514. *The Orientation of Fluoranthene-4 : 12-disulphonic Acid.*

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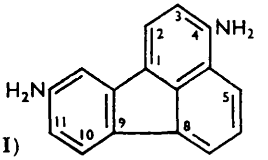
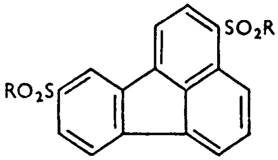
Fluoranthene-4 : 11- and -4 : 12-disulphonanilide have been synthesised. The second substance is identical with that obtained from the disulphonation product of fluoranthene, which is thus fluoranthene-4 : 12-disulphonic acid.[1]

Evidence advanced to show that the product obtained by disulphonation of fluoranthene is the 4 : 12-disulphonic acid [1] is not conclusive since it rests on the assumption that fusion of the acid with sodium hydroxide to give 4 : 12-dihydroxyfluoranthene is unattended by rearrangement. A rigorous proof of the constitution of the acid is now given. 4 : 12-Diaminofluoroanthene [2] (I), when diazotised and treated with sulphur dioxide, gives fluoranthene-4 : 12-disulphonyl chloride (II; R = Cl), which with aniline yields the disulphonanilide (II; R = NHPh), identical with that obtained from the disulphonation product of fluoranthene. This product is therefore fluoranthene-4 : 12-disulphonic acid (II; R = OH). Comparison of the chromatographic behaviour of the acid with that of naphthalene-2-sulphonic and -2 : 7-disulphonic acid showed that it contained a little monosulphonic acid and a trace of fluoranthene.



(I)



(II)

Fluoranthene-4 : 11-disulphonanilide has been synthesised from 4 : 11-diaminofluoranthene obtained from the corresponding carboxylic acid by the Curtius reaction.

Experimental

Fluoranthene-4 : 12-disulphonanilide.—Heating 4 : 12-diacetamidofluoranthene [2] (4 g.) with 30% hydrochloric acid (100 c.c.) for 2 hr. at 115° gave 4 : 12-diaminofluoranthene dihydrochloride, which was suspended in water (12 c.c.) and 38% hydrochloric acid (25 c.c.) and added in one operation to sodium nitrite (2·5 g.) in water (5 c.c.) at −10°. After 15 min. addition of cooled acetone (100 c.c.) precipitated the tetrazonium salt which was filtered off, washed with acetone, and at 10° added with stirring to a mixture of acetic acid (50 c.c.) saturated with sulphur dioxide, 38% hydrochloric acid (2 c.c.), and cuprous chloride (0·5 g.). The mixture was kept at 10—20° for 10 min., at 40° for 10 min., and at 80° for 10 min., cooled, and mixed with 10% hydrochloric acid (50 c.c.). The disulphonyl chloride which separated was washed with water, and dried in a vacuum at 35° (yield 3·45 g.). The compound was heated for ½ hr. in aniline (20 c.c.) at 95°, diluted with ethanol, and when poured into 10% hydrochloric acid gave *fluoranthene-4 : 12-disulphonanilide*, m. p. 271° (from chlorobenzene) (Found : C, 65·7; H, 4·1; N, 5·4; S, 12·2. $C_{28}H_{20}O_4N_2S_2$ requires C, 65·6; H, 3·9; N, 5·5; S, 12·5%).

Heating sodium fluoranthenedisulphonate with phosphorus pentachloride for 3 hr. at 145° gave the disulphonyl chloride, which (10 g.) was stirred with aniline (50 g.) at 95°. The magma obtained by cooling was stirred with 10% hydrochloric acid, and the crude fluoranthene-4 : 12-disulphonanilide after repeated crystallisation from *o*-dichlorobenzene, aniline, and chlorobenzene had m. p. 273°, undepressed when mixed with a sample prepared as above.

Fluoranthene-4 : 11-disulphonanilide.—Pyridine (18 g.) was added to fluoranthene-4 : 11-dicarboxylic acid (97 g.) in dry *o*-dichlorobenzene (3200 g.) with stirring at 145—155°, and then

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[1] Campbell and Keir, *J.*, 1955, 1233.

[2] Campbell, Leadill, and Wilshire, *J.*, 1951, 1404.

thionyl chloride (82·5 g.) in 10 min. After 20 min. the excess of thionyl chloride was removed by a current of air. Diethylaniline (25 g.) and portions of sodium azide (total 48 g.) in water (132 g.) were added with brisk stirring at 0—5° to the suspension of the acid chloride. 10% Hydrochloric acid (5 g.) was added and the mixture stirred at 0—5° for 7 hr. and at 20—22° for 7 hr. The resulting azide was washed successively with ethanol, water, and ethanol, and then dried as thoroughly as possible at the pump. The azide in toluene (750 g.) was freed from ethanol and water by distilling off toluene (350 g.) at 100—110 mm. The mixture was then heated at atmospheric pressure on the water-bath until reaction set in, the reaction being moderated by cooling if necessary. After ½ hr. on the water-bath the mixture was boiled for ½ hr., then cooled somewhat, absolute ethanol (145 g.) added, and the mixture boiled for 3 hr. Cooling deposited the *dicarbamate* (40 g.), m. p. 234—235° after crystallisation from chlorobenzene (charcoal) (Found : C, 69·9; H, 5·2; N, 7·7. $C_{22}H_{20}O_4N_2$ requires C, 70·2; H, 5·4; N, 7·5%).

The dicarbamate (100 g.) was added during 1 hr. to 73% sulphuric acid (1500 g.) at 130°, preferably after air has been displaced from the reaction vessel by nitrogen. After being stirred at 130—135° for ¾ hr. the mixture was allowed to cool completely without stirring. The disulphate separated, was washed with 60% sulphuric acid, suspended in water, and stirred with ammonia and ice. 4 : 11-*Diaminofluoranthene* separated and its solution in chloroform (1600 c.c.) after treatment with activated charcoal with light petroleum (b. p. 50—70°, 1350 c.c.) gave yellow plates or red matted needles, m. p. 162—163° (40 g.) (Found : C, 82·6; H, 5·5. $C_{16}H_{12}N_2$ requires C, 82·7; H, 5·2%).

The diamine (4·6 g.) in water (20 c.c.) and 20% hydrochloric acid (7 c.c.) was added to 38% hydrochloric acid (40 c.c.), and to the resulting suspension sodium nitrite (3·4 g.) in water (7 c.c.) was added in one operation with stirring at −10°. After 10 min. the solution was added at 0—5° to a mixture of acetic acid (160 c.c.) saturated with sulphur dioxide, 38% hydrochloric acid (7 c.c.), and cuprous chloride (1·6 g.). The mixture was heated for 15 min. to 70°, maintained at 70—80° for ½ hr., and mixed with water (150 c.c.) at 20°. Crude fluoranthene-4 : 11-disulphonyl chloride (6 g.) separated and when heated (1 hr.) with excess of aniline yielded the *disulphonanilide*, m. p. 303—305° after two crystallisations from *o*-dichlorobenzene (Found : C, 65·9; H, 4·0; N, 5·6%).

Chromatographic Behaviour of Fluoranthene-4 : 12-*disulphonic Acid, etc.*—The sulphonic acids were placed about 1 cm. from the centre of a 15 mm. Whatman No. 1 filter paper which was placed in a desiccator so that the centre of the paper rested on the end of a capillary tube dipping into a tube of the developing solution. A mixture of butanol (40 ml.), ethanol (10 ml.), water (49 ml.), and concentrated aqueous ammonia (1 ml.) was shaken and the butanol layer used as developer, and the aqueous layer placed in the desiccator to saturate the atmosphere. The chromatogram was examined in ultraviolet light; the spots produced showed that the monosulphonic acids travel much more rapidly to the edge of the paper than do the disulphonic acids. The fluoranthenedisulphonic acid was shown to contain only a small amount of monosulphonic acid along with a trace of fluoranthene.

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