358. *Preparation of Some Fluorinated α-Aminoanthraquinones. Sulphonation and Subsequent Reactions of Fluorinated Anthraquinones.*

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Sulphonation of β- but not α-fluoroanthraquinones has been achieved. The products readily exchanged the sulphonic acid group for chlorine when treated with sodium chlorate in hydrochloric acid. The chlorine has then been replaced by a sulphonamido-group and hydrolysis yields fluorinated α-aminoanthraquinones. Some interesting dyes have thence been made.

Mono- and di-fluoroanthraquinones have recently been prepared in a satisfactory manner.[1] We now report their sulphonation and conversion into fluorinated aminoanthraquinones. Three such quinones have previously been reported in patents.[2,3]

With narrowly defined conditions for its isolation 2,6-difluoroanthraquinone-1-sulphonic acid can be obtained in 78% yield. Yellow 1-chloro-2,6-difluoroanthraquinone results on treatment of this acid with sodium chlorate in boiling hydrochloric acid, and on reaction with toluene-*p*-sulphonamide[4] and hydrolysis of the resulting sulphonamide in hot sulphuric acid affords orange 1-amino-2,6-difluoroanthraquinone in good yield.

Similarly the 1-chloro-2-fluoroanthraquinone,[1] on reaction with toluene-*p*-sulphonamide and subsequent hydrolysis, gave the bright-red 1-amino-2-fluoroanthraquinone.

For comparison we have repeated with some modifications the preparation of 1-amino-6- or -7-fluoroanthraquinone.[3] According to the literature the α-sulphonation of 2-fluoroanthraquinone takes place in the fluorine-free benzene ring: 2-fluoroanthraquinone-5- and -8-sulphonic acid are equally probable as products.

The sulphonation of 1-fluoro- and 1,5-difluoro-anthraquinone could not be achieved. After 4—5 hours' heating at 125—130° with oleum red water-soluble products were obtained from which no sulphonic acid could be isolated.

A few simple dyes prepared[5] from the aminofluoroanthraquinones indicate possibilites

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[1] Valkanas and Hopff, *J. Org. Chem.*, 1962, **27**, 3680.
[2] Johnson, U.S.P. 2,013,657; *Chem. Abs.*, 1935, **29**, 6904.
[3] Ciba, Swiss P. 289,992, 292,690—2; *Chem. Abs.*, 1954, **48**, 11,800.
[4] Scott and Allen, *Org. Synth.*, 1938, **18**, 15, 72; Coll. Vol. II, 1943, 128, 539.
[5] Seidel, Diss., E.T.H., Zurich, 1960; *Chimia*, 1961, **15**, 193.

of improved stability and colour. For instance, the colour shift to green produced by fluorine in *NN'*-di-(7-fluoro-anthraquinon-1-yl)isophthalamide is encouraging.

The replacement of the chlorine in the 1-chlorofluoroanthraquinones by an amino-group was also attempted by reaction with ammonia under pressure.[6] In general, the products prepared were of low fluorine content; 1-chloro-2,6-difluoroanthraquinone gave a product of correct fluorine content but the amine proved difficult to separate from the unchanged starting material.

EXPERIMENTAL

Sulphonation of 2,6-*Difluoroanthraquinone.*—2,6-Difluoroanthraquinone [1] (20 g.) was added to oleum (47 ml., made from 40 ml. of 24% oleum and 7 ml. of 66% oleum), and mercury acetate (0·5 g.) was then added with stirring. The temperature was gradually raised during 1 hr. to 125—130° where it was maintained for 5 hr. The product, after being cooled to 40—50°, was poured into hot water (500 ml.) containing traces of sodium chlorate and the resulting mixture was boiled and filtered. The filtrate was mixed hot with sodium carbonate (10 g.) and left at room temperature for 40 hr. 2,6-Difluoroanthraquinone-1-sulphonic acid was precipitated and was washed with a saturated sodium sulphate solution and dried at 110—115°. The yield was 22 g. (78·5%).

1-*Chloro*-2,6-*difluoroanthraquinone.*—Sodium 2,6-difluoroanthraquinone-1-sulphonate (18 g.) was dissolved in a hot (60—70°) mixture of water (1 l.) and concentrated hydrochloric acid (120 ml.) and then kept at 90—95° with stirring while sodium chlorate (70 g.) in water (150 ml.) was added during 1 hr. The solution was further kept at 90—95° until precipitation ceased (1½ hr.). The yellow *chloro-derivative* was filtered off hot, washed with hot water, and dried (yield, 17·3 g., 79·5%). Recrystallised from chlorobenzene, it had m. p. 237—238° and dissolved in sulphuric acid giving an intense red colour (Found: C, 60·15; H, 1·8; F, 13·4; Cl, 12·7. $C_{14}H_5ClF_2O_2$ requires C, 60·3; H, 1·8; F, 13·65; Cl, 12·75%).

2,6-*Difluoro*-1-*toluene*-p-*sulphonamidoanthraquinone.*—1-Chloro-2,6-difluoroanthraquinone (10 g.), toluene-*p*-sulphonamide (8 g.), copper acetate (4 g.), potassium carbonate (4 g.), and *o*-dichlorobenzene (100 ml.) were heated slowly to the b. p. and kept under reflux (180—185°) for 4—5 hr. Aftdr cooling, the mixture was filtered and the precipitate washed with boiling alcohol and water and then dried. The resulting *anthraquinonesulphonamide* recrystallised from anisole, giving greenish-yellow crystals (12·2 g., 84%), m. p., 249—250° (Found: C, 61·1; H, 3·1; N, 3·4; F, 9·3. $C_{21}H_{13}F_2NO_4S$ requires C, 61·1; H, 3·15; N, 3·4; F, 9·2%).

1-*Amino*-2,6-*difluoroanthraquinone.*—The sulphonamide (6 g.) was heated with stirring in concentrated sulphuric acid (50 ml.) for 1 hr. at 60—65°, then poured on ice, to precipitate the amine, which was filtered off, washed to neutrality with water, and dried. From anisole the *amine* formed brilliant orange crystals, m. p. 229—230° (3·6 g., 95·7%) (Found: C, 64·8; H, 2·7; N, 5·4; F, 14·0. $C_{14}H_7F_2NO_2$ requires C, 64·9; H, 2·7; N, 5·4; F, 14·6%).

2-*Fluoro*-1-*toluene*-p-*sulphonamidoanthraquinone.*—1-Chloro-2-fluoroanthraquinone [1] (5 g.), toluene-*p*-sulphonamide (4 g.), copper acetate (2 g.), potassium carbonate (2 g.), and *o*-dichlorobenzene (60 ml.) were heated slowly to the b. p. and kept under reflux for 8 hr. The mixture, after being cooled, was filtered and the *amide* was washed with boiling alcohol and water and dried. Recrystallised from anisole, it had m. p. 262—263° (5·6 g., 81·6%) (Found: N, 3·8; F, 5·1. $C_{21}H_{14}FNO_2$ requires N, 3·85; F, 5·2%).

1-*Amino*-2-*fluoroanthraquinone.*—The preceding sulphonamide (5 g.) was hydrolysed as described above. The *amine*, recrystallised from anisole, was bright red and had m. p. 228—229° (3·2 g., 96%) (Found: N, 5·8; F, 7·6. $C_{14}H_8FNO_2$ requires C, 5·8; F, 7·9%).

Sulphonation of 2-*Fluoroanthraquinone.*—2-Fluoroanthraquinone [1] (20 g.) was added to oleum (50 ml., made from 40 ml. of 24% oleum and 10 ml. of 66% oleum), and mercury sulphate (0·5 g.) was added with stirring. The solution was kept for 5 hr. at 125—130°, then cooled to room temperature and poured into hot water (60—70°; 700 ml.); this mixture was heated to the b. p. and filtered hot. The filtrate, while still hot, was mixed with sodium carbonate (15 g.) and kept at room temperature for 48 hr. The precipitate of sodium 6- or 7-fluoro-anthraquinone-1-sulphonate was filtered off, washed with saturated sodium sulphate solution to neutrality, and dried (yield, 24·7 g., 85%).

1-*Chloro*-6- *or* -7-*fluoroanthraquinone.*—The preceding salt (20 g.), treated as in the case

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[6] Whelen, U.S.P. 2,100,527; *Chem. Abs.*, 1938, **32**, 960.

described above, afforded the bright yellow 1-chloro-compound, m. p. 209—210° (from chlorobenzene) (14·1 g., 89%).

6- *or* 7-*Fluoro*-1-*toluene*-p-*sulphonamideanthraquinone*.—The sulphonamide (10 g.), m. p. 256—260°, prepared from the preceding the chloro-compound, was heated with stirring in concentrated sulphuric acid (50 ml.) for 1 hr. The resulting solution was poured on ice, and the free *amine* filtered off and washed with water to neutrality. Recrystallised from chlorobenzene it formed red crystals, m. p. 203—204° (6·1 g., 95%) (Found: N, 5·8; F, 7·55, 7·4. $C_{14}H_8FNO_2$ requires N, 5·8; F, 7·9%).

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