SYNTHESIS

of

METHYLATED FLUORANTHENES

THESIS

PRESENTED BY

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of the

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The following papers have been, or are about to be submitted to the Chemical Society.

(1) The Condensation of Fluorene with Acetone. Part V. Contrasting Reactions of Magnesium 9 - Fluorenyl Bromide and of Lithium 9 - Fluorenyl with αβ - Unsaturated Ketones.

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(2) The Condensation of Fluorene with Acetone. Part VI. Methylated Di - and Tetrahydrofluoranthenes. Synthesis of 2:3:4 - Trimethylfluoranthene.

Received by the Chemical Society, 15th June 1948.

(3) The Condensation of Fluorene with Acetone. Part VII. Synthesis of 1:3 Dimethyl - and 1:2:3 - Trimethylnaphthalenes.

To be submitted to the Chemical Society shortly.

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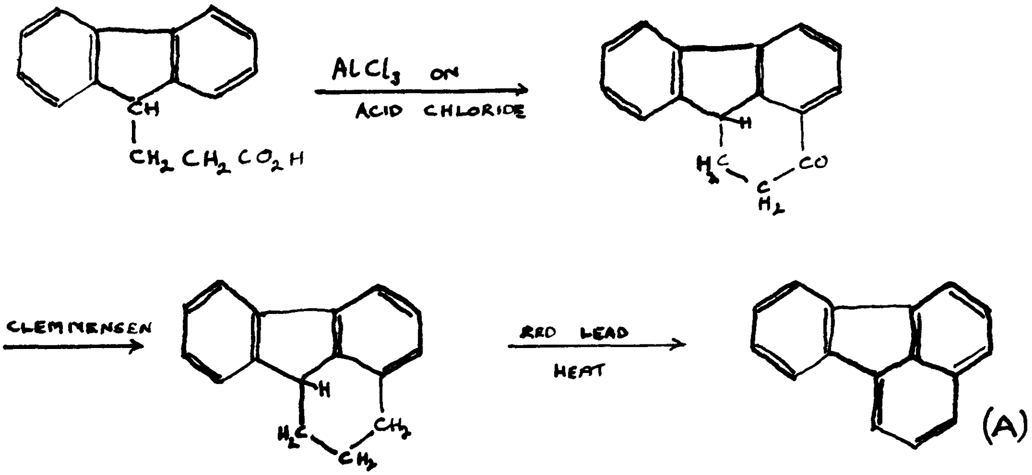
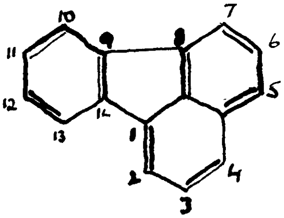
Introduction

The hydrocarbon fluoranthene was first isolated in a pure condition by Goldschmidt (ref.1 and 2) from mercury ores (1877) and very soon afterwards by Fittig and Gebhard (ref.3 and 4) from a high boiling fraction of coal tar.

Its structure remained in doubt until 1929 when von Braun and Anton (ref.5) deduced, from the nature of its degradation products, the formula (A) which is now generally accepted. The same two workers confirmed (ref.5) this structure of fluoranthene by the synthesis here outlined.



Of the different systems of reference which have been suggested for fluoranthene the second one introduced by von Braun and Anton (ref.6;cf.ref.5) has been adopted throughout this thesis:-



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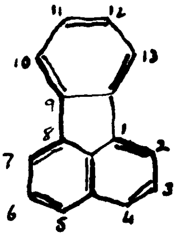
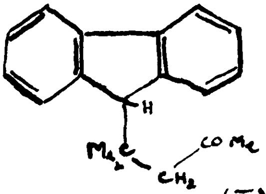
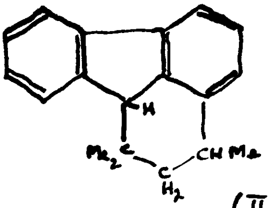


Methylated derivatives of fluoranthene were first described by France, Tucker and Forrest (ref.7) They showed (ref.8) that fluorene and acetone in the presence of potassium hydroxide give methyl β-9-fluorenyl-β-methyl-n-propyl ketone (I). Treatment of this compound with hydriodic acid in boiling acetic acid produced a 2:2:4 - trimethyl - 1:2:3:4 - tetrahydro-fluoranthene (II) whilst hydrogen bromide in acetic acid yielded 2:2:4 - trimethyl - 1:2 - dihydro-fluoranthene (III) (ref.7).



(I)



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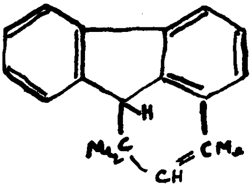


(III)

It was later established (ref.9) that dehydrogenation of (III) with selenium gives 2:4 - dimethylfluoranthene whose structure was confirmed by synthesis from 1:3 - dimethylnaphthalene.

In addition (III) heated with zinc chloride or phosphorus pentoxide gave a compound which appeared to be 2:3:4 - trimethylfluoranthene, a reaction involving the migration of a methyl group. Such methyl group migration under acidic reagents is however a well-recognised change, e.g., the ready conversion of (ref.10 and 11)

That the compound obtained from (III) with zinc chloride or phosphorus pentoxide was in fact 2:3:4 - trimethylfluoranthene required confirmation. To this end its synthesis was undertaken as the first objective of this research.

Pages 8,9,10 and 11 summarise the lines upon which related work developed.

Summary.

A. 2:3:4 - Trimethylfluoranthene has been synthesised from 1:2:3 - trimethylnaphthalene and *O*- bromonitrobenzene (page 37).

B. Since starting materials for the existing syntheses of 1:2:3- trimethylnaphthalene were not available alternative methods of preparation were sought. Two have been found (a) from benzyl methyl ketone and ethyl cyano-acetate. (page 16).
(b) from hemimellitene and succinic anhydride. (page 18).

C. During the search for such alternative methods, three preparations of 1:3 - dimethylnaphthalene - used in the synthesis of 2:4 - dimethylfluoranthene (ref.9) - were established

(a) from benzyl methyl ketone and ethyl cyanoacetate (page 14).

(b) from 1 - phenyl - 2:4:4 - trimethylbutadiene (page 20).

(c) from 1 - phenyl - 2:4 - dimethylbutadiene (page 21).

D. The possibility of preparing 2:3:4 - trimethylfluoranthene from α -diphenylene - $\beta\delta$ - dimethyl - $\Delta^{\alpha\gamma}$ - pentadiene (page 56) has been successfully investigated.

α - Diphenylene - βδ - dimethyl - $\Delta^{\alpha\gamma}$ - pentadiene was obtained by the action of magnesium 9 - fluorenyl bromide on mesityl oxide (page 34)

Treatment of the diene with hydriodic acid and boiling acetic acid gave three products (page 55):-

(a) 2:3:4 - trimethylfluoranthene - involving ring closure and migration of a methyl group but without reduction (page 56).

(b) 2:4:4 - trimethyl - 1:2:3:4 - tetrahydrofluoranthene - involving ring closure and reduction but no methyl group migration (page 56).

(c) 2 - methyl - 4 (9-fluorenyl) - pentane - involving reduction only (page 56).

E. The same diene has been cyclised, with hydrogen bromide and stannic chloride, to 2:4:4 -trimethyl - 1:4 (?3:4 ~~2:3~~?) - dihydrofluoranthene (page 58) from which various fluoranthene derivatives have been prepared by oxidation and reduction reactions (page 59-60).

F. Further assurance of the structure of α - diphenylene - βδ - dimethyl - $\Delta^{\alpha\gamma}$ - pentadiene (the same diene as in D and E) was sought in the reaction of <u>lithium</u> 9 - fluorenyl on mesityl oxide since such lithium compounds almost invariably give high yields of carbinol produced by addition to the carbonyl group (1:2 - addition) of αβ-unsaturated ketones. It has been established that the product was not the expected diene but methyl β-9-fluorenyl-β-methyl-n-propyl ketone resulting from 1:4 - addition. (page 38).

G. The reactions of both magnesium 9-fluorenyl bromide and of lithium 9-fluorenyl with such other αβ-unsaturated ketones as chalcone (page 36,39), benzylidene acetone (page 35,40), ethylidene acetone (page 35) and 3-methyl-pent-2-en-4-one (page 35,43) have been examined. In some cases interpretation of the results proved difficult but it has been shown that in the case of magnesium 9-fluorenyl bromide there was no evidence of 1:4 addition (which would produce ketones). In contrast lithium 9-fluorenyl has been shown to react with the above αβ-unsaturated ketones solely by 1:4-addition (yielding saturated ketones).

H. Various further fluoranthene derivations have been prepared from the products obtained in G:-

(a) 2:4 - diphenylfluoranthene : by reduction, cyclisation and dehydrogenation of phenyl β-9-fluorenyl-β phenylmethyl ketone (product of lithium 9-fluorenyl and chalcone) (page 41).

(b) 2-phenyl - 4-methylfluoranthene : similarly from methyl β-9-fluorenyl - β-phenylethyl ketone (product of lithium 9-fluorenyl and benzylidene acetone)(Page 42).

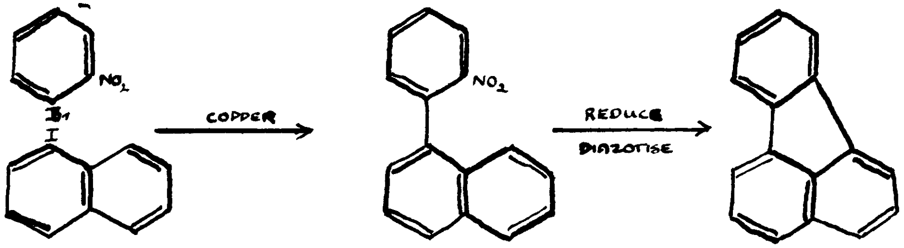
(c) 2:3 : 2':3' - tetramethyl - 4-4' - difluoranthyl from the ketone product of lithium 9-fluorenyl and 3-methyl-pent-2-ene-4-one by reduction (giving a pinacol) with subsequent cyclisation and dehydrogenation (page 44): and from the same ketone by reduction to the carbinol, a 2:3:4 - trimethyltetrahydrofluoranthene.

I. Lithium 1-indenyl has been shown to react with chalcone (page 65) and benzylidene acetone (page 65) solely by 1:4 - addition giving saturated ketones.

J. The preparation of lithium 10 - benzanthryl and of benzanthrene 10 - carboxylic acid has been achieved, (PAGE 66).

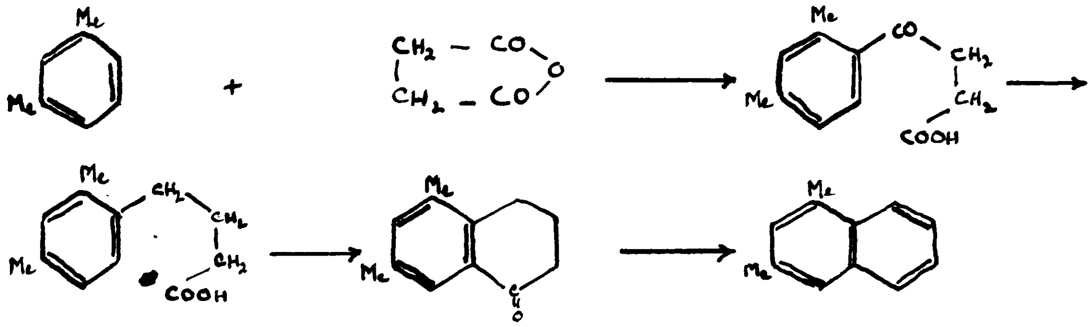
I Synthesis of Methylnaphthalenes.

Since fluoranthene may be obtained from α-iodonaphthalene and *o*- bromonitrobenzene thus:-



it was thought probable that various methylfluoranthenes might be obtained, by a similar series of reactions, from the corresponding methyl naphthalenes, e.g., 1:3 - dimethyl and 1:2:3 - trimethylnaphthalenes. In fact 2:4 - dimethylfluoranthene has recently (ref.9) been prepared from 1:3 - dimethylnaphthalene.

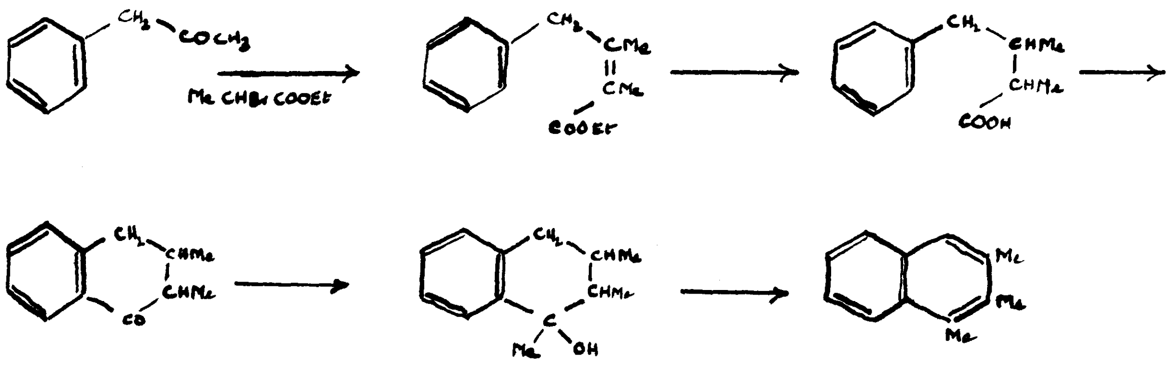
Barnett and Sanders (ref.12) synthesised 1:3 - dimethylnaphthalene in this way



The hydrocarbon was obtained in about 30% yield.

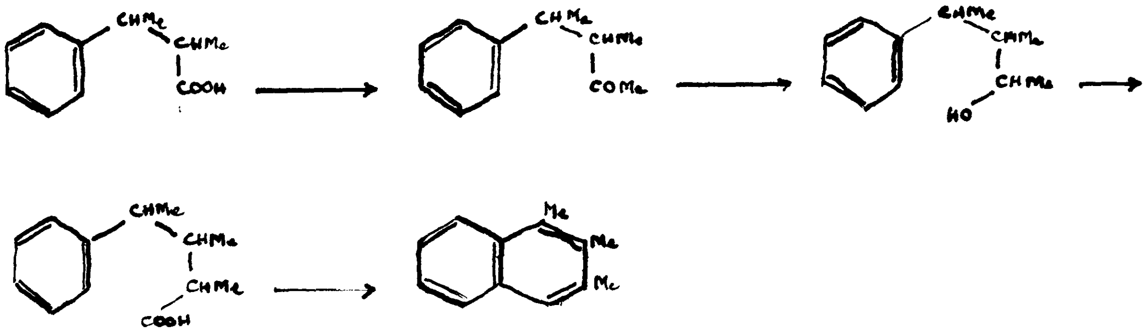
For 1:2:3 - trimethylnaphthalene, three syntheses are available.

(1) Ruzicka and Ehman (ref.13)



No yields are given for this synthesis.

(2) Ruzicka and Ehman (ref.13)



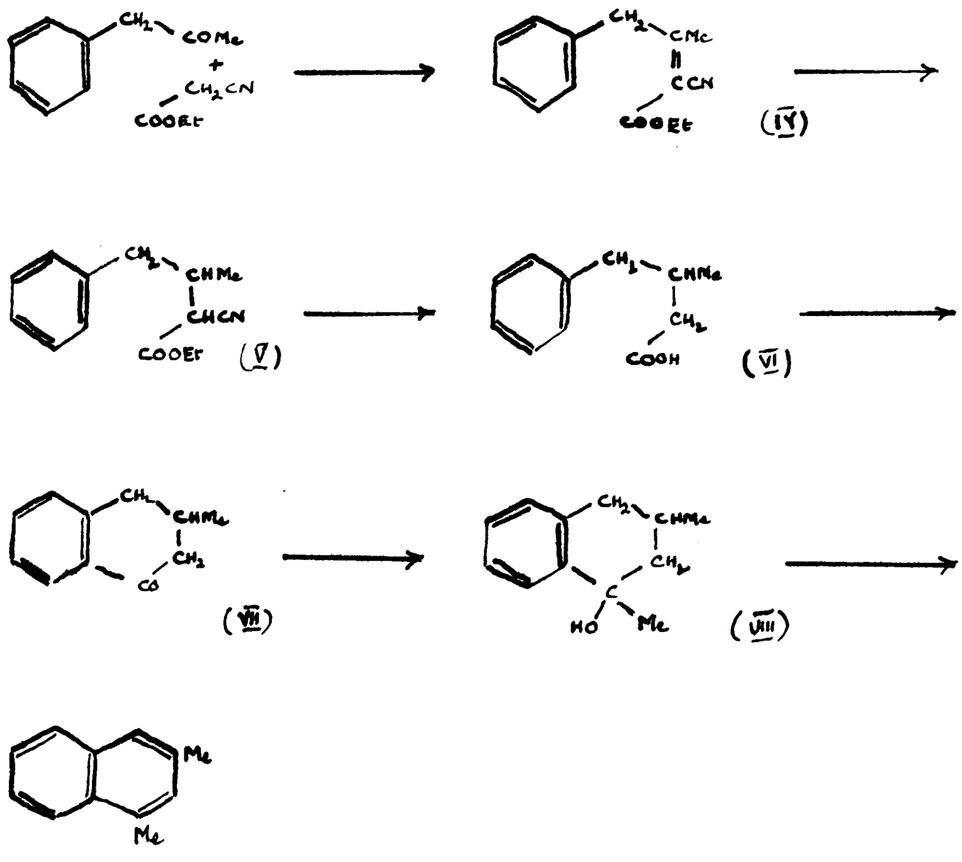
Again no yields are indicated.

(3) Hewett (ref.14) obtained a good yield of 1:2:3 - trimethylnaphthalene by chloromethylation of 2:3 - dimethylnaphthalene followed by catalytic hydrogenation of the chloromethyl compound.

Since starting materials for these syntheses were in short supply, alternative methods of preparation were sought. The first to be attempted was suggested by (1) above, and seemed particularly suitable since it was a source of both the desired compounds.

Benzyl methyl ketone was prepared from magnesium benzyl chloride and acetic anhydride (ref.15) and its

2:4 - dinitrophenylhydrazone, mp. 150-152°, obtained. The ketone was condensed with ethyl cyanoacetate in the presence of ammonium acetate and acetic acid, and in benzene solution (ref.16) to give ethyl 1-methyl-2-phenylethylidene - cyanoacetate (IV) in 73% yield. The replacement of acetic acid and ammonium acetate by trichloracetic acid and ammonium trichloracetate reduced the reaction time considerably, but failed to make any improvement in yield.

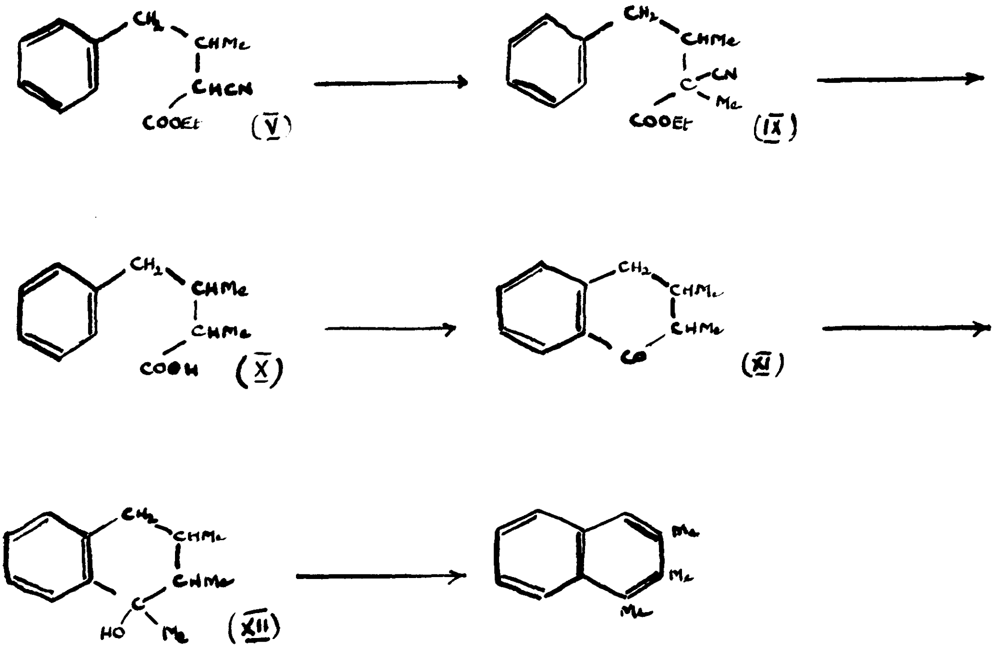


Since hydrolysis, with sulphuric acid, acetic acid and water, of the unsaturated ester (IV) proved unsatisfactory, reduction of the ethylenic double bond was attempted. Catalytic hydrogenation (IV) proceeded smoothly and rapidly with hydrogen in the presence of palladium charcoal (ref.17), the solvent being ethanol. The presence of potassium hydroxide or the use of glacial acetic acid instead of ethanol had little effect on either the reaction time or the yield of ethyl 1- methyl - 2-phenylethyl - cyanoacetate (V). (V)was also obtained, though in much reduced yield, by simultaneous condensation and reduction of benzyl methyl ketone and ethyl cyanoacetate, with acetic acid as solvent and palladium charcoal as hydrogenation catalyst. (cf. ref.18)

Hydrolysis of both the cyano - and carbethoxy - groups of (V) was carried out with sulphuric acid, water and acetic acid. On distillation of the product, decarboxylation of the intermediate malonic acid derivative occurred and 3-benzylbutyric acid (VI) was obtained in 90% yield. Cyclisation of(VI) was readily effected with phosphorus Pentachloride followed by stannic chloride giving 1-keto-3-methyl - 1:2:3:4 - tetrahydronaphthalene(VII) as a colourless liquid which was characterised by means of its 2:4 - dinitrophenylhydrazone m.p. 241-2° and its semicarbazone m.p. 179-188°.

In the first attempted reaction of magnesium methyl iodide and (VII), the ketone was added slowly to a cooled solution containing the theoretical quantity of magnesium methyl iodide but (VII) was recovered unchanged. However, when excess magnesium methyl iodide was slowly added to a cooled solution of (VII) a good yield of *1-hydroxy - 1:3-dimethyl - 1:2:3:4 - tetrahydronaphthalene* (VIII) was obtained (cf. ref.13). The carbinol (VIII) was dehydrated with potassium bisulphate and dehydrogenation of the resulting dihydrodimethylnaphthalene with palladium charcoal catalyst (ref.19) gave 1:3 - dimethylnaphthalene (picrate m.p. 115-117°; *S* - trinitro-benzenate m.p. 132-4°). By this method there was obtained an overall yield, based on benzyl methyl ketone of 15%.

The synthesis, described above, may be readily adapted to yield 1:2:3 - trimethylnaphthalene instead of the dimethyl compound. Since the saturated ester (V) has a hydrogen atom activated by both a nitrile -and a carbethoxy - grouping replacement of this hydrogen by methyl was attempted. With molecular proportions of sodium ethoxide, methyl iodide and (V) the yield of *ethyl 2-methyl - 2-cyano - 3-benzylbutyrate* (IX) was only 50%. Doubling the quantities of sodium ethoxide and methyl iodide however greatly increased the yield of (IX). Analyses of various samples of this compound failed to agree entirely with the theoretical values but this may be explained by the hydrolytic action of the sodium ethoxide, in ethanol, on the cyano group.

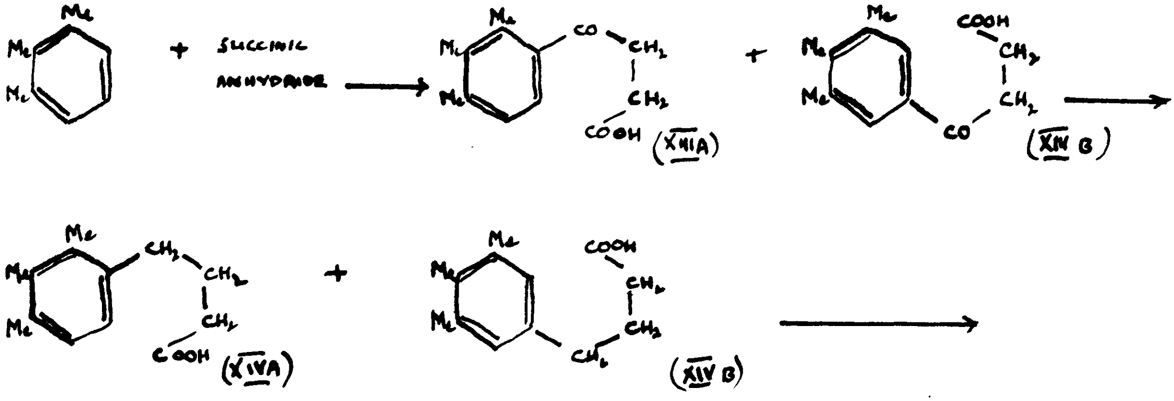


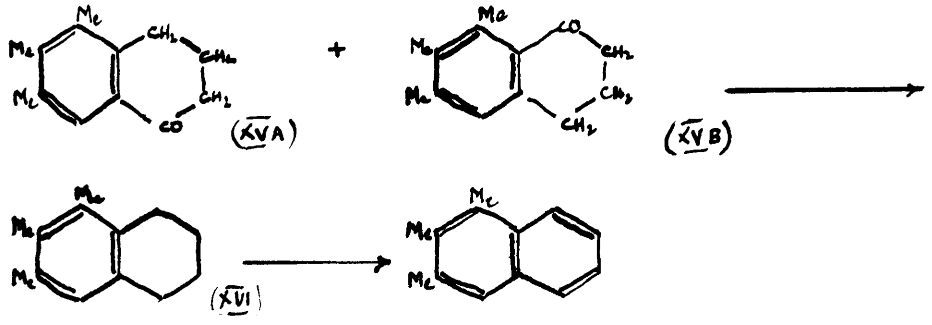
Hydrolysis of (IX) was carried out as for the ester (V) but it was not found possible to isolate a pure specimen of 2-methyl-3-benzyl-butyric acid (X) since even after 24 hours refluxing there still remained some of the acid amide produced by partial hydrolysis of the nitrile group. The identity of the acid amide was indicated by the formation of the ketone (XI) on treatment with 80% sulphuric acid and sodium nitrite. Cyclisation of the acid (X) was achieved in good yield with phosphorus pentachloride and stannic chloride, giving 1-keto-2:3-dimethyl - 1:2:3:4:-tetrahydronaphthalene (XI) which was characterised by means of its 2:4-dinitrophenylhydrazone mp. 201-203°.

With excess magnesium methyl iodide, 1-hydroxy - 1:2:3 - trimethyl - 1:2:3:4 - tetrahydronaphthalene (XII) was obtained. Dehydration and dehydrogenation of (XII) proceeded with selenium at 300° giving 1:2:3 - trimethylnaphthalene, (Picrate mp. 141-2°, styphnate mp. 142-4° S - trinitrobenzenate mp. 142-4°)

The overall yield for this synthesis based on benzyl methyl ketone was 14%.

Another synthesis starting with hemimellitene (1:2:3-trimethylbenzene) gave 1:2:3-trimethyl-naphthalene in less satisfactory yield. This is a method similar to that used by Barnett and Sanders (ref.12) for the preparation of 1:3-dimethylnaphthalene.

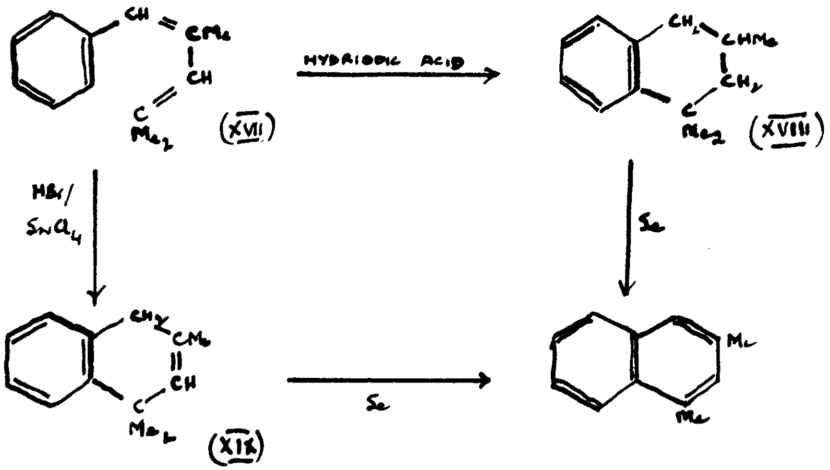




Hemimellitene was condensed by a Friedel-Crafts reaction in chlorobenzene, with succinic anhydride. Although the product consisted of a mixture of isomers (4- and 5- hemimellitoyl-propionic acids, (XIIIA and (XIIIB) no attempt was made to separate the two constituents since both gave the same product at a later stage of the synthesis. Reduction of the keto-acids by the Clemmensen method using acetic acid, proceeded readily to give 4- and 5- hemimellityl-n-butyric acids (XIVA and XIVB). These acids were cyclised to the corresponding tetralone derivatives - 1 - keto - 5:6:7 (and 6:7:8) - trimethyl - 1:2:3:4 - tetrahydronaphthalene (XVA and XVB) by means of 80% sulphuric acid. A derivative was obtained with 2:4 - dinitrophenyl - hydrazine. Analysis figures for this derivative were satisfactory though no sharp melting point could be obtained (probably due to the 2:4 dinitrophenylhydrazone being mixture a of isomers).

5:6:7 - Trimethyl - 1:2:3:4 - tetrahydronaphthalene (XVI) was obtained by Clemmensen reduction of the mixture of ketones, i.e., the isomerism introduced in the first stage of the synthesis had now been eliminated. Dehydrogenation of 5:6:7 - trimethyl -1:2:3:4 - tetrahydronaphthalene yielded a small amount of 1:2:3 - trimethylnaphthalene. The small overall yield (3.5%) and the scarcity of hemimellitene render this synthesis impracticable for the preparation of 1:2:3 - trimethylnaphthalene.

1:3 - Dimethylnaphthalene was also obtained by the following methods:-

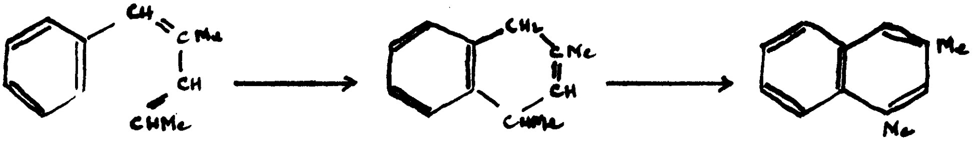


Magnesium benzyl chloride was condensed with mesityl oxide to give 1-phenyl - 2:4:4 - trimethylbutadiene (XVII) (ref.20) Two methods of ring closure of this compound were found to be effective:-

(a) Boiling hydriodic acid and glacial acetic acid gave a colourless liquid which was probably 1:1:3 - trimethyl-1:2:3:4 - tetrahydronaphthalene (XVIII) and which on treatment with selenium yielded 1:3 - dimethylnaphthalene in 10% yield.

(b) A solution of (XVII) in benzene was saturated with hydrogen bromide and stannic chloride added to the cooled solution. The product was a colourless liquid whose analysis corresponded to that of 1:1:3 - trimethyl - 1:4 - dihydronaphthalene (XIX). Dehydrogenation with selenium gave a 66% overall yield (from XVII) of 1:3 - dimethylnaphthalene.

2. In a similar manner 1 - phenyl - 2:4 - dimethylbutadiene - prepared from magnesium benzyl chloride and ethylidene acetone - gave a small yield of 1:3 - dimethylnaphthalene on treatment with hydrogen bromide and stannic chloride (to give 1:3 - dimethyl - 1:4 - dihydronaphthalene) followed by dehydrogenation, i.e.,



This method of cyclisation from α-phenylbutadienes by means of hydrogen bromide and stannic chloride appears to be new.

Application of the same process to phenylbutadiene, however, yielded polymers instead of the expected dihydronaphthalene.

The ethylidene acetone used in the last synthesis of 1:3 - dimethylnaphthalene was prepared from acetone and acetaldehyde with aqueous potassium cyanide as condensing agent (ref.21). Owing to the small yield obtained under these conditions (about 15%) search was made for an alternative method of preparation:-

(a) acetaldehyde was added slowly to excess acetone containing anhydrous calcium sulphate. No reaction had occurred after 15 hours.

(b) when zinc chloride was added to a mixture of acetone and acetaldehyde a large amount of heat was evolved. The product was a yellow liquid bp. 110-120° whose derivatives did not correspond to those of ethylidene acetone.

(c) ammonium acetate and acetic acid as condensing agents gave a liquid b.p. 110-120 which was not ethylidene acetone.

In view of the success of the method used by Cope (ref.16) (see page 14) for condensation of ketones with reactive methylene compounds the following condensations were tried.

(a) benzyl methyl ketone and cyanoacetamide.

(b) benzyl methyl ketone and ethyl acetoacetate.

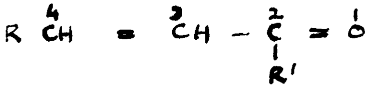
(c) fluorenone and ethyl acetoacetate.

No success was attained under these conditions, the reactants being recovered unchanged.

The failure of 1 - phenyl - 2:4:4 - trimethyl-butadiene (XVIII) and of 1 - phenyl - 2:4 - dimethyl- XVII / butadiene to give Diels-Alder adducts with benzoquinone or maleic anhydride is interesting. (see page 55).

II. Contrasting reactions of magnesium 9 - fluorenyl bromide and of lithium 9 - fluorenyl with $\alpha\beta$ - unsaturated ketones.

The reaction of a Grignard reagent with an $\alpha\beta$ - unsaturated aldehyde.

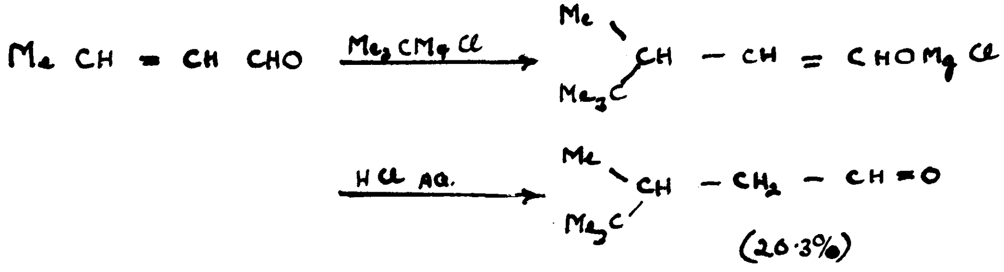
i.e. 

$R\overset{4}{C}H = \overset{3}{C}H - \underset{R'}{\overset{2}{C}} = \overset{1}{O}$ where $R' = H$

appears to lead almost invariably to 1:2 - addition, the product being an unsaturated secondary carbinol. Thus crotonaldehyde reacts with magnesium phenyl bromide to give propenylphenylcarbinol

$$MeCH = CH\,CHO \xrightarrow{PhMgBr} MeCH = CH - CH(Ph)OH$$

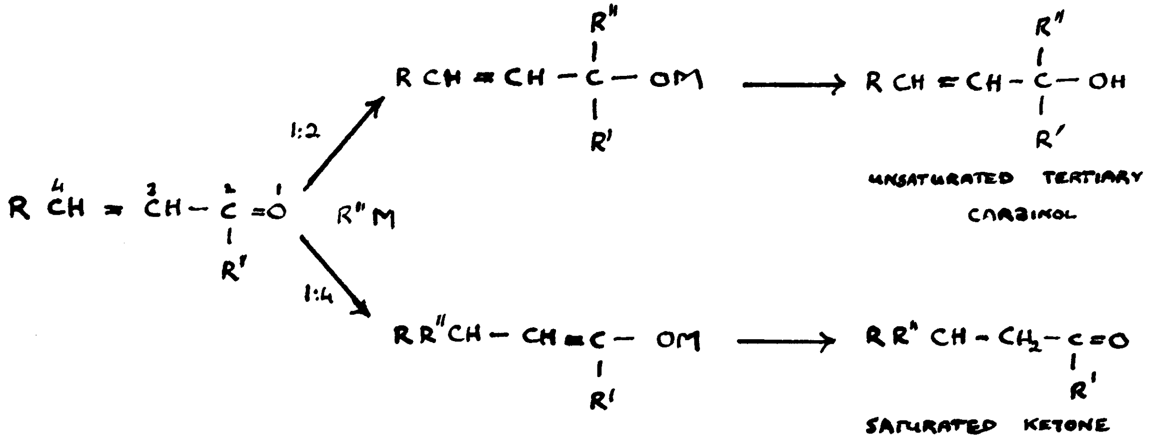
However two exceptions to this rule are recorded:- crotonaldehyde reacts with magnesium tertiary butyl and tertiary amyl halides (ref.22) to give, by 1:4 - addition, saturated aldehydes thus:-



Even here 30% of the 1:4 - addition product was isolated.

In contrast the reactions of Grignard compounds with $\alpha\beta$ -unsaturated <u>ketones</u> vary considerably. Such reactions have been extensively studied by Kohler and later by Gilman and co-workers, who extended their investigations to other organo-metallic compounds.

In general an organo-metallic compound may react with an αβ -unsaturated ketone according to this scheme:-



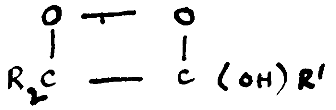
i.e., 1:2 - addition gives an unsaturated tertiary carbinol and 1:4 - addition a saturated ketone.

It might be suggested that 1:4 - addition which is, in effect, addition to the ethylenic bond is really due to direct 3:4 - addition but so far no addition of a Grignard reagent to an isolated ethylenic bond has been achieved. Rupe and Liechtenhan (ref.23) investigating the reaction of magnesium methyl iodide and carvone obtained two compounds one by 1:2 - addition and the other undoubtedly by 1:4 - addition. Their assumption that this was due to 3:4 - addition is most unlikely.

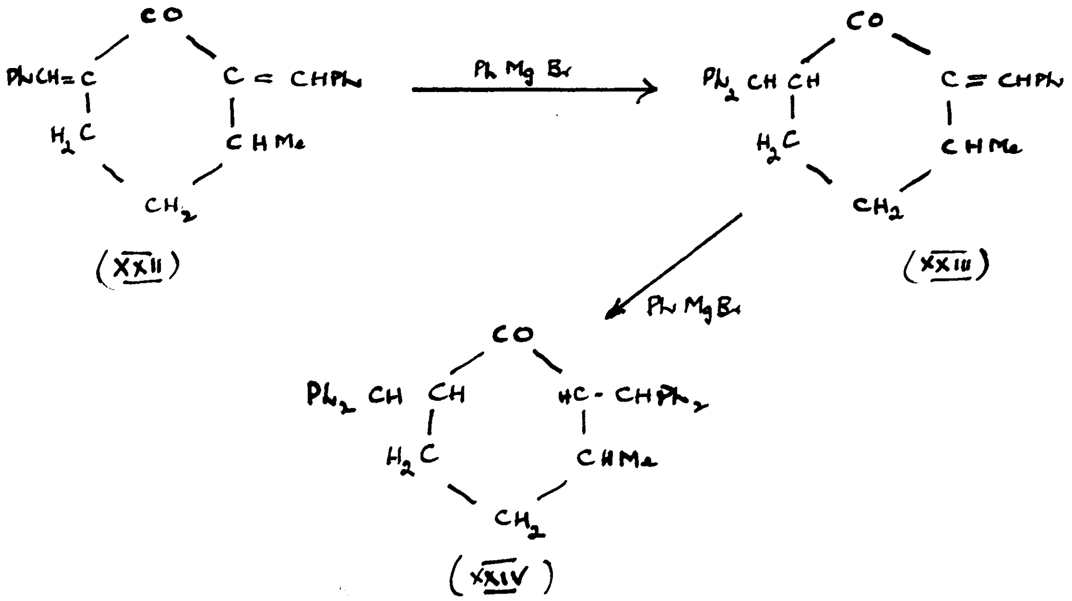
Kohler (ref.24) provided support for the theory of 1:4 - addition by isolating the intermediate enols [$RR''CH-CH=C(OH)R'$)

e.g. $$PhCH=CPhCOPh \xrightarrow{PhMgBr} [Ph_2CH-CPh=C(OMgBr)Ph]$$
$$\longrightarrow Ph_2CH-CPh=C(OH)Ph \quad (\underline{XX})$$
$$\longrightarrow Ph_2CH-CHPh-COPh \quad (\underline{XXI})$$

i.e. α-phenylchalcone with magnesium phenyl bromide followed by hydrolysis gave 1:2:3:3 - tetraphenylprop-1-enol (XX) in crystalline form and its transition into the isomeric 1:2:2 - triphenylethyl phenyl ketone (XXI) could be observed. In comparable reactions where the enols could not be isolated as solids their transformation into ketones could be observed and their existence demonstrated by the formation of peroxides which are yellow crystalline solids of formula,

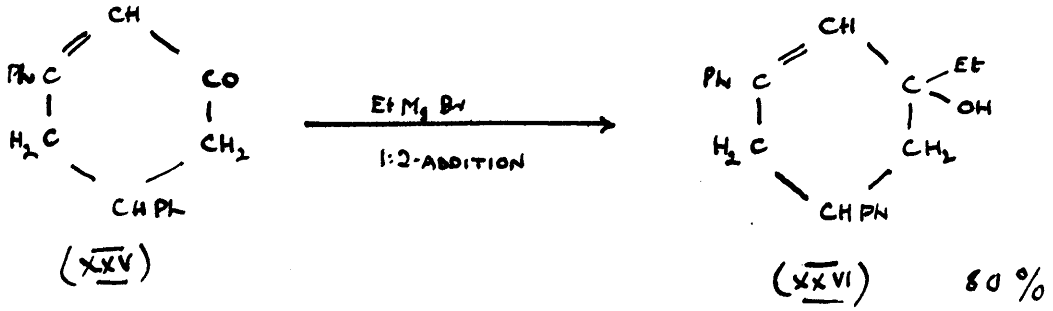


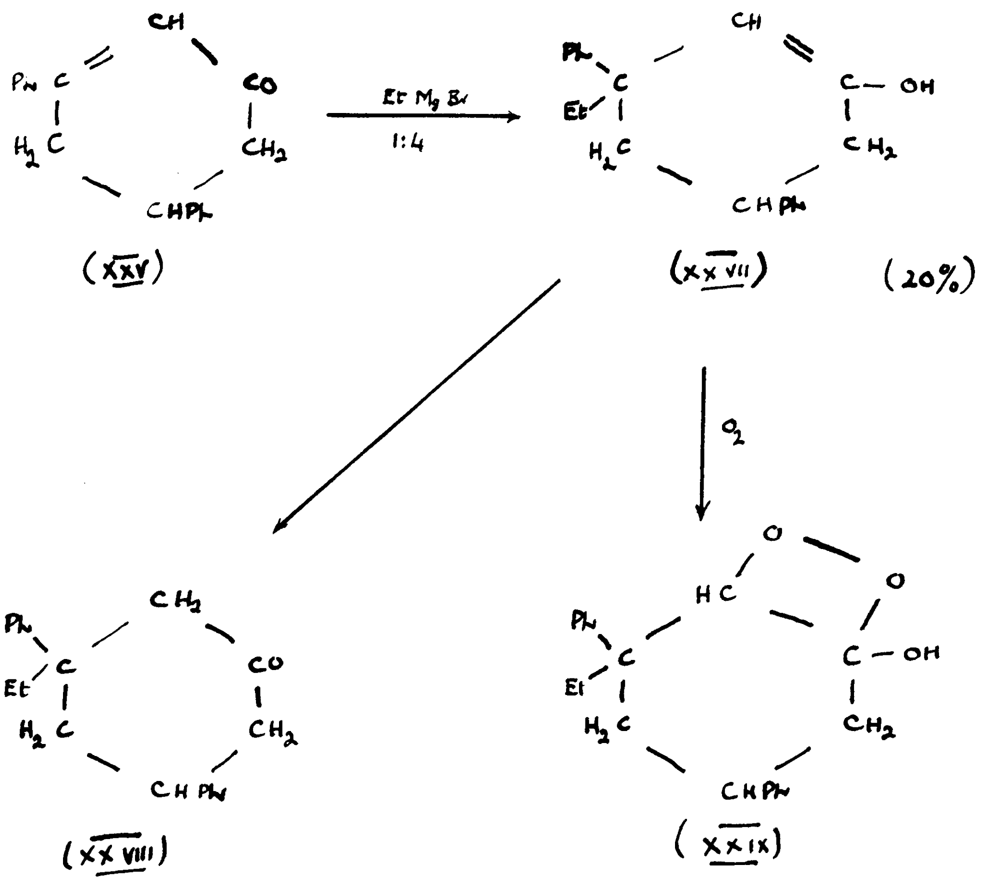
Later Kohler (ref.25) showed that addition of Grignard reagents to αβ -unsaturated ketones was not exclusively 1:4 - but that in many cases 1:2 - addition also occurred. e.g. 2:6 - benzylidene - 3 - methylcyclohexanone (XXII) by the action of magnesium phenyl bromide gave, after hydrolysis, 2 - benzylidene - 6 - benzhydryl - 3 - methylcyclohexanone (XXIII) and ultimately 2:6 - dibenzhydryl - 3 - methylcyclohexanone (XXIV)



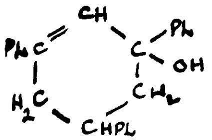
The addition of the Grignard reagent was clearly 1:4.

On the other hand, magnesium ethyl bromide reacted with 3:5 - diphenylcyclohex-2-enone (XXV) to give a mixture of 80% tertiary carbinol (XXVI) (by 1:2-addition) and 20% enol (XXVI) (by 1:4-addition). The constitution of (XXVII) xxvii was proved by its spontaneous transformation into the ketone (XXVIII) and by oxidation to the peroxide (XXIX)





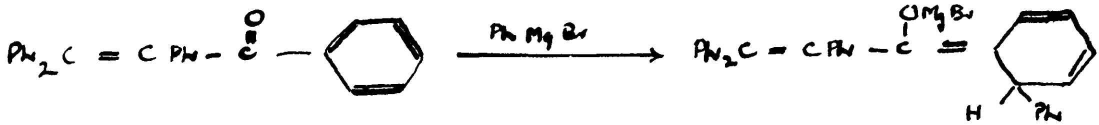
That the nature of the Grignard reagent has an important directive influence is shown by the fact that, although in the above example magnesium <u>ethyl</u> bromide gives a mixture of 1:2 and 1:4 - addition products (XXVI) and (XXVII), with magnesium <u>phenyl</u> bromide 1:2-addition takes place exclusively to give 1:3:5 - triphenylcyclohex-2-enol.



The results of a series of experiments carried out by Kohler (ref.26; see also ref.27) show the differences between the action of alkyl and aryl Grignard reagents and effects of changes in the ketone itself.

Substance	% 1:4-Addition with $PhMgBr$	with $EtMgBr$
$PhCH=CHCOMe$	12	60
$PhCH=CHCOEt$	40	71
$PhCH=CHCOPr^{\beta}$	88	100
$PhCH=CHCOBu^{\gamma}$	100	100
$PhCH=CHCOPh$	94	99
$Ph_2C=CHCOPh$	0	18
$PhCH=CPhCOPh$	100	100
$PhCMe=CHCOPh$	44	41

The tendency to 1:4 - addition is so strong that it takes place even when a double bond of a benzene ring has to be used to make it possible. Thus, Kohler and Nygaard (ref.28) found that although the <u>saturated</u> ketone $Ph_2CH-CH.Ph.CO.Ph$ reacted in the normal way with magnesium methyl iodide and magnesium phenyl bromide, the corresponding <u>unsaturated</u> ketone was quite unreactive in ether. However, when this latter was heated in benzene with magnesium phenyl bromide 1:4 - addition occurred but it involved a phenyl nucleus:-



When however this ortho position is occupied, forcing the conditions gives the normal 1:4 - addition (ref.29; see also ref.30, 31, 32, 33)

It has been shown that when there are two substituents on the β-carbon—atom 1:4 - addition is greatly reduced (ref.26) or entirely suppressed (ref.28). Forced conditions bring about addition but only by conscripting a "double bond" of the benzene ring. That normal addition can occur under forced conditions, has also been shown (ref.29).

Similarly magnesium <u>alkyl</u> halides give 1:2 - addition products. Thus Gry (ref.34) obtained tertiary alcohols and no 1:4 products by the action of magnesium methyl iodide, magnesium-ethyl bromide, magnesium isobutyl chloride and magnesium isoamyl bromide. Mesityl oxide appears to give 1:2 - addition with <u>all</u> Grignard reagents: no 1:4 - product has been isolated. Thus Fellenberg (ref.35) by the use of magnesium methyl iodide obtained $Me_2C = CHCMe = CH_2$. This was obtained by improved methods by Jitkon and Bogert (ref.36). I had myself prepared it independently by exactly this method. Fellenberg (ref.20) also obtained $PhCH = CMe - CH = CMe_2$ by the action of magnesium benzyl chloride on mesityl oxide, andIhave confirmed this result.

Gilman and co-workers extended the scope of the investigation to the reaction - of organo metallic compounds such as $PhLi (Na, K)$, $PhCaI$, $PhMnI$, Ph_3Al

Kirby (ref.37) surveyed the literature and deduced the following generalisations:-

1. The proportion of 1:2 - addition decreases as R' changes in the order Me, Et, Buγ, Ph.
2. Where R is phenyl, the proportion of 1:4 - addition is less than where R is methyl. Two groups on the β-carbon atom greatly decrease 1:4 - addition.
3. If R is aryl radicle the 1:2 - directing influence of monosubstitution on the β-C - atom is overcome and 1:4 - addition occurs.
4. Substitution on the α-C - atom favours 1:4 - addition.
5. Temperature and solvent seem to have little effect on the relative proportions of 1:2 - and 1:4 - addition.
6. For Grignard reagents, 1:2 - addition was found increasingly in the order R = tertiary alkyl, alkyl, aryl, methyl, though there are exceptions.
7. Explanations based on steric hindrance of the Grignard reagent, the particular halogen, or proportions of R_2 Mg to RMgX were inadequate.

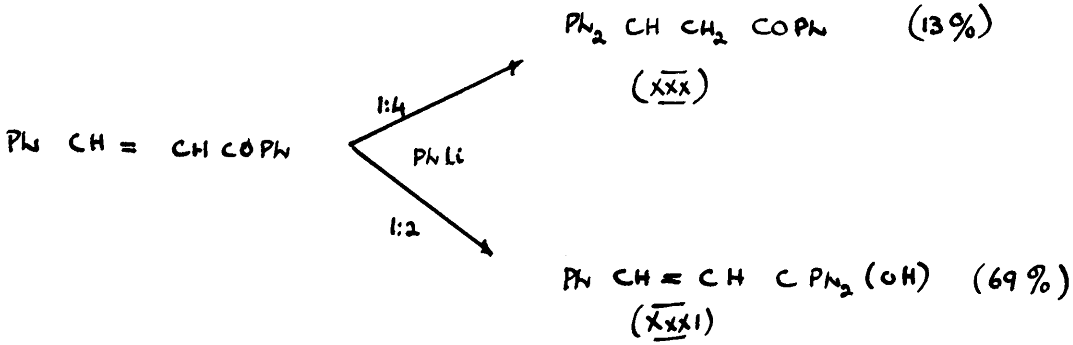
The preparation of organo-metallic compounds other than Grignard reagents introduced further complications.

Thus Gilman and Kirby show that whilst magnesium phenyl bromide adds to chalcone by 1:4 - addition to give ββ - diphenylpropiophenone (XXX)

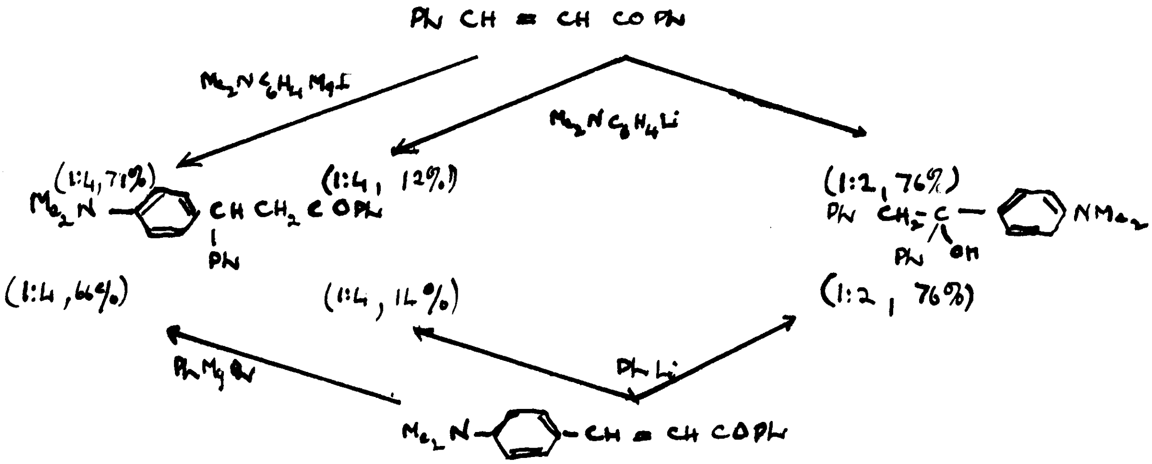
$$\text{Ph CH = CH COPh} \xrightarrow[\text{hydrolysis}]{\text{Ph Mg Br and}} \text{Ph}_2\text{ CH CH}_2\text{ COPh}$$

(XXX)

lithium phenyl gives not only the 1:4 - product (13%) but predominantly the 1:2 - product (69%) diphenylstyryl carbinol (XXXI)



Lüttringhaus (ref.38) who isolated the carbinol (XXXI) failed at first to detect the ketone (XXX) but later (ref.39) confirmed Gilman and Kirby's claim. Gilman and Kirby's extension of the work may be represented thus:-

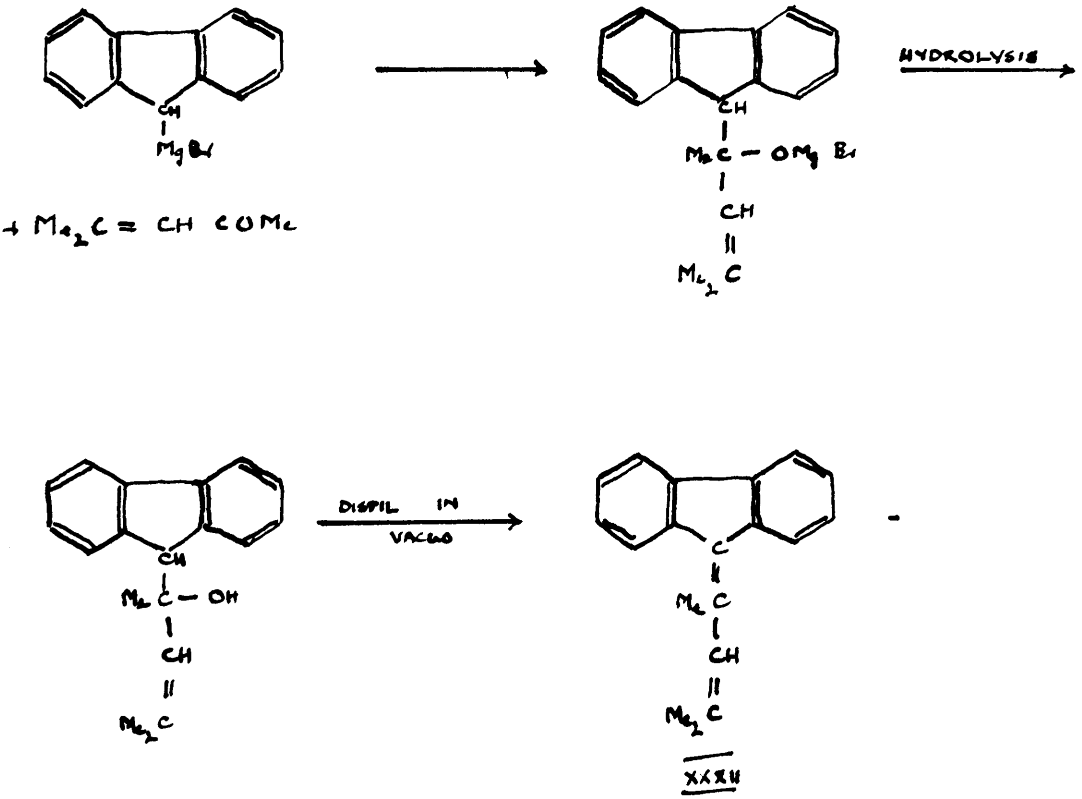


i.e., whilst addition of Grignard reagents proceeds by a 1:4 - process, organo lithium compounds add predominantly by 1:2 - addition though 1:4 - addition takes place to a lesser degree.

Up to the present, no work appears to have been carried out on the reaction of metallofluorene derivatives and αβ - unsaturated ketones. I have investigated the behaviour of magnesium 9 - fluorenyl bromide and of lithium 9 - fluorenyl on mesityl oxide, chalcone, benzylidene acetone, ethylidene acetone and 3 - methyl - pent - 2 - ene - 4 - one.

Although interpretation of results in several cases was difficult since the products of reaction were oils, it can be stated that in the addition of magnesium 9 - fluorenyl bromide to these αβ - unsaturated ketones reaction took place with the carbonyl group only i.e., 1:2 - addition: there was no evidence of 1:4 - addition. On the other hand the reaction of lithium 9-fluorenyl with these same ketones proceeded entirely by 1:4 - addition there being no evidence of 1:2 - addition.

In particular, work herein described has shown that magnesium 9-fluorenyl bromide combines with mesityl oxide solely in the 1:2 - position. On account of experimental difficulties inherent in working with fluorenyl derivatives no attempt was made to isolate the intermediate carbinol, but this was dehydrated, during distillation to give the diene, α - diphenylene -βδ - dimethyl - $\Delta^{\alpha\gamma}$ - pentadiene (XXXII)



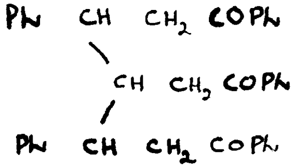
XXXII

This compound had already been isolated by the action of the same Grignard reagent (ref.8) on diacetonealcohol, presumably by intermediate formation of mesityl oxide. The yield of the crystalline, phototropic substance (XXXII) was 30% based on unrecovered fluorene. The remainder of the reaction product gave no reaction with 2:4 - dinitrophenylhydrazine. These results are entirely in agreement with those previously mentioned (page 30) for the reaction of magnesium alkyl or aryl halides with mesityl oxide - addition is invariably solely with the keto-group i.e. 1:2 - addition.

This reaction was carried out under conditions which are generally classed as "forced" i.e. mesityl oxide was added to a stirred suspension of magnesium 9-fluorenyl bromide in xylene and the mixture maintained at 125° for 2½ hours. However, Kirby (ref.37) states that while changes of temperature and solvent may help to bring about a reaction they do not disturb the ratio of 1:2 - to 1:4 - addition. Gilman and Kirby (ref.40) in reference to the use of calcium phenyl iodide write "other studies with benzhydryl metallic compounds indicate the possibility of thermally converting a 1:2 - addition product to a 1:4 - addition product but we have not seen any experimental evidence for this idea". Lüttringhaus and Scholtis (ref.41) attempted unsuccessfully to convert the 1:2-addition product derived from lithium phenyl and chalcone into the 1:4-addition product.

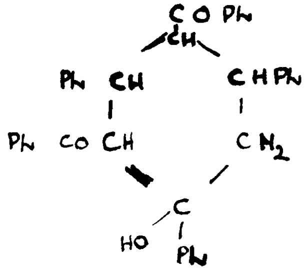
Similar condensations were attempted between magnesium 9-fluorenyl bromide and ethylidene acetone, benzylidene acetone and benzylidene acetophenone (chalcone) but no crystalline addition products could be isolated. The thick yellow oils obtained gave in each case, fluorenone, and benzoic acid from the benzylidene acetone and chalcone adducts in good yield. Tests for ketones with 2:4-dinitrophenylhydrazine and with hydroxylamine gave negative results. This was surprising for ethylidene acetone gives both 1:2 and 1:4 - addition with magnesium ethyl bromide (41.4% and 38.16% respectively) and with magnesium tert-butyl bromide, (16.7% and 54% respectively) (ref.22; see also ref.26 and 34). Similarly benzylidene acetone and chalcone give high yields of 1:4 - addition products with certain Grignard reagents (ref.25 and 26).

In the reaction of magnesium 9-fluorenyl bromide and chalcone there was obtained a white solid, m.p. 252-254° which failed to give fluorenone on treatment with sodium dichromate in glacial acetic acid and which did not form a 2:4-dinitrophenylhydrazone. Kostanecki (ref.76 and 77) obtained from the reaction of benzaldehyde and acetophenone a high melting solid to which they assigned the formula



However, it is unlikely that a compound of this type would fail to form ketone derivatives. It is therefore possible that the substance m.p. 252-254° is 1:3:5-triphenyl - 2:4-diphenylcarbonyl-cyclohexene.

where the carbonyl groups are hindered by phenyl groups. This structure is supported by analysis figures. An attempt to prepare the same compound from chalcone and acetophenone dissolved in ether with pyridine and potassium hydroxide added, gave a different compound m.p. 245-247° which may be

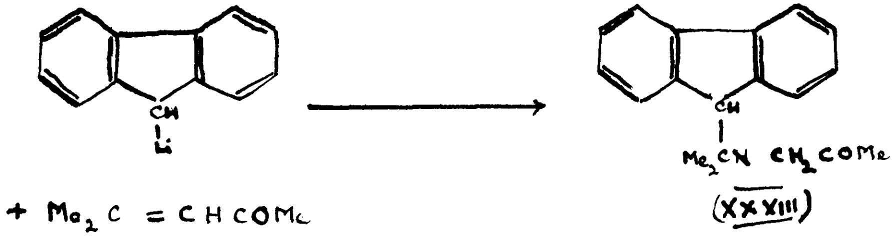


i.e. 1:3:5 - triphenyl - 2:4 - diphenylcarbonylcyclohexanol.

Addition of cuprous bromide or iodide to the xylene suspension of magnesium 9-fluorenyl bromide followed by addition of mesityl oxide merely decreased the yield of the 1:2-addition product (ref.42 and 43.)

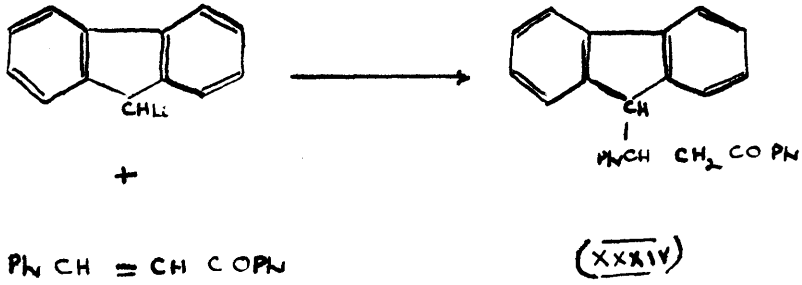
It is well known that lithium organo-compounds react similarly to Grignard reagents with carbonyl compounds and generally give improved yields of carbinols. In addition they often react when Grignard reagents fail to do so (ref.44 and 32). Similarly lithium organo-compounds react with $\alpha\beta$-unsaturated ketones to give almost invariably high yields of carbinols (1:2-addition) even when the corresponding Grignard reagents give high yields of saturated ketones (1:4-addition). Gilman and Kirby (ref.40) using lithium reagents obtained invariably high yields of carbinols (1:2-addition) but also isolated saturated ketones (1:4-addition) in small yield (cf. ref 38 and 41). Koelsch and Rosenwald (ref.45) obtained the unusual 1:4-addition of lithium phenyl in the reaction with 8-phenyl-perinaphthindan - 7:9-dione but the reaction was somewhat abnormal since it involved the "double bond" of an aromatic ring.

Hence it is surprising to find that lithium 9 - fluorenyl not only does not react with the highly reactive carbonyl group of mesityl oxide, as do all Grignard reagents (including magnesium 9-fluorenyl bromide), but gives in petroleum (b.p. $67-69^{\circ}$) at the boiling point for ½ hr. a good yield (52%) of the saturated ketone, methyl β-9-fluorenyl-β-methyl-n-propyl ketone (XXXIII), by 1:4 - addition. Its 2:4-dinitrophenylsemicarbazone was prepared.



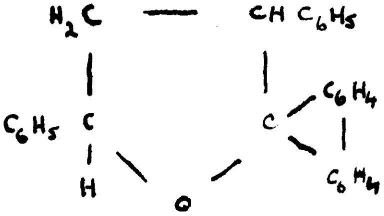
That none of the 1:2-addition product was present was shown by exposing the solid fractions obtained in the reaction, to sunlight, no colour change occurring: the presence of the phototropic substance (XXXII; page 34) would have been shown by pink specks.

Lithium 9-fluorenyl added likewise (1:4-addition) to chalcone, forming phenyl β-9-fluorenyl-β-phenylethyl ketone (XXXIV) in 55% yield m.p. 126-7°.



(XXXIV)

Taylor and Connor (ref.46) prepared it (27% yield in 1 week) m.p. 127-128° (corr.) by the action of fluorene and chalcone in the presence of sodium ethoxide but, except for analysis, did not establish its suggested structure. Its constitution was however called in question by Pinck and Hilbert (ref.47) who, following the method used by Tucker (ref.48) for the Michael condensation of fluorene and mesityl oxide, claim that fluorene condenses with chalcone by the action of concentrated sodium hydroxide in pyridine solution to give a compound $C_{28}H_{22}O$, m.p. 128°, to which they assign the structure,



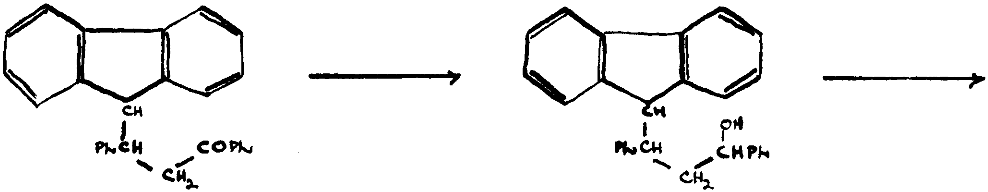
"since this compound failed to form a phenylhydrazone and a carbazide and failed to show an OH - absorption in the infra-red".

Pinck and Hilbert's work has now been repeated and the compound $C_{28}H_{22}O$ found to be identical with that obtained with lithium 9-fluorenyl and chalcone.

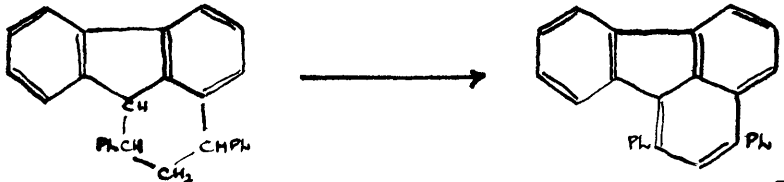
Oxidation of (XXXIV) gave fluorenone (42%) and benzoic acid (26%). These oxidation results do not, of course, differentiate between 1:2 - and 1:4-addition but indicate that the substance under investigation is a condensation product of fluorene and chalcone.

2:4-dinitrophenylhydrazine gave with (XXXIV) an orange reaction product which could not be purified but the preparation of an <u>oxime</u> indicated that the substance was indeed phenyl β-9-fluorenyl-β-phenylethyl ketone (XXXIV).

Since the ultimate object of these researches was the synthesis of substituted fluoranthenes it was decided to attempt to confirm the structure of the fluorene-chalcone, Michael addition product (XXXIV) by converting it to 2:4 - diphenylfluoranthene. This was successfully achieved in the following manner:-



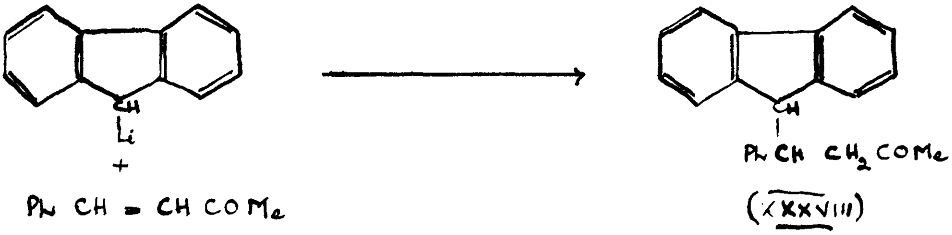
(XXXIV) (XXXV)



(XXXVI) (XXXVII)

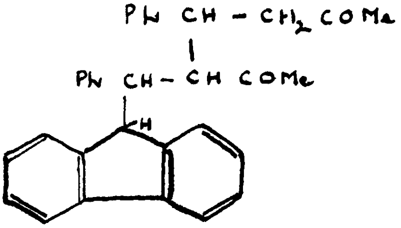
The ketone (XXXIV) was reduced by means of aluminium isopropoxide in isopropanol or hydrogen and Raney nickel in ethanol to *αγ-diphenyl - γ - 9 - fluorenyl - propanol* (XXXV) which on heating at 100° for 5 mins. in a mixture of concentrated sulphuric and glacial acetic acids gave *2:4-diphenyl-1:2:3:4-tetrahydrofluoranthene* (XXXVI) (cf. ref.7). Dehydrogenation of (XXXVI) with selenium at 300° yielded *2:4 - diphenylfluoranthene* (XXXVII) which formed a stable *picrate* though its *s* - trinitrobenzenate was unstable.

In a similar manner, *methyl β-9-fluorenyl-β-phenylethyl ketone* (XXXVIII) was obtained in the reaction of lithium 9-fluorenyl with benzylidene acetone.

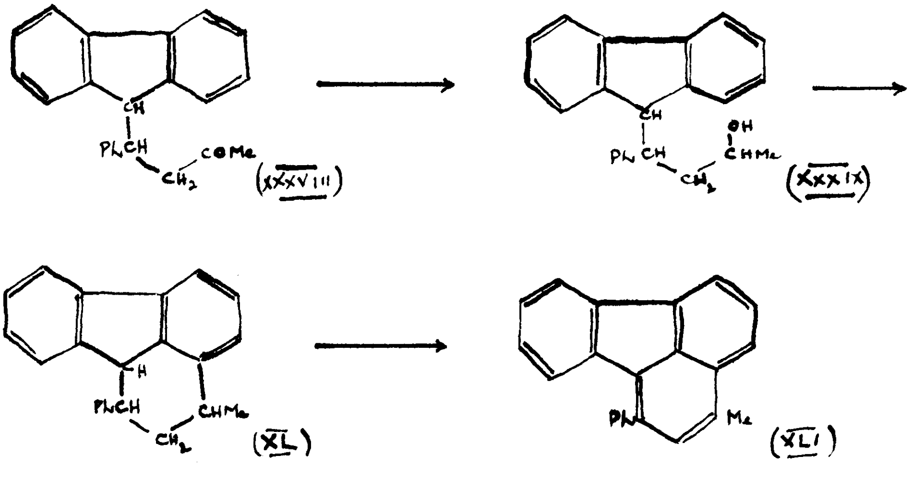


(XXXVIII)

It is interesting to note that Taylor and Connor (ref.46) by the action of fluorene and benzylidene acetone in the presence of sodium ethoxide obtained a substance which they believed to be a "trimolecular compound", m.p. 250°, of the type



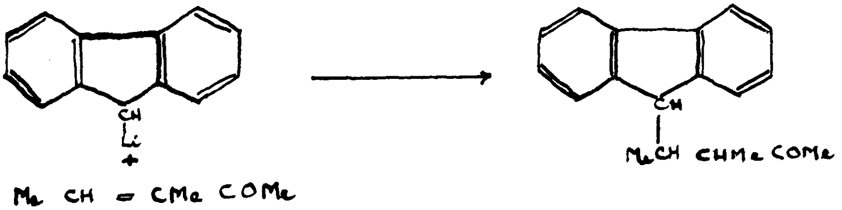
No trace of this substance was observed in the present series of experiments. The ketone (XXXVIII) which formed a <u>2:4-dinitrophenylhydrazone</u> and an <u>oxime</u>, was also obtained by condensation of fluorene with benzylidene acetone in the presence of pyridine and concentrated sodium hydroxide solution. As additional confirmation of the structure 2-phenyl-4-methylfluoranthene was prepared thus:-



<u>α-Methyl-γ-phenyl-γ-9-fluorenyl-propanol</u> (XXXIX) was obtained from (XXXVIII) by catalytic reduction with Raney nickel catalyst in ethanol, and cyclised to <u>2-phenyl-4-methyl-1:2:3:4-tetrahydrofluoranthene</u> (XL)

with concentrated sulphuric acid and glacial acetic acids. 2-Phenyl-4-methylfluoranthene (XLI) was then obtained by dehydrogenation of (XL) with selenium at 300°. The hydrocarbon formed a s-trinitrobenzenate but its picrate rapidly dissociated on standing.

In the reaction of lithium 9-fluorenyl with 3-methylpent-2-en-4-one no crystalline condensation product was isolated. However, the principal fraction obtained on distillation; a heavy red oil, b.p. 210-215°/15 mm., gave a 2:4-dinitrophenylhydrazone whose analysis corresponded to that of the desired compound, methyl β-9-fluorenyl-β-methyl-isopropyl ketone, (XLII).



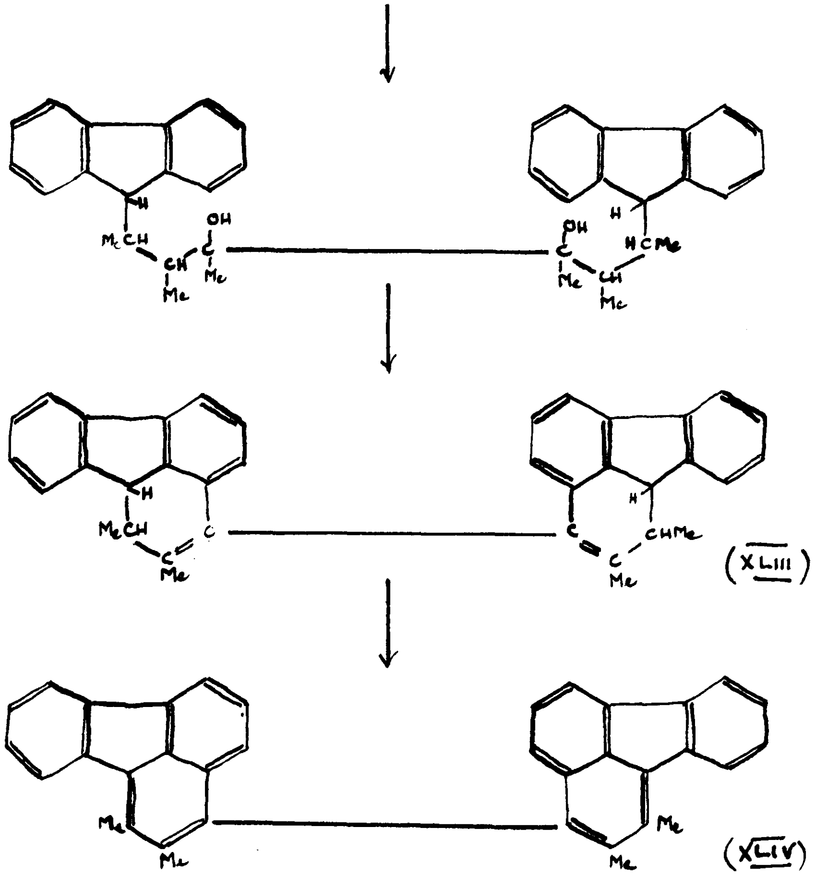
(XLII)

Oxidation of the oil yielded fluorenone.

It was hoped that catalytic reduction followed by cyclisation and dehydrogenation of this compound would yield 2:3:4-trimethylfluoranthene whose synthesis was a primary object of this research. This did not at first occur:-

Reduction of the ketone using Raney nickel as catalyst and a trace of alkali gave an oil which resisted crystallisation but which reacted vigorously with magnesium methyl iodide suggesting that it was indeed a carbinol. The crude oil was treated as before with glacial acetic and concentrated sulphuric acids. The product, m.p. 210-212°, did not correspond to either of the 2:3:4-trimethyl - 1:2:3:4-tetrahydrofluoranthenes already known (see pages 56,59). Analysis figures suggested that pinacol reduction of the ketone had probably occurred i.e.

2 molecules of ketone (XLII)



the product of cyclisation was 2:3:2':3'-tetramethyl - 1:2:1':2'-tetrahydro - 4-4'-difluoranthyl (XLIII). On dehydrogenation this yielded 2:3:2':3'-tetramethyl - 4-4' - difluoranthyl (XLIV) whose picrate and s - trinitrobenzenate were unstable.

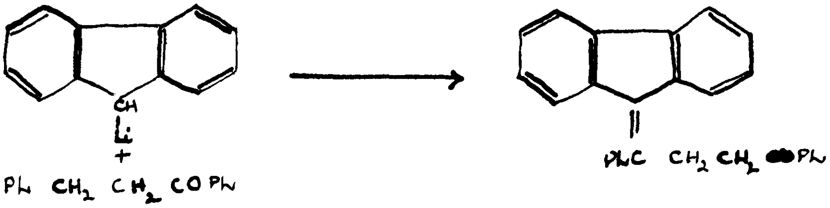
Catalytic reduction with Raney nickel catalyst but no alkali proceeded very slowly. The oil which was obtained was treated with concentrated sulphuric and glacial acetic acids in the usual way and crystallisation from ethanol yielded a minute quantity of 2:3:4-trimethyl-1:2:3:4-tetrahydrofluoranthene (LIVB, page 54)

It will be observed that lithium 9-fluorenyl resembles sodium and potassium 9-fluorenyl in that all react with mesityl oxide by 1:4-addition (ref.48). It is interesting to note that the nature of the solvent does not affect the result - the lithium experiments being conducted in petroleum, the sodium ones in ether whilst potassium 9-fluorenyl was probably formed in mesityl oxide-pyridine. These observations on the 1:4-addition of lithium, sodium and potassium derivatives of fluorene are of special interest since potassium phenyl adds exclusively to the 1:2-position of other $\alpha\beta$-unsaturated ketonic systems (ref.37)

It is clear that steric effects have no influence on the course of these reactions since

(a) as shown above the 9-fluorenyl radicle can be induced to add to the 2- or the 4- position of an αβ-unsaturated ketone by using either the magnesium or the lithium derivative (cf. ref.49)

(b) it was found that lithium 9-fluorenyl reacts with benzylacetophenone (phenyl β-phenylethyl ketone), in which addition to the carbonyl group alone is possible, to give, after hydrolysis and dehydration, α-diphenylene-βδ-diphenylbutene in 20% yield.



Catalytic reduction yielded α-9-fluorenyl-βδ-diphenylbutane.

In the course of these investigations the preparation of magnesium 9-fluorenyl bromide (ref.50 and 8) by the action of magnesium ethyl bromide on fluorene was greatly improved. This resulted from following the course of the reaction and estimating the yield of Grignard reagent by measuring the ethane evolved. Thus it was found that

(a) the period of heating in xylene could be reduced from 12 hours to 3 hours.

(b) the replacement of xylene by p-cymene reduced the period to 1 hour.

(c) replacement by isoamyl ether reduced the period to 1 hour.

The yield of ethane was the same (40%) in each case but the product from isoamyl ether coalesced into larger and harder masses and that from p-cymene was less reactive. A great improvement was effected when it was found that two molecules of magnesium ethyl bromide to one of fluorene in boiling xylene for 3 hours - raised the yield of ethane to 92%. That the increased yield was not due to independent reaction of magnesium ethyl bromide with excess of ethyl bromide or xylene was settled by a blank experiment omitting fluorene from the reaction mixture.

An attempt to confirm the high yield of magnesium 9-fluorenyl bromide by carbonation was disappointing, fluorene 9- carboxylic acid being obtained in 13% yield. The cause is probably mechanical since the solid, pale green Grignard reagent, on treatment with carbon dioxide, coats with an impervious white layer retaining unchanged green reagent.

Again, the reaction of magnesium 9-fluorenyl bromide, prepared by the revised method, gave with acetone, 9-fluorenyl-dimethyl-carbinol in approximately 30% yield i.e. there was little improvement on that reported by Maitland and Tucker (ref.8) The acetyl derivative of 9-fluorenyl-dimethyl-carbinol was prepared.

The preparation of lithium 9-fluorenyl proved troublesome. The use of lithium methyl in ether (ref.51) followed by heating with fluorene in xylene as for the preparation of the corresponding magnesium 9-fluorenyl bromide, proved unsatisfactory. No gas (methane) was evolved and addition of mesityl oxide to the reaction mixture gave subsequently an almost theoretical recovery of fluorene. This negative result was probably due to the great stability of lithium methyl (ref.52). I am unable to understand the comparable preparation of lithium 9-fluorenyl by Miller and Bachman (ref.53 ; cf. also Gilman and co-workers, ref.54, who state that lithium methyl cannot be satisfactorily prepared in petroleum, b.p. 28-38°, because of its insolubility). Similarly lithium n-butyl prepared in sulphur-free benzene (ref.55) gave with fluorene, low yields of butane and after carbonation a low yield (5%) of fluorene 9 - carboxylic acid. The preparation of lithium n-butyl in petroleum (67-69°) (ref.56,54,57) in four hours and heating the product with fluorene in the same solvent for one hour gave however lithium 9 - fluorenyl in 76% yield - estimated by Gilman's titration method - (ref.58 and 59) which by carbonation gave fluorene - 9 - carboxylic acid (66% on total fluorene used and 100% on unrecovered fluorene). It will be seen incidentally that this provides the best method for preparing fluorene 9 - carboxylic acid from fluorene.

Attempts to prepare 9-acetylfluorene (ref.53 and 60) were unsuccessful, the actions of acetyl chloride, acetic anhydride, and ethyl acetate giving almost complete recovery of fluorene.

Following the addition of the fluorene radicle to the 1:4 - position of $\alpha\beta$-unsaturated ketones, it was hoped that lithium 9-fluorenyl would react with tiglic nitrile (α-methylcrotononitrile) in a similar manner, thus providing a ready synthesis of 2:3-dimethylfluoranthene. No such addition product was obtained.

Michael Reactions with Fluorene and Fluorene 9-carboxylic Esters

The ease with which fluorene underwent direct Michael addition to the ethylenic double bonds of chalcone and benzylidene acetone (see pages 40,42) in the presence of sodium hydroxide and pyridine led to a search for the most suitable conditions for such condensations of fluorene with various $\alpha\beta$-unsaturated ~~chalcone~~ ketones (chalcone, benzylidene acetone, O-nitrochalcone, benzylidene acetone, desoxybenzoin, 3-methyl-pent-2-en-4-one) and with tiglic nitrile. The results of this investigation are shown in the accompanying table (page 51) and may be summarised thus:-

(1) 3-Methyl-pent-2-en-4-one, o-nitrochalcone, benzylidene desoxybenzoin and tiglic mitrile failed to react under the conditions employed.

(2) In two cases only with mesityl oxide a very small yield of methyl β-9-fluorenyl-β-methyl n-propyl ketone (XXXIII); page 38) was obtained. This is surprising for this same ketone is readily prepared by the reaction of fluorene and acetone in the presence of powder potassium hydroxide (ref.8), a reaction in which mesityl oxide is probably produced as an intermediate.

(3) Benzylidene acetone gives methyl β-9-fluorenyl - β-phenylethyl ketone (XXXVIII; page 41) in good yield only when pyridine and concentrated sodium hydroxide solution are used as condensing agents.

(4) β-9-Fluorenyl - β-phenylethyl phenyl ketone (XXXIV); page 39) was obtained by condensation of fluorene and chalcone under a variety of conditions. The success of this reaction is probably due to the small solubility in ether, pyridine and dioxan, of the product which slowly crystallises out.

MICHAEL CONDENSATION OF FLUORENE

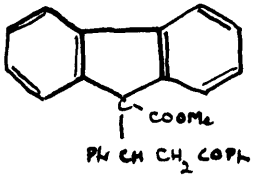
	Reactant	Reagent	Solvent	Conditions		% Ketonic products
				Temp.	Time	
1.	Mesityl oxide	60% NaOH	Pyridine	60°	1.5 hrs.	-
2.	Mesityl oxide	diethylanine	-	reflux	2.5 hrs.	-
3.	Mesityl oxide	powder KOH	-	60°	20 min.	9%
4.	Mesityl oxide	powder KOH	Pyridine	18°	24 hrs.	4%
5.	Mesityl oxide	alcoholic NaOEt	ethanol	78°	2 hrs.	-
6.	Mesityl oxide	powder KOH	nitromethane	60°	15 min.	-
7.	Mesityl oxide	$PhCH_2Me_3N$ OH	mesityl oxide	60°	30 min.	-
8.	Mesityl oxide	powder KOH	-	60°	2 hrs.	-
9.	Mesityl oxide	60% NaOH	pyridine	18°	5 days	-
10.	Tiglic mitrile	$PhCH_2Me_3N$ OH	dioxan	60°	1.5 hrs.	-
11.	Tiglic nitrile	piperidine	ethanol	78°	48 hrs.	-
12.	Benzylidene acetone	60% NaOH	pyridine	60°	1.5 hrs.	-
13.	Benzylidene acetone	60% MaOH	pyridine	18°	5 days	22%
14.	Benzylidene acetone	powder KOH	ether/pyridine	18°	5 days.	10%
15.	Chalcone	powder KOH	dioxan/pyridine	18°	48 hrs.	-
16.	Chalcone	NaO -Me	MeOH/pyridine	18°	48 hrs.	-
17.	Chalcone	50% KOH	dioxan	18°	5 days	50%
18.	Chalcone	powder KOH	ether/pyridine	18°	20 hrs.	64%
19.	Chalcone	powder KOH	dioxan	18°	5 days	45%

Michael addition reactions with the methyl or ethyl ester of fluorene 9-carboxylic acid and benzalacetone, chalcone and mesityl oxide were even less successful. In most cases fluorene - 9 - carboxylic acid was isolated, but in a few instances other substances were obtained:-

(1) With atomised potassium as condensing agent in the condensation of the ethyl ester with mesityl oxide diethyl 9-9' - difluorenyl - 9-9'-dicarboxylate ~~ester~~ was obtained.

(2) When chalcone replaced mesityl oxide in (1) a substance was isolated which gave this analysis - C, 71.4; H, 4.8%.

(3) Chalcone, methyl-fluorene 9-carboxylate, ether and potassium hydroxide yielded two substances-aa acid which proved identical with the product of (2) and a neutral substance m.p. 180-182 which on warming with dilute sodium hydroxide formed phenyl β-9-fluorenyl-β-phenylethyl ketone i.e. the substance was probably mainly the ester,



though analysis figures were not very satisfactory.

III Synthesis of Methylfluoranthenes

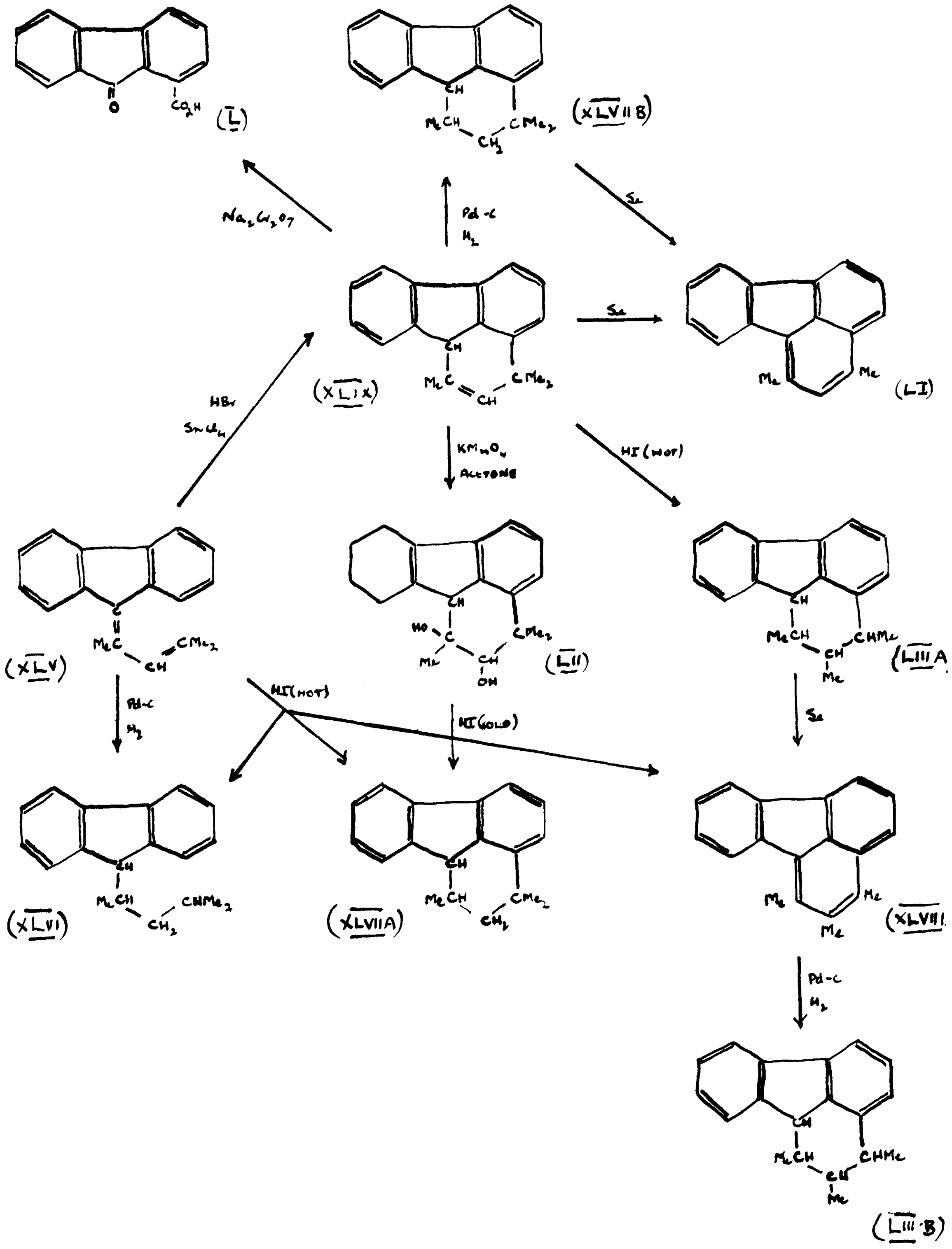
In the reaction of magnesium 9-fluorenyl bromide and mesityl oxide there was isolated a phototropic substance to which was ascribed the structure (XLV) (see page 34) i.e. the substance formed by 1:2 - addition, to the conjugated system of mesityl oxide, followed by dehydration. This structure is supported by the following evidence:-

(1) oxidation with sodium dichromate and acetic acid yielded fluorenone indicating the presence of a substituent on the 9-position of the fluorene nucleus.

(2) it forms a picrate.

(3) catalytic hydrogenation with palladium charcoal and hydrogen at atmospheric pressure indicates the presence of two double bonds. Since oxidation of the reduced product, 2-methyl-4-(9-fluorenyl)-pentane (XLVI) yields fluorenone the bonds reduced must be in the side chain.

The formula (XLV) contains a diene system $\rangle C=CMe-CH=CMe_2$ and would be expected to give a Diels Alder addition product with maleic anhydride. However repeated attempts to obtain such an adduct in xylene, propionic acid or nitrobenzene as solvent or with a large excess of molten maleic anhydride, were all unsuccessful. An attempt to prepare the sulphone of (XLV) with liquid sulphur dioxide in a sealed tube failed. It is interesting to note that the same failure



occurred in the attempted preparation of Diels Alder adducts of Ph CH = CMe - CH = CMe$_2$ and Ph CH = CMe - CH =NCMe$_2$ (see page 13). This failure of a conjugated ethylenic system to undergo the typical diene reaction is, however, not unique. Becker and Strating (ref.61) failed to add maleic anhydride to 1-diphenylenebutadiene (assumed to be intermediately formed from 9-hydroxy - 9-allyl-fluorene) and Bachman and Hatton (ref.62) found that 4-methyl-1:3-pentadiene failed to react with maleic anhydride and with benzo-quinone even in the presence of anti-oxidants and at high temperatures.

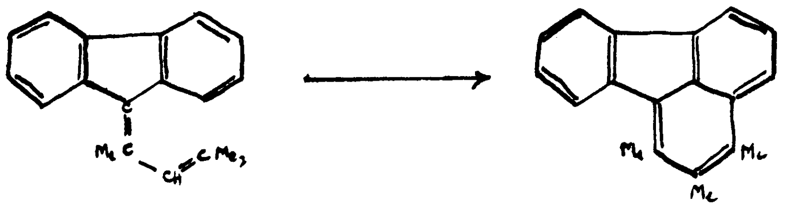
Various methods were tried to cyclise the compound (XLV) to derivatives of fluoranthene.

The first reagent used was anhydrous aluminium chloride with carbon disulphide, nitrobenzene and chlorobenzene as solvents. Since no success was attained a mixture of aluminium chloride and sodium chloride (ref.63) was used - also unsuccessfully.

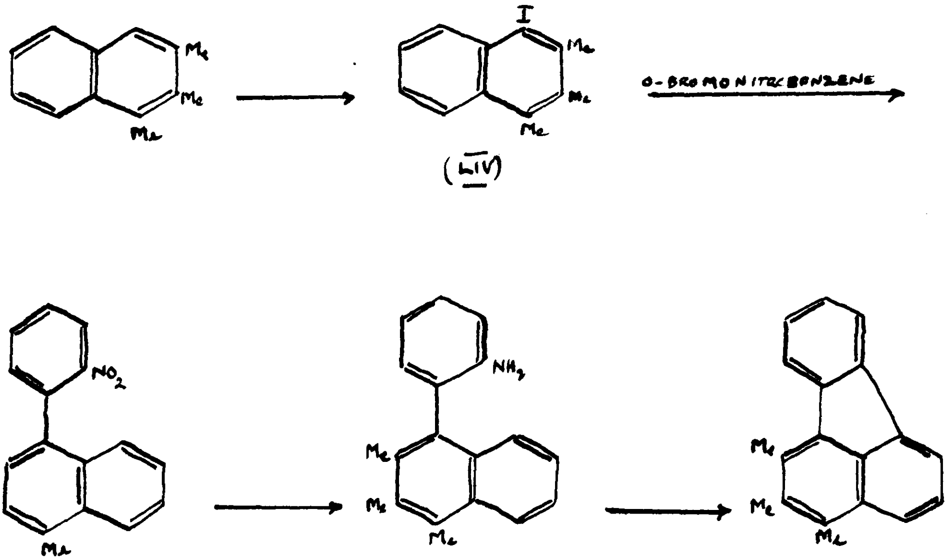
A mixture of phosphoric acid and phosphorus pentoxide (ref.64) likewise met with no success.

Maitland and Tucker (ref.8) obtained two compounds by the action of hydriodic acid and glacial acetic acid on (XLV) (a) substance m.p. 51-55° (b) a substance m.p. 101-3°. This work has now been repeated and the structures of the compounds assigned. The compound (a) (m.p. 51-55°) was found to be identical with that obtained by catalytic hydrogenation of (XLV) viz. 2-methyl-4-(9-fluorenyl)-pentane (XLVI). The analytical figures formerly obtained (ref.8.) for this compound are in approximate agreement for either formula, $C_{19}H_{20}$ or $C_{19}H_{22}$. Repeat analysis confirmed the formula as $C_{19}H_{22}$. (XLVI), then, is obtained by direct reduction of the double bonds and further refluxing with hydriodic acid causes no change. The substance (b) m.p. 101-103° was not at first obtained in this series of experiments and was finally isolated, on one occasion only, when hydriodic acid(d, 1.50) was used in place of (d, 1.70). At this stage the structure of 2:4:4 - trimethyl - 1:2:3:4 - tetrahydrofluoranthene (XLVIIA) produced by ring closure and reduction was provisionally (see page 59) assigned. In the course of these reactions a fairly large yield of a <u>third</u> substance not previously isolated from this reaction, was obtained. This proved to be 2:3:4-trimethylfluoranthene (XLVIII) whose constitution had already been clearly indicated by Forrest and Tucker (ref.9). The mechanism for the formation of this compound is not quite clear since it involves the migration of a methyl group either before or after cyclisation and also the formation of an unsaturated ring in the presence of a strong reducing agent.

i.e.



The identity of the compound (XLVIII) has now been conclusively established by the synthesis from 1:2:3-trimethylnaphthalene of 2:3:4-trimethylflauranthene which proved identical with(XLVIII)



(LIV)

(LV)

(LVI)

Iodination of 1:2:3-trimethylnaphthalene with sodium iodide, sodium nitrate and acetic acid, (cf.ref.9) or powdered iodine and concentrated nitric acid in benzene (ref.65) yielded pale yellow needles, m.p. 127-9° which contained nitrogen (6.1%) and iodine (13.7%). No formula has so far been assigned to this compound. With potassium iodide, potassium iodate and acetic acid (ref.66) <u>1-iodo -2:3:4- trimethylnaphthalene</u> (LIV) was obtained. An Ullmann reaction (cf. ref.67 and 68) with (LIV) and *o*-bromonitrobenzene yielded two products

(a) colourless needles m.p. 122-4° which did not contain nitrogen

(b) a small yield of the desired *1-(2'-nitrophenyl)-2:3:4-trimethylnaphthalene* (LV). Catalytic hydrogenation of (LV) with hydrogen and Raney nickel in ethanol yielded *1-(2'-aminophenyl)- 2:3:4-trimethylnaphthalene* (LVI) which on diazotisation and treatment of the diazo-solution with copper bronze gave 2:3:4-trimethylfluoranthene (ref.69 and 9).

The use of hydrogen bromide as a cyclising agent for α-diphenylene-βδ-dimethyl- $\Delta^{\alpha\gamma}$pentadiene (XLV) (page 54) gave a white solid, insensitive to light which rapidly changed back to the phototropic (XLV). This white solid was dissolved in benzene and anhydrous stannic chloride in benzene added to the cooled solution. There was obtained a good yield of a white crystalline solid. That this compound is probably *2:4:4 -trimethyl - 1:4 (? 3:4) - dihydrofluoranthene* (XLIX page 54) (the position of the double bond cannot be certified) is supported by the following evidence:-

(1) Oxidation of (XLIX) with sodium dichromate in acetic acid yielded fluorenone 1-carboxylic acid (L) proving conclusively that ring formation to the 1-position of the fluorene nucleus had occurred (*vide*, ref.7).

(2) Heating (XLIX) with selenium at 300° gave, by elimination of hydrogen and methyl, 2:4-dimethylfluoranthene (LI) (ref.9) which was identified by its trinitrobenzenate.

(3) Catalytic hydrogenation with palladium charcoal and hydrogen indicated the presence of one double bond, a substance $C_{19}H_{20}$ m.p. 85-87° being obtained. Since migration of methyl groups is unlikely in such a reaction and since dehydrogenation yields 2:4-dimethylfluoranthene the substance is probably 2:4:4-trimethyl-1:2:3:4-tetrahydrofluoranthene (XLVIIB, page 54). It was different from (XLVIIA) which was obtained by the action of hot hydriodic acid on α-diphenylene-βδ-dimethyl-$\Delta^{\alpha\gamma}$-pentadiene (page 56)

(4) When (XLIX) was oxidised with potassium permanganate in acetone there was produced 2:4:4-trimethyl-2:3 (?1:2)-dihydroxy-1:2:3:4-tetrahydrofluoranthene (LII, PAGE 54) which was reduced with hydriodic acid in glacial acetic acid in the cold. The product, a hydro-carbon m.p. 103-4° was 2:4:4-trimethvl-1:2:3:4-tetrahydrofluoranthene which was identical with(XLVIIA.)

(5) Reduction of (XLIX) with a hot solution of hydriodic acid in glacial acetic acid gave a hydrocarbon different from that obtained by catalytic hydrogenation. Since dehydrogenation with selenium yielded 2:3:4- trimethyl-

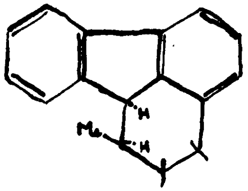
fluoranthene, it is believed that in this case, too, the hot hydriodic acid solution has caused migration of one of the methyl groups to give *2:3:4-trimethyl-1:2:3:4-tetrahydrofluoranthene* (LIIIA) Catalytic hydrogenation of 2:3;4-trimethylfluoranthene produced a second and different *2:3:4-trimethyl-1:2:3:4-tetrahydrofluoranthene* (LIIIB)

It is interesting to note that whereas the above 2:4:4-trimethyl - (1:4 ? 3:4) - dihydrofluoranthene under the action of hot hydriodic acid gives by migration of a methyl group, 2:3:4-trimethyl - 1:2:3:4-tetrahydrofluoranthene (LIIIA), the corresponding 2:2:4-trimethyl - 1:2-dihydrofluoranthene gives without methyl group migration, the normal hydrogenation product. In this latter case, methyl group migration can however be brought about by heating with zinc chloride or phosphorus pentoxide (ref.7)

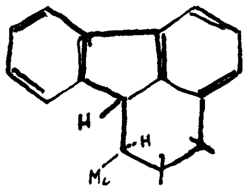
It will be seen that two pairs of compounds (XLVIIA and B; LIIIA and B) have been prepared with apparently the same structure but which are not identical. The occurrence of these compounds may be explained on the grounds of stereo- ~~geometrical~~ isomerism.

Considering compounds (XLVIIA and B)i.e. the two 2:4:4-trimethyl - 1:2:3:4-tetrahydrofluoranthenes, it will be observed that such a structure has two asymmetric carbon atoms and hence two stereo- ~~geometrical~~ isomers (A) and

(B) are theoretically possible.



(A)



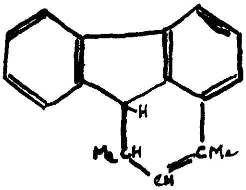
(B)

Similarly 2:3:4-trimethyl - 1:2:3:4-tetrahydrofluoranthene (LIII A and B) contains three asymmetric carbon atoms and could theoretically exist as 8 pairs of optical isomers. Since LIIIB is obtained by catalytic hydrogenation it is possible that in this case all the hydrogen atoms may be on the same side of the plane of the ring.

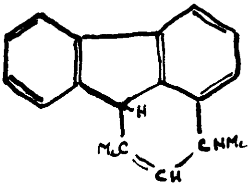
Catalytic hydrogenation of 2:4-dimethylfluoranthene with palladium-charcoal and hydrogen yielded two products.

(a) 2:4-dimethyl - 1:2:3:4-tetrahydrofluoranthene m.p. 115-117°.

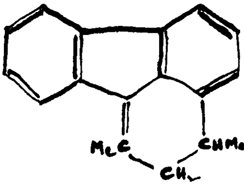
(b) a small amount of substance m.p. 84-86° which contains one double bond in the methylated ring and may therefore be represented by (C), (D) or (E).



(C)



(D)



(E)

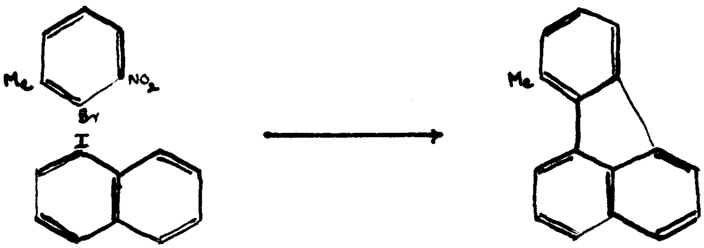
Of these (C) seems to be the most likely structure since (D) requires that the two hydrogen atoms have been added in the 1:4-position of 2:4-dimethylfluoranthene - unusual for catalytic hydrogenation - and (E) leaves the readily reducible "isopropylidene fluorene" double bond untouched i.e. the second product is 2:4-dimethyl-2:3- (? 1:2, 3:4)-dihydrofluoranthene.

A strong blue green fluorescence in ultra-violet light is shown by XLVIII, XLIX, XLVIIA, LI, 2:4-diphenylfluoranthene and 2-phenyl-4-methylfluoranthene. XLVIIB unlike its isomer shows no colour.

Syntheses of Other Methylfluoranthenes.

It was hoped to synthesise several other methylfluoranthenes by reactions similar to those employed in the preparation of 2:3:4-trimethylfluoranthene

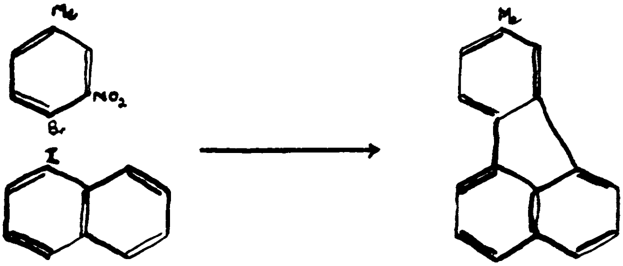
(1) 10-Methylfluoranthene



1 - Iodonaphthalene was condensed with 2-bromo-3-nitrotoluene by heating with copper bronze, the principal product being 1- (2′-nitro-5′-methylphenyl)- naphthalene. Reduction of the nitro group proceeded readily with hydrogen and Raney nickel catalyst, forming 1-(2′-amino-5′-methylphenyl)-naphthalene. On diazotisation and heating with copper, a small amount of solid whose ethanolic solution gave a blue

fluorescence in ultraviolet light and which gave an S-trinitrobenzenate was isolated. The product was not obtained pure.

(2) 11-Methylfluoranthene



The reaction of 3-nitro-4-bromotoluene with 1-iodonaphthalene in the presence of copper bronze yielded 2-2'-dinitro-4-4'-dimethyldiphenyl and a large amount of heavy oil from which no crystalline material could be obtained even after distillation under reduced pressure or chromotography (alumina). Catalytic reduction of the oil using Raney nickel was therefore attempted but no acid - soluble substance was obtained.

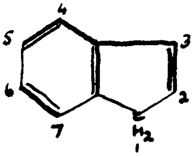
(3) 2:6-Dimethylfluoranthene

No success was achieved in the synthesis of this compound since all attempts to iodinate 2:6 - dimethylnaphthalene failed.

Since direct iodination of naphthalene and some of its methyl-derivatives proved difficult the condensation of naphthalene and of 1:3 - dimethylnaphthalene with O - nitrotriazen by the various modifications of the Gomberg-Hey method (ref.70) were attempted, but without success.

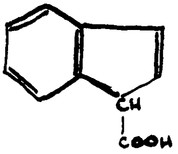
IV. Reactions of lithium 1-indenyl and lithium 10-benzanthryl.

Since the methyl group of indene



was known to behave in certain reactions in a similar manner to that of fluorene i.e. indene readily forms magnesium 1-indenyl bromide by "double decomposition" with magnesium ethyl bromide (ref. 73 and 74) an investigation of the preparation and reactions of lithium 1-indenyl with $\alpha\beta$-unsaturated ketones was undertaken.

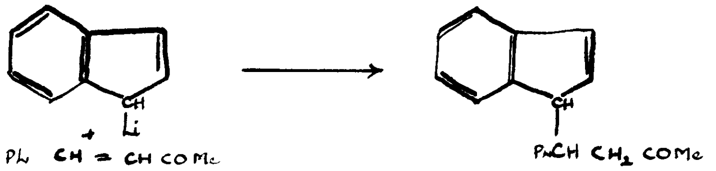
Lithium 1-indenyl was successfully prepared under exactly the same conditions as lithium 9-fluorenyl. Indene in petroleum (67-69°) was added to lithium n-butyl prepared in petroleum. Almost at once a white gelatinous precipitate of lithium 1-indenyl was formed. Evolution of butane was more rapid (84% in 40 mins.) than in the corresponding fluorene preparation, probably owing to the more reactive methylene group of indene. Carbonation of the mixture with a stream of dry air-free carbon dioxide gave indene 1-carboxylic acid (LVII) in 38% yield.



(LVII)

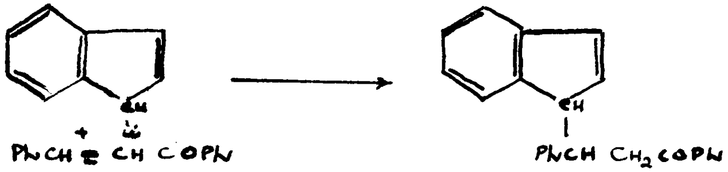
With mesityl oxide, lithium 1-indenyl gave two oils from which no crystalline material or derivatives could be obtained though one of them gave a red oil with 2:4-dinitrophenylhydrazine. Neither fraction reacted with magnesium methyl iodide

Benzylidene acetone and lithium 1-indenyl gave one product - methyl β-1-indenyl-β-phenylethyl ketone (LVIII) WHich was a viscous red oil. Its 2:4-dinitrophenylhydrazone was prepared.



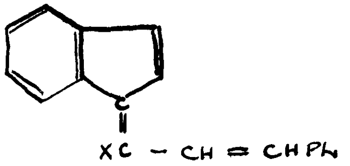
(LVIII)

Similarly, lithium 1-indenyl reacts with chalcone to give a very high yield of phenyl β-1-indenyl-β-phenylethyl ketone (LIX) which gave a 2:4-dinitrophenylhydrazone.



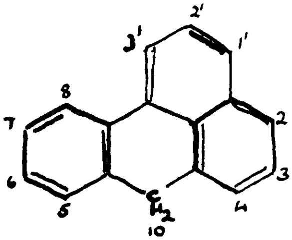
(LIX)

It will be observed that lithium 1-indenyl reacts like lithium 9-fluorenyl i.e., with benzylidene acetone and with chalcone, lithium 1-indenyl gives only the 1:4-addition products (saturated ketones). As was to be anticipated, the unsaturated compounds (of the type LX) produced by 1:2-addition followed by dehydration were not obtained. ~~However~~, this may have been due to polymerisation which would be expected to occur readily.

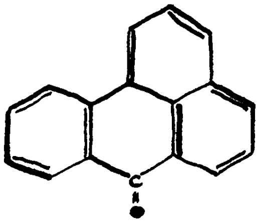


(LX)

Another hydrocarbon which contains a reactive methylene group is benzanthrene (LXI) which can be obtained from *meso*-benzanthrone (LXII).

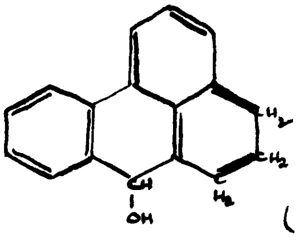


(LXI)



(LXII)

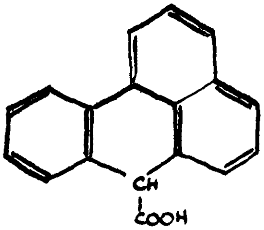
Reduction of *meso*-benzanthrone with zinc, concentrated hydrochloric acid and glacial acetic acid, yields the carbinol (LXIII),



(LXIII)

which on distillation from zinc dust, or from a mixture of zinc chloride and sodium chloride (1:5) gives benzanthrene (LXI) (ref.75).

Lithium 10-benzanthryl, a dark brown solid was readily formed in petroleum (67-69°) by the reaction of benzanthrene and lithium n-butyl. The evolution of butane was rather slower than with fluorene and indene but was complete when the mixture had been refluxed for 2 hours. Treatment of lithium 10-benzanthryl with a stream of dry air-free carbon dioxide gave a small yield (20%) of benzanthrene 10-carboxylic acid (LXIII).



(LXIII).

Experimental.

I. Synthesis of Methylnaphthalenes.

1:3-Dimethyl and 1:2:3-trimethylnaphthalenes from benzyl methyl ketone. Benzyl methyl ketone - Prepared by the method of Newman and Booth (ref.15). Its 2:4-dinitrophenylhydrazone was obtained as orange needles from ethyl acetate, m.p. 150-2°. (Found: C, 57.5; H, 4.6; N, 17.75. $C_{15} H_{14} O_4 N_4$ requires C, 57.3; H, 4.5; N, 17.8%)

Ethyl 1-Methyl - 2-phenylethylidene - cyanoacetate (IV, page 14) -

The following attempts were made to increase the yield of 73% in three hours reported by Cope (ref.16):-

(1) Benzyl methyl ketone (6.7g.), ethyl cyanoacetate (5.7g), trichloracetic acid and trichloracetamide (1.6g.) and benzene WERE REFLUXED but no reaction occurred till ammonium acetate (1.5g.) was added. The yield of (IV) was then 61% in 2.5 hours.

(2) Trichloracetic acid (3g.) alone was added as condensing agent. The addition of ammonium trichloracetate was necessary to start the reaction which yielded 56% of ester after 2 hours.

Ethyl 1 - methyl - 2-phenylethylcyanoacetate (V, page 14) -

(a) By catalytic hydrogenation at atmospheric pressure using palladium-charcoal (ref.17) and ethanol. ~~When~~

When hydrogenation was complete the catalyst was recoveredby filtration and most of the alcohol removed from the filtrate. The remaining oil was shaken with dilute hydrochloric acid (to remove traces of amine resulting from reduction of the nitrile group) then extracted with benzene and dried with sodium sulphate. On removal of the solvent ethyl 1-methyl-2-phenylethyl-cyanoacetate was obtained as a colourless liquid, b.p. 175-7°/9 mm. (Yield 80%). (Found: C, 72.9; H, 7.2; N, 6.3. $C_{14}H_{17}O_2N$ requires C, 72.7; H, 7.4: N, 6.1 %).

(b) Benzyl methyl ketone (13.4g.), ethyl cyanoacetate (11.3 g.), ammonium acetate (0.8 g.), acetic acid (2 g.) ethanol (25 ml) and palladium charcoal (ref.17) (1g.) were stirred vigorously in an atmosphere of hydrogen. After 25 hours the theoretical volume of hydrogen had been absorbed. On working up as before the ester (V) was obtained. (7.0g.; yield 30%).

3 - Benzyl-butyric acid (VI, page 14). - (V) (10g.) in glacial acetic acid (20 ml.), concentrated sulphuric acid (10 ml.) and water (10 ml.) was refluxed for 7 hours. After cooling, water was added and the oil which separated extracted with carbon tetrachloride. 3-Benzylbutyric acid distilled as a pale yellow oil, b.p. 275-7°. (7.1g.; yield 90%). (Found: C, 74.3;

H, 7.7. Calc. for $C_{11}H_{14}O_2$: C, 74.2; 1 , 7.4%)

<u>1-Keto-3-methyl-1:2:3:4-tetrahydronaphthalene (VII,</u> page 14). - To a solution of (VI) (8g.) in benzene (80 ml.) was added phosphorus pentachloride (11.2g.) in portions. After standing at room temperature for nearly 1 hour, most of the phosphorus pentachloride was in solution. The mixture was warmed on a steam-bath for 5 mins. then cooled till the benzene showed signs of freezing. At this point, anhydrous stannic chloride (12.4 ml.) in benzene (12.4 ml.) was added rapidly with swirling and an orange-red complex separated. After standing 15 mins. in ice-water the mixture was hydrolysed by ice, followed by concentrated hydrochloric acid (40 ml.). Ether (5 ml.) was added to hasten hydrolysis and the mixture was shaken till all the complex had dissolved. After separation the organic layer was washed with several portions of 5% hydrochloric acid, water, 5% sodium hydroxide and water. The solvent was removed and 1-keto-3-methyl-1:2:3:4-tetrahydronaphthalene distilled - a colourless liquid, b.p. 152-5°/9 mm. (6.8g; yield 94%). Its 2:4-dinitrophenylhydrazone crystallised in scarlet needles from benzene, m.p. 241-2°. (Found: C, 60.1; H, 4.5. Calc. for $C_{17}H_{16}O_4N_4$: C, 60.0; H, 4.7%). Its <u>semicarbazone</u> was obtained as pale-brown to salmon,

rectangular plates from methanol, m.p. 179-88°. (Found: C, 66.1; H, 6.8; N, 19.4. $C_{15}H_{15}ON_3$ requires C, 66.4; H, 6.9; N, 19.4%).

<u>1-Hydroxy - 1:3-dimethyl - 1:2:3:4-tetrahydronaphthalene</u> (VIII), page 14). -
An ethereal solution of magnesium methyl iodide prepared from magnesium (6g; 0.25g.atom), methyl iodide (35.5g; 0.25 mole) and ether(150 ml.) (ref.71) was added slowly to a solution of (VII) (10g; 0.0625 mole) in ether (10 ml) cooled in ice-salt freezing mixture. After standing overnight the Grignard reagent was decomposed with ammonium chloride solution, the ether layer separated and the aqueous layer extracted with ether. Distillation of the residue after removal of the ether gave <u>1-hydroxy - 1:3-dimethyl - 1:2:3:4-tetrahydronaphthalene</u> as a pale yellow liquid b.p. 103-5°/0.9 mm (7.25g; yield 66%). (Found: C, 82.0; H, 88. $C_{12}H_{16}O$ requires C,81.8; H, 9.1%)
<u>1:3-Dimethylnaphthalene</u> - (VIII) (9g.) and anhydrous potassium bisulphate (9g.) were heated at 150° till no more water collected in the upper part of the tube (3 hours). On cooling the potassium bisulphate was filtered off. The filtrate was heated initially at 220° with palladium-charcoal (ref.17) in a tube constantly flushed with carbon dioxide. The temperature was gradually raised, reaching 260° after 1.5 hours. The product

was extracted with ether and distillation gave 1:3-dimethylnaphthalene b.p. 115-120°/10 mm. (picrate, m.p. 115-7°; s-trinitrobenzenate, m.p. 132-4°). (7g.; yield 86%)

Ethyl 2-methyl-2-cyano-3-benzylbutyrate (IX, page 17) - (Cf. ref.72) A solution of sodium ethoxide in ethanol was prepared by dissolving sodium (3g.) in ethanol (63 ml.) When the freshly prepared solution had cooled to about 50° the ester (V, page 17) (18g.) was added gradually, followed by slow addition, with shaking of methyl iodide (18g.). The reaction mixture was then refluxed for 2 hours, most of the alcohol distilled off and the residue diluted with water. The oil which separated was extracted with benzene. Distillation yielded ethyl 2-methyl-2-cyano-3-benzylbutyrate as a pale yellow liquid, b.p. 160-5°/10 mm. (16g.: yield 84%).

2-Methyl-3-benzylbutyric acid (X, page 17). - (IX) (16g.), glacial acetic acid (32 mls), concentrated sulphuric acid (16 ml.), and water (16 ml.) were refluxed for 24 hours. The mixture was diluted with water and the oil which separated, estracted with carbon tetrachloride. On evaporation of the solvent, 2-methyl-3-benzylbutyric acid was obtained as a yellow oil, b.p. 278-281° (12g; yield 95%). From this oil there separated a white solid which contained nitrogen and which is probably the acid amide obtained by hydrolysis of the cyano group. This supposition proved to be correct since treatment with sodium nitrite and 80% sulphuric acid gave rise to the ketone (XI)

1-Keto-2:3-dimethyl-1:2:3:4-tetrahydronaphthalene (XI, page 17). - Cyclisation of (X) was carried out exactly as that of 3-benzylbutyric acid (page 70) giving 1-keto-2:3-dimethyl-1:2:3:4-tetrahydronaphthalene as a colourless liquid b.p. 155-160°/11 mm. (Yield 92%) (Found: C, 82.5; H, 8.05. $C_{12}H_{14}O$ requires C, 82.8; H 8.0%). Its 2:4-dinitrophenylhydrazone crystallised in small red needles from ethyl acetate, m.p. 201-3°. (Found: C, 60.9; H, 5.0: N, 16.0. $C_{18}H_{18}O_4N_4$ requires C, 61.0; H, 5.1; N, 15.8%).

1-Hydroxy-1:2:3-trimethyl-1:2:3:4-tetra hydronaphthalene (XII, page 17). - Prepared by the action of magnesium methyl iodide on (XI), the method being that used for the preparation of (VIII, page 71). The product was a colourless liquid b.p. 120-125°/9 mm. (Yield 6g. from 10g. of ketone). The discrepancy observed between the analytical and theoretical figures for this compound was probably due to partial dehydration of the carbinol during distillation.

1:2:3-Trimethylnaphthalene. - The liquid obtained above (10g.) was heated with the theoretical quantity of selenium for 5 hours at 300°. The residue was extracted with benzene and on removal of the solvent, 1:2:3-trimethylnaphthalene was obtained as a yellow oil (5g.: yield 73%) and was identified by means of its picrate, m.p. 141-2°, and styphnate, m.p. 142-4°. The *S-trinitrobenzenate* was obtained as yellow needles from ethanol m.p. 154-6° (Found: N, 10.9. $C_{19}H_{17}O_6N_3$ requires N, 11.0%).

1:2:3-Trinethylnaphthalene from hemimellitene (With J. Forrest).

4-and5-Hemimellitoyl-propionic acids. (XIIIA & B, page 18).- Finely ground, anhydrous aluminium chloride was added slowly in portions to a suspension of succinic anhydride (17g.) in chlorobenzene (136 ml.) containing hemimellitene (17g.). Hydrochloric acid was evolved and the mixture darkened. The flask was shaken at intervals. After standing overnight the complex was decomposed with a mixture of ice and concentrated hydrochloric acid, ether (10 ml.) being added to accelerate the reaction. The organic layer was washed with dilute hydrochloric acid, then with sodium carbonate solution. Solid sodium carbonate was then added to keep the solution alkaline and the chlorobenzene removed by steam distillation. The mixture of 4-and 5-hemimellitoylpropionic acids, obtained on acidification was crystallised from benzene-petroleum (60-80°) giving white needles m.p. 142-5° (10.5g; yield 30%). (Found: C, 70.8; H, 7.5. $C_{13}H_{16}O_3$ requires C, 70.9; H, 7.3%)

4-and 5-Hemimellitylbutyric acids (XIVA and B, page 18).- The mixture of acids (XIIIA and B) (10.5g.) was boiled for 7 hours with zinc (80g.) in concentrated hydrochloric and glacial acetic acid (2:1 by volume; 450 ml), the solution being saturated at intervals with hydrochloric acid gas. The acid product 4-and5-hemimellitylbutyric acids, separated as a solid and was crystallised from petroleum (60-80°) in colourless rhombs m.p. 95° (7g.; yield 80%) (Found (after drying in vacuum): C, 75.6; H, 8.7. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.7%).

1-Keto-5:6:7 (and 6:7:8)-trimethyl-1:2:3:4-tetra hydronaphthalene (XVA and B, page 19). - The mixture of(XIVA and B) (7g.) was heated on a waterbath with 80% sulphuric acid (83 ml.) with frequent agitation for 1.5 hours then poured into water. The aqueous solution was extracted with chloroform and the unchanged acid removed from the extract with sodium carbonate solution. The neutral chloroform layer was then washed with water and dried over calcium chloride. On removal of the chloroform the residual oil solidified on cooling and 1-keto-5:6:7 (and 6:7:8) - trimethyl-1:2:3:4-tetrahydronaphthalene crystallised from methanol in pale yellow rhombs, m.p. 52-53° (4.5g.; yield 70%). (Found: C, 82.8; H, 5.7. $C_{13}H_{16}O$ requires C, 82.3; H, 5.7%). The 2:4-dinitrophenylhydrazone was obtained as dark orange crystals from anisole, m.p. about 210°. (Found: C, 61.7; H, 5.25; N, 15.3. $C_{19}H_{20}O_4N_4$ requires C, 61.95; H, 5.4; N, 15.2%).

5:6:7-Trimethyl-1:2:3:4-tetrahydronaphthalene (XVI, page 19).- The ketones (XVA and B) (4.5g.) were boiled for 7 hours with zinc (30g.) in concentrated hydrochloric acid and glacial acetic acid (2:1; 160 ml.) the reaction mixture being saturated at intervals with hydrochloric acid gas. The oil which separated from the acid mixture was extracted with carbon tetrachloride, the extract washed with water and dried with sodium sulphate. After removal of the solvent and distillation, 5:6:7-trimethyl-1:2:3:4-tetrahydronaphthalene, b.p. 135-137°/11 mm. (2.3g; yield 55%).

1:2:3-Trimethylnaphthalene. - (XVI) (2.3g.) was heated with selenium (2.05g.) at 295-300° for 5 hours and the residue extracted with carbon tetrachloride. After removal of the solvent, distillation gave a pale yellow oil b.p. 155-160°/10 mm, (0.8g.; yield 35%), whose picrate, styphnate and s-trinitrobenzenate corresponded to those of 1:2:3-trimethylnaphthalene.

Cyclisation and dehydrogenation of 1-phenyl-2:4:4-trimethylbutadiene, (XVII, page 20). -

(a) (XVII) (10g.) in glacial acetic acid (25 ml.) was refluxed for 10 hours with hydriodic acid (8 ml.; d, 1.70). The reaction mixture was treated with sulphurous acid to remove iodine and the oil which separated was extracted with ether. After drying, and removal of the solvent, the residue distilled as a colourless liquid, b.p. 115-120°/20 mm., probably 1:1:3-trimethyl-1:2:3:4-tetrahydronaphthalene (XVIII), page 20). This liquid was heated at 220° with sulphur for 3 hours, the residue extracted with ether and distilled giving 1:3-dimethylnaphthalene (0.9g.; yield 10%).

(b) (XVII) (10g.) in dry benzene (20 ml.) was treated with hydrogen bromide for 20 mins., the resulting dark solution cooled in ice and stannic chloride (15 ml.) in benzene (15 ml.) added. After standing 0.5 hr. in ice-water, the stannic chloride complex was decomposed with ice and concentrated hydrochloric acid, ether being added to hasten decomposition. The benzene layer was then shaken with several portions of dilute hydrochloric acid, water, dilute sodium hydroxide solution and water. After drying and removal of the solvent, the residue was distilled giving 1:1:3-trimethyl-1:4- dihydronaphthalene (XIX, page 20) b.p. 105-110°/9 mm. (7.5g.; yield 75%). (Found: C, 90.5; H, 9.4. $C_{13}H_{16}$ requires C, 90.7; H, 9.3%).

(XIX) (7.5g.) on heat~~ed~~ing with selenium for 5 hours at 300° yielded 1:3-dimethylnaphthalene (4.5g; yield 66%).

1-Phenyl-2:4-dimethylbutadiene (page 21). - To an ether solution of magnesium benzyl chloride, prepared from magnesium (4.25g.), benzyl chloride (22.1g.) and ether (100 ml.), was added ethylidene acetone (ref.21) (14g.) and the mixture allowed to stand overnight. After decomposition with dilute hydrochloric acid, the ether layer gave 1-phenyl-2:4-dimethylbutadiene as a colourless liquid, b.p. 110-115°/20 mm. (12.7g.; yield 48%). (Found: C, 91.1; H, 8.6. $C_{12}H_{14}$ requires C, 91.1; H, 8.9%)

1:3-Dimethylnaphthalene. - 1-Phenyl-2:4-dimethylbutadiene was treated with hydrobromic acid and stannic chloride, as above, giving a colourless liquid, b.p. 150-160°/30 mm., which was probably 1:3-dimethyl-1:4-dihydronaphthalene (page 21) (3g; yield 60%). This liquid on heating with sulphur for 3 hours yielded a small quantity of 1:3-dimethylnaphthalene as its picrate.

II. Contrasting Reactions of Magnesium 9-Fluorenyl Bromide and of lithium 9-Fluorenyl with $\alpha\beta$-Unsaturated Ketones.

Magnesium 9-Fluorenyl Bromide. - (Ref. 8 and 50). The results of various carbonation experiments are summarised in the table:-

Solvent	EtMgBr per Mole fluorene	Time	% ethane	Wt. of acid /mole fluorene
xylene	1 mole	2 hr. 50 min.	40	18g.
xylene	2.5 mole	3 hr.	92	27g.
p-cymene	1 mole	1 hr. 20 min.	41	9g.
p-cymene	1 mole	1 hr.	43	12g.
p-cymene	2.5 mole	45 min.	85	6g.
amyl ether	1 mole	2 hr.	52	6g.
amyl ether	2.5 mole	2 hr.	72	-

The following improvements were introduced:-

(1) the volume of ethane evolved was used to trace the course of the reaction and indicated that 3 hrs. heating (xylene) was sufficient.

(2) an excess of magnesium ethyl bromide increased the yield of ethane to 91% i.e. revised quantities:- ethyl bromide (45.5g.; 2.5 mole), magnesium (10g.; 2.5 atoms), ether (100 ml.), fluorene (27.7g.; 1 mole) and xylene

(85 ml.)

(3) during the heating in xylene, intermittent stirring was found to be advantageous.

9-Fluorenyl-dimethylcarbinyl acetate. - Obtained from 9-fluorenyl-dimethylcarbinol, in stellar clusters of colourless prismatic rods, m.p. 115-116°, crystallised from methanol. (Found: C, 81.1; H, 6.6. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%).

α-Diphenylene -$\beta\delta$-dimethyl-$\Delta^{\alpha\gamma}$ -pentadiene, (XXXII, page 34). -

(a) To magnesium 9-fluorenyl bromide prepared from fluorene (41.5g; 0.25g.mol.) was added mesityl oxide (24g; 0.25g.mol.) Vigorous stirring and heating at 125° were maintained for 2.5 hours, the Grignard reagent turning from green to brown. The reaction mixture was treated with dilute hydrochloric acid, the aqueous layer extracted with ether and the xylene-ether extracts combined. After removal of the solvents the remaining liquid was distilled, four fractions being obtained:-

(i) 150-180°/12 mm. fluorene (11.2g., 27% recovery).

(ii) 180-225°/12 mm. reddish oil from which a solid slowly crystallised. Recrystallisation from petroleum (40-60°) gave white needles which turned pink on exposure to light, m.p. 80-82° (1.1g.)

(iii) 225-235°/12 mm. Thick oil which on crystallisation from petroleum (40-60°) gave more phototropic substance (α-diphenylene - $\beta\delta$-dimethyl - $\Delta^{\alpha\gamma}$-pentadiene) (14.7g.). i.e. total yield 15.8g. or 30% on unrecovered fluorene.

(iv) 225-280°/12 mm. Red oil from which a small quantity of 9-9'-difluorenyl was obtained.

Tests for ketones with 2:4-dinitrophenylhydrazine were negative for all four fractions.

(b) Mesityl oxide was added as before to magnesium 9-fluorenyl bromide (prepared from 21g. fluorene) containing cuprous iodide (0.5g.). Tests with 2:4-dinitrophenylhydrazine were negative and the yield of (XXXII) fell to 2.5% on unrecovered fluorene.

(c) Cuprous bromide (0.5g.) replaced cuprous iodide in (b). The yield of (XXXII) was again low (8%) and tests for ketones with 2:4-dinitrophenylhydrazine were negative.

Reactions of magnesium 9-fluorenyl bromide (pages 35-7).

(a) With ethylidene acetone. - Ethylidene acetone (7g.) was added slowly to a suspension of magnesium 9-fluorenyl bromide prepared from fluorene (14g.). When addition was complete the mixture was heated at 130° for 1.5 hrs. with constant stirring. After decomposition with dilute hydrochloric acid, extraction with benzene and removal of the solvent the residue was distilled.

(i) 165-185°/11 mm. - fluorene (4g., 28% recovery)

(ii) 215-235°/11 mm. - a heavy red oil (5.1g.) which resisted crystallisation and which failed to give a 2:4-dinitrophenylhydrazone.

(b) Benzylidene acetone - Benzylidene acetone (18.3g.) in xylene (40 ml.) was added to magnesium 9-fluorenyl bromide and the mixture heated ~~at~~ for 1.5 hours. On working up as before two fractions were obtained.

(i) 165-200°/14 mm. - fluorene (6.2g.; 29% recovery)

(ii) 270-280°/14 mm. - heavy red oil (10g.) which did not give a reaction with hydroxylamine, or 2:4-dinitrophenylhydrazine.

Oxidation of fraction (ii) Oil (1.3g.) was refluxed for 1.5 hours with sodium dichromate (4g.) and glacial acetic acid (25 ml.) then more dichromate added (3g.) and refluxing continued for 1.5 hours. The reaction mixture was poured into water and the solid which separated extracted with ether. The ether layer was shaken with dilute sodium carbonate solution. The alkaline extract gave benzoic acid (0.14g.) and the ether layer fluorenone (0.2g.)

(c) Chalcone. - To magnesium 9-fluorenyl bromide prepared from fluorene (21g.) was added chalcone (26g.) in xylene (70 ml.). After heating at 130° for 1.5 hours, working up as before gave

(i) before distillation there separated a colourless solid, crystallised from glacial acetic acid, m.p. 252-254 which is possibly *1:3:5-triphenyl-2:4-diphenylcarbonyl-cyclohexene* (page 36) (6.4g.) (Found: C, 88.2; H, 5.9. $C_{38}H_{30}O_2$ requires C, 88.0; H, 5.8%).

Chalcone (2.08g.) and acetophenone (0.96g.) in ether (10 ml) with pyridine (1 ml.) and potassium hydroxide (0.56g.) were allowed to stand for five days, acidified with dilute hydro-chloric acid and the solid crystallised from glacial acetic acid in colourless needles m.p. 249-250°. This may be *1:3:5-triphenyl-2:4-diphenyl-carbonyl-cyclohexanol*. (Found: C, 84.8; H, 6.1. $C_{38}H_{32}O_3$ requires C, 85.0; H, 6.0%).

(ii) 165-200°/15 mm. - fluorene (6.9g; 36% recovery).

(iii) 204-210°/0.2 mm.-orange oil (yield 5.1g.) (Found: C, 87.15; H, 5.95%). Oxidation with sodium dichromate and glacial acetic acid gave fluorenone and benzoic acid.

(iv) 235-245°/0.1 mm.- reddish oil (yield 6.0g.) (Found; C, 88.29; H, 6.32%).

(v) Difluorenyl, crystallised from benzene, m.p. 245° (yield 2.3g.).

Lithium 9-fluorenyl (page 48). -

(a) Fluorene in ether was added to lithium methyl in ether and the mixture refluxed. Since no gas was evolved, xylene was added and the mixture heated at 140° for about 2 hours.

Still no gas was collected. Acetyl chloride was then added and the mixture refluxed for 1 hour. 94% of the original fluorene was recovered.

(b) As in (a) with mesityl oxide in place of acetyl chloride. The fluorene was recovered unchanged.

(c) n-Butyl chloride replaced methyl iodide in the above experiments. On the addition of fluorene in xylene and removal of ether, no butane was collected but carbonation with dry air-free carbon dioxide gave a 9% yield of fluorene 9-carboxylic acid.

(d) Lithium n-butyl was prepared from n-butyl chloride in dry thiophene-free benzene (ref.55). Refluxing was maintained till all the lithium had dissolved (14 hrs.), fluorene in benzene added and THE mixture refluxed for 4 hours. A 12% yield of butane, was recorded whilst carbonation gave fluorene 9-carboxylic acid (5% yield).

(e) (Ref.57) n-butyl chloride (13.5g; 10% excess) in petroleum (67-69°) (45 ml.) was added rapidly to a stirred suspension of lithium (2·03g.), which had been "atomised" in liquid paraffin, in boiling petroleum (45 ml.) After 4 hours continuous stirring and refluxing under an atmosphere of nitrogen all the lithium had dissolved. Titration of the solution indicated a 76% yield of lithium n-butyl, the whole solution containing 0.11 mole of lithium compound. Fluorene (16.6g; 0.1 mole) in hot petroleum (60ml.), was now added the reaction mixture immediately becoming bright orange. Refluxing was maintained for 1 hour, the butane evolved (1900 ml. at N.T.P.; 85%) being scrubbed with concentrated sulphuric acid and collected in a graduated vessel.

Carbonation of lithium 9-fluorenyl (page 48). - Lithium 9-fluorenyl prepared as above was treated for 1.5 hours at room temperature with a stream of dry, air-free carbon dioxide, the orange colour rapidly disappearing. After acidification, fluorene 9-carboxylic acid was filtered off, washed with benzene and crystallised from glacial acetic acid (14g.; yield 67% or 100% on unrecovered fluorene). Unchanged fluorene (5.6g.) was recovered from the benzene-petroleum washings. No improvement was observed when solid carbon dioxide replaced gaseous carbon dioxide.

Reactions of Lithium 9-fluorenyl.

(a) Methyl β-9-fluorenyl-β-methyl-n-propyl ketone (XXXIII, page 38). - To lithium 9-fluorenyl, prepared from fluorene (16.6g.) in petroleum was added mesityl oxide (9.8g.) in petroleum ($67-69^{\circ}$) (40 ml.) Refluxing in an atmosphere of nitrogen was maintained for 0.5 hr. The reaction mixture was allowed to stand overnight, acidified with dilute hydrochloric acid and the aqueous layer extracted with benzene. After removal ofthe benzene and petroleum the residue was distilled:-

(i) 160-210°/12 mm. - fluorene (2.2g.; 13% recovery)

(ii) 210-235°/12 mm. - viscous red oil which solidified on standing. Recrystallisation from ethanol gave white needles, m.p. 77-8°, of methyl β-9-fluorenyl-β-methyl-n-propyl-ketone (12g; yield 52% on unrecovered fluorene). Its 2:4-dinitrophenylhydrazone, m.p. 200-202°, was identical with a sample previously prepared. Its *2:4-dinitrophenylsemicarbazone*, prepared in methanol containing a trace of sulphuric acid, crystallised from glacial acetic acid in pale yellow pointed needles m.p. 225-228° (with effervescence) (Found: C, 63.9; H, 5.1; N, 14.1. $C_{26}H_{25}O_5N_5$ requires C, 64.1; H, 5.1; N, 14.4%)

(b) Phenyl-β-9-Fluorenyl-β-phenylethyl ketone (XXXIV); page 39). - Chalcone (10.4g.; 0.05 mole) in petroleum (50 ml.) was added to lithium 9-fluorenyl prepared from fluorene (8.3g.; 0.05 mole). The reaction mixture was refluxed for 1 hour, acidified with dilute hydrochloric acid and extracted with benzene. After removal of the solvents the solid which separated was filtered off from a small amount of oil and boiled with alcohol to remove any unchanged fluorene (0.5g.) The solid which remained and the first crystals to separate from the alcohol

extract then crystallised from benzene - alcohol in colourless prisms m.p. 125-7° of phenyl β-9-fluorenyl-β-phenylethyl ketone. (10.5g.; yield 55% on total fluorene). (Found: C, 89.7; H, 5.7; mol. wt. 354. Calc. for $C_{28}H_{22}O$: C, 89.8; H, 5.8%; mol.wt. 374). Its *oxime* was obtained as rectangular prisms from methanol, s. 155° m.p. 162°. (Found: C, 86.3; H, 5.9; N, 3.6. $C_{28}H_{23}ON$ requires C, 86.4; H, 5.9; N, 3.6%) An orange solid was formed with 2:4-dinitrophenylhydrazine but a pure product could not be prepared.

Oxidation of XXXIV. - (XXXIV) (1.5g.) was refluxed as before with sodium dichromate (6g.) and glacial acetic acid (25 ml.). On working up benzoic acid (0.4g; 26%) and fluorenone (42%) were obtained.

(c) *Methyl β-9-fluorenyl-β-phenylethylketone* (XXXVIII, page 41). Benzylidene acetone (14.6g.) was added to lithium 9-fluorenyl prepared from fluorene (16.6g.). Distillation of the product gave:-

(i) 165-200°/20 mm. - fluorene (5.4g; 32% recovery)

(ii) 195-205°/0.5 mm. - thick orange oil which crystallised slowly from ethanol in prisms of *methyl β-9-fluorenyl-β-phenylethyl ketone* m.p. 99-101° (5.2g; yield 17% or 25% on unrecovered fluorene). (Found: C, 88.6; H, 6.4. $C_{23}H_{20}O$ requires C, 88.45; H, 6.4%) Its *2:4-dinitrophenylhydrazone* crystallised in orange-r red prisms from glacial acetic acid, m.p. 167-9°. (Found: C, 70.8; H, 4.9; N, 11.3. $C_{29}H_{24}O_4N_4$ requires C, 70.7; H, 4.9; N, 11.4%).

Its <u>oxime</u> crystallised from methanol in small, colourless needles, m.p. 155-159°. (Found: C, 84.3; H, 6.3; N, 4.7. $C_{23}H_{21}ON$ requires C, 84.4; H, 6.4; N, 4.3%).

A mixture of fluorene (1.66g.) and benzylidene acetone (1.46g.) in pyridine (15 ml.) and concentrated sodium hydroxide (1 ml.) was allowed to stand, with occasional shaking, for five days. On being acidified with dilute hydrochloric acid an oil separated and was extracted with carbon tetrachloride. It crystallised from ethanol (during several days) in prisms of methyl β-9-fluorenyl-β-phenylethyl ketone, m.p. 99-101°, prepared above. (0.7g.; yield 22%).

(d) <u>With 3-methyl-pent-2-en-4-one</u> (page 43). - 3-Methyl-pent-2-en-4-one (4.9g; 0.05g.mol.) in petroleum (67-69°) (20 ml.) was added slowly to lithium 9-fluorenyl prepared from fluorene (8.3g.). After working up as before there was obtained fluorene (2.6g.; 31% recovery) and a heavy oil, b.p. 210-215°/15 mm., which was principally <u>methyl β-9-fluorenyl-β-methylisopropyl ketone</u> (XLII, page 43) (3.8g.; yield 29%). Its <u>2:4-dinitrophenylhydrazone</u> crystallised in orange-red prisms from anisole, m.p.

184-7°. (Found: C, 67.4; H, 5.3; N, 12.5. $C_{25}H_{24}O_4N_4$ requires C, 67.6; H, 5.4; N, 12.6%)

Oxidation of (XLII) as before yielded fluorenone (yield 30%)

(e) α-Diphenylene-βδ-diphenylbutene (page 46). - Phenyl β-phenylethyl ketone (benzylacetophenone) (5.2g.) in petroleum was added to lithium 9-fluorenyl, prepared from fluorene (4.2g.) and the mixture refluxed for 5 mins. After the usual treatment, a crystalline solid was obtained. Extraction with boiling ethanol removed unchanged fluorene (0.2g.) and the residue crystallised from benzene - ethanol in needles of α-diphenylene-βδ diphenylbutene, m.p. 147-9° (1.9g.; yield 20%). (Found: C, 93.8; H, 6.05. $C_{28}H_{22}$ requires C, 93.85; H, 6.15%).

Catalytic reduction (palladium-charcoal-ethanol-hydrogen) of α-diphenylene -βδ -diphenylbutene yielded colourless nodules from ethanol of α-9-fluorenyl-βδ- diphenylbutane m.p. 96-98°. (Found: C, 93.4; H, 6.5). $C_{28}H_{24}$ requires C, 93.3; H, 6.7%).

Synthesis of 2:4-diphenylfluoranthene

αγ-Diphenyl-γ-9-fluorenyl-propanol (XXXV, page 40).- (a) Phenyl β-9-fluorenyl β-phenylethyl ketone (XXXIV, page 40) (1.0g.) in isopropanol (barium oxide dried) (15 ml.) was mixed with a solution of aluminium isopropoxide [aluminium (1g.), isopropanol (15 ml.), mercuric chloride, trace]. The mixture was slowly distilled until the distillate failed to give a positive test for acetone (2:4-dinitrophenyl-hydrazine). Practically all the isopropanol was then removed, the residue treated with dilute hydrochloric acid and extracted with benzene. After evaporation the residue crystallised after several weeks from acetic acid.

(b) The ketone (XXXIV) (10g.) in suspension in ethanol (treated with Raney nickel) (80 ml.) was shaken with hydrogen in the presence of Raney nickel and a trace of sodium hydroxide. The evaporated ethanol filtrate gave a glass-like solid which, as above, crystallised extremely slowly from acetic acid in greenish nodules, m.p. 98-105° of *αγ-diphenyl-γ-9-fluorenyl-propanol* (Found: C, 89.8; H, 6.2. $C_{28}H_{24}O$ requires C, 89.4; H, 6.4%). It gave, from boiling pyridine, a *3:5-dinitrobenzoyl derivative* which crystallised in orange needles from a colourless solution in benzene to which petroleum (60-80°) was added, softening at 199° melting at 202°. (Found: C, 73.8; H, 4.8; N, 4.9. $C_{35}H_{26}O_6N_2$ requires C, 73.7; H, 4.6; N, 4.9%).

2:4-Diphenyl-1:2:3:4-tetrahydrofluoranthene (XXXVI, page 41)- The carbinol (XXXV) (4.1g.) in glacial acetic acid (15 ml.) was treated with a solution of concentrated sulphuric acid

(15 ml.) in glacial acetic acid (15 ml.) and the mixture heated (5 mins.) on the steam bath. The addition of water precipitated a solid which crystallised from glacial acetic acid in needles of *2:4-diphenyl-1:2:3:4-tetrahydrofluoranthene*, m.p. 209-211° (2.4g.; yield 61%). (Found: C, 93.8; H, 6.1. $C_{28}H_{22}$ requires C, 93.85; H, 6.15%).

2:4-Diphenylfluoranthene (XXXVII, page 41).- Dehydrogenation of the above tetrahydro-compound (1.5g.) was achieved with selenium at 250-300° for 5 hours (or palladium-charcoal at 260 for 3 hours.) The residue was extracted with carbon tetrachloride and crystallised from glacial acetic acid in green-fluorescing needles softening at 153°, mp. 158-160°, of *2:4-diphenylfluoranthene*. (0.9g; yield 60%). (Found: C, 94.8; H, 5.2. $C_{28}H_{18}$ requires C, 94.2; H, 5.1%). Its *picrate* crystallised from ethanol in orange needles m.p. 162-164° (Found: C, 69.8; H, 3.6; N, 7.3. $C_{28}H_{18}\cdot C_6H_3O_7N_3$ requires C, 70.0; H, 3.6; N, 7.2%). *S* - Trinitrobenzene gave an unstable complex.

Synthesis of 2-Phenyl-4-Methylfluoranthene.

α-Methyl-γ-phenyl-γ-9-fluorenylpropanol (XXXIX, page 42)- Methyl β-9-fluorenyl-β-phenyl-ethyl ketone (XXXVIII, page 42) (4.7g.) was shaken in ethanol solution with hydrogen and

Raney nickel, a trace of sodium hydroxide being added. Evaporation of the filtrate gave a sticky solid, which crystallised slowly from ethanol in white nodules, of doubtful purity, of *α-methyl-γ-phenyl-γ-9-fluorenyl-propanol* m.p. 87-89°. (3.4g; yield 77%).

2-Phenyl-4-methyl-1:2:3:4-tetrahydrofluoranthene. (XL, page 42). - The above carbinol (2.4g.) was heated at 100° for 5 mins. with a mixture of glacial acetic (20 ml.) and concentrated sulphuric (10 ml.) acids. Dilution with water yielded a solid which was crystallised from acetic acid then benzene-alcohol giving colourless needles, m.p. 211-213°, of *2-phenyl-4-methyl-1:2:3:4-tetrahydrofluoranthene*. (1.5g; yield 66%). (Found: C, 93.3; H, 6.6. $C_{23}H_{20}$ requires C, 93.2; H, 6.75%).

2-Phenyl-4-Methylfluoranthene (XLI, page 42). - XL (0.5g.) was heated with selenium at 250° for 2 hours and then at 280° for 3 hours. The residue was extracted with carbon tetrachloride, the solvent evaporated and the solid which remained crystallised from glacial acetic acid (charcoal) in yellow-fluorescing needles of *2-phenyl-4-methyl fluoranthene*, m.p. 148-151°. (0.3g; yield 61%). (Found: C, 94.5; H, 5.4. $C_{23}H_{16}$ requires C, 94.5; H, 5.5%). Its *s-trinitrobenzenate* was obtained as fine yellow needles from ethanol m.p. 174-7°. (Found: C, 69.0; H, 3.7. $C_{29}H_{19}O_6N_3$ requires C, 68.9; H, 3.8%). Its picrate was unstable.

Synthesis of 2:3:2':3'-tetramethyl-4-4'-difluoranthyl (XLIV, page 44).

(a) Methyl β-9-fluoranyl-β-methylisopropyl ketone (XLII, page 43) (1.2g.) was shaken in ethanol solution in an atmosphere of hydrogen with Raney nickel catalyst activated with a little sodium hydroxide. On evaporation an oil (1.0g.) which resisted crystallisation was obtained.

The oil (0.8g.) was dissolved in glacial acetic acid and concentrated sulphuric acid (14 ml and 7 ml.) and warmed for 5 mins. on the steam bath. Dilution with water gave a white solid which crystallised from benzene-alcohol in small colourless needles, softening at 208° and melting at 210-212°, of 2:3:2':3'-tetramethyl - 1:2:1':2'-tetrahydro-4:4'-difluoranthyl (XLIII, page 44) (0.4g.); yield 54%). (Found: C, 93.65; H, 6.2. $C_{36}H_{30}$ requires C, 93.5; H, 6.5%).

(b) The hydro-carbon (XLIII) (0.3g.) was heated with selenium at 270-290° for 5 hours and the residue extracted with carbon tetrachloride. Crystallisation from glacial acetic acid (charcoal) gave yellow-brown needles, m.p. 162-164°, of 2:3:2':3'-tetramethyl-4:4'-difluoranthyl. (0.2g; yield 72%). (Found: C, 94.3; H, 5.5. $C_{30}H_{26}$ requires C, 94.3; H, 5.7%). Its picrate and s-trinitrobenzenate were both unstable.

(c) When catalytic reduction of the ketone (XLII) was carried out without alkali (to lessen the risk of pinacol reduction) absorption of hydrogen, though very slow, was steady. Treatment of the oily product with glacial acetic acid and concentrated sulphuric acid~~s~~ yielded an oil which was passed through a chromatographic column (alumina/benzene). A band which fluoresced blue in ultra-violet light was washed through, evaporated and the residue dissolved in ethanol. Seeding the solution with a crystal ~~with~~ of 2:3:4-trimethyl-1:2:3:4-tetrahydrofluoranthene (LIIIB, page 54) yielded a small quantity of this substance. The remaining oil resisted crystallisation.

Michael condensations with methyl fluorene-9-carboxylate

(Page 52).

~~(a)~~ Mesityl oxide: using atomised potassium as condensing agent gave colourless prisms from benzene-alcohol of diethyl 9-9'-difluorenyl-~~9-9'-difluorenyl~~-9-9'-dicarboxylate, m.p. 165-7°. (Found: C, 80.9; H, 5.5. $C_{32}H_{26}O_4$ requires C, 81.0; H, 5.5%).

III. Synthesis of Methylfluoranthenes.

α-Diphenylene - βδ-dimethyl- $\Delta^{\alpha\gamma}$-pentadiene (XLV, page 54). - For preparation see page 80

Oxidation of (XLV). - (XLV) (0.5g.), sodium dichronate (2.6g.) and glacial acetic acid (20 ml.) were refluxed for 1.5 hours, more dichromate (2.0g.) added and refluxing continued for 1.5 hours. The reaction mixture was poured into dilute sulphuric acid. The product was fluorenone (0.26g.; yield 70%).

Picrate of XLV. - Prepared in ethanol solution and crystallised from ethanol as orange-red needles of picrate m.p. 106-7°. (Found: C, 63.3; H, 4.5. $C_{19}H_{18}\cdot C_6H_3O_7N_3$ requires C, 63.2; H, 4.4%).

2-Methyl-4-(9-fluorenyl)-pentane (XLVI, page 54). (XLV) (2.5g.) was shaken in ethanol (100 ml.) at atmospheric pressure with hydrogen and pa~~pp~~lladium charcoal (ref.17) The absorption of hydrogen (466 ml.) corresponded to the reduction of two double bonds. After filtering and evaporation of most of the alcohol, 2-methyl-4-(9-fluorenyl)-pentane was obtained in colourless needles, crystallised from methanol, m.p. 51-55° (1.9g.; yield 75%). (Found: C, 91.1; H, 8.9. Calc. for $C_{19}H_{22}$: C, 91.2; H, 8.8%).

Oxidation of (XLVI, page 53).- (XLVI) (0.25g.) was oxidised, as above, with sodium dichromate in acetic acid. Fluorenone was obtained (0.1g; yield 57%).

Hydriodic acid on XLV, (Page 52).- Using the method of Maitland and Tucker (ref.8) with hydriodic acid (d,1.70) there was obtained:-

(i) 2-Methyl-4-(9-fluorenyl)-pentane (XLVI, page 54) m.p. 51-55° (0.2g.; yield 13%).

(ii) 2:3:4-Trimethylfluoranthene (XLVIII, page 54) (0.19g; yield 14%) which was identified by mixed melting point determination.

When hydriodic acid (d,1.50) was used, on one occasion only a small quantity of white plates m.p. 103-4° was obtained:- 2:4:4-trimethyl-1:2:3:4-tetrahydrofluoranthene (XLVIIA, page 54). (Found: C, 91.9; H, 7.8. Calc. for $C_{19}H_{20}$: C, 91.9; H, 8.1%).

Synthesis of 2:3:4-trimethylfluoranthene.

1-Iodo-2:3:4-trimethylnaphthalene (LIV, page 57).- 1:2:3-Trimethylnaphthalene (10.0g.), prepared from 2:3-dimethylnaphthalene (ref.14), was dissolved in glacial acetic acid (15 ml.) and potassium iodide (6.6g.) added followed by potassium iodate (9.6g.). The mixture was refluxed till it acquired a pale straw coloured tint (~ 6 hours). The solution was decanted from unchanged potassium iodate, shaken with sodium bisulphite solution and extracted with carbon tetrachloride. Evaporation gave a dark oil which crystallised from methanol (charcoal) in white needles, turning brown in air, of *1-iodo-2:3:4-trimethylnaphthalene* m.p. 110-112° (6.4g.; yield 37%). (Found: C, 52.7; H, 4.3; I, 42.9. $C_{13}H_{13}I$ requires C, 52.7; H, 4.4; I, 42.9%).

1-(2'-Nitrophenyl)-2:3:4-trimethylnaphthalene (LV, page57).- 1-Iodo-2:3:4-trimethylnaphthalene (2.09g.) and *o*-bromonitrobenzene (1.40g.) were heated together at 210-215°. Copper bronze (2.0g.) was added at intervals and heating continued with occasional stirring for 3 hours. The mixture was finally heated to 250° for 5 mins. and the residue extracted with dry ether. Crystallisation of the oil obtained gave (i) pale straw coloured needles, m.p. 126-127°, which contained halogen but no nitrogen, (Found: C, 62.3; H, 5.1%) - the nature of this compound has not been investigated. (ii) a sticky oil which after vacuum sublimation crystallised from ethanol in yellow diamond-shaped plates m.p. 111-114° of *1-(2'-nitrophenyl)-2:3:4-trimethylnaphthalene* (1.0g.; yield 51%). (Found: C, 78.2; H, 5.9; N, 4.9. $C_{19}H_{17}O_2N$ requires C, 78.3; H, 5.8; N, 4.8%).

1-(2'-Aminophenyl)-2:3:4-trimethylnaphthalene (LVI, page 54)- 1-(2'-Nitrophenyl)-2:3:4-trimethylnaphthalene (0.7g.) was reduced with hydrogen in the presence of Raney Nickel and a trace of sodium hydroxide. When theoretical absorption had occurred, the solvent, ethanol, was removed, the remaining oil extracted with dilute hydro-chloric acid and the acid layer basified with dilute sodium hydroxide solution. The oil was extracted with carbon tetrachloride. The basic oil resisted crystallisation (0.5g; yield 63%)

2:3:4-Trimethylfluoranthene. - 1-(2'-Aminophenyl)-2:3:4-trimethylnaphthalene (0.5g.) was diazotised in dilute sulphuric acid. Excess nitrite was destroyed by addition of a small quantity of urea, the yellow solution filtered and warmed on a steambath for 0.5 hr. with copper bronze. The copper was extracted several times with boiling ethanol. The blue-fluorescent solution was concentrated and 2:3:4-trimethylfluoranthene slowly separated. A complex formed with 2:4:7-trinitrofluorenone, crystallised from benzene in bright scarlet needles, m.p. 208-210°. (Found: C, 68.7; H, 3.9; N, 7.5. $C_{19}H_{16}\cdot C_{13}H_5O_7N_3$ requires C, 68.7; H, 3.8; N, 7.5%).

2:4:4-Trimethyl-1:4-(?3:4)-dihydrofluoranthene (XLIX, page 54). XLV (page 54) (1.0g.) was suspended in glacial acetic acid (15 ml.) and hydrogen bromide passed in. The substance gradually dissolved but when the solution was saturated with hydrogen bromide a white solid precipitated. This was filtered off, washed with glacial acetic acid, dissolved in dry benzene (10 ml.) and the solution cooled. Stannic chloride (4 ml.) in dry benzene (10 ml.) was then added rapidly. After standing (20 min.) in ice-water the mixture was hydrolysed with concentrated hydrochloric acid and a little ether. The organic layer was separated, washed with dilute hydrochloric acid, water, dilute sodium hydroxide solution and water. After extraction with carbon tetrachloride and evaporation, a pale yellow oil was obtained. This crystallised from ethanol in colourless plates of <u>2:4:4-trimethyl-1:4(?3:4)- dihydrofluoranthene</u>, m.p. 106-7°. (0.8g; yield 80%). (Found: C, 92.7; H, 7.2. $C_{19}H_{18}$ requires C, 92.7; H, 7.3%).

<u>Oxidation of XLIX</u> (page 54).- (XLIX) (0.4g.) sodium dichromate (4.6g.) and glacial acetic acid were refluxed in the usual way. Pouring into water gave an orange solid which crystallised from glacial acetic acid in orange needles of fluorenone-1-carboxylic acid (L, page 54).

<u>Dehydrogenation of XLIX</u> (page 54).- (XLIX) (0.2g.) was heated with selenium at 300° for five hours. The residue was extracted with ether and the solvent evaporated. The solid residue was 2:~~3~~:4-~~tr~~dimethylfluoranthene (~~XLVIII~~,LI, page 54) whose identity was confirmed by the preparation

of its s-trinitrobenzenate.

2:4:4-Trimethyl-1:2:3:4-tetrahydrofluoranthene (XLVIIB, page 54).-

XLIX (0.246g.) was hydrogenated with palladium-charcoal (ref.17) in ethanol (50 ml.) Evaporation of the solvent and recrystallisation from ethanol gave colourless needles of 2:4:4-trimethyl-1:2:3:4-tetrahydrofluoranthene, m.p. 85-7° (0.23g.; yield 93%). (Found: C, 91.4; H, 7.8. $C_{19}H_{20}$ requires C, 91.9; H 8.1%).

Dehydrogenation of XLVIIB, prepared above, was achieved by heating with selenium for 5 hours at 300°. The residue was extracted with ethanol and the extract evaporated. The solution slowly deposited 2:4-dimethylfluoranthene, m.p. 113-115°, (LI, page 54), whose s-trinitrobenzenate, m.p. 223° was prepared.

2:4:4-Trimethyl-2:3 (?1:2)-dihydroxy-1:2:3:4-tetrahydrofluoranthene (LII, page 54). - (XLIX) (0.5g.) was dissolved in acetone (10 ml.) and potassium permanganate (0.5g.) added in portions with frequent shaking, then left overnight. On filtration and evaporation of the filtrate, a colourless solid separated. 2:4:4-Trimethyl-2:3 (?1:2) - dihydroxy-1:2:3:4-tetrahydrofluoranthene was obtained from glacial acetic acid in colourless needles, m.p. 189-193° (0.2g; yield 35%). (Found: C, 81.3; H, 6.9.

$C_{19}H_{20}O_2$ requires C, 81.4; H, 7.1%).

2:4:4-Trimethyl-1:2:3:4-tetrahydrofluoranthene (XLVIIA, page 54).-
(LII), prepared above, (0.2g.) in glacial acetic acid (15 ml.) was treated with hydriodic acid (d,1.70; 7 ml.) and allowed to stand for 24 hours. The solid which separated was filtered off and crystallised from ethanol m.p. 103-4°. Mixed m.p. with (XLVIIA) obtained by the action of hydriodic acid on (XLV) was undepressed.

2:3:4-Trimethyl-1:2:3:4-tetrahydrofluoranthene (LIIIA, page 54).-
(XLIX) (0.5g.) glacial acetic acid (25 ml.) and hydriodic acid (d,1.70; 4 ml.) were refluxed for 5 hours. The reaction mixture was poured into sodium bisulphite solution and the oil which separated extracted with carbon tetrachloride. Removal of the solvent and crystallisation from ethanol yielded colourless needles m.p. 102-4° of *2:3:4-trimethyl-1:2:3:4-tetrahydrofluoranthene* (Found: C, 91.8; H, 8.0. $C_{19}H_{20}$ requires C, 91.9; H, 8.1%).

Dehydrogenation of this compound with selenium yielded 2:3:4-trimethylfluoranthene from which the *s*-trinitrobenzenate was prepared.

2:4:4-Trimethyl-1:2:3:4-tetrahydro~~naphthalene~~FLUORANTHENE (LIIIB, page 54).- Attempts to hydrogenate 2:3:4-trimethylfluoranthene using Adams catalyst in acetic acid or in ethyl acetate showed that hydrogen was absorbed but no product could be isolated. Similarly boiling hydriodic acid failed to effect reduction. Microhydrogenation using palladium black in glacial acetic acid indicated the presence of two double bonds. Hydrogenation using Cheronis' catalyst gave excellent results: (2:3:4-trimethylfluoranthene (0.122g.), Cheronis' catalyst (2g.) in ethanol (20 ml) which had been distilled from Raney nickel catalyst). Practically theoretical absorption took place in 80 mins. The solution was filtered, the palladium charcoal extracted with boiling ether and filtrates evaporated to dryness. Crystallisation of the residue first from glacial acetic acid and then from methanol (blue-fluorescent solution) gave hair-fine needles, m.p. 107-9°, of 2:3:4-trimethyl-1:2:3:4-tetrahydrofluoranthene (LIIIB, PAGE 54) (0.098g; yield 72%). (Found: C, 91.8; H, 8.1. $C_{19}H_{20}$ requires C, 91.9; H, 8.1%). Heated in benzene solution with2:4:7-trinitrofluorenone it gave an addition product, crystallising from benzene in dark, scarlet prisms, m.p. 190-2° decomposing at 200° (Found: C, 68.3; H, 4.3; N, 7.6. $C_{19}H_{20}$ requires C, 68.2; H, 4.4; N, 7.5%).

Catalytic hydrogenation of 2:4-dimethylfluoranthene (LI, page 54).- 2:4 Dimethylfluoranthene was hydrogenated using twice its weight of palladium charcoal (ref.17), in ethanol. Absorption ceased after four hours when an amount of hydrogen approximately equivalent to that required for hydrogenation of one double bond had been absorbed. The filtered evaporated solution deposited prisms which crystallised as nacreous leaflets of 2:4-dimethyl-1:2:3:4-tetrahydrofluoranthene, m.p. 115-117°. (Found: C, 92.3; H, 7.5. $C_{18}H_{18}$ requires C, 92.3; H, 7.7%). Concentration of the ethanolic filtrate gave a very small amount of yellow plates which crystallised from methanol as pale green prisms of 2:4-dimethyl-2:3 (?1:2, 3:4)-dihydrofluoranthene, softening at 73°, melting at 84-86°. (Found: C, 92.9; H, 6.8. $C_{18}H_{16}$ requires C, 93.1; H, 6.9%).

Synthesis of 10-methylfluoranthene.

1-(2'-Amino-5'-methylphenyl)-naphthalene (page 62). - 1-(2'-Nitro-5'-methylphenyl)-naphthalene (0.526g.) in ethanol was shaken in an atmosphere of hydrogen with Raney nickel catalyst. The evaporated filtrate deposited white needles - which were recrystallised from ethanol - of 1-(2'-amino-5'-methylphenyl)-naphthalene, m.p. 113-115° (0.31g.; yield 65%). (Found: C, 87.4; H, 6.4; N, 6.1. $C_{17}H_{15}N$ requires C, 87.5; H, 6.4; N, 6.0%).

<u>10-Methylfluoranthene</u> (?) The above amine (0.5g.) was diazotised with sodium nitrite and dilute sulphuric acid, the excess nitrite destroyed by addition of a small quantity of urea and the diazo solution filtered. Copper bronze (0.5g.) was added and the mixture warmed on a steam bath for 40 mins. Extraction of the copper with boiling ethanol and concentration gave a blue fluorescent solution from which a small amount of impure <u>s</u>-trinitrobenzenate, m.p. ~ 200°, was isolated.

IV. Reactions of lithium 1-indenyl and lithium 10-benzanthryl.

Lithium 1-indenyl. - Lithium n-butyl (0.11 mole) was prepared as before (see page 84) and indene (11.6g; 0.1 mole) added in petroleum (67-69°) (60 ml.) After about 2 mins. a white gelatinous precipitate was formed and butane was evolved rapidly (1870 ml. at N.T.P.; yield 84%). Stirring and refluxing were continued for 40 mins.

Indene-1-carboxylic acid (LVII, page 64).- Lithium 1-indenyl prepared as above was treated with a rapid stream of dry air-free carbon dioxide for 1.5 hrs. and left overnight in an atmosphere of carbon dioxide. Addition of water and acidification of the aqueous layer yielded indene-1-carboxylic acid as yellow needles from ethanol softening at 222° m.p. 230° (4g; yield 25% or 38% on unrecovered indene.) The petroleum layer gave unchanged indene (4g.; 34% recovery).

Reactions with lithium 1-indenyl (page 64).

(a) With mesityl oxide.- Mesityl oxide (9.8g.; 0.1 mole) was added to lithium 1-indenyl prepared as above, the reaction mixture refluxed ~~for~~ (0.5 hr.) and allowed to stand overnight. After acidification with dilute hydrochloric acid, extraction with carbon tetrachloride and evaporation of the solvent the residual oil was distilled:-

(i) under 150°/12 mm. indene and mesityl oxide.

(ii) 170-175°/12 mm. pale yellow liquid which gave a heavy red oil with 2:4-ditrophenylhydrazine. Attempts to crystallise this derivative were unsuccessful.

(iii) 220-235°/12 mm. - very viscous red oil which did not react with 2:4-dinitrophenylhydrazine.

(b) With benzylidene acetone. - Benzylidene acetone (146g.; 0.1 mole) in petroleum was added to lithium 1-indenyl prepared from indene (11.6g.), the reaction mixture refluxed for 0.5 hr. and allowed to stand overnight. Distillation of the product gave (i) a small quantity of indene and benzylidene acetone.

(ii) b.p. 240-250°/12 mm. Methyl β-1-indenyl β-phenylethyl ketone (LVIII, page 65), a viscous red oil which resisted crystallisation. (Found: C, 86.8; H, 7.2. $C_{19}H_{18}O$ requires C, 87.0; H, 6.9%). Its 2:4-dinitrophenylhydrazone crystallised in red prisms from glacial acetic acid, m.p. 200-202°. (Found: C, ; H, . $C_{25}H_{22}O_4N_4$ requires C, 67.8; H, 5.0 %). (Values obtained were unsatisfactory).

(c) With chalcone. Chalcone (5.2g.) was added to lithium 1-indenyl prepared from indene (2.9g.), the mixture turning from white to reddish-orange. After standing overnight, dilute hydrochloric acid was added and the mixture extracted with carbon tetrachloride. The oil obtained on evaporation of the solvent was crystallised (very slow) from ethanol and recrystallised from glacial acetic acid in small yellowish prisms m.p. 115-116° of phenyl-β-1-indenyl-β-phenylethyl ketone (LIX, page 65) (7.0g.; yield 86%) (Found: C, 88·2; H, 6·3. $C_{24}H_{20}O$ requires C, 88·8; H, 6·2%). Its 2:4-dinitrophenylhydrazone crystallised from benzene in small orange needles m.p. 202-4° (Found: C, 71·4; H, 4·8; N, 11·0. $C_{30}H_{24}O_4N_4$ requires C, 71·4; H, 4·8; N, 11·1%).

Lithium 10-benzanthryl (page 66).- To lithium n-butyl prepared in the usual manner from lithium (0.5g.) was added benzanthrene (5.4g.; 0.025 mole) in petroleum (67-69°) (20 ml.). A dark chocolate coloured solid appeared almost at once, butane being evolved. (52%; 2 hours refluxing.).

Benzanthrene 10-carboxylic acid (LXIII, page 67).- Lithium 10-benzanthryl prepared as above was stirred vigorously under a rapid stream of dry air-free carbon dioxide for two hours, the colour changing from dark-brown to orange. The mixture was hydrolysed with water and the aqueous layer on acidification with dilute hydrochloric acid gave a solid which crystallised from ethanol in yellow needles, softening at 170°, m.p. 174-5°, of benzanthrene 10-carboxylic acid (1.25g.; yield 20%).

(Found: C, 83.4; H, 4.6. $C_{18}H_{12}O_2$ requires C, 83.1; H, 4.65%). The petroleum layer gave a thick oil which appeared to bea mixture of benzanthrene and benzanthrone.

Michael Condensation of benzanthrene and chalcone.- Benzanthrene (1.08g.) and chalcone (1.04g.) were dissolved in dry ether (5 ml.) and pyridine (1 ml.), potassium hydroxide (0.56g.) being added. The mixture was allowed to stand for five days during which time a yellow solid crystallised out. This was filtered off and recrystallised from benzene-ethanol, m.p. 250-252°; (yield 1.0g.) (Found: C, 92.3; H, 4.11). No derivative was obtained with 2:4-dinitrophenylhydrazine, hydroxylamine or semicarbazide. The substance was recovered unchanged after 24 hours refluxing with sodium dichromate and acetic acid.

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