FLUORANTHENE STUDIES

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ABSTRACT

3-Acetamido- and 3-amino-fluoranthene are brominated in the 2-position. Two new fluoranthene compounds are reported: 2-bromo-3-acetamidofluoranthene and 2-bromofluoranthene. The theoretical implications of these results are discussed.

INTRODUCTION

Comparatively few disubstituted derivatives of fluoranthene* have been made by further reaction on monosubstituted derivatives and not too much is known regarding the directive influence of these substituents. It is known that, in general, compounds containing meta-directing groups in the 3-position undergo further substitution in the 9-position. 3-Bromofluoranthene on further bromination gives the 3,8-dibromo compound. On the basis of these data, Campbell and Keir (3) postulated in 1955, that a metadirecting group in ring A would direct to position 9 and an ortho-para directing group would direct to position 8. In the following year Kloetzel, King, and Menkes (4) showed that the above rule was over-simplified, as 3-acetamidofluoranthene was found to nitrate in the 2-position. They considered that the greater activating influence of the acetamido group activates the ring to which it is attached and substitution occurs in the same ring. It seemed desirable to study further examples of strongly activating directors such as the acetamido and amino groups under brominating conditions.

3-Acetamidofluoranthene (III) was brominated at room temperature in pyridine to give the 2-bromo-3-acetamido derivative (IV). Hydrolysis of IV in pyridine – methanol – sodium hydroxide gave 2-bromo-3-aminofluoranthene (II).

Attempts to establish the orientation of the bromine in IV by diazotization and a Sandmeyer reaction on 2-amino-3-acetamidofluoranthene (X) failed. The usual high sulphuric acid concentration required for diazotization of weak, insoluble amines of this type resulted in tar formation. This was due to the instability of the amine sulphate, as this salt, prepared in ether, decomposed when separated from the ether.

The 2-position of the bromine atom has been established in the following manner. If the two substituents are in the same ring, oxidation of IV would destroy this ring, whereas if the groups were in different rings, only the ring containing the amino group could be destroyed and a bromo-1-fluorenonecarboxylic acid would result. Oxidation with chromic anhydride in glacial acetic acid gave 1-fluorenonecarboxylic acid (V) identical with an authentic sample. That the bromine is in the 2-position in the A ring has been established through the 2-nitro-3-acetamido compound (VI) whose orientation was previously established by Kloetzel *et al.* (4). By hydrolysis and deamination of VI they obtained 2-nitrofluoranthene (VII) and by reduction 2-aminofluoranthene (VIII).

Attempted diazotization of VIII under the conventional high-acid concentration required for weak insoluble amines gave an unsatisfactory product. In this diazotization (and in the diazotization of I for practice) side reactions were largely avoided by isolation of the amine sulphate which was then dissolved in a concentrated sulphuric and acetic

*For excellent reviews of fluoranthene chemistry up to 1951, see references 1 and 2.

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acid mixture and diluted for diazotization. This valuable method is fully described in the experimental preparation mentioned. A Sandmeyer reaction on the diazonium sulphate solution gave an authentic sample of 2-bromofluoranthene (IX). By deamination of II, IX is also obtained. Thus the orientation of the bromine in the original bromination has been established.

The direct bromination of 3-aminofluoranthene (I) is recorded in a German patent by Meyer and Falta (5), but they did not establish the orientation of the halogen. They

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report a melting point of 166–167° C, but our purest product by their method melted at 152–158° C. Comparison of the nuclear magnetic resonance spectra indicates that this is an impure specimen of 2-bromo-3-aminofluoranthene which melts at 176–177° C. Thus direct bromination of 3-aminofluoranthene (II) occurs largely in the 2-position, but a purer product is obtained via the 3-acetamidofluoranthene (III).

These results substantiate those of Kloetzel *et al*. that an intensely activating substituent in fluoranthene causes further substitution in the same ring.

EXPERIMENTAL

3-Nitrofluoranthene was prepared by the method of Garascia, Fries, and Ching (6), reduced to 3-aminofluoranthene (I), and acetylated to the 3-acetamido derivative (III) by following the directions of Kloetzel, King, and Menkes (4).

2-Bromo-3-acetamidofluoranthene (IV)

Bromine (5 ml) was added, with stirring, to a solution of 3-acetamidofluoranthene (10.0 g) in technical grade pyridine (700 ml). The reaction was allowed to proceed at room temperature for 10 hours. The crude product was precipitated by addition of water (2 liters), filtered off, and washed successively with 10% aqueous solutions of sodium hydroxide and sodium bisulphite. The resulting material was placed in pyridine (20 ml) and heated to the boiling point. The insoluble material was filtered from the hot pyridine solution and discarded. The filtrate was treated with charcoal and then sufficient water was added to cause crystallization when the pyridine-water solution cooled. The 2-bromo-3-acetamidofluoranthene (7–8 g) was obtained as yellow flakes which melted at 266–267° C (decomp.). Found: N, 4.2; Br, 23.3; acetyl, 13.1%. Calc. for C₁₈H₁₂NBrO: N, 4.1; Br, 23.6; acetyl, 12.7%.

2-Bromo-3-aminofluoranthene (II)

The previous 2-bromo-3-acetamidofluoranthene (10.3 g) was hydrolyzed by heating under reflux for 12 hours in a solution of methanol (600 ml), pyridine (400 ml), and sodium hydroxide (30 g). A small amount of insoluble material was filtered off and discarded. The crude product was precipitated by dilution to 4 liters with water. The collected material was washed with water, dried, and dissolved in boiling pyridine. A small amount of insoluble material was filtered off and the filtrate was heated with charcoal. Sufficient water was added to cause crystallization when the solvent cooled. 2-Bromo-3-aminofluoranthene (7.2 g) was thus obtained as beautiful yellow needles, m.p. 176–177° C (decomp.). Found: N, 4.6; Br, 27.6%. Calc. for $C_{16}H_{10}NBr$: N, 4.7; Br, 27.0%.

Oxidation of 2-Bromo-3-aminofluoranthene

This was accomplished by heating 2-bromo-3-aminofluoranthene (2.0 g) under reflux for 5 hours with sodium dichromate (20 g) in glacial acetic acid (100 ml). This treatment caused evolution of bromine in gaseous form. The reaction mixture was poured into a solution of concentrated sulphuric acid (100 ml) in water (700 ml). The solid which precipitated was filtered off and heated in an aqueous solution of sodium carbonate. The insoluble material was filtered from the carbonate solution and discarded. The filtrate from the diluted reaction mixture was extracted with benzene. The benzene extract was in turn treated with carbonate solution, and the carbonate solutions combined. Acidification of the carbonate solution with sulphuric acid produced crude 1-fluorenonecarboxylic acid. The acid was dried and taken up in boiling o-xylene (100 ml). The acid was recovered by extraction with aqueous carbonate solution and acidified. Recrystallization from glacial acetic acid gave 1-fluorenonecarboxylic acid (0.53 g), m.p. 185–189° C. Admixture with an authentic sample prepared by oxidation of fluoranthene by the method of Fieser and Seligman (7) gave no depression in melting point. Comparison of the infrared spectra also proved the identity.

Treatment of the two samples of 1-fluorenonecarboxylic acid with p-nitrophenylhydrazine gave the same derivative as fine yellow-orange microcrystals which melted at 307–308° C and with no depression on mixing.

Preparation of 2-Bromofluoranthene (IX)

(a) from 2-Aminofluoranthene (VIII)

2-Nitrofluoranthene (VII) was made from 3-acetamidofluoranthene (III) as shown on the flow sheet according to the directions of Kloetzel *et al.* (4). Reduction of the nitro group gave 2-aminofluoranthene (VIII).

Crude 2-aminofluoranthene (2.0 g) was stirred in dry ether (170 ml) and the insoluble material filtered off. Concentrated sulphuric acid (1 ml) was added with stirring to the amine solution. The amine sulphate was filtered off, allowed to dry, and finely ground. The salt was dissolved in a vigorously stirred solution of concentrated sulphuric acid (75 ml) and glacial acetic acid (75 ml) with gentle warming. The solution was cooled and 150 g of ice and water were added rapidly with stirring to precipitate the amine salt in finely divided condition. The salt was diazotized at 15-20° C by addition of sodium nitrite (1.6 g) in water (10 ml). The diazonium solution was poured, with stirring, into a solution of cuprous bromide (15 g) in 48% hydrobromic acid (70 ml) and water (30 ml). The mixture was heated slowly, with stirring, to 95° C. The cooled reaction mixture was diluted with water and the precipitate filtered off. The dried material was stirred with hot benzene and the insoluble material discarded. The aqueous filtrate from above was also extracted with benzene. The benzene extracts were combined and washed with an aqueous sodium hydroxide and sodium bisulphite solution. The benzene was then washed with concentrated sulphuric acid until further washing caused no visible change in the benzene solution. The benzene solution was now washed with an aqueous sodium carbonate solution, which was discarded. The benzene was removed by evaporation to dryness. Sublimation of the solid residue, at approximately 100° C under high vacuum, gave 2-bromofluoranthene (1.1 g) as a light yellow powder, m.p. 102-104° C. Found: C, 67.7; H, 3.39; Br, 27.3; N, 1.17%. Calc. for C16H9Br: C, 68.4; H, 3.23; Br, 28.4%. The analysis indicates some nitrogen containing impurity was present.

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

Sodium nitrite (0.75 g) was added slowly with stirring to a solution of concentrated sulphuric acid and water (4.2 ml) at room temperature. The solution was then cooled to -5° C and finely ground 2-bromo-3aminofluoranthene (1.16 g) was then added with vigorous stirring over a 15-minute period, the temperature being maintained at -5° C. Stirring was continued for another 45 minutes at this temperature. Then precooled 50% hypophosphorous acid (85 ml) was added to the stirred solution at such a rate that the temperature did not exceed 5° C. This took about $2\frac{1}{2}$ hours. After 1 week, at 2–3° C, the reaction mixture was diluted with water to 1 liter. The precipitate was allowed to coagulate and then filtered off. The dried material was treated with benzene (250 ml) as previously described under (a). The sublimed pale yellow 2-bromofluoranthene (0.75 g) melted at 101-103° C. Found: C, 68.3; H, 3.32; Br, 28.8%. Calc. for C16H9Br: C, 68.4; H, 3.23; Br, 28.4%. A mixed melting point with sample (a) showed no depression.

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