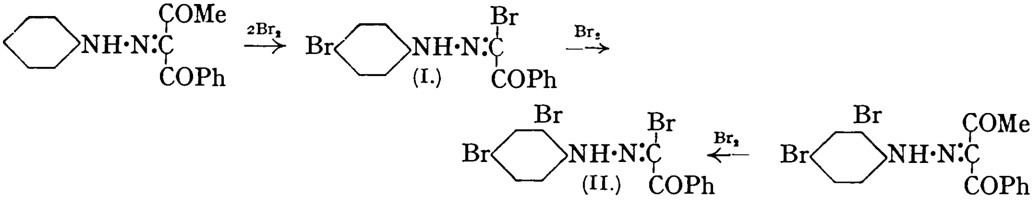
117. *The Action of Bromine upon Arylazobenzoylacetones.*

By F. D. Chattaway and R. J. Lye.

Bromine acts upon the similarly constituted compounds, $\mathrm{Ar{\cdot}NH{\cdot}N{:}CAc{\cdot}COR}$, formed by coupling diazonium salts with benzoyl-, acetyl-, or formyl-acetone (R = Ph, Me, or H), in the same way as it does upon arylazoacetoacetates (see preceding paper). Its action upon the arylazobenzoylacetones is now described.

When two molecular equivalents of bromine act at the ordinary temperature upon phenylazobenzoylacetone dissolved in acetic acid containing a little water or sodium acetate, *ω-bromophenylglyoxal*-p-*bromophenylhydrazone* (I) is produced.



Further action of bromine upon this compound, even when excess is used, only takes place at a higher temperature; a second atom then enters the nucleus in an *o*-position, and *ω-bromophenylglyoxal*-2 : 4-*dibromophenylhydrazone* (II) is produced. This compound is also formed when one molecular equivalent of bromine acts at the ordinary temperature upon 2 : 4-*dibromophenylazobenzoylacetone* dissolved in acetic acid in the presence of sodium acetate.

The corresponding *ω-bromophenylglyoxal*-2 : 4 : 6-*tribromophenylhydrazone* is similarly obtained from 2 : 4 : 6-*tribromophenylazobenzoylacetone.*

In glacial acetic acid solution, in absence of water or sodium acetate, the action of bromine upon phenylazobenzoylacetone causes, in addition to similar substitution in the phenyl nucleus, successive substitution in the acetyl group, 4-bromo-1 : 2 : 3-triketo-1-phenylbutane-2-phenylhydrazone and 4 : 4-dibromo-1 : 2 : 3-triketo-1-phenylbutane-2-phenylhydrazone being formed.

Compounds containing either one or two bromine atoms in the acetyl group are formed practically quantitatively as successive stages in the bromination of 2 : 4-dibromophenylazobenzoylacetone and of 2 : 4 : 6-tribromophenylazobenzoylacetone, and can easily be isolated, but the regulation of the bromination of phenylazobenzoylacetone is more difficult, only the product of the action of three molecules of bromine, 4 : 4-*dibromo*-1 : 2 : 3-*triketo*-1-*phenylbutane*-2-p-*bromophenylhydrazone*, $\mathrm{C_6H_4Br{\cdot}NH{\cdot}N{:}CBz{\cdot}CO{\cdot}CHBr_2}$, being easily isolated.

The action of chlorine upon the arylazobenzoylacetones is more difficult to regulate than that of bromine, and though the acetyl group as a whole is very readily replaced by chlorination in glacial or slightly diluted acetic acid, the conditions under which substitution in the acetyl group alone occurs have not yet been found.

The bromine atom in the ω-bromophenylglyoxalarylhydrazones is very reactive, and is readily replaced by various other groups, *e.g.*, NHPh.

Bromine atoms substituted in the acetyl group cannot be similarly replaced, since reagents such as ammonia or potassium acetate bring about elimination of hydrogen bromide and ring closure with formation of derivatives of 4-hydroxypyrazole (cf. preceding paper). 4-*Hydroxy*-3-*benzoyl*-1-(2′ : 4′-*dibromophenyl*)*pyrazole*, thus obtained from 4-*bromo*-1 : 2 : 3-*triketo*-1-*phenylbutane*-2-(2′ : 4′-*dibromophenylhydrazone*), on further bromination yields 5-*bromo*-4-*hydroxy*-3-*benzoyl*-1-(2′ : 4′-*dibromophenyl*)*pyrazole*, which is also obtained by the elimination of hydrogen bromide from 4 : 4-dibromo-1 : 2 : 3-triketo-1-phenylbutane-2-(2′ : 4′-dibromophenylhydrazone).

Experimental.

Phenylazobenzoylacetone.—9 G. of aniline (1 mol.) were diazotised (40 c.c. conc. HCl, 7 g. $NaNO_2$) and the solution was added slowly to a well-stirred solution of 18 g. of benzoylacetone

(1 mol. + excess) in 100 c.c. of ice-cold EtOH containing 80 g. of cryst. sodium acetate in suspension. Phenylazobenzoylacetone began to separate almost at once; it crystallised from EtOH in golden prisms, m. p. 90—95° (yield, 90%) (Found : N, 10·4. Calc. for $C_{16}H_{14}O_2N_2$: N, 10·5%). Beyer and Claisen (*Ber.*, 1888, **21**, 1705) give m. p. 99°.

In a similar way other coupled products of benzoylacetone were made. 2 : 4-*Dibromophenylazobenzoylacetone*, yellow flattened prisms with domed ends, from AcOH, m. p. 160° (Found : Br, 37·8. $C_{16}H_{12}O_2N_2Br_2$ requires Br, 37·7%); *acetyl* derivative compact, colourless, four-sided prisms, m. p. 171°, from EtOH (Found : Br, 34·6. $C_{18}H_{14}O_3N_2Br_2$ requires Br, 34·3%). 2 : 4 : 6-*Tribromophenylazobenzoylacetone*, dull yellow, rhombic plates, m. p. 112°, from AcOH (Found : Br, 47·9. $C_{16}H_{11}O_2N_2Br_3$ requires Br, 47·7%); *acetyl* derivative, long, slender, flattened, colourless prisms, m. p. 159°, from EtOH (Found : Br, 44·4. $C_{18}H_{13}O_3N_2Br_3$ requires Br, 44·0%).

ω-*Bromophenylglyoxal*-p-*bromophenylhydrazone* (I).—3·2 G. of Br (2 mols.) in 4 c.c. of AcOH were added to a cooled solution of 2·7 g. of phenylazobenzoylacetone (1 mol.) and 2·7 g. of NaOAc (2 mols.) in 20 c.c. of AcOH. On standing and addition of water, the p-*bromophenylhydrazone* (I) separated; it crystallised from AcOH in very pale yellow needles, m. p. 197° (yield, 60%) (Found : Br, 42·0. $C_{14}H_{10}ON_2Br_2$ requires Br, 41·9%).

The ω-*anilino*-compound, prepared from 0·5 g. of the *p*-bromophenylhydrazone and excess of aniline in boiling EtOH (10 c.c.), separated on cooling, and crystallised from EtOH in long, flattened, obliquely-truncated, yellow prisms, m. p. 165° (Found : Br, 20·1. $C_{20}H_{16}ON_3Br$ requires Br, 20·3%). It is phototropic and becomes deep red on exposure to light.

Further Action of Bromine (1 *mol.*) *upon* ω-*Bromophenylglyoxal*-p-*bromophenylhydrazone*.—1 G. of Br (1 mol.) in 3 c.c. of AcOH was added to a hot solution of 2 g. of ω-bromophenylglyoxal-*p*-bromophenylhydrazone (1 mol.) in 20 c.c. of AcOH. On cooling, ω-*bromophenylglyoxal*-2 : 4-*dibromophenylhydrazone* (II) separated quantitatively. It crystallised from EtOH in long, slender, colourless prisms, which became yellow on exposure to light; m. p. 122° (Found : Br, 52·2. $C_{14}H_9ON_2Br_3$ requires Br, 52·1%).

The ω-*anilino*-compound crystallised from EtOH in long, slender, pale yellow prisms, m. p. 137° (Found : Br, 33·7. $C_{20}H_{15}ON_3Br_2$ requires Br, 33·8%).

ω-*Bromophenylglyoxal*-2 : 4 : 6-*tribromophenylhydrazone*.—1·6 G. of Br (1 mol.) in 4 c.c. of AcOH were added to a cooled solution of 5 g. of 2 : 4 : 6-tribromophenylazobenzoylacetone (1 mol.) and 1·4 g. of NaOAc (1 mol.) in 35 c.c. of AcOH. On addition of H_2O the ω-*bromo*-compound separated. It crystallised from AcOH in a mass of small, colourless, hair-like needles, m. p. 132° (yield, 60%) (Found : Br, 59·3. $C_{14}H_8ON_2Br_4$ requires Br, 59·3%).

ω-*Chlorophenylglyoxal*-2 : 4 : 6-*tribromophenylhydrazone*.—Cl was bubbled in a slow stream through a suspension of 2 : 4 : 6-tribromophenylazobenzoylacetone in AcOH. Heat was evolved and a clear solution formed, from which, on addition of H_2O, ω-*chlorophenylglyoxal*-2 : 4 : 6-*tribromophenylhydrazone* separated. It crystallised from EtOH in felted, colourless needles, m. p. 142° (Found : Cl, 7·1; Br, 48·1. $C_{14}H_8ON_2ClBr_3$ requires Cl, 7·2; Br, 48·4%).

ω-*Anilinophenylglyoxal*-2 : 4 : 6-*tribromophenylhydrazone*, prepared by boiling either of the above ω-halogeno-compounds with aniline in EtOH, crystallised from EtOH in pale yellow, flattened prisms, m. p. 118° (Found : Br, 43·8. $C_{20}H_{14}ON_3Br_3$ requires Br, 43·5%).

4 : 4-*Dibromo*-1 : 2 : 3-*triketo*-1-*phenylbutane*-2-p-*bromophenylhydrazone*.—4·8 G of Br (3 mols.) in 5 c.c. of AcOH were added to a solution of 2·7 g. of phenylazobenzoylacetone (1 mol.) in 10 c.c. of AcOH at about 40°. HBr was copiously evolved and a deep red solution formed, from which, on cooling, the above *compound* (3·5 g.) separated. It crystallised from boiling $CHCl_3$–EtOH in long, flattened, golden-yellow needles, m. p. 177° (decomp.) (Found : Br, 48·0. $C_{16}H_{11}O_2N_2Br_3$ requires Br, 47·7%).

4-*Bromo*-1 : 2 : 3-*triketo*-1-*phenylbutane*-2-(2′ : 4′-*dibromophenylhydrazone*), prepared by adding 1·6 g. of Br (1 mol.) in 3 c.c. of AcOH to a boiling solution of 4·3 g. of 2 : 4-dibromophenylazobenzoylacetone (1 mol.) in 20 c.c. of AcOH, separated (4·6 g.) on cooling; it crystallised from boiling C_6H_6 in small, flattened, yellow prisms, m. p. 170° (decomp.) (Found : Br, 47·2. $C_{16}H_{11}O_2N_2Br_3$ requires Br, 47·7%).

The corresponding 4 : 4-*dibromo*-compound, prepared similarly, formed slender, flattened, deep yellow prisms from C_6H_6, m. p. 187° (decomp.) (Found : Br, 55·2. $C_{16}H_{10}O_2N_2Br_4$ requires Br, 55·0%).

4-*Bromo*- and 4 : 4-*dibromo*-1 : 2 : 3-*triketo*-1-*phenylbutane*-2-(2′ : 4′ : 6′-*tribromophenylhydrazone*) formed long, slender, lemon-yellow prisms from $CHCl_3$, m. p. 158° (decomp.) (Found : Br, 55·1. $C_{16}H_{10}O_2N_2Br_4$ requires Br, 55·0%), and flattened, deep yellow prisms from C_6H_6, m. p. 156° (decomp.) (Found : Br, 60·5. $C_{16}H_9O_2N_2Br_5$ requires Br, 60·5%), respectively.

4-*Hydroxy*-3-*benzoyl*-1-(2′ : 4′-*dibromophenyl*)*pyrazole*.—5 G. of finely powdered 4-bromo-1 : 2 : 3-triketo-1-phenylbutane-2-(2′ : 4′-dibromophenylhydrazone) (1 mol.) were added in portions to a boiling solution of 2 g. of KOAc (excess) in 20 c.c. of EtOH. Sufficient heat was evolved to keep the solution boiling, and a pale yellow solution was formed. On cooling, and addition of H_2O, the 4-*hydroxy-pyrazole* separated almost quantitatively. It crystallised from AcOH in very pale yellow, slender, flattened prisms, m. p. 171° (Found : Br, 38·2. $C_{16}H_{10}O_2N_2Br_2$ requires Br, 37·9%).

5-*Bromo*-4-*hydroxy*-3-*benzoyl*-1-(2′ : 4′-*dibromophenyl*)*pyrazole*, similarly prepared from the 4 : 4-dibromo-butane, crystallised from AcOH in colourless flattened prisms, m. p. 127° (Found : Br, 47·85. $C_{16}H_9O_2N_2Br_3$ requires Br, 47·9%). This compound was also obtained by the action of 0·3 g. of Br (1 mol.) upon a boiling solution of 0·5 g. of 4-hydroxy-3-benzoyl-1-(2′ : 4′-dibromophenyl)pyrazole (1 mol.) in 5 c.c. of AcOH.

4-*Hydroxy*-3-*benzoyl*-1-(2′ : 4′ : 6′-*tribromophenyl*)*pyrazole*, prepared by the action of alc. KOAc upon 4-bromo-1 : 2 : 3-triketo-1-phenylbutane-2-(2′ : 4′ : 6′-tribromophenylhydrazone), crystallised from boiling AcOH in colourless prisms, m. p. 206° (Found : Br, 48·1. $C_{16}H_9O_2N_2Br_3$ requires Br, 47·9%). The *acetyl* derivative, prepared by warming it with Ac_2O and a drop of conc. H_2SO_4, crystallised from EtOH in long, slender, colourless prisms, m. p. 140° (Found : Br, 44·4. $C_{18}H_{11}O_3N_2Br_3$ requires Br, 44·2%).

5-*Bromo*-4-*hydroxy*-3-*benzoyl*-1-(2′ : 4′ : 6′-*tribromophenyl*)*pyrazole* was prepared both by brominating 4-hydroxy-3-benzoyl-1-(2′ : 4′ : 6′-tribromophenyl)pyrazole and by heating 4 : 4-dibromo-1 : 2 : 3-triketo-1-phenylbutane-2-(2′ : 4′ : 6′-tribromophenylhydrazone) with alc. KOAc. It separated from AcOH in colourless compact prisms, m. p. 178° (Found : Br, 55·6. $C_{16}H_8O_2N_2Br_4$ requires Br, 55·2%). Its *acetyl* derivative crystallised from EtOH in colourless flattened prisms with domed ends, m. p. 117° (decomp.) (Found : Br, 51·6. $C_{18}H_{10}O_3N_2Br_4$ requires Br, 51·4%).

THE QUEEN'S COLLEGE LABORATORY, OXFORD. [*Received, February* 14*th*, 1933.]