

PART A

STUDIES OF 1-SUBSTITUTED FLUORANTHENES

PART B

SYNTHESIS OF SOME 3,6-DISUBSTITUTED FLUORENONES

By

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ABSTRACT

PART A

1-Nitro-, 1-acetamido- and 1-bromofluoranthene unlike the corresponding 2- and 3-substituted fluoranthenes all dibrominate in positions 4 and 9. The theoretical implication of this has been discussed. With excess bromine and heat on 1-nitrofluoranthene, six bromines entered the structure and the nitro group was completely lost. 1-Acetamido- and 1-bromofluoranthene tribrominate in positions 4,8 and 9. Side chain bromination of 1-acetamidofluoranthene was accomplished using pyridine hydrobromide perbromide. Both 1-bromo- and 1-hydroxyfluoranthene have been synthesized from the amine through diazonium reactions. 3-Acetamidofluoranthene was found to brominate in position 2 in carbon tetrachloride just as it did in acetic acid and in carbon tetrachloride: acetic acid 1:2.

1-Nitro- and 1-acetamidofluoranthene have been nitrated to give dinitro derivatives. A mono nitro derivative was also obtained in the case of the acetamido compound. The orientations of these compounds have not been rigidly established. New amino and acetamido compounds have been derived from these. During the course of this work, twenty-one new compounds have been synthesized.

PART B

Following the scheme of Charlesworth and Mathiapparanam (1) for the synthesis of 3,6-disubstituted unsymmetrical fluorenones, the synthesis of 3-chloro-6-nitrofluorenone and 3-fluoro-6-nitrofluorenone have been accomplished. In the process, twelve intermediate compounds have been synthesized. 4-Iodo-2-methyl-4'-benzophenone and 5-acetamido-2-(p-nitrobenzoyl)-benzoic acid have also been synthesized but the above scheme did not achieve the synthesis of 3-iodo-6-nitrofluorenone. Alternate schemes have been proposed. During the course of this work, 16 new compounds have been synthesized.

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TABLE OF CONTENTS
.....

PART A

	<u>Page</u>
INTRODUCTION	1
LITERATURE SURVEY	4
General	4
Addition Compounds of Fluoranthene	6
Oxidation of Fluoranthene	6
Reduction of Fluoranthene	7
Oxidation of Substituted Fluoranthenes	9
Monosubstituents in Fluoranthene	
1) Halogens	11
2) Nitro Groups	12
3) Other Mono Substituents	14
Disubstituents in Fluoranthene	
1) Bromination	15
2) Nitration	22
3) Other Disubstituents	27
Orientation of Disubstituted Fluoranthenes	31
Polysubstituents in Fluoranthene	33
Substituents in Tetrahydrofluoranthene	33
DISCUSSION OF RESULTS	39
Synthesis of 1-Nitrofluoranthene	41
Bromination of 1-Nitrofluoranthene	42
Bromination of 1-Acetamidofluoranthene	48
Bromination of 3-Acetamidofluoranthene	53
Bromination of 1-Aminofluoranthene	54
Bromination of 1-Bromofluoranthene	55
Theoretical Implications of Dibromination of 1-Nitro-, 1-Acetamido- and 1-Bromofluoranthene	56
Nitration of 1-Nitrofluoranthene	59
Nitration of 1-Acetamidofluoranthene	60
EXPERIMENTAL	
Instruments and Materials Used	62
1) Preparation of 10% Sodium Amalgam	63
2) Synthesis of 1,2,3,10b-Tetrahydrofluoranthene	63
3) Synthesis of 1-Nitrofluoranthene	64
4) Synthesis of 1-Nitro-4,9-Dibromofluoranthene	65
5) Synthesis of 1-Amino-4,9-Dibromofluoranthene by Reduction of the Nitro Compound	65
6) Synthesis of 1-Acetamido-4,9-Dibromofluoranthene by Acetylation of the Amine	66
7) Oxidation of 1-Nitro-4,9-Dibromofluoranthene to give 4- Nitro-6-Bromofluorenone-1-Carboxylic Acid	66
8) Preparation of Cuprous Bromide	67

	<u>Page</u>
9) Synthesis of 1,4,9-Tribromofluoranthene from 1-Amino-4,9-Dibromofluoranthene	67
10) Oxidation of 1-Amino-4,9-Dibromofluoranthene	68
11) Oxidation of 1-Acetamido-4,9-Dibromofluoranthene	69
12) Synthesis of 3,8-Dibromofluoranthene	69
13) Oxidation of 3,8-Dibromofluoranthene	69
14) Decarboxylation of 2,7-Dibromofluorenone-1-Carboxylic Acid to 2,7-Dibromo-9-Fluorenone	70
15) Oxidation of 2,7-Dibromofluorene to 2,7-Dibromofluorenone..	71
16) Deamination of 1-Amino-3,8-Dibromofluoranthene to 3,8-Dibromofluoranthene	71
17) Attempted Monobromination of 1-Nitrofluoranthene	72
18) Attempted Monobromination of 1-Nitrofluoranthene with N-Bromosuccinimide	72
19) Preparation of Pyridine Hydrobromide Perbromide	73
20) Attempted Monobromination of 1-Nitrofluoranthene with Pyridinium Hydrobromide Perbromide	73
21) Attempted Polybromination of 1-Nitrofluoranthene Beyond the Dibromo stage	73
22) Polybromination of 1-Nitrofluoranthene to give Hexabromofluoranthene	74
23) Synthesis of 1-Aminofluoranthene	74
24) Synthesis of 1-Acetamidofluoranthene	75
25) Attempted Bromination of 1-Acetamidofluoranthene in Pyridine	75
26) Attempted Bromination of 1-Acetamidofluoranthene in Acetic Acid	75
27) Attempted Bromination of 1-Acetamidofluoranthene in Dimethyl Sulfoxide	76
28) Synthesis of 1-Acetamido-4,8,9-Tribromofluoranthene and 1-Acetamido-4,8,9,(?)-Tetrabromofluoranthene	76
29) Bromination of 1-Acetamidofluoranthene to give 1-Acetamido-4,9-Dibromofluoranthene	77
30) Hydrolysis of 1-Acetamido-4,9-Dibromofluoranthene to give 1-Amino-4,9-Dibromofluoranthene	78
31) Synthesis of 1-Amino-4,8,9-Tribromofluoranthene by Hydrolysis of the Amide	78
32) Attempted Hydrolysis of 1-Acetamido-4,8,9,(?)-Tetrabromofluoranthene to 1-Amino-4,8,9,(?)-Tetrabromofluoranthene	79
33) Synthesis of 3,8,9-Tribromofluoranthene From 3,8-Dibromofluoranthene	80
34) Deamination of 1-Amino-4,8,9-Tribromofluoranthene to give 3,8,9-Tribromofluoranthene	80
35) Synthesis of 1,4,8,9-Tetrabromofluoranthene from 1-Amino-4,8,9-Tribromofluoranthene	81
36) Side Chain Bromination of 1-Acetamidofluoranthene with Pyridine Hydrobromide Perbromide	82
37) Bromination of 3-Acetamidofluoranthene with Bromine in Carbon Tetrachloride	82
38) Attempted Bromination of 1-Aminofluoranthene	83
39) Synthesis of 1-Bromofluoranthene and 1-Hydroxyfluoranthene.	84
40) Attempted Bromination of 1-Bromofluoranthene	85

	<u>Page</u>
41) Bromination of 1-Bromofluoranthene to 1,4,8,9-Tetrabromofluoranthene	86
42) Bromination of 1-Bromofluoranthene to 1,4,9-Tribromofluoranthene	86
43) Synthesis of 1,(?)-Dinitrofluoranthene	87
44) Reduction of 1,(?)-Dinitrofluoranthene to 1,(?)-Diaminofluoranthene	87
45) Acetylation of 1,(?)-Dinitrofluoranthene to 1,(?)-Diacetamidofluoranthene "in situ"	88
46) Synthesis of 1-Acetamido-Mononitrofluoranthene	88
47) Synthesis of 1-Acetamido-Monoaminofluoranthene	89
48) Synthesis of 1-Acetamido-Dinitrofluoranthene	89
49) Hydrolysis of 1-Acetamido-Dinitrofluoranthene to give the Dinitroamine Hydrochloride	89
 SUMMARY	 91
 RECOMMENDATIONS FOR FUTURE WORK	 96
 BIBLIOGRAPHY	 101
 INFRA RED SPECTRA	 105

LIST OF TABLES AND FIGURES

	<u>Page</u>
Table I - Nitration Products of Fluoranthene	14
Table II - Bromination of 2- and 3-Substituted Fluoranthenes Nitration of 2- and 3-Substituted Fluoranthenes	40
Table III - Bromination of 1-Substituted Fluoranthenes	57
Infra Red Spectra	105

PART B

	<u>Page</u>
INTRODUCTION	130
LITERATURE SURVEY	132
Oxidation of Fluorene	134
Synthesis of Fluorenones	
1) Oxidation of Fluorenes	136
2) From Phenanthraquinones	137
3) From Diphenic Acids	138
4) From Ortho Carboxy Diphenyl Derivatives	140
5) From 2-Substituted Benzophenones	141
6) From Fluoranthene	142
7) Direct Substitution	144
8) From Miscellaneous Compounds	146
9) Method of Charlesworth and Mathiaram	148
DISCUSSION OF RESULTS	
Synthesis of 3-Chloro-6-Nitrofluorenone	155
Synthesis of 3-Fluoro-6-Nitrofluorenone	156
Attempted Synthesis of 3-Iodo-6-Nitrofluorenone	156
Proposed Synthesis of 3-Iodo-6-Nitrofluorenone	159
EXPERIMENTAL	
1) Synthesis of 4-Amino-2-Methyl-4'-Nitrobenzophenone	162
2) Synthesis of 4-Chloro-2-Methyl-4'-Nitrobenzophenone	163
3) Synthesis of 5-Chloro-2-(p-Nitrobenzoyl)-Benzoic Acid	163
4) Synthesis of 5-Chloro-2-(p-Nitrobenzoyl)-Benzoyl Chloride ..	164
5) Activation of Sodium Azide	164
6) Synthesis of 5-Chloro-2-(p-Nitrobenzoyl)-Benzoic Acid Azide	165
7) Synthesis of 5-Chloro-2-(p-Nitrobenzoyl)-Aniline	165
8) Synthesis of 3-Chloro-6-Nitrofluorenone and 2-Hydroxy- 4-Chloro-4'-Nitrobenzophenone	166
9) Synthesis of 4-Fluoro-2-Methyl-4'-Nitrobenzophenone	167
10) Synthesis of 5-Fluoro-2-(p-Nitrobenzoyl)-Benzoic Acid	168
11) Synthesis of 5-Fluoro-2-(p-Nitrobenzoyl)-Benzoyl Chloride...	168
12) Synthesis of 5-Fluoro-2-(p-Nitrobenzoyl)-Benzoic Acid Azide	169
13) Synthesis of 5-Fluoro-2-(p-Nitrobenzoyl)-Aniline	169
14) Synthesis of 3-Fluoro-6-Nitrofluorenone and 2-Hydroxy- 4-Fluoro-4'-Nitrobenzophenone	170
15) Synthesis of 4-Iodo-2-Methyl-4'-Nitrobenzophenone	171
16) Attempted Oxidation of 4-Iodo-2-Methyl-4'-Nitrobenzophenone to 5-Iodo-2-(p-Nitrobenzoyl)-Benzoic Acid	172
17) Synthesis of 5-Acetamido-2-(p-Nitrobenzoyl)-Benzoic Acid	172

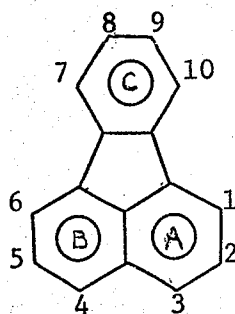
	<u>Page</u>
SUMMARY	174
RECOMMENDATIONS FOR FUTURE WORK	176
BIBLIOGRAPHY	178
INFRA RED SPECTRA	181

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PART A

STUDIES OF 1-SUBSTITUTED FLUORANTHENES

INTRODUCTION

The directive properties of substituents in the fluoranthene nucleus have provided exciting though formidable research over the past twenty years. Even as late as 1964 R.D. Brown (1) in a discussion of non-alternant hydrocarbons concluded that fluoranthene deserves closer study, both theoretically and experimentally. Much work has been done on the further substitution of 3-substituted fluoranthenes. In this laboratory over the past five years, similar studies have been done on 2- as well as 3-substituted fluoranthenes.



In 1955 Campbell and Keir (2) found that 3-carboxy, 3-carbomethoxy, 3-cyano and 3-nitrofluoranthene were all brominated in position 9, and that direct sulfonation of fluoranthene gave 3,9-fluoranthenedisulfonic acid. These reactions coupled with the fact that bromination of 3-bromofluoranthene gave 3,8-dibromofluoranthene caused them to draw an analogy to disubstitution in monosubstituted diphenyl, and postulate that a meta-directing group in ring A of fluoranthene would direct a second substituent

to position 9, and that an ortho-para directing group in the same ring would direct a second substituent to position 8. This was shown to be an oversimplification since Kloetzel et al. (3) in 1956 found that 3-acetamidofluoranthene was nitrated in position 2 rather than in position 8. They suggested, that in this case, substitution occurred in the same ring because the acetamido group is a highly activating substituent. Charlesworth and Blackburn (4) further substantiated this by demonstrating that 3-acetamido and 3-aminofluoranthene were brominated in position 2.

Charlesworth and Dolenko (19) showed that 2-nitrofluoranthene undergoes bromination in position 9, whereas 2-acetamidofluoranthene brominates in position 3. Recently Charlesworth and Lithown (30) showed that nitration of 3-nitro and 3-acetamidofluoranthene occurred in the 9 and 2 positions respectively.

From the foregoing it can be seen that nitration goes the same way as bromination whether the initial substituents were in the 3 or 2-positions. Furthermore a mono substituted fluoranthene has never been found to substitute into ring B of the fluoranthene nucleus.

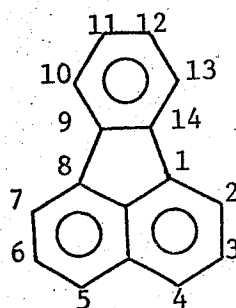
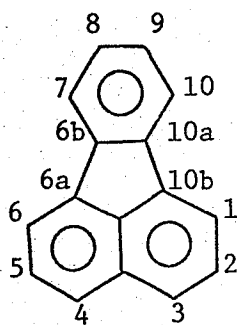
Up to this point further substitution of the final position in ring A (i.e. 1-substituted fluoranthenes) had never been reported. Wilshire (personal communication) attempted nitration of 1-nitrofluoranthene, but was unable to isolate any useful products. It seemed therefore particularly desirable to brominate (and possibly nitrate) 1-nitro-, 1-acetamido- and 1-bromofluoranthene. These substituents were chosen because of their interesting directive properties. The nitro group is highly deactivating and meta directing, whereas near the opposite end of the activity scale the acetamido group is highly activating and ortho-para

directing. The bromo group occupies a unique position in that it is slightly deactivating but ortho-para directing.

As can be observed from earlier paragraphs (also Table II page 40) much work had been done on further bromination of 2- and 3-nitro, 2- and 3-acetamido and 2- and 3-bromofluoranthenes. Somewhat less has been reported on nitration of the corresponding compounds. The products from the reactions of the 1-substituted fluoranthenes would be isolated, their orientations established and the results compared with analogous reactions of the substituents in the 2 and 3 positions. One might expect similar behavior in further substitution regardless of whether the initial substituents were in positions 1,2 or 3. Experimentation, however, proved otherwise.

LITERATURE SURVEY*

The structure of fluoranthene, a colorless crystalline hydrocarbon of molecular formula $C_{16}H_{10}$ and melting at $109.5 - 110.5^\circ$ is depicted below. The numbering system in formula 1a is now used almost

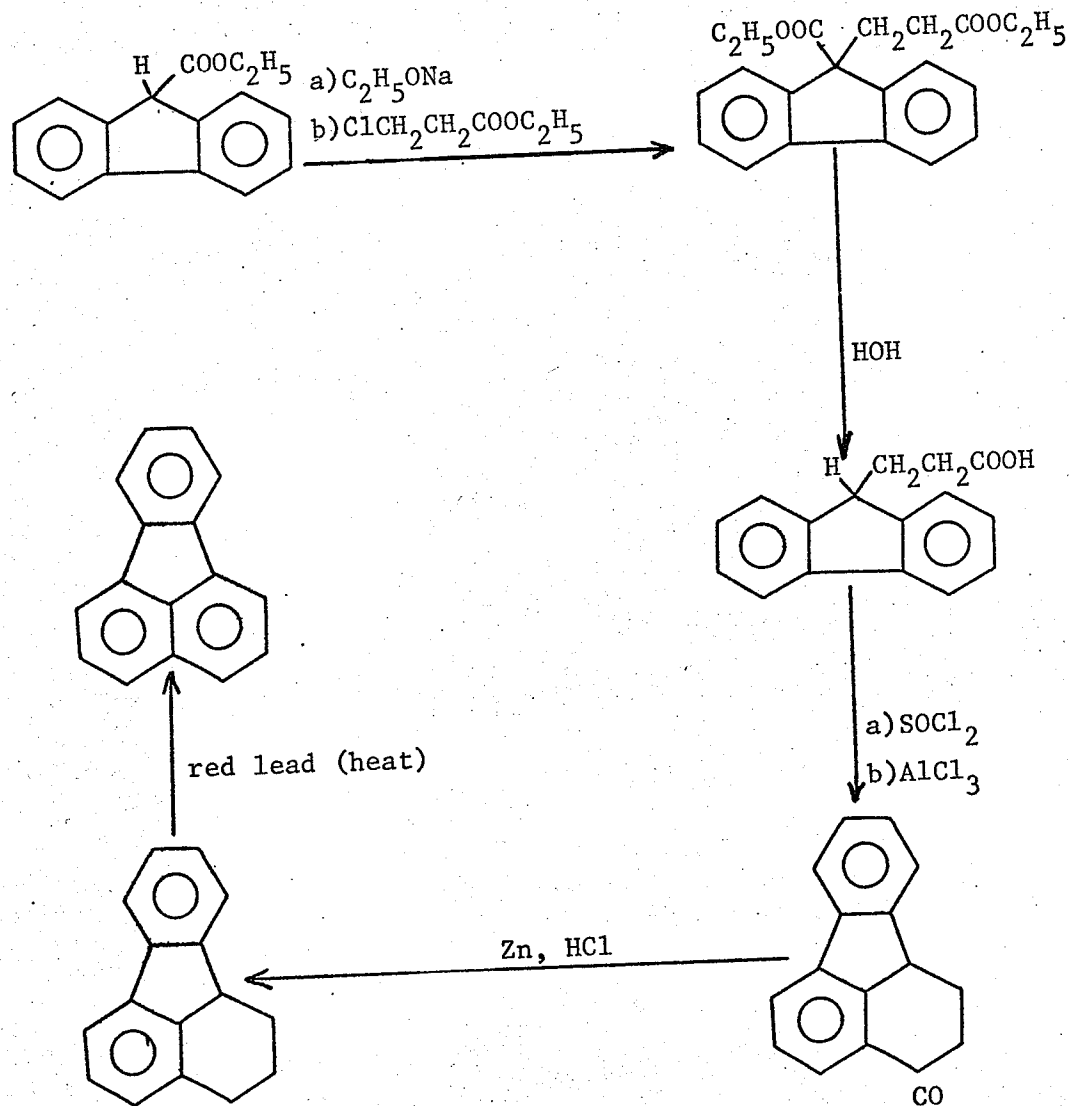


exclusively throughout the world. The numbering system in 1b is in accordance with the Richter system of notation and until quite recently was used by most European chemists. The notation in 1a will be used throughout this thesis. It is both interesting and informative to note that the following hydrocarbon molecules can be discerned in the fluoranthene structure: benzene, naphthalene, fluorene, indan, acenaphthene, diphenyl and cyclopentane.

Fluoranthene was discovered independently by Fittig and Gebhard (6) and by Goldschmidt (7) in 1877. Goldschmidt obtained fluoranthene by fractional distillation and crystallization of a mixture of hydrocarbons

* An excellent review of fluoranthene chemistry up to 1951 is contained in reference (5).

known as idrialene which had previously been obtained by extraction of the mercury ores of Idria by Dumas (8) and Laurent (9). Fittig and Gebhard isolated fluorethane from the high boiling fraction of coal tar. Little interest was shown in the compound until 1929 when von Braun and Anton (10) proved the structure of fluorethane by synthesis from ethyl-9-fluorenicarboxylate and β -chloroethylpropionate. This is illustrated below.

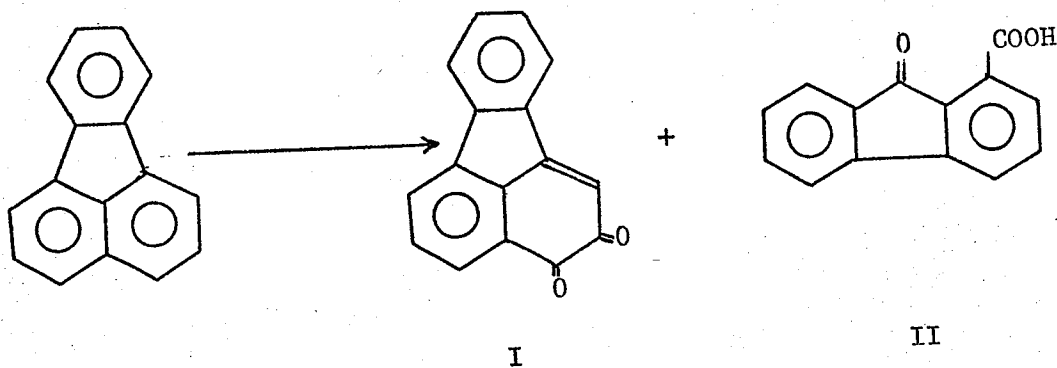


Addition Compounds of Fluoranthene (11, 12, 13)

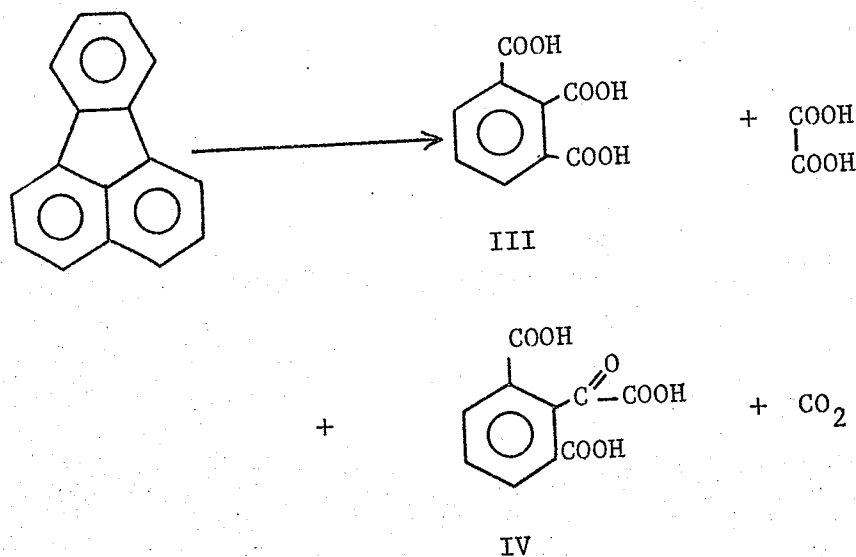
Fluoranthene closely resembles naphthalene and pyrene in its propensity for forming molecular complexes with nitro compounds. These complexes, often used for characterization, include the picrate, m.p. 185 - 186°; the 1,3,5-trinitrobenzene complex, m.p. 205-206°; the 1,3-dinitrobenzene complex, m.p. 77°; the 2,4-dinitrotoluene complex, m.p. 75.5° and several others.

Oxidation of Fluoranthene (5)

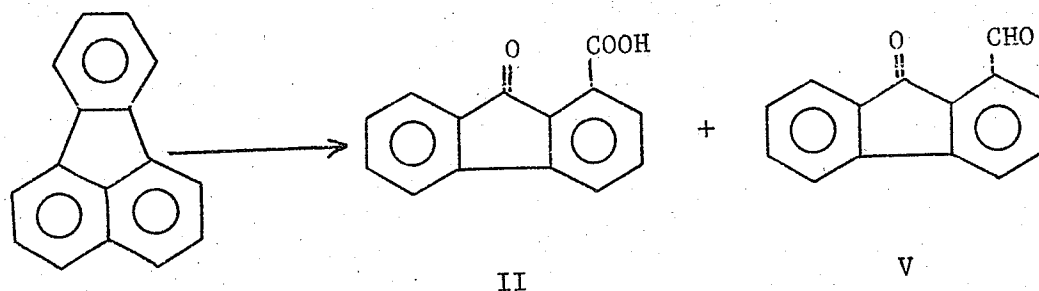
The products of oxidation of fluoranthene vary greatly with the oxidizing conditions. Oxidation with potassium chromate in dilute sulfuric acid and chromic anhydride or potassium chromate in acetic acid yields 2,3-fluoranthenequinone (I) and 1-fluorenonedicarboxylic acid (II) as the principal products. II is also produced in good yield with chromic



anhydride in acetic acid or with aqueous permanganate as was found by this author. Prolonged treatment with alkaline permanganate yields hemimellitic acid (III), oxalic acid, carbon dioxide, with some 2,6-dicarboxyphenylglyoxylic acid (IV).



Ozonolysis in glacial acetic acid gives a mixture of 1-fluorenonecarboxylic acid (II) and 1-fluorenonealdehyde (V).



Reduction of Fluoranthene

Goldschmiedt (13) in 1880 prepared hydrogenated derivatives of fluoranthene but was unable to characterize the products obtained. In a detailed investigation completed in 1930, von Braun and Manz (14) reported that reduction of the hydrocarbon with sodium amalgam and alcohol, or with phosphorus and hydriodic acid below 180°, gave almost a quantitative yield of 1,2,3,10b-tetrahydrofluoranthene (VI). Above 200°, they obtained an inseparable mixture of products. Catalytic hydrogenation of fluoranthene under pressure using 20% palladium-charcoal as catalyst, gave VI as the