

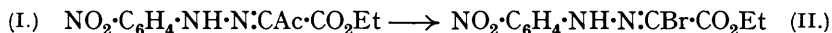
116. *The Action of Bromine upon Nitrophenylazoacetoacetates and Related Compounds.*

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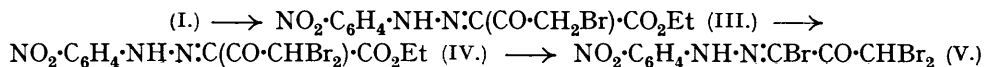
WHEN halogens react with arylazoacetoacetates, either the aryl nucleus or the acetyl group may be substituted, or the acetyl group and even the carbethoxy-group replaced by halogen (*Proc. Roy. Soc.*, 1932, **135**, 282; **137**, 489).

The *nitrophenylazoacetoacetates* (I), which are readily formed by the action of the nitrophenyldiazonium salts upon ethyl acetoacetate, behave similarly, the nitro-group merely preventing or hindering substitution in the aryl nucleus. In but one case, that of *o*-nitrophenylazoacetoacetate, was bromine found to enter the nucleus and then only very slowly when excess was used.

In cold, slightly diluted acetic acid, bromine replaces the acetyl group and produces *nitrophenylhydrazones* of ethyl α -bromoglyoxylate (II), bromine not entering the nucleus under these conditions :



In boiling glacial acetic acid, on the other hand, bromine displaces hydrogen in the acetyl group, producing first *nitrophenylazo- γ -bromoacetoacetates* (III), then *nitrophenylazo- $\gamma\gamma$ -dibromoacetoacetates* (IV), and finally displaces the carbethoxy-group, *nitrophenylhydrazones* of $\beta\beta\omega$ -tribromo- α -ketopropaldehyde (V) being the end products :

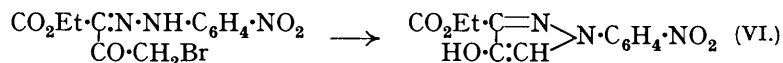


In the case of the *o*-nitrophenylazoacetoacetate, when excess of halogen is used and reaction takes place in glacial acetic acid at 100°, bromine enters the nucleus in the para-position and the final product is $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-4-bromo-2-nitrophenylhydrazone.

The constitution of the γ -bromoacetoacetates has been proved by their synthesis from nitrophenyldiazonium salts and ethyl γ -bromoacetoacetate under the normal conditions.

The action of bromine upon the *o*-, *m*-, and *p*-nitrophenylhydrazones of α -ketopropaldehyde (prepared by coupling acetoacetic acid with the nitrophenyldiazonium salts, carbon dioxide being lost in the reaction: $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl} + \text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H} \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{CHAc}$) has also been studied. The final products are the nitrophenylhydrazones of $\beta\beta\omega$ -tribromo- α -ketopropaldehyde identical with those obtained by the action of excess of bromine on the azoacetoacetates, ω -bromo- α -ketopropaldehydenitrophenylhydrazones and $\beta\omega$ -dibromo- α -ketopropaldehydenitrophenylhydrazones being formed as intermediate stages. Bromine enters the nitrophenyl residue only in the case of α -ketopropaldehyde-*o*-nitrophenylhydrazone; then, as before, it enters in the para-position, and the final product is $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-4-bromo-2-nitrophenylhydrazone.

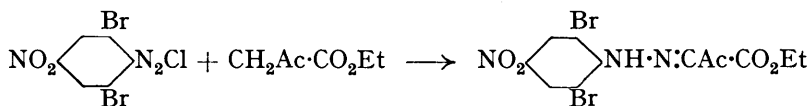
When treated with alcoholic potassium acetate, the azo- γ -bromoacetoacetates and the azo- $\gamma\gamma$ -dibromoacetoacetates lose hydrogen bromide, ring closure taking place with the formation of 4-hydroxy- and 5-bromo-4-hydroxy-pyrazole derivatives respectively:



5-Bromo-4-hydroxypyrazoles can also be obtained by brominating the 4-hydroxypyrazoles in boiling acetic acid.

The bromine atoms in the α -bromoglyoxylates and the ω -bromo- α -ketopropaldehydes are similarly very reactive and are easily replaced by other groups; *e.g.*, alcoholic ammonia replaces the halogen by an amino-group.

Although bromine is not introduced into the phenyl nucleus by the action of bromine upon the *m*- and *p*-nitrophenylazoacetoacetates, even when excess is used, compounds with bromine in the nucleus can easily be made by coupling the appropriate brominated nitrophenyldiazonium salts with ethyl acetoacetate; *e.g.*,



The action of bromine upon ethyl 2 : 6-dibromo-4-nitrophenylazoacetoacetate and ethyl 2-bromo-4-nitrophenylazoacetoacetate, thus prepared, resembles closely its action on the unsubstituted nitrophenylazoacetoacetates themselves.

EXPERIMENTAL.

Ethyl p-Nitrophenylazoacetoacetate (I).—A solution of 25 g. of *p*-nitroaniline (1 mol.) in 30 c.c. of boiling AcOH was poured, with constant stirring, into 300 c.c. of cold conc. HCl to obtain a fine pulp of crystals. This was diazotised at 0–5° with 15 g. of NaNO₂ (1 mol.) in 70 c.c. of H₂O. The diazonium solution was filtered and added slowly to a well-stirred cooled mixture of 30 g. of ethyl acetoacetate (1 mol. + excess) in 50 c.c. of EtOH and 50 c.c. of H₂O containing 350 g. of cryst. NaOAc. *Ethyl p*-nitrophenylazoacetoacetate separated as a yellow solid. It crystallised from EtOH in yellow, long, slender needles, m. p. 127° (Found : N, 14.9. C₁₂H₁₃O₅N₃ requires N, 15.05%). In a similar manner were obtained *ethyl 2-bromo-4-nitrophenylazoacetoacetate*, light yellow, very slender prisms from EtOH, m. p. 130° (Found : Br, 22.1. C₁₂H₁₂O₅N₃Br requires Br, 22.3%), *ethyl 2 : 6-dibromo-4-nitrophenylazoacetoacetate*, bright yellow, long, slender needles from EtOH, m. p. 135° (Found : Br, 36.4. C₁₂H₁₁O₅N₃Br₂ requires Br, 36.6%), *ethyl o*-nitrophenylazoacetoacetate, deep yellow leaflets from light petroleum, m. p. 93° (Found : N, 14.9%), and *ethyl m*-nitrophenylazoacetoacetate, yellow, long, slender, four-sided prisms from EtOH, m. p. 128° (Found : N, 14.9%).

α -Ketopropaldehyde-*p*-nitrophenylhydrazone, CH₃·CO·CH:N·NH·C₆H₄·NO₂.—A diazonium solution prepared from 15 g. of *p*-nitroaniline (1 mol.) was added slowly at 0° to 15 g. of aceto-

acetic acid in 275 c.c. of H₂O containing 200 g. of cryst. NaOAc. *α*-Ketopropaldehyde-*p*-nitrophenylhydrazone began to separate almost immediately, CO₂ being given off. It crystallised from EtOH in bright yellow, hair-like needles, m. p. 217° (Found : N, 20.3. C₉H₉O₃N₃ requires N, 20.3%).

In a similar way were prepared *α*-ketopropaldehyde-2-bromo-4-nitrophenylhydrazone, which separates first from a solution in AcOH in a labile form as light yellow needles which gradually dissolve in the mother-liquor, a stable polymorphic form then separating as yellow, compact, four-sided prisms, m. p. 187° (Found : Br, 28.2. C₉H₈O₃N₃Br requires Br, 27.95%); *α*-ketopropaldehyde-2 : 6-dibromo-4-nitrophenylhydrazone, pale yellow, four-sided prisms with domed ends from C₆H₆, m. p. 151° (Found : Br, 44.0. C₉H₇O₃N₃Br₂ requires Br, 43.8%); *α*-ketopropaldehyde-*o*-nitrophenylhydrazone, deep yellow, long, hair-like needles from EtOH, m. p. 128° (Found : N, 20.3%); *α*-ketopropaldehyde-*m*-nitrophenylhydrazone, clusters of pale yellow, slender needles from EtOH, m. p. 152° (Found : N, 20.1%); and *α*-ketopropaldehyde-4-bromo-2-nitrophenylhydrazone, pale yellow, very slender needles from AcOH, m. p. 176° (Found : Br, 28.0%).

Ethyl α-Bromoglyoxylate-*p*-nitrophenylhydrazone (II).—1.65 G. of Br (1 mol.) in 3 c.c. of AcOH were added to a solution of 2.8 g. of *p*-nitrophenylazoacetate (1 mol.) and 2 g. of cryst. NaOAc (1 mol. + excess) in 40 c.c. of AcOH. *Ethyl α*-bromoglyoxylate-*p*-nitrophenylhydrazone slowly separated as a yellow solid. It crystallised from AcOH as a labile form in long, pale yellow needles which gradually redissolved whilst bright yellow, compact rhombic plates of a stable form separated, m. p. 203° (Found : Br, 25.2. C₁₀H₁₀O₄N₃Br requires Br, 25.3%). The following compounds were similarly prepared: *ethyl α*-bromoglyoxylate-2-bromo-4-nitrophenylhydrazone, very pale yellow, long, slender needles from EtOH, m. p. 126° (Found : Br, 40.2. C₁₀H₉O₄N₃Br₂ requires Br, 40.5%); *ethyl α*-bromoglyoxylate-2 : 6-dibromo-4-nitrophenylhydrazone, very pale yellow, slender prisms from EtOH, m. p. 144° (Found : Br, 50.3. C₁₀H₈O₄N₃Br₂ requires Br, 50.6%); *ethyl α*-bromoglyoxylate-*o*-nitrophenylhydrazone, yellow, four-sided, flattened prisms from EtOH, m. p. 137° (Found : Br, 25.1%); *ethyl α*-bromoglyoxylate-*m*-nitrophenylhydrazone, yellow compact tablets from EtOH, m. p. 149° (Found : Br, 25.0%). *Ethyl α*-aminoglyoxylate-*p*-nitrophenylhydrazone was quantitatively formed when *ethyl α*-bromoglyoxylate-*p*-nitrophenylhydrazone was stirred into EtOH saturated with NH₃. It crystallised from aq. EtOH in yellow, slender prisms, m. p. 181° (Found : N, 22.1. C₁₀H₁₂O₄N₄ requires N, 22.2%).

The following compounds were similarly prepared: *ethyl α*-aminoglyoxylate-2-bromo-4-nitrophenylhydrazone, deep yellow, slender prisms from EtOH, m. p. 124.5° (Found : Br, 24.0. C₁₀H₁₁O₄N₄Br requires Br, 24.15%); *ethyl α*-aminoglyoxylate-2 : 6-dibromo-4-nitrophenylhydrazone, bright yellow, slender prisms from EtOH, m. p. 191° (Found : Br, 39.2. C₁₀H₁₀O₄N₄Br₂ requires Br, 39.0%); *ethyl α*-aminoglyoxylate-*o*-nitrophenylhydrazone, red, long, flattened, four-sided prisms from EtOH, m. p. 123° (Found : N, 22.2%).

Ethyl p-Nitrophenylazo-*γ*-bromoacetate (III).—(1) 11 G. of *p*-nitroaniline (1 mol.) were diazotised, and the solution slowly added to 20 g. of *γ*-bromoacetoacetic ester (1 mol. + excess) in 50 c.c. of EtOH and 50 c.c. of H₂O containing 150 g. of cryst. NaOAc. *Ethyl p*-nitrophenylazo-*γ*-bromoacetate, collected after 6 hr., crystallised from EtOH in light yellow, slender prisms, m. p. 163° (Found : Br, 22.2. C₁₂H₁₂O₅N₃Br requires Br, 22.3%).

(2) 3.3 G. of Br (1 mol.) in 3 c.c. of AcOH were added to a solution of 5.6 g. of *ethyl p*-nitrophenylazoacetate (1 mol.) in 25 c.c. of AcOH. *Ethyl p*-nitrophenylazo-*γ*-bromoacetate separated on cooling, and crystallised from EtOH in light yellow, slender prisms, m. p. 163°, identical with the product obtained above. The yield was quantitative.

By similar methods were also obtained *ethyl 2-bromo-4-nitrophenylazo-γ*-bromoacetate, yellow hair-like needles from EtOH, m. p. 138° (Found : Br, 36.4. C₁₂H₁₁O₅N₃Br₂ requires Br, 36.6%); *ethyl 2 : 6-dibromo-4-nitrophenylazo-γ*-bromoacetate, pale yellow, long, slender prisms from EtOH, m. p. 118° (Found : Br, 46.5. C₁₂H₁₀O₅N₃Br₂ requires Br, 46.5%); *ethyl o*-nitrophenylazo-*γ*-bromoacetate, bright yellow, slender, flattened prisms from C₆H₆-light petroleum (b. p. 60—80°), m. p. 145° (Found : Br, 22.1%); *ethyl m*-nitrophenylazo-*γ*-bromoacetate, pale yellow, long, slender needles from EtOH, m. p. 122° (Found : Br, 22.0%).

Action of Bromine (2 mols.) upon Ethyl p-Nitrophenylazoacetate. *Formation of Ethyl p*-Nitrophenylazo-*γγ*-dibromoacetate (IV).—6.6 G. of Br (2 mols.) in 4 c.c. of AcOH were added to a boiling solution of 5.6 g. of *ethyl p*-nitrophenylazoacetate (1 mol.) in 2.5 c.c. of AcOH. On cooling, *ethyl p*-nitrophenylazo-*γγ*-dibromoacetate separated; it crystallised from EtOH in pale yellow, long, slender prisms, m. p. 134° (Found : Br, 36.8. C₁₂H₁₁O₅N₃Br₂ requires Br, 36.6%).

By similar methods were also obtained *ethyl 2-bromo-4-nitrophenylazo- γ -dibromoacetoacetate*, pale yellow, long, slender prisms from EtOH, m. p. 167° (Found: Br, 46.4. $C_{12}H_{10}O_5N_3Br_3$ requires Br, 46.5%); *ethyl 2:6-dibromo-4-nitrophenylazo- γ -dibromoacetoacetate*, yellow, irregular, rhombic plates from EtOH, m. p. 153° (Found: Br, 53.9. $C_{12}H_9O_5N_3Br_4$ requires Br, 53.75%); *ethyl o-nitrophenylazo- γ -dibromoacetoacetate*, deep yellow, large, irregular, lustrous plates from petroleum (b. p. 60—80°), m. p. 116° (Found: Br, 36.4%); *ethyl m-nitrophenylazo- γ -dibromoacetoacetate*, pale yellow, slender, short, hair-like prisms from EtOH, m. p. 117° (Found: Br, 36.6%).

Action of Excess of Bromine upon Ethyl p-Nitrophenylazoacetoacetate and of Bromine (3 mols.) upon α -Ketopropaldehyde-p-nitrophenylhydrazone. Formation of $\beta\beta\omega$ -Tribromo- α -ketopropaldehyde-p-nitrophenylhydrazone (V).—(1) 14 G. of Br in 10 c.c. of AcOH were added to a solution of 5.6 g. of ethyl p-nitrophenylazoacetoacetate in 25 c.c. of AcOH, and the mixture heated for 12 hr. on a water-bath. $\beta\beta\omega$ -Tribromo- α -ketopropaldehyde-p-nitrophenylhydrazone separated slowly; it crystallised from AcOH in light yellow, thin, flattened prisms, m. p. 194° (Found: Br, 54.2. $C_9H_6O_3N_3Br_3$ requires Br, 54.0%).

(2) 3.6 G. of Br (3 mols.) in 5 c.c. of AcOH were added to a boiling solution of 2 g. of α -ketopropaldehyde-p-nitrophenylhydrazone (1 mol.) in 15 c.c. of AcOH. $\beta\beta\omega$ -Tribromo- α -ketopropaldehyde-p-nitrophenylhydrazone separated as a yellow solid on cooling; after crystn. from AcOH it was identical with the compound prepared as above.

By similar methods have been prepared $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-2-bromo-4-nitrophenylhydrazone, pale yellow, long, slender needles from AcOH, m. p. 186° (Found: Br, 60.9. $C_9H_5O_3N_3Br_4$ requires Br, 61.1%); $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-2:6-dibromo-4-nitrophenylhydrazone, pale yellow, flattened prisms from AcOH, m. p. 128° (Found: Br, 66.2. $C_9H_4O_3N_3Br_5$ requires Br, 66.4%); $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-m-nitrophenylhydrazone, pale yellow, long, slender prisms from AcOH, m. p. 158° (Found: Br, 53.8%); $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-o-nitrophenylhydrazone (by the action of 3 mols. of Br upon α -ketopropaldehyde-o-nitrophenylhydrazone), deep yellow, very long, slender prisms from AcOH, m. p. 145.5° (Found: Br, 53.7%); $\beta\beta\omega$ -tribromo- α -ketopropaldehyde-4-bromo-2-nitrophenylhydrazone (by the prolonged action of excess of Br upon ethyl o-nitrophenylazoacetoacetate or α -ketopropaldehyde-o-nitrophenylhydrazone, and also by the action of 3 mols. of Br upon α -ketopropaldehyde-4-bromo-2-nitrophenylhydrazone), yellow, thin, flattened prisms from AcOH, m. p. 160° (Found: Br, 60.8%).

Action of Bromine (1 mol.) upon α -Ketopropaldehyde-p-nitrophenylhydrazone. Formation of ω -Bromo- α -ketopropaldehyde-p-nitrophenylhydrazone.—4.8 G. of Br (1 mol.) in 6 c.c. of AcOH were added to a solution of 8 g. of α -ketopropaldehyde-p-nitrophenylhydrazone (1 mol.) and 4 g. of cryst. NaOAc (1 mol. + excess) in 100 c.c. of AcOH. After 1 hr., on addition of H_2O , ω -bromo- α -ketopropaldehyde-p-nitrophenylhydrazone separated in practically quant. yield. It crystallised from AcOH in yellow, large, four-sided, obliquely truncated prisms, m. p. 233° (Found: Br, 27.9. $C_9H_8O_3N_3Br$ requires Br, 27.95%).

In a similar manner were prepared ω -bromo- α -ketopropaldehyde-2-bromo-4-nitrophenylhydrazone, pale yellow, very slender needles from EtOH, m. p. 162° (Found: Br, 43.5. $C_9H_7O_3N_3Br_2$ requires Br, 43.8%); ω -bromo- α -ketopropaldehyde-2:6-dibromo-4-nitrophenylhydrazone, pale yellow, slender, long, flattened prisms from EtOH, m. p. 156° (Found: Br, 53.7. $C_9H_6O_3N_3Br_3$ requires Br, 54.0%); ω -bromo- α -ketopropaldehyde-o-nitrophenylhydrazone, yellow, long, slender, deep, flattened, irregular prisms from AcOH, m. p. 185° (Found: Br, 28.1%); ω -bromo- α -ketopropaldehyde-m-nitrophenylhydrazone, pale yellow, short needles from EtOH, m. p. 214° (Found: Br, 27.8%).

Action of Bromine (2 mols.) upon α -Ketopropaldehyde-p-nitrophenylhydrazone. Formation of $\beta\omega$ -Dibromo- α -ketopropaldehyde-p-nitrophenylhydrazone.—9.6 G. of Br (2 mols.) in 8 c.c. of AcOH were added to a solution of 8 g. of α -ketopropaldehyde-p-nitrophenylhydrazone (1 mol.) in 30 c.c. of AcOH at 90°. On cooling, $\beta\omega$ -dibromo- α -ketopropaldehyde-p-nitrophenylhydrazone separated. It crystallised from AcOH in clusters of small yellow needles, m. p. 228° (Found: Br, 43.7. $C_9H_7O_3N_3Br_2$ requires Br, 43.8%).

In a similar manner were obtained $\beta\omega$ -dibromo- α -ketopropaldehyde-2-bromo-4-nitrophenylhydrazone, deep yellow, large prisms from EtOH, m. p. 177° (Found: Br, 54.1. $C_9H_6O_3N_3Br_3$ requires Br, 54.0%); $\beta\omega$ -dibromo- α -ketopropaldehyde-2:6-dibromo-4-nitrophenylhydrazone, yellow, long, slender needles from EtOH, m. p. 136° (Found: Br, 61.1. $C_9H_5O_3N_3Br_3$ requires Br, 61.1%); $\beta\omega$ -dibromo- α -ketopropaldehyde-o-nitrophenylhydrazone, deep yellow, very long, slender prisms from EtOH, m. p. 175° (Found: Br, 43.6%).

ω -Amino- α -ketopropaldehyde-p-nitrophenylhydrazone was obtained in quant. yield by stirring

ω -bromo- α -ketopropaldehyde-*p*-nitrophenylhydrazone into sat. alc. NH_3 . It separated from EtOH in scarlet, long, slender prisms, m. p. 240° (decomp.) (Found : N, 25.4. $\text{C}_9\text{H}_{10}\text{O}_3\text{N}_4$ requires N, 25.2%). ω -Amino- α -ketopropaldehyde-*o*-nitrophenylhydrazone, similarly prepared, crystallised from EtOH in scarlet, long, slender, four-sided prisms, m. p. 174° (Found : N, 25.0%).

ω -Anilino- α -ketopropaldehyde-*p*-nitrophenylhydrazone, prepared by boiling an alc. solution of ω -bromo- α -ketopropaldehyde-*p*-nitrophenylhydrazone with aniline, crystallised from EtOH in deep yellow, large, somewhat flattened prisms, m. p. 167° (Found : N, 18.8. $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_4$ requires N, 18.8%). ω -Anilino- α -ketopropaldehyde-*o*-nitrophenylhydrazone, similarly prepared, crystallised from EtOH in orange, long, slender, flattened prisms, m. p. 140° (Found : N, 18.6%).

4-Hydroxy-3-carbethoxy-1-(4'-nitrophenyl)pyrazole (VI).—1.5 G. of KOAc (1 mol.) were added in small quantities at a time to 5 g. of ethyl *p*-nitrophenylazo- γ -bromoacetoacetate (1 mol.) in 75 c.c. of boiling EtOH; the solution darkened and KBr separated. On cooling, and addition of H_2O , 4-hydroxy-3-carbethoxy-1-(4'-nitrophenyl)pyrazole separated as a light brown solid. It crystallised from EtOH in colourless hair-like needles, m. p. 220° (Found : N, 14.9. $\text{C}_{12}\text{H}_{11}\text{O}_5\text{N}_3$ requires N, 15.15%). Its acetyl derivative, made by warming it with $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$, crystallised from EtOH in colourless flattened prisms with domed ends, m. p. 167° (Found : N, 13.4. $\text{C}_{14}\text{H}_{13}\text{O}_6\text{N}_3$ requires N, 13.2%).

In a similar manner were obtained : 4-Hydroxy-3-carbethoxy-1-(2'-bromo-4'-nitrophenyl)pyrazole, colourless, long, slender, flattened prisms from EtOH, m. p. 189° (Found : Br, 22.6. $\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_3\text{Br}$ requires Br, 22.45%); acetyl derivative, colourless, long, slender, four-sided prisms from EtOH, m. p. 138.5° (Found : Br, 20.0. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_3\text{Br}$ requires Br, 20.1%); 4-hydroxy-3-carbethoxy-1-(2' : 6'-dibromo-4'-nitrophenyl)pyrazole, colourless rectangular plates from EtOH, m. p. 170° (Found : Br, 37.0. $\text{C}_{12}\text{H}_9\text{O}_5\text{N}_3\text{Br}_2$ requires Br, 36.8%); acetyl derivative, clusters of colourless small plates from EtOH, m. p. 148° (Found : Br, 33.2. $\text{C}_{14}\text{H}_{11}\text{O}_6\text{N}_3\text{Br}_2$ requires Br, 33.5%); benzoyl derivative, prepared by a Schotten-Baumann reaction, in colourless compact prisms from EtOH, m. p. 143° (Found : Br, 29.6. $\text{C}_{18}\text{H}_{13}\text{O}_6\text{N}_3\text{Br}_2$ requires Br, 29.7%); 4-hydroxy-3-carbethoxy-1-(2'-nitrophenyl)pyrazole, colourless, large, six-sided prisms from C_6H_6 , m. p. 153° (Found : N, 15.1%); acetyl derivative, colourless, compact, elongated, six-sided prisms from EtOH, m. p. 115° (Found : N, 13.3%); 4-hydroxy-3-carbethoxy-1-(3'-nitrophenyl)pyrazole, colourless, long, very slender prisms from EtOH, m. p. 199° (Found : N, 15.0%); acetyl derivative, colourless, slender, flattened prisms from EtOH, m. p. 140.5° (Found : N, 13.0%).

Bromination of 4-Hydroxy-3-carbethoxy-1-(4'-nitrophenyl)pyrazole. Formation of 5-Bromo-4-hydroxy-3-carbethoxy-1-(4'-nitrophenyl)pyrazole (as VI).—0.8 G. of Br (1 mol.) in 2 c.c. of AcOH were added to a boiling solution of 1 g. of 4-hydroxy-3-carbethoxy-1-(4'-nitrophenyl)pyrazole in 15 c.c. of AcOH; on cooling, 5-bromo-4-hydroxy-3-carbethoxy-1-(4'-nitrophenyl)pyrazole separated. It crystallised from AcOH in colourless, slender, four-sided prisms, m. p. 163° (Found : Br, 22.6. $\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_3\text{Br}$ requires Br, 22.45%). Its acetyl derivative crystallised from EtOH in colourless, irregular, rhombic plates, m. p. 126° (Found : Br, 19.8. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_3\text{Br}$ requires Br, 20.1%).

5-Bromo-4-hydroxy-3-carbethoxy-1-(4'-nitrophenyl)pyrazole, identical in all respects with the above compound, was also obtained by adding 2 g. of KOAc (1 mol.) to a boiling solution of 6 g. of ethyl *p*-nitrophenylazo- $\gamma\gamma$ -dibromoacetoacetate in 80 c.c. of EtOH. On cooling, and addition of H_2O , it separated as a light brown solid.

The following have been prepared by both of the above methods : 5-bromo-4-hydroxy-3-carbethoxy-1-(2'-bromo-4'-nitrophenyl)pyrazole, colourless, long, slender prisms from EtOH, m. p. 218° (Found : Br, 36.6. $\text{C}_{12}\text{H}_9\text{O}_5\text{N}_3\text{Br}_2$ requires Br, 36.8%); acetyl derivative, colourless, thin, flattened prisms from EtOH, m. p. 108° (Found : Br, 33.5. $\text{C}_{14}\text{H}_{11}\text{O}_6\text{N}_3\text{Br}_2$ requires Br, 33.5%); 5-bromo-4-hydroxy-3-carbethoxy-1-(2' : 6'-dibromo-4'-nitrophenyl)pyrazole, colourless, compact, rectangular prisms with domed ends from EtOH, m. p. 209.5° (Found : Br, 46.5. $\text{C}_{12}\text{H}_8\text{O}_5\text{N}_3\text{Br}_3$ requires Br, 46.7%); acetyl derivative, colourless, irregular, rhombic plates from EtOH, m. p. 126° (Found : Br, 43.0. $\text{C}_{14}\text{H}_{10}\text{O}_6\text{N}_3\text{Br}_3$ requires Br, 43.1%); 5-bromo-4-hydroxy-3-carbethoxy-1-(2'-nitrophenyl)pyrazole, colourless, long, compact, four-sided prisms from EtOH, m. p. 161° , which turn brown on exposure to light (Found : Br, 22.5%); acetyl derivative, colourless, compact, rectangular, flattened prisms from EtOH, m. p. 111° (Found : Br, 19.9%); 5-bromo-4-hydroxy-3-carbethoxy-1-(3'-nitrophenyl)pyrazole, colourless, compact, flattened prisms with domed ends from EtOH, m. p. 167° (Found : Br, 22.3%).