

The Amination of Anthraquinone with Hydroxylamine in Sulphuric Acid.

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This reaction affords a mixture of 1- and 2-amino- and 1 : 4-, 1 : 5-, 1 : 6-, 1 : 7-, 1 : 8-, and 2 : 7-diamino-anthraquinone. Substitution occurs equally in the α - or the β -positions.

THE direct amination of aromatic compounds with hydroxylamine in concentrated sulphuric acid catalysed by ferrous sulphate was first described by Turski (G.P. 287,756), who claimed that 1-aminoanthraquinone could be isolated from the product, although Kniatowna (*Bull. Soc. chim.*, 1924, **35**, 207) found that this was not easy. Subsequently, a vanadium catalyst was used as an alternative and the hydroxylamine was produced *in situ* from a nitroparaffin (Turski, B.P. 564,610; 626,661). Separation and identification of the principal products has now been achieved by chromatography on very active alumina. Since the present work was carried out (in 1944), Rao, Shah, and Venkataraman (*Proc. Indian Acad. Sci.*, 1951, **34**, 354) and Hoyer (*Kolloid Z.*, 1951, **121**, 121) described the qualitative behaviour of individual aminoanthraquinones and selected two-component mixtures on alumina with benzene or methylene chloride as solvent, but there is no record of quantitative chromatographic examination of a complex mixture.

A two-stage chromatographic procedure, supplemented by fractional crystallisation (see Experimental section) was worked out which effectively separated the nine components in the product. The results (see Table) show that the reaction is far more complicated than was originally suspected. Not only is 1-aminoanthraquinone formed but also at least an equal amount of 2-aminoanthraquinone, and both compounds are aminated further to produce diaminoanthraquinones. Apart from the very small amount of 1 : 4-diaminoanthraquinone produced when a vanadium catalyst is used, all the diaminoanthraquinones have the two substituents in different rings. Vanadium is a more active catalyst than ferrous iron, but the reaction takes a similar course. The reaction still occurs, though much more slowly, in sulphuric acid containing no added catalyst. No special precautions were taken to use specially purified sulphuric acid but the amount of iron and other metals present in that used was extremely small.

The mechanism of amination is still obscure. Some suggestions have been made, for example by Keller and Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 1122), that the active agent is the NH_2^+ ion but the most recent text-books on chemical kinetics and the mechanism of reactions say nothing on the matter. Our results for anthraquinone indicate that, whatever the reactive species may be, it produces random substitution, α - and β -positions being attacked with equal facility.

EXPERIMENTAL

Amination of Anthraquinone.—(a) *With an iron catalyst.* Ferrous sulphate crystals (0.9 g.) were dissolved in 90% sulphuric acid (120 g.), and anthraquinone (10 g.) followed by hydroxylamine sulphate (9 g., 1.17 equiv. of $\text{NH}_2\cdot\text{OH}$) was added to the stirred solution. The addition of the latter caused the precipitation of anthraquinone but it re-dissolved on warming to 100—

110°. The temperature was raised to 160° during 45 min. and kept at 160—165° for 4 hr. After cooling to 80° the mixture was poured into ice and water, and the product filtered off, washed with dilute aqueous ammonia, and dried (yield 10.48 g.). The crude product was extracted (Soxhlet) with chlorobenzene (2.5 l.), and the insoluble residue discarded. On cooling, the extract deposited reddish crystals (2.8 g.), m. p. ca. 298°, which were filtered off and examined separately. The chlorobenzene solution was passed through a column (24 × 2") containing activated alumina (Type "O" as supplied by Peter Spence & Sons Ltd., Widnes) under slight pressure (4" water). The column was developed with chlorobenzene containing 5% of pyridine, bands being developed as shown in the Table, and separated with the same solvents. The amines, recovered by removal of the solvent (the last traces by steam), crystallised from an appropriate solvent, and were converted into acetyl and benzoyl derivatives and identified by comparison with authentic specimens.

A portion (1 g.) of the small fraction which crystallised from the original solution in chlorobenzene was dissolved in pyridine (50 c.c.), and the solution diluted with chlorobenzene (150 c.c.), then chromatographed on alumina (12 × 1") with the same mixed solvent, giving mainly 2-amino-, 1 : 7- and 2 : 7-diamino-, and traces of 1-amino- and 1 : 6-diamino-anthraquinones.

The combined yields of the individual amines isolated are given in the Table. The compounds bracketed together were separated as one band and identified as shown later.

(b) *With a vanadium catalyst.* A similar experiment in which vanadium pentoxide (0.3 g.) was used instead of ferrous sulphate gave 10.75 g. of product, which was extracted with chlorobenzene, giving 0.65 g. of insoluble matter (discarded), a crystalline less-soluble fraction, subsequently chromatographed separately (1.45 g.), and a solution which was chromatographed as described above.

The combined yields are also given in the Table.

| Order of elution | Colour of band | FeSO ₄ catalyst | | V catalyst | | M. p. (pure) |
|---|------------------|----------------------------|---------------|------------|---------------|--------------|
| | | Yield (g.) | M. p. (crude) | Yield (g.) | M. p. (crude) | |
| Anthraquinone | Pale yellow | 3.7 | 281° | 2.75 | — | 284° |
| 1-Amino-anthraquinone ... | Orange-red | 1.45 | 245 | 1.82 | 247—249° | 251 |
| 1 : 5-Diamino- " ... | Orange-red | 0.18 | 320—322 | 0.53 | 300—310 | 320 |
| 2-Amino- " ... | Orange to red | 2.36 | 296—300 | 1.80 | 306—308 | 304 |
| 1 : 8-Diamino- " ... | Orange to red | 0.13 | | 0.20 | 265—267 | 265 |
| 1 : 6-Diamino- " ... | Red | 0.10 | 280—290 | 0.45 | 288—292 | 297 |
| 1 : 4-Diamino- " ... | Violet | — | (indef.) | 0.05 | ~230 | 268 |
| 1 : 7-Diamino- " ... | Orange-yellow | 0.20 | 300 | 0.15 | 286—289 | 292 |
| 2 : 7-Diamino- " ... | Yellow-orange | 0.15 | (indef.) | 0.35 | 310—325 | >330 |
| Insoluble matter (discarded) | — | 1.05 | — | | | |
| Aminohydroxy-anthraquinone, etc. + loss by difference | Deep purple lake | 1.16 | — | 2.00 | — | — |
| <i>Yields (% wt.) on unrecovered anthraquinone :</i> | | | | | | |
| 1-Amino-anthraquinone | | 22.9 | | 25.1 | | |
| 2- " | | 37.4 | | 24.8 | | |
| Total diamines | | 12.0 | | 23.8 | | |

(c) *Without added catalyst.* When no metallic catalyst was used the product was resolved into unchanged anthraquinone (5.06 g.), 1-amino- (1.3 g.), 2-amino- (1.36 g.), and traces of 1 : 5-, 1 : 8-, and 2 : 7-diaminoanthraquinone.

(d) *With a vanadium catalyst in stronger acid.* An experiment was carried out in 98% sulphuric acid as described under (b). An exothermic reaction took place at 120° and the amination was allowed to proceed at 130° for 20 min. The composition of the product was very similar to that already described except that, in addition, a very small amount (<0.1 g.) of 2 : 6-diaminoanthraquinone (dibenzoyl derivative, m. p. 372—376°) was isolated from the sparingly soluble fraction.

Separation of Bands of Mixed Amines.—Pairs of amines which tended to run together were separately identified as follows :

2-Amino- and 1 : 8-diaminoanthraquinone. The former separated on recrystallisation from nitrobenzene, leaving the 1 : 8-diaminoanthraquinone in the mother-liquors. These were boiled with a little benzoyl chloride, and the yellow crystals of 1 : 8-dibenzamidoanthraquinone were filtered off and hydrolysed to the diamino-compound in 80% sulphuric acid at 100°.

1:4- and 1:6-Diaminoanthraquinone. The presence of the very small amount of 1:4-diaminoanthraquinone was revealed by the violet appearance of the leading edge of the band. It was readily removed from the recovered mixture by extraction with cold benzene.

1:7- and 2:7-Diaminoanthraquinone. These were separated by passing a solution in chlorobenzene containing 25% of pyridine through a small column of alumina. The less soluble fraction separating from the original chlorobenzene solution was conveniently chromatographed along with the mixture of 1:7- and 2:7-diamino-compounds recovered from the large column.

Amination of Aminoanthraquinones.—Vanadium pentoxide (0.075 g.) was added to 90% sulphuric acid (30 g.), followed by either 1- or 2-aminoanthraquinone (2.75 g.) and hydroxylamine sulphate (1 g.), and the mixture was heated to 160° in 45 min. and kept at that temperature for 4 hr. The yields were as follows: from 1-aminoanthraquinone, unchanged material (1.73 g.) and 1:5- (0.07 g.), 1:8- (0.12 g.), 1:6- (0.1 g.), 1:7- (0.15 g.), 1:4- (trace) diaminoanthraquinone; from 2-aminoanthraquinone: unchanged material (1.45 g.) and 1:6- (0.12 g.), 2:6- (0.08 g.), 2:7- (0.32 g.) diaminoanthraquinone.

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