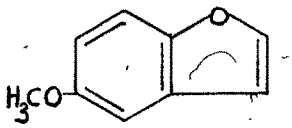
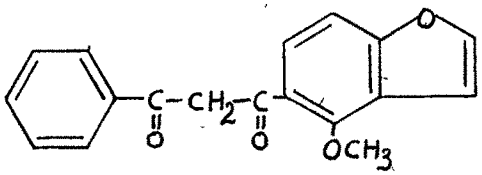
CHAPTER III

Synthesis of some dibenzofurans from dihydroxy derivatives of diphenyl, diphenyl methane, benzophenone and diphenyl sulfone :

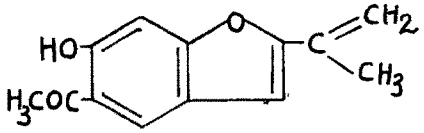
A large number of natural products having the furan ring system have been isolated from various plants. 5-Methoxy-benzofuran (I), pongamol (II), euparin (III) and egonol (IV) are a few examples of this group.



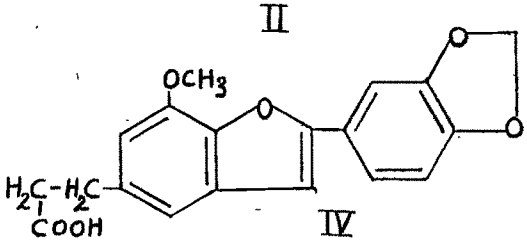
I



II

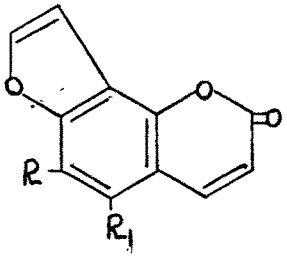


III

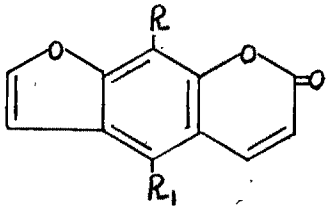


IV

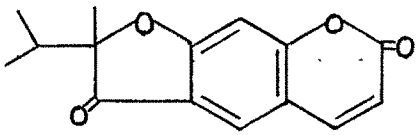
A large number of furocoumarins have also been isolated from plants. For example, angelicin (V), pimpinellin (VI), psoralene (VII), bergapten (VIII), xanthotoxin (IX), isopimpinellin (X) and oreoselone (XI).



	R	R_1
Angelicin (V)	H	H
Pimpinellin (VI)	OCH_3	OCH_3

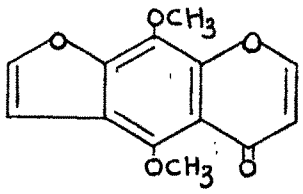


	R	R_1
Psoralene (VII)	H	H
Bergapten (VIII)	H	OCH_3
Xanthotoxin (IX)	OCH_3	H
Isopimpinellin (X)	OCH_3	OCH_3

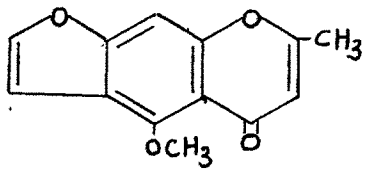


XI

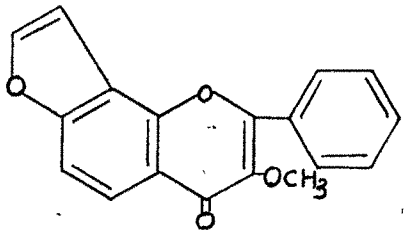
Another group consists of furochromones and furoflavones. Khellin (XII), visnagin (XIII) and karanjin (XIV) are a few members of this group.



XII

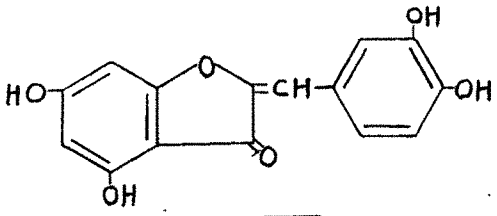


XIII

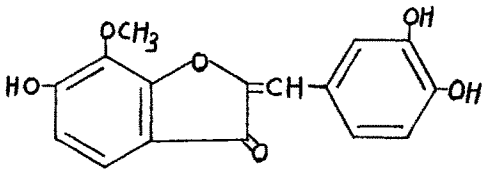


XIV

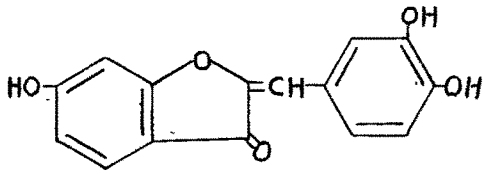
Still another group of benzofuran derivatives are the aurones. They are glycosides of hydroxylated benzylidenecoumaranones. Aureusidin (XV), leptosidin (XVI) and sulfuretin (XVII) are a few members of this group.



XV



XVI



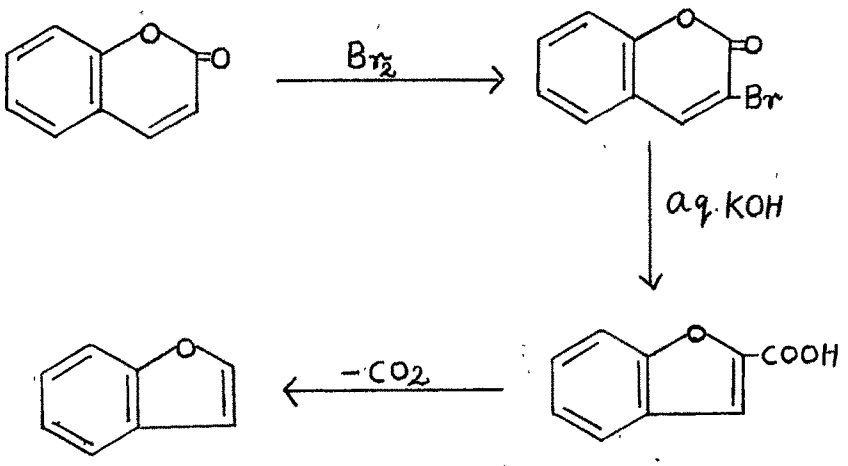
XVII

Besides these, there are other compounds of varied structures containing the furan ring system.

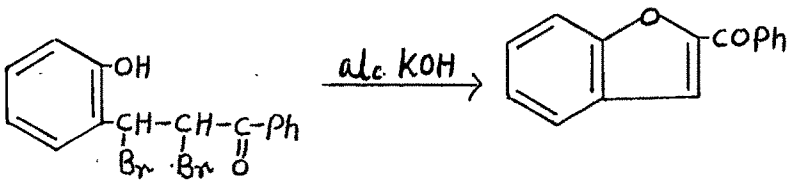
Syntheses of benzofuran derivatives :

There are several ways in which a furan ring can be built up on an aromatic nucleus. Some of the methods are briefly mentioned below :-

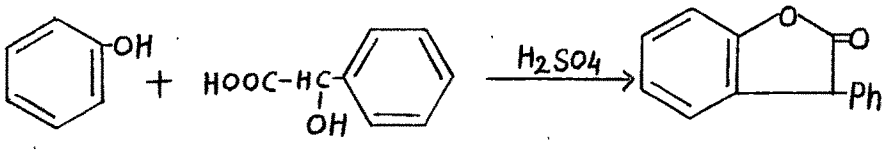
(i) The classical synthesis of benzofuran involves bromination of coumarin and treatment of the resulting 3-bromocoumarin with alkali to get benzofuran-2-carboxylic acid (coumarilic acid) which on decarboxylation gives benzofuran[1,2].



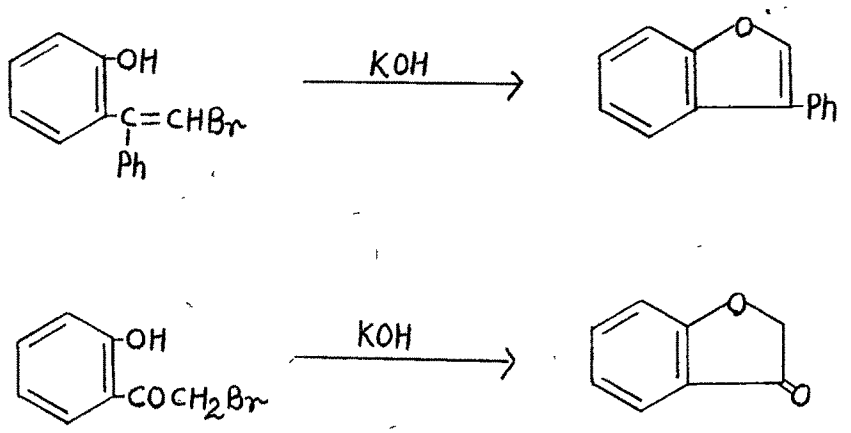
(ii) The dibromide of a chalcone[3] on treatment with alcoholic potassium hydroxide gives a benzofuran derivative.



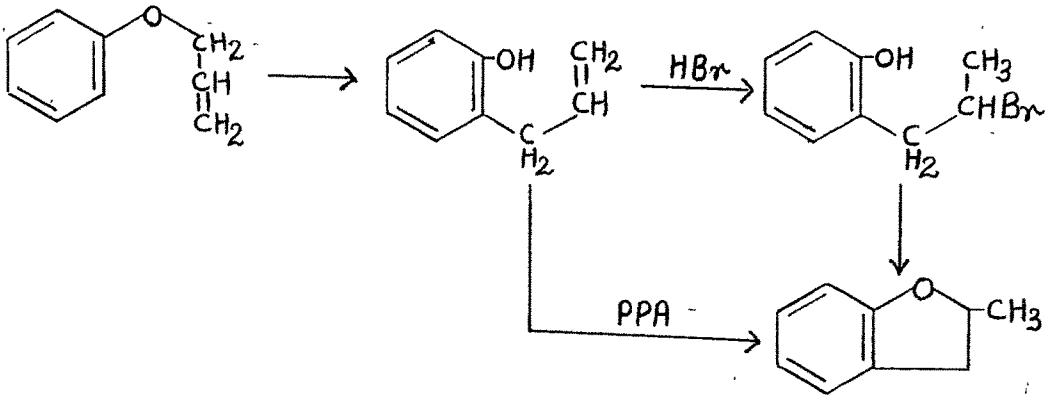
(iii) α-Hydroxyphenyl acetic acid condenses with phenol in presence of sulfuric acid to yield a furan derivative[4,5,6]. Thus, when mandelic acid is condensed with phenol, 3-phenylcoumaran-2-one is formed.



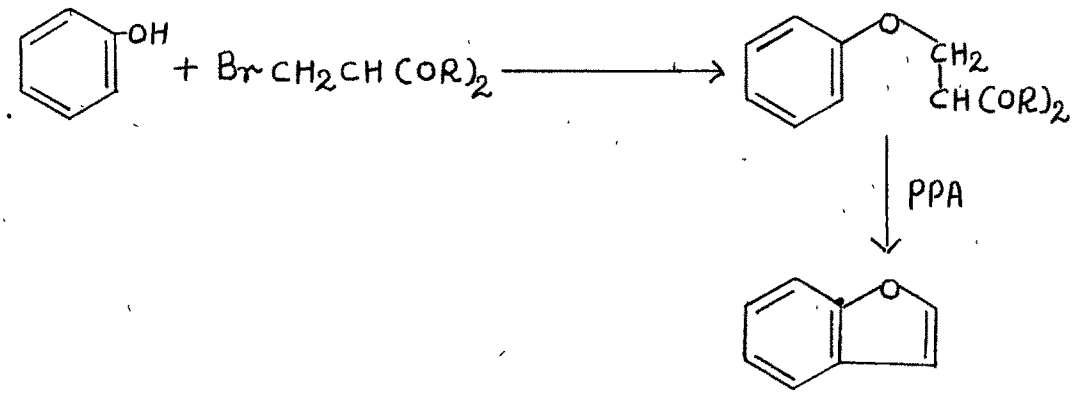
(iv) A related synthesis involves the action of alkali on o-hydroxy-β-halostyrenes[7]. 3-Phenylbenzofuran can be prepared in this way; and if o-hydroxybromoacetophenone is used, 3-coumaranone results[8].

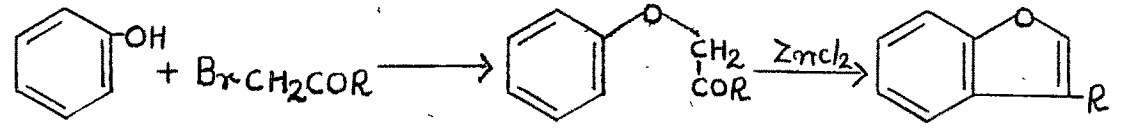


(v) Benzofuran can be obtained by the catalytic cyclodehydrogenation of o-ethylphenol[9], and 2,3-dihydrobenzofurans can be prepared by the cyclisation of o-allylphenols on heating with hydrobromic acid or with pyridine hydrochloride[10,11,12,13].

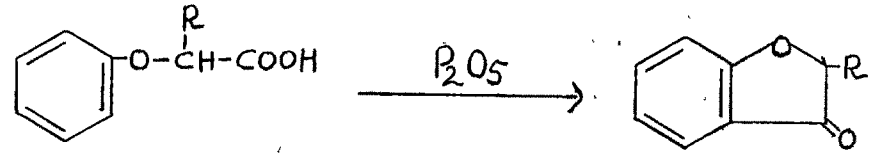


(vi) Ring closure of phenoxy carbonyl compounds or their acetals can be effected with the help of reagents like conc. sulfuric acid, anhydrous zinc chloride or polyphosphoric acid to get the furan derivative[14,15,16,17].



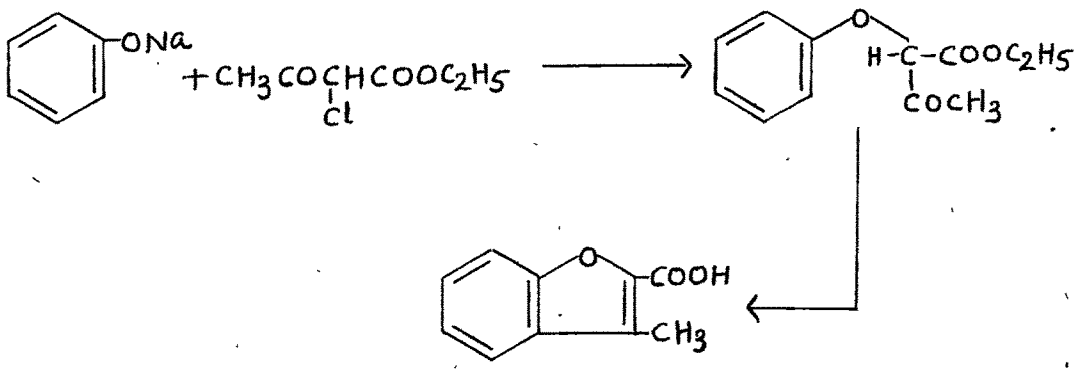


(vii) Phenoxy acetic acids undergo similar cyclisations when heated with phosphorus pentoxide to yield coumaran-3-ones[18,19,20].



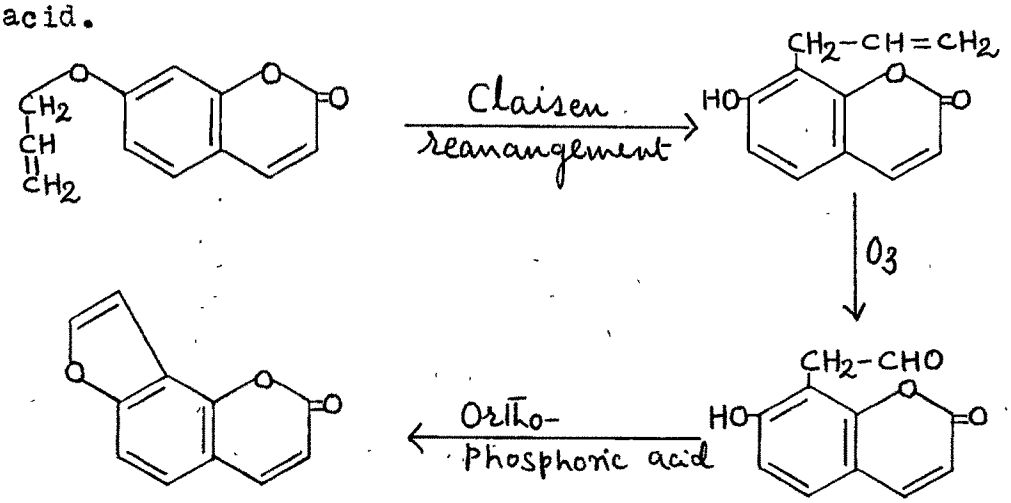
(viii) Another method is illustrated by the condensation of sodium phenoxide with ethyl chloroacetoacetate

in which 3-methyl benzofuran-2-carboxylic acid is obtained[21].



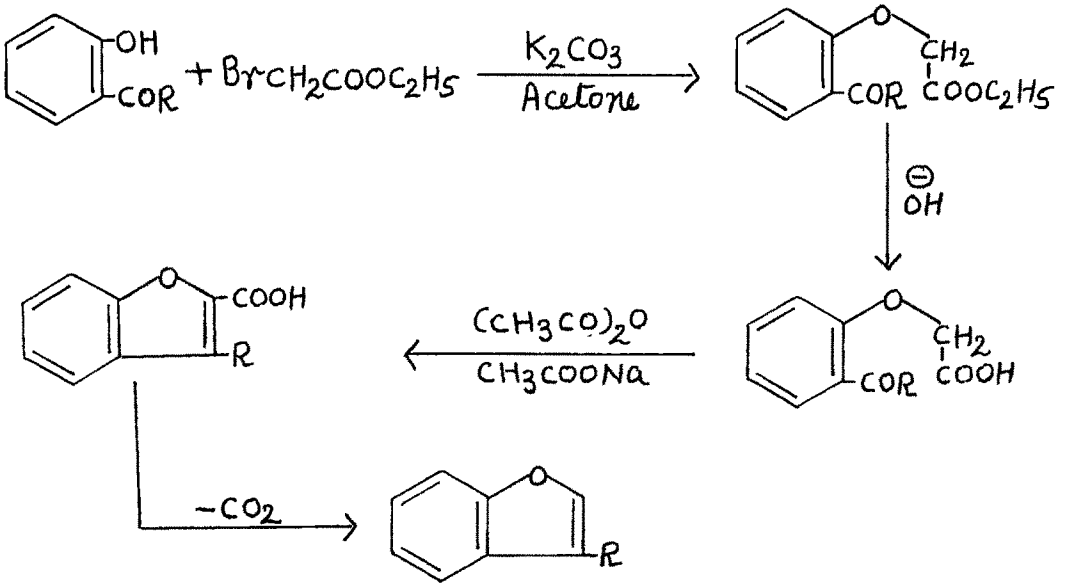
Condensations of this type are often effected with zinc chloride, sulfuric acid and similar reagents[22].

(ix) Aneja, Mukerjee and Seshadri[23] in the course of their work on the synthesis of furocoumarins developed another method in which they subjected the o-hydroxy allyl derivatives to ozonolysis and cyclised the o-hydroxyacetaldehyde derivative formed with ortho-phosphoric acid.

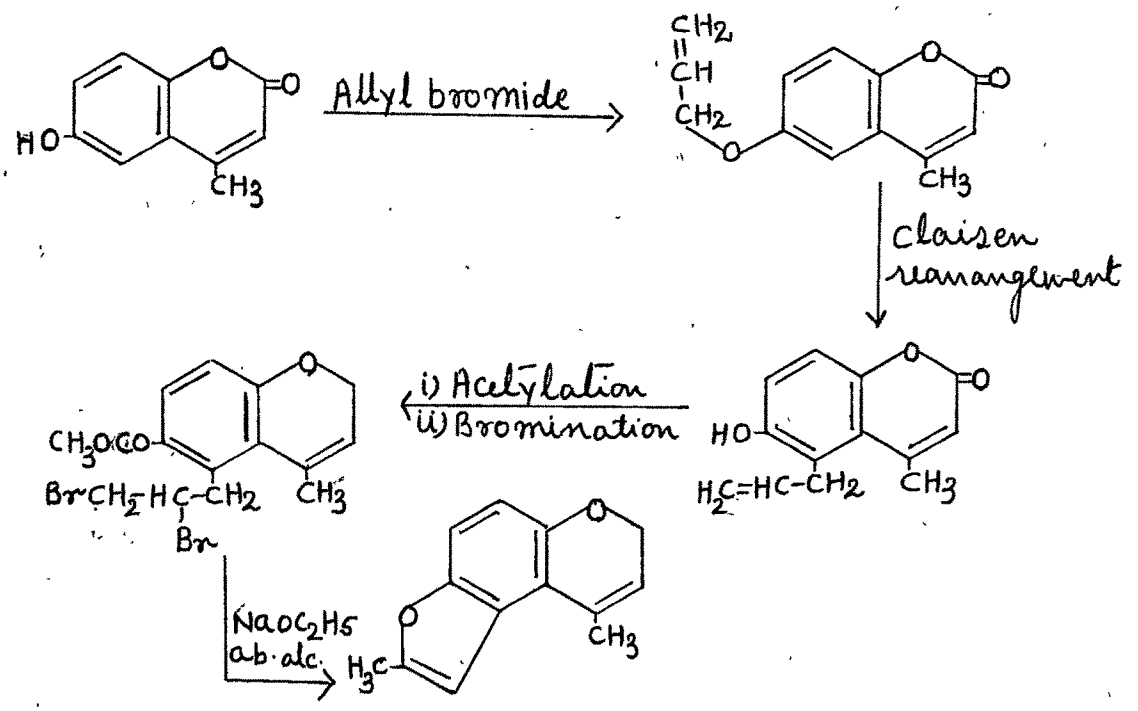


The oxidation of the allyl derivative to the formyl derivative can also be achieved with osmium tetroxide[24].

(x) A method which is extensively used for the synthesis of furan derivatives consists in the condensation of bromo acetic ester with an o-hydroxy aldehyde or an o-hydroxyketone and subsequent hydrolysis and cyclisation of the phenoxy acetic acid derivative formed with sodium acetate and acetic anhydride. Simultaneous decarboxylation has been observed in many cases.



(xi) Kaufmann et al.[25] in their work on the synthesis of furocoumarins developed a method for the synthesis of furan derivatives from o-hydroxy allyl derivatives. It can be illustrated with the synthesis of a furocoumarin derivative.



When the present work was started there were only two references in the literature on the synthesis of dibenzofuranyls viz. the synthesis of 5,5'-di(3-methylbenzofuranyl) by Mathai and Sethna[26] and the synthesis of 5,5'-di(3-methylbenzofuranyl)ketone by Balani and Sethna[27]. The present work deals with the synthesis of some bibenzofuranyl, bi(benzofuranyl) methane, bi(benzofuranyl)ketone and bi(benzofuranyl)sulfone.

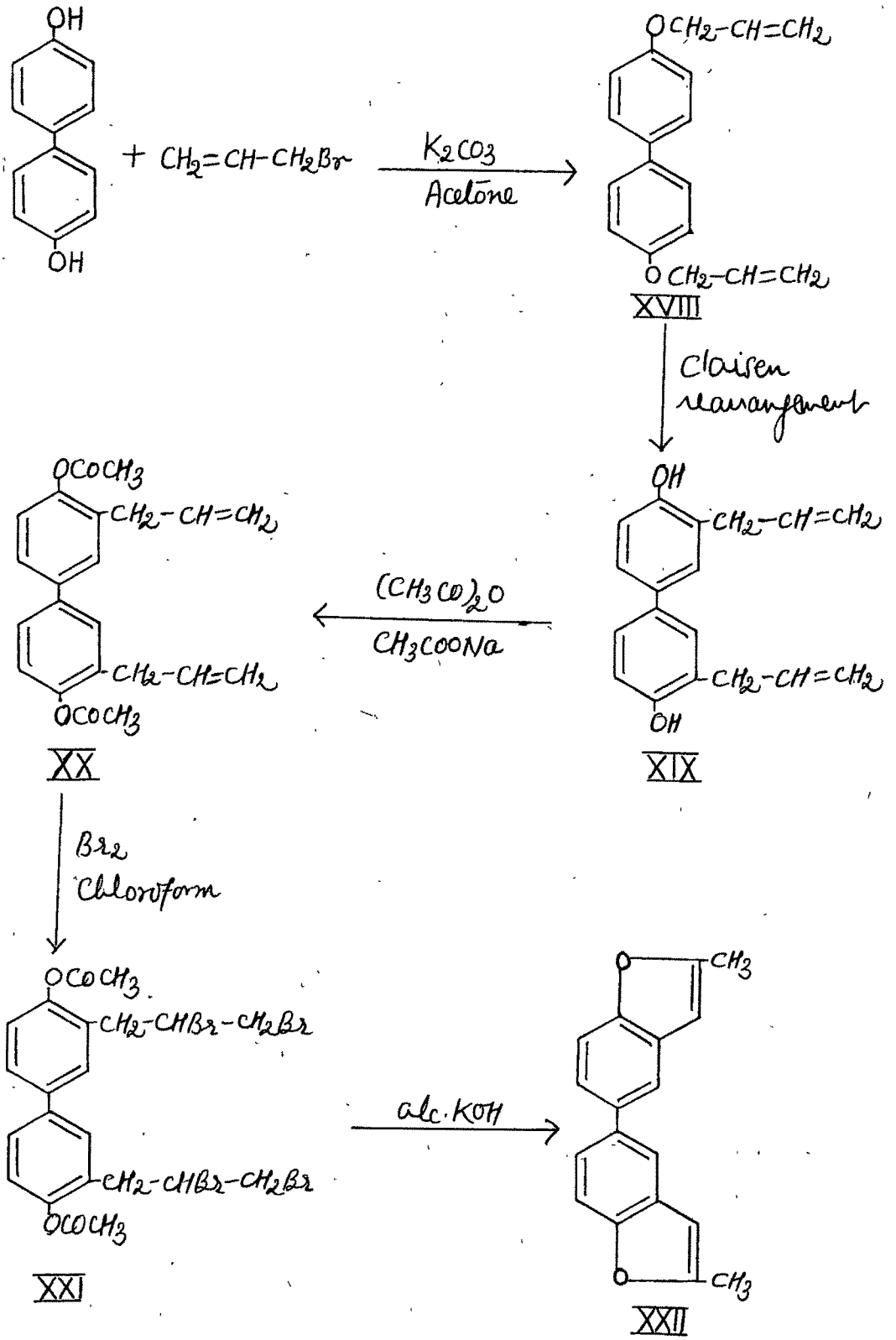
Synthesis of bi(2-methyl-5-benzofuranyl) :

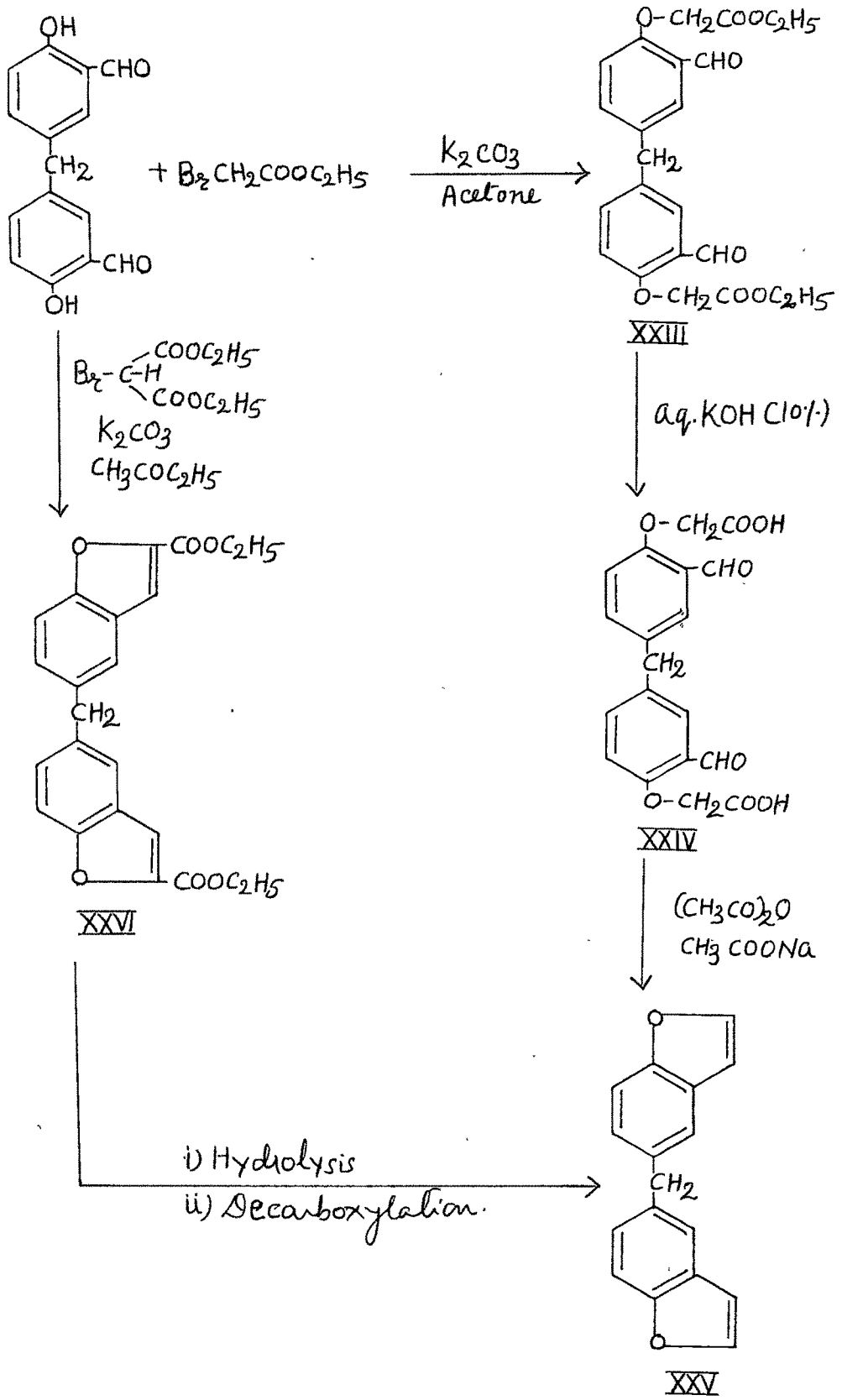
4,4'-Dihydroxydiphenyl on condensation with allyl bromide in presence of anhydrous potassium carbonate in dry acetone gave 4,4'-diallyloxy diphenyl (XVIII). It was subjected to Claisen rearrangement by heating in diphenyl ether when alkali soluble 3,3'-diallyl-4,4'-dihydroxydiphenyl

(XIX) was obtained. Attempt to cyclise the above allylphenol did not succeed. Original allylphenol was recovered unchanged. Therefore, Kaufmann method[25] was adopted. The above allylphenol (XIX) was converted into 3,3'-diallyl-4,4'-diacetoxydiphenyl (XX) by heating with acetic anhydride and fused sodium acetate. The alkali insoluble product obtained was brominated in chloroform solution. The bromo derivative showed a single spot in TLC. The tetrabromo derivative (XXI) was subjected to cyclisation using alcoholic potassium hydroxide when the the desired bi(2-methyl-5-benzofuranyl) (XXII) was obtained. U.V. λ max. (chloroform) 270 nm. I.R.865 cm^{-1} (Furan ring breathing).

Synthesis of bi(5-benzofuranyl)methane :

3,3'-Diformyl-4,4'-dihydroxydiphenyl methane, prepared as described on page No.138 , on condensation with ethyl bromoacetate in the presence of anhydrous potassium carbonate in dry acetone gave 3,3'-diformyl-4,4'-di(carbethoxy-methoxy)diphenyl methane (XXIII). It was then hydrolysed with alkali (10 %) to the corresponding dicarboxylic acid (XXIV) which on cyclisation with acetic anhydride and freshly fused sodium acetate gave bi(5-benzofuranyl)methane (XXV). The same bi(5-benzofuranyl)methane was obtained by the condensation of 3,3'-diformyl-4,4'-dihydroxydiphenyl methane with diethyl bromomalonate[28], when di(2-carbethoxy-5-benzofuranyl)methane (XXVI) was obtained, which on hydrolysis and decarboxylation with copper and quinoline gave bi(5-benzo-furanyl)methane (XXV). U.V. λ max.(chloroform) 250, 282 nm. I.R.890 cm^{-1} (Furan ring breathing).


OH
OH
+ CH2=CH-CH2Br
K2CO3
Acetone
O CH2-CH=CH2
O CH2-CH=CH2
XVIII
Claisen rearrangement
OH
CH2-CH=CH2
CH2-CH=CH2
OH
XIX
(CH3CO)2O
CH3COONa
OCOCH3
CH2-CH=CH2
CH2-CH=CH2
OCOCH3
XX
Br2
Chloroform
OCOCH3
CH2-CHBr-CH2Br
CH2-CHBr-CH2Br
OCOCH3
XXI
alc. KOH
CH3
CH3
XXII

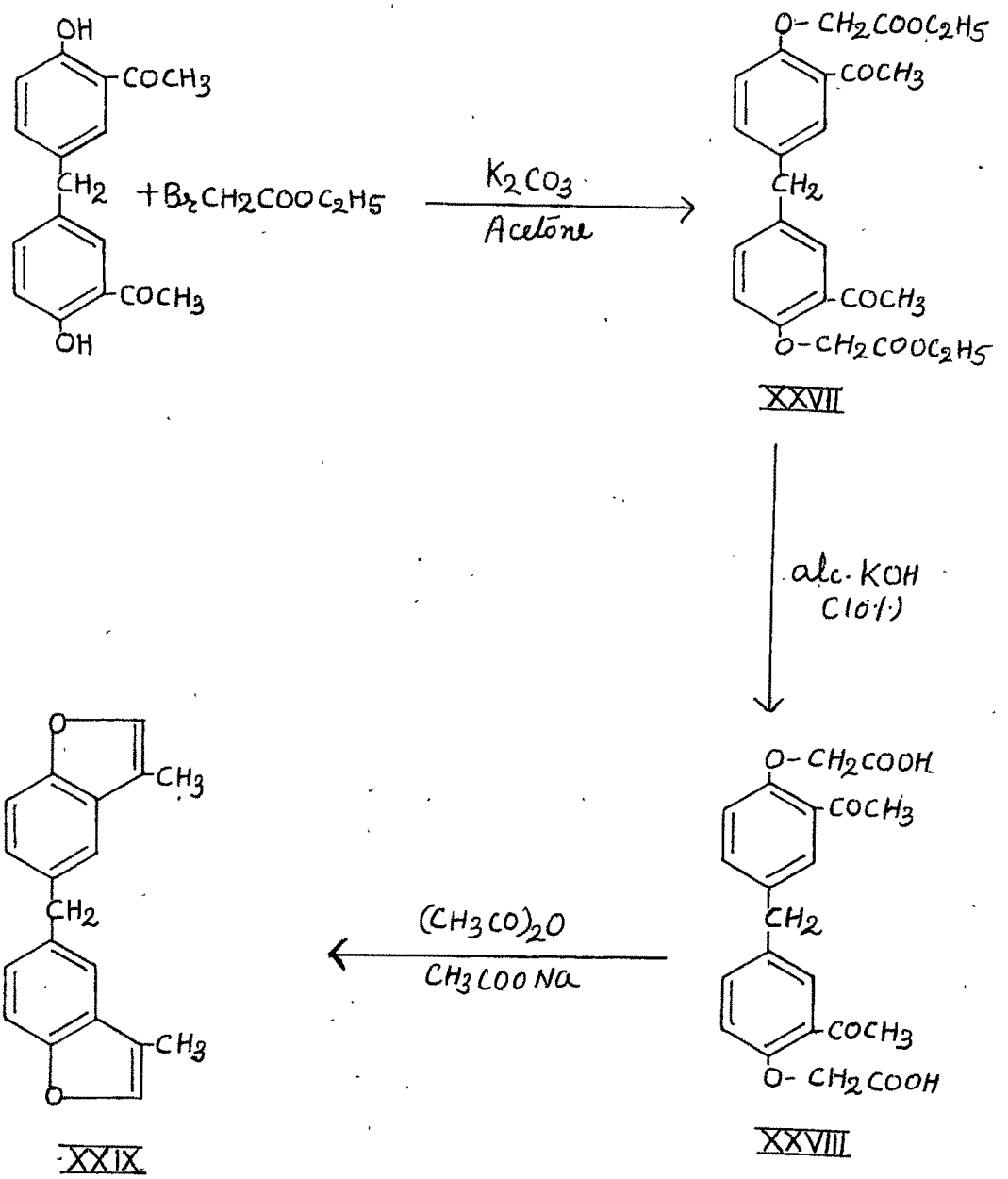

OH
CHO
CH2
CHO
OH
+ Br2CH2COOC2H5
K2CO3
Acetone
O-CH2COOC2H5
CHO
CH2
CHO
O-CH2COOC2H5
XXIII
aq. KOH (10%)
Br-C-H
COOC2H5
COOC2H5
K2CO3
CH3COC2H5
O-CH2COOH
CHO
CH2
CHO
O-CH2COOH
XXIV
(CH3CO)2O
CH3COONa
COOC2H5
CH2
COOC2H5
XXVI
i) Hydrolysis
ii) Decarboxylation.
CH2
XXV

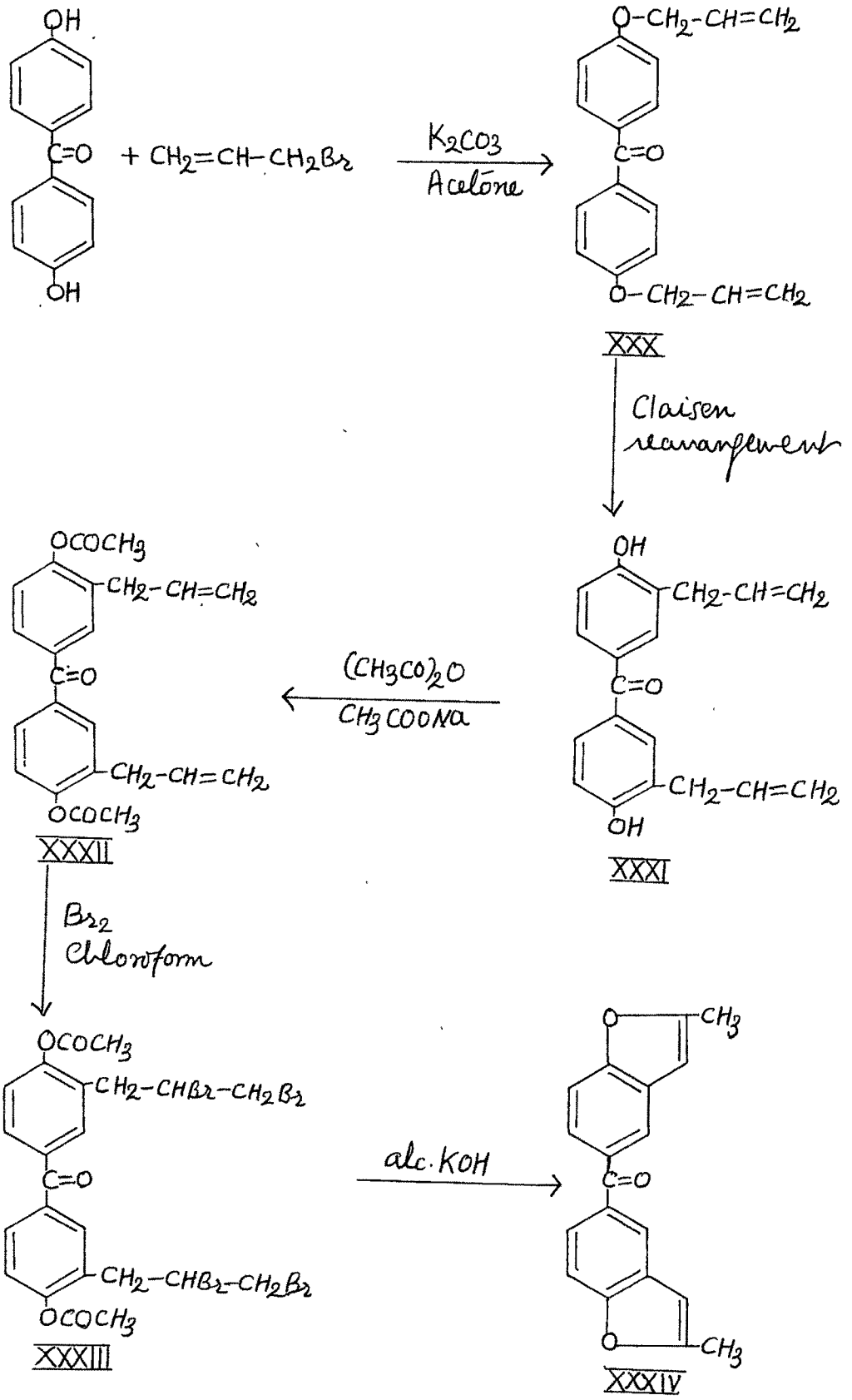
Synthesis of bi(3-methyl-5-benzofuranyl)methane :

3,3'-Diacetyl-4,4'-dihydroxydiphenyl methane, prepared as described on page 79, on condensation with ethyl bromoacetate in the presence of anhydrous potassium carbonate and dry acetone gave 3,3'-diacetyl-4,4'-di (carbethoxymethoxy)diphenyl methane (XXVII) which on alkaline hydrolysis (10 %) gave the corresponding dicarboxylic acid (XXVIII). This was treated with sodium acetate and acetic anhydride when through simultaneous cyclisation and decarboxylation, bi(3-methyl-5-benzofuranyl)methane (XXIX) was obtained. U.V. λ max. (chloroform) 256, 284 mμ. I.R. 900 $cm.^{-1}$ (Furan ring breathing).

Synthesis of bi(2-methyl-5-benzofuranyl)ketone :

4,4'-Dihydroxybenzophenone on condensation with allyl bromide in presence of anhydrous potassium carbonate in dry acetone gave 4,4'-diallyloxy benzophenone (XXX). It was subjected to Claisen rearrangement by heating in diphenyl ether when alkali soluble 3,3'-diallyl-4,4'-dihydroxybenzophenone (XXXI) was obtained. Attempt to cyclise the above allylphenol with Conc. Sulfuric acid did not succeed. Original allylphenol was recovered unchanged. Therefore, Kaufmann method[25] was adopted. The above ketone (XXXI) was converted into 3,3'-diallyl-4,4'-diacetoxybenzophenone (XXXII) by heating with acetic anhydride and fused sodium acetate. The alkali insoluble product obtained was brominated in


OH
COCH3
CH2
+Br CH2 COOC2H5
K2CO3
Acetone
O- CH2 COOC2H5
COCH3
CH2
COCH3
O-CH2 COOC2H5
XXVII
alc. KOH
(10%)
O-CH2COOH
COCH3
CH2
COCH3
O- CH2 COOH
XXVIII
(CH3CO)2O
CH3COONa
CH3
CH2
CH3
XXIX


OH
C=O
+ CH2=CH-CH2Br2
K2CO3
Acetone
O-CH2-CH=CH2
C=O
O-CH2-CH=CH2
XXX
Claisen rearrangement
OH
CH2-CH=CH2
C=O
CH2-CH=CH2
OH
XXXI
(CH3CO)2O
CH3COONa
OCOCH3
CH2-CH=CH2
C=O
CH2-CH=CH2
OCOCH3
XXXII
Br2
Chloroform
OCOCH3
CH2-CHBr2-CH2Br2
C=O
CH2-CHBr2-CH2Br2
OCOCH3
XXXIII
alc. KOH
CH3
O
C=O
O
CH3
XXXIV

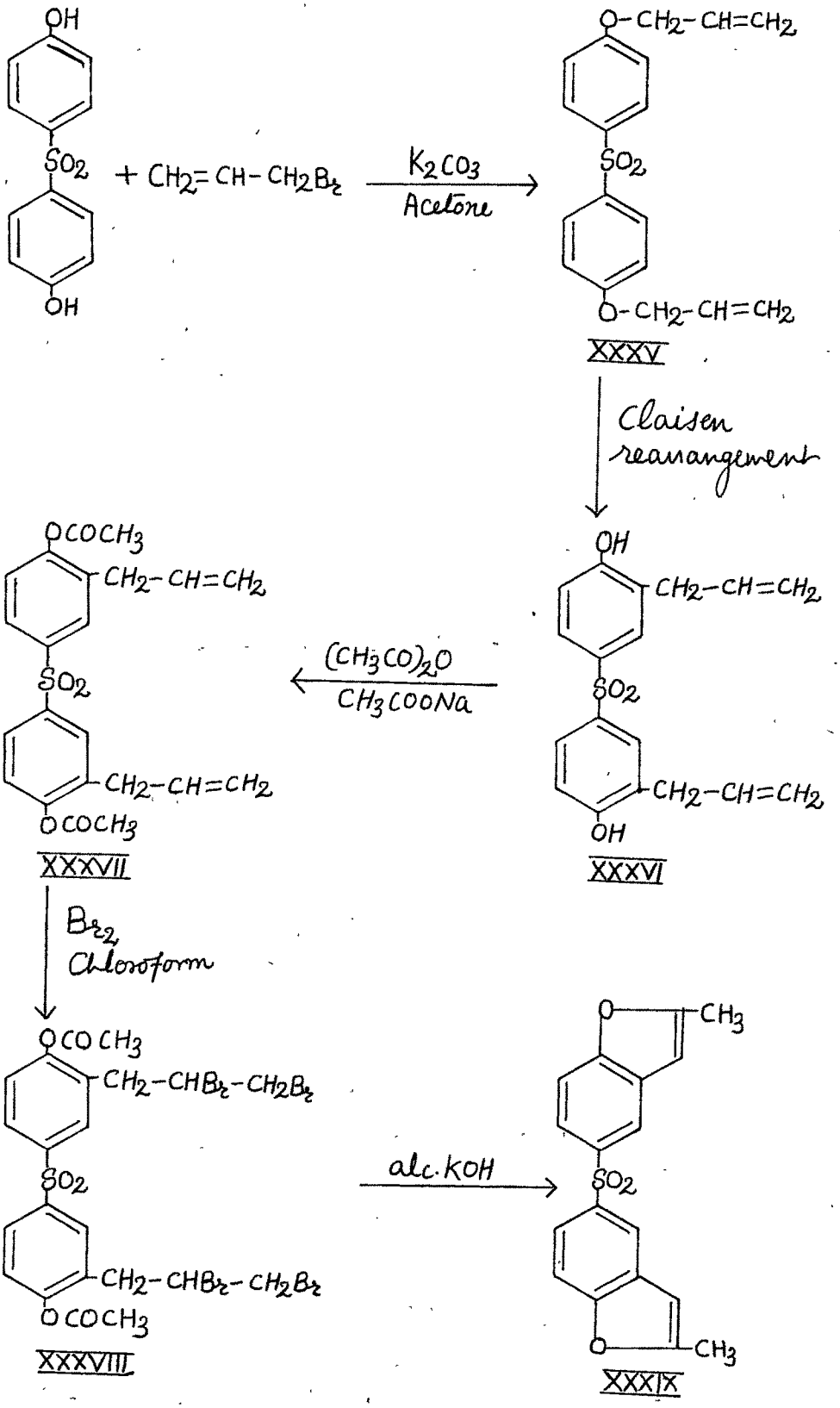
chloroform solution. The bromo derivative showed a single spot in TLC. The tetrabromo derivative (XXXIII) was subjected to cyclisation using alcoholic potassium hydroxide when the desired bi(2-methyl-5-benzofuranyl)ketone (XXXIV) was obtained. U.V. λmax. (chloroform) 244, 302 nm . I.R. 860 cm^{-1} (Furan ring breathing).

Synthesis of bi(2-methyl-5-benzofuranyl)sulfone :

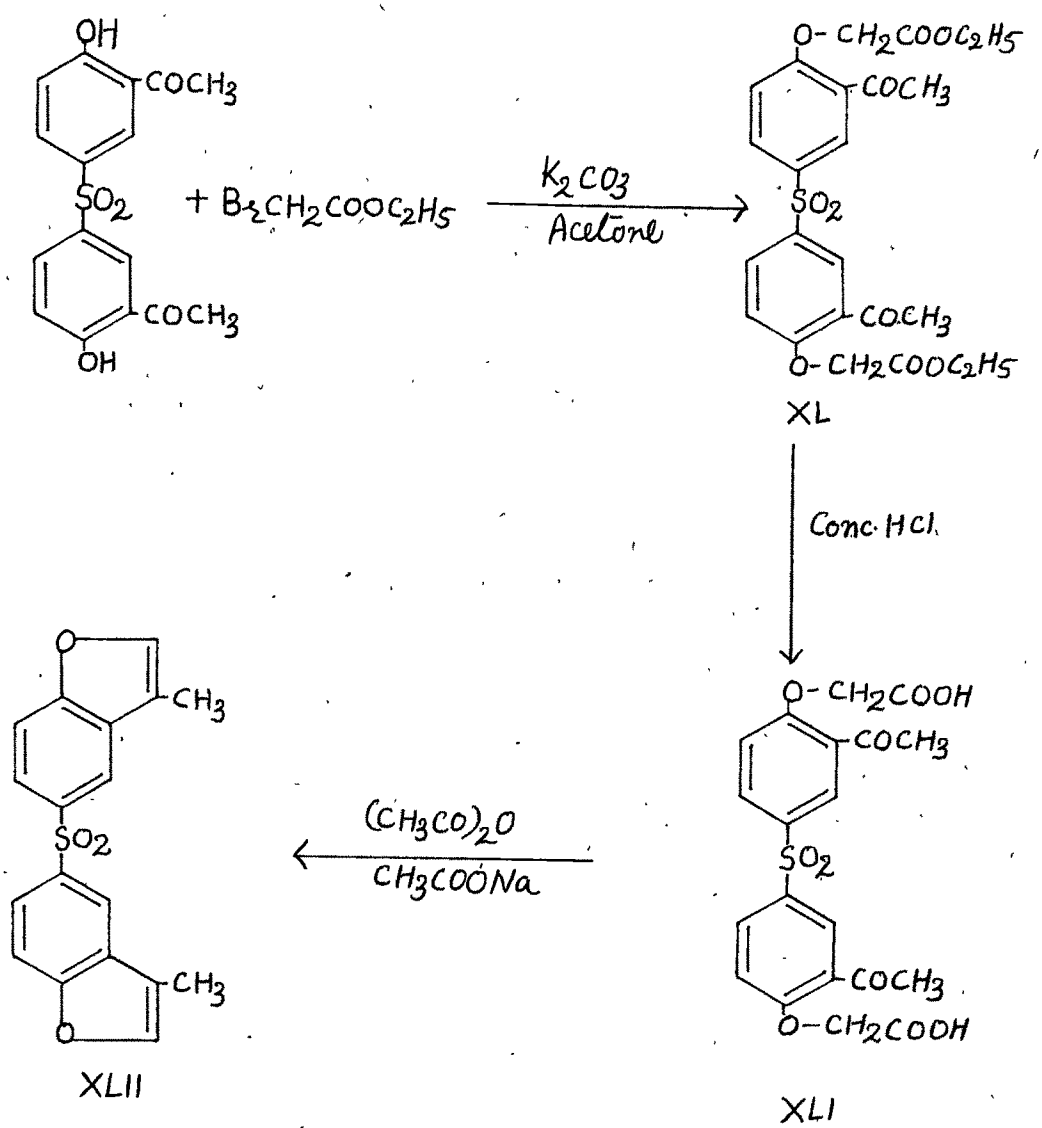
4,4'-Dihydroxydiphenyl sulfone on condensation with allyl bromide in presence of anhydrous potassium carbonate in dry acetone gave the 4,4'-diallyloxy diphenyl sulfone (XXXV). It was subjected to Claisen rearrangement by heating in diphenyl ether when alkali soluble 3,3'-diallyl-4,4'-dihydroxydiphenyl sulfone (XXXVI) was obtained. The above sulfone was acetylated and the diacetoxy derivative (XXXVII) was brominated using chloroform as the solvent. The tetrabromo derivative (XXXVIII) which could not be crystallised was subjected directly to cyclisation using alcoholic potassium hydroxide when alkali insoluble bi(2-methyl-5-benzofuranyl)sulfone (XXXIX) was obtained. U.V. λ max. (chloroform) 244, 290 nm . I.R. 885 cm^{-1} (Furan ring breathing).

Synthesis of bi(3-methyl-5-benzofuranyl)sulfone :

3,3'-Diacetyl-4,4'-dihydroxydiphenyl sulfone, prepared as described on page 86 , on condensation with


OH
SO2
+ CH2=CH-CH2Br2
K2CO3
Acetone
O-CH2-CH=CH2
SO2
O-CH2-CH=CH2
XXXV
Claisen rearrangement
OH
CH2-CH=CH2
SO2
CH2-CH=CH2
OH
XXXVI
(CH3CO)2O
CH3COONa
OCOCH3
CH2-CH=CH2
SO2
CH2-CH=CH2
OCOCH3
XXXVII
Br2
Chloroform
OCOCH3
CH2-CHBr2-CH2Br2
SO2
CH2-CHBr2-CH2Br2
OCOCH3
XXXVIII
alc. KOH
O
CH3
SO2
O
CH3
XXXIX

ethyl bromoacetate in the presence of anhydrous potassium carbonate in dry acetone gave 3,3'-diacetyl-4,4'-di(carbethoxymethoxy)diphenyl sulfone (XL), which on acid hydrolysis gave the 3,3'-diacetyl-4,4'-di(carboxymethoxy)diphenyl sulfone (XLI). The above dicarboxylic acid on refluxing with fused sodium acetate and acetic anhydride yielded bi(3-methyl-5-benzofuranyl)sulfone (XLII). U.V. λ max. (chloroform) 248, 284 nm. I.R. 885 cm^{-1} (Furan ring breathing).


OH
COCH3
SO2
+ BrCH2COOC2H5
K2CO3
Acetone
O-CH2COOC2H5
COCH3
SO2
COCH3
O-CH2COOC2H5
XL
Conc. HCl
O-CH2COOH
COCH3
SO2
COCH3
O-CH2COOH
XLI
(CH3CO)2O
CH3COONa
CH3
SO2
CH3
XLII

EXPERIMENTAL.

Condensation of 4,4'-dihydroxydiphenyl with allyl bromide :

4,4'-Diallyloxy diphenyl :

A mixture of 4,4'-dihydroxydiphenyl (2 g.), allyl bromide (2.5 ml.) and anhydrous potassium carbonate (5 g.) in dry acetone was refluxed for 12 hr. The product obtained on removal of solvent was crystallised from glacial acetic acid in yellow shining plates (2 g.), m.p. 151-52°.

Analysis : Found : C, 80.87 ; H, 6.64 %.

$C_{18}H_{18}O_2$ requires : C, 81.20 ; H, 6.12 %.

3,3'-Diallyl-4,4'-dihydroxydiphenyl :

4,4'-Diallyloxydiphenyl (0.5 g.) was refluxed with diphenyl ether (5 ml.) for 2 hr. The reaction mixture was cooled and diluted with solvent ether. Allylphenol was extracted with sodium hydroxide solution (10 %). The product obtained on acidification of the clear alkaline extract was dried and crystallised from benzene-petroleum ether mixture in white needles (0.2 g.), m.p. 79-81°.

Analysis : Found : C, 81.66 ; H, 6.46 %.

$C_{18}H_{18}O_2$ requires: C, 81.20 ; H, 6.77 %.

3,3'-Diallyl-4,4'-diacetoxydiphenyl :

The above allylphenol (0.5 g.) was dissolved in acetic anhydride (10 ml.) and heated with freshly fused sodium acetate (1 g.) on a steam bath for 5 hr. and the

reaction mixture was then poured in cold water. The separated alkali insoluble product crystallised from alcohol in white shining plates (0.5 g.), m.p. 88-89°.

Analysis : Found : C, 75.86 ; H, 6.56 %.

$C_{22}H_{22}O_4$ requires: C, 75.40 ; H, 6.28 %.

The tetrabromo derivative :

The above diacetoxy derivative (0.5 g.) was dissolved in chloroform (25 ml.) and cooled in an ice bath. Bromine (0.5 g.) in chlofoform (10 ml.) was added dropwise with continuous stirring. After all the bromine was added, the reaction mixture was stirred for half an hour more. The product obtained on removal of the solvent crystallised from benzene-petroleum ether mixture in white needles (0.6 g.), m.p. 155-57°.

Analysis : Found : C, 39.75; H, 3.68; Br, 48.24 %.

$C_{22}H_{22}O_4Br_4$ requires : C, 39.40; H, 3.28; Br, 47.75 %.

It showed a single spot in TLC.

Bi-(2-methyl-5-benzofuranyl) :

The above tetrabromo derivative (0.5 g.) was dissolved in absolute alcohol (100 ml.) and refluxed with potassium hydroxide (1 g.) for 4 hr. The product obtained on removal of alcohol was crystallised from alcohol in light pink shining plates (0.15 g.), m.p. 148-49°.

Analysis : Found : C, 82.68 ; H, 5.58 %.

$C_{18}H_{14}O_2$ requires: C, 82.45 ; H, 5.34 %.

It showed a single spot in TLC.

Condensation of 3,3'-diformyl-4,4'-dihydroxydiphenyl methane with ethyl bromoacetate : 3,3'-Diformyl-4,4'-di-(carbethoxymethoxy)diphenyl methane :

A mixture of 3,3'-diformyl-4,4'-dihydroxydiphenyl methane (1 g.), ethyl bromoacetate (2 ml.) and anhydrous potassium carbonate (3 g.) was refluxed in dry acetone for 15 hr. An oily product was obtained on removal of acetone which was treated with water and left overnight. The product obtained crystallised from benzene-petroleum ether mixture in white needles (0.5 g.), m.p. 107-08°.

Analysis :Found : C, 64.37 ; H, 5.73 %.

$C_{23}H_{24}O_8$ requires : C, 64.50 ; H, 5.60 %.

3,3'-Diformyl-4,4'-di-(carboxymethoxy)diphenyl methane :

The above ester (1 g.) was heated with potassium hydroxide solution (20 ml. ; 10 %) on a steam bath for 3 hr. The product obtained on acidification crystallised from dilute alcohol in pale yellow needles (0.5 g.), m.p. 247° (decomp.).

Analysis : Found : C, 60.96 ; H, 4.41 %.

$C_{19}H_{16}O_8$ requires : C, 61.30 ; H, 4.30 %.

Bi-(5-benzofuranyl)methane :

A mixture of 3,3'-diformyl-4,4'-di(carboxymethoxy) diphenyl methane (0.5 g.), acetic anhydride (3 ml.) and freshly fused sodium acetate (1 g.) was refluxed for half an hour. The reaction mixture was then poured in water and left overnight. The separated product was

crystallised from petroleum ether. Yield 0.1 g. M.p. 75-76°.

Analysis : Found : C, 82.24 ; H, 5.03 %.

$C_{17}H_{22}O_2$ requires : C, 82.23 ; H, 4.84 %.

It showed a single spot in TLC.

Condensation of 3,3'-diformyl-4,4'-dihydroxydiphenyl methane with diethyl bromomalonate : Di-(2-carbethoxy-5-benzofuranyl) methane :

3,3'-Diformyl-4,4'-dihydroxydiphenyl methane (1 g.) was refluxed with diethyl bromomalonate (2 ml.) and anhydrous potassium carbonate (5 g.) in dry ethyl methyl ketone (25 ml.) on a steam bath for 15 hr. The solvent was removed and water was added. The product obtained crystallised from alcohol in white needles (0.5 g.), m.p. 134°.

Analysis :Found : C, 70.65 ; H, 5.28 %.

$C_{23}H_{20}O_6$ requires : C, 70.40 ; H, 5.10 %.

Di-(2-carboxy-5-benzofuranyl)methane :

The above ester (0.5 g.) was refluxed with alcoholic potassium hydroxide solution (10 ml.; 20 %) for 1 hr. The product obtained on acidification was crystallised from dilute alcohol in small white needles (0.2 g.), m.p. 317°.

Analysis : Found : C, 67.59 ; H, 3.92 %.

$C_{19}H_{12}O_6$ requires : C, 67.86 ; H, 3.57 %.

Decarboxylation :

The above dicarboxylic acid (0.5 g.) was refluxed

with copper powder (0.2 g.) in quinoline (15 ml.) for half an hour and the solution was filtered hot. Conc. hydrochloric acid was added to the filtrate. The separated product was crystallised from petroleum ether in brown shining leaflets (0.1 g.), m.p. 75-76°. It showed a single spot in TLC.

Mixed m.p. with the furan prepared by ethyl bromoacetate method as described above was not depressed.

Condensation of 3,3'-diacetyl-4,4'-dihydroxydiphenyl methane with ethyl bromoacetate : 3,3'-Diacetyl-4,4'-di-(carbethoxymethoxy)diphenyl methane :

A mixture of 3,3'-diacetyl-4,4'-dihydroxydiphenyl methane (1 g.), ethyl bromoacetate (2 ml.) and anhydrous potassium carbonate (5 g.) was refluxed in dry acetone for 16 hr. The product obtained on removal of acetone was washed with water and crystallised from alcohol in white shining leaflets (1 g.), m.p. 126°.

Analysis : Found : C, 65.64 ; H, 6.11 %.

$C_{25}H_{28}O_8$ requires : C, 65.78 ; H, 6.18 %.

3,3'-Diacetyl-4,4'-di-(carboxymethoxy)diphenyl methane :

The above ester (1 g.) was refluxed with alcoholic potassium hydroxide solution (20 ml. ; 10 %) for 1 hr. The product obtained on acidification of the clear alkaline solution was crystallised from dilute alcohol in white shining needles (0.5 g.), m.p. 201-02°.

Analysis : Found : C, 63.49 ; H, 5.00 %.

$C_{21}H_{20}O_8$ requires : C, 63.30 ; H, 5.03 %.

Bi-(3-methyl-5-benzofuranyl)methane :

The above dicarboxylic acid (1 g.) was refluxed with freshly fused sodium acetate (4 g.) and acetic anhydride (10 ml.) for 4 hr. The reaction mixture was poured in water. The separated product was crystallised from alcohol. Yield 0.5 g., M.p. 102-03°.

Analysis :Found : C, 82.47 ; H, 5.59 %.

$C_{19}H_{16}O_2$ requires : C, 82.60 ; H, 5.79 %.

It showed a single spot in TLC.

Condensation of 4,4'-dihydroxybenzophenone with allyl bromide : 4,4'-Diallyloxybenzophenone :

A mixture of 4,4'-dihydroxybenzophenone (2 g.), allyl bromide (2.5 ml.) and anhydrous potassium carbonate (5 g.) in dry acetone was refluxed for 8 hr. The product obtained on removal of solvent was crystallised from alcohol in white shining plates (1.5 g.), m.p. 128-29°.

Analysis : Found : C, 77.34 ; H, 5.70 %.

$C_{19}H_{18}O_3$ requires : C, 77.55 ; H, 6.12 %.

3,3'-Diallyl-4,4'-dihydroxybenzophenone :

4,4'-Diallyloxybenzophenone (0.5 g.) was refluxed with diphenyl ether (5 ml.) for 2 hr. The reaction mixture was cooled and diluted with solvent ether. Allylphenol was extracted with sodium hydroxide solution (10 %). The product obtained on acidification of the clear alkaline extract was

dried and crystallised from benzene-petroleum ether mixture in white needles (0.2 g.), m.p. 120-22°.

Analysis : Found : C, 77.59 ; H, 5.71 %.

$C_{19}H_{18}O_3$ requires : C, 77.55 ; H, 6.12 %.

3,3'-Diallyl-4,4'-diacetoxybenzophenone :

The above allyl-phenol (0.5 g.) was dissolved in acetic anhydride (7 ml.) and heated with freshly fused sodium acetate (1 g.) on a steam bath for 5 hr. The reaction mixture was poured in cold water and left overnight. The separated alkali insoluble product crystallised from petroleum ether (60-80°) in white needles (0.5 g.), m.p. 89-91°.

Analysis : Found : C, 73.13 ; H, 6.07 %.

$C_{23}H_{22}O_5$ requires : C, 73.00 ; H, 5.82 %.

The tetrabromo derivative :

The above diacetoxy derivative (0.5 g.) was dissolved in chloroform (25 ml.) and cooled in an ice bath. Bromine (0.5 g.) in chloroform (10 ml.) was added dropwise with continuous stirring. After all the bromine was added, the reaction mixture was stirred for half an hour more. The product obtained on removal of the solvent crystallised from benzene-petroleum ether mixture in white buds (0.5 g.), m.p. 157-58°.

Analysis : Found : C, 40.00; H, 3.12; Br, 46.21 %.

$C_{23}H_{22}O_5Br_4$ requires : C, 39.54; H, 3.15; Br, 45.83 %.

It showed a single spot in TLC.

Bi-(2-methyl-5-benzofuranyl)ketone :

The above tetrabromo derivative (0.5 g.) was dissolved in absolute alcohol (30 ml.) and refluxed with potassium hydroxide (1 g.) for 4 hr. The product obtained on removal of alcohol was crystallised from alcohol in brown plates (0.1 g.), m.p. 128-30°.

Analysis : Found : C, 78.29; H, 5.09 %.

$C_{19}H_{14}O_3$ requires : C, 78.60; H, 4.83 %.

It showed a single spot in TLC.

Condensation of 4,4'-dihydroxydiphenyl sulfone with allyl bromide : 4,4'-Diallyloxydiphenyl sulfone :

A mixture of 4,4'-dihydroxydiphenyl sulfone (2 g.), allyl bromide (2.5 ml.) and anhydrous potassium carbonate (5 g.) in dry acetone was refluxed for 8 hr. The product obtained on removal of the solvent was crystallised from alcohol in white shining plates (1.5 g.), m.p. 141-42°.

Analysis : Found : C, 65.61 ; H, 5.15 %.

$C_{18}H_{18}O_4S$ requires : C, 65.46 ; H, 5.45 %.

3,3'-Diallyl-4,4'-dihydroxydiphenyl sulfone :

4,4'-Diallyloxydiphenyl sulfone (1 g.) was refluxed in diphenyl ether (10 ml.) for 2 hr. The reaction mixture was cooled and diluted with solvent ether. The rearranged product was extracted with sodium hydroxide solution (10 %). The product obtained on acidification of

the clear alkaline extract was dried and crystallised from xylene in white needles (0.6 g.), m.p. 151-52°.

Analysis : Found : C, 65.31 ; H, 5.15 %.

$C_{18}H_{18}O_4S$ requires : C, 65.46 ; H, 5.45 %.

Bi-(2-methyl-5-benzofuranyl)sulfone :

The above allylphenol (1 g.) was heated with acetic anhydride (5 ml.) and fused sodium acetate (2 g.) on a steam bath for 4 hr. The reaction mixture was then poured in water. An oily product obtained was taken up in chloroform and purified by sodium hydroxide treatment. Chloroform layer was dried and to it bromine (1 g.) in chloroform (10 ml.) was added dropwise with stirring. The solvent was then removed by evaporation. The oily bromo derivative obtained was refluxed with potassium hydroxide (1.5 g.) in absolute alcohol (20 ml.) for 6 hr. The alcohol was evaporated and the residue treated with water. The separated product was filtered and crystallised from alcohol in yellowish brown buds (0.2 g.), m.p. 154-55°.

Analysis : Found : C, 66.68 ; H, 4.58 %.

$C_{18}H_{14}O_4S$ requires : C, 66.26 ; H, 4.29 %.

It showed a single spot in TLC.

Condensation of 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfone with ethyl bromoacetate : 3,3'-Diacetyl-4,4'-di-(carbethoxymethoxy)diphenyl sulfone :

A mixture of 3,3'-diacetyl-4,4'-dihydroxydiphenyl

sulfone (2 g.), ethyl bromoacetate (2.5 g.) and anhydrous potassium carbonate (5 g.) in dry acetone was refluxed for 15 hr. The product obtained on removal of the solvent was crystallised from alcohol in white needles (2 g.), m.p. 139-40°.

Analysis : Found : C, 57.38 ; H, 5.16 %.

$C_{24}H_{26}O_{10}S$ requires : C, 56.91 ; H, 5.13 %.

3,3'-Diacetyl-4,4'-di(carboxymethoxy)diphenyl sulfone :

The above ester (1 g.) was dissolved in glacial acetic acid (15 ml.) and conc. hydrochloric acid (15 ml.) was added to it. The whole reaction mixture was refluxed for 3 hr. and then poured in water. The separated product was purified by sodium bicarbonate treatment and was crystallised from dilute alcohol in white needles (0.5 g.), m.p. 222° (decomp.).

Analysis : Found : C, 53.40 ; H, 3.80 %.

$C_{20}H_{18}O_{10}S$ requires : C, 53.34 ; H, 4.00 %.

Bi-(3-methyl-5-benzofuranyl)sulfone :

The above dicarboxylic acid (0.5 g.) was refluxed with freshly fused sodium acetate (2 g.) and acetic anhydride (8 ml.) for 1 hr. and the reaction mixture was poured in water. The pasty product obtained solidified on treatment with sodium bicarbonate solution. The bicarbonate insoluble product was crystallised from dilute alcohol in pale brown needles (0.1 g.), m.p. 152-53°.

Analysis : Found : C, 66.13 ; H, 4.00 %.

$C_{18}H_{14}O_4S$ requires: C, 66.26 ; H, 4.29 %.

It showed a single spot in TLC.

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