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523. 1 : 1′-*Difluorodianthron*-9-*ylidene and an Attempted Synthesis of* 4 : 4′-*Dibromodianthron*-9-*ylidene.*

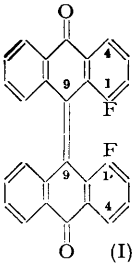
By Ernst D. Bergmann and H. J. E. Loewenthal.

Although 1 : 1′-substituents such as OMe, Br, or Me destroy the thermochromism of dianthron-9-ylidene, the small fluorine atom does not, since 1 : 1′-difluorodianthron-9-ylidene (I), which has been synthesized, is thermochromic.

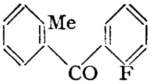
The bromine atom in 1-bromoanthraquinone is unusually labile.

It had been shown that substituents (*e.g.*, Br, Me, OMe) in the 1 : 1′-positions of dianthron-9-ylidene destroy the thermochromism of the parent substance (Bergmann and Loewenthal, *Bull. Soc. chim.*, 1952, **19**, 66). In view of the theoretical significance of this effect, it seemed worthwhile to establish whether it is dependent on the volume of the substituents. This is indeed so. 1 : 1′-Difluorodianthron-9-ylidene (I) has been synthesized and proved thermochromic; its solutions in diphenyl ether became, reversibly, green on heating.

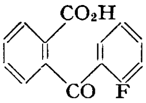
For the synthesis of (I), 4-fluoroanthrone (V) was prepared. *o*-Fluorobenzonitrile and *o*-tolylmagnesium bromide gave 2′-fluoro-2-methylbenzophenone (II). Selenium dioxide, which has been applied to similar cases before (*Organic Reactions*, 1949, **5**, 173), oxidized (II) to 2-*o*-fluorobenzoylbenzoic acid (III). The corresponding 2-*o*-fluorobenzylbenzoic acid (IV) was cyclized to (V). This was dehydrogenated with ferric chloride (Dimroth, *Ber.*, 1901, **34**, 219) to the corresponding dianthron-9-yl (VI), and the enol form of the latter with *p*-benzoquinone (Schönberg and Ismail, *J.*, 1944, 307) gave the desired 1 : 1′-difluorodianthron-9-ylidene (I). It is interesting that in distinction from other 1 : 1′-disubstituted dianthronyls, (VI) enolizes as easily as the unsubstituted parent compound.



(I)



(II)



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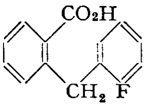
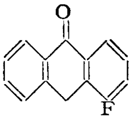


(IV)



(V)

In connection with these experiments, an attempt was made to prepare 4 : 4′-dibromodianthron-9-ylidene, the only symmetrically dibrominated compound of this series still unknown. This was thwarted by the surprising lability of the bromine atoms, which is paralleled by, but far greater than, that of the bromine atoms in bromo-substituted *o*-benzoylbenzoic acids towards alkaline reducing agents (Bergmann and Loewenthal, *loc. cit.*). As the routes analogous to the synthesis of (V) appeared to be very cumbersome, the possibility of the reduction of 1-bromoanthraquinone to 1-bromoanthrone (VII) was explored; it was known (Attree and Perkin, *J.*, 1931, 144; Barnett and Matthews, *J.*, 1923, **123**, 2549) that, *e.g.*, 1-chloro- and 1-methoxy-anthraquinone give, by this method, the corresponding 1-substituted anthrones. Indeed, reduction of 1-bromoanthraquinone with copper and concentrated sulphuric acid gave a product which was extremely unstable in air and for this reason could not be the known stable alternative reduction product 4-bromoanthrone. Ferric chloride oxidation of the crude product, which is considered to be (VII), gave a dianthron-9-yl, presumably the 4 : 4′-dibromo-compound (VIII); but in spite of repeated recrystallisations, bromine analysis gave low values. Further dehydrogenation of (VII) with *p*-benzoquinone gave a strongly thermochromic product which, however, according to the bromine analysis contained only 24% of a dibromodianthron-9-ylidene.

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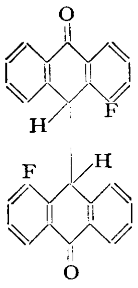
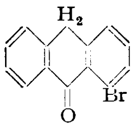
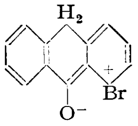
The instability of the bromine atom in these compounds is somewhat surprising; perhaps it is due to the existence of zwitterionic forms, *e.g.*, (VII*a*). The halogen atoms in 1-halogenoanthraquinones are known to be readily reduced out (cf. Kirchner, *Annalen*, 1887, **238**, 345); *e.g.*, refluxing these compounds in nitrobenzene in presence of copper powder and potassium acetate causes hydrogenolysis of the C–Hal bond (Ullmann and Minajeff, *Ber.*, 1912, **45**, 687).



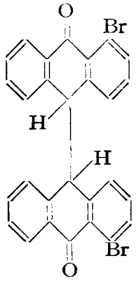
(VI)



(VII)



(VII*a*)



(VIII)

EXPERIMENTAL

2'-*Fluoro-2-methylbenzophenone* (II).—From *o*-fluorobenzoic acid (Schiemann, *J. pr. Chem.*, 1934, **140**, 97), the nitrile (b. p. 92—95°/22 mm.) was prepared *via* the amide, according to Borsche and Wagner-Roemmich (*Annalen*, 1941, **546**, 273), in 62% yield. A solution of the nitrile (17·5 g.) in dry benzene (100 ml.) was added to *o*-tolylmagnesium bromide [from *o*-bromotoluene (30·4 g.) and magnesium (4·1 g.) in ether (125 ml.)]. The ether was distilled off, and the benzene solution refluxed for 7 hr. and worked up as usual for this type of reaction (see, *e.g.*, Schlenk and Bergmann, *ibid.*, 1928, **464**, 34). The *ketone* (II) distilled as an almost colourless oil, b. p. 125—130/1 mm. (23·5 g., 76·5%), $n_{\rm D}^{20}$ 1·5800 (Found : C, 78·8; H, 5·1. $C_{14}H_{11}OF$ requires C, 78·5; H, 5·1%). The 2 : 4-dinitrophenylhydrazone separated after several days. Recrystallization from ethyl acetate–ethanol gave orange needles, m. p. 184°.

2-o-*Fluorobenzoylbenzoic Acid* (III).—The preceding ketone (8·7 g.) and selenium dioxide (11 g.) were refluxed together in nitrobenzene (50 ml.) for 4 hr. After cooling, the mixture was diluted with ether, filtered from selenium, and extracted with a total of 90 ml. of 10% sodium carbonate solution. The alkaline extracts were saturated with carbon dioxide, treated with charcoal, and filtered. Acidification gave the crude *acid*, m. p. 138—139·5° (5·2 g., 56%). Recrystallization from benzene–heptane and subsequently from water raised the m. p. of the colourless needles to 140° (Found : C, 69·1; H, 4·1. $C_{14}H_9O_3F$ requires C, 68·9; H, 3·7%).

2-o-*Fluorobenzylbenzoic Acid* (IV).—This acid was obtained from the keto-acid (3·8 g.) by means of activated zinc dust and ammonia (Bergmann and Loewenthal, *loc. cit.*) (yield, 3·4 g., 94·5%). The *acid* formed colourless needles, m. p. 116—117°, from heptane and depressed the m. p. of *o*-benzylbenzoic acid which melts at the same temperature (Found : C, 72·5; H, 4·9. $C_{14}H_{11}O_2F$ requires C, 73·0; H, 4·8%).

4-*Fluoroanthrone* (V).—Cyclisation of the preceding acid (3·2 g.) with sulphuric acid (20 ml.) at room temperature proceeded slowly. Recrystallization of the *anthrone* from methanol gave 2·25 g. (76%) of yellowish needles, m. p. 143° (Found : C, 79·1; H, 4·5. $C_{14}H_9OF$ requires C, 79·2; H, 4·3%).

1 : 1'-*Difluorodianthron-9-yl* (VI).—A mixture of 4-fluoroanthrone (V) (2·2 g.), glacial acetic acid (11 ml.), ferric chloride (2·2 g.), and sodium acetate (2·2 g.) was kept at 100° for 1·5 hr. After cooling and dilution with ice-cold methanol, the greyish crystals were filtered off (yield, 1·8 g.). Addition of water to the filtrate gave a second crop of 0·2 g. (total yield, 91%). Recrystallization from benzene–heptane gave the *product* as slightly yellow prisms, m. p. 212·5—213° (Found : C, 79·2; H, 4·0. $C_{28}H_{16}O_2F_2$ requires C, 79·6; H, 3·7%).

1 : 1'-*Difluorodianthron-9-ylidene* (I).—The dianthronyl (1·4 g.) was enolized (Bergmann and Loewenthal, *loc. cit.*) in less than 10 min. Oxidation of the dianthranol with *p*-benzoquinone proceeded without occurrence of the usual transient green colour; 1 : 1'-*dianthronylidene* was precipitated immediately in 86% yield (1·2 g.). From chloroform–xylene, it crystallized in very pale yellow needles, m. p. >360°. It was slightly, but definitely thermochromic (reversibly) in boiling diphenyl ether, and remained unchanged on irradiation of its solution

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(Found : C, 80·0; H, 3·6; F, 8·7, 9·0. $C_{28}H_{14}O_2F_2$ requires C, 80·8; H, 3·3; F, 9·0%). The fluorine determination was carried out according to Clark (*Analyt. Chem.*, 1951, **23**, 659), and the estimation of carbon and hydrogen according to Bodenheimer and Goldstein (*Bull. Res. Council Israel*, 1953, **3**, in the press).

4 : 4′-*Dibromodianthron*-9-*yl* (?) (VIII).—1-Bromoanthraquinone (3·0 g.), prepared by cyclisation of 2-benzoyl-3-bromobenzoic acid (von Pechmann, *Ber.*, 1879, **12**, 2123; cf. Bergmann and Loewenthal, *loc. cit.*) with sulphuric acid at 160—180°, was dissolved in concentrated sulphuric acid (45 ml.), and copper powder (3 g.) was added in portions at 25—30°, with stirring. The colour changed slowly from red to greenish-brown. After 0·5 hr., the mixture was slowly heated to 50°, whereupon a yellow precipitate was formed. After 1 hr., the mixture was poured on ice, and the precipitate washed, dried *in vacuo*, and extracted thoroughly with chloroform. The filtered extract was evaporated to a small volume, and boiling ethanol (40 ml.) added. There separated yellowish crystals (1·0 g.), m. p. 235—237° (open capillary). By addition of water to the filtrate, a second crop (1·1 g.) of the same m. p. was obtained. As the m. p. of the product, when determined in an evacuated capillary, was 131—137° (after sintering), the 1-bromoanthrone (VII) which appears to have been formed is evidently oxidized with extreme ease. It could, therefore, not be obtained analytically pure and was dehydrogenated directly with ferric chloride. Thus were obtained 1·75 g. (58%) of the dianthron-9-yl (VIII), m. p. 246—247°. Repeated recrystallization from benzene–ethanol gave pale yellow needles of m. p. 248—249°, which, however, contained less than the theoretical quantity of bromine (Found : Br, 23·0%). Enolized and oxidized in the normal manner, they gave a highly thermochromic (hot xylene) yellow product (m. p. 290—300°); however, the treatment had resulted in loss of most of the bromine (Found : Br, 7·0%).

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[*Received, April* 15*th*, 1953.]