231. *New Intermediates and Dyes. Part VIII.* 1,4-Disubstituted Derivatives of 2-Butylanthraquinone: Dyes for Cellulose Acetate Rayon, Nylon, and Terylene.*

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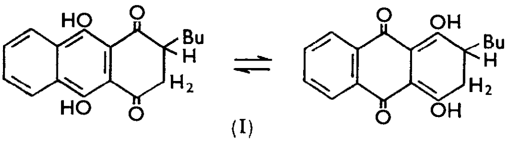
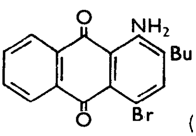
The orientation of 2-butyl-1,4-dihydroxyanthraquinone (2-butylquinizarin) was established by conversion into the 1,4-diamino-analogue.

A series of 1-amino-4-alkylamino- and -4-arylamino-2-butylanthraquinones was prepared, and the effects of the n-butyl group and of the 4-substituent on the dyeing properties on cellulose acetate rayon, Nylon, and Terylene were examined. Strong and bright dyeings were obtained from 1-amino-4-butylamino-, -4-methoxyalkylamino-, and -4-*p*-hydroxyethylanilino-2-butylanthraquinone.

THE orientated 1,4-diamino-2-butylanthraquinone[1] was boiled with sodium dithionite in aqueous-alcoholic sodium hydroxide, and the resulting product heated with sulphuric acid at 130—140° to give 2-butylquinizarin, m. p. 125°. According to Marschalk and his co-workers,[2] the latter was obtained on treatment of leucoquinizarin with butyraldehyde under nitrogen, followed by aeration, but no proof of orientation was recorded. On repeating this experiment, we obtained orange prisms, m. p. 125°, identical with the above, in excellent yield. Chromatographic procedures showed its homogeneity, and no unchanged quinizarin was isolated. We also converted 1,4-diaminoanthraquinone into 2-butylquinizarin by a similar procedure, the amino-groups being replaced by hydroxyl in the presence of alkaline dithionite. In both cases, the intermediate (I) was probably formed:



(I)



(II)

The 2-butylquinizarin obtained from quinizarin was also partly converted into the orientated 1,4-diamino-2-butylanthraquinone; this was achieved by heating it with aqueous ammonia (*d* 0·88) at 140—150° in a sealed tube, and the resulting product was chromatographed to yield the above diamine and considerable amounts of a monoamino-monohydroxy-2-butylanthraquinone.

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* Part VII, *J.*, 1959, 3928.

[1] Part VI, *J.*, 1958, 3497.

[2] Marschalk, Koenig, and Ouroussoff, *Bull. Soc. chim. France*, 1936, 1545.

Replacement of α-halogeno-groups by amino-groups in anthraquinone derivatives (Ullmann and Bincer [3]) affords a valuable method of preparing intermediates and dyes. No substitution of the amino-group occurred when 1-amino-2-butylanthraquinone was heated with excess of alcoholic methylamine in a sealed tube at 125—130° for 3 hours. The principal product of interaction of 1-amino-4-bromo-2-butylanthraquinone (II) and alcoholic methylamine at 125°, in presence of anhydrous sodium acetate and copper acetate, was the intensely violet 1-amino-2-butyl-4-methylaminoanthraquinone. Purification of this and allied products was effected by chromatography, which we consider is essential in this series of compounds. Similarly prepared in good yields were the deep violet 1-amino-4-ethylamino-, -4-propylamino-, -4-butylamino-, and -4-pentylamino-2-butylanthraquinone. The deep violet 4-hexylamino-analogue was obtained by refluxing the bromo-compound (II) with hexylamine in presence of sodium and copper acetates and a trace of copper bronze. More drastic conditions, *viz.*, 150—160° for 10—20 hours, were required to replace the bromo-group in compound (II) when preparing the deep violet 1-amino-2-butyl-4-isopropylamino- and -4-s-butylamino-anthraquinone, both being obtained in only low yield; these derivatives gave strongly adsorbed bright blue bands on the alumina column, and in both cases there was a lower bluish-red zone, which afforded 1-amino-2-butylanthraquinone: in addition, in the case of the isopropyl derivative, a little 1,4-diamino-2-butylanthraquinone was isolated, probably owing to some decomposition of isopropylamine.

Elimination of bromine in the anthraquinone series was reported by Ullmann and Minajeff,[4] who heated 4-chloro-1-methylanthraquinone with potassium acetate and copper in nitrobenzene, and isolated 1-methylanthraquinone, and by Bayer,[5] who recorded a similar elimination of both bromine atoms in 2-acetamido-1,3-dibromoanthraquinone.

1-Amino-2-butyl-4-isobutylaminoanthraquinone was prepared by the usual method, at 150—155°, but attempts to introduce the t-butylamino-group failed.

By a similar method to that used for the hexylamino-analogue, 1-amino-2-butyl-4-2′-ethylhexylaminoanthraquinone was prepared, but interaction of 1-amino-4-bromo-2-butylanthraquinone and 2,2-difluoro- and 2,2,2-trifluoro-ethylamine gave only traces of the required substituted derivative, bromine being eliminated and 1-amino-2-butylanthraquinone isolated.

On reaction with hydroxyalkylamines, *e.g.*, monoethanolamine and 1-aminopropan-2-ol, the bromo-derivative (II), at 120—125° in a sealed tube, afforded in both cases small amounts of 1,4-diamino-2-butylanthraquinone, separated by chromatography from the main products, *viz.*, the dark violet 1-amino-2-butyl-4-2′-hydroxyethylamino- and -4-2′-hydroxypropylamino-butylanthraquinone. Some decomposition of the hydroxyalkylamine was evident, and a similar side reaction was noted [1] in the reaction of ethanolamine with 2-butyl-1-nitroanthraquinone. The appropriate methoxyalkylamines similarly afforded the deep violet 1-amino-2-butyl-4-2′-methoxyethylamino- and -4-3′-ethoxypropylamino-anthraquinone. 1-Amino-2-butyl-4-cyclohexylaminoanthraquinone was prepared in a sealed tube, but the refluxing procedure, with the appropriate amine, gave the deep bluish-red 1-amino-4-benzylamino-, the violet -4-anilino-, and -4-*o*-, -*m*-, and -*p*-toluidino-derivatives of 2-butylanthraquinone. Similar reaction of the bromo-compound (II) with 4-aminophenethyl alcohol, but in pentyl alcohol, yielded the dark violet 1-amino-2-butyl-4-*p*-2′-hydroxyethylanilinoanthraquinone; however, preparation of the deep violet *o*-2′-hydroxyethylanilino-analogue required reaction at 130—140° for 8 hr. in a sealed tube.

In general, introducing the butyl group into anthraquinonoid dyes for cellulose acetate rayon and Nylon reduced the rate of dyeing, thus producing somewhat weaker shades; on Terylene, differences in shade were negligible. The butyl group had little effect on

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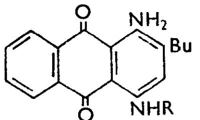
[3] Ullmann and Bincer, *Ber.*, 1916, **49**, 747.
[4] Ullmann and Minajeff, *Ber.*, 1912, **45**, 687.
[5] Bayer, B.P. 261,270, 275,299.

the tone of the dyeings, apart from a slight bathochromic effect in certain cases of the dyeing of Nylon. Fastness to sublimation, light, and burnt-gas fumes were similar to those recorded for analogous derivatives not containing the butyl group, but this group led to better washing-fastness on all these fibres.

The influence on the dyeing properties with variation of the radical R in the series (III) is summarised as follows:

R = Alkyl: dyeings were weaker than those of the 1,4-diamino-2-butyl derivative, but much bluer; the 4-butylamino-derivative gave the strongest and brightest colour of the series on cellulose acetate rayon, Nylon, and Terylene; branched-chain alkylamino-compounds afforded weak shades.



(III)

R = Hydroxyalkyl: increased dyeing power was shown on all three fibres by introduction of the hydroxyl group, but the resulting blue shades were redder than those given by the alkylamino-analogues.

R = Methoxyalkyl: shades on all three fibres were stronger, brighter, and redder than those derived from the 4-alkylamino- or 4-hydroxyalkylamino-compounds, and had excellent fastness to light.

R = Cyclohexyl and benzyl: on cellulose acetate rayon and Nylon, weak violet dyeings resulted, and on Terylene a blue of moderate strength; the benzylamino-derivative gave bluer shades than the cyclohexylamino-compound.

R = Aryl: in general, dyeings were of a greener tone than those of all the above derivatives, but affinity was lower.

R = Hydroxyalkylphenyl: the affinity of the dye was greatly increased for cellulose acetate and Nylon at ordinary temperatures, and dyeings had good all-round fastness, especially to light and washing.

In the series (III), R is bathochromic in the order, *p*-hydroxyalkylphenyl = *p*-tolyl > phenyl = *m*-tolyl > *o*-tolyl > alkyl > hydroxyalkyl > methoxyalkyl > cyclohexyl > benzyl > H; the affinity of the dyes was methoxyalkyl > hydroxyalkyl > H = hydroxyalkylphenyl > n-alkyl > isoalkyl > benzyl > cyclohexyl = phenyl = tolyl.

EXPERIMENTAL

2-*Butyl*-1,4-*dihydroxyanthraquinone*.—(*a*) (cf. ref. 2) Quinizarin (10 g.) was reduced to the leuco-compound by sodium dithionite (20 g.) and 1·5% aqueous sodium hydroxide (800 ml.), and the mixture was heated with butyraldehyde (6·5 g.) at 40—45° under nitrogen; aeration gave a solid (11·3 g., 91·6%), m. p. 118—120°. Chromatography in benzene on alumina gave only orange needles (from benzene), m. p. 125° (Found: C, 72·8; H, 5·45. Calc. for $C_{18}H_{16}O_4$: C, 73·0; H, 5·4%). The use of 1,4-diaminoanthraquinone in place of quinizarin in the above experiment also yielded 2-butylquinizarin, in 81% yield.

(*b*) 1,4-Diamino-2-butylanthraquinone (0·6 g.; from 1-amino-4-bromo-2-butylanthraquinone) was ground with ethanol (15 ml.) and added to a boiling solution of sodium dithionite (10 g.) in 15% aqueous sodium hydroxide (120 ml.). After 1 hr., the resulting dark brown solid was collected, washed, dried at 100°, and heated with sulphuric acid (5 ml.) at 130—140° for 4 min., and the mixture was then added to water (100 ml.); the resulting solid was collected, washed, dried at 100°, and extracted with boiling benzene, to yield 2-butylquinizarin (0·1 g.), m. p. and mixed m. p. 125°.

Orientation of 2-*Butylquinizarin*.—2-Butylquinizarin (1 g.), prepared by method (*a*), was heated with aqueous ammonia (*d* 0·88; 6 ml.) and sodium dithionite (0·25 g.) in a sealed tube at 140—150° for 8 hr. Aeration of the resulting aqueous suspension for 1 hr. gave a violet solid. This was extracted with warm 5% aqueous sodium hydroxide, and the insoluble solid was collected (0·8 g.; m. p. 125—130°). Dissolution in toluene, followed by chromatography, gave three principal zones: (i) a bluish-violet zone which on extraction with ethanol afforded dark violet needles with a metallic lustre (0·1 g.), m. p. 210—211° (Found: C, 73·4; H, 5·8; N, 9·1. Calc. for $C_{18}H_{18}O_2N_2$: C, 73·5; H, 6·2; N, 9·5%), not depressed on admixture with 1,4-diamino-2-butylanthraquinone, m. p. 211—212°; more strongly adsorbed zones were (ii) a reddish-violet zone, yielding purple prisms (from ethanol), (0·14 g.), m. p. 142—144° (Found: C, 72·8; N, 5·95; N, 4·1. $C_{18}H_{17}O_3N$ requires C, 73·2; H, 5·8; N, 4·7%), and (iii) a deep purple zone, giving a dark violet powder (0·2 g.), m. p. 204—210° (Found: C, 70·2; H, 5·7; N, 4·6%), of undetermined constitution. It is probable that the product from band (ii) was a *monoamino-2-butylmonohydroxyanthraquinone.*

Replacement of Bromine in 1-Amino-4-bromo-2-butylanthraquinone.—*1-Amino-2-butyl-4-methylaminoanthraquinone.* Pure 1-amino-4-bromo-2-butylanthraquinone (II), m. p. 151—152°, was used for this and succeeding experiments. The bromo-derivative (1 g.), 33% alcoholic methylamine (20 ml.), fused sodium acetate (1 g.), and copper acetate (0·1 g.) were heated at 120—125° for 3 hr. in a sealed tube, then added to warm water. The resulting dark violet solid was chromatographed in toluene (all chromatography was on alumina) to give a small bluish red zone, readily eluted, and a main intense blue zone which on extraction with ethanol afforded intensely violet needles with a metallic lustre (0·58 g., 67·5%), m. p. 181°, of *1-amino-2-butyl-4-methylaminoanthraquinone* (Found: C, 73·8; H, 6·55; N, 9·3. $C_{19}H_{20}O_2N_2$ requires C, 74·0; H, 6·5; N, 9·1%).

1-Amino-2-butyl-4-ethylaminoanthraquinone. The bromo-derivative (II) (1 g.) and 33% alcoholic ethylamine (16 ml.), as above, gave a main dark blue band and thence the *4-ethylamino-derivative,* which crystallised from ethanol in intensely violet needles with a bronze lustre (0·58 g., 64·4%), m. p. 161—162° (Found: C, 74·4; H, 6·75; N, 8·6. $C_{20}H_{22}O_2N_2$ requires C, 74·5; H, 6·9; N, 8·7%). Dyeings and fastness properties were similar to those derived from the methylamino-derivative, but the tones were somewhat bluer.

1-Amino-2-butyl-4-propylaminoanthraquinone. Compound (II) (1 g.), propylamine (10 ml.), ethanol (4 ml.), fused sodium acetate (1 g.), and copper acetate (0·1 g.), in a sealed tube at 130—135° for 4 hr., gave a violet solid (0·84 g.; m. p. 125—130°); the derived bright blue alumina zone gave, on extraction with ethanol, the *propylamino-derivative,* which crystallised from pyridine in dark violet needles with a bronze lustre (0·54 g., 57·5%), m. p. 160—161° (Found: C, 74·7; H, 7·1; N, 8·25. $C_{21}H_{24}O_2N_2$ requires C, 75·0; H, 7·2; N, 8·3%).

1-Amino-2-butyl-4-isopropylaminoanthraquinone. On proceeding as above for the propylamino-derivative, but with isopropylamine, much bromo-derivative (II) was recovered. After reaction at 150—160° for 10 hr., the resulting dark violet solid (0·92 g.) was chromatographed in toluene to yield a lower bluish-red zone which was eluted and gave dark red needles (0·18 g., 23%), m. p. 174—175° (Found: N, 4·85%; Br, nil), of 1-amino-2-butylanthraquinone (mixed m. p. 174—175°). A bright blue zone was extracted with ethanol, to give, from ethanol, dark violet needles with a metallic lustre (0·16 g., 17%), m. p. 143—144°, of *1-amino-2-butyl-4-isopropylaminoanthraquinone* (Found: C, 74·8; H, 7·05; N, 8·15. $C_{21}H_{24}O_2N_2$ requires C, 75·0; H, 7·2; N, 8·3%). In addition to the above two isolated compounds, a trace of 1,4-diamino-2-butylanthraquinone, m. p. and mixed m. p. 210—211°, was extracted by ethanol from an intermediate bluish-red zone.

1-Amino-2-butyl-4-butylaminoanthraquinone. By the method used for the methylamino-derivative, butylamine (8 ml.) and ethanol (5 ml.) with compound (II) (1 g.) gave a deep blue zone, and thence the *4-butylamino-derivative,* which crystallised from pyridine in deep violet needles with a bronze lustre (0·56 g., 57·2%), m. p. 114—115° (Found: C, 75·2; H, 7·3; N, 7·9. $C_{22}H_{26}O_2N_2$ requires C, 75·4; H, 7·5; N, 8·0%). This compound dyed cellulose acetate and Nylon brighter and stronger shades than other alkylamino-analogues, but similar blue shades were obtained on Terylene.

1-Amino-2-butyl-4-iso- and -s-butylaminoanthraquinone. After reaction of isobutylamine at 150—155° for 6 hr., the resulting solid was chromatographed to give a blue zone and thence, by ethanol, dark violet needles with a blue lustre (0·48 g., 49%), of the *4-isobutylamino-derivative* (Found: C, 75·5; H, 7·4; N, 8·0%); this had weak tinctorial power, but the shades were greener than those derived from the n-butyl analogue. The use of alcoholic s-butylamine at 150—160° for 20 hr., gave a dark violet solid (0·65 g.; m. p. 135—140°), which on chromatography in toluene yielded 1-amino-2-butylanthraquinone (0·24 g., 30·9%), m. p. and mixed m. p. 174—175°, and an upper blue zone which gave, from ethanol, clusters of violet needles (0·12 g., 12·5%), m. p. 127—128° with softening at 120° (Found: C, 75·3; H, 7·5; N, 7·9%), of *1-amino-2-butyl-4-s-butylaminoanthraquinone.*

1-Amino-2-butyl-4-pentylaminoanthraquinone. The bromo-compound (II) (1 g.) and pentylamine (10 ml.), as usual, at 125—130° for 4 hr., gave a solid (0·95 g.) and thence, by toluene, an intense blue zone, and deep violet needles (from ethanol), m. p. 112—113° (0·54 g., 51%) (Found: C, 76·0; H, 7·6; N, 7·6. $C_{23}H_{28}O_2N_2$ requires C, 75·8; H, 7·7; N, 7·7%). This *diamine* dyed cellulose acetate a reddish-blue, and Nylon and Terylene a blue shade.

1-*Amino*-2-*butyl*-4-*hexylaminoanthraquinone*. The bromo-derivative (II) (1 g.) was refluxed with hexylamine (25 ml.; b. p. 127—131°) in presence of anhydrous sodium acetate (1 g.), copper acetate (0·1 g.), and a trace of copper bronze. Removal of excess of hexylamine by distillation with steam, and purification of the resulting dark reddish-blue residue (0·95 g.; m. p. 114—120°), gave a bright blue zone and thence by ethanol dark violet needles (0·7 g., 66·2%), m. p. 106—107° (Found: C, 75·65; H, 7·8; N, 7·2. $C_{24}H_{30}O_2N_2$ requires C, 76·2; H, 8·0; N, 7·4%). Dyeing properties of this *quinone* were similar to those of the pentyl analogue.

1-*Amino*-2-*butyl*-4-2′-*ethylhexylaminoanthraquinone*. The refluxing method, with 2-ethylhexylamine (10 ml.; b. p. 165—168°), afforded a deep blue zone (eluted by toluene), and thence dark violet needles (from ethanol) with a slight bronze cast (0·52 g., 46%), m. p. 118—119° (Found: C, 76·6; H, 8·3; N, 6·8. $C_{26}H_{34}O_2N_2$ requires C, 76·85; H, 8·4; N, 6·9%). This *derivative* was only of weak tinctorial power.

1-*Amino*-2-*butyl*-4-2′-*hydroxyethylaminoanthraquinone*. The bromo-derivative (II) (1 g.), monoethanolamine (8 ml.), anhydrous sodium acetate (1 g.), copper acetate (0·1 g.), and ethanol (6 ml.) were heated at 120—125° for 2 hr. in a sealed tube. Adding the mixture to water gave a violet solid (0·86 g.; m. p. 145—150°), and a further amount (0·11 g.) was obtained from the filtrate by extraction with ether. Chromatography of the combined products in toluene gave a readily eluted orange-red zone, a small purple zone which gave a few violet crystals, m. p. 208—209°, probably of impure 1,4-diamine, and a main dark blue zone which afforded dark violet needles with a bronze lustre (from ethanol) (0·64 g., 65·3%), m. p. 178—179°, of the 2′-*hydroxyethylamino-derivative* (Found: C, 71·1; H, 6·4; N, 8·1. $C_{20}H_{22}O_3N_2$ requires C, 71·0; H, 6·5; N, 8·3%). This dyed cellulose acetate, Nylon, and Terylene similar blue shades to those obtained from the analogue free from the 2-butyl group.

1-*Amino*-2-*butyl*-4-2′-*hydroxypropylaminoanthraquinone*, prepared similarly, crystallised from ethanol in dark violet needles (0·52 g., 53%), m. p. 189—190° (Found: C, 71·7; H, 6·8; N, 8·05. $C_{21}H_{24}O_3N_2$ requires C, 71·6; H, 6·9; N, 7·95%), and had similar dyeing properties.

1-*Amino*-2-*butyl*-4-2′-*methoxyethylaminoanthraquinone*. The bromo-derivative (II) (1 g.) and 2-methoxyethylamine (8 g.), with sodium acetate (1 g.), copper acetate (0·1 g.), and ethanol (6 ml.) at 125—130° for 8 hr. in a sealed tube yielded a dark violet solid (0·94 g.) and thence deep violet needles with an intense bronze lustre (0·68 g., 69%), m. p. 128—129° (Found: C, 71·4; H, 6·8; N, 7·9. $C_{21}H_{24}O_3N_2$ requires C, 71·6; H, 6·9; N, 7·95%). This *methoxy-compound* dyed cellulose acetate a bright royal blue, and Nylon and Terylene a bright reddish-blue, of considerable tinctorial power.

1-*Amino*-2-*butyl*-4-3′-*methoxypropylaminoanthraquinone*. The use of 3-methoxypropylamine, as above, afforded long violet needles with a bronze lustre (from ethanol) (0·44 g., 43·2%), m. p. 113—114° (Found: C, 71·9; H, 7·0; N, 7·7. $C_{22}H_{26}O_3N_2$ requires C, 72·1; H, 7·1; N, 7·65%). The dyeings were slightly greener than those of the methoxyethylamino-analogue, but on all three fibres were strong and bright; fastness to washing was particularly good.

1-*Amino*-2-*butyl*-4-*cyclohexylaminoanthraquinone*. By the sealed tube method, as in the case of the methoxyethylamino-derivative above, cyclohexylamine (6 ml.) and the compound (II) (1 g.) gave a main deep blue zone (eluted by toluene) and thence dark violet needles with a bronze lustre (from ethanol) (0·76 g., 72·4%), m. p. 168°, of the *cyclohexylamino-derivative* (Found: C, 76·3; H, 7·4; N, 7·35. $C_{24}H_{28}O_2N_2$ requires C, 76·6; H, 7·5; N, 7·4%). This showed poor affinity for all three fibres, yielding weak violet shades.

1-*Amino*-4-*benzylamino*-2-*butylanthraquinone*. The bromo-derivative (II) (1 g.) was refluxed with benzylamine (14 ml.), anhydrous sodium acetate (1 g.), and copper acetate (0·1 g.) for 6 hr. Chromatography in toluene gave a clear blue zone, and thence deep bluish-violet needles (from alcohol) (0·21 g.; 19·6%), m. p. 173—174° (Found: C, 77·8; H, 6·3; N, 7·3. $C_{25}H_{24}O_2N_2$ requires C, 78·1; H, 6·3; N, 7·3%). All dyeings were much redder than those of the 4-alkylamino-analogues, and tinctorial power was only moderate.

Derivatives (III) *where* R = *aryl*. Aniline (15 ml.), sodium acetate (1 g.), and copper acetate (0·1 g.) were heated at 140° for 5 min. to remove moisture, and the bromo-derivative (II) (1 g.) was added. The mixture was heated (reflux) at 180—185° for 10 hr., then filtered and added to warm dilute aqueous hydrochloric acid. The resulting insoluble violet solid was collected, washed, and dried (1·0 g.; m. p. 150—155°); the usual procedure gave a violet-blue zone (eluted by toluene) and thence dark violet needles (from ethanol), which crystallised from pyridine in similar needles with a metallic lustre (0·66 g., 64·1%), m. p. 166° (Found:

C, 77·6; H, 6·05; N, 7·4. $C_{24}H_{22}O_2N_2$ requires C, 77·8; H, 6·0; N, 7·6%), of 1-*amino*-4-*anilino*-2-*butylanthraquinone*. Dyeings were somewhat weaker than the shades formed by the analogue free from the butyl group. Similarly prepared, the o-*toluidino-derivative* crystallised from pyridine in dark violet needles (0·56 g., 52·2%), m. p. 145° (Found: C, 77·9; H, 6·3; N, 7·25. $C_{25}H_{24}O_2N_2$ requires C, 78·1; H, 6·3; N, 7·3%); the 4-m-*toluidino-analogue* crystallised from pyridine in dark violet needles (0·74 g., 68·4%), m. p. 150° (Found: C, 78·1; H, 6·1; N, 7·3%), and the 4-p-*toluidino-derivative* gave dark violet needles (from ethanol) (0·72 g., 66·6%), m. p. 168—169° (Found: C, 77·9; H, 6·2; N, 7·2%). The rate of dyeing was very slow for all three toluidino-derivatives, the weak shades produced being greener than those derived from the anilino-derivative.

2-Aminophenethyl alcohol, b. p. 155—165°/4 mm. (3 g.), and the bromo-compound (II) (1 g.), with the usual procedure, at 130—140° in a sealed tube for 8 hr., afforded, after chromatography in *o*-dichlorobenzene, a principal bright blue zone, which yielded deep purple needles with a bronze lustre (from ethanol) (0·52 g., 45%), m. p. 65°, of 1-*amino*-2-*butyl*-4-o-2'-*hydroxyethylanilinoanthraquinone* (Found: C, 75·15; H, 6·5; N, 6·4. $C_{26}H_{26}O_3N_2$ requires C, 75·4; N, 6·3; N, 6·8%). Its low m. p. precluded its use as a dye for cellulose acetate and Nylon, but Terylene was dyed a blue shade.

The isomeric 4-p-2'-*hydroxyethylanilino-derivative* was obtained by refluxing 4-aminophenethyl alcohol (2 g.) and compound (II) (1 g.) in pentyl alcohol (12 ml.) in presence of sodium acetate (1 g.) and copper acetate (0·1 g.) and a trace of copper bronze for 8 hr.; chromatography in toluene gave an intense blue zone, extracted with alcohol; final crystallisation from pyridine yielded dark violet needles (0·5 g., 43·2%), m. p. 166—167° (Found: C, 75·1; H, 6·4; N, 6·8%). This compound dyes all three fibres a deep blue shade, and washing and light fastness properties were excellent.

The authors thank Dr. J. B. Dickey, Director, Tennessee Eastman Co., U.S.A., for gifts of chemicals, and Yorkshire Dyeware and Chemical Co., Ltd., for facilities for dyeing tests; the junior author thanks the Trustees of the Courtaulds' Scientific and Educational Trust Fund for a Scholarship.

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[*Received, October* 13*th*, 1959.]