

## 66. The Formation and Reductive Scission of Bis-compounds from Enols.

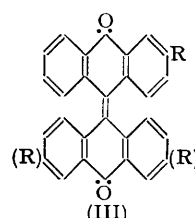
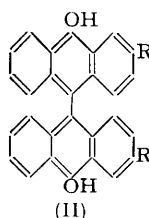
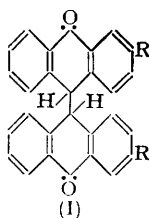
By WILLIAM BRADLEY and LEONARD J. WATKINSON.

On being heated with azobenzene phenols may undergo substitution or self-union with loss of hydrogen (either one atom or two atoms per mol.). Anthrone gives 9 : 9'-dihydro-9 : 9'-dianthrone, 2-methyl-1-naphthol affords 3 : 3'-dimethyldi-1-naphthyl-4 : 4'-quinone, and  $\alpha$ -naphthol yields 2-anilino-1 : 4-naphthaquinone 4-anil. 4-Methyl-1-naphthol gives the same anil and in addition 1 : 2-di-(3-anilino-1 : 4-dihydro-4-oxo-1-naphthylidene)ethane. Analogous compounds result by the use of 3 : 3'-dimethyl- and 3 : 3'-dibromo-azobenzene. With dilute nitric acid the ethane derivative gives 1 : 2-di-(1 : 4-dihydro-3-hydroxy-4-oxo-1-naphthylidene)ethane and this has been derived also from 4-methyl-1 : 2-naphthaquinone.

1 : 1 : 2 : 2-Tetrabenzoylthane is reduced to dibenzoylmethane by magnesium in hot pyridine or aqueous pyridine. Amongst analogous compounds only 1 : 2-dibenzoyl-1 : 2-di-*p*-toluoylthane behaves similarly; others afford furan derivatives or do not react. Magnesium subiodide also gives furans, but reductive fission is not observed either with this reagent or with Raney nickel and hydrogen.

It has generally been held<sup>1,2</sup> that the self-union of phenols begins with the transfer of hydroxylic hydrogen from the phenol to the oxidant, the resulting aryloxy-radicals rearranging and then uniting through carbon. The conditions under which the transfer of hydrogen occurs vary with the oxidant, and for this reason it seemed of interest to study the process of self-union by using aromatic azo-compounds. It was believed that azo-compounds would function solely as neutral, un-ionised hydrogen acceptors, and that their use would enable a simple view of the self-union process to be put forward. Experiment showed that by-products were usually formed, however, and that in some instances the reaction was complex.

Although most azo-compounds are reduced with ease the literature records few examples of their use as hydrogen acceptors. Quinol and diethyl azodicarboxylate afford benzoquinone and diethyl hydrazinedicarboxylate,<sup>3</sup> 2 : 7-dibromo-9-hydroxyfluorene and azobenzene give 2 : 7-dibromofluorenone,<sup>4</sup> and 3-methyl-1-phenylpyrazol-5-one yields di-(3-methyl-1-phenylpyrazol-5-on-4-yl) on being heated with azobenzene.<sup>5</sup> In the present investigation it has been found that anthrone readily yields dianthrone-9-yl (I; R = H), together with aniline and hydrazobenzene (identified as benzidine) on being heated with azo-



benzene, but that dianthrone-9-yl is stable towards this reagent. Self-union as a result of dehydrogenation with azobenzene appears thus as a property of enolic forms and this accords with the results of Barnett, Cook, and Matthews<sup>1</sup> who employed other oxidants. 3-Chloro-anthr-10-one is dehydrogenated, more rapidly than anthrone, to 3 : 3'-dichlorodianthrone-9-yl (I; R = Cl); this too was stable. Similar results were obtained on using 3 : 3'-dimethyl-azobenzene. When the azo-compounds were used in large excess, azobenzene and its

<sup>1</sup> Barnett, Cook, and Matthews, *J.*, 1923, 1994.

<sup>2</sup> Cosgrove and Waters, *J.*, 1951, 388.

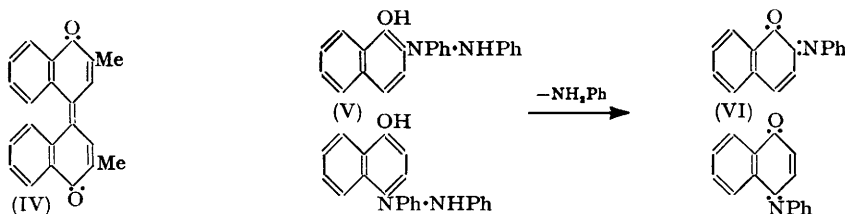
<sup>3</sup> Diels and Fritzsche, *Ber.*, 1911, **44**, 3018.

<sup>4</sup> Pinck and Hilbert, *J. Amer. Chem. Soc.*, 1946, **68**, 2740.

<sup>5</sup> Passerini and Losco, *Gazzetta*, 1938, **68**, 485.

dimethyl derivative dehydrogenated anthrone at about the same rate; with a smaller excess the rate was faster with the latter, possibly because the product was less soluble in this medium. 10 : 10'-Dihydroxydi-9-anthryl (II; R = H) yielded dianthron-9-ylidene (III; R = H), anthrone, and anthraquinone on being heated with azobenzene at 180°, and the same products resulted in the absence of the azo-compound. The 3 : 3'-dichloro-derivative (II; R = Cl) and azobenzene gave the related dianthronylidene.

2-Methyl-1-naphthol afforded 3 : 3'-dimethyl-1-naphthyl-4 : 4'-quinone (IV), identical with the product obtained by the use of ferric chloride.<sup>6</sup> With  $\alpha$ -naphthol the product was 2-anilino-1 : 4-naphthaquinone 4-anil, identical with the product derived by heating 4-benzeneazo-1-naphthol with aniline and aniline hydrochloride.<sup>7</sup> This derivative probably arose by the addition of  $\alpha$ -naphthol to azobenzene, giving one or both of the hydrazines (V), from which aniline was lost, giving one or both of the anils (VI). 2-Anilino-1 : 4-naphthaquinone 4-anil may be assumed to result from (VI) by the addition of aniline and dehydrogenation. A related reaction, the addition of  $\beta$ -naphthylamine to azodicarboxylic

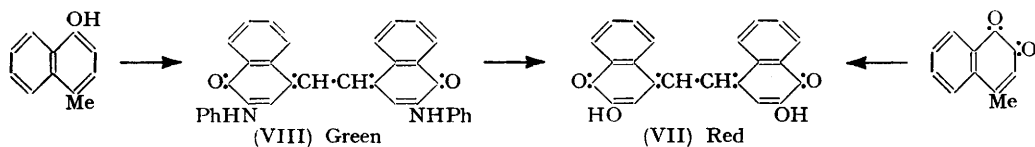


ester to form 2-amino-1-naphthylhydrazine-*NN'*-dicarboxylic ester, has been described by Diels.<sup>8</sup>

4-Methyl-1-naphthol gave 2-anilino-1 : 4-naphthaquinone 4-anil and two other products. That, C<sub>34</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>, formed in larger amount, was green, insoluble in aqueous sodium hydroxide, and stable in hot hydrochloric acid. Oxidation with chromium trioxide gave phthalic acid, and heating with soda-lime gave aniline. Nitric acid (30%) afforded a brown product from which violet-red rhombs were derived by extraction with acetone; these gave a blue solution in sodium hydroxide, and subsequent acidification afforded violet-red plates (B), C<sub>22</sub>H<sub>14</sub>O<sub>4</sub>.

4-Methyl-1-naphthol and 3 : 3'-dibromoazobenzene afforded analogously 2-*m*-bromo-anilino-1 : 4-naphthaquinone 4-*m*-bromoanil and a green crystalline compound, C<sub>34</sub>H<sub>22</sub>O<sub>2</sub>N<sub>2</sub>Br<sub>2</sub>, from which substance B resulted on oxidation with nitric acid. With *m*-azotoluene the products were 2-*m*-toluidino-1 : 4-naphthaquinone 4-3'-methylanil and a green crystalline compound, C<sub>36</sub>H<sub>28</sub>O<sub>2</sub>N<sub>2</sub>.

Distillation of substance B gave naphthalene. Methylation afforded a violet-red dimethyl derivative, C<sub>22</sub>H<sub>12</sub>O<sub>2</sub>(OMe)<sub>2</sub>, and acetylation a violet-red diacetyl derivative, C<sub>22</sub>H<sub>12</sub>O<sub>2</sub>(OAc)<sub>2</sub>. Addition of sodium dithionite to the blue solution of substance B in aqueous sodium hydroxide gave a yellow solution which rapidly became blue again in air. Acetic anhydride and boric acid gave a deep blue colour. Together, the evidence suggested that substance B was a quinone containing two naphthalene nuclei, two 4-carbonyl groups, and two 3-hydroxyl groups. This was confirmed by the preparation of a tetra-acetyl



derivative, C<sub>22</sub>H<sub>12</sub>(OAc)<sub>4</sub>, on reductive acetylation, and a yellow bisquinoxaline derivative, C<sub>34</sub>H<sub>22</sub>N<sub>4</sub>, with *o*-phenylenediamine. The properties indicated that substance B was 1 : 2-di-(1 : 4-dihydro-3-hydroxy-4-oxonaphthylidene)ethane (VII), and this was confirmed by

<sup>6</sup> Lesser, *Annalen*, 1914, **402**, 44.

<sup>7</sup> Fischer and Hepp, *Ber.*, 1888, **21**, 676.

<sup>8</sup> Diels, *Ber.*, 1922, **55**, 1524.

its catalytic reduction to a tetrahydro-derivative and by a synthesis from 4-methyl-1 : 2-naphthaquinone which yielded substance B on being heated with either azobenzene or alcoholic potassium hydroxide.

With the structure of compound (VII) established, the constitution of the green, crystalline compound which results by the action of azobenzene on 4-methyl-1-naphthol is regarded as 1 : 2-di-(3-anilino-1 : 4-dihydro-4-oxonaphthylidene)ethane (VIII). Analogously, the products obtained from 3 : 3'-dibromo- and 3 : 3'-dimethyl-azobenzene are regarded as the dibromo- and dimethyl derivatives of (VIII), the substituents being in the arylamino-groups. Reductive acetylation of the quinone (VIII) afforded the diacetyl derivative of a dihydro-compound.

In agreement with the constitution (VIII) for the product from 4-methyl-1-naphthol, 2 : 4-dimethyl-1-naphthol did not react with azobenzene, and the results suggest further that with 4-methyl-1-naphthol the 2-position enters into reaction first, probably by the mechanism already suggested.<sup>9</sup>

Like  $\alpha$ -naphthol, 4-chloro-1-naphthol affords 2-anilino-1 : 4-naphthaquinone 4-anil with azobenzene, but the products from 4-ethyl-, 2-chloro-, 2-chloro-4-methyl-, and 2 : 4-dichloro-1-naphthol could not be obtained pure. Methyl 1-naphthyl ether did not react. 2-Anilino-1 : 4-naphthaquinone 4-anil has been obtained previously in several related reactions, *e.g.*, by heating 4-methyl-, 4-benzyl-, or 4-diethoxycarbonylmethyl-1 : 2-naphthaquinone with aniline in alcohol.<sup>10</sup> In these examples the 4-substituent is replaced by aniline, and this adds further support to the view<sup>9</sup> that in its reaction with azobenzene 4-methyl-1-naphthol yields 4-methyl-1 : 2-naphthaquinone 2-anil and an equimolecular amount of aniline at a stage preceding the formation of 2-anilino-1 : 4-naphthaquinone 4-anil. The formation of 1 mol. of aniline from 1 mol. each of azobenzene and 4-methyl-1-naphthol was shown in other experiments.

The following observations were made in the course of the work. In the preparation of 3-chloroanthr-10-one by Barnett and Wiltshire's method,<sup>11</sup> the reduction of 2-*p*-chlorobenzoylbenzoic acid by zinc dust and ammonia gave 3-*p*-chlorophenylphthalide as the main product unless the reduction proceeded vigorously.

On being exposed to air and sunlight the dichlorodianthr-9-ylidene (III; R = Cl) gave a dichloromesonaphthadanthr-9-ylidene and hydrogen peroxide, the formation of which was observed earlier<sup>12</sup> as a by-product of the oxidation of helianthrone to mesonaphthadanthr-9-ylidene by means of oxygen and ultraviolet light.

No evidence of self-union was found when several open-chain compounds which were capable of enolisation were heated with azobenzene. Of (a) diethyl malonate, (b) ethyl acetoacetate, (c) diethyl oxaloacetate, (d) acetoacetanilide, (e) acetylacetone, (f) benzoylacetone, and (g) dibenzoylmethane, only (c), (d), and (e) reacted readily with azobenzene; in each case aniline was formed. In the presence of pyridine, (b) and (f) also reduced azobenzene. Homogeneous products were not obtained. Further, tetraethyl 1 : 1 : 2 : 2-ethanetetra-carboxylate, diethyl  $\alpha\alpha'$ -diacetosuccinate, and its dianilide, diethyl  $\beta\beta'$ -diacetyl- $\alpha\alpha'$ -dioxoadipate, 1 : 1 : 2 : 2-tetra-acetylene, 1 : 2-diacetyl-1 : 2-dibenzoylene, and 1 : 1 : 2 : 2-tetrabenzoylene, derived by the self-union of the compounds (a)–(f), did not give homogeneous products: there was evidence of reaction, exception in the first case, and again the formation of aniline was more marked in the presence of pyridine.

Neither 1 : 9-pyrazoloanthrone nor mesobenzanthrone undergoes self-union on being heated with azobenzene at 180°, although the reaction occurs readily at room temperature with mesobenzanthrone and sodioaniline,<sup>13</sup> and at 140–160° with 1 : 9-pyrazoloanthrone and alcoholic potassium hydroxide.<sup>14</sup>

Hitherto no self-union of this type has been reversed. We have now found that 1 : 1 : 2 : 2-tetrabenzoylene can be reduced to dibenzoylmethane in 8% yield by means of magnesium and pyridine or aqueous pyridine, and it is probable that the reaction is

<sup>9</sup> Bradley and Watkinson, *Chem. and Ind.*, 1954, 1482.

<sup>10</sup> Fieser and Bradsher, *J. Amer. Chem. Soc.*, 1939, **61**, 417.

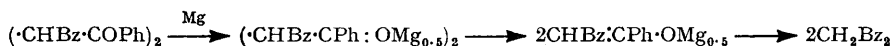
<sup>11</sup> Barnett and Wiltshire, *J.*, 1928, 1822.

<sup>12</sup> Brockmann and Muhlman, *Ber.*, 1949, **82**, 348.

<sup>13</sup> Bradley and Sutcliffe, *J.*, 1954, 708.

<sup>14</sup> Mayer and Heil, *Chem.-Ztg. Fortschrittber.*, 1929, 56; G.P. 255,641.

analogous to the reduction of *p*-benzoquinone to quinol, the metal becoming attached to carbonyl oxygen at the first stage. The more usual course of reaction, the formation of a pinacol,<sup>15</sup> is hindered in the present example because of steric considerations.



The reaction is not general. Tetramethyl ethane-1 : 1 : 2 : 2-tetracarboxylate did not react with magnesium; 1 : 1 : 2 : 2-tetra-acetylene formed a stable magnesium enolate. No fission was observed with 1 : 2-dibenzoyl-1 : 2-di-*p*-chlorobenzoyl- or 1 : 2-di-*p*-anisoyl-1 : 2-dibenzoyl-ethane, but 1 : 2-dibenzoyl-1 : 2-di-*p*-toluoyl-ethane afforded a product which gave a copper derivative having approximately the same m. p. as copper  $\omega$ -*p*-toluoylacetophenone. Diethyl  $\alpha\alpha$ -diacetylsuccinate gave ethyl 2 : 3-dihydro-3-1'-hydroxyethylidene-2-oxofuran-4-carboxylate (IX), (with cyclisation and elimination of alcohol.

Gomberg and Bachmann<sup>16</sup> have shown that the system Mg + MgI<sub>2</sub> reacts with ketones to give ketyls, which then dimerise to pinacols. With this reagent 1 : 1 : 2 : 2-tetrabenzoyl-ethane affords 3 : 4-dibenzoyl-2 : 5-diphenylfuran, and 1 : 1 : 2 : 2-tetra-acetylene gives correspondingly 3 : 4-diacetyl-2 : 5-dimethylfuran, the main reaction being neither pinacol-formation nor reductive scission but the elimination of water. Neither 1 : 2-diacetyl-1 : 2-dibenzoyl-ethane nor 1 : 1 : 2 : 2-tetra(ethoxycarbonyl)ethane was cleaved by this reagent. None of the tetra-acetylenes afforded diacylmethanes with Raney nickel and hydrogen.

## EXPERIMENTAL

*Dianthron-9-yl*.—Azobenzene (0.9 g.) and anthrone (3.8 g.; m. p. 153—154°) were melted together at 160—170°. In a few minutes crystals separated and after 15 min. the suspension was cooled and extracted with alcohol (3 × 15 c.c.). The extract was evaporated, and the resulting solid was ground and kept in contact with concentrated hydrochloric acid (20 c.c.) for 20 min. The acid solution was filtered and mixed with anhydrous sodium sulphate (3 g.) dissolved in a small volume of water, and the solid which formed was collected. After being dried the residue was extracted with chloroform; a white insoluble solid remained which gave benzidine with sodium hydroxide. The chloroform extract contained azobenzene and dianthron-9-yl, m. p. and mixed m. p. ca. 255°; acetylation gave a derivative, m. p. 278—281° (10 : 10'-diacetoxydi-9-anthryl prepared by Barnett and Matthews's method,<sup>17</sup> had m. p. 279—282°).

Azobenzene (3.64 g.) and anthrone (0.97 g.), heated for 4 hr. at 95—100°, gave dianthron-9-yl (80%). When azobenzene (0.5 g.) and anthrone (3 g.) were heated for 4 hr. at 180° in the absence of light and air, the cooled product on extraction with dilute hydrochloric acid afforded a solution from which 2 : 4 : 6-tribromoaniline (1.2 g.) separated on the addition of bromine water.

Dianthron-9-yl was recovered unaltered after being further heated at 180° with azobenzene.

Azobenzene (2 g.) and 10 : 10'-dihydroxydi-9-anthryl (1 g.) reacted at 180° in the dark and *in vacuo* during 4 hr. to give aniline and dianthron-9-ylidene, and at this temperature the diol alone decomposed. Diol prepared by Barnett and Matthews's method<sup>17</sup> gave anthrone and dianthron-9-ylidene. Diol obtained by Meyer's method,<sup>18</sup> when heated in carbon dioxide at 180°, gave anthraquinone and dianthron-9-ylidene.

*3-Chloroanthr-10-one*.—Zinc dust (150 g.) was added slowly and with cooling to a stirred suspension of *o-p'*-chlorobenzoylbenzoic acid (50 g.) in water (150 c.c.) and ammonia (300 c.c.; *d* 0.880). The suspension cleared and, when the addition of zinc dust was complete, a concentrated solution (5 c.c.) of copper sulphate was added; the reactants were then stirred under reflux on the water-bath. It was necessary to raise the temperature during 2 hr. because of the vigorous foaming which occurred at 70°; thereafter heating was continued for 36 hr. The reduction was complete when a portion of the product precipitated by the addition of hydrochloric acid dissolved completely in aqueous sodium carbonate. The main portion was then

<sup>15</sup> Bachmann, *J. Amer. Chem. Soc.*, 1944, **55**, 1179.

<sup>16</sup> Gomberg and Bachmann, *ibid.*, 1927, **49**, 236.

<sup>17</sup> Barnett and Matthews, *J.*, 1923, 380.

<sup>18</sup> Meyer, *Ber.*, 1909, **42**, 143.

filtered; addition of concentrated hydrochloric acid to the filtrate precipitated 2-carboxy-4'-chlorodiphenylmethane. The residue was extracted with hot dilute aqueous ammonia, and the filtered extracts were combined and acidified. The total yield of the reduced acid was 40 g. After being washed with water and crystallised from alcohol the acid had m. p. 130—132° (Barnett and Wiltshire<sup>11</sup> give m. p. 132°).

Cyclisation gave 3-chloroanthr-10-one, m. p. 154—155°, and this on acetylation afforded 9-acetoxy-2-chloroanthracene, m. p. 142—143° (Barnett and Wiltshire<sup>11</sup> record m. p.s 155° and 143°).

**3-*p*-Chlorophenylphthalide.**—When in the preceding preparation zinc powder was used instead of dust, reaction was less vigorous and the *phthalide* crystallised from alcohol in colourless needles, m. p. 124° (Found: Cl, 14.3.  $C_{14}H_9O_2Cl$  requires Cl, 14.5%). The same compound was also obtained, together with impure 2-carboxy-4'-chlorodiphenylmethane, by the reduction of *o*-*p*-chlorobenzoylbenzoic acid by the method of B.I.O.S. Report No. 1493, p. 47. The phthalide is neutral but combines slowly with warm aqueous sodium hydroxide. Vigorous reduction with zinc dust, ammonia, and aqueous sodium hydroxide gave 2-carboxy-4'-chlorodiphenylmethane.

**3 : 3'-Dichlorodianthr-9-ylidene.**—Azobenzene (3.6 g.) and 3-chloroanthr-10-one (1 g.) were heated for 3 hr. at 100° and the product was worked up as with anthrone. The yield of dianthr-onylidene was 0.85 g.; it was characterised by heating it with acetic anhydride and pyridine to give 10 : 10'-diacetoxy-3 : 3'-dichlorodi-9-anthryl, m. p. and mixed m. p. 308° (Found: C, 70.8; H, 3.7. Calc. for  $C_{32}H_{22}O_4Cl_2$ : C, 71.0; H, 4.1%). When azobenzene (0.8 g.) and 3-chloroanthr-10-one (2 g.) were heated under the same conditions and the cooled product was extracted with dilute hydrochloric acid, addition of concentrated hydrochloric acid to the filtered extract gave benzidine, isolated as the sulphate (1 g.).

**3 : 3'-Dichloro-10 : 10'-dihydroxydi-9-anthryl** (1 g.) gave **3 : 3'(or 3 : 6')-dichlorodianthr-9-ylidene** on being heated for 4 hr. at 180° *in vacuo* with azobenzene (3.6 g.). Neither **3 : 3'(or 3 : 6')-dichlorodianthr-9-ylidene** nor **3 : 3'-dichlorohelianthrone** reacted with azobenzene under these conditions.

**Azobenzene and 3 : 3'-Dimethylazobenzene as Dehydrogenating Agents.**—(a) Anthrone (0.5 g.) and **3 : 3'-dimethylazobenzene** (2.2 g.) were heated together at 100° for 1.5 hr. The product was then cooled and extracted with acetone (15 c.c.); the residue of dianthr-onyl weighed 0.16 g. Use of an equivalent amount of azobenzene (1.82 g.) gave 0.06 g.

When 0.095 g. of anthrone was used and heating was for 1 hr. the yields of dianthr-onyl were 0.037 g. on use of azobenzene and 0.041 g. with its **3 : 3'-dimethyl** derivative.

(b) **3-Chloroanthrone** (0.5 g.) was kept at 100° with azobenzene (1.82 g.). Precipitation of **3 : 3'-dichlorodi-9-anthr-onyl** occurred in 5 min.; after 1.5 hr. the yield was 0.28 g. **3 : 3'-Dimethylazobenzene** under the same conditions gave 0.29 g.

**Action of Light on 3 : 3'(or 3 : 6')-Dichlorodianthr-9-ylidene.**—A 0.1% solution of the dichlorodianthr-onylidene was introduced into 12 tubes which were then lightly stoppered. Six were exposed to sunlight and the remainder were kept in the dark. After 30 min. 5 c.c. of solution from an exposed tube were shaken with water (10 c.c.), and the aqueous solution was shaken with 10% potassium iodide solution (1 c.c.), 2N-sulphuric acid (1 c.c.), and starch solution (0.5 c.c.); a blue colour developed after 2 min. Similar treatment of a non-irradiated solution gave no evidence of hydrogen peroxide. The intensity of the blue colour increased up to 6.5 hours' exposure and was then constant for a further 14 hours' exposure.

**Action of Azobenzene on  $\alpha$ -Naphthol.**—Azobenzene (1.5 g.) and  $\alpha$ -naphthol (1.4 g.), heated for 9 hr. at 180° in a sealed evacuated tube, afforded a black, viscous mass. This was dissolved in benzene and chromatographed on alumina. The lowest band (azobenzene) was removed and the next was eluted and re-chromatographed; separation into two bands occurred. The lower was eluted and the solute recovered and crystallised from light petroleum (b. p. 60—80°). Red needles (0.25 g.), m. p. 182°, were obtained which did not depress the m. p. of 2-anilino-1 : 4-naphthaquinone 4-anil prepared from 4-phenylazo-1-naphthol, aniline, and aniline hydrochloride. The absorption spectra of the two products in "AnalaR" concentrated sulphuric acid were identical ( $\lambda_{max}$ , 261.5, 277.5, 360, 530  $\mu$ ).

**3 : 3'-Dimethyldi-1-naphthyl-4 : 4'-quinone.**—2-Methyl-1-nitronaphthalene<sup>19</sup> was reduced and the derived amine was diazotized and converted into 2-methyl-1-naphthol by Lesser's method.<sup>6</sup> 2-Methyl-1-naphthol (0.15 g.) and azobenzene (0.18 g.) were heated for 10 hr. at 180° *in vacuo*. The cooled product was extracted with light petroleum (b. p. 40—60°); the grey

<sup>19</sup> Fierz-David, *Helv. Chim. Acta*, 1937, 20, 1027.



powder [0.13 g., m. p. 250° (decomp.)] which remained undissolved showed the same absorption spectrum in "AnalaR" concentrated sulphuric acid as the authentic dinaphthylquinone (IV) (0.001% solutions; a Unicam S.P. 500 Spectrophotometer), *viz.*:

$\lambda_{\max.}$ (m $\mu$ ) .....	222	245	290	442	662
$10^{-3} \epsilon$ .....	>50, >50	8.0, 7.0	9.0, 8.0	6.0, 6.5	14.2, 12.5

*Reaction of 4-Methyl-1-naphthol with Azobenzene.*—1-Methylnaphthalene was converted into the 4-sulphonic acid by Steige's method,<sup>20</sup> and this into the naphthol according to Fieser and Bradsher.<sup>10</sup> At the final stage it was advantageous to purify the product by short-path distillation (Towers model T 331 still). The molten crude product was degassed at 75° for 2 hr. and then distilled during 2 hr. while the temperature was raised from 80° to 95°. Recrystallisation from ligroin (b. p. 40–60°) gave prisms, m. p. 84–85°, which did not change on storage. 4-Methyl-1-naphthol (3 g.) and azobenzene (3.6 g.) were heated for 12 hr. at 150° in a sealed evacuated tube. The cooled melt was extracted with benzene and the extract separated from the green crystals (1.8 g.) which remained undissolved. The benzene solution was chromatographed on alumina; there resulted a strongly adsorbed, dark band and two others, the lower of which was azobenzene. The middle band on elution with benzene gave dark red material (0.3 g.; m. p. 171–173°) from which was obtained by recrystallisation from light petroleum (b. p. 60–80°) 2-anilino-1:4-naphthaquinone 4-anil as red needles, m. p. and mixed m. p. 180–181° (Found: C, 81.3; H, 5.2; N, 8.6. Calc. for C<sub>22</sub>H<sub>16</sub>ON<sub>2</sub>: C, 81.5; H, 4.9; N, 8.7%). The absorption spectra of 0.001% solutions of the two preparations in "AnalaR" concentrated sulphuric acid were identical [ $\lambda_{\max.}$  255 ( $\epsilon$  2050), 270 ( $\epsilon$  2200), 360 ( $\epsilon$  1100), 525 m $\mu$  ( $\epsilon$  8000)].

The green crystals, when extracted for a day with acetone, afforded a soluble, colourless portion (m. p. >360°; 0.2 g.). Further crystallisation of the residue from 1:2:4-trichlorobenzene gave flat, thin, green needles of 1:2-di-(3-anilino-1:4-dihydro-4-oxonaphthylidene)-ethane (A), m. p. >360° (Found: C, 82.8; H, 4.9; N, 6.1. C<sub>34</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub> requires C, 82.9; H, 4.9; N, 5.7%). At all stages of purification the product exhibited a strong bronze reflex.

*Reactions of product (A).* (a) The diketone (0.1 g.) was recovered unaltered after being heated in a sealed tube with concentrated hydrochloric acid (10 c.c.) and alcohol (10 c.c.) for 12 hr. at 150°. (b) It (2 g.) was stirred into cold dilute nitric acid (20 c.c.; *d* 1.18), then kept overnight; the solid was collected, washed acid-free with water, and added to a solution of sodium dithionite (0.5 g.) and sodium hydroxide (2 g.) in water (50 c.c.); a dark blue solution was formed and from this golden platelets rapidly separated. These were collected, washed with 15% aqueous sodium hydroxide until the filtrate was no longer brown, and then added to water (50 c.c.). The resulting dark blue solution was filtered and then acidified. A red-brown precipitate was formed which on drying and crystallisation from 1:2:4-trichlorobenzene (1 l.) afforded red-violet, thin plates (0.65 g.), m. p. 345° (decomp.) (Found: C, 76.7; H, 4.0. C<sub>22</sub>H<sub>14</sub>O<sub>4</sub> requires C, 77.2; H, 4.1%), of 1:2-di-(1:4-dihydro-3-hydroxy-4-oxonaphthylidene)-ethane (B); the crystals had a marked greenish-yellow reflex.

*Constitution of the ketone (B).* (a) Zinc dust (5 g.) and the product (B) (0.3 g.) in a bent Pyrex tube were covered with zinc dust. On being heated the mixture afforded naphthalene as a sublimate, m. p. and mixed m. p. 80°, unaltered by naphthalene. (b) Methylation. Methyl sulphate (0.1 c.c.) was heated with a solution of the product (B) (0.1 g.) in water (8 c.c.) containing sodium hydroxide (0.25 g.) on the water-bath and shaken at intervals for 30 min. during which further methyl sulphate (0.1 c.c.) and 25% sodium hydroxide (0.25 c.c.) were added; the initial blue colour disappeared. The precipitated dimethyl derivative was washed with dilute sodium hydroxide, then water, dried (yield 0.1 g.), and crystallised from *o*-dichlorobenzene (10 c.c.), giving red-violet needles (35 mg.), m. p. 283° (decomp.) [Found: C, 77.4; H, 4.8; OMe, 15.9. C<sub>22</sub>H<sub>12</sub>O<sub>2</sub>(OMe)<sub>2</sub> requires C, 77.8; H, 4.9; OMe, 16.8%]. The *dimethyl compound* is insoluble in dilute aqueous sodium hydroxide but dissolves to a yellow solution on the addition of sodium dithionite. (c) Reductive acetylation. The product (B) (0.4 g.) was methylated as in (b) and the washed and dried product was dissolved in boiling acetic anhydride (10 c.c.) containing a drop of pyridine. On the addition of zinc dust (1 g.) in small amounts the solution rapidly became pale yellow. It was refluxed for 15 min., then filtered and cooled. The solid which separated was collected and washed with dilute acetic acid and water. The *dimethyl ether diacetate* of the dihydro-compound crystallised from acetic anhydride as pale

<sup>20</sup> Steige, *Helv. Chim. Acta.*, 1930, **13**, 173.

cream-coloured needles, m. p. 291—292° (Found : C, 73.2; H, 5.3.  $C_{26}H_{24}O_6$  requires C, 73.6; H, 5.3%). (d) Acetylation. Product (B) (0.1 g.), on being boiled for 10 min. with acetic anhydride (2 c.c.) containing a drop of pyridine, changed to red-violet needles. After being cooled, the 1 : 2-di-(3-acetoxy-1 : 4-dihydro-4-oxonaphthylidene)ethane was collected, washed with benzene, and recrystallised from chlorobenzene. The pure compound had m. p. 260° (decomp.) (Found : C, 73.4; H, 4.3.  $C_{26}H_{18}O_6$  requires C, 73.9; H, 4.2%). On being heated with a saturated solution of boric acid in acetic anhydride (2 c.c.), the product (B) (0.05) dissolved to form a deep royal-blue solution from which dark bluish-purple needles separated. (e) Zinc dust (1 g.) was added quickly in small successive amounts to a boiling suspension of the product (B) (0.2 g.) in acetic anhydride (5 c.c.) containing a drop of pyridine. The yellow solution was filtered and then kept; a yellow precipitate was collected, washed with dilute acetic acid and water, and crystallised from acetic anhydride. The pale yellow needles of 1 : 2-di-(3 : 4-diacetoxy-1-naphthyl)ethylene had m. p. 277—278° [Found : C, 70.3; H, 5.0; *M* (Rast), 460, 520.  $C_{30}H_{24}O_8$  requires C, 70.3; H, 4.7%; *M*, 512%]. (f) *o*-Phenylenediamine (0.5 g.) and product (B) (0.5 g.) were refluxed for 3.5 hr. in 1 : 2 : 4-trichlorobenzene (5 c.c.) containing glacial acetic acid (1 c.c.). Crystals of 1 : 2-di-(1 : 2-benzophenazin-3-yl)ethane were formed on cooling; and these were washed with benzene and recrystallised from 1 : 2 : 4-trichlorobenzene as bright yellow needles, m. p. >360° (Found : N, 11.6, 11.7.  $C_{34}H_{22}N_4$  requires N, 11.5%). (g) Preparation from 4-methyl-1 : 2-naphthaquinone. (i) Azobenzene (1 g.) and 4-methyl-1 : 2-naphthaquinone<sup>10</sup> (0.05 g.; m. p. 108—109°) were heated for 5 hr. at 110° in an evacuated sealed tube. The cooled product was extracted with light petroleum (b. p. 40—60°), then with acetone, and finally the dark brown residue was crystallised from 1 : 2 : 4-trichlorobenzene, giving red-violet needles, m. p. 345° (decomp.), of 1 : 2-di-(1 : 4-dihydro-3-hydroxy-4-oxonaphthylidene)ethane. A 0.001% solution of the present preparation, like one of the product from 4-methyl-1-naphthol and azobenzene, had  $\lambda_{max}$  at 250, 305, 420, and 660 m $\mu$ . (ii) An identical product was obtained when 4-methyl-1 : 2-naphthaquinone (0.1 g.) was added to a refluxing solution of potassium hydroxide (1 g.) in ethyl alcohol (5 c.c.) and heated for 30 min. The solution became green immediately and brownish-yellow after 15 min. On addition to water (50 c.c.) a dark blue colour developed. Further addition of hydrochloric acid gave a maroon precipitate; this was washed and dried (0.04 g.). Crystallisation from 1 : 2 : 4-trichlorobenzene gave red-violet needles.

*Constitution of product (A).* (a) Chromium trioxide (5 g.) was added gradually during 2 hr. to a stirred suspension of product (A) (1.5 g.) in glacial acetic acid (50 c.c.). After a further 2 hours' boiling the suspension was filtered and the filtrate added to water (200 c.c.) containing concentrated sulphuric acid (2 c.c.). The resulting suspension was heated and stirred on the water-bath, and the brown solid (0.5 g.) was collected. Purification gave white needles, m. p. ca. 125° (sublimation), which afforded fluorescein on being heated with resorcinol and sulphuric acid. (b) A mixture of zinc dust (10 g.) and product (A) (0.5 g.) was added during 30 min. to refluxing acetic anhydride (50 c.c.). The suspension was then filtered and the filtrate was added to ice. After being kept overnight the pale green, granular precipitate was washed and dried (0.5 g.). Purification from chlorobenzene (charcoal) gave pale cream-coloured crystals, m. p. 274—275° (decomp.) (Found : C, 79.2; H, 5.3; N, 4.65.  $C_{38}H_{30}O_4N_2$  requires C, 78.9; H, 5.2; N, 4.8%). (c) A mixture of soda-lime (10 g.) and product (A) (1 g.) was heated in a slow current of nitrogen. Aniline distilled; it was collected in water and weighed as 2 : 4 : 6-tribromoaniline (0.5 g., equiv. to aniline, 0.1 g.). In a second experiment the yield of aniline was 0.1 g. from 0.5 g. of product (A).

*Formation of Aniline in the Action of Azobenzene on 4-Methyl-1-naphthol.*—Azobenzene (3.6 g.) and 4-methyl-1-naphthol (3.2 g.) were heated at 160° for 12 hr. in a sealed evacuated tube. The product was then transferred to a Pozzi-Escott apparatus and steam-distilled. The yield of aniline as determined by titration with acidified bromide-bromate was 1.5 g. The 2 : 4 : 6-tribromoaniline produced in the estimation weighed 5.1 g., equiv. to 1.4 g. of aniline. Repetition of the experiment using azobenzene (7.2 g.) and 4-methyl-1-naphthol (3.2 g.) gave 2.0 g. of aniline (by direct titration), or 1.75 g. of aniline (calc. from the yield of 2 : 4 : 6-tribromoaniline).

*Action of 3 : 3'-Dimethylazobenzene on 4-Methyl-1-naphthol.*—3 : 3'-Dimethylazobenzene (4.2 g.) and 4-methyl-1-naphthol (3.0 g.) were heated for 12 hr. at 150° in a sealed, evacuated tube, then treated with benzene, giving an insoluble 1 : 2-di-(1 : 4-dihydro-4-oxo-3-m-toluidino-naphthylidene)ethane which crystallised from 1 : 2 : 4-trichlorobenzene in dark green needles (bronze reflex), m. p. >360° (Found : C, 83.0; H, 5.4; N, 5.75.  $C_{36}H_{28}O_2N_2$  requires C, 83.0; H, 5.4; N, 5.4%). The benzene solution, chromatographed on alumina, gave two bands; the more mobile contained 3 : 3'-dimethylazobenzene and white material, m. p. >360°; the less

mobile band yielded red needles, m. p. 145°, of 2-*m*-toluidino-1 : 4-naphthaquinone 4-3'-methylanyl (Found : C, 81.7; H, 5.4; N, 8.2.  $C_{24}H_{20}ON_2$  requires C, 81.8; H, 5.7; N, 7.95%).

*Action of 3 : 3'-Dibromoazobenzene on 4-Methyl-1-naphthol.*—3 : 3'-Dibromoazobenzene<sup>21</sup> (3.4 g.), and 4-methyl-1-naphthol (1.6 g.) were treated as in the experiment with the dimethyl analogue. Extraction of the crude product with benzene gave a dark residue (0.9 g.) and a solution (C). The solid was extracted with acetone, and then crystallised (0.5 g.) from 1 : 2 : 4-trichlorobenzene. 1 : 2-Di-(3-*m*-bromoanilino-1 : 4-dihydro-4-oxonaphthylidene)ethane is a brownish solid, m. p. >360° (Found : C, 62.7, 63.2; H, 3.5, 3.3; N, 4.1, 3.9; Br, 26.5, 24.8.  $C_{34}H_{22}O_2N_2Br_2$  requires C, 62.75; H, 3.4; N, 4.3; Br, 24.6%), which is blue-green in thin layers. Oxidation of 0.5 g. with nitric acid (20 c.c.; *d* 1.18), as in the experiment with the corresponding product from 4-methyl-1-naphthol and azobenzene, gave 1 : 2-di-(1 : 4-dihydro-3-hydroxy-4-oxonaphthylidene)ethane identical with the compound (B) derived from the azobenzene product (A) ( $\lambda_{\max}$ , at 250, 305, 420, and 660  $\mu$ ). Solution (C) was chromatographed on alumina. Two mobile bands were formed, the lower containing 3 : 3'-dibromoazobenzene and white material m. p. >360°. The upper band was eluted; recovery of the dissolved solid and crystallisation from light petroleum (b. p. 40–60°) gave 2-*m*-bromoanilino-1 : 4-naphthaquinone 4-3'-bromoanil as red needles, m. p. 192° (Found : C, 54.9; H, 3.1; N, 5.7.  $C_{22}H_{14}ON_2Br_2$  requires C, 54.8; H, 2.9; N, 5.8%).

*Action of Azobenzene on 4-Chloro-1-naphthol.*—After being heated at 150° for 12 hr. in a sealed, evacuated tube azobenzene (3.62 g.) and 4-chloro-1-naphthol (3.56 g.) afforded a black product. This was extracted with light petroleum (b. p. 60–80°) and the soluble portion was chromatographed on alumina. The most mobile band consisted of azobenzene; next followed a red band and this was eluted with light petroleum. The eluate afforded red needles (Found : C, 81.1; H, 5.0; N, 9.0%); m. p. 183° not depressed by 2-anilino-1 : 4-naphthaquinone 4-anil.

#### *Reduction experiments.*

In the preparation of *sym.*-tetra-acylethanes from diacylmethanes by the action of iodine on sodio-derivatives in ether it was often advantageous to extract the ether-insoluble part of the product because of the low solubility of many tetra-acylethanes in the medium.

*Reduction of 1 : 1 : 2 : 2-Tetrabenzoylthane.*—(a) Magnesium powder (0.1 g.) was heated for 48 hr. at 90–95° with a solution of 1 : 1 : 2 : 2-tetrabenzoylthane<sup>22</sup> (0.8 g.) in pyridine (10 c.c.). The resulting suspension was filtered, and the filtrate was diluted, acidified, and extracted with ether. The extract, washed with water and then shaken with saturated aqueous copper acetate, gave the copper derivative of dibenzoylmethane (0.05), m. p. and mixed m. p. 211°. When the experiment was repeated with the addition of water (2 c.c.) at such a rate as to maintain slow evolution of hydrogen, the same copper derivative (0.06 g.) was obtained.

There was no evidence of fission when 1 : 2-dibenzoyl-1 : 2-di-*p*-chlorobenzoylthane and 1 : 2-di-*p*-anisoyl-1 : 2-dibenzoylthane were treated similarly, but 1 : 2-dibenzoyl-1 : 2-di-*p*-toluoylthane gave 0.04 g. of a *copper derivative*, m. p. *ca.* 230° (decomp.) (of benzoyl-*p*-toluoylmethane), m. p. 236° (decomp.) (Found : C, 71.1; H, 5.0; Cu, 11.8.  $C_{22}H_{26}O_4Cu$  requires C, 71.5; H, 4.8; Cu, 11.8%).

(b) To a solution of magnesium subiodide, prepared from magnesium (0.1 g.) and iodine (0.25 g.) in benzene (7 c.c.) and ether (3.5 c.c.), was added one of 1 : 1 : 2 : 2-tetrabenzoylthane (0.9 g.) in benzene (60 c.c.), and the mixture was shaken 2 hr. A resultant precipitate was filtered off and the filtrate was shaken with a small volume of dilute sulphuric acid. Evaporation of the benzene-ether solution gave a crystalline residue and this was extracted with a small volume of aqueous methanol or acetone; 1 : 1 : 2 : 2-tetrabenzoylthane remained undissolved. From the extracts needles separated and these afforded 3 : 4-dibenzoyl-2 : 5-diphenylfuran, m. p. and mixed m. p. 141° (Found : C, 84.1; H, 4.4. Calc. for  $C_{30}H_{20}O_3$  : C, 84.1; H, 4.7%); a further quantity was obtained by ether-extraction of the aqueous acid washings.

1 : 1 : 2 : 2-Tetra-acetylthane.—Similar treatment of 1 : 1 : 2 : 2-tetra-acetylthane (1 g.) with magnesium (0.24 g.) and iodine (0.63 g.) in benzene-ether gave a bulky precipitate of the magnesium derivative of the tetraketone. From the benzene-ether solution were obtained unchanged material and 3 : 4-diacetyl-2 : 5-dimethylfuran, m. p. 62–63° (Found : C, 66.8; H, 6.5. Calc. for  $C_{10}H_{12}O_3$  : C, 66.7; H, 6.7%), identical with the product obtained by the action of sulphuric acid<sup>23</sup> or hydrochloric acid<sup>24</sup> on the tetraketone.

<sup>21</sup> Gabriel, *Ber.*, 1876, **9**, 1407.

<sup>22</sup> Abell, *J.*, 1912, 997.

<sup>23</sup> Mullikan, *Amer. Chem. J.*, 1893, **15**, 532.

<sup>24</sup> Zanetti, *Gazzetta*, 1893, **23**, II, 307.



A solution of hydrazine hydrate (1.2 g.) in glacial acetic acid (5 c.c.) was added with stirring at 0° to one of 3 : 4-diacetyl-2 : 5-dimethylfuran (3.6 g.) in acetic acid (10 c.c.). Water (50 c.c.) and then 4% sodium hydroxide were added until a cream-coloured precipitate resulted. This was collected, washed with a small volume of water, then crystallised twelve times from hot water. The *monohydrazone* formed long needles, m. p. 136—140° (decomp.) (Found : C, 62.2; H, 7.2; N, 14.5.  $C_{10}H_{14}O_2N_2$  requires C, 61.9; H, 7.2; N, 14.4%). On being kept for several days the mother-liquors afforded a small quantity of another product, m. p. 244—246° (decomp.) (Found : N, 28.9.  $C_{10}H_{16}ON_4$  requires N, 26.9%), which was probably the *dihydrazone*.

*Diethyl  $\alpha\alpha'$ -Diacetylsuccinate*.—Magnesium powder (0.2 g.) was heated for 48 hr. with a solution of diethyl  $\alpha\alpha'$ -diacetylsuccinate (0.85 g.) in pyridine (10 c.c.). The colour became light purple-brown, then deep yellow-brown. The filtered solution was mixed with water, acidified, and then extracted with ether. The extract, washed with water, gave a pale yellow-brown crystalline precipitate when it was shaken with saturated cupric acetate solution. The product was washed with water, then ether; crystallised from benzene, it had m. p. 220° (decomp.) (Found : C, 49.4; H, 4.7; Cu, 13.1. Calc. for  $C_{20}H_{22}O_{10}Cu$  : C, 49.4; H, 4.5; Cu, 13.1%) and was identical with the copper derivative of ethyl 2 : 3-dihydro-3-1'-hydroxyethylidene-2-oxofuran-4-carboxylate. The copper compound decomposed in contact with dilute sulphuric acid to form white needles (from alcohol) of the ester, m. p. 106° (Found : C, 56.7; H, 5.7. Calc. for  $C_{10}H_{12}O_5$  : C, 56.6; H, 5.7%) not depressed by a sample prepared by heating diethyl  $\alpha\alpha'$ -diacetylsuccinate at 170—190°, extraction with dilute alkali, and acidification.<sup>25</sup>

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<sup>25</sup> Knorr and Haber, *Ber.*, 1894, **27**, 1159.