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 The nitro-group in 2-methyl-1-nitroanthraquinone has been replaced by alkylamino-groups, and the derived products have been compared with the 1-alkylamino-anthraquinone analogues.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

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[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%).

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