crystalline products obtained. The compound with m.p. 256–258° was acetylated by heating it in acetic anhydride – sulfuric acid (12), giving a product, m.p. 193–194°, corresponding to the triacetate of emodin (14). The infrared spectrum (KBr) of the product, m.p. 256–258°, was identical with that of emodin.

Thin-Layer Chromatography

Thin-layer chromatography was performed on silica gel G made up in water (15) (method 1) and on silica gel G made up in 0.5 *N* oxalic acid (16) (method 2). The plates were dried at room temperature for 15 min and at 100° for 30 min. Examination of the total pigment by method 1 with petroleum ether – ethyl acetate (9:1) gave three spots: yellow, light pink, and dark pink (in order of decreasing R_f values). The first two appeared to be the major components, showed pronounced "tailing", and were identified as pachybasin and chrysophanol, respectively; the third spot corresponded to emodin.

Repetition of the thin-layer chromatography by method 2 with benzene – ethyl acetate (9:1) gave six spots. The first, and largest, spot was a mixture of pachybasin and chrysophanol, and the third was emodin. The fractions from the chromatography were also examined by both methods to give the results noted in Tables I–III.

Purification of Emodin

The commercial sample of emodin had m.p. 253–257° and showed two closely spaced spots on thin-layer chromatography by method 2. An ether solution of the sample was extracted with 10% NH_4OH, and the ammonia extract was acidified and re-extracted with ether. The product was recrystallized from chloroform, had m.p. 258–260°, and showed only one spot on thin-layer chromatography.

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Fluoranthene studies. II. Bromination of 2-nitro- and 2-acetamido-fluoranthene

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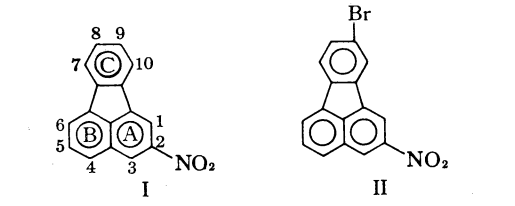
As the result of the nitration of 3-acetamidofluoranthene in the 2-position, Kloetzel *et al.* (1) postulated that a strongly activating substituent in the A ring of fluoranthene would cause further substitution to occur in the same ring. This was further substantiated in 1964 when Charlesworth and Blackburn (2), in the first paper of this series, showed that 3-acetamido- and 3-amino-fluoranthene were brominated in the 2-position.

It seemed desirable to study the influence of strongly activating and deactivating substituents in other positions in the A ring, particularly the 2-position. The directive properties of the 2-acetamido and the 2-nitro groups are reported in this note.

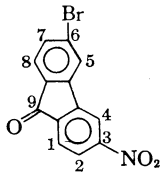
2-Nitrofluoranthene (I) was brominated

in nitrobenzene at room temperature to give 9-bromo-2-nitrofluoranthene (II). The 9-position of the bromine was established in the following manner. Oxidation of II with chromic acid gave an acidic substance which contained both nitrogen and bromine, thus indicating that the unsubstituted ring of the naphthalene nucleus, i.e. the B ring, had cleaved as expected, giving 3-nitro-6-bromofluorenone-1-carboxylic acid and, on decarboxylation, 3-nitro-6-bromofluorenone (III).

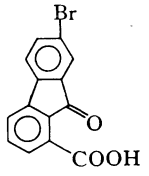


I

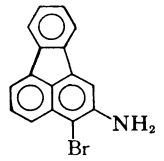
II



III



IV



V

Hydrogenation of II followed by acetylation gave 9-bromo-2-acetamidofluoranthene. This compound was also oxidized with chromic acid and yielded an acidic product IV which contained bromine, but no nitrogen, thus indicating that the A ring had cleaved. The oxidation products III and IV indicated that the bromine atom must be in the C ring of II. IV was found to have the same melting point as 7-bromofluorenone-1-carboxylic acid. Admixture with an authentic sample prepared by the bromination of fluorenone-1-carboxylic acid by the method of Campbell *et al.* (3) gave no depression in the melting point.

Hydrogenation of I followed by acetylation yielded 2-acetamidofluoranthene. On bromination and removal of the acetyl group, 3-bromo-2-aminofluoranthene (V) was obtained. Elimination of the amino group in the conventional manner gave a compound identical with 3-bromofluoranthene prepared from 3-aminofluoranthene.

The above results demonstrate that Campbell and Kier's rule (4) for deactivating substituents and the rule of Kloetzel *et al.* (1) for strongly activating substituents are also applicable to substituents in the 2-position.

2-Chloro-, 2-iodo-, and 2-fluoro-fluoranthene have been prepared from 2-aminofluoranthene by following the method which was developed by Charlesworth and Blackburn (2) for the diazotization of weak polycyclic amines and which led to 2-bromofluoranthene.

EXPERIMENTAL

A supply of 2-nitrofluoranthene (I) was built up from fluoranthene (Matheson, P1214) through the eight steps employed by Kloetzel *et al.* (1).

9-Bromo-2-nitrofluoranthene (II)

2-Nitrofluoranthene (3.0 g) was stirred in nitrobenzene (50 ml), and a small amount of insoluble material was removed by filtration. Bromine (1.28 ml) was added dropwise to the above solution at room temperature. Stirring was continued for 3 h, during which time a solid precipitated. The mixture was filtered and the precipitate washed with cold ethanol (50 ml, 95%). It was then recrystallized from glacial acetic acid (charcoal). 9-Bromo-2-nitrofluoranthene (2.2 g, 56%) was thus obtained as flat yellow plates, m.p. 240–243 °C.

Anal. Calcd. for $C_{16}H_8O_2NBr$: C, 58.9; H, 2.45; N, 4.29; Br, 24.5. Found: C, 58.6; H, 2.85; N, 4.13; Br, 24.8.

9-Bromo-2-acetamidofluoranthene

The previous 9-bromo-2-nitrofluoranthene (2.2 g) was reduced by hydrogenation in absolute ethanol (110 ml) in the presence of platinum oxide (0.025 g) at a pressure of 40 p.s.i. for 24 h. The catalyst was filtered off and the amine precipitated with a 10% solution of sodium hydroxide. The precipitate was collected, washed with water, and dried. The crude amine (1.8 g) thus obtained had a melting point range of 115–122 °C. Since various methods of purification failed to yield an analytically pure sample of the amine, some of the crude amine (0.6 g) was dissolved in benzene (60 ml). Acetic anhydride (0.8 ml) was added and the mixture stirred for 1 h, during which time a solid precipitated. The mixture was filtered and the precipitate was washed with benzene and allowed to dry. The crude product (0.49 g) was crystallized from glacial acetic acid (charcoal) as yellow needles which melted at 251–253 °C.

Anal. Calcd. for $C_{18}H_{12}ONBr$: C, 64.1; H, 3.26; N, 4.15; Br, 23.7. Found: C, 64.7; H, 3.84; N, 4.16; Br, 23.8.

Oxidation of 9-Bromo-2-acetamidofluoranthene

Chromium trioxide (1.2 g) in water (7.0 ml) and glacial acetic acid (5.0 ml) was added slowly, with

stirring, to a mixture of 9-bromo-2-acetamidofluoranthene (0.64 g) in glacial acetic acid (75 ml) at room temperature. The resulting mixture was stirred overnight and then refluxed for 2 h. Removal of half the solvent by distillation, and precipitation with water gave the crude product (0.41 g). Crystallization from glacial acetic acid (charcoal) yielded pure 7-bromofluorenone-1-carboxylic acid (IV) as orange-red needles which melted at 226–229 °C.

Anal. Calcd. for $C_{14}H_7O_3Br$: Br, 26.37. Found: Br, 26.35.

Admixture with an authenic sample of 7-bromofluorenone-1-carboxylic acid prepared by the method of Campbell *et al.* (3) gave no depression in the melting point.

Oxidation of 9-Bromo-2-nitrofluoranthene (II)

An oxidizing solution was prepared by dissolving chromic oxide (2.0 g) in water (12 ml) and glacial acetic acid (8.0 ml). This solution was added, with stirring, to a mixture of 9-bromo-2-nitrofluoranthene (1.0 g) in glacial acetic acid (140 ml). The reaction mixture was stirred at room temperature for 12 h and then refluxed for a further 8 h. Upon removal of half the solvent by distillation and cooling, 6-bromo-3-nitrofluorenone-1-carboxylic acid (0.4 g) separated as bright-yellow crystals which melted at 283.5–286 °C.

Anal. Calcd. for $C_{14}H_6O_5NBr$: C, 48.3; H, 1.74; N, 4.02; Br, 23.0. Found: C, 48.6; H, 1.69; N, 3.94; Br, 23.4.

Decarboxylation of 6-Bromo-3-nitrofluorenone-1-carboxylic Acid

The above bromonitro acid (0.22 g) was refluxed in pyridine (25 ml) with a trace of copper powder for 11 h. The cooled reaction mixture was poured into dilute hydrochloric acid and the precipitate filtered off. The dried material was stirred with hot benzene, and a small amount of insoluble material was filtered off and discarded. The aqueous acid filtrate was also extracted with benzene. The benzene extracts were combined and washed with aqueous sodium carbonate solution (15%) until there was no visible change in the carbonate solution, and then with water. The benzene solution was dried with anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure left a solid residue which, when treated with decolorizing charcoal and recrystallized from glacial acetic acid, gave beautiful golden needles (0.028 g) of 6-bromo-3-nitrofluorenone (III), m.p. 327–330 °C.

Anal. Calcd. for $C_{13}H_6O_3NBr$: C, 51.4; H, 1.99; N, 4.61; Br, 26.3. Found: C, 51.6; H, 2.45; N, 4.34; Br, 23.4.

It is evident from the analysis that the decarboxylation was accompanied by a little debromination. This was not unexpected, since the lability of bromine in the 3-position of fluorenone has long been known (5).

3-Bromo-2-acetamidofluoranthene

Bromine (1.1 ml) was added, with stirring, to a solution of 2-acetamidofluoranthene (2.4 g), prepared by the method of Kloetzel *et al.* (1), in pyridine (150 ml). Stirring was continued at room temperature for 11 h. The crude product was precipitated with water (400 ml), filtered off, and washed successively with 10% solutions of sodium hydroxide and sodium bisulfite and finally with water. It was then dissolved in boiling pyridine (45 ml), a small amount of insoluble material being filtered off and discarded. The filtrate was treated with charcoal, and sufficient water was added to bring about precipitation when the pyridine–water solution cooled. 3-Bromo-2-acetamidofluoranthene (3.0 g, 94%) was thus obtained as straw-colored needles, m.p. 223.5–225.5 °C.

Anal. Calcd. for $C_{18}H_{12}ONBr$: N, 4.11; Br, 23.1. Found: N, 4.15; Br, 23.7.

3-Bromo-2-aminofluoranthene (V)

3-Bromo-2-acetamidofluoranthene (2.3 g) was added to a mixture of methanol (125 ml), pyridine (85 ml), and sodium hydroxide (7.2 g). The resulting solution was heated to the boiling point and the reaction mixture was allowed to reflux for 12 h. On dilution to 1 l with water, a yellow flocculent precipitate was formed. This was collected, washed with water, dried, and dissolved in boiling pyridine. After treatment with charcoal, sufficient water was added to cause crystallization when the solution cooled. The 3-bromo-2-aminofluoranthene (1.6 g) thus obtained melted at 150.5–152 °C, with slight decomposition.

Anal. Calcd. for $C_{16}H_{10}NBr$: N, 4.73; Br, 27.0. Found: N, 4.41; Br, 26.9.

Deamination of 3-Bromo-2-aminofluoranthene (V)

Sodium nitrite (0.6 g) was added cautiously, with stirring, to a solution of concentrated sulfuric acid (45 ml) and water (3.2 ml) at room temperature. When all the sodium nitrite had dissolved the solution was cooled to −5 °C. Finely ground 3-bromo-2-aminofluoranthene (1.0 g) was added slowly, with vigorous stirring, to the above solution over a period of 15 min, the temperature being maintained at −5 °C. Stirring was continued at this temperature for 1 h. Pre-cooled hypophosphorous acid (65 ml) was then added at such a rate (2½ h) that the temperature at no time rose above 5 °C. The reaction mixture was then allowed to stand at 2–3 °C for 4 days, after which time the product was allowed to coagulate, filtered off, dried, and dissolved in hot benzene, a small amount of insoluble material being discarded. The benzene solution was washed with concentrated sulfuric acid until the acid layer no longer became colored, then with 10% sodium carbonate solution, and finally with water. It was dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the solid residue was crystallized twice from 95% ethanol (charcoal). 3-Bromofluoranthene (0.3 g) was thus obtained as pale-yellow needles which melted at 104.0–105.5 °C.

Anal. Calcd. for $C_{16}H_9Br$: Br, 28.4. Found: Br, 28.1.

The melting point is in good agreement with previous literature figures (m.p. 103 °C (6) and 110 °C (7)). Admixture with an authenic sample of

3-bromofluoranthene obtained by a Sandmeyer reaction on 3-aminofluoranthene gave no depression in the melting point. Comparison of the infrared spectra of the two samples also confirmed their identity.

2-Chlorofluoranthene

The method was that used by Charlesworth and Blackburn (2) for the corresponding 2-bromofluoranthene.

2-Aminofluoranthene (4.0 g) was diazotized as described and allowed to react with a pre-cooled solution of cuprous chloride (20 g) in concentrated hydrochloric acid (150 ml) and water (30 ml). The solid left after evaporation of the benzene was subjected to sublimation twice at approximately 95 °C under a high vacuum. 2-Chlorofluoranthene (1.3 g) was obtained as pale-yellow needles, m.p. 87.5–88.5 °C.

Anal. Calcd. for $C_{16}H_9Cl$: Cl, 15.0. Found: Cl, 15.0.

2-Iodofluoranthene

2-Aminofluoranthene diazotized as described was poured into a cold solution of potassium iodide (30.0 g) in water (100 ml). The resulting mixture was allowed to stand overnight and worked up as previously described. The 2-iodofluoranthene was obtained by crystallization of the crude product from 95% ethanol. It melted at 124.0–125.5 °C.

Anal. Calcd. for $C_{16}H_9I$: I, 38.7. Found: I, 37.2.

2-Fluorofluoranthene

This substance was prepared by a modified Schiemann reaction as described by Fletcher and Namkung (8) for 3-fluorofluoranthene.

2-Aminofluoranthene (1.5 g) treated by this method gave a product which, after two sublimations at 80° (high vacuum) and recrystallization from 95% ethanol (charcoal), melted at 88–89 °C (0.2 g).

Anal. Calcd. for $C_{16}H_9F$: C, 87.3; H, 4.08; F, 8.63. Found: C, 87.4; H, 4.50; F, 8.54.

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Erratum: Pyrrole chemistry. IV. The preparation and some reactions of brominated pyrrole derivatives

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(Ref. Can. J. Chem. 43, 409 (1965))

On page 409, paragraph 2, line 6 should read "containing mostly the 5-formyl-2-ester along with some of the 4-formyl-2-ester."

On page 414, paragraph 2, line 3 should read "From the formyl-2-ester, m.p. 121–122°, was obtained methyl 2,4-pyrroledicarboxylate, m.p. 126–127°;" and line 6 should read "From the formyl-2-ester, m.p. 92–93°, was obtained methyl 2,5-pyrroledicarboxylate, m.p. 128.5–129.5°".

On page 414, paragraph 3, line 1 should read "The now proven methyl 5-formyl-2-pyrrolecarboxylate (m.p. 92–93°) was converted into its oxime, m.p. 123–124°, and dehydrated with hot acetic anhydride (28) to the corresponding methyl 5-cyano-2-pyrrolecarboxylate. Similarly the 4-formyl-2-ester was converted by way of its oxime, m.p. 204–205°, into methyl 4-cyano-2-pyrrolecarboxylate."

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