Elimination of N-*Substituents from Derivatives of* 1-*Aminoanthraquinone.*

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The *N*-methyl, *N*-ethyl, *N*-*n*-butyl, *N*-*tert.*-butyl, *N*-benzyl, *N*-*p*-nitrobenzyl, and *N*-dimethyl derivatives of 1-aminoanthraquinone have been studied in regard to their behaviour towards oxidants, sulphuric acid, and alumina. Elimination of the *N*-substituent can occur in almost every case, the mechanism of the reaction depending on the group displaced.

In experiments on the preparation of *N*-alkyl derivatives of indanthrone Bradley and Leete (*J.*, 1951, 2138) found that 1-chloroanthraquinone and 2-methylaminoanthraquinone condensed to form 1 : 2′-dianthraquinonylamine, the methyl group being eliminated as formaldehyde. This demethylation has now been studied in greater detail. In the examples mentioned demethylation was favoured by the use of nitrobenzene as solvent and the addition of cupric acetate and an alkali such as potassium carbonate. The same authors also found that *NN*′-dimethylindanthrone was demethylated when its solution in *o*-dichlorobenzene was heated with alumina. The properties of several other *N*-derivatives of 1-aminoanthraquinone, including the ethyl, *n*-butyl, *tert.*-butyl, benzyl, *p*-nitrobenzyl, and dimethyl derivatives, have now been studied under a wider range of conditions.

In concentrated sulphuric acid the *tert.*-butyl derivative is easily decomposed, even in the cold, with formation of 1-aminoanthraquinone. No other member of the series shows this property which thus appears to depend on the tertiary character of the alkyl group.

Heating with alumina in *o*-dichlorobenzene caused elimination of the *N*-substituent in several instances, the relative extent (%) under comparable conditions being methyl (0), ethyl (0·3), *n*-butyl (0·9), *tert.*-butyl (70), benzyl (35). It is probable that alumina reacts with the bases converting them into 'onium salts in the first stage of the change.

A different order of elimination was found when the bases were heated with nitrobenzene or with nitrobenzene, cupric acetate, and potassium carbonate: the *tert.*-butyl derivative was then almost unaffected, whilst 1-benzylaminoanthraquinone readily gave 1-aminoanthraquinone and benzaldehyde, and 1-*p*-nitrobenzylaminoanthraquinone afforded 1-aminoanthraquinone and *p*-nitrobenzaldehyde somewhat less readily.

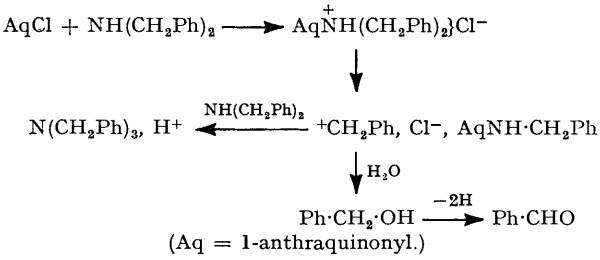
In further experiments it was shown that 1-benzylaminoanthraquinone was stable to boiling acetic acid or chlorobenzene, but benzaldehyde was formed at 240° to the extent of 4% in naphthalene and 15% in diphenyl. Heating in nitrobenzene at 205° formed 38% of benzaldehyde, and even heating *in vacuo* at 220° gave 13·5% of the same product. These experiments indicated that the benzyl group could be lost by oxidation and that 1-benzylaminoanthraquinone itself could furnish the necessary atoms of oxygen. The addition of another quinone (1-chloroanthraquinone) to a solution of 1-benzylaminoanthraquinone in nitrobenzene did not augment the yield of benzaldehyde, but an increase to 53—59% was observed when the nitrobenzene contained both 1(or 2)-chloroanthraquinone and cupric acetate. In the presence of toluene-*p*-sulphonic acid nitrobenzene did not oxidise 1-benzylaminoanthraquinone.

There appear to be three mechanisms by which 1-benzylaminoanthraquinone could yield benzaldehyde. Sachs and Kempk (*Ber.*, 1902, **35**, 1224) showed that *N*-benzyl-2 : 4-dinitroaniline and potassium permanganate yielded *N*-benzylidene-2 : 4-dinitroaniline, dehydrogenation having occurred. Other investigations point to the occurrence of α-oxidation of the *N*-substituent. Waters (*J.*, 1946, 827) found that certain *tert.*-amines were α-chlorinated by chlorine or *N*-chloroimides before dealkylation occurred. Leonard and Rekenstorf (*J. Amer. Chem. Soc.*, 1945, **67**, 49) observed that 2-diethylaminoethanol gave diethylamine and glycollic aldehyde with lead tetra-acetate, and considered that an α-hydrogen atom of the 2-hydroxyethyl group was replaced by acetoxy, that hydrolysis ensued, and that the resulting 1 : 2-dihydroxyethyldiethylamine decomposed to give the observed products. A somewhat similar conclusion was reached by Horner (*Angew. Chem.*,

1950, **62**, 359) who regarded the dealkylation of tertiary amines with benzoyl peroxide as passing through an *N*-α-benzoyloxyalkyldialkylamine. Finally, amine oxides have been regarded as intermediates in the dealkylation of amines by oxidation (Dodonov, *J. Gen. Chem. Russ.*, 1944, **14**, 960).

In the present instance the formation of benzaldehyde when 1-benzylaminoanthraquinone is heated *in vacuo*, where no second reactant is present, is likely to proceed by hydrogen transfer from the benzylamino- to the quinone group, a benzylideneaminoanthraquinol resulting. The hydrolysis of the imine requires the intervention of water and this should be available by elimination from the anthraquinol nucleus at the temperature employed. In agreement with fact dehydrogenation should be favoured by the use of nitrobenzene as solvent. Debenzylation occurred to a remarkably high degree (30%) when nitrobenzene was replaced by diphenyl ether. It is possible that in this instance an ether peroxide was the active dehydrogenating agent.

Conversion of 1-chloroanthraquinone into 1-dimethylamino- and 1-piperidino-anthraquinone by heating with the appropriate base proceeded normally, but when dibenzylamine, di-*n*-butylamine, or diethylamine was used the products were 1-benzylamino-, 1-*n*-butylamino-, and 1-ethylamino-anthraquinone respectively. In the reaction with dibenzylamine, benzaldehyde and tribenzylamine were formed as by-products, which suggests that the reactions concerned are:



Experimental

1-Benzylaminoanthraquinone.—In confirmation of Seer's work (*Monatsh.*, 1910, **31**, 371) 1-aminoanthraquinone reacts even with an excess of benzyl chloride to form the monobenzyl derivative. A more convenient preparation of this compound is to heat 1-chloroanthraquinone (54 g.) and benzylamine (100 g.) at 180° for 2 hr. 1-Benzylaminoanthraquinone dissolves in cold concentrated sulphuric acid, forming a greenish-yellow solution from which it is precipitated unchanged on the addition of water. The bluish-red solution in acetic anhydride changes to deep violet on the addition of boroacetic anhydride and heating. The derivative is more soluble in organic solvents, and less strongly adsorbed on alumina, than is 1-aminoanthraquinone.

Elimination of the benzyl group. (*a*) In a series of experiments 1-benzylaminoanthraquinone (2·5 g.) was heated with other reactants in an oil-bath, usually for 6 hr. The product was transferred to a 1-l. flask, benzene being used to collect the last traces, water (500 c.c.) was then added, and the product distilled in steam. The residue, consisting of 1-aminoanthraquinone and unchanged 1-benzylaminoanthraquinone, was dissolved in chlorobenzene and the proportion of the constituents determined after chromatography on alumina. 1-Benzylaminoanthraquinone passed through the column; 1-aminoanthraquinone was eluted by the use of acetone. A saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid was added to the steam-distillate which was then again distilled in steam. The crystalline residue of benzaldehyde 2 : 4-dinitrophenylhydrazone was collected, washed with light petroleum (b. p. 60—80°), dried, and weighed. The tabulated results were obtained; values in parentheses indicate the extent of debenzylation.

In the chlorobenzene and acetic acid experiments the reactants were heated under reflux; in all other experiments the oil-bath temperature was 240°. In each instance 20 c.c. of chlorobenzene, acetic acid, or nitrobenzene were used.

(*b*) 1-Benzylaminoanthraquinone (0·19 g.) was recovered unchanged after 0·2 g. had been kept for 48 hr. at the room temperature in 5 c.c. of concentrated sulphuric acid. At 110° sulphonation occurred.

(*c*) When heated under reflux with 4 g. of alumina ("B.D.H., for Chromatographic Adsorption") in 20 c.c. of *o*-dichlorobenzene, 1-benzylaminoanthraquinone (0·4 g.) gave 1-aminoanthraquinone (0·1 g.; m. p. 250—251°); 0·2 g. of 1-benzylaminoanthraquinone, m. p. 188—189°, was recovered.

Ref. no.	Other reactants	1-Aminoanthraquinone (g.) *	Benzaldehyde 2 : 4-dinitrophenylhydrazone (g.)
1	$Ph{\cdot}NO_2$	0·7 (39%)	0·88 (38%)
2	$Ph{\cdot}NO_2$, K_2CO_3 (2 g.)	0·56 (31%)	0·67 (29%)
3	$Ph{\cdot}NO_2$, $Cu(OAc)_2$ (1·5 g.)	0·47 (26%)	0·59 (26%)
4	$Ph{\cdot}NO_2$, $Cu(OAc)_2$ (1·5 g.), 1-chloroanthraquinone (2 g.)	None	1·32 (57%), 1·23 (53%)
5	$Ph{\cdot}NO_2$, 1-chloroanthraquinone (2 g.)	None	0·82 (36%), 0·88 (38%)
6	$Ph{\cdot}NO_2$, $Cu(OAc)_2$ (1·5 g.), 2-chloroanthraquinone (2 g.)	None	1·35 (59%)
7	$Ph{\cdot}NO_2$, p-$C_6H_4Me{\cdot}SO_3H$ (1 g.)	None	None
8	Naphthalene (12 g.)	Trace	0·01 (0·4%)
9	Diphenyl (10 g.)	—	0·34 (15%)
10	Diphenyl ether (20 g.)	0·55 (31%)	0·66 (29%)
11	PhCl	None	None
12	PhCl, 1-chloroanthraquinone (2 g.)	None	None
13	PhCl, $Cu(OAc)_2$ (1·5 g.), 1-chloroanthraquinone (2 g.)	None	None
14	$CH_3{\cdot}CO_2H$	None	None
15	$CH_3{\cdot}CO_2H$, $Cu(OAc)_2$ (1·5 g.)	Trace	0·01, 0·01 (0·4%)

* Where "None" occurs in this column, it is probable that 1-aminoanthraquinone was formed but condensed with 1- or 2-chloroanthraquinone to yield a dianthraquinonylamine.

1-p-*Nitrobenzylaminoanthraquinone*.—(*a*) 1-Aminoanthraquinone (6·5 g.) and *p*-nitrobenzyl chloride (5 g.), heated under reflux in trichlorobenzene (250 c.c.) for 4 hr., gave a deep red solution from which a tar separated after evaporation and cooling. Repeated treatment with acetic acid (charcoal) gave bright red needles (m. p. 258—259°; 0·3 g.) identical with the compound obtained more conveniently as follows. (*b*) An intimate mixture of *p*-nitrobenzyl bromide (9 g.) and the dry potassium derivative of 1-toluene-*p*-sulphonamidoanthraquinone (5 g.) was heated at 170°. A vigorous reaction ensued, a viscous, yellow liquid resulted, and after 5 min. addition to alcohol gave a yellow solid. Crystallisation from alcohol–acetone gave hexagonal rods (4 g.), m. p. 212—213° (Found: C, 66·0; H, 4·3; N, 5·3; S, 6·0. $C_{28}H_{20}O_6N_2S$ requires C, 65·7; H, 3·9; N, 5·5; S, 6·2%). 1-(N-p-*Nitrobenzyltoluene*-p-*sulphonamido*)*anthraquinone* dissolved in pyridine with a yellow colour, changed to wine-red on the addition of methanolic potassium hydroxide. Heating with acetic acid caused decomposition, and this was also noticed during the preparation of the compound if the stated time was exceeded. On being heated at 213° for 10 min. the pure compound became red and 1-p-*nitrobenzylaminoanthraquinone* was isolated from the product by chromatography on alumina from benzene.

A solution of 1-(*N*-*p*-nitrobenzyltoluene-*p*-sulphonamido)anthraquinone (2·8 g.) in concentrated sulphuric acid (20 c.c.) was kept at the room temperature for 15 min. and then added to water. After neutralisation with sodium carbonate the solid (2·1 g.) was collected. Crystallisation from chlorobenzene gave bright red needles, m. p. 261—262° (Found: C, 69·9; H, 3·5; N, 7·7. $C_{21}H_{14}O_4N_2$ requires C, 70·4; H, 3·9; N, 7·8%). 1-*p*-Nitrobenzylaminoanthraquinone is more strongly adsorbed on alumina than is 1-benzylaminoanthraquinone. It gives a deep violet colour with boroacetic anhydride in acetic anhydride. Like 1-benzylaminoanthraquinone the 1-*p*-nitrobenzyl analogue (2·87 g.) decomposes in nitrobenzene (20 c.c.) at 240° (oil-bath) during 6 hr. Isolated by the standard procedure the products were 1-aminoanthraquinone (0·28 g., 16%) and *p*-nitrobenzaldehyde 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 308—310°; 0·28 g., 10%); the percentages quoted indicate the extent of elimination of the *p*-nitrobenzyl group. 1-*p*-Nitrobenzylaminoanthraquinone was recovered unaltered after being heated (0·1 g.) with 10 c.c. of concentrated sulphuric acid at 120° for 6 hr.

2-p-*Nitrobenzylaminoanthraquinone*.—*p*-Nitrobenzyl chloride (3·5 g.) and the potassium salt of 2-toluene-*p*-sulphonamidoanthraquinone (Bradley and Leete, *J.*, 1951, 2137) (2 g.), heated for 30 min. at 190° and subsequently worked up as for the 1-derivative, gave buff-coloured leaflets (1·3 g.), m. p. 181—183° (Found: N, 5·3; S, 5·9. $C_{28}H_{20}O_6N_2S$ requires N, 5·5; S, 6·2%). 2-(N-p-*Nitrobenzyltoluene*-p-*sulphonamido*)*anthraquinone* forms an orange solution in pyridine, changed first to green, then to dull brown, on the addition of methanolic potassium hydroxide. A solution containing 0·5 g. in concentrated sulphuric acid (20 c.c.), heated on the steam-bath for 30 min., then cooled and added to water, gave 2-p-*nitrobenzylaminoanthra-*

quinone which crystallised from *o*-dichlorobenzene in orange needles, m. p. 255—256° (Found: C, 70·4; H, 4·1; N, 7·9. $C_{21}H_{14}O_4N_2$ requires C, 70·4; H, 3·9; N, 7·8%).

1-m-*Chlorobenzylaminoanthraquinone*.—1-Aminoanthraquinone (3 g.) was refluxed with *m*-chlorobenzyl chloride (5 g.) in *o*-dichlorobenzene (20 c.c.) for 6 hr. The product was mixed with benzene, the solution chromatographed on alumina, and the main red band eluted with benzene. Evaporation gave 1-m-*chlorobenzylaminoanthraquinone* which crystallised from chlorobenzene in red needles (2 g.), m. p. 209—211° (Found: C, 72·6; H, 4·0; N, 4·1; Cl, 10·2. $C_{21}H_{14}O_2NCl$ requires C, 72·5; H, 4·0; N, 4·0; Cl, 10·2%). *Ethyl*-N-*nitrosoaminoanthraquinone* resulted when finely powdered sodium nitrite (0·33 g.) was added to a stirred solution of 1-ethylaminoanthraquinone (1 g.) in acetic acid (12·5 c.c.) at 50°. The yellow precipitate, washed, dried, and purified by dissolution in boiling chlorobenzene, filtration, and cooling of the filtrate, gave crystals, m. p. 170—171° (Found: C, 68·4; H, 4·3; N, 10·3. $C_{16}H_{12}O_3N_2$ requires C, 68·5; H, 4·3; N, 10·0%).

Action of Light.—A solution of 1-*N*-nitrosoethylaminoanthraquinone (0·26 g.) in benzene (15 c.c.) was refluxed in bright sunlight for 2 hr. The colour changed from yellow to red. Chromatographed on alumina the cooled solution gave a bluish-red band which readily passed through the column. On the addition of light petroleum (b. p. 60—80°) to the eluate red needles (0·12 g.) separated, having m. p. 113—115°, not depressed by mixing with authentic 1-ethylaminoanthraquinone.

A similar decomposition occurred in benzene or in alcohol on exposure to sunlight at the room temperature. In the dark, even heating under reflux in alcohol for 3 hr. did not cause decomposition. However, the addition of benzoyl peroxide to the refluxing alcoholic solution caused rapid decomposition even in the absence of light.

Solutions of 1-*N*-nitrosomethylaminoanthraquinone in benzene or alcohol decomposed similarly on exposure to sunlight.

1-tert.-*Butylaminoanthraquinone*.—1-Chloroanthraquinone (4 g.) was heated with *tert.*-butylamine (16 c.c.) at 200° for 5 hr. The semi-solid product was dried in air and extracted with dilute ammonia, then with water, and finally it was crystallised from acetic acid. Deep red needles (3 g.), m. p. 132—133° (Found: C, 77·1; H, 6·2; N, 4·8. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1; N, 5·0%), separated. 1-tert.-*Butylaminoanthraquinone* is more soluble than 1-aminoanthraquinone in the common organic solvents; it is also less strongly absorbed on alumina. The bluish-red colour of the solution in acetic anhydride remains unaltered even on long heating with boroacetic anhydride.

Elimination of the tert.-*butyl group*. (*a*) A solution of 0·1 g. of 1-*tert.*-butylaminoanthraquinone in 10 c.c. of concentrated sulphuric acid was kept at the room temperature for 3 hr. and then added to water. After neutralisation with dilute ammonia the solid was collected, dried, and chromatographed from benzene on alumina. The main band was strongly adsorbed and on elution with acetone it gave 0·078 g. of 1-aminoanthraquinone, m. p. and mixed m. p. 249—250°. The yield corresponded to 98% dealkylation.

(*b*) 1-*tert.*-Butylaminoanthraquinone (0·5 g.), heated with alumina (4 g.) as described for 1-benzylaminoanthraquinone, gave 1-aminoanthraquinone (0·28 g.) and 1-*tert.*-butylaminoanthraquinone (0·15 g.).

In an unsuccessful attempt to prepare 1-*tert.*-butylaminoanthraquinone from 1-chloroanthraquinone and N-tert.-*butyltoluene*-p-*sulphonamide* the last was prepared from toluene-*p*-sulphonyl chloride (26 g.), *tert.*-butylamine (14 c.c.), and pyridine (70 c.c.). It crystallised from aqueous ethanol in colourless hexagonal rods (15·5 g.), m. p. 112—113° (Found: C, 58·0; H, 7·3; N, 6·4; S, 14·1. $C_{11}H_{17}O_2NS$ requires C, 58·1; H, 7·5; N, 6·2; S, 14·1%).

1-n-*Butylaminoanthraquinone*.—1-Chloroanthraquinone (4 g.), heated with *n*-butylamine (15 c.c.) at 180° for 3 hr., gave a solid which after extraction several times with dilute ammonia and then water was crystallised from acetic acid. Deep red needles (2 g.), m. p. 81—82° (Found: C, 77·8; H, 6·0; N, 4·9. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·0; N, 5·0%), were obtained. 1-n-*Butylaminoanthraquinone* is more soluble in organic solvents and less strongly adsorbed on alumina than 1-aminoanthraquinone. The bluish-red solution in acetic anhydride becomes dull purple on heating with boroacetic anhydride.

Elimination of the n-*butyl group*. (*a*) Heated in an oil-bath at 240° for 24 hr., 1-*n*-butylaminoanthraquinone (0·5 g.), cupric acetate (0·5 g.), anhydrous potassium carbonate (0·5 g.), and nitrobenzene (10 c.c.) gave unchanged 1-*n*-butylaminoanthraquinone (0·3 g.; m. p. 80°), and an unidentified yellow product after isolation and chromatography. 1-Aminoanthraquinone was absent.

(*b*) Heated with alumina as described for 1-benzylaminoanthraquinone, 1-*n*-butylamino-

anthraquinone (0·4 g.) gave 0·03 g. of 1-aminoanthraquinone (m. p. 245°); 0·3 g. of 1-*n*-butylaminoanthraquinone, m. p. 78—80°, was recovered. 1-Aminoanthraquinone could not be detected after 1-*n*-butylaminoanthraquinone (0·1 g.) had been kept in concentrated sulphuric acid at the room temperature for 6 hr.; 0·09 g. of the starting material, m. p. 78—80°, was recovered. There was no indication of dealkylation after heating of 0·5 g. with 20 c.c. of concentrated sulphuric acid at 110° for 5 hr.

1-*Ethylaminoanthraquinone. Elimination of the Ethyl Group.*—(*a*) Heated in an oil-bath at 240° for 24 hr., 1-ethylaminoanthraquinone (1 g.), cupric acetate (1 g.), anhydrous potassium carbonate (1 g.), and nitrobenzene (20 c.c.) gave 0·035 g. of 1-aminoanthraquinone, m. p. 250° (4% dealkylation).

(*b*) Heated with alumina as described for 1-benzylaminoanthraquinone, 1-ethylaminoanthraquinone (0·4 g.) gave 1-aminoanthraquinone (0·01 g.; m. p. 245—248°); 0·3 g. of 1-ethylaminoanthraquinone was recovered.

No trace of 1-aminoanthraquinone was found when 1-ethylaminoanthraquinone (0·1 g.) was kept in 10 c.c. of concentrated sulphuric acid for 24 hr. at the room temperature; 0·07 g. of the starting material was recovered. Only unchanged material (0·08 g.) was found on repetition of the experiment at 120° for 6 hr.

1-*Methylaminoanthraquinone.*—This compound was recovered unchanged after being heated with alumina in boiling chlorobenzene, or with concentrated sulphuric acid at 120° for 6 hr. Similarly, 1-dimethylaminoanthraquinone (0·09 g.) was recovered after heating of 0·1 g. in concentrated sulphuric acid (5 c.c.) at 90° for 8 hr.

Condensation of Dibenzylamine with 1-*Chloroanthraquinone.*—(a) *Formation of* 1-*benzylaminoanthraquinone.* 1-Chloroanthraquinone (2 g.), potassium acetate (1 g.), and dibenzylamine (10 c.c.) were heated in an oil-bath at 190° for 2 hr. When cool, the solid was collected and washed with methanol (yield, 1 g.; m. p. 187—189°, not depressed on mixing with authentic 1-benzylaminoanthraquinone). Crystallisation from acetic acid gave rosettes of bright red needles, m. p. 188—189° (Found: C, 80·7; H, 5·1; N, 4·4. Calc. for $C_{21}H_{15}O_2N$: C, 80·4; H, 4·8; N, 4·5%). The filtrate from the original reaction product was neutralised by the addition of hydrochloric acid, heated (charcoal), and filtered. The colourless crystals which separated, washed with hydrochloric acid and then dried, had m. p. 265—266°, not depressed by mixing with dibenzylamine hydrochloride, m. p. 266°, and depressed to 220° by benzylamine hydrochloride (Found: C, 71·5; H, 7·1; N, 5·8; Cl, 15·3. Calc. for $C_{14}H_{16}NCl$: C, 71·9; H, 6·8; N, 7·0; Cl, 15·2%).

(b) *Formation of tribenzylamine.* 1-Chloroanthraquinone (5 g.) and dibenzylamine (25 c.c.) were heated under reflux for 4 hr. The product was cooled and extracted with 200 c.c. of ether, and the extract was shaken with hydrochloric acid. A white precipitate formed and this was collected, washed with ether, and then extracted with 30 c.c. of pyridine. On the addition of water the extract gave a white solid (0·8 g.), m. p. 89—90°, not depressed on admixture with an authentic sample of tribenzylamine.

(c) *Formation of benzaldehyde.* Experiment (a) was repeated, but the reaction product was acidified and then distilled in steam. A saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid added in excess to the distillate gave 0·4 g. of a yellow solid, m. p. 240—241°, not depressed on admixture with an authentic sample of benzaldehyde 2 : 4-dinitrophenylhydrazone.

*Di-*n-*butylamine and* 1-*Chloroanthraquinone. Formation of* 1-n-*Butylaminoanthraquinone.*—1-Chloroanthraquinone (4 g.) and di-*n*-butylamine (10 c.c.) were heated at 190° for 4 hr. The resulting solid was collected, extracted several times with dilute ammonia, then crystallised from acetic acid. The product (1 g.) formed deep red needles, m. p. 78—80°, not depressed on admixture with an authentic sample of 1-*n*-butylaminoanthraquinone.

Diethylamine and 1-*Chloroanthraquinone. Formation of Ethylaminoanthraquinone.*—A carefully purified sample of diethylamine (12 c.c.) was heated with 1-chloroanthraquinone (4 g.) at 160° for 4 hr. The resulting solid was collected and extracted with dilute ammonia, and the residue was dried and finally chromatographed from benzene on alumina. The main portion passed through the column readily and the eluate when mixed with light petroleum (b. p. 60—80°) afforded 2·1 g. of bright red needles, m. p. 122—123° (Found: C, 76·4; H, 5·1; N, 5·8. Calc. for $C_{16}H_{13}O_2N$: C, 76·5; H, 5·2; N, 5·6%), not depressed on admixture with an authentic specimen of 1-ethylaminoanthraquinone. The red solution in acetic anhydride changed to violet on the addition of boroacetic anhydride and heating.

1-*Piperidinoanthraquinone.*—Following G.P. 136,777, 1-chloroanthraquinone (5 g.) and piperidine (14 c.c.) were heated on a steam-bath for 10 hr. The product crystallised from ethyl

alcohol in red leaflets (4 g.), m. p. 118—119° (Found: C, 77·9; H, 5·8; N, 4·9. Calc. for $C_{19}H_{17}O_2N$: C, 78·3; H, 5·8; N, 4·8%). 1-Piperidinoanthraquinone forms a bluish-red solution in acetic anhydride, rendered paler on heating with boroacetic anhydride.

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