# 15. *The Action of Bases on 1-Diazoanthraquinone-2-sulphonate and its Derivatives.*

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The action of various bases on 1-diazoanthraquinone-2-sulphonate and on two of its derivatives, having anilino- and bromo-substituents in the 4-position, has been investigated. The mixture of products was separated by chromatographic adsorption, the results being tabulated below.

The so-called exchange reaction between bases and diazo-compounds (*inter al.*, Griess, *Ber.*, 1886, **19**, 313) was apparently first studied in the anthraquinone series by Wacker (*Ber.*, 1902, **35**, 2593, 3922), who investigated the interaction of what was then regarded as 1-diazoanthraquinone-2-sulphonate with a number of bases. He found that, in nearly all cases, the primary product of the reaction, the diazoaminoanthraquinonesulphonic acid, decomposed with the regeneration of the parent aminoanthraquinonesulphonic acid. As is now known, the acid used by Wacker was the 1-aminoanthraquinone-6-sulphonic acid and not the 2-sulphonic acid. More recently (E.P. 321,217 of 1929) it has been observed that acid wool dyes result from the interaction of bases with 1-diazoanthraquinone-2-sulphonates which are substituted in the 4-position. Although it is recorded that the dyes are not homogeneous, no attempt appears to have been made to elucidate their composition.

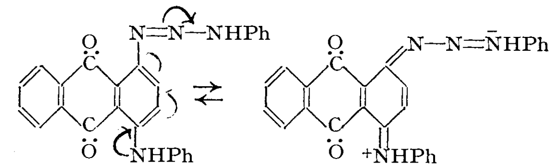
We have now examined the interaction of the diazo-compounds prepared from 1-aminoanthraquinone-2-sulphonic acid (I), 1-amino-4-anilinoanthraquinone-2-sulphonic acid (II) and 4-bromo-1-aminoanthraquinone-2-sulphonic acid (III) with a number of primary aliphatic and aromatic bases under conditions similar to those described in the above-mentioned patent. It was not found possible to separate the products by fractional crystallisation, but resolution was readily effected by chromatographic adsorption of alcoholic solutions of the mixture of sodium salts on alumina. The results are as follows :

| Diazo-compound from | Base. | Product. | Yield, %. |
|---|---|---|---|
| (I) | Aniline | (I) | 100 |
| (I) | Ammonia | (I) | 50 |
| | | 1-Hydroxyanthraquinone-2-sulphonic acid | 50 |
| (II) | Aniline | (II) | 15 |
| | | 1-Anilinoanthraquinone-3-sulphonic acid (IV) | 45 |
| | | 1 : 4-Dianilinoanthraquinone-2-sulphonic acid (V) | 40 |
| (II) | *p*-Toluidine | (II) | 10 |
| | | (IV) | 50 |
| | | 4-Anilino-1-*p*-toluidinoanthraquinone-2-sulphonic acid | 40 |
| (II) | *m*-4-Xylidine | (II) | 62 |
| | | (IV) | 32 |
| | | 4-Anilino-1-*m*-4′-xylidenoanthraquinone-2-sulphonic acid | 6 |
| (III) | Aniline | (II) | 10 |
| | | (III) | 20 |
| | | (IV) | 40 |
| | | (V) | 30 |
| (III) | Ammonia | 1 : 4-Diaminoanthraquinone-2-sulphonic acid | 94 |
| | | 4 : 4′-Diamino-1 : 1′-dianthraquinonyl-3 : 3′-disulphonic acid | 5—6 |
| (III) | Methylamine | 1-Amino-4-methylaminoanthraquinone-2-sulphonic acid | 100 |

(The yields are calculated upon the reaction product separated, the sulphonic acids being weighed as sodium salts.)

Although the experimental data are insufficient to warrant any theoretical conclusions, it is perhaps permissible to direct attention to the marked effect of a substituent in the 4-position in facilitating the reduction of the diazo-group or its replacement by NAr. This is due possibly to the formation of the reactive mesomeride (VII) from (VI).

(VI.)



(VII.)

## EXPERIMENTAL.

The following general conditions were used in carrying out the reactions summarised above. To a well-stirred suspension of copper bronze (0·003 part) in the base (3 parts) at 0° the diazo-compound, from the appropriate amino-anthraquinonesulphonic acid (1 part), was added during 1 hour (solid bases were used in ethereal solution). After the reaction, which proceeded vigorously with evolution of nitrogen, had moderated, the mixture was heated at 60° for 30 minutes, the excess of base after the addition of aqueous sodium hydroxide removed in steam, the deeply coloured aqueous solution filtered, and the soluble products precipitated by the addition of brine. The mixture of salts was collected, dissolved in alcohol, and purified by chromatographic adsorption on alumina towers.

*Aniline and* 1-*Diazoanthraquinone*-2-*sulphonate*.—Interaction of aniline with the diazo-compound (9·8 g.) gave a crystalline red salt (10 g.). The chromatogram, after development with alcohol was, apart from a trace of tarry impurity, homogeneous, forming an orange-red zone. This was eluted with water and the substance so obtained crystallised from this solvent in small red prisms identified as sodium 1-aminoanthraquinone-2-sulphonate (Found: N, 4·4; S, 9·8; Na, 7·0. Calc. for $C_{14}H_8O_5NSNa$: N, 4·3; S, 9·8; Na, 7·1%). It gave on bromination 2 : 4-dibromo-1-aminoanthraquinone, crystallising from pyridine in scarlet needles, m. p. 222—223°, both alone and in admixture. On reduction, the sulphonic acid gave 1-aminoanthraquinone, the following conditions being used for this and similar reductions (I.C.I., Lodge, and Tatum, E.P. 322576): The sodium salt of the sulphonic acid (1 g.) and glucose (1 g.) were dissolved in water, and aqueous sodium hydroxide (20%; 2 c.c.) added gradually with stirring at 100°. The base crystallised from benzene in ruby needles, m. p. 243°, both alone and in admixture; the acetyl derivative had m. p. 218°.

In another experiment a suspension of the diazo-compound (10 g.) in water (50 c.c.) was mixed with a solution of aniline in glacial acetic acid (32%; 10 c.c.), the mixture cooled to 0°, and aqueous sodium hydroxide (15%) added with vigorous stirring until the solution was alkaline. The sodium diazoamino-compound (12 g.) was precipitated by the addition of an equal volume of brine, collected, and washed with brine and with benzene to remove tar. The dry salt (10 g.) was dissolved in water (50 c.c.), and sulphuric acid (25%; 250 c.c.) gradually added, the reaction being completed by warming at 50°. Vigorous evolution of nitrogen occurred and the odour of phenol became evident. After completion of the reaction, steam was passed through the solution and phenol was identified in the distillate as tribromophenol, m. p. 95° (0·7 g.). The cooled solution remaining after the steam-distillation deposited a sparingly soluble solid (*A*); this was removed, and the filtrate saturated with salt, which precipitated sodium 1-aminoanthraquinone-2-sulphonate (4 g.), identified as described above. The solid (*A*) (4·5 g.) was extracted with hot water (750 c.c.), which on cooling deposited a crystalline substance (0·3 g.). This separated from acetic acid in copper-coloured leaflets, m. p. 248°, darkening at 238°. Analysis showed this to be the *aniline* salt of 1-diazophenylaminoanthraquinone-2-sulphonic acid (Found: C, 62·3; H, 4·4; N, 11·0. $C_{26}H_{20}O_5N_4S$ requires C, 62·4; H, 4·0; N, 11·2%), the identity being confirmed by comparison with a specimen of the salt prepared from the diazoamino-sulphonic acid.

*Ammonia and* 1-*Diazoanthraquinone*-2-*sulphonate*.—The diazo-compound (10 g.) was added to aqueous ammonia (100 c.c. containing ammonia, *d* 0·880, 30 c.c.); addition of copper bronze was unnecessary. After the evolution of nitrogen was complete, sodium hydroxide (10%; 50 c.c.) was added, the excess of ammonia boiled off, and an equal volume of brine added to the cooled solution. The reddish-brown sodium salt (10 g.; N, 2·8; Na, 6·9%), which separated, was chromatographed, alcohol developing two zones, the upper being bright red and the lower yellow. The upper zone (2·8 g. from the salt, 6 g.) was sodium 1-aminoanthraquinone-2-sulphonate; from the lower zone a salt (2·7 g.), crystallising in yellow needles, was obtained. This was identified as sodium 1-hydroxyanthraquinone-2-sulphonate, yielding on bromination 2 : 4-dibromo-1-hydroxyanthraquinone, m. p. 232—233° (Found: Br, 42·0. Calc. for $C_{14}H_6O_3Br_2$: Br, 41·9%).

*Aniline and* 1-*Diazo*-4-*anilinoanthraquinone*-2-*sulphonate*.—The black reaction product (16 g.) from the diazo-compound (10 g.) was chromatographed from an alcoholic solution, the tower on being developed with alcohol giving, in addition to a small zone of tar, three zones: (*A*) rose-violet, (*B*) blue and (*C*) green. The salt (4·5 g.), *sodium* 1-*anilinoanthraquinone*-3-*sulphonate*, from (*A*) crystallised from water in long brownish-red needles with a golden metallic lustre (Found: C, 57·4; H, 2·6; N, 3·2; Na, 5·6. $C_{20}H_{12}O_5NSNa$ requires C, 57·85;* H, 2·9; N, 3·3; Na, 5·5%). The p-*toluidine* salt crystallised from dilute methyl alcohol, in which it dissolved to give a port-wine coloured solution, in purple prismatic needles, decomp. 290°, after sintering at 286—288°, but the temperature of decomposition varied considerably with the rate of heating (Found: C, 66·2; H, 4·6; N, 5·9. $C_{27}H_{22}O_5N_2S$ requires C, 66·7; H, 4·5; N, 5·8%).

The salt (1·5 g.) from (*B*) crystallised from water in light blue needles with a coppery glance and was identified as sodium 1-amino-4-anilinoanthraquinone-2-sulphonate (Found: N, 6·6; S, 7·6; Na, 5·6. Calc. for $C_{20}H_{13}O_5N_2SNa$: N, 6·7; S, 7·7; Na, 5·5%) by the preparation of the p-*toluidine* salt, which crystallised from its royal-blue solution in dilute methyl alcohol in purple prismatic needles, decomp. 269—270°, sintering at 263° (Found: C, 64·9; H, 4·6. $C_{27}H_{23}O_5N_3S$ requires C, 64·7; H, 4·6%). The identity was confirmed by the reduction of the sulphonic acid to 1-amino-4-anilinoanthraquinone, m. p. 203°, both alone and in admixture (Found: N, 8·8. Calc. for $C_{20}H_{14}O_2N_2$: N, 8·9%).

The salt (4·5 g.) from (*C*) crystallised from water in long steel-black needles giving a green aqueous solution. It was identified as *sodium* 1 : 4-*dianilinoanthraquinone*-2-*sulphonate* by analysis (Found: N, 5·9; S, 6·0; Na, 4·5. $C_{26}H_{17}O_5N_2SNa$ requires N, 5·7; S, 6·5; Na, 4·7%) and by reduction to 1 : 4-dianilinoanthraquinone, blue-black needles from benzene, m. p. 214° (Found: N, 7·2. Calc. for $C_{26}H_{18}O_2N_2$: N, 7·2%). The p-*toluidine* salt of the sulphonic acid crystallised from dilute acetone in deep purple, almost black, needles, decomp. 252°, the solution in alcohol or acetone being green (Found: C, 68·7; H, 4·3; N, 7·2. $C_{33}H_{27}O_5N_3S$ requires C, 68·6; H, 4·7; N, 7·3%).

p-*Toluidine and* 1-*Diazo*-4-*anilinoanthraquinone*-2-*sulphonate*.—This reaction was carried out with an ethereal solution of the base and the diazo-compound (14 g.). The purple-black aqueous solution was filtered to remove a black solid (*K*; 3 g.) and deposited a black salt (10g.) after the addition of brine. This was dissolved in alcohol and chromatographed, yielding, in addition to a small zone containing tarry impurities, three zones: a red-violet zone (*X*), a blue zone (*Y*) and a green zone (*Z*). Elution of (*X*) with water gave a salt (5 g.) identified as sodium 1-anilinoanthraquinone-3-sulphon-

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* Calculated on the assumption that the residue in the boat was sodium carbonate.

ate by the preparation of its *p*-toluidine salt (see above). The blue zone (*Y*) gave a salt (1 g.) recognised as sodium 1-amino-4-anilinoanthraquinone-2-sulphonate by reduction to 1-amino-4-anilinoanthraquinone and by the preparation of its *p*-toluidine salt. From the green zone (*Z*) a salt (2 g.) crystallising from water in bluish-black needles was obtained; this was *sodium* 4-*anilino*-1-p-*toluidinoanthraquinone*-2-*sulphonate* (Found : N, 5·5; S, 6·2; Na, 4·6. $C_{27}H_{19}O_5N_2SNa$ requires N, 5·5; S, 6·3; Na, 4·5%). It was characterised by the preparation of its *p*-toluidine salt, which crystallised from dilute methyl alcohol in short stout prisms, m. p. 231—232°, identical with the salt described below. On reduction with glucose, 1-*anilino*-4-p-*toluidinoanthraquinone* was obtained, crystallising from benzene–alcohol in blue-black needles, m. p. 250° (Found : C, 80·6; H, 5·2; N, 6·9. $C_{27}H_{20}O_2N_2$ requires C, 80·2; H, 4·9; N, 6·9%).

The sparingly soluble substance (*K*) crystallised from its emerald-green solution in dilute methyl alcohol in black prisms, m. p. 231—232°, and was the p-*toluidine* salt of 4-anilino-1-*p*-toluidinoanthraquinone-2-sulphonic acid (Found : C, 67·0; H, 5·0; N, 7·3; S, 5·4. $C_{34}H_{29}O_5N_3S,H_2O$ requires C, 67·0; H, 5·1; N, 6·9; S, 5·9%). On admixture with alkali and distillation in steam, *p*-toluidine was identified in the distillate by the preparation of its acetyl derivative, m. p. 144—145°, both alone and in admixture; the residue after reduction with glucose gave 1-anilino-4-*p*-toluidinoanthraquinone.

m-4-*Xylidine and* 1-*Diazo*-4-*anilinoanthraquinone*-2-*sulphonate*.—Interaction of the diazo-compound (10 g.) with *m*-4-xylidine (purified through its acetyl derivative) (25 g.) in the presence of freshly precipitated copper (0·1 g.) proceeded readily at 0° and the reaction was completed by heating at 70—80° for 0·5 hour. An alcoholic solution of the black salt (10 g.) isolated in the usual manner was chromatographed and gave three zones : a rose-violet zone (*L*), a blue zone (*M*) and a green zone (*N*). The yields varied considerably in different experiments and the values recorded are only very approximate. The zone (*L*) (31%) gave on elution sodium 1-anilinoanthraquinone-3-sulphonate; *p*-toluidine salt, decomp. 290°; the zone (*M*) (62%) gave sodium 1-amino-4-anilinoanthraquinone-2-sulphonate, *p*-toluidine salt, decomp. 270°. Elution of the zone (*N*) gave on evaporation of the water a somewhat gummy *salt* (6%) which after repeated re-towering was ultimately obtained as an almost black powder crystallising from its green aqueous solution in black needles (Found : N, 5·2. $C_{28}H_{21}O_5N_2SNa$ requires N, 5·4%). The p-*toluidine* salt of 4-*anilino*-1-m-4′-*xylidinoanthraquinone*-2-*sulphonate* crystallised from dilute methyl alcohol in black needles, decomp. 250° (Found : C, 68·8; H, 5·2. $C_{35}H_{31}O_5N_3S$ requires C, 69·4; H, 5·1%). On reduction 1-*anilino*-4-m-4′-*xylidinoanthraquinone* was obtained, crystallising from benzene or ligroin (b. p. 100—120°) in deep blue needles, m. p. 232—233° (Found : C, 80·7; H, 5·3. $C_{28}H_{22}O_2N_2$ requires C, 80·4; H, 5·2%).

This substance was prepared also by the digestion of 4-chloro-*m*-xylene (5 g.) with 1-amino-4-anilinoanthraquinone (0·5 g.) in the presence of freshly precipitated copper (0·1 g.) and sodium acetate (0·2 g.) for 3 hours. The reaction mixture was distilled in steam, and the residue digested with hydrochloric acid for 0·5 hour, collected, and recrystallised from benzene, 1-anilino-4-*m*-4′-xylidinoanthraquinone (0·7 g.) being obtained in blue needles, m. p. 232—233°.

*Ammonia and* 1-*Diazo*-4-*bromoanthraquinone*-2-*sulphonate*.—Aqueous ammonia (*d* 0·880; 10 c.c.) and copper bronze (0·1 g.) were added to a paste of the diazo-compound (10 g.) in water (100 c.c.). The reaction, which was vigorous, was completed by heating at 70—80° for 0·5 hour. After the addition of aqueous sodium hydroxide, the solution was boiled to expel ammonia, and the product precipitated from the filtered solution by the addition of salt. An alcoholic solution of the black powder (8·5 g.) was chromatographed, yielding two zones, a red and a blue. The former on elution with water gave a red powder (5%) crystallising from hot water in red plates with a golden metallic lustre (Found : N, 4·0. $C_{28}H_{14}O_{10}N_2S_2Na_2$ requires N, 4·3%). The p-*toluidine* salt of 4 : 4′-*diamino*-1 : 1′-*dianthraquinonyl*-3 : 3′-*disulphonic acid* crystallised from dilute methyl alcohol in deep red, prismatic needles, m. p. 234—235°. For analysis it was dried at 100°, but it still apparently contained solvent (Found : C, 57·3; H, 4·6; N, 6·4. $C_{42}H_{34}O_{10}N_4S_2,3H_2O$ requires C, 57·8; H, 4·6; N, 6·4%). This disulphonic acid was conveniently prepared by digesting sodium 4-bromo-1-aminoanthraquinone-2-sulphonate (2 g.) in water (100 c.c.) with copper powder (0·1 g.) and a drop of alkali for 3 hours.

On reduction with glucose in the usual manner, 4 : 4′-*diamino*-1 : 1′-*dianthraquinonyl* was obtained, which crystallised from *m*-4-xylidine in small red plates, m. p. 356—358°. This base was very sparingly soluble in the ordinary organic media, but it dissolved readily in acetic–hydrochloric acid (Found : N, 6·3. $C_{28}H_{16}O_4N_2$ requires N, 6·3%). 2 : 2′-*Dibromo*-4 : 4′-*diamino*-1 : 1′-*dianthraquinonyl*, prepared by the action of bromine on the sodium salt of the disulphonic acid, crystallised from nitrobenzene in red plates with a brilliant green iridescence, m. p. 415—416° (Found : N, 4·9; Br, 26·3. $C_{28}H_{14}O_4N_2Br_2$ requires N, 4·6; Br, 26·6%). Both these dianthraquinonyl derivatives dissolved in sulphuric acid to yield colourless solutions, becoming green on the addition of boric acid.

Elution of the blue-violet zone with water gave a black salt (90%), which was purified by conversion into its sparingly soluble, crystalline, scarlet hydrochloride. The hydrochloride, which readily dissociated, was reconverted into the sodium salt by the addition of aqueous sodium hydroxide. *Sodium* 1 : 4-*diaminoanthraquinone*-2-*sulphonate* crystallised from water, in which it was readily soluble, in small, dark violet needles (Found : N, 8·0. $C_{14}H_9O_5N_2SNa$ requires N, 8·2%). On bromination, the salt gave 2 : 4-dibromo-1-aminoanthraquinone, m. p. 221°, and on reduction 1 : 4-diaminoanthraquinone was obtained, crystallising in black needles, m. p. 267—268°, from dilute alcohol (Found : N, 11·9. Calc. for $C_{14}H_{10}O_2N_2$ : N, 11·8%) and yielding a diacetyl derivative, m. p. 268°.

*Methylamine and* 1-*Diazo*-4-*bromoanthraquinone*-2-*sulphonate*.—This reaction, carried out with the diazo-compound (10 g.) and methylamine (10 g.) in water (100 c.c.), gave a violet-blue powder (8 g.) which was homogeneous in the tower. *Sodium* 1-*amino*-4-*methylaminoanthraquinone*-2-*sulphonate* crystallised from water in blue needles (Found : N, 7·6; S, 9·6. $C_{15}H_{11}O_5N_2SNa$ requires N, 7·9; S, 9·6%). Reduction gave 1-amino-4-methylaminoanthraquinone, violet rhombohedra from toluene, m. p. 198° (Found : C, 71·5; H, 4·6; N, 11·5. Calc. for $C_{15}H_{12}O_2N_2$ : C, 71·4; H, 4·8; N, 11·1%). The acetyl derivative separated from methyl ethyl ketone in brown leaflets, m. p. 282°. Gattermann (*Annalen*, 1912, **393**, 160) gives m. p. 195° and 278° respectively for the base and its acetyl derivative.

*Aniline and* 1-*Diazo*-4-*bromoanthraquinone*-2-*sulphonate*.—An alcoholic solution of the mixture of sodium salts (15 g.) from the diazo-compound (16 g.) was chromatographed yielding four zones : (*S*) rose-violet, (*T*) blue, (*U*) red and (*V*) green. From (*S*), sodium 1-anilinoanthraquinone-3-sulphonate (4 g.) was eluted and identified as its *p*-toluidine salt, decomp. 290°; from (*T*), sodium 1-amino-4-anilinoanthraquinone-2-sulphonate (1 g.), *p*-toluidine salt, decomp. 269°; and from (*U*), sodium 4-bromo-1-aminoanthraquinone-2-sulphonate (2 g.) (Found : N, 3·2; Br, 20·1; Na, 5·7. Calc. for $C_{14}H_7O_5NBrSNa$ : N, 3·5; Br, 19·8; Na, 5·7%). The p-*toluidine* salt crystallised from alcohol in red leaflets, seen under the microscope to consist of prismatic needles, decomp. 252°, both alone and in admixture (Found : C, 51·4; H, 3·5. $C_{15}H_{17}O_5N_2BrS$ requires C, 51·5; H, 3·5%). The green zone (*V*) gave sodium 1 : 4-dianilinoanthraquinone-2-sulphonate (3 g.); *p*-toluidine salt, decomp. 252°.

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