667. *New Intermediates and Dyes. Part IX.* Reactions of 2-Methyl-1-nitro- and 1-Amino-2-methyl-anthraquinone; Derived Dyes for Cellulose Acetate Rayon.*

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Mononitration of 2-methylanthraquinone has been studied in detail, and the amines derived by reduction separated. The nitro-group in 2-methyl-1-nitroanthraquinone has been replaced by alkylamino-groups, and the derived products have been compared with the 1-alkylamino-anthraquinone analogues.

1-Amino-4-bromo-2-methylanthraquinone has been converted into some 4-alkylamino- and 4-arylamino-derivatives, which are dyes for acetate rayon. In presence of sodium and cupric acetates, or sodium acetate alone, reaction of the 4-bromo-compound with alkylamines is accompanied by debromination, to yield 1-amino-2-methylanthraquinone.

2-Methylanthraquinone, when nitrated by a modification of the method of Locher and Fierz,[1] gives 81·5% of 2-methyl-1-nitroanthraquinone, which is reduced by aqueous sodium sulphide, again in 81% yield, to the red 1-amino-2-methylanthraquinone, and this has been oriented by Eder, Widner, and Bütler.[2] After isolation of 77·3% of the 1-nitro-compound from the acid nitration liquors, the more soluble product was reduced and the resulting amine chromatographed in trichlorobenzene on alumina to yield the 1-amine and small amounts of the orange 2-amino-3-methylanthraquinine and a red diamino-2-methylanthraquinone. Thus, the major nitration product was accompanied by *ca.* 4% of 2-methyl-3-nitroanthraquinone and 3% of a dinitro-derivative.

1-Amino-4-bromo-2-methylanthraquinone was converted by the Sandmeyer reaction into 1,4-dibromo-2-methylanthraquinone; the 4-bromo- and the 1,4-dibromo-derivative reacted with toluene-*p*-sulphonamide in boiling pentyl alcohol to yield 1-amino-2-methyl-4-toluene-*p*-sulphonamido- and 2-methyl-1,4-ditoluene-*p*-sulphonamido-anthraquinone, respectively, both of which on hydrolysis afforded 1,4-diamino-2-methylanthraquinone.

Replacement of the 1-nitro-group by the appropriate alkylamine in ethanol at 140° (sealed tube) yielded 1-methylamino- (66%), 1-ethylamino- (73%), 1-n-propylamino- (78%), 1-isopropylamino- (76%, after reaction for 24 hr.), 1-n-butylamino- (79%), 1-isobutylamino- (53%), 1-n-pentylamino- (61%), and 1-n-hexylamino-2-methylanthraquinone (53%); these derivatives are dark red to purple.

1,2′-Hydroxyethylamino-2-methylanthraquinone was obtained in only 5% yield by heating the nitro-quinone with monoethanolamine and ethanol at 130—140°, the main product being 1-amino-2-methylanthraquinone, formed probably by the reducing action of the monoethanolamine. Heating 1-bromo-2-methylanthraquinone with ethanolic ethanolamine at 125—130° afforded an improved yield (14%) of the 1,2′-hydroxyethylamino-derivative but some debromination occurred and 2-methylanthraquinone was isolated. 1-Cyclohexylamino-2-methylanthraquinone (65% yield) was prepared by refluxing the 1-nitro-quinone with cyclohexylamine; heating with benzylamine alone in a sealed tube at 130—140° converted the nitro-quinone into 1-amino-2-methylanthraquinone and 1-benzylamino-2-methylanthraquinone (28%); refluxing it with aniline gave purple 1-anilino-2-methylanthraquinone in 55% yield. In all the above cases, chromatography was used for purification, and this procedure is generally useful for alkylamino-anthraquinones.

For comparison, the 1-alkylaminoanthraquinones were prepared from 1-chloroanthraquinone by reaction with the appropriate ethanolic alkylamine at 130—140°, with

* Part VIII, *J.*, 1960, 1125.

[1] Locher and Fierz, *Helv. Chim. Acta*, 1927, **10**, 642.
[2] Eder, Widmer, and Bütler, *Helv. Chim. Acta*, 1924, **7**, 341.

no additive, in a sealed tube, yields being 60—88%. When sodium anthraquinone-1-sulphonate was refluxed with aqueous-ethanolic n-hexylamine for 24 hours, only a low yield of 1-n-hexylaminoanthraquinone was obtained, the sulphonate being mainly unchanged; an analogous reaction was observed on heating the sulphonate with aqueous-ethanolic methylamine in a sealed tube at 130—140°.

Reaction of 1-amino-4-bromo-2-methylanthraquinone with the appropriate ethanolic alkylamine in a sealed tube at 130—140° was effected (*a*) in presence of sodium and cupric acetates, (*b*) in presence of sodium acetate, and (*c*) with no such additions. Methylamine thus afforded (*a*) the violet 1-amino-2-methyl-4-methylaminoanthraquinone (54%) and 1-amino-2-methylanthraquinone (20%), (*b*) 1-amino-2-methylanthraquinone (33%), 1-amino-2-methyl-4-methylaminoanthraquinone (20%), and a copper-coloured, strongly fluorescent product (*ca.* 10%), and (*c*) mainly unchanged product (65%) and the above 4-methylamino-derivative (24%). Chromatography was used in all experiments. The elimination of bromine, to give 1-amino-2-methylanthraquinone is not novel; Bayer [3] states that, in the presence of copper, 2-acetamido-1,3-dibromoanthraquinone affords 2-acetamidoanthraquinone, and Ullmann and Minajeff [4] heated 4-chloro-1-methylanthraquinone in nitrobenzene with potassium acetate and copper powder, obtaining 1-methylanthraquinone.

The above reaction (*a*) was extended by using the appropriate alkylamine, yielding 1-amino-4-ethylamino- (34%), -4-n-propylamino- (22%), and -4-n-butylamino-2-methylanthraquinone (10%), with increasing formation (33%, 47%, and 73%, respectively) of 1-amino-2-methylanthraquinone. As formation of the violet 4-n-alkylamino-derivatives decreased with increase in the length of the aliphatic chain of the amine, with a corresponding increase in the amount of 1-amino-2-methylanthraquinone, this reaction was not extended. The use of method (*b*) above gave 1-amino-4-ethylamino- (22%), -4-n-propylamino- (17%), -4-n-butylamino- (30%), -4-n-pentylamino- (30%), -4-n-hexylamino- (30%), and -4-n-octylamino-anthraquinone (22%). In all cases, 1-amino-2-methylanthraquinone was also formed in yields of *ca.* 40% in each case, with little variation in amount whichever alkylamine were used. In this reaction (*b*), however, small amounts of yellowish-brown solid with a strong green fluorescence in organic solvents were isolated; analyses indicated that the proportion of nitrogen to oxygen was in the ratio of 2 : 1, but the constitution of such compounds was not established.

Reaction (*c*), in which no additive was used, showed no dehalogenation and yielded much 1-amino-4-bromo-2-methylanthraquinone (45—65%), and the respective 4-alkylamino-1-amino-2-methylanthraquinones were obtained as follows; alkyl = ethyl (28%), n-propyl (32%), n-butyl (35%), isobutyl (25%), n-pentyl (43%), n-hexyl (47%), n-octyl (52%), 2′-ethylhexyl (58%), and cyclohexyl (59%), respectively. The usual method of heating in a sealed tube at 130—140° was modified in the last four cases above, where refluxing was used. In general, this method (*c*) was found to be the most useful for preparing the 4-alkylamino-1-amino-2-methylanthraquinones.

Dyeings were carried out on secondary cellulose acetate rayon, in presence of soap solution, at 85° for 1 hour, and the 2-methylanthraquinone derivatives were compared with anthraquinone analogues. Introduction of a 2-methyl group into 1-alkylaminoanthraquinones had a bathochromic effect, and dyeings were bluish-red; 1-anilino-2-methylanthraquinone, however, had poorer affinity than 1-anilinoanthraquinone. With 4-alkylamino-1-amino-2-methylanthraquinones, only slight modifications of shade and depth of the blue dyeings were noted, compared with the anthraquinone analogues; increasing the length of the 4-alkylamino-chain gave dyeings progressively weaker, and redder in shade, and the deepest dyeings were obtained with 1-amino-2-methyl-4-methylaminoanthraquinone.

[3] Bayer, G.P. 261,270; *Friedlander*, **11**, 558.
[4] Ullmann and Minajeff, *Ber.*, 1912, **45**, 687.

Experimental

Nitration of 2-Methylanthraquinone.—2-Methylanthraquinone (20 g., 1 mol.) was dissolved in 98% sulphuric acid (100 ml.), and finely ground potassium nitrate (10 g., 1·1 mol.) was added during 1 hr. at 0—5°; the mixture was stirred for 18 hr., the temperature being allowed to rise to 20°. Water (4 ml.) was then added and the solution heated to 90—95° during 1 hr., kept at this temperature for 30 min., and then allowed to cool. The separated solid was collected (filtrate *A*) and washed with aqueous sulphuric acid and then with warm water until free from acid (18·6 g., 77·3%; m. p. 267—269°). Crystallisation from acetic acid gave pale yellow needles, m. p. 272—273°, of 2-methyl-1-nitroanthraquinone (Locker and Fierz [1] give m. p. 269—270°). The acid filtrate *A*, when added to ice (1 kg.), yielded a purplish-brown solid (*B*) (4·4 g.), m. p. 241—242°, which did not alter appreciably in m. p. on crystallisation; subsequent reduction, however, showed that this was a mixture of nitro-compounds.

1-*Amino*-2-*methylanthraquinone.*—2-Methyl-1-nitroanthraquinone (2·5 g.) was dissolved in boiling ethanol and added to a stirred solution of crystalline sodium sulphide (15 g.) in water (150 ml.) at 70°. The mixture was boiled for 30 min., the ethanol removed, and the residue cooled; red crystals then separated (1·8 g., 81%); crystallisation from ethanol yielded red needles, m. p. 204—205°, of the 2-amine (lit.,[1] m. p. 202°). This amine was also obtained by heating the nitro-compound with aqueous-ethanolic ammonia at 130—140° in a sealed tube for 6 hr.

Reduction, as described, of the above solid (*B*) (2 g.) afforded a reddish-brown solid (1·6 g.), which was chromatographed in trichlorobenzene on alumina and the main zone eluted with the same solvent, giving 1-amino-2-methylanthraquinone (0·4 g.), m. p. and mixed m. p. 205°. A moderately strongly adsorbed red band was extracted with ethanol, giving a solid (0·15 g.) which crystallised from benzene in red prisms, m. p. 195—196°, of a diamino-2-methylanthraquinone (Found: C, 71·5; H, 4·9; N, 10·9. Calc. for $C_{15}H_{12}N_2O_2$: C, 71·45; H, 4·75; N, 11·1%). A more strongly adsorbed orange band was extracted with ethanol, from which separated orange needles (0·17 g.), m. p. 260—261° (Found: C, 75·6; H, 4·4; N, 6·1. Calc. for $C_{15}H_{11}NO_2$: C, 76·0; H, 4·6; N, 5·9%), not depressed on admixture with 2-amino-3-methylanthraquinone, m. p. 262—263° (kindly supplied by Dr. Nursten), obtained by Nursten and Bradley.[5]

Yields of amines isolated on reduction of the solid (*B*) correspond to 0·88 g. of 1-amino-, 0·33 g. of diamino-, and 0·374 g. of 3-amino-2-methylanthraquinone, equivalent to 0·99 g. (4·1%), 0·408 g. (1·2%), and 0·42 g. (1·4%) of the respective nitro-compounds. The total yield of 2-methyl-1-nitroanthraquinone in the above nitration was 19·6 g., 81·5%.

1-*Amino*-4-*bromo*-2-*methylanthraquinone.*—1-Amino-2-methylanthraquinone (5 g., 1 mol.), acetic acid (50 ml.), and bromine (3·5 g., 1·04 mol.) gave an orange solid (5·9 g.), which crystallised from toluene in red needles, m. p. 248° (decomp.) (Locher and Fierz [1] give m. p. 247°).

1,4-*Dibromo*-2-*methylanthraquinone.*—The above monobromo-derivative (4 g.) was dissolved in 98% sulphuric acid (30 ml.), and sodium nitrite (2·4 g.) was added slowly with stirring at 0—5°. The colour changed from greenish-yellow to brownish-yellow; stirring was then continued for 30 min., and the mixture added to ice; the pale cream precipitate of diazo-compound was collected and dissolved in hydrobromic acid (30 ml.; *d* 1·49) and treated with a solution of cuprous bromide (4 g.) in hydrobromic acid (30 ml.) and warmed on the water-bath; the mixture became purple, and after 1 hr. was added to water and the resulting yellowish-brown solid was collected, washed, dried, dissolved in toluene, filtered from a little insoluble matter, and chromatographed on alumina. The main yellow band was extracted with ethanol and afforded yellow needles (4·2 g.), m. p. 169°, of the *dibromo-derivative* (Found: C, 47·7; H, 2·2; Br, 42·3. $C_{15}H_8Br_2O_2$ requires C, 47·4; H, 2·1; Br, 42·1%). A small strongly adsorbed orange-brown band was not examined.

1 *Amino*-2-*methyl*-4-*toluene*-p-*sulphonamidoanthraquinone.*—This crystallised from ethanol in violet needles with a metallic reflex, m. p. 282—283° (Found: C, 65·0; H, 4·5; N, 6·9. Calc. for $C_{20}H_{18}N_2O_4S$: C, 65·05; H, 4·4; N, 6·9%). Ruggli and Merz [6] give m. p. 271—272°.

[5] Nursten and Bradley, *J.*, 1953, 924.
[6] Ruggli and Merz, *Helv. Chim. Acta*, 1929, **12**, 71.

2-*Methyl*-1,4-*ditoluene*-p-*sulphonamidoanthraquinone*.—The ditoluene-*p*-sulphonamido-derivative crystallised from ethanol in golden-yellow needles, m. p. 207° (Found: C, 62·1; H, 4·4; N, 5·2. Calc. for $C_{29}H_{24}N_2O_6S_2$: C, 62·15; H, 4·3; N, 5·0%). Ruggli and Merz [6] prepared this compound from 1,4-dichloro-2-methylanthraquinone and gave m. p. 204—205°.

1,4-*Diamino-2-methylanthraquinone*.—Hydrolysis [6] of the above mono- and di-toluene-*p*-sulphonamido-derivatives gave the diamine, which crystallised from benzene in violet needles, m. p. 247—248° (Found: C, 71·6; H, 4·6; N, 11·0. Calc. for $C_{15}H_{12}N_2O_2$: C, 71·4; H, 4·7; N, 11·1%).

N-*Substituted* 1-*Amino-2-methylanthraquinones*.—2-Methyl-1-nitroanthraquinone (1 g.) was heated with the appropriate ethanolic amine (15 ml.) at 130—140° in a sealed tube for 2 hr. (24 hr. in the case of the isopropyl analogue), or the nitro-compound was refluxed with the appropriate amine for 5—8 hr., the latter method being denoted " r " below. The products were purified by chromatography. Thus prepared were the 1-alkylamino-derivatives of 2-methylanthraquinone, where alkyl was: *methyl*, dark red needles (from ethanol) (this solvent was used in other cases unless stated otherwise), m. p. 112—113° (Found: C, 76·2; H, 5·05; N, 6·0. $C_{16}H_{13}NO_2$ requires C, 76·5; H, 5·2; N, 5·75%), *ethyl*, dark purple needles with a bronze reflex, m. p. 124—125° (Found: C, 76·8; H, 5·6; N, 5·3. $C_{17}H_{15}NO_2$ requires C, 77·0; H, 5·65; N, 5·3%), *n-propyl*, dark purple needles, m. p. 102° (Found: C, 77·15; H, 6·0; N, 5·1. $C_{18}H_{17}NO_2$ requires C, 77·45; H, 6·1; N, 5·0%), *isopropyl*, deep red needles, m. p. 133° (Found: C, 77·4; H, 6·0; N, 5·0%), *n-butyl*, dark purple needles, m. p. 86—87° (Found: C, 77·5; H, 6·4; N, 4·6. $C_{19}H_{19}NO_2$ requires C, 77·8; H, 6·5; N, 4·8%), *isobutyl*, purplish-brown needles with a green reflex, m. p. 109° (Found: C, 77·85; H, 6·6; N, 5·0%), *n-pentyl*, reddish-brown prisms with a metallic reflex, m. p. 105—106° (Found: C, 78·1; H, 6·7; N, 4·5. $C_{20}H_{21}NO_2$ requires C, 78·15; H, 6·65; N, 4·6%), *n-hexyl*, dark purple needles with a green reflex, m. p. 99—100° (Found: C, 87·3; H, 7·25; N, 4·3. $C_{21}H_{23}NO_2$ requires C, 78·5; H, 7·15; N, 4·35%), and 2′-*hydroxyethyl*, reddish-brown needles with a metallic reflex, m. p. 141—142° (Found: C, 72·5; H, 5·4; N, 4·9. $C_{17}H_{15}NO_3$ requires C, 72·6; H, 5·3; N, 5·0%). The *cyclohexylamino*- (r), dark red needles, m. p. 108—109° (Found: C, 78·8; H, 6·5; N, 4·4. $C_{21}H_{21}NO_2$ requires C, 79·0; H, 6·5; N, 4·3%), *benzylamino*-, brownish-red needles, m. p. 126—127° (Found: C, 80·95; H, 5·3; N, 4·2. $C_{22}H_{17}NO_2$ requires C, 80·75; H, 5·2; N, 4·3%), and *anilino-derivatives* (r), purple needles with a metallic reflex (from benzene), m. p. 230° (Found: C, 80·4; H, 4·7; N, 4·6. $C_{21}H_{15}NO_2$ requires C, 80·6; H, 4·8; N, 4·5%), were also obtained.

1-2′-Hydroxyethylamino-2-methylanthraquinone was best prepared by heating 1-bromo-2-methylanthraquinone (1·25 g.) with monoethanolamine (7 ml.) and ethanol (7 ml.) in a sealed tube at 125—130° for 3 hr.

1-*Methylaminoanthraquinone*.—(*a*) 1-Chloroanthraquinone (1 g.) was heated with 33% ethanolic methylamine solution (15 ml.) at 130—140° in a sealed tube for 2 hr. Orange-red needles (0·47 g.) were deposited on cooling, and a further amount (0·3 g.) was derived by adding the filtrate to water. Chromatography (benzene–alumina) gave red needles (from ethanol), m. p. 170°, of 1-methylaminoanthraquinone (Found: C, 75·8; H, 4·7; N, 5·8. Calc. for $C_{15}H_{11}NO_2$: C, 76·0; H, 4·65; N, 5·9%).

(*b*) Sodium anthraquinone-1-sulphonate (1 g.) was heated with 33% aqueous methylamine (15 ml.) at 130—140° in a sealed tube for 2 hr. The pink reaction mass was warmed with 5% aqueous sodium hydroxide, and the red solid collected; acidification of the filtrate gave the sulphonic acid (0·7 g.). The red solid was chromatographed as above, to give only 0·2 g. of 1-methylaminoanthraquinone, m. p. and mixed m. p. 169—170°.

Other 1-*Alkylaminoanthraquinones*.—These were prepared by method (*a*) above, from the appropriate ethanolic alkylamine, and purified by chromatography (benzene–alumina): 1-*ethylamino*- (0·65 g.), red needles (from ethanol; this solvent was used in similar cases), m. p. 124—125° (Found: C, 76·3; H, 5·15; N, 5·3. $C_{16}H_{13}NO_2$ requires C, 76·3; H, 5·2; N, 5·55%), 1-*n-propylamino*- (0·64 g.), red needles, m. p. 152° (Found: C, 76·7; H, 5·6; N, 5·1. $C_{17}H_{15}NO_2$ requires C, 77·0; H, 5·65; N, 5·3%), 1-*n-butylamino*- (0·83 g.), red prismatic needles, m. p. 81—82° (Found: C, 77·4; H, 6·0; N, 5·3. $C_{18}H_{17}NO_2$ requires C, 77·4; H, 6·1; N, 5·05%), 1-*isobutylamino*- (0·8 g.), red needles, m. p. 135—136° (Found: C, 77·2; H, 6·0; N, 5·0%), and 1-*n-pentylamino-anthraquinone* (0·92 g.), dark red needles, m. p. 78—79° (Found: C, 77·9; H, 6·3; N, 4·7. $C_{19}H_{19}NO_2$ requires C, 77·9; H, 6·5; N, 4·75%).

1-*n-Hexylaminoanthraquinone* (0·53 g.), red prismatic needles, m. p. 82—83° (Found: C, 78·2; H, 6·5; N, 4·7. $C_{20}H_{21}NO_2$ requires C, 78·1; H, 6·85; N, 4·55%), was prepared by

refluxing 1-chloroanthraquinone (1 g.) with n-hexylamine (10 ml.) for 6 hr., adding the whole to water, and collecting the solid, which was chromatographed. Similarly prepared from cyclohexylamine (10 ml.) was 1-*cyclohexylaminoanthraquinone* (1·05 g.), red needles, m. p. 108—109° (Found: C, 78·5; H, 6·1; N, 4·7. $C_{20}H_{19}NO_2$ requires C, 78·7; H, 6·2; N, 4·6%). Refluxing 1-chloroanthraquinone (1 g.) with aniline (10 ml.) for 24 hr. gave, after chromatography, 1-chloroanthraquinone (0·07 g.), m. p. 161°, a strongly adsorbed small royal-blue band, and a main reddish-violet band which afforded red plates (0·9 g.), m. p. 148°, of 1-anilinoanthraquinone (Found: C, 80·2; H, 4·3; N, 4·6. Calc. for $C_{20}H_{13}NO_2$: C, 80·3; H, 4·3; N, 4·7%). Ullmann and Fodor [7] prepared this compound, m. p. 147—148°, by refluxing 1-chloroanthraquinone and aniline in presence of cupric and potassium acetates.

1-*Amino*-2-*methyl*-4-*methylaminoanthraquinone*.—(*a*) 1-Amino-4-bromo-2-methylanthraquinone (1 g.), 33% ethanolic methylamine (10 ml.), anhydrous sodium acetate (1 g.), and cupric acetate (0·1 g.) were heated at 130—140° in a sealed tube for 3 hr.; addition to water gave a purple solid, which on chromatography (toluene–alumina) yielded a main intense purple zone; this was extracted with ethanol, giving a solid, that crystallised from ethanol in violet needles with a bronze reflex (0·45 g.), m. p. 234°, of the 4-*methylamino-derivative* (Found: C, 71·9; H, 5·4; N, 10·7. $C_{16}H_{14}N_2O_2$ requires C, 72·2; H, 5·25; N, 10·5%); a lower orange zone yielded 1-amino-2-methylanthraquinone (0·15 g.), m. p. and mixed m. p. 204°.

(*b*) In absence of cupric acetate, but otherwise as above, the derived products were chromatographed (toluene–alumina), giving orange-red, yellow, blue, and a strongly adsorbed violet band, in that order. The orange-red band gave 1-amino-2-methylanthraquinone (0·25 g.), m. p. 204°; the blue zone yielded the above methylamino-derivative (0·17 g.), m. p. 234°, and the violet band afforded a trace of product which separated from pyridine in dark plates with a green reflex (0·01 g.), m. p. 245°, probably mainly 1,4-diamino-2-methylanthraquinone. The yellow band was extracted with ethanol and gave an orange solution with a strong green fluorescence, yielding copper-coloured needles (0·1 g.), m. p. 194—195° (Found: C, 78·9; H, 5·1; N, 9·6. $C_{19}H_{16}N_2O$ requires C, 79·2; H, 5·55; N, 9·7%), which had lost oxygen.

(*c*) In absence of both sodium and cupric acetate, 1-amino-4-bromo-2-methylanthraquinone (1 g.) and 33% ethanolic methylamine (10 ml.) at 130—140° in a sealed tube for 3 hr. afforded unchanged bromo-compound (0·54 g.), m. p. 248° (decomp.), and 1-amino-2-methyl-4-methylaminoanthraquinone (0·2 g.), m. p. 234°.

1-*Amino*-4-*ethylamino*-2-*methylanthraquinone*.—(i) Reaction as in (*a*) above, with ethylamine, gave 1-amino-2-methylanthraquinone (0·25 g.) and 1-*amino*-4-*ethylamino*-2-*methylanthraquinone* (0·3 g.), violet needles (from ethanol), m. p. 235° (Found: C, 72·7; H, 5·8; N, 9·7. $C_{17}H_{16}N_2O_2$ requires C, 72·9; H, 5·7; N, 10·0%).

(ii) Reaction as in (*b*) above gave the same two products (0·2 g. each) and a yellowish-brown solid (0·02 g.), m. p. 153°, giving a strong green fluorescence in toluene.

(iii) 1-Amino-4-bromo-2-methylanthraquinone (1 g.) and 33% ethanolic ethylamine (10 ml.), without an additive, yielded unchanged bromo-compound (0·5 g.), m. p. 248° (decomp.), and the 4-ethylamino-derivative (0·25 g.), m. p. 235°.

1-*Amino*-2-*methyl*-4-*n-propylaminoanthraquinone*.—(*a*) n-Propylamine (5 ml.) and the 4-bromo-compound (1 g.) in ethanol (5 ml.) afforded, after chromatography (toluene–alumina) of the derived products, 1-amino-2-methylanthraquinone (0·35 g.) and the 4-*n-propylamino-compound* (0·2 g.), violet needles with a bronze reflex (from ethanol), m. p. 230° (Found: C, 73·1; H, 6·05; N, 9·4. $C_{18}H_{18}N_2O_2$ requires C, 73·45; H, 6·05; N, 9·5%).

Method (*b*) (cf. above) gave two products (0·3 g. and 0·14 g., respectively), and a trace of yellow solid (0·02 g.), m. p. 140°, giving a strong green fluorescence in toluene.

Method (*c*) (cf. above) afforded unchanged bromo-derivative (0·5 g.) and the 4-n-propylamino-compound (0·3 g.).

1-*Amino*-4-*n-butylamino*-2-*methylanthraquinone*.—Method (*a*) (cf. above) gave 1-amino-2-methylanthraquinone (0·6 g.) and, from a royal-blue alumina band, the 4-*n-butylamino-derivative* (0·1 g.), which crystallised from ethanol in violet-blue needles, m. p. 198—199° (Found: C, 73·8; H, 6·1; N, 9·0. $C_{19}H_{20}N_2O_2$ requires C, 74·0; H, 6·25; N, 9·05%).

Method (*b*) gave the same two products (0·3 g. each) and a middle greenish-yellow band yielding golden-yellow needles (from ethanol) (0·05 g.), m. p. 140°, of an unidentified *substance* (Found: C, 80·1; H, 6·0; N, 7·95%).

[7] Ullmann and Fodor, *Annalen*, 1911, **380**, 317.

Method (*c*) (cf. above) gave unchanged bromo-compound (0·45 g.) and the 4-n-butylamino-derivative (0·35 g.).

1-*Amino*-4-*isobutylamino*-2-*methylanthraquinone*.—Method (*c*) only was used in this case. 1-Amino-4-bromo-2-methylanthraquinone (1 g.), isobutylamine (5 ml.), and ethanol (5 ml.) at 130—140° in a sealed tube for 3 hr. gave unchanged bromo-compound (0·6 g.) and the 4-*isobutylamino-derivative* (0·25 g.), blue needles (from ethanol), m. p. 260° (Found: C, 73·8; H, 6·3; N, 9·1%):

1-*Amino*-2-*methyl*-4-*n-pentylaminoanthraquinone*.—Methods (*b*) and (*c*) were examined for the n-pentyl-, n-hexyl-, and n-octyl-amino-analogues. Method (*b*) yielded 1-amino-2-methylanthraquinone (0·3 g.), a substance which crystallised from ethanol in golden-yellow needles (0·1 g.), m. p. 110° (Found: C, 79·1; H, 6·8; N, 8·5%), and 1-*amino*-2-*methyl*-4-*n-pentylaminoanthraquinone* (0·3 g.), which crystallised from ethanol in bluish-violet needles, m. p. 180° (Found: C, 74·6; H, 6·9; N, 8·5. $C_{20}H_{22}N_2O_2$ requires C, 74·5; H, 6·8; N, 8·7%).

Method (*c*) gave the bromo-compound (0·35 g.) and the 4-n-pentylamino-derivative (0·4 g.).

1-*Amino*-2-*methyl*-4-*n-hexylaminoanthraquinone*.—(*b*) The bromo-compound (1 g.), n-hexylamine (10 ml.), and sodium acetate (1 g.) were refluxed for 12 hr.; the resulting product was chromatographed (toluene–alumina), giving 1-amino-2-methylanthraquinone (0·3 g.), a yellow band giving a yellowish-brown amorphous product (0·04 g.), m. p. 202°, and a strongly adsorbed blue band affording the 4-*n-hexylamino-derivative* (0·3 g.), which crystallised from ethanol in violet prisms with a metallic reflex, m. p. 139—140° (Found: C, 75·1; H, 7·0; N, 8·4. $C_{21}H_{24}N_2O_2$ requires C, 75·0; H, 6·85; N, 8·3%).

Method (*c*) gave the bromo-compound (0·32 g.) and the 4-n-hexylamino-derivative (0·45 g.).

1-*Amino*-2-*methyl*-4-*n-octylaminoanthraquinone*.—(*b*) Refluxing as above gave 1-amino-2-methylanthraquinone (0·28 g.), a small orange-yellow band yielding an orange-yellow substance (0·02 g.), m. p. 90° (Found: C, 78·9; H, 7·4; N, 6·75%), and a strongly adsorbed blue band giving 1-*amino*-2-*methyl*-4-*n-octylaminoanthraquinone* (0·25 g.), which crystallised from ethanol in blue needles, m. p. 134° (Found: C, 75·5; H, 7·5; N, 7·6. $C_{23}H_{28}N_2O_2$ requires C, 75·8; H, 7·7; N, 7·7%).

Method (*c*) led to a violent reaction, and after 12 hours' refluxing the product yielded unchanged bromo-derivative (0·2 g.) and the 4-n-octylamino-compound (0·6 g.), m. p. and mixed m. p. 134°.

1-*Amino*-4-2′-*ethylhexylamino*-2-*methylanthraquinone*.—In this case, only method (*c*) was used. Refluxing the bromo-derivative (1 g.) with 2-ethylhexylamine (10 ml.) for 12 hr. afforded unchanged bromo-compound (0·2 g.) and the 4-2′-*ethylhexylamino-derivative* (0·66 g.), blue needles (from ethanol), m. p. 95° (Found: C, 75·6; H, 7·75; N, 7·6. $C_{23}H_{28}N_2O_2$ requires C, 75·8; H, 7·7; N, 7·7%).

1-*Amino*-4-*cyclohexylamino*-2-*methylanthraquinone*.—Refluxing [method (*c*)] gave the bromo-compound (0·25 g.) and the 4-*cyclohexylamino-derivative* (0·62 g.), blue needles with a bronze reflux (from ethanol), m. p. 180° (Found: C, 75·1; H, 6·6; N, 8·5. $C_{21}H_{22}N_2O_2$ requires C, 75·4; H, 6·6; N, 8·4%).

The authors thank the British Silk Dyeing Co., and Messrs. Hickson and Welch, Ltd., for awards of Scholarships (G. D. W.), also Yorkshire Dyeware and Chemical Co., Ltd., for gifts of chemicals.

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[*Received, March 2nd,* 1962.]