AZOIC DYES*

Part IX. The Behaviour of \( \omega \)-Benzoyl-2-acetyl-1-naphthol towards Diazonium Salts

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The members of the Naphtol AS series derived from 2-hydroxy-3-naphthoic acid and similar \( \sigma \)-hydroxycarboxylic acids yield orange, red and deeper colours. The attachment of an arylazo group to a carbon atom in an aliphatic group being one method for preparing yellow dyes, the I.G. in 1921 introduced Naphtol AS–G, which is bisacetoacet-\( \sigma \)-tolidide, as a "napthilol" for the production of yellow shades; coupled on the fibre with diazotised chloranilines lemon-yellow shades could be obtained. The poor substantivity and the moderate light fastness of the Naphtol AS–G shades then led to the introduction of Naphtol AS–LG, L\( _3 \)G and L\( _4 \)G, the constitution of which has been elucidated by Desai and Mehta.\(^1\) The first two are arylides of terephthaloyl diacetic acid and the last is 2-acetoacetamido- 6-ethoxybenzthiazole. With specified diazonium salts the bright yellow shades from Naphtol AS–L\( _4 \)G possess very high light fastness. It is to be noted, however, that on account of its adequacy for general purposes Naphtol AS–G continues to be widely used for dyeing yellow azoic shades.

The present work is an investigation of the utility, as azoic coupling components, of diketones prepared by the action of sodamide,\(^2\) potassium carbonate\(^3\) or sodium ethoxide\(^4\) on \( \sigma \)-benzoyloxyaryl methyl ketones. A substance such as 2-benzoylacetetyl-1-naphthol (I) has two coupling positions, and the comparative reactivity of these sites for diazonium couplings is of interest. Further, the introduction of a 1:3-diketone group in a dye or a 2-hydroxy-3-naphthanilide type of coupling component might offer a useful method for modifying shades.

2-Benzoylacetetyl-1-naphthol (I) was obtained by the action of anhydrous potassium carbonate in toluene on 2-acetyl-1-naphthol benzoate in very good yield.\(^2\) The diketone (I) gave weak dyeings when used as a "napthol" and coupled with diazotised Fast Red Base B (5-nitro-\( \sigma \)-anisidine) and Scarlet Base GG (2:5-dichloroaniline); the shades lacked fastness to soaping and light. Treatment of the dyeings with potassium dichromate and copper sulphate did not improve the fastness.

The diketone (I), when coupled in substance with one or more moles of diazotised aniline in alcoholic sodium hydroxide solution, yielded the disazo dye (II). Coupling in alcoholic sodium carbonate or pyridine solution with diazotised aniline (1 mole) yielded a mixture of the disazo dye (II) and a monoazo dye (III), which were separated by careful fractional crystallisation from acetic acid, the latter being less soluble. It was observed that boiling the monoazo dye (III) with acetic acid for a long time during crystallisation yielded a third product, which was ultimately found to be the corresponding flavone (IV). The monoazo dye (III), when dyed as a ‘naphthol’, and developed with diazotised Fast Red Salt B, gave brown shades which bled considerably during soaping.

The disazo dye was unaffected by treatment with concentrated sulphuric acid in the cold, while the monoazo dye, either by treatment with concentrated sulphuric acid in the cold or by refluxing with glacial acetic acid gave the flavone (IV) by cyclisation. In view of the ring closure taking place only in the case of the monoazo dye, it is evident that the coupling must have taken place in the 4-position. However, to confirm the constitution of the monoazo dye as (III), it was also prepared by an unambiguous method. 2-Acetyl-1-naphthol (V) was coupled with diazotised aniline to obtain 4-benzeneazo-2-acetyl-1-naphthol (VI). Condensation of (VI) with ethyl benzoate in presence of sodium, sodium ethoxide or sodamide was not successful. The benzoate (VII), prepared under the conditions specified, readily underwent rearrangement with potassium carbonate in toluene, and
gave 4-benzeneazo-2-benzoyleacetyl-1-naphthol (III) identical with the monoazodye obtained by coupling (I) with diazotised aniline. It was observed that 4-nitro-2-acetyl-1-naphthol benzoate (VIII), prepared by the benzylation of 4-nitro-2-acetyl-1-naphthol, did not undergo rearrangement to the corresponding diketone under these conditions.

The benzeneazo-naphtha flavone (IV) on reduction with acetic acid and zinc dust, gave the acetamido derivative (IX). Even when the reduction was carried out in a large volume of alcohol with the addition of 1–2 moles of acetic acid, the acetamido derivative (IX), and not the amine (X), was obtained. Reduction with iron and hydrochloric acid in alcoholic solution gave amorphous red products. The deacetylation of (IX) proved difficult since it remained unaffected when treated either with 30 per cent. hydrochloric acid or 10 per cent. sodium hydroxide solution. The aminoflavone (X) could however be very readily obtained by reduction of (IV) by hydrogen under pressure in presence of Raney nickel. When the diketone (III) was reduced under these conditions, the corresponding amine could not be isolated since it was very unstable. However, when (III) was reduced with sodium hydrosulphite in alcoholic alkali, the aminoflavone (X) was obtained, reduction of the azo-group and cyclisation of the diketone taking place simultaneously.

When the diketone (I) was coupled with diazotised 2:5-dichloroaniline (1 mole) in pyridine or alcoholic sodium hydroxide solution, it gave the disazodye (II; C₆H₅Cl₂ instead of Ph). However, coupling in alcoholic sodium carbonate solution with diazotised 2:5-dichloroaniline (1 mole) gave the disazo dye (II; C₆H₅Cl₂ instead of Ph), together with about 5 per cent. of the monoazo dye (III; C₆H₅Cl₂ instead of Ph), which was isolated as the flavone (IV; C₆H₅Cl₂ instead of Ph). The same monoazo dye was also obtained by the rearrangement of (VII; C₆H₅Cl₂ instead of Ph) with potassium carbonate in toluene.

In order to prepare a diketone which does not have a nuclear site for coupling as in (I), ω-benzoyl-1-acetyl-2-naphthol (XI) was prepared by the rearrangement of 1-acetyl-2-naphthyl benzoate with sodium ethoxide.
The diketone (XI) when coupled in sodium hydroxide solution with diazo- 
tised aniline gave a red substance, which appeared to be a mixture of the 
desired azo dye (XII) and 1-benzeneazo-2-naphthol. 1-Acetyl-2-naphthol 
undergoes a similar displacement on treatment with diazonium salts.5 
Application of (XI) in azoic dyeing by the normal process of impregnation 
from an aqueous alkaline solution was not possible. The diketone (XI) 
coupled readily in alcohol-sodium acetate solution and gave \( \omega \)-benzoyl-
\( \omega \)-benzeneazo-1-acetyl-2-naphthol (XII); but on account of the influence 
of alcohol in lowering the substantivity of the diketone towards cellulose, 
a very weak yellow shade, loose to soaping, was obtained when (XI) was 
applied to cotton yarn from an alcoholic sodium acetate solution and deve-
loped with diazotised 2:5-dichloroaniline.

With a view to studying the effect of a benzamido group \( p \)-to the 
hydroxyl in the diketone (I), the synthesis of (XV) was then undertaken. 
4-Benzamido-1-naphthol did not undergo the Nencki reaction to give the 
2-acetyl compound, from which (XV) could be prepared. The azo dye 
from acetonaphthol and diazotised metanilic acid was reduced by alkaline 
sodium hydrosulphite to give the aminonaphthol (XIII), which on treatment 
with excess of benzoyl chloride gave the dibenzoyl derivative (XIV). Re-
arrangement of (XIV) with potassium carbonate in toluene gave the diketone 
(XV). As a "naphthol" (XV) gave a pink shade with diazotised \( \alpha \)-amino-
anthraquinone, which was loose to soaping and had a light fastness of only
2-3. The diketone (XV) on treatment with concentrated sulphuric acid in the cold gave 6-benzamido-7:8-benzoflavone (XVI).

Condensation of (XIII) with ethyl acetoacetate gave (XVII); the yellowish brown shades produced by development with diazonium salts had poor fastness to light.

5-Benzamido-2-hydroxyacetophenone (XVIII) was prepared by the Fries migration of 4-benzamidophenyl acetate. The benzoate of (XVIII) on treatment with sodamide in benzene gave the diketone (XIX). The diketone was not substantive to cotton, and when developed with diazotised dichloroaniline, it gave a weak brown shade with poor light fastness. The diketone (XIX) could be cyclized as usual to 6-benzamido-flavone (XX).

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**EXPERIMENTAL**

2-Benzoylacetyl-1-naphthol (I)

2-Acetyl-1-naphthyl benzoate (15 g.), toluene (75 c.c.) and freshly ignited potassium carbonate (45 g.) were refluxed under stirring for 8 hours. The deep orange potassium salt was filtered and treated with dilute acetic acid. The diketone (12 g.) crystallised from acetone in bright orange needles, m.p. 147° (Mahal and Venkataraman,\(^2\) 147°).

**Coupling of the diketone (I) with diazotised aniline**

The diketone (1·5 g.) was pasted with 10% sodium hydroxide solution (10 c.c.) and dissolved in alcohol (50 c.c.). The solution was diluted with water (10–15 c.c.) and after adding sodium acetate (4 g.), cooled to 0° and coupled with aniline (1·5 g., 3 mols.) in hydrochloric acid (4·5 c.c.) diazотised with sodium nitrite (1·2 g.). The bright red dye (2·1 g.) crystallized from acetic acid in thin, elongated plates, m.p. 168–70° (Found: N, 11·2\(\text{C}_{91}\text{H}_{92}\text{O}_{3}\text{N}_{4}\) requires N, 11·2%). A little more of the disazo dye was obtained from the filtrate by acidification. The substance also crystallized from the same solvent in a second form with m.p. 204–5°. It gives a brown colour with ferric chloride and a deep cherry red colour with concentrated sulphuric acid. The dye was recovered unchanged from its solution in concentrated sulphuric acid, no cyclization to a flavone taking place under the usual conditions.

When the diketone was coupled under similar conditions using one mole of diazotised aniline, the dye that separated out proved to be (II). The
filtrate on acidification gave a sticky substance, which dissolved in concentrated sulphuric acid with a bright green fluorescence, indicating the presence of unreacted diketone.

When the diketone (I) (0.5 g.) in 10% sodium carbonate solution (10 c.c.), alcohol (100 c.c.) and sodium acetate (1 g.), was coupled with diazotised aniline (1 mol.) and stirred for one hour, a deep red solution was obtained which was acidified with dilute hydrochloric acid and the orange red dye collected (0.6 g.). The dye was taken up in acetic acid (20 c.c.), heated to about 110° and the resulting mixture was filtered immediately. The residue (0.2 g.) crystallised from alcohol-acetic acid mixture in thin short orange rods, m.p. 201–2° (Found: N, 7.3. C_{25}H_{18}O_{5}N_{5} requires N, 7.2%). The monoazo dye gives a brown colour with ferric chloride and a cherry red colour with concentrated sulphuric acid. From the acetic acid mother-liquors, the disazo dye (II), m.p. 168–70°, was recovered.

The diketone (I) (0.5 g.) was then dissolved in pyridine (20 c.c.) and coupled with one mol. of diazotised aniline. The dark red solution, on dilution and acidification with hydrochloric acid, gave an orange red dye, which could be separated into mono- (III) and disazo (II) dyes as in the previous case; about 0.12 g. of the pure monoazo and 0.1 g. of the disazo dye were obtained.

4-Benzeneazo-2-acetyl-1-naphthol (VI)

The bright red dye, prepared in the usual manner from acetanapthol and diazobenzene chloride, crystallised from acetic acid or chlorobenzene in reddish orange needles, m.p. 143° (Found: N, 9.8. C_{15}H_{14}O_{3}N_{2} requires N, 9.7%). It gives a deep brown colour with ferric chloride and a violet colour with concentrated sulphuric acid.

4-Benzeneazo-2-acetyl-1-naphthyl benzoate (VII)

The dye (VI) (2 g.), pyridine (10 c.c.) and benzoyl chloride (1.5 g.) were refluxed for six hours in the oil-bath at 140°. The solution was poured over crushed ice and hydrochloric acid. The dark red sticky product was taken up in ether, washed with ice-cold dilute hydrochloric acid, water, and finally with ice-cold sodium carbonate solution. Removal of the solvent and crystallisation from alcohol gave orange prismatic needles (1.7 g.), m.p. 153° (Found: N, 7.1. C_{25}H_{18}O_{5}N_{5} requires N, 7.2%).

4-Benzeneazo-2-benzoylacetyl-1-naphthol (III)

A mixture of the benzoate (1 g.), toluene (20 c.c.) and potassium carbonate (4 g.) was refluxed for 8 hours. The dark red potassium salt was filtered, washed with benzene and decomposed with dilute acetic acid. The brownish
red diketone (0·65 g.) crystallised from acetic acid or alcohol-acetic acid in short orange rods, m.p. 201–2° (Found: N, 7·4. \( \text{C}_{28}\text{H}_{18}\text{O}_5\text{N}_2 \) requires N, 7·2%). A mixed m.p. with the monoazo dye (III) obtained by direct coupling of the diketone showed no depression.

6-Benzeneazo-7: 8-benzoflavone (IV)

4-Benzeneazo-2-benzoylethyl-1-naphthol (III) (0·2 g.) was refluxed with glacial acetic acid for 30 minutes, and cooled. The flavone (IV) crystallised in shining yellow needles, m.p. 271° (Found: N, 7·2. \( \text{C}_{28}\text{H}_{18}\text{O}_5\text{N}_2 \) requires N, 7·4%). The substance does not give a ferric chloride colour and is insoluble in aqueous or alcoholic alkali.

Treatment of the dye (III) with cold concentrated sulphuric acid also yielded the same flavone (IV).

4-Nitro-2-acetyl-1-naphthyl benzoate (VIII)

4-Nitro-2-acetyl-1-naphthol (2·5 g.), prepared by the nitration of 2-acetyl-1-naphthol with 40% nitric acid at room temperature, pyridine (15 c.c.) and benzoyl chloride (1·5 c.c.) were heated on the water-bath for 30 minutes and the solution poured over ice and hydrochloric acid. The semi-sticky solid which separated was taken up in ether washed with dilute hydrochloric acid, water and cold sodium carbonate solution respectively, the ether extract dried and the solvent removed. The semi-sticky solid crystallised from alcohol in short colourless plates (1·5 g.), m.p. 126–27° (Found: N, 4·0. \( \text{C}_{19}\text{H}_{18}\text{O}_5\text{N} \) requires N, 4·2%).

6-Acetamido-7: 8-benzoflavone (IX) was obtained by reduction of the flavone (IV) with zinc dust in acetic acid solution. It crystallised from acetic acid in small lustrous, yellow needles, which melted with darkening in colour at 306–7° (Found: N, 4·3. \( \text{C}_{21}\text{H}_{15}\text{O}_5\text{N} \) requires N, 4·2%).

6-Amino-7: 8-benzoflavone (X)

(i) The benzeneazoflavone (IV) (0·5 g.) was suspended in alcohol (30 c.c.), Raney nickel catalyst added and shaken with hydrogen under pressure (40 lbs.) for two hours when the flavone slowly went into solution. The catalyst was filtered off and the yellow filtrate diluted with water, the product which separated (0·25 g.) crystallised from alcohol in long, shining yellow needles, m.p. 220° (Found: N, 4·6. \( \text{C}_{15}\text{H}_{18}\text{O}_2\text{N} \) requires N, 4·8%). It dissolves in concentrated sulphuric acid giving a colourless solution with a bright bluish violet fluorescence.

(ii) The dye (III) (0·1 g.), dissolved in alcohol (20 c.c.) and 10% sodium hydroxide solution (1 c.c.) was warmed to about 70°, and reduced by sodium
hydrosulphite till the colour of the solution changed from deep red to yellowish red. After heating for a few minutes, the solution was acidified with dilute acetic acid, concentrated and cooled. The aminoflavone \((X)\) crystallised from alcohol in long, shining yellow needles.

**Coupling of the diketone \((I)\) with diazotised \(2:5\)-dichloroaniline**

The diketone \((I)\) \((0.5\, \text{g})\), dissolved in pyridine \((20\, \text{c.c.})\) was coupled in the usual manner with one mole of diazotised \(2:5\)-dichloroaniline. The dye, precipitated by dilution and acidification with hydrochloric acid, crystallised from acetic acid in fluffy aggregates of red needles \((0.2\, \text{g})\), m.p. 215–16º (Found: \(\text{N, 8.9}\). \(\text{C}_{31}\text{H}_{18}\text{Cl}_{4}\text{O}_{3}\text{N}_{4}\) requires \(\text{N, 8.9}\%\)). The disazo dye \((\text{II}; \text{C}_{6}\text{H}_{9}\text{Cl}_{2} \text{instead of Ph})\) gives a light brown colour with ferric chloride. The filtrate, after separation of the disazo dye, on dilution and crystallisation, gave the unreacted diketone \((0.2\, \text{g})\).

The diketone \((I)\) \((0.5\, \text{g})\) dissolved in alcoholic sodium carbonate solution was then coupled with one mol. of diazotised \(2:5\)-dichloroaniline. The dye was boiled in acetic acid \((50\, \text{c.c.})\) and a small quantity of a yellowish-orange solid which separated was immediately filtered off. It crystallised from a large volume of acetic acid in thin yellow rods \((30\, \text{mg})\), m.p. 295–96º (Found: \(\text{N, 6.4}\). \(\text{C}_{25}\text{H}_{14}\text{Cl}_{2}\text{O}_{2}\text{N}_{2}\) requires \(\text{N, 6.2}\%\)). It does not give any ferric chloride colour and is not soluble in aqueous or alcoholic alkali. Analysis and its properties indicated that it was the flavone \((\text{IV}; \text{C}_{6}\text{H}_{9}\text{Cl}_{2} \text{instead of Ph})\). From the acetic acid mother liquor, the disazo dye \((0.2\, \text{g})\) was obtained.

4-(2': 5'-Dichloro)-benzeneazo-2-acetyl-1-naphthol (\(\text{VI}; \text{C}_{6}\text{H}_{3}\text{Cl}_{2} \text{instead of Ph}\)).

Acetonaphthol was coupled with diazotised \(2:5\)-dichloroaniline, and the red dye crystallised from chlorobenzene in long needles, m.p. 229–30º (Found: \(\text{N, 8.1}\). \(\text{C}_{18}\text{H}_{12}\text{Cl}_{2}\text{O}_{2}\text{N}_{2}\) requires \(\text{N, 7.8}\%\)).

4-(2': 5'-Dichloro)-benzeneazo-2-acetyl-1-naphthyl benzoate \((\text{VII}; \text{C}_{6}\text{H}_{3}\text{Cl}_{2} \text{instead of Ph})\)

The dye \((\text{VI}; \text{C}_{6}\text{H}_{3}\text{Cl}_{2} \text{instead of Ph})\) was benzyolated by refluxing with benzoyl chloride in pyridine. The benzoate crystallised from alcohol in yellowish orange needles, m.p. 184–5º (Found: \(\text{N, 6.1}\). \(\text{C}_{25}\text{H}_{16}\text{Cl}_{2}\text{O}_{3}\text{N}_{2}\) requires \(\text{N, 6.0}\%\)).

6-(2': 5'-Dichloro)-benzeneazo-7: 8-benzoflavone (\(\text{IV}; \text{C}_{6}\text{H}_{3}\text{Cl}_{2} \text{instead of Ph}\))

The benzoate on treatment with potassium carbonate in toluene rearranged to the yellowish red diketone \((\text{III}; \text{C}_{6}\text{H}_{3}\text{Cl}_{2} \text{instead of Ph})\), m.p. 238–40º, which was converted into the corresponding flavone \((\text{IV}; \text{C}_{6}\text{H}_{3}\text{Cl}_{2} \text{instead of Ph})\).
instead of Ph) by treatment with boiling glacial acetic acid, when it crystallised in thin yellow rods, m.p. 295–96° (Found: N, 6.3. \( C_{25}H_{14}Cl_{2}O_{2}N_{2} \) requires N, 6.2%), identical with the corresponding flavone obtained by direct coupling of the diketone with diazotised 2:5-dichloraniline followed by treatment with acetic acid.

\( \omega \)-Benzeneazo-\( \omega \)-benzoyl-1-acetyl-2-naphthol (XII)

The diketone (XI) (0.3 g.), prepared by the rearrangement of 1-acetyl-2-naphthol benzoate with sodium ethoxide,\(^4\) was dissolved in alcohol (20 c.c.) and sodium acetate (1 g.) added, when the solution became greenish in colour. The solution was cooled and coupled with one mol. of diazotised aniline. The orange dye was filtered (0.3 g.), which crystallised from alcohol in small orange plates, m.p. 162° (Found: N, 7.2. \( C_{25}H_{18}O_{2}N_{2} \) requires N, 7.2%). It gives a deep brown colour with ferric chloride.

4-Amino-2-acetyl-1-naphthol (XIII)

2-Acetyl-1-naphthol (5 g.) was dissolved in aqueous sodium hydroxide solution and coupled with diazotised metanilic acid (5 g.). The deep red coloured alkaline solution of the dye was heated to 70°, and hydro-sulphite (9 g.) was slowly added till the colour of the solution became pale yellow. The orange crystalline amine which separated (3.5 g.) crystallised from dilute alcohol in orange needles, m.p. 122–23° (Found: N, 6.9. \( C_{15}H_{11}O_{2}N \) requires N, 7.0%). It gave a brown colouration with ferric chloride.

4-Benzamido-2-acetyl-1-naphthyl benzoate (XIV)

4-Amino-2-acetyl-1-naphthol (XIII) (3 g.) in pyridine (10 c.c.) was mixed with benzoyl chloride (6 c.c.) and refluxed for 30 minutes. The yellow product (3 g.), obtained on stirring the solution into dilute hydrochloric acid, crystallised from alcohol in colourless needles, m.p. 175–6° (Found: N, 3.2. \( C_{28}H_{19}O_{4}N \) requires N, 3.4%).

4-Benzamido-2-benzoylacetyl-1-naphthol (XV)

(XIV) (1 g.), anhydrous potassium carbonate (4 g.) and benzene (15 c.c.) were refluxed for 8 hours, the orange potassium salt filtered and stirred into dilute acetic acid and the product which separated was filtered. It crystallised from glacial acetic acid in orange needles, m.p. 232° (Found: N, 3.2. \( C_{25}H_{19}O_{4}N \) requires N, 3.4%).

6-Benzamido-\( \alpha \)-naphthaflavone (XVI), obtained by treatment of (XV) with cold concentrated sulphuric acid, crystallised from glacial acetic acid in plates, m.p. 273° (Found: N, 3.2. \( C_{26}H_{16}O_{3}N \) requires N 3.6%).
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4-Acetoacetamido-2-acetyl-1-naphthol (XVII)

4-Amino-2-acetyl-1-naphthol (XIII) (3 g.) and acetoacetic ester (3 c.c.) were refluxed for 6$\frac{1}{2}$ hours in chlorobenzene (25 c.c.) with a few drops of one N caustic soda solution. The residue, after distilling off chlorobenzene, was dissolved in caustic soda and reprecipitated by acid. The product (1.5 g.) crystallised from alcohol (Norit) in long yellow needles, m.p. 183°. (Found: N, 4.6. $C_{18}H_{14}O_{4}N$ requires N, 4.9%). It gives a dark green colour with ferric chloride.

2-Acetyl-4-benzamidophenol (XVIII)

4-Benzamidophenyl acetate (7 g.) was dissolved in dry acetylene tetra-chloride (70 c.c.), aluminium chloride (10 g.) added and the mixture heated for 2 hours at 140–45°. The solution was stirred into ice and hydrochloric acid and carbon tetrachloride steam distilled. The yellow product (4 g.) crystallised from alcohol (Norit) in colourless needles, m.p. 155°. (Found: N, 5.2. $C_{15}H_{18}O_{8}N$ requires N, 5.5%). It gives a blue colour with ferric chloride.

$\omega$-Benzoyl-2-hydroxy-5-benzamidoacetophenone (XIX)

2-Acetyl-4-benzamidophenyl benzoate was obtained by refluxing (XVIII) for 1$\frac{1}{2}$ hours with benzoyl chloride in pyridine. It crystallised from alcohol in colourless needles, m.p. 168–69° (Found: N, 3.8. $C_{22}H_{17}O_{4}N$ requires N, 3.9%).

2-Acetyl-4-benzamidophenyl benzoate (4.6 g.), benzene (100 c.c.) and sodamide (5 g.) were refluxed for 4 hours and the yellow product that separated was treated with dilute hydrochloric acid. It crystallised from glacial acetic acid in yellow needles, m.p. 210°. (Found: N, 3.8. $C_{22}H_{17}O_{4}N$ requires N, 3.9%). It gives an olive brown colour with ferric chloride.

The flavone (XX), obtained by treatment of the diketone (XIX) with cold concentrated sulphuric acid, crystallised from alcohol in colourless plates, m.p. 291° (Found: N, 4.1. $C_{22}H_{15}O_{9}N$ requires N, 4.1%).

Summary

The utility, as azoic coupling components, of diketones prepared by the action of sodamide and similar reagents on o-benzoyloxaryl methyl ketones has been investigated. 2-Benzoylacetyl-1-naphthol gives weak dyeings when used as a “naphthol” for impregnation of cotton, and development with diazonium salts. The shades lacked fastness to soaping and light. On coupling the diketone in substance with diazonium salts, mono- and disazo dyes were obtained; the constitution of the former, which could
have two possible structures, has been proved to be 4-benzeneazo-2-benzoyl-
acetyl-1-naphthol by an unambiguous synthesis from 4-benzeneazo-2-acetyl-
1-naphthol through the corresponding benzoate. The monoazo dye from
1-benzoylacetetyl-2-naphthol has been prepared. 4-Benzamido-2-benzoyl-
acetyl-1-naphthol and 4-acetoacetamido-2-acetyl-1-naphthol have also been
studied as "naphthols".

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