

## New Intermediates and Dyestuffs for Synthetic Fibres. Part VI.<sup>1</sup> 1-Arylaminoanthraquinones

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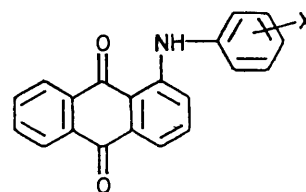
The synthesis of a series of 1-arylaminoanthraquinones and 2-substituted 1-anilinoanthraquinones is described; principal factors influencing the colour of the dyes are discussed, together with u.v. and i.r. data. Condensation of 1-chloroanthraquinone with 4-aminopyridine gives rise to 1-hydroxyanthraquinone and 1-aminoanthraquinone in addition to the anticipated 1-(4-pyridylamino)anthraquinone. Data obtained indicate the stabilisation of the dyes by strong hydrogen-bonding, a factor compatible with the high fastness to light shown by these dyes on synthetic fibres.

1-ANILINOANTHRAQUINONE, a pink dyestuff for synthetic fibres, results from the condensation of 1-chloroanthraquinone with aniline, together<sup>1</sup> with numerous by-products. Several 1-arylaminoanthraquinones have been prepared from condensation of arylamines with 1-nitroanthraquinone<sup>2</sup> or anthraquinone-1-sulphonic acid,<sup>3</sup> and from 1-aminoanthraquinones and halogenobenzenes.<sup>4-6</sup>

Condensation of arylamines with 1-chloroanthraquinone and with 2-substituted and 1-nitro- or 1-chloroanthraquinones gave the majority of the dyes (I) and (II), respectively; an excess of arylamine was used, with nitrobenzene, *NN*-dimethylformamide (DMF), or pentyl alcohol as solvent. The use of DMF as solvent has been shown<sup>7</sup> to yield the arylaminoanthraquinone (I), 1-methylaminoanthraquinone, or a mixture thereof, depending on the basicity of the arylamine, a factor substantiated in this work by the sole formation of the arylaminoanthraquinone (I) with the more reactive aminophenylethanols and by the formation of (I) and 1-methylaminoanthraquinone with the less basic 4-aminobenzylidene trifluoride. The ethoxycarbonyl derivatives (32)—(34) were also prepared from the acid chlorides or by esterification of the corresponding acids; the amino-derivatives were obtained by reduction of the nitro-analogues or by condensation of 1-aminoanthraquinone with bromonitrobenzenes. All crude reaction products showed the presence of deeply coloured by-products,<sup>1</sup> although in the present work compounds (I) and (II) only were isolated during chromatographic purification.

The mass spectrum of the product from 1-chloroanthraquinone and 4-aminopyridine indicated the formation of some 4-di(anthraquinon-1-yl)aminopyridine ( $P^+$  at  $m/e$  506); similar tertiary amines have been shown<sup>8</sup> to result during the condensation of aminopyridines with halogenonitrobenzenes. Also isolated from this reaction were 1-hydroxyanthraquinone and 1-aminoanthraquinone. 1-Hydroxyanthraquinone has been previously<sup>9</sup> reported as a minor (2%) by-product in some Ullmann reactions, but the formation of 1-aminoanthraquinone has not been noted; it appears to be specific to reactions involving 4-aminopyridine; reaction of 2-chloroanthraquinone with 4-aminopyridine was found to yield some

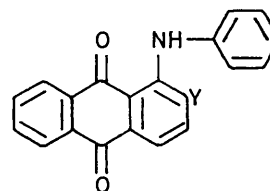
2-aminoanthraquinone. The formation of 1-aminoanthraquinone probably results from hydrolysis of the tautomeric form (III); this species would also be more



(I)

X =

(1) H	(16) NO <sub>2</sub>	(31) 4-CO <sub>2</sub> H
(2) 2-OMe	(17) 2-Cl	(32)† 2-CO <sub>2</sub> Et
(3) 3-OMe	(18) 3-Cl	(33)† 3-CO <sub>2</sub> Et
(4) 4-OMe	(19) 4-Cl	(34) 4-CO <sub>2</sub> Et
(5)† 2-OEt	(20)† 2-Br	(35)† 4-SO <sub>2</sub> Me
(6)† 3-OEt	(21)† 3-Br	(36)† 4-CN
(7)† 4-OEt	(22) 4-Br	(37) 4-COMe
(8) 2-Me	(23)† 2-F	(38)† XC <sub>6</sub> H <sub>4</sub> = 2-pyridyl
(9) 3-Me	(24)† 3-F	(39)† XC <sub>6</sub> H <sub>4</sub> = 3-pyridyl
(10) 4-Me	(25)† 4-F	(40)† XC <sub>6</sub> H <sub>4</sub> = 4-pyridyl
(11)† 2-C <sub>2</sub> H <sub>4</sub> OH	(26) 2-CF <sub>3</sub>	(41) 2-NH <sub>2</sub>
(12)† 3-CH(OH)Me	(27) 3-CF <sub>3</sub>	(42) 3-NH <sub>2</sub>
(13)† 4-C <sub>2</sub> H <sub>4</sub> OH	(28)† 4-CF <sub>3</sub>	(43) 4-NH <sub>2</sub>
(14) 2-NO <sub>2</sub>	(29) 2-CO <sub>2</sub> H	(44)† 4-NMe <sub>2</sub>
(15) 3-NO <sub>2</sub>	(30) 3-CO <sub>2</sub> H	



(II)

Y =

(45)† NO <sub>2</sub>	(48)† CO <sub>2</sub> Et
(46) Me	(49) Cl
(47) CO-NH <sub>2</sub>	

† New compound

susceptible to the known formation of 1-hydroxyanthraquinone in reactions in the presence of alkaline earth acetates.

The  $\pi$ - $\pi^*$  absorption maxima at 252 and 323 nm in the electronic spectrum of anthraquinone are associated<sup>10</sup>

<sup>6</sup> W. Bradley and F. P. Williams, *J. Chem. Soc.*, 1959, 360.

<sup>7</sup> W. M. Lord and A. T. Peters, *J. Chem. Soc. (C)*, 1968, 783.

<sup>8</sup> A. T. Peters, *J. Soc. Dyers and Colourists*, 1970, 86, 77.

<sup>9</sup> N. I. Artemyev and A. E. Kretov, *J. Appl. Chem. U.S.S.R.*, 1953, 26, 1219, 1249.

<sup>10</sup> T. Hayashi and M. Matsuo, *Bull. Chem. Soc. Japan*, 1962, 35, 1500.

<sup>1</sup> Part V, W. M. Lord and A. T. Peters, *J. Chem. Soc. (C)*, 1971, 3600.

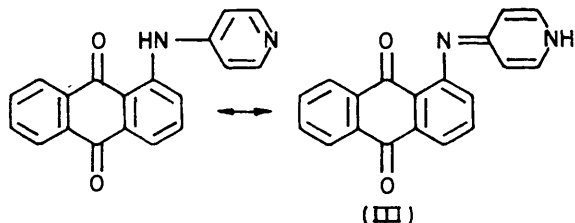
<sup>2</sup> Bayer, G.P. 115,048.

<sup>3</sup> Bayer, G.P. 175,024.

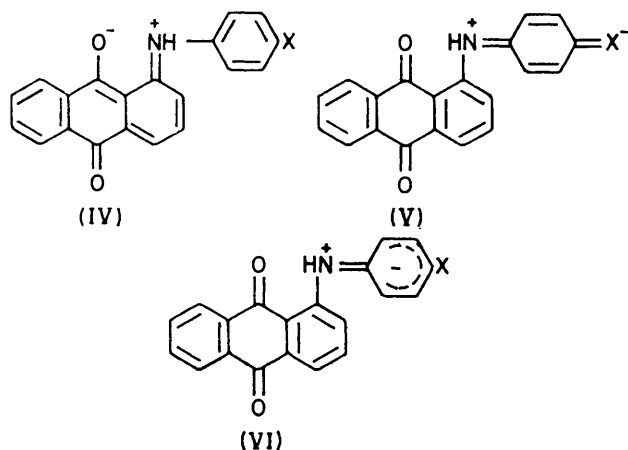
<sup>4</sup> J. Arzent and V. Slavic, *Coll. Czech. Chem. Comm.*, 1969, 34, 3576.

<sup>5</sup> F. Ullmann and O. Fodor, *Annalen*, 1911, 380, 317.

with the benzenoid character of the chromophore, and those at 262 and 272 nm are designated 'quinonoid' bands. In the spectra of compounds (I) and (II), one



or both of the latter bands is absent, in agreement with the general lowering<sup>11</sup> of the quinonoid character resulting from substitution at the 1-position. The long-wavelength band is significantly affected in the spectrum of (I) by the nature of the substituent X; electron donor groups enhance the contribution of the polar structures (IV) by intramolecular electron transfer between the substituent and the anthraquinone nucleus, with resultant bathochromic shift. Electron acceptor groups X give a hypsochromic shift, additional structures (V) and (VI) opposing the contribution of the more bathochromic (IV).



Observed shifts in the long wavelength absorption band on introduction of various donor and acceptor groups X into structure (I) show<sup>12</sup> a generally linear relation with Hammett  $\sigma$ -constants for substitution of X at the 3-position, and with Jaffe  $\sigma^*$  constants for substitution at the 4-position. Similar correlations for a small range of compounds (I) have been reported<sup>10</sup> to show a linear relations between  $\lambda_{\max}$  and Hammett  $\sigma$ -values, but a 'concave' relation with the  $\sigma$ -constants of Brown.<sup>13</sup> Relations between  $\sigma$ -constants and shifts in  $\lambda_{\max}$  have been observed in other classes of dye, e.g. 1-acylaminoanthraquinones,<sup>14</sup> 7-substituted 3,4-phthaloylacridones,<sup>15</sup> nitrodiphenylamines,<sup>16</sup> and 4-aminoazobenzenes.<sup>17,18</sup> In the case of compounds (I), steric factors<sup>19</sup> interfere with

<sup>11</sup> R. A. Morton and W. R. Earlam, *J. Chem. Soc.*, 1941, 159.

<sup>12</sup> W. M. Lord, Ph.D. Thesis, University of Bradford, 1970.

<sup>13</sup> H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

<sup>14</sup> T. Hayashi and R. Shibata, *Bull. Chem. Soc. Japan*, 1961, **34**, 1116.

<sup>15</sup> W. Bradley and H. Kaiwar, *J. Chem. Soc.*, 1960, 2859.

conclusions based solely on electronic changes. The presence in aminoanthraquinones of steric interactions is shown in the  $\epsilon_{\max}$  values of the long wavelength band of 1-methylaminoanthraquinone (7100), 1-dimethylaminoanthraquinone (4900) and 1-anilinoanthraquinone (4900) in ethanolic solution; 1-N-ethyl anilinoanthraquinone shows<sup>20</sup>  $\epsilon_{\max}$  1970 in carbon tetrachloride. The modification of the electronic effects of substituents X in (I) due to steric factors is further indicated in comparing the effect of X when present either in the phenyl ring or in the anthraquinone nucleus. Thus, introduction of a 1-methoxy-group into anthraquinone ( $\lambda_{\max}$  327 nm) results in a blue shift of 53 nm [cf. a shift of 7 nm between dye (1) ( $\lambda_{\max}$  508 nm) and dye (4), (515 nm)]; similarly, 1-aminoanthraquinone ( $\lambda_{\max}$  475 nm) shows a blue shift of 148 nm as compared with anthraquinone, but dye (43) ( $\lambda_{\max}$  518 nm) is only 10 nm 'more bathochromic' than dye (1). Correlations between  $\sigma$ -values of X and blue shifts are thus not absolute and although the relationship is generally linear,<sup>12</sup> steric factors result in several anomalies. The inductive polar character of the trifluoromethyl group results in hypsochromic shifts in the anticipated order: *o* > *m* > *p* (486, 492, and 496 nm, respectively), but with many other substituents, shifts anticipated on the basis of electronic effects are not observed, e.g. dye (7),  $\lambda_{\max}$  510, and dye (5),  $\lambda_{\max}$  515; and dye (16),  $\lambda_{\max}$  482, and dye (15),  $\lambda_{\max}$  486; dyes (3),  $\lambda_{\max}$  506, and (8),  $\lambda_{\max}$  504 nm, show a red shift of 2 and 4 nm, respectively.

In the range of dyes (1)–(44), shifts in  $\lambda_{\max}$  from 521 nm [dyes (2) and (44)] to 481 nm [dye (14)] occur, the overall range of 40 nm being much lower than that observed for similar substitution in 4-aminoazobenzenes,<sup>17</sup> indicating the lower electron mobility in 1-aryl-aminoanthraquinones.

Substitution at the 2-position of the anthraquinone molecule [dyes (II)] results in a slight hypsochromic shift due to the electron donor alkyl group; dyes (8) and (46) have similar  $\lambda_{\max}$  values (504 and 505 nm), the red shift in comparison with dye (1) being relatable<sup>10</sup> to repulsion between the methyl group and the  $\beta$ -CH group of the anthraquinone or the phenyl ring, respectively. Marked bathochromic shifts, strongest for dye (38) ( $\lambda_{\max}$  523 nm) occur where Y is an electron acceptor, these shifts resulting from additional resonance structures (VII) acting in conjunction with (IV).

Shifts in (CO) i.r. bands of compounds (I) show only a random relationship<sup>12</sup> with the  $\sigma$ -constants of X, although an 'S-shaped relationship' has been reported<sup>10</sup> for a more limited range of 1-arylaminoanthraquinones. Values of  $\nu(\text{NH})$  could not be obtained by the KBr disc technique except for the dyes (41)–(43) and (47), which gave identifiable data for the primary amino-group.

<sup>16</sup> M. Day and A. T. Peters, *J. Soc. Dyers and Colourists*, 1969, **85**, 8.

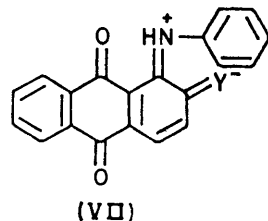
<sup>17</sup> I. Bridgman and A. T. Peters, *J. Soc. Dyers and Colourists*, 1970, **86**, 519.

<sup>18</sup> H. P. Mehta and A. T. Peters, unpublished work.

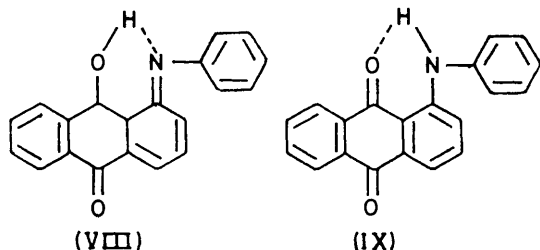
<sup>19</sup> R. H. Peters and H. H. Sumner, *J. Chem. Soc.*, 1953, 2101.

<sup>20</sup> N. S. Dokunikhin and T. N. Kurduomova, *J. Gen. Chem. (U.S.S.R.)*, 1958, **58**, 2021.

Many dyes in which an amino-group is in a strongly H-bonded environment show  $\nu(\text{NH})$  readily by KBr disc techniques, e.g. indigo<sup>21</sup> and 2-nitrodiphenylamines,<sup>16</sup> although absence of a  $\nu(\text{NH})$  band in the spectrum of



indanthrone<sup>22</sup> has led to the formulation of alternative structures for this dye, on the basis of which 1-anilinoanthraquinone would require structures of type (VIII), which are unacceptable owing to the absence of a  $\nu(\text{C}=\text{N})$  band in the i.r. spectrum. Values for  $\nu(\text{NH})$  of the secondary amino-group in 1-arylaminoanthraquinones



have been previously obtained<sup>10</sup> by the Nujol mull technique; however we were unable to obtain any reproducible data from spectra in this medium. Although reported<sup>10</sup> as being of limited solubility, we found that compounds (I) gave satisfactory  $\nu(\text{NH})$  data from dilute solutions in carbon tetrachloride, but the band intensities were low.

The low intensity of the  $\nu(\text{NH})$  bands of compounds (I) and (II) is more consistent with the strongly intramolecular H-bonded configuration (IX).

Molecular models of structures (I) confirm a limited rotation about the N-C(I) bond and indicate the necessary close proximity of the amino hydrogen atom to the carbonyl group in a rigid configuration. In 1-amino- and 1-methylaminoanthraquinone, configurations are less rigid and rotation of the amino group allows the possibility of both H-bonded and non-bonded orientations.

All the anthraquinones (I) and (II) dyed polyester fibres in deep orange-red to bluish-red shades, which, with the exception of those due to dyes containing primary amino-groups in the phenyl ring, showed a very high stability to light fading, viz. a factor of rating of 7–8 by standard<sup>23</sup> assessment methods. This is compatible with the existence of these dyes in a stable configuration with stabilisation of the ground state (IX) and the polar excited state (IV) by strong intramolecular H-bonding.

\* Experimental details not included here are available as Supplementary Publication No. SUP 20804 [for details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20], which also includes u.v. and i.r. data for compounds (1)–(49).

#### EXPERIMENTAL \*

M.p.s are corrected. Microanalyses were performed by Research Laboratory Dr. C. Janssen, Beerse, Belgium. All crude dyes were purified on activated alumina (type H; 100–200 mesh; Laporte); strongly adsorbed dark-coloured zones<sup>1</sup> were not investigated, unchanged 1-chloroanthraquinone was collected as in the initial eluate, and the pure dyes were extracted from the principal bluish-red zones with ethanol.

*Excess of Arylamine as Reaction Solvent.*—1-Chloroanthraquinone (2 g), arylamine (10 g), and potassium carbonate (1 g) were stirred at 180–200° for 6 h; the mixture was then added to 50% hydrochloric acid (500 ml) and filtered, giving crude products in 90–100% yields. Prepared by this method were dyes (2)–(10), (17)–(19), and (22)–(25).

*Nitrobenzene as Reaction Solvent.*—1-Chloroanthraquinone (4 g), arylamine (5 g), and nitrobenzene (30 ml) were stirred for 10–15 h at 170–180° in the presence of copper(II) acetate (0.1 g). After removal of nitrobenzene by steam distillation, crude dyes were purified as above, giving compounds (12), (20), (21), (26), (32), (33), and (35)–(37).

Extraction with benzene of the crude products derived from use of 2-nitro- and 4-nitro-aniline removed only unchanged arylamine and 1-chloroanthraquinone. Dyes (14)–(16) were obtained by recrystallisation from pyridine of the benzene-insoluble material.

1-Chloroanthraquinone (5 g) was heated at 130–140° for 15 h in nitrobenzene (15 ml) with 2-aminopyridine (7.5 g) in the presence of anhydrous sodium acetate (5 g); steam distillation left a reddish-brown residue (8.7 g), m.p. 142–144°, chromatography of which gave, from a deep scarlet zone, 1-(2-pyridylamino)anthraquinone (25%), dark red needles, m.p. 226° (from ethanol) (Found: C, 75.8; H, 3.7; N, 9.3.  $\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}_2$  requires C, 76.0; H, 4.0; N, 9.3%). 3-Aminopyridine similarly gave 1-(3-pyridylamino)anthraquinone (27%), dark red prisms, m.p. 178–179° (from ethanol) (Found: C, 75.8; H, 4.0; N, 9.3%).

4-Aminopyridine, treated similarly, gave a brick red product. Extraction of the crude product (2.5 g) with benzene and chromatography of the extract, gave, from an upper deep orange zone, 1-hydroxyanthraquinone (0.11 g) and, from a lower deep scarlet zone, 1-aminoanthraquinone (0.7 g); a strongly adsorbed dark brown zone was not investigated and 1-chloroanthraquinone (0.18 g) was eluted. Benzene-insoluble material showed  $M^+$  300, with minor contaminant at  $m/e$  506. High resolution mass measurement on the latter ion agreed with the molecular formula ( $\text{C}_{33}\text{H}_{18}\text{N}_2\text{O}_4$ ) of 4-di(anthraquinon-1-yl)aminopyridine; this was removed during recrystallisation, which gave 1-(4-pyridylamino)anthraquinone, deep red needles, m.p. 320–324° (from pyridine) (Found: C, 75.8; H, 3.8; N, 9.2%).

*NN-Dimethylformamide as Reaction Solvent.*—Dyes (26) and (27) were obtained as previously<sup>7</sup> described. 1-Chloroanthraquinone and 4-aminobenzylidene trifluoride gave 1-methylaminoanthraquinone (43%) and 1-(4-trifluoromethylanilino)anthraquinone (39%), red needles, m.p. 148° (from ethanol) (Found: C, 68.4; H, 3.3; F, 15.5; N, 3.8.  $\text{C}_{21}\text{H}_{12}\text{F}_3\text{NO}_2$  requires C, 68.7; H, 3.3; F, 15.3; N, 3.8%).

<sup>21</sup> R. W. Brode, E. G. Pearson, and G. M. Wyman, *J. Amer. Chem. Soc.*, 1954, **76**, 1034.

<sup>22</sup> G. M. Wyman, *J. Amer. Chem. Soc.*, 1956, **78**, 4599.

<sup>23</sup> 'Standard Methods for the Determination of the Colour Fastness of Textiles,' The Society of Dyers and Colourists, 1962, p. 46.

No 1-methylaminoanthraquinone was isolated during similar syntheses of dyes (11), (13), and (25).

*Miscellaneous Syntheses.*—1-Chloroanthraquinone (7.25 g) and aminobenzoic acids (6.2 g) were refluxed for 12 h in pentyl alcohol (75 ml) in the presence of potassium acetate (6.2 g), copper(II) acetate (0.2 g), and copper powder (0.2 g). Crude products, crystallised from glacial acetic acid, gave dyes (29)—(31).

Dye (29), refluxed in ethanol in the presence of concentrated sulphuric acid, gave dye (32); dyes (30) and (31) were converted by way of the corresponding acid chlorides into dyes (33) and (34).

1-Chloroanthraquinone (5 g) and *NN*-dimethyl-*p*-phenylenediamine (3 g) were refluxed for 15 h in pentyl alcohol (50 ml) in the presence of potassium carbonate (3 g), copper(II) acetate (0.4 g), and copper(I) bromide (0.1 g). Steam distillation left a dark blue residue (6.8 g); from a deep violet zone on alumina was obtained 1-(4-*dimethylaminoanilino*)anthraquinone (27%), m.p. 228° (from ethanol) (Found: C, 77.4; H, 5.4; N, 8.3.  $C_{22}H_{18}NO_2$  requires C, 77.2; H, 5.3; N, 8.2%).

1-(3-Nitroanilino)anthraquinone was obtained<sup>24</sup> from 1-

<sup>24</sup> Cassella, G.P. 889,595.

<sup>25</sup> T. Hargreaves, H. G. Eyles, and A. T. Peters, *J. Chem. Soc. (C)*, 1968, 2431.

aminoanthraquinone and 3-bromonitrobenzene. Reduction of dyes (14) and (15) with sodium dithionite<sup>5</sup> in aqueous sodium hydroxide gave dyes (41) and (42); reduction of dye (16) with sodium sulphide<sup>5</sup> gave dye (43).

Condensation of 2-substituted 1-nitroanthraquinones with aniline gave 1-anilino-2-carbamoylanthraquinone,<sup>25</sup> 1-anilino-2-methylanthraquinone,<sup>26</sup> and 1-anilino-2-ethoxycarbonylanthraquinone (67%), m.p. 158—159° (from ethanol) (Found: C, 74.4; H, 4.6; N, 3.8.  $C_{23}H_{17}NO_4$  requires C, 74.4; H, 4.6; N, 3.8%). 1-Chloro-2-nitroanthraquinone and aniline afforded 1-anilino-2-nitroanthraquinone (41%), m.p. 187—189° (from ethanol) (Found: C, 69.8; H, 3.4; N, 8.3.  $C_{20}H_{12}N_2O_4$  requires C, 69.8; H, 3.5; N, 8.4%).

2-Chloroanthraquinone was nitrated<sup>26</sup> to give 2-chloro-1-nitroanthraquinone, m.p. 245° (from *o*-dichlorobenzene) (lit.,<sup>27</sup> 280—281°) (Found: C, 58.2; H, 1.8; Cl, 12.0; N, 4.7. Calc. for  $C_{14}H_6ClNO_4$ : C, 58.45; H, 2.1; Cl, 12.3; N, 4.9%). Condensation of this product with aniline gave 1-anilino-2-chloroanthraquinone, m.p. 158—160° (from ethanol) (lit.,<sup>27</sup> 204—205°) (Found: C, 71.8; H, 3.1; Cl, 10.0; N, 4.2. Calc. for  $C_{20}H_{12}ClNO_2$ : C, 72.0; H, 3.4; Cl, 10.1; N, 4.2%).

[3/450 Received, 28th February, 1973]

<sup>26</sup> G. D. Wood and A. T. Peters, *J. Chem. Soc.*, 1962, 3373.

<sup>27</sup> W. Bradley and E. Leete, *J. Chem. Soc.*, 1951, 2129.