution in acetic acid as a labile form in pale yellow, hair-like prisms which gradually redissolved with the separation of the stable form in yellow, rectangular, dense, somewhat flattened prisms, m. p. 168° (Found : Cl, 14.6%); α -ketopropaldehyde-p-bromophenylhydrazone, very pale yellow, slender prisms from light petroleum, m. p. 143° (Found : Br, 33.1. $C_9H_8ON_2Br$ requires Br, 33.2%).

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