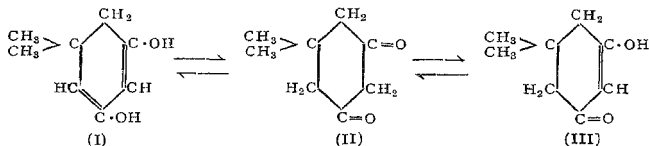


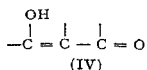
COUPLING OF METHONE WITH TETRAZONIUM COMPOUNDS.

By *Balkrishna H. Iyer.*

Methone is known in literature by three other names, *viz.*, (1) 5:5-dimethyldihydroresorcinol, (2) 5:5-dimethyl-1:3-cyclohexanedione, and (3) dimedone. As the different names would warrant, methone owns chameleonic structure. Claims are made for a di-enol structure (I) (Haas, *J.C.S.*, 1906, 89, 187 and 387), a diketo structure (II) (Vorländer and Erig, *Annalen*, 1897, 294, 314) and a hydroxy ketonic structure (III) (Crossley and Le Sueur, *J.C.S.*, 1902, 81, 821; 1903, 83, 110; Vorländer, *Z. Anal. Chem.*, 1929, 77, 241; Klein and Linser, *Mikrochem.* 1929 *Preglfestschrift*, p. 204; Chakravarti *et al*, *J. Indian Inst. Sci.*, 1931, 14A, 141; Iyer and Chakravarti, *Ibid.*, 1931, 14A, 157).



The structures (I) and (III) are interesting as both of them contain conjugated double bonded systems with the difference that in (I) the system consists of two ethylenic linkages and in (III) the system is made up of one ethylenic linkage and one carbonyl linkage. In a system like (IV) the ethylenic linkage is more reactive than the carbonyl group (*cf.* Sen-Gupta, *J.C.S.*, 1915, 107, 1347; Sen and Bose, *J. Indian Chem. Soc.*, 1927, 4, 51). Hence in methone too this part is expected to be more reactive than the keto group.

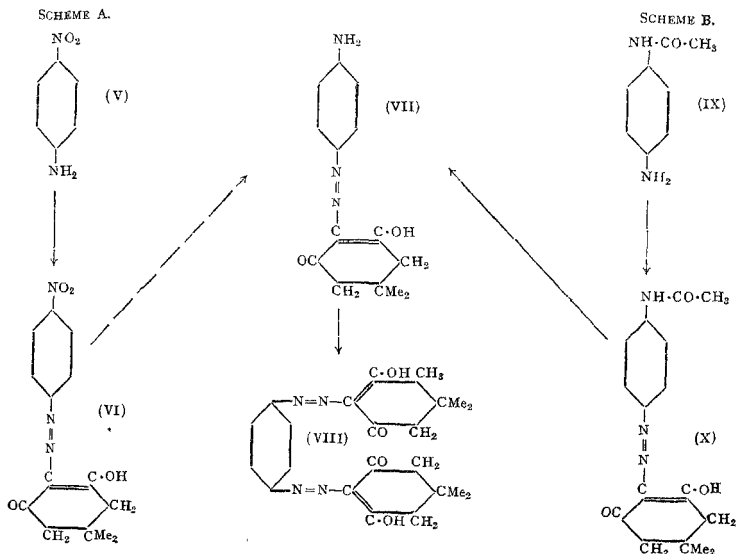


The presence of the *gem*-dimethyl group also makes methone very interesting for a study of its behaviour towards different substances.

The present work forms part of a systematic study of the reactivity of methone undertaken in these laboratories. Iyer and Chakravarti (*J. Indian Inst. Sci.*, 1934, 17A, 41) found that the azo-compounds with methone had good dyeing properties for silk and wool.

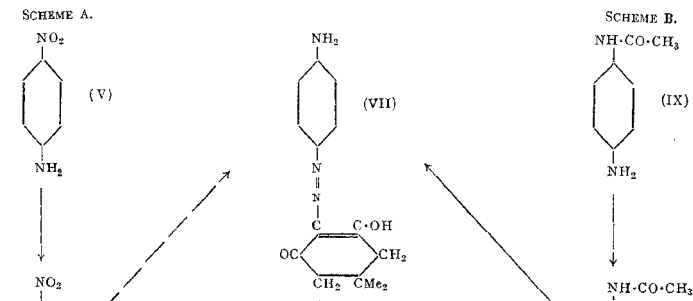
Their observation regarding the fastness of these dyes have been corroborated by the later findings of a foreign patentee (I.G. E.P., 461,965. *cf. J. Soc. Dyers and Col.*, 1937, 53, 294). The patent claims that those products which do not contain water-solubilising groups dye cellulose acetate rayon, cellulose ester and ether lacquers, and vinyl, urea-aldehyde and phenol-aldehyde synthetic resins, yellow shades of good fastness to light. The present work was also to verify the possibility of preparing substantive cotton dyes from methone.

Methone has now been successfully coupled with the tetrazonium compounds of *p*-phenylenediamine, benzidine, *o*-tolidine and *o*-dianisidine and the resulting products have been characterised. When attempts were made to prepare compound (VIII) directly by coupling two molecules of methone with one molecule of the tetrazonium compound of *p*-phenylenediamine obtained according to Schoutissen (*J. Amer. Chem. Soc.*, 1933, 55, 4535) no product could be isolated owing to the decomposition that followed the coupling stage. The preparation of the desired product was next attempted by the available



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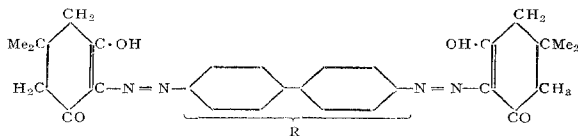
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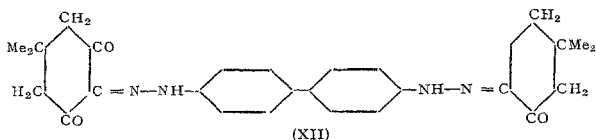
Insert " which is in the *ortho*-position to the carbon atom " between the words ' atom ' and ' bearing '.

two indirect methods (schemes A and B). Both these methods operate on the principle that the coupling of two molecules of methone takes place in two successive stages, one molecule entering at each stage. The first method (scheme A) was to diazotise *p*-nitraniline (V) and couple with one molecule of methone when *p*-nitrobenzene-azo-2-hydroxy-4-dimethyl-6-keto- Δ^1 -tetrahydrobenzene (VI) was obtained. On attempting to reduce it to the corresponding amino compound (VII) scission at the azo link occurred and the desired amino product could not be isolated. The second indirect method (scheme B) was from *p*-amino-acetanilide (IX) which was diazotised and coupled with one molecule of methone to yield *p*-acetaminobenzene-azo-2-hydroxy-4-dimethyl-6-keto- Δ^1 -tetrahydrobenzene (X). This was hydrolysed with 30% sulphuric acid to *p*-aminobenzene-azo-2-hydroxy-4-dimethyl-keto-6- Δ^1 -tetrahydrobenzene (VII), which was in turn diazotised and coupled with another molecule of methone when the desired benzene-1:4-disazo-di-2-hydroxy-4-dimethyl-6-keto- Δ^1 -tetrahydrobenzene (VIII) resulted. Tetrazotisation of benzidine, *o*-tolidine and *o*-dianisidine was carried out in the usual manner and the compounds (IX), (X) and (XI) were obtained.

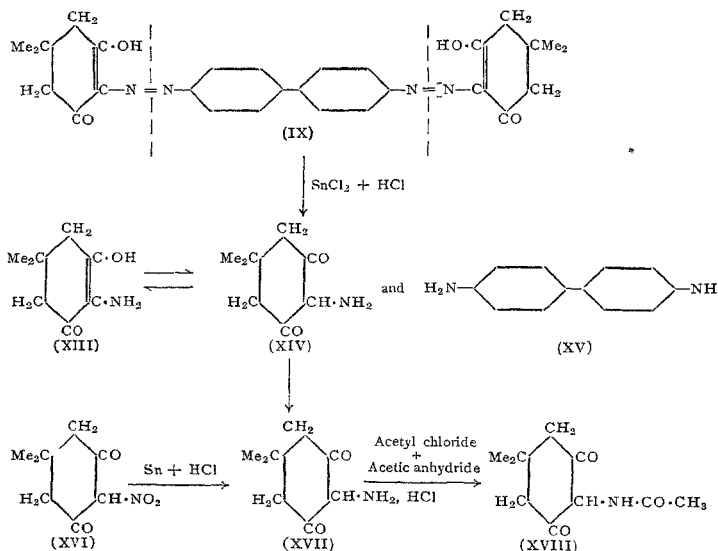


(IX), R = diphenyl, (X), R = 3,3'-dimethyldiphenyl; (XI), R = 3,3'-dimethoxydiphenyl.

The -OH group in methone is more phenolic than alcoholic in character. The laws of orientation regulating the formation of products of coupling between diazonium salts and phenolic bodies would indicate that in the case of methone, the azo-addendum should replace one of the -H atoms of the methylene group occupying the *para*-position of the -OH group. On the other hand, it is known (*cf.* Mills and Nixon, *J.C.S.*, 1930, 2512; Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1936, 58, 2050) that in coupling diazonium salts with substances exhibiting keto-enol tautomerism, the azo-addendum attaches itself to the carbon atom bearing the enolic-OH and is linked to it by the double bond. In view of these observations and also because the present series of coupled products may have either the true azo structure (VIII, IX, X and XI) or the plausible hydrazo-diketo form (XII) (*cf.* Lifschitz, *Ber.*, 1914, 47, 1401), investigation of their structure is of particular interest.



In order to give a rigid chemical proof for assigning azo-enol structures for the present series of compounds, diphenyl-4:4'-disazo-di-2-hydroxy-4-dimethyl-6-keto- Δ^1 -tetrahydrobenzene (IX) was subjected to the characteristic azo-scission by reduction with stannous chloride when 4-amino-1:1-dimethyldihydroresorcin (XIV) and benzidine (XV) were produced.

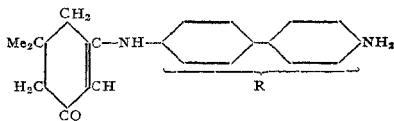


Benzidine was identified from its melting point with a genuine sample. The identity of 4-amino-1:1-dimethyldihydroresorcin (not isolated) was proved in an indirect manner. It may have the tautomeric formulæ as represented by (XIII) and (XIV). Haas (*J.C.S.*, 1907, 91, 1441) who prepared this compound for the first time, has recorded

that this base could not be isolated in a pure condition. Its hydrochloride and acetyl derivatives are stable crystalline substances. Hence the hydrochloride (XVII) obtained from the reduction mixture was acetylated and the product identified as 4-acetamino-1:1-dimethyl-dihydroresorcin (XVIII) from its melting point with a genuine sample prepared according to Haas (*loc. cit.*).

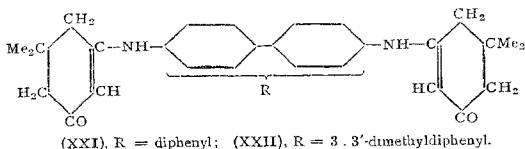
Although the inclusion of benzidine nucleus in the structure of the present series of compounds would indicate the possibility of their dyeing cotton fabrics to a substantive colour, experiments proved that all these dyes were absolutely fugitive to cotton. On the other hand, silk and woollen fabrics were dyed with great facility to fast shades ranging from light yellow to bright orange. This observation supports the view that many of the substantive cotton dyes are better adapted for the dyeing of wool than of cotton (*cf.* Cain and Thorpe, *The Synthetic Dyestuffs*, 1918, p. 37). Chrome mordanting prior to dyeing brought about a heavier shade. As all but one (VII) of the present series of compounds were insoluble in dilute acids, dyeing was carried out in baths containing the dyestuff in fine suspension. The insolubility of the compounds is one of the drawbacks for their technical application. It is hoped that the introduction of a solubilising group like the sulphonic acid group either in methone or in the azo-addendum will remove this disability. *p*-Aminobenzene-azo-2-hydroxy-4-dimethyl-6-keto- Δ^1 -tetrahydrobenzene (VII) imparts fast shades varying from flesh colour to deep orange to leather.

Molecular proportions of methone and each of benzidine and *o*-tolidine, condensed in alcoholic solution to form 4:4'-diamino-diphenyl-3-keto-5:5-dimethyl- Δ^1 -tetrahydrobenzene (XIX) and 4:4'-diamino-3:3'-dimethyldiphenyl-3-keto-5:5-dimethyl- Δ^1 -tetrahydrobenzene (XX) respectively, by the elimination of one molecule of water (*cf.* Haas, *loc. cit.*).



(XIX), R = diphenyl; (XX), R = 3:3'-dimethyldiphenyl.

When two molecules of methone react with one molecule each of these two amines, 4:4'-diaminodiphenyl-*s*-bis-3-keto-5:5-dimethyl- Δ^1 -tetrahydrobenzene (XXI) and 4:4'-diamino-3:3'-dimethyldiphenyl-*s*-bis-3-keto-5:5-dimethyl- Δ^1 -tetrahydrobenzene (XXII) are formed respectively by the elimination of two molecules of water.



Curiously enough, *ortho*-, *meta*- and *para*-nitranilines did not at all condense with methone even though various condensing agents were tried. Perhaps the presence of a negative group like the NO_2 -group lessens the basicity of the substance as to prevent its combining with an acidic substance like methone.

EXPERIMENTAL.

Methone was prepared according to the method described in *Organic Synthesis*, 1935, 15, 14.

For the sake of brevity, the suffix 'methone' is used in the following part instead of "2-hydroxy-4-dimethyl-6-keto- Δ^1 -tetrahydrobenzene", while naming the products of the coupling reactions.

Coupling of methone with diazotised p-nitraniline and p-aminoacetanilide.

p-Nitrobenzeneazo-methone (VI).—A solution of *p*-nitraniline (3.45 g.) in water (30 c.c.) and concentrated hydrochloric acid (11 c.c.) was diazotised under ice cooling with sodium nitrite (1.75 g.) in water (17.5 c.c.). This diazonium solution was gradually added to an ice-cooled solution of methone in alcohol (30 c.c.) to which a solution of sodium acetate (3.5 g.) in water (30 c.c.) had already been added. A yellow precipitate separated which was filtered out, boiled with water to remove unreacted methone, filtered again and dried on the porous plate. Yield of the crude product was 6.5 g. It dissolves in alkali to a crimson solution and can be precipitated therefrom by mineral acid. It is soluble in methyl and ethyl alcohols, acetone, benzene, toluene and glacial acetic acid; gives characteristic yellow coloration with concentrated sulphuric acid. Crystallised from benzene in yellow, thick rectangular plates, m.p. 215–16°. (Found: N, 14.53; $\text{C}_{14}\text{H}_{15}\text{O}_4\text{N}_2$ requires N, 14.53 per cent.)

p-Acetaminobenzeneazo-methone (X).—To a solution of *p*-aminoacetanilide (7.5 g.) in hot water (60 c.c.), concentrated hydrochloric acid (10 c.c.) was added when the hydrochloride of the base separated out in finely divided form. This was diazotised with sodium nitrite (3.5 g.). The diazonium solution thus obtained was carefully neutralised with 33% caustic soda under ice-cooling and just acidified

with acetic acid. This diazonium solution was gradually poured on to a solution of methone (7 g.) in alcohol (50 c.c.) containing sodium acetate (21 g.) in water (60 c.c.). The orange yellow precipitate obtained was boiled with water, filtered and dried on porous plate; yield, 13.7 g. Substance is slightly soluble in 2N sodium carbonate and readily in 2N caustic soda, from which it can be precipitated by mineral acid. It gives yellow coloration with concentrated sulphuric acid. It is very sparingly soluble in boiling water, acetone, chloroform and ethyl acetate and insoluble in ligroin, ether and benzene. It is soluble in pyridine and hot glacial acetic acid; crystallised from methyl or ethyl alcohol in light, silky, orange-yellow needles, m.p. 250–55° (decomp.). (Found: N, 13.60; $C_{16}H_{19}O_3N_3$ requires N, 13.95 per cent.)

*Hydrolysis of p-acetaminobenzeneazo-methone (X): Formation of p-aminobenzeneazo-methone (VII).—*p-Acetaminobenzeneazo-methone (14 g.) was well mixed with 30% sulphuric acid (500 c.c.) and heated under reflux on a water-bath for 12 hours. Later it was boiled under reflux over a free flame till all the solid had gone into solution. If the preliminary heating was not done on the water-bath enormous frothing occurred during boiling. The resulting solution was diluted with water (500 c.c.) and made alkaline under ice-cooling with 30% caustic soda. The small quantity of crimson precipitate which separated out was extracted with chloroform. Then the aqueous portion was extracted several times with ethyl acetate after saturation with sodium chloride. The substance is soluble both in 2N caustic soda and 2N hydrochloric acid; gives yellow coloration with concentrated sulphuric acid. It is soluble in acetone, methyl and ethyl alcohols, acetic acid and benzene, very easily in chloroform, pyridine and ethyl acetate and insoluble in water, carbon tetrachloride, ether and petrol. Crystallised from methyl or ethyl alcohol in beautiful ruby red light needles, m.p. 225° (decomp.). (Found: N, 15.88; $C_{14}H_{17}O_2N_3$ requires N, 16.22 per cent.)

p-Aminobenzeneazo-methone (1 g.) was re-acetylated with a mixture of acetyl chloride (5 c.c.) and acetic anhydride (2.5 c.c.) and the resulting product identified as (X).

*Coupling of methone with p-aminobenzeneazo-methone (VII): Formation of Benzene-1:4-disazo-di-methone (VIII):—*p-Aminobenzeneazo-methone (2.59 g.) was dissolved in water (50 c.c.) containing concentrated hydrochloric acid (3 c.c.) and diazotised in the usual manner with sodium nitrite (0.7 g.). The diazonium solution was added on to methone (1.4 g.) dissolved in alcohol (10 c.c.) and containing sodium acetate (4 g.) in water (15 c.c.). The brick-red massy product thus obtained is soluble in chloroform, toluene, xylene and

pyridine and insoluble in most of the other organic solvents. Gives orange coloration with concentrated sulphuric acid. Crystallised in copper coloured plates from glacial acetic acid, m.p. 275–80° (decomp.). (Found: N, 13.38; $C_{22}H_{20}O_4N_4$ requires N, 13.66 per cent.)

Coupling of methone with tetrazotised benzidine, o-tolidine and o-dianisidine.

Diphenyl-4:4'-disazo-di-methone (IX).—To benzidine (4.6 g.) dissolved in hot water (70 c.c.), concentrated hydrochloric acid (10 c.c.) was added and tetrazotised in the usual manner with sodium nitrite (3.5 g.) in water (35 c.c.). This tetrazonium solution was carefully neutralised with caustic soda under thorough cooling and then acidified with acetic acid. This was poured on to a solution of methone (7 g.) in alcohol (50 c.c.) containing sodium acetate (21 g.) in water (60 c.c.). The separated orange precipitate was filtered out after standing at ordinary temperature for 1½ hours, washed with water and dried on porous plate; yield, 10.2 g. Substance is practically insoluble in most of the organic solvents, gives blood-red coloration with concentrated sulphuric acid and can be crystallised from glacial acetic acid or pyridine in chocolate coloured feathery crystals, m.p. 285° (decomp.). (Found: N, 11.39; $C_{28}H_{30}O_4N_4$ requires N, 11.52 per cent.)

3:3'-Dimethyldiphenyl-4:4'-disazo-di-methone (X).—*o*-Tolidine (5.3 g.) was tetrazotised and coupled with methone (7 g.) in the same way as in the previous experiment; yield, 11.6 g. The substance gives blood-red coloration with concentrated sulphuric acid. It is practically insoluble in methyl and ethyl alcohols, acetone, carbon tetrachloride, ethyl acetate and petrol and slightly soluble in chloroform, acetic acid, pyridine, benzene, toluene and xylene. It crystallised from xylene with one molecule of xylene of crystallisation; m.p. 263–65° (decomp.) (Found: N, 9.19; $C_{30}H_{34}O_4N_4$, $C_6H_4.Me_2$ requires N, 9.03 per cent.) When crystallised from amyl alcohol. (Found: N, 10.739; $C_{30}H_{34}O_4N_4$ requires N, 10.895 per cent.)

Xylene of crystallisation.—The above substance (0.3959 g.) was heated in an air oven during 16 hours at 150–60° until constant weight was attained. The loss in weight was 0.0661 g. (Found: xylene, 16.70 per cent.; $C_{30}H_{34}O_4N_4.C_6H_4.Me_2$ requires xylene, 17.10 per cent.); m.p. of the de-xyleneated product also was the same as above.

3:3'-dimethoxydiphenyl-4:4'-disazo-di-methone (XI).—*o*-Di-anisidine (3.05 g.) was tetrazotised and coupled with methone (3.5 g.) in a similar manner as described before. The resulting red product gave blood-red coloration with concentrated sulphuric acid. The

substance was crystallised from pyridine, m.p. 290–92° (decomp.). (Found; N, 10.14; $C_{20}H_{24}O_6N_4$ requires N, 10.26 per cent.)

Reduction of diphenyl-4:4'-disazo-di-methone (IX).—Diphenyl-4:4'-disazo-di-methone (5 g.) mixed with water (100 c.c.) was gradually treated with 50 c.c. of a solution of stannous chloride in concentrated hydrochloric acid (40 g. in 100 c.c.) on the water-bath during one hour. The insolubility of the substance was retarding the process of reduction. After one hour the contents were refluxed on a free flame for 15 minutes. The resulting solution, when cooled, yielded a crystalline precipitate (A) of benzidine hydrochloride from which the base was generated and identified as benzidine.

The filtrate from (A) was repeatedly heated on a water-bath and saturated with H_2S till no further stannous sulphide separated out. The final filtrate was evaporated to dryness when it yielded the hydrochloride of 4-amino-1:1-dimethyldihydroresorcin (3.7 g.). It was dried in a desiccator overnight and then treated with a mixture of acetyl chloride (5 c.c.) and acetic anhydride (4 c.c.) on the water-bath for one hour. Then it was boiled with a small quantity of methyl alcohol, evaporated to dryness, kept in a desiccator overnight and finally extracted with petrol (b.p. 40–60°); treated with norite and yielded on evaporation needle-like crystalline substance identified as 4-acetamino-1:1-dimethyldihydroresorcin (XVIII) from its m.p. 115–16° with a genuine sample prepared according to Haas (*loc. cit.*) from methone.

Dyeing Experiments.

Dyeing experiments were carried out with cotton, silk and woollen fabrics according to the instructions given in *The Synthetic Dyestuffs* by Cain and Thorpe, p. 317. The cotton fabric was purified by boiling with soap solution and subsequent washing with water; silk was purified by boiling with soap solution in two successive stages and finally washing with water acidulated with dilute sulphuric acid; woollen fabric was purified by boiling in a bath containing a little ammonia and then washing with water. Silk and woollen fabrics were dyed from acid baths kept as 95–100° containing 2 per cent. of the dye-stuff. In addition to either dilute sulphuric or acetic acid, sodium sulphate and potassium hydrogen sulphate were added to dye silk and wool respectively. Cotton fabrics were dyed from alkaline baths containing sodium carbonate, sodium sulphate and sodium chloride. In all cases but one (VII), the dye was brought into a fine state of division in the bath, either by dissolving it in alkali and precipitating by acid, or by dissolving in glacial acetic acid and precipitating with water. In the case of (VII) which was soluble in dilute acids there was no

difficulty. The present series of compounds dyed silk and wool to shades varying from light yellow to bright orange and fast to washing and sunlight. These dyes were entirely fugitive to cotton. The fastness of the colour was tried by washing with hot soap solution, several times, immediately after taking the fabrics from the dye bath.

Compound (VII) dyes leather in shades varying from light skin colour to bright orange depending upon the proportion of the dye used and the length of steeping. The shades were fast to light. The grain side of the leather took up the dye better than the flesh side. Only vegetable tanned leather was tried in these experiments. The process employed was as follows: the leather was first de-tanned by treating with borax, washed with water, dyed from an acid bath kept at 50°, washed with water, oiled and dried.

Condensation of methone with benzidine and o-tolidine.

4: 4'-Diaminodiphenyl-3-keto-5: 5-dimethyl- Δ^1 -tetrahydrobenzene (XIX).—Methone (3.5 g.) and benzidine (4.6 g.) in absolute alcohol (100 c.c.) were boiled under reflux for 3 hours on a water-bath. At the end of the period alcohol was distilled out and the residue boiled with water to remove unreacted benzidine and methone. The solid thus obtained was again treated with a small quantity of dilute sodium carbonate and washed with water. Then it was dissolved in the minimum quantity of dilute hydrochloric acid, filtered, the filtrate alkalisied with 2N sodium hydroxide and the resulting solid crystallised from alcohol, m.p. 217–18°. (Found: N, 9.25; $C_{20}H_{22}ON_2$ requires N, 9.15 per cent.) Very light yellow coloured substance, soluble in methyl alcohol, acetic acid and pyridine, sparingly in acetone and practically insoluble in ethyl acetate, benzene, carbon tetrachloride and ether. Alcoholic solution gives coloration with ferric chloride.

4: 4'-Diamino-3:3'-dimethyldiphenyl-3-keto-5: 5-dimethyl- Δ^1 -tetrahydro-benzene (XX).—Methone (3.5 g.) and o-tolidine (5.3 g.) were condensed together and the product isolated and purified in the above manner and crystallised from alcohol; m.p. 245°. (Found: N, 8.48; $C_{20}H_{26}ON_2$ requires 8.38 per cent.)

The substance is insoluble in ether, acetone and ethyl acetate and soluble in methyl alcohol and acetic acid.

4: 4'-Diaminodiphenyl-s-bis-3-keto-5: 5-dimethyl- Δ^1 -tetrahydro-benzene (XXI).—Methone (7 g.) and benzidine (4.6 g.) in absolute alcohol (150 c.c.) were boiled under reflux for 3 hours on a water bath. The residue got after removing the alcohol was successively washed with dilute sodium carbonate, hydrochloric acid and water and finally

crystallised from glacial acetic acid in yellow coloured light plates; m.p. 339–41° (decomp.). (Found: N, 6.72; $C_{25}H_{32}O_2N_2$ requires N, 6.54 per cent.)

4: 4'-Diamino-3: 3-dimethyldiphenyl-s-bis-3-keto-5: 5-dimethyl- Δ^1 -tetrahydro-benzene (XXII).—Methone (7 g.) and *o*-tolidine (5.3 g.) were condensed together in the above manner and the product crystallised from glacial acetic acid; m.p. 320° (decomp.). (Found: N, 6.17; $C_{30}H_{30}O_2N_2$ requires N, 6.14 per cent.)

SUMMARY.

1. Methone has been coupled with the tetrazonium compounds of benzidine, *o*-tolidine and *o*-dianisidine and the resulting products have been definitely established to possess azo-enol structure.

2. The present series of azo-compounds dye silk, wool and leather in shades varying from yellow to orange and fast to light. They are fugitive to cotton.

3. Methone has been condensed with benzidine and *o*-tolidine in mono- and di-molecular proportions.

The author's grateful thanks are due to Prof. P. C. Guha, D.Sc., F.N.I., and Dr. G. C. Chakravarti, D.Sc., for their keen interest in the present piece of work and also to Mr. C. T. Krishnaswamy for supplying him with tanned leather and helping him in testing the dyeing properties on it.

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