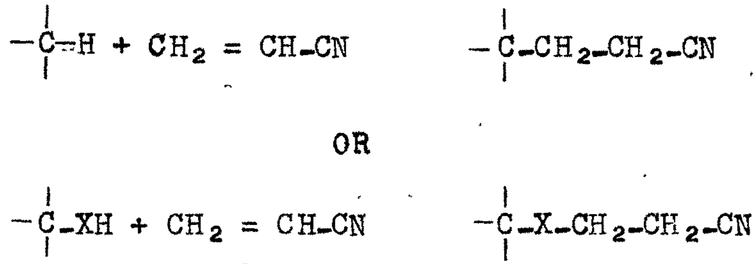
CHAPTER I

Cyanoethylation of some dihydroxy derivatives of diphenyl, diphenyl methane, benzophenone and diphenyl sulfone and the synthesis of bichromonyl derivatives :

Acrylonitrile reacts readily by addition with a variety of organic and inorganic compounds that possess a reactive hydrogen atom, with the formation of β-substituted propionitrile derivatives. The propionitrile residue $-CH_2-CH_2-CN$, is termed the β-cyanoethyl or 2-cyanoethyl group, and the reaction is therefore known as cyanoethylation



$$-\overset{|}{\underset{|}{C}}-H + CH_2 = CH-CN \qquad -\overset{|}{\underset{|}{C}}-CH_2-CH_2-CN$$

OR

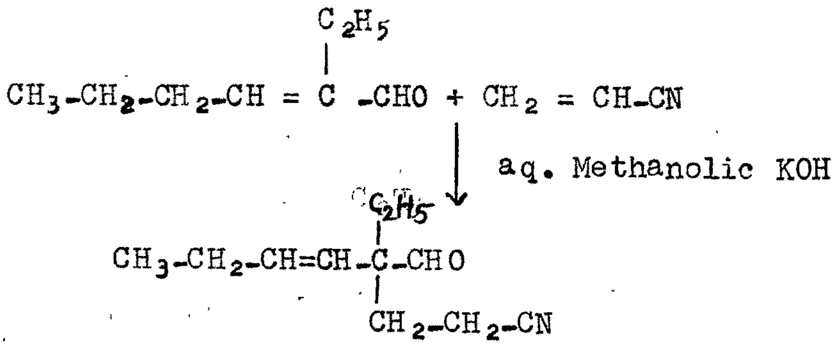
$$-\overset{|}{\underset{|}{C}}-XH + CH_2 = CH-CN \qquad -\overset{|}{\underset{|}{C}}-X-CH_2-CH_2-CN$$

where X is an electronegative atom such as N, O, S, P and As. Thus the reaction may be effected with hydroxyl compounds, thiols, nitrogen compounds, some carbon compounds, hydrochloric acid, hydrogen cyanide, hydrobromic acid, sodium bisulfite and hydrazoic acid as well as with arsines, boranes, germanes, phosphines, silanes and stannanes, In general, all compounds excepting carboxylic and sulfonic acid, containing reactive hydrogen atom add to acrylonitrile, Multiple cyanoethylation takes place, provided the compound contains several active hydrogen atoms.

The earlier work on cyanoethylation has been reviewed by Bruson[1]. Another more recent review is by Bikales[2].

Applications of the reaction :

Cyanoethylation may be effected on carbon if the substrate has at least one hydrogen atom adjacent to one or more powerful electron withdrawing groups, such as carbonyl, nitrile, nitro or sulfone. Rogers[3] carried out cyanoethylation of compounds containing a reactive methylene group, e.g. benzyl cyanide on cyanoethylation gave α-phenyl glutaronitrile. Many reactive methylene compounds have been cyanoethylated successfully[4,5]. If several hydrogen atoms are available, mixtures of mono-, di-, and tri-cyanoethylated products are obtained, e.g. cyanoethylation of acetaldehyde gives a mixture of mono- and di-cyanoethylene aldehydes[6]. Bruson and Riener[7] have cyanoethylated α-ethyl-β-propyl-acrolein, even though an α-hydrogen atom is lacking and obtained a 50 % yield of the product (A).



$$CH_3-CH_2-CH_2-CH=\overset{C_2H_5}{\overset{|}{C}}-CHO + CH_2=CH-CN \xrightarrow{\text{aq. Methanolic KOH}} CH_3-CH_2-CH=CH-\underset{CH_2-CH_2-CN}{\underset{|}{\overset{C_2H_5}{\overset{|}{C}}}}-CHO$$

Apparently, shifting of a hydrogen atom and the double bond permits the introduction of cyanoethyl group in the rearranged product. Acetone and acrylonitrile in equimolecular proportions give a small amount of mono-cyanoethylation product[8] with three moles of acrylonitrile in the presence of sodium hydroxide or Triton B. The crystalline tricyanoethylation derivative[9,10] is obtained in 75-80 % yield and upon further cyanoethylation a tetra addition product can be isolated.

Alicyclic ketones react like their aliphatic analogs but more readily. Aromatic aliphatic ketones react very readily, e.g. acetophenone, p-methoxyacetophenone, p-methyl acetophenone, p-chloro and p-bromo phenyl acetophenones give tricyanoethylation products in good yields[11]. Several 1,3-diketones fail to react with acrylonitrile. The explanation is that the high degree of acidity effectively neutralises the catalyst. It is essential that the reaction mixture be alkaline to moist litmus for the reaction to occur[12]. In general, reactive methylene compounds are more reactive than methyl groups. Although cyanoethylation takes place normally at the position α to the carbonyl group, there is at least one report of γ-cyanoethylation in the case of a steroid[13].

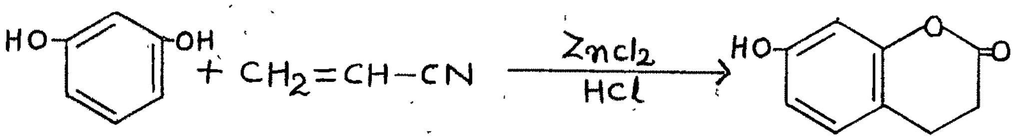
Nuclear cyanoethylation has been carried out on a number of aromatic compounds. Mesitylene and o-xylene react more readily than benzene and chlorobenzene in the presence of anhydrous aluminium chloride[14]. Chatterjee et al.[15] carried out nuclear cyanoethylation of anisole and its derivatives successfully.

Hydroxy compounds react readily with acrylonitrile in the presence of a strongly basic catalyst to form β-alkoxy propionitriles. Water reacts with acrylonitrile to give β-β'-dicyanoethyl ether[16,17,18]. Practically all primary alcohols react with acrylonitrile rapidly when the more active basic catalysts are used. Secondary alcohols react somewhat slowly but tertiary alcohols require drastic conditions. Tertiary alcohols are used as solvents in most cyanoethylation reactions, carried out below 50°. Primary and secondary, but not tertiary hydroxy groups in glycols and polyhydric alcohols are cyanoethylated[19,20,21].

Complex substances such as cellulose, starch and polyvinyl alcohols do not give cyanoethylation products. Oximes and hydroperoxides may also be cyanoethylated in the presence of strong base to form oximino-ethers in 60-90 % yields[22,16].

Phenols require relatively high temperatures of 90-150° and the presence of alkaline catalysts. Simple phenol gives β-phenoxy propionitrile in good yield[23]. Various substituted phenols, such as m-chlorophenol,[23] β-naphthol[23], cresols, xylenols, hydroxybiphenyls[24] and bisphenols[25] react with acrylonitrile to yield the corresponding cyanoethyl ethers[26,27,28]. However, the cyanoethylation of β-naphthol in the presence of an equimolecular amount of sodium hydroxide suspended in benzene yields 2-hydroxy-1-naphthalene propionitrile in excellent yield[29]. The Cyanoethylation of 6-bromo-2-naphthol gives a 10 % yield of the corresponding cyanoethyl ether,[30] whereas 2-naphthol gives a 79 % yield of β-(2-naphthoxy) propionitrile when Triton B is used as a catalyst[26].

Polyhydric phenols such as hydroquinone, catechol and resorcinol can be cyanoethylated in the presence of 1 % by weight of basic catalyst at 120-40° to yield the mono- or di-cyanoethyl ether depending upon the amount of acrylonitrile used[23]. When resorcinol is cyanoethylated in the presence of hydrochloric acid and zinc chloride as the catalyst the lactone of β-(2,4-dihydroxyphenyl)propionic acid is obtained[30].

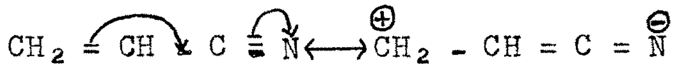


In the presence of Triton B, resorcinol gives a 40 % yield of 1,3-di-(β-cyanoethoxy)benzene[31]. The presence of electronegative substituents tend to hinder the reaction[32]. Thus, halogenated phenols add only slowly to acrylonitrile, whereas p-nitrophenol and methyl salicylate apparently do not react at all[30]. The cyanoethylation of p-cresol in the presence of anhydrous aluminium chloride gives 6-methyl-3,4-dihydrocoumarin along with 2-(2-cyanoethyl)-4-methylphenol[33].

Ammonia and most amines react with acrylonitrile without the aid of a catalyst[34]. As a general rule, acyclic secondary amines react more slowly than do primary amines. The size and branching of the substituent alkyl groups affect the rate of the reaction and yield. Thus, di-n-propylamine gives a 88 % yield of cyanoethylated product, whereas, di-isopropylamine gives only a 12 % yield[35,36]. Cyclic secondary amines are considerably more reactive than the acyclic secondary amines. The use of a strong base has been recommended to catalyse the cyanoethylation of certain amines[37].

The hydrogen atoms of hydrazine are active in cyanoethylation. The $-NH_2$ hydrogen atom of hydroxylamine is more reactive than the hydroxyl hydrogen atom and cyanoethylation yields $HONHCH_2CH_2CN$. Amides, imides and lactams are readily cyanoethylated. A number of aromatic aliphatic sulfonamides can be cyanoethylated. Compounds such as phosphines, phosphine oxides, phosphonates and phosphinates readily yield the 2-cyanoethyl derivatives[32,38].

Mechanism : Various mechanisms have been postulated for the cyanoethylation reaction. Some of them take into account the normal polarisation of acrylonitrile. The nitrile group is a powerful electronegative substituent and attracts electrons from the -CH = CH- double bond of acrylonitrile molecule. The β-carbon atom is thereby rendered relatively positive and the nitrogen atom relatively negative. It can be indicated in structure I.



$$CH_2 = CH - C \equiv N \longleftrightarrow \overset{\oplus}{C}H_2 - CH = C = \overset{\ominus}{N}$$

(I)

Thus, the true acrylonitrile molecule is a resonance hybrid of the above two canonical structures. The molecule is therefore susceptible to attack by nucleophilic reagents at the β-position. These nucleophiles may be anions such as alkoxide ions, or neutral molecules having an unshared pair of electrons such as amines.

The generally accepted reaction mechanism for cyanoethylation may be summarised as follows using methyl alcohol as the active hydrogen compound. The strongly basic catalyst abstracts the hydroxyl hydrogen atom of the alcohol, producing an alkoxide ion.

$$CH_3OH + \underset{\text{(Base)}}{:B} \longrightarrow CH_3\overset{\ominus}{O} + H{:}B \text{ ------- (a)}$$

The methoxide ion attacks the relatively positive carbon atom of acrylonitrile, forming the intermediate ion II which is stabilised by resonance.

$$CH_3\overset{\ominus}{O} + CH_2 = CH - CN \rightleftharpoons \left[CH_3OCH_2 - \overset{\ominus}{C}H - CN \longleftrightarrow CH_3OCH_2CH = C = \overset{\ominus}{N}\right]$$

(II) -------- (b)

The anion then reacts with a substance capable of donating a proton, to produce the final product, 3-methoxy propionitrile (III) and the methoxide ion is regenerated.

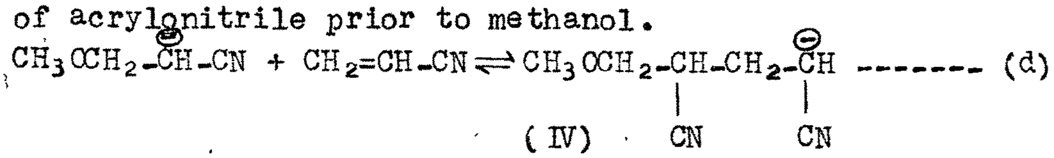
$$CH_3OCH_2\text{-}\overset{\ominus}{C}H\text{-}CN + CH_3OH \rightleftharpoons CH_3OCH_2\text{-}CH_2\text{-}CN + CH_3\overset{\ominus}{O} \text{ ---- (c)}$$

(III)

The methoxide ion can start the process of equation (b) again, thus confirming the need for only a small quantity of catalyst. Neutralisation of (II) may also take place with other active hydrogen compounds if present, e.g. water or another solvent. If so, an anion other than methoxide will be produced which, in turn, may participate in equation (b). It is to be noted that all steps in the sequence are reversible[32].

The validity of this mechanism has recently been confirmed by kinetic investigations by Ogata and Okano[39] and Feit and Zilkha[40]. The rate of the reaction was found to be proportional to the concentrations of alkoxide ion and of acrylonitrile, independent of metal cation, and to increase with increasing basic strength of the alkoxide ion. These results indicate that the slow, rate determining step is equation (b), whereas equation (c) must be very rapid. This is in agreement with the known behaviour of anions.

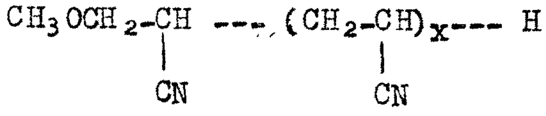
The anionic polymerisation of acrylonitrile can be explained on the basis of the above mechanism. Anion from step (II) should be capable of adding another molecule of acrylonitrile prior to methanol.



$$CH_3OCH_2\text{-}\overset{\ominus}{C}H\text{-}CN + CH_2{=}CH\text{-}CN \rightleftharpoons CH_3OCH_2\text{-}\underset{CN}{CH}\text{-}CH_2\text{-}\underset{CN}{\overset{\ominus}{C}H} \text{ ------- (d)}$$

(IV)

The product (IV) could then repeat the process to produce eventually polyacrylonitrile (V).

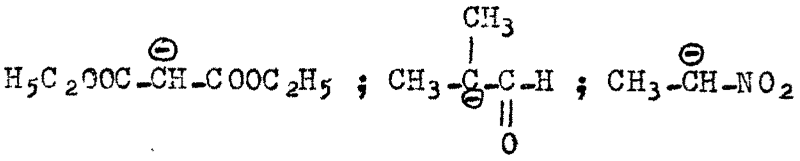


$$CH_3OCH_2\text{-}\underset{CN}{CH}\text{ --- }(CH_2\text{-}\underset{CN}{CH})_x\text{--- }H$$

(V)

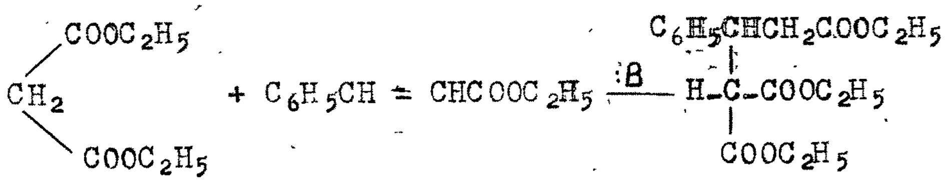
The fact that essentially no polymer is formed under most ordinary cyanoethylation conditions provides additional evidence that reaction (c) must be very rapid.

The above mechanism is believed to apply to all base catalysed cyanoethylations, such as those of alcohols, mercaptans, phosphines and carbon compounds activated by the presence of adjacent electronegative groups. Carbanions of the following type are formed with strong bases and may then react in the normal way with acrylonitrile.



$$H_5C_2OOC\text{-}\overset{\ominus}{C}H\text{-}COOC_2H_5 \;;\; CH_3\text{-}\underset{\ominus}{\overset{CH_3}{C}}\text{-}\underset{O}{\overset{}{C}}\text{-}H \;;\; CH_3\text{-}\overset{\ominus}{C}H\text{-}NO_2$$

This variation is a specific case of the classical Michael addition of nucleophilic reagents to α-β-unsaturated compounds and illustrates the formal analogy of cyanoethylation to this well-known reaction.



<u>Catalysts</u> : Cyanoethylation reaction generally requires the presence of an alkaline catalyst. Catalysts generally employed for the purpose are the amides, alkoxides, cyanides hydrides, hydroxides and oxides of sodium and potassium as well as the alkali metals themselves. Quaternary ammonium hydroxides such as benzyl trimethyl ammonium hydroxide (Triton B) and choline are strongly basic and are used advantageously. Holsten[25] carried out cyanoethylation of bisphenols using Triton B or sodium as the basic catalyst, but they observed excessive polymerisation of acrylonitrile. The same difficulty was observed by Cook and Reed[24] in the cyanoethylation of dihydric phenols using sodium or Triton B as a catalyst. However, with sodium methoxide as the catalyst, polymerisation of acrylonitrile was only slight.

Good results are obtained when sodium tertiary butoxide is used as a catalyst. It was found to be more effective than sodium methoxide because of its greater basicity. Cuprous chloride is added as a stabilizer of acrylonitrile[41]. Large number of phenols have been cyanoethylated using Triton B as a catalyst. The presence of Triton B increases the yield in the cyanoethylation of anilines of lower basic strength[42]. Cyanoethylation of phenols using copper compounds[43] such as cupric oxide, cupric hydroxide and copper salts of organic acids has been carried out with good results. Excess catalyst had no effect. Concentration of the catalyst may vary from 0.01 to 10 % of the weight of the phenol. Cupric acetate has been found to be highly effective catalyst for the mono-cyanoethylation of a variety of aromatic amines. It is effective even with sterically hindered o-substituted amines. It improves the yield and also shorter time is required[44]. Ketones can be mono-cyanoethylated in the presence of a $\overset{+2}{Cu}$, $\overset{+}{Cu}$, $\overset{+3}{Co}$, $\overset{+2}{Co}$, $\overset{+3}{Ni}$, $\overset{+2}{Ni}$, Ag, Zn, $\overset{+4}{Pb}$, $\overset{+2}{Pb}$, $\overset{+3}{Mn}$, $\overset{+2}{Mn}$, $\overset{+3}{Fe}$, $\overset{+2}{Fe}$, Cd salts of C_4-C_8-aliphatic aromatic carboxylic acids[45]. Catalysts such as zinc chloride, zinc bromide, boron trifluoride or $BF_3.Et_2O$ have been used to cyanoethylate secondary amines[46]. Kambe and Yasuda[47] have reported potassium fluoride as a catalyst in the cyanoethylation of ethylcyanoacetate. Merchant[48] has used saturated potassium carbonate solution as a catalyst in the cyanoethylation of hydroxy coumarins. Sometimes organic bases such as pyridine, quinoline, dimethylaniline and trimethylamine are used as the cyanoethylation catalysts[48,23]. A mixture of cyclohexylamine and acetic acid has been used as a catalyst in the mono cyanoethylation of ketones[49]. Many alcohols have been cyanoethylated in the presence of quaternary ammonium type resins (Amberlite IRA - 400)[50]. Anion exchange resins are also used[51]. Howk and Langkammerer[52] have used cross-linked polyquaternary ammonium hydroxide resin as a catalyst and have obtained mono cyanoethylated products in high yields.

Solvents and temperature :

Cyanoethylation reactions are frequently highly exothermic and require safety measures to ensure control of the reaction. This may be achieved in part by the use of inert solvents such as acetonitrile, benzene, dioxan, pyridine, toluene or tertiary-butyl alcohol. Tertiary-butyl alcohol is particularly a good solvent since it dissolves appreciable amounts of potassium hydroxide to give an effective catalyst solution. The reaction of acrylonitrile with phenols takes place at a temperature in the range of 120-40°. Feit et al.[53] have discussed the effect of solvent composition on the kinetics of the cyanoethylation of methanol. They have also discussed the cyanoethylation of methanol in mixed methanol-aprotic solvents[54] such as dimethyl sulfoxide, dimethyl formamide, dimethyl formamide-dioxan (1 : 1), dioxan, tetrahydrofuran and benzene. Depending upon the aprotic solvent the rate of the reaction decreased in the order dimethyl sulfoxide > dimethyl formamide >> tetrahydrofuran $\simeq$ dioxan > benzene. Yun et al.[55] have carried out cyanoethylation of alkyl aromatic compounds such as toluene, m-xylene, isopropylbenzene, mesitylene, diphenylmethane and tetralin at 200-300° in the presence of sodium tert-butoxide in an autoclave. In some cases an excess of reactants may be used as diluents under some circumstances, as in the cyanoethylation of cellulose, excess acrylonitrile is a suitable reaction medium.

Reversibility of the reaction : Decyanoethylation :

Cyanoethylation reaction is usually carried out at moderate temperatures. High temperatures tend to reverse the cyanoethylation and therefore, lower yields are obtained. β-β'-Dicyanoethyl ether yields water and acrylonitrile when heated to about 200° in the presence of an alkaline material[56].

$$NCCH_2CH_2OCH_2CH_2CN \rightleftharpoons 2CH_2 = CHCN + H_2O$$

β-Alkoxy and β-aryloxy propionitriles get decyanoethylated when heated with an alkaline material or with uncyanoethylated bases[57,58].

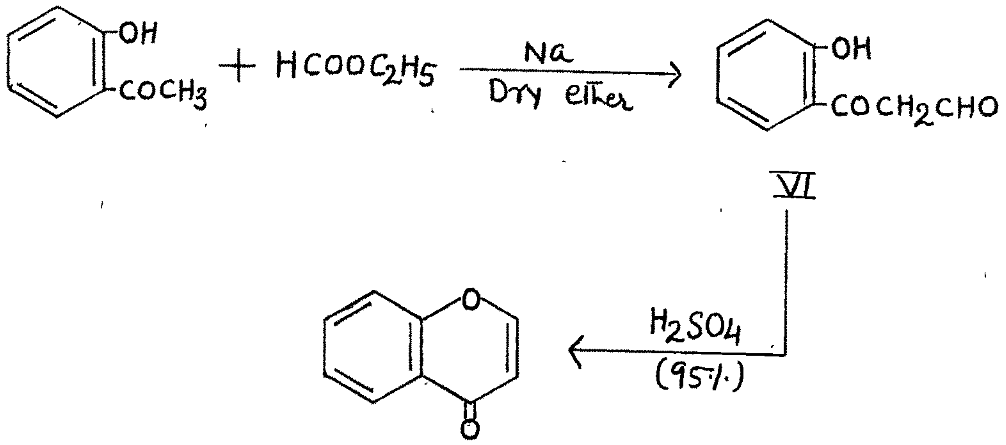
$$ROCH_2CH_2CN + NaOH\ (5\ \%) \longrightarrow ROH$$

$$ROCH_2CH_2CN + C_6H_5NH_2 + 0.025\ g.\ NaOH \xrightarrow{10\ hrs.} C_6H_5NHCH_2CH_2CN + ROH$$

The reaction of aromatic amines with N-mono and N,N-dicyanoethylated α- and β-amino acids result in the formation of the decyanoethylation products[59].

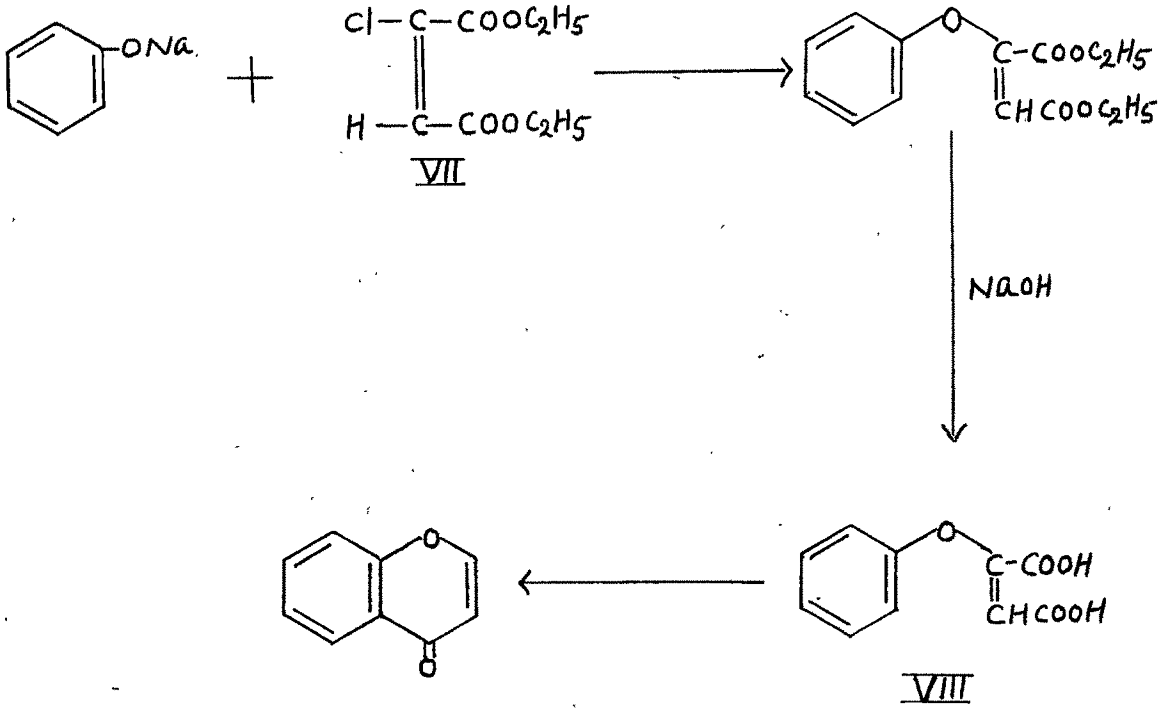
Present work :

While there are a number of methods available for the synthesis of 2-methyl chromones, 2-phenyl chromones (flavones) and 3-phenyl chromones (isoflavones) there are only a couple of methods available for the synthesis of chromones without any substituents in the heterocyclic ring. In one of the methods o-hydroxy acetophenone is treated with ethyl formate in presence of sodium and the intermediate keto aldehyde VI is cyclised in the presence of sulfuric acid (95 %) to chrome[60].



Use of diethyl oxalate gives 2-carbethoxychromones[61]. Hydrolysis and decarboxylation of these esters give the chromones unsubstituted in the heterocyclic ring. The yields are generally poor.

Phenols can be converted into β-phenoxyacrylic acids by adding their sodium derivatives to ethyl acetylene dicarboxylate. Similar products are also formed when ethyl chloro fumarate VII is treated with sodium phenoxide. The β-phenoxy acrylic acids VIII obtained by saponification of the esters can be cyclised to chromones either with acetyl chloride or sulfuric acid[62] or through the acid chloride with anhydrous aluminium chloride[63].



Cyanoethylation of phenols provides a good method for the preparation of chromone derivatives, unsubstituted in the heterocyclic ring. The intermediate β-phenoxypropionitriles can be hydrolysed to the corresponding acids and the acids cyclised to chromanones using cyclising agents such as anhydrous hydrofluoric acid[64] or conc. sulfuric acid. Alternatively, the corresponding acylchorides can be cyclised using Friedal-Crafts catalysts such as anhydrous aluminium chloride[65]. Heininger[66] cyclised β-aryloxy propionitriles to chromanones through the intermediate formation of chromanimines. Bachman and Levine[31] cyclised various β-aryloxy propionitriles to chromanones using either sulfuric acid or phosphoric acid. These chromanones can be dehydrogenated to chromones by using palladium on charcoal or selenium dioxide.

Merchant et al.[48,67,68] have built up a γ-pyrone ring on various hydroxy coumarins through cyanoethylation. There is no reference in the literature to the synthesis of bichromonyl derivatives from diphenyl derivatives through cyanoethylation. It was therefore thought of interest to study the cyanoethylation of dihydroxy diphenyls and use the intermediate cyanoethyl derivatives to synthesise bichromonyls. The application of this reaction to 2,2'-dihydroxydiphenyl, 4,4'-dihydroxydiphenyl, 2,2'-dihydroxydiphenyl methane ; 4,4'-dihydroxydiphenyl methane, 2,2'-dihydroxybenzophenone, 4,4'-dihydroxybenzophenone, and 4,4'-dihydroxydiphenyl sulfone has now been studied.

The cyanoethylation of 4,4'-dihydroxydiphenyl methane, 2,2'-dihydroxydiphenyl, 4,4'-dihydroxybenzophenone and 4,4'-dihydroxydiphenyl sulfone was studied using a number of condensing agents such as, sodium hydroxide, sodium methoxide, cuprous chloride, cupric oxide and Triton B. It was found that the highest yields were obtained when cupric oxide was used as a condensing agent. In the case of 4,4'-dihydroxydiphenyl however the best yield was obtained when sodium hydroxide was used as a condensing agent.

Comparative study of some catalysts :

A comparative study of the efficacy of the different catalysts was made with some dihydroxydiphenyl derivatives. The yields were as follows :-

Phenolic Compound	Product	Catalyst and % yield of the cyanoethylation product				
		NaOH	NaOMe	Cu_2Cl_2	CuO	Triton B
4,4'-Dihydroxy-diphenyl methane	4,4'-Di(β-cyanoethoxy) diphenyl methane	1.6	32.7	0.7	71.9	55.5
2,2'-Dihydroxy-diphenyl	2,2'-Di(β-cyanoethoxy) diphenyl	6.4	no reaction	6.4	22.3	no reaction
4,4'-Dihydroxy-diphenyl	4,4'-Di(β-cyanoethoxy) diphenyl	25.5	6.4*	9.5	1.5	no reaction
4,4'-Dihydroxy-benzophenone	4,4'-Di(β-cyanoethoxy) benzophenone	10.0	26.8	30.1	56.8	40
4,4'-Dihydroxy-diphenyl sulfone	4,4'-Di(β-cyanoethoxy) diphenyl sulfone	8.8	polymeric product	no reaction	31.6	no reaction

* Cook and Reed have reported a yield of 47 % with sodium methoxide as a catalyst when the reaction was carried out under pressure.

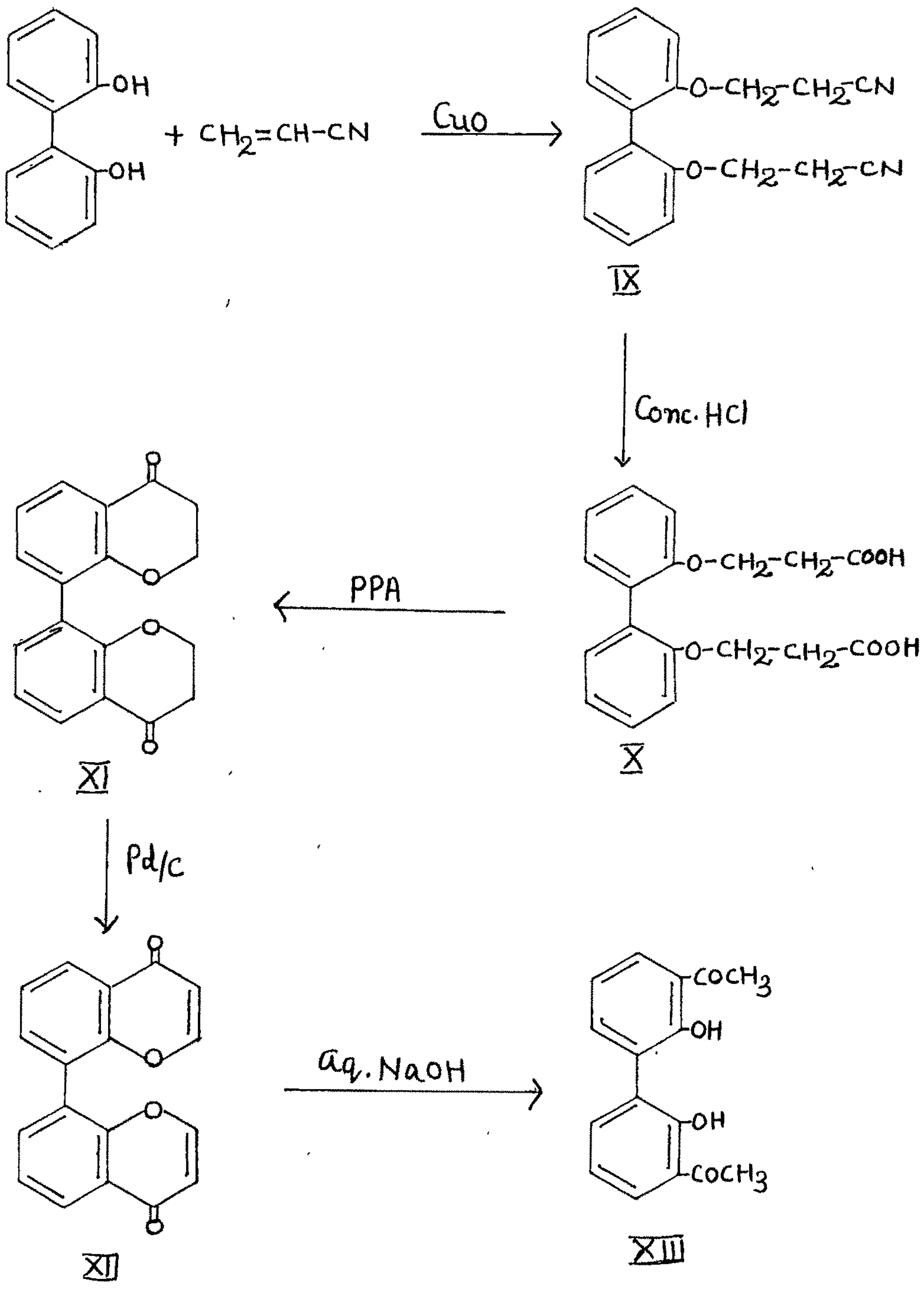
Synthesis of 8,8'-bichromonyl :

2,2'-Dihydroxydiphenyl on reaction with acrylonitrile in the presence of cupric oxide gave 2,2'-di-(β-cyanoethoxy) diphenyl (IX) which, when hydrolysed with conc. hydrochloric acid gave 2,2'-di(β-carboxyethoxy)diphenyl (X). This acid was cyclised in the presence of polyphosphoric acid to the bichromanonyl derivative (XI). It gave in I.R.a band at 1680 cm.$^{-1}$, characteristic of a carbonyl group and in U.V. λ max (dioxan) 252 and 328 nm. It was dehydrogenated in the presence of palladium on charcoal in boiling diphenyl ether to bichromonyl derivative. 8,8'-Bichromonyl structure (XII) was assigned to the dehydrogenated product. Its I.R. showed absorption at 1640 cm.$^{-1}$, characteristic of a carbonyl group and in U.V.λmax. (dioxan) 251 and 306 nm. 68A It gave a hydroxyketone on alkaline hydrolysis as seen by a blue colouration with alcoholic ferric chloride, solubility in alkali and the formation of a di-(2,4-dinitrophenylhydrazone) derivative with 2,4-dinitrophenylhydrazine. It has been assigned the 2,2'-dihydroxy-3,3'-diacetyl diphenyl structure (XIII). I.R. 1625 cm.$^{-1}$ (C=O), 3200 cm.$^{-1}$ (b, H.B).

This incidentally provides a method for the preparation of this ketone. It could not be prepared by the Friedel-Crafts acetylation of 2,2'-dihydroxydiphenyl or through the Fries migration of 2,2'-diacetoxydiphenyl. The 5,5'-diacetyl derivative is formed in these reactions.

Synthesis of 6,6'-bichromonyl :

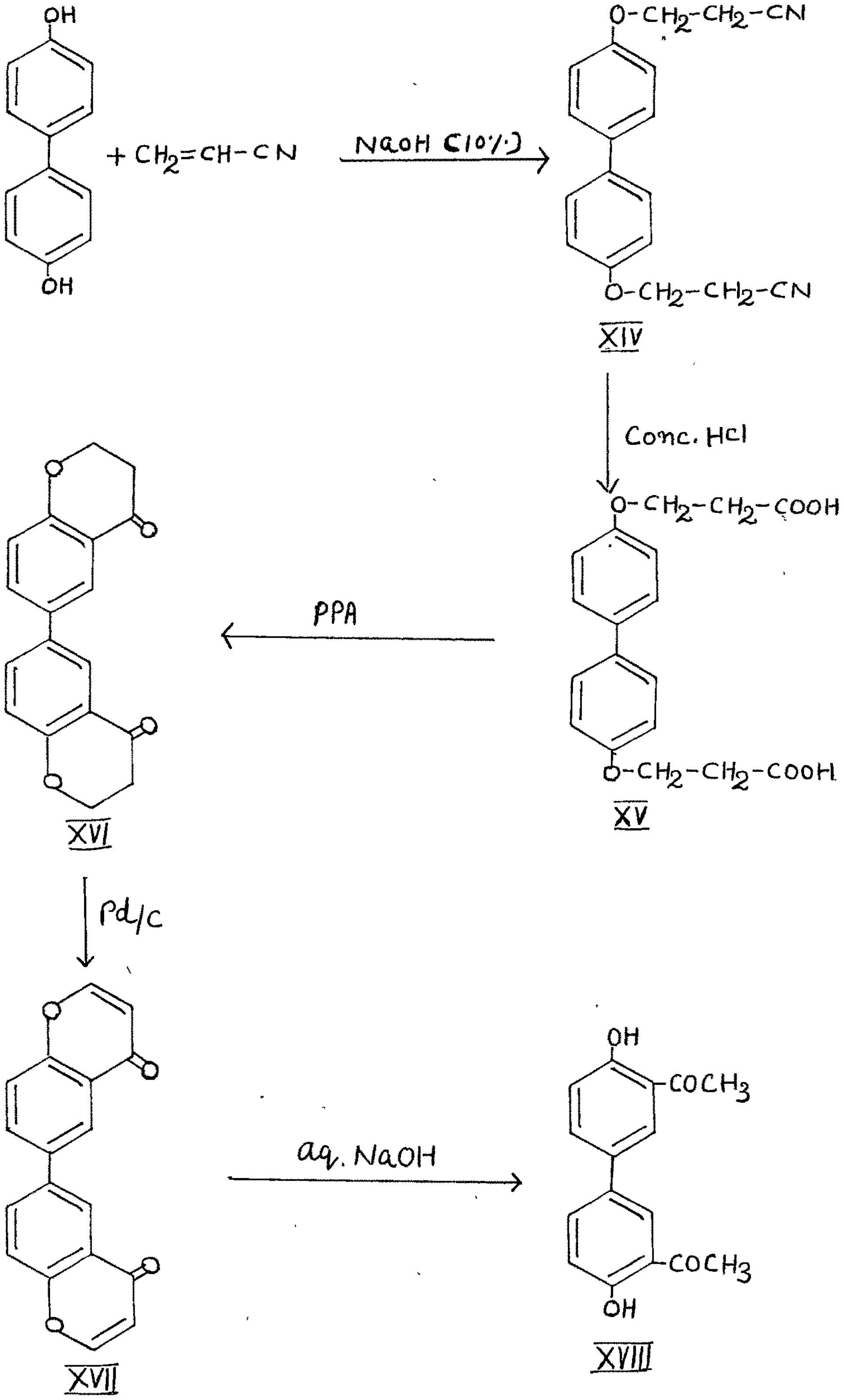
4,4'-Dihydroxydiphenyl on condensation with

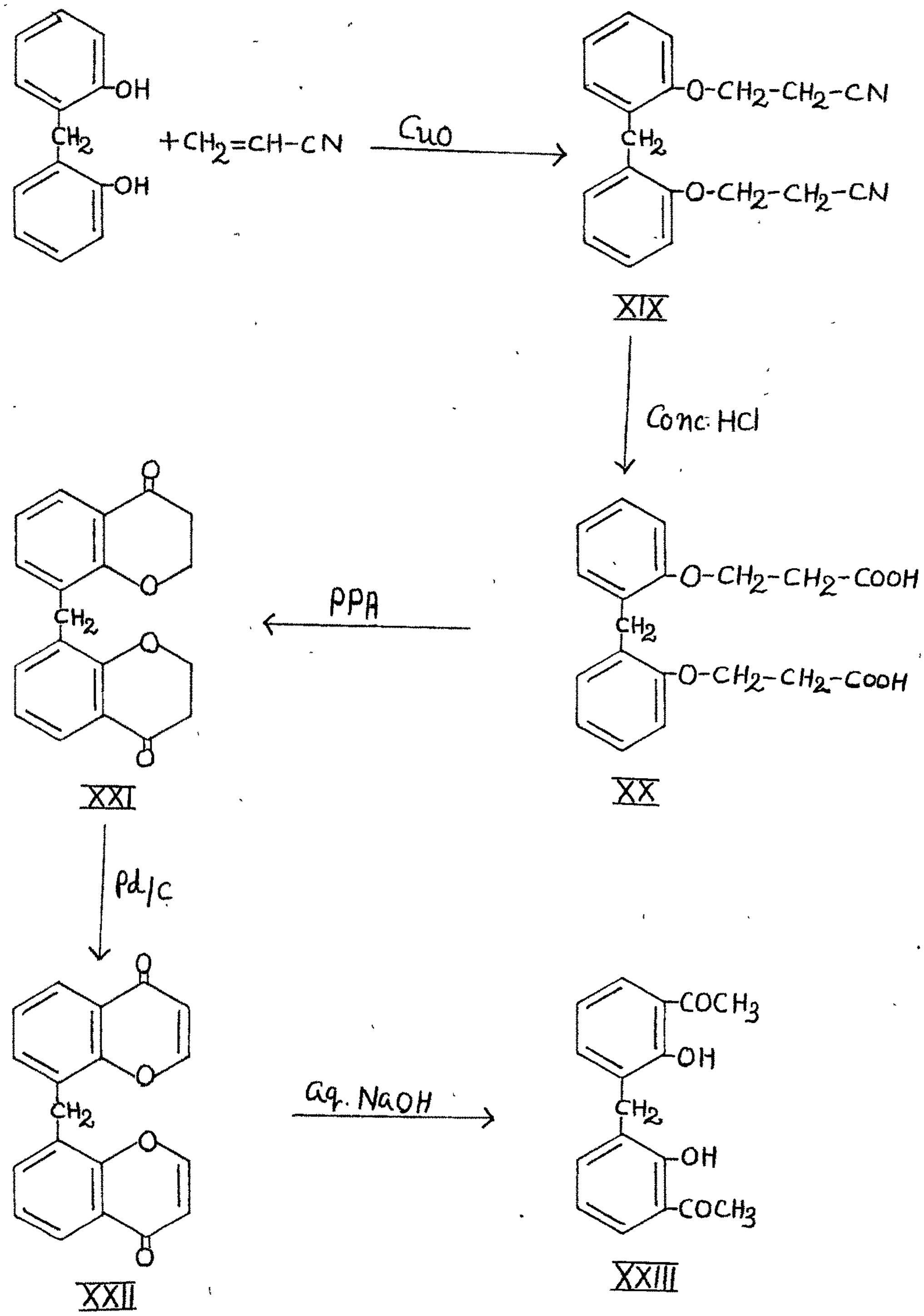

OH
OH
+ CH2=CH-CN
CuO
O-CH2-CH2-CN
O-CH2-CH2-CN
IX
Conc. HCl
O-CH2-CH2-COOH
O-CH2-CH2-COOH
X
PPA
XI
Pd/c
XII
aq. NaOH
COCH3
OH
OH
COCH3
XIII

acrylonitrile in the presence of Sodium hydroxide yielded 4,4'-di-(β-cyanoethoxy)diphenyl (XIV). It was identical with the compound prepared according to Cook and Reed[24] using sodium methoxide as the condensing agent. The above cyano derivative on acid hydrolysis gave 4,4'-di-(β-carboxyethoxy)diphenyl (XV). This dicarboxylic acid was cyclised in the presence of polyphosphoric acid to the corresponding bichromanonyl derivative (XVI). I.R. 1675 $cm.^{-1}$ (C=0). U.V. λ max (dioxan) 248, 330 nm. It was dehydrogenated with palladium on charcoal to the bichromonyl derivative. 6,6'-Bichromonyl structure (XVII) was assigned to the dehydrogenated product. I.R. 1645 $cm.^{-1}$ (C=0). U.V. λ max (dioxan) 250, 278, 310 nm. On alkaline hydrolysis it gave the known 3,3'-diacetyl-4,4'-dihydroxydiphenyl (XVIII). Mixed m.p. with an authentic specimen prepared according to Nara Boon-long[69] by the Fries migration of 4,4'-diacetoxydiphenyl was not depressed.

Synthesis of 8,8'-bichromonyl methane :

2,2'-Dihydroxydiphenyl methane on condensation with acrylonitrile in the presence of cupric oxide gave 2,2'-di-(β-cyanoethoxy)diphenyl methane (XIX). On acid hydrolysis it yielded the corresponding dicarboxylic acid (XX) which on cyclisation in the presence of polyphosphoric acid gave the bichromanonyl derivative (XXI). I.R. 1685 $cm.^{-1}$ (C=0). U.V. λ max (dioxan) 254, 320 nm. The bichromanonyl derivative was dehydrogenated using palladised charcoal (10 %) in boiling diphenyl ether. 8,8'-Bichromonyl methane structure (XXII) was


OH
OH
+ CH2=CH-CN
NaOH (10%)
O-CH2-CH2-CN
O-CH2-CH2-CN
XIV
Conc. HCl
O-CH2-CH2-COOH
O-CH2-CH2-COOH
XV
PPA
XVI
Pd/C
XVII
aq. NaOH
OH
COCH3
COCH3
OH
XVIII

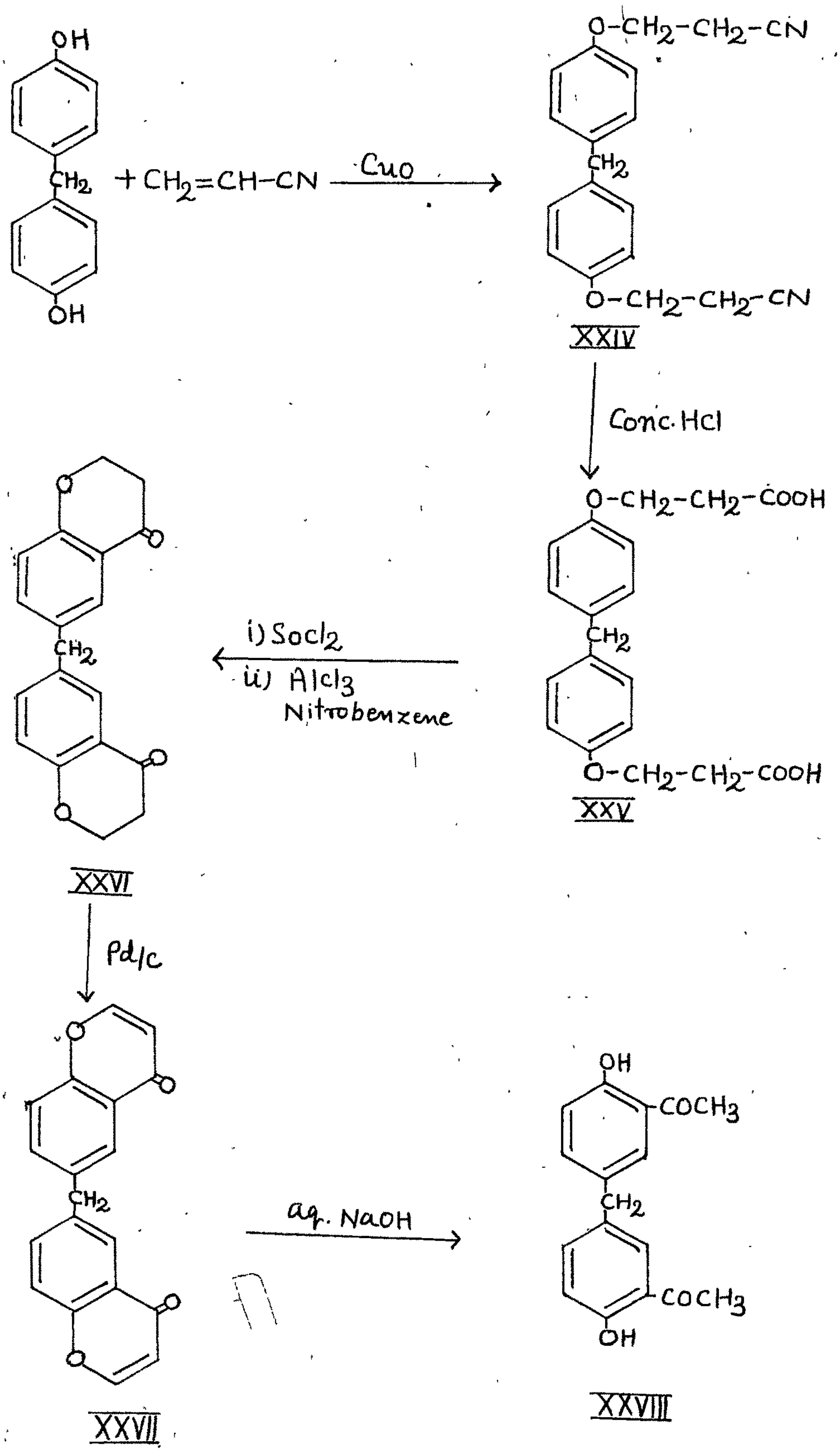

OH
CH2
OH
+CH2=CH-CN
CuO
O-CH2-CH2-CN
CH2
O-CH2-CH2-CN
XIX
Conc. HCl
O-CH2-CH2-COOH
CH2
O-CH2-CH2-COOH
XX
PPA
O
CH2
O
O
O
XXI
Pd/C
O
O
CH2
O
O
XXII
aq. NaOH
COCH3
OH
CH2
OH
COCH3
XXIII

assigned to the dehydrogenated product. I.R. 1630 $cm.^{-1}$ (C=O). U.V. λ max (dioxan) 242, 296, 306 nm. On alkaline hydrolysis it gave an o-hydroxy ketone as seen by a violet colouration with alcoholic ferric chloride solution, solubility in alkali and the formation of a di-(2,4-dinitrophenylhydrazone) derivative. 2,2'-Dihydroxy-3,3'-diacetyldiphenyl methane structure (XXIII) was assigned to this ketone. I.R. 1630 $cm.^{-1}$ (C=O), 3200 $cm.^{-1}$ (b, H.B).

This ketone could not be prepared by the Friedel-Crafts acetylation of 2,2'-dihydroxydiphenyl methane or by the Fries migration of 2,2'-diacetoxydiphenyl methane as in both these cases the 5,5'-diacetyl derivative is obtained.

Synthesis of 6,6'-bichromonyl methane :

4,4'-Dihydroxydiphenyl methane when condensed with acrylonitrile in the presence of cupric oxide gave 4,4'-di(β-cyanoethoxy)diphenyl methane (XXIV) m.p. 115-16°. Holsten[25] prepared the same compound using a mixture of sodium-tert-butoxide and cuprous chloride. They have reported the same m.p. The above cyano derivative on hydrolysis with conc. hydrochloric acid yielded the corresponding dicarboxylic acids (XXV), which was converted into its acid chloride using thionyl chloride. The acid chloride was cyclised using anhydrous aluminium chloride to the corresponding bichromanonyl derivative (XXVI). I.R. 1680 $cm.^{-1}$ (C=O) U.V. λ max (dioxan) 252, 324 nm. It was dehydrogenated in the presence of palladium on charcoal, using diphenyl ether as the solvent. 6,6'-Bichromonyl methane structure (XXVII) was assigned to the


OH
CH2
OH
+ CH2=CH-CN
CuO
O-CH2-CH2-CN
CH2
O-CH2-CH2-CN
XXIV
Conc. HCl
O-CH2-CH2-COOH
CH2
O-CH2-CH2-COOH
XXV
i) SOCl2
ii) AlCl3
Nitrobenzene
CH2
XXVI
Pd/C
CH2
XXVII
aq. NaOH
OH
COCH3
CH2
COCH3
OH
XXVIII

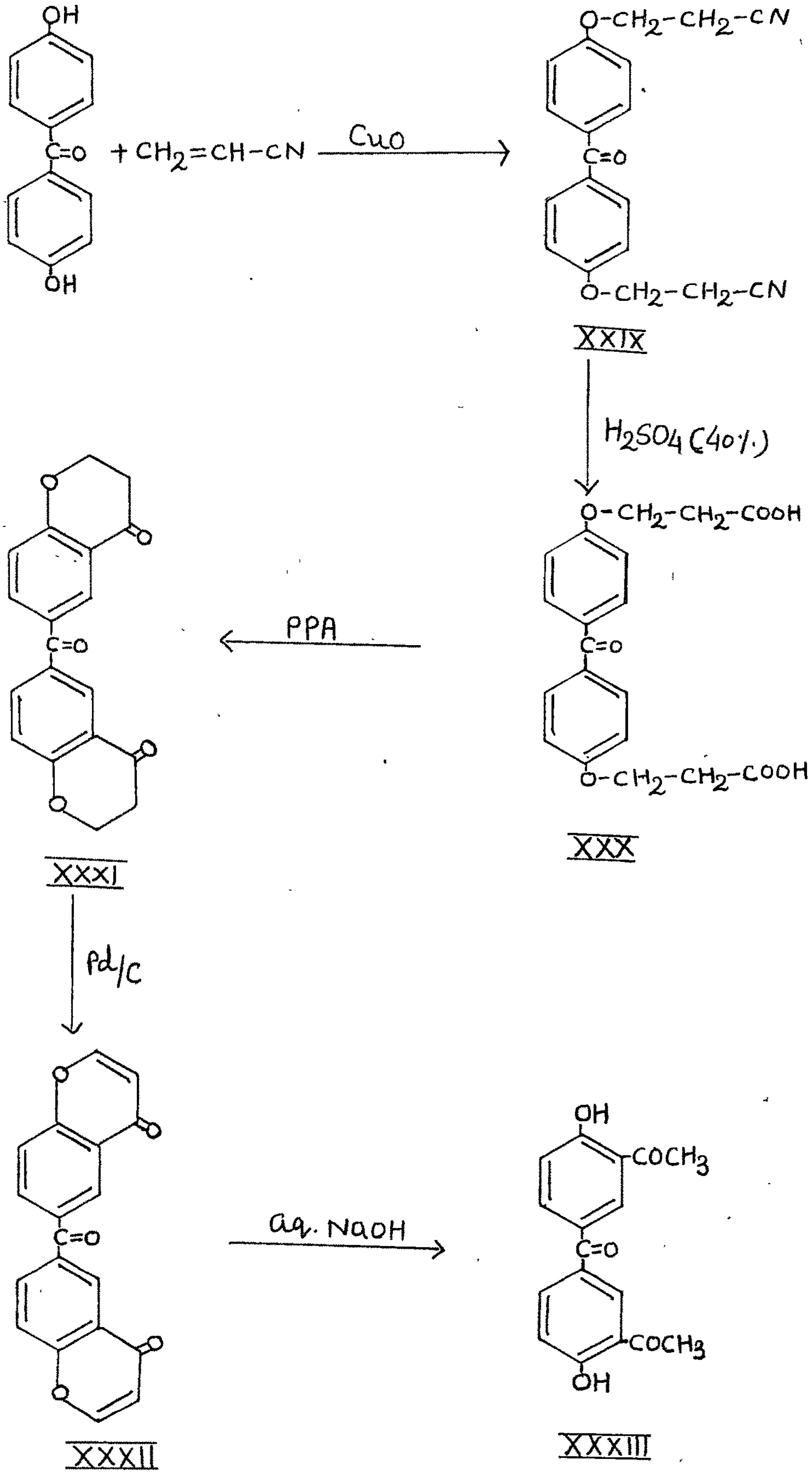
dehydrogenated product. I.R. 1650 $cm.^{-1}$ (C=O). U.V. λ max. (dioxan), 252, 300, 310 mμ. On alkaline hydrolysis it gave 3,3'-diacetyl-4,4'-dihydroxydiphenyl methane (XXVIII). Mixed m.p. with an authentic sample prepared by the Fries migration of 4,4'-diacetoxydiphenyl methane described on page 79 was not depressed.

<u>Synthesis of 6,6'-bichromonyl ketone</u> :

4,4'-Dihydroxybenzophenone when condensed with acrylonitrile in the presence of cupric oxide gave 4,4'-di-(β-cyanoethoxy)benzophenone (XXIX). This nitrile on hydrolysis with sulfuric acid (40 %) yielded the corresponding dicarboxylic acid (XXX), which was cyclised in the presence of polyphosphoric acid to the corresponding bichromanonyl ketone (XXXI). I. R. 1690 $cm.^{-1}$ (C=O). U.V. λ max (EtOH), 246, 266, 282 mμ. This was dehydrogenated to bichromonyl ketone. 6,6'-Bichromonyl ketone structure (XXXII) was assigned to the dehydrogenated product. I.R. 1645 $cm.^{-1}$ (C=O). U.V. λ max (EtOH), 252, 286, 296, 306 mμ. On alkaline hydrolysis it gave the known 3,3'-diacetyl-4,4'-dihydroxybenzophenone (XXXIII). Mixed m.p. with an authentic sample prepared according to Balani and Sethna[70] by the Fries migration of 4,4'-diacetoxybenzophenone was not depressed.

<u>Synthesis of 6,6'-bichromonyl sulfone</u> :

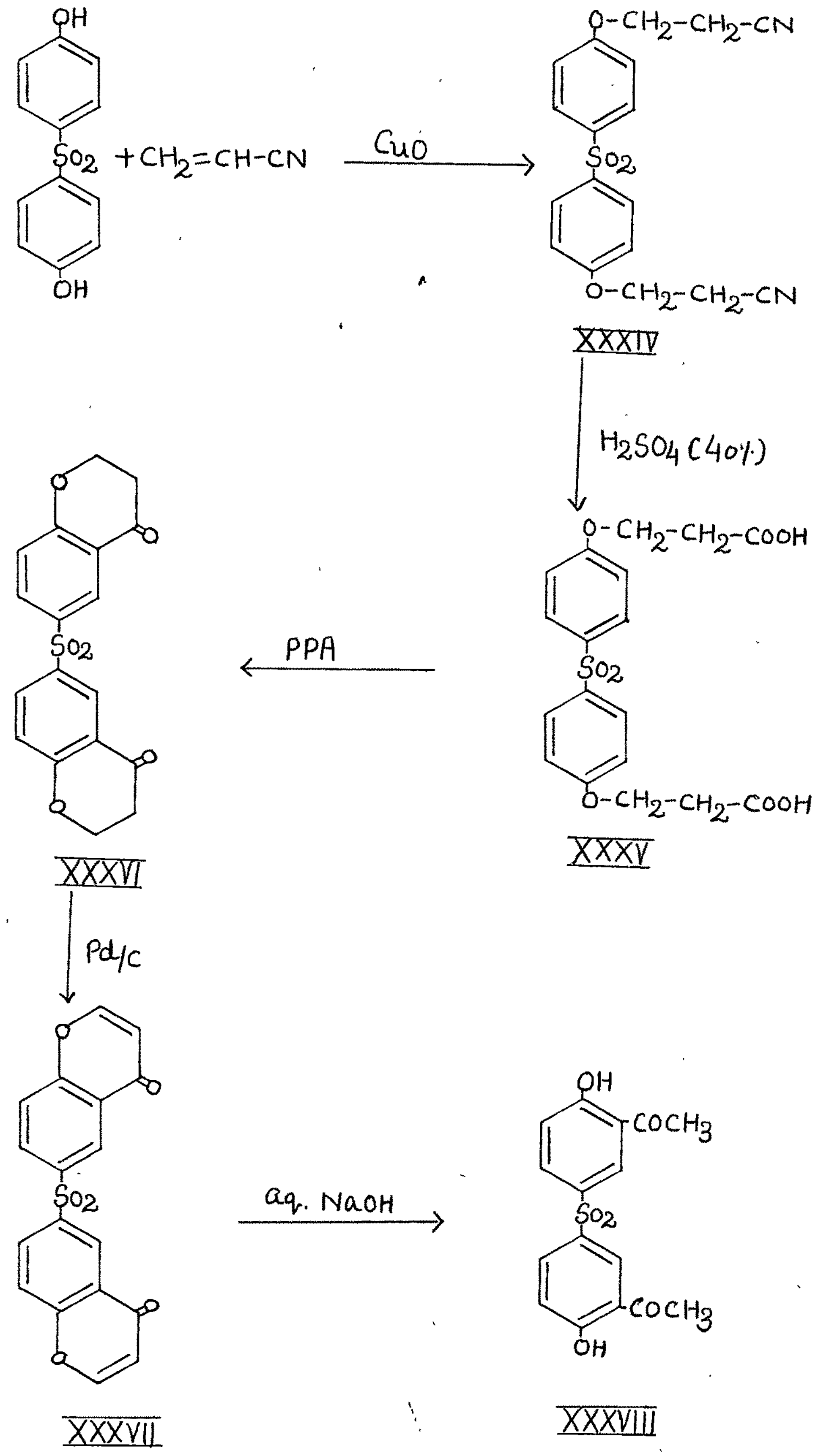
4,4'-Dihydroxydiphenyl sulfone on cyanoethylation with acrylonitrile in the presence of cupric oxide gave


OH
C=O
OH
+ CH₂=CH-CN
CuO
O-CH₂-CH₂-CN
C=O
O-CH₂-CH₂-CN
XXIX
H₂SO₄ (40%)
O-CH₂-CH₂-COOH
C=O
O-CH₂-CH₂-COOH
XXX
PPA
C=O
XXXI
Pd/C
C=O
XXXII
aq. NaOH
OH
COCH₃
C=O
COCH₃
OH
XXXIII

4,4'-di-(β-cyanoethoxy)diphenyl sulfone (XXXIV) which on hydrolysis with sulfuric acid (40 %) yielded 4,4'-di-(β-carboxyethoxy)diphenyl sulfone (XXXV). This dicarboxylic acid on cyclisation with polyphosphoric acid gave bi-(6-chromanonyl)sulfone (XXXVI). I.R. 1690 $cm.^{-1}$ (C=O). U.V. λ max (Chloroform), 248, 310 nm. This when dehydrogenated using palladised charcoal in boiling diphenyl ether gave 6,6'-bichromonyl sulfone (XXXVII). I.R. 1630 $cm.^{-1}$ (C=O). U.V. λ max (chloroform), 270, 294, 304 nm. It gave 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfone (XXXVIII) when subjected to alkaline hydrolysis. Mixed m.p. with an authentic specimen prepared according to Kulkarni[71] by the oxidation of 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide was not depressed.

Attempted cyanoethylation of 2,2'-dihydroxybenzophenone :

2,2'-Dihydroxybenzophenone on refluxing with acrylonitrile in the presence of condensing agents such as cupric oxide, cuprous chloride, sodium methoxide, etc., did not undergo any reaction. When sodium hydroxide was used as the condensing agent, xanthone was obtained instead of the cyanoethylated product. M.p. and mixed m.p. with an authentic sample of xanthone prepared by the distillation of salol according to Holleman[72] was not depressed.


OH
SO2
OH
+CH2=CH-CN
CuO
O-CH2-CH2-CN
SO2
O-CH2-CH2-CN
XXXIV
H2SO4 (40%)
O-CH2-CH2-COOH
SO2
O-CH2-CH2-COOH
XXXV
PPA
SO2
XXXVI
Pd/c
SO2
XXXVII
aq. NaOH
OH
COCH3
SO2
COCH3
OH
XXXVIII

EXPERIMENTAL

Cyanoethylation of 2,2'-dihydroxydiphenyl : 2,2'-Di-(β-cyanoethoxy)diphenyl :

A mixture of 2,2'-dihydroxydiphenyl (2 g.), acrylonitrile (5 ml.) and cupric oxide (0.2 g.) was refluxed on a steam bath for 30 hr. The reaction mixture was then treated with chloroform and the chloroform layer was washed successively with dilute sodium hydroxide solution, dilute hydrochloric acid and finally with water. The product obtained on removal of the solvent crystallised from alcohol in white plates (0.7 g.), m.p. 100-01°.

Analysis : Found : C, 74.13; H, 5.57; N, 9.22 %.

$C_{18}H_{16}N_2O_2$: requires : C, 74.00; H, 5.48; N, 9.59 %.

2,2'-Di-(β-carboxyethoxy)diphenyl :

The above cyano derivative (1 g.) was refluxed with conc. hydrochloric acid (50 ml.) for 4 hr. The product separating on cooling was extracted with sodium bicarbonate solution. The product obtained on acidification of the bicarbonate extract was crystallised from dilute alcohol in light pink plates (0.5 g.), m.p. 157-59°.

Analysis : Found : C, 65.54; H, 5.24 %.

$C_{18}H_{18}O_6$: requires : C, 65.46; H, 5.45 %.

8,8'-Bichromanonyl :

The above dicarboxylic acid (0.5 g.) was heated with polyphosphoric acid (20 g., P_2O_5; 10 ml. o-phosphoric acid) on a steam bath for 7 hr. It was then poured into ice cold water and kept overnight. The separated product was filtered, washed with sodium bicarbonate solution and crystallised from acetic acid in pale yellow needles (0.15 g.), m.p. 229-30°.

Analysis : Found : C, 73.16 ; H, 4.55 %.
$C_{18}H_{14}O_4$ requires : C, 73.50 ; H, 4.76 %.

8,8'-Bichromonyl :

A mixture of 8,8'-bichromanonyl (0.5 g.) in diphenyl ether (5 ml.) and palladised charcoal (10 % ; 0.25 g.) was refluxed for 7 hr. and filtered hot. The product obtained on cooling crystallised from glacial acetic acid in brown shining needles (0.2 g.), m.p. 326°.

Analysis : Found : C, 74.69 ; H, 3.81 %.
$C_{18}H_{10}O_4$ requires : C, 74.50 ; H, 3.45 %.

2,2'-Dihydroxy-3,3'-diacetyldiphenyl :

8,8'-Bichromonyl (50 mg.) was refluxed with sodium hydroxide solution (10 ml; 10 %) for 20 minutes. The clear alkaline solution was acidified with conc. hydrochloric acid. The separated product crystallised from alcohol in pale yellow needles, m.p. 167-68°. It gave a violet colouration with alcoholic ferric chloride solution.

Analysis : Found : C, 71.14 ; H, 4.81 %.
$C_{16}H_{14}O_4$ requires : C, 71.10 ; H, 5.18 %.

The di-(2,4-dinitrophenylhydrazone) :

The above ketone was dissolved in alcohol and 2,4-dinitrophenylhydrazine in alcohol was added. The product separating on standing crystallised from diphenyl ether. M.P. 302-03° (decomp.).

Analysis : Found : N, 17.60 %.

$C_{28}H_{22}N_8O_{10}$: requires : N, 17.78 %.

Cyanoethylation of 4,4'-dihydroxydiphenyl : 4,4'-Di-(β-cyanoethoxy)diphenyl :

A mixture of 4,4'-dihydroxydiphenyl (2 g.), acrylonitrile (10 ml.), and sodium hydroxide solution (2 ml.; 10 %) was refluxed on a steam bath for 25 hr. The reaction mixture was worked up as before. The product obtained was crystallised from alcohol in yellowish brown plates (0.8 g.), m.p. 180-81°.

Analysis : Found : C, 73.60; H, 5.32; N, 9.20 %.

$C_{18}H_{16}N_2O_2$: requires : C, 74.00; H, 5.48; N, 9.59 %.

4,4'-Di-(β-carboxyethoxy)diphenyl :

The above cyano derivative (1 g.) in hot acetic acid (25 ml.) was refluxed with conc. hydrochloric acid (20 ml.) for 7 hr. The reaction mixture was then diluted with water and the separated product was purified by sodium bicarbonate extraction. It crystallised from glacial acetic acid in silky grey plates (0.4 g.), m.p. 241-42°.

Analysis : Found : C, 65.86 ; H, 5.33 %.
$C_{18}H_{18}O_6$ requires : C, 65.46 ; H, 5.45 %.

6,6'-Bichromanonyl :

4,4'-Di-(β-carboxyethoxy)diphenyl (0.5 g.) was heated with polyphosphoric acid (20 g.; P_2O_5 ; 10 ml. o-phosphoric acid) on a steam bath for 7 hr. The product obtained on working up as before crystallised from glacial acetic acid in pale yellow needles (0.2 g.), m.p. 205-06°.

Analysis : Found : C, 73.07; H, 4.37 %.
$C_{18}H_{14}O_4$ requires : C, 73.05; H, 4.76 %.

6,6'-Bichromonyl :

A mixture of 6,6'-bichromanonyl (0.5 g.) in diphenyl ether (5 ml.) and palladised charcoal (10 %; 0.25 g.) was refluxed for 7 hr. and filtered hot. The product separating on cooling crystallised from glacial acetic acid. M.P. 298-99° (decomp.). Yield 0.1 g. It gave light blue fluorescence with conc. sulfuric acid.

Analysis : Found : C, 74.82 ; H, 3.06 %.
$C_{18}H_{10}O_4$ requires : C, 74.50 ; H, 3.45 %.

Hydrolysis :

6,6'-Bichromonyl (50 mg.) was refluxed with sodium hydroxide solution (10 ml. ; 10 %) for 10 minutes. The product obtained on acidification of the clear alkaline solution crystallised from acetic acid. M.P. and mixed m.p. with 3,3'-diacetyl-4,4'-dihydroxydiphenyl, prepared by the

Fries migration of 4,4'-diacetoxydiphenyl according to Boon-Long[62] was 209-10°.

Cyanoethylation of 2,2'-dihydroxydiphenyl methane : 2,2'-Di-(β-cyanoethoxy)diphenyl methane :

A mixture of 2,2'-dihydroxydiphenyl methane (2 g.), acrylonitrile (5 ml.) and cupric oxide (0.2 g.) was refluxed on a steam bath for 30 hr. The reaction mixture was worked up as before. The product obtained was crystallised from alcohol in pale yellow needles (2.2 g.), m.p. 146-47°.

Analysis : Found : C, 74.27; H, 5.62; N, 8.97 %.

$C_{19}H_{18}N_2O_2$ requires : C, 74.50; H, 5.88; N, 9.15 %.

2,2'-Di-(β-carboxyethoxy)diphenyl methane :

The above cyano derivative (1 g.) was refluxed with conc. hydrochloric acid (50 ml.) for 20 hr. The product obtained on cooling and diluting with water was filtered, washed with water and extracted with sodium bicarbonate solution. The product obtained on acidification of the bicarbonate extract crystallised from dilute alcohol in light pink needles (0.4 g.), m.p. 170-71°.

Analysis : Found : C, 66.24 ; H, 5.49 %

$C_{19}H_{20}O_6$ requires : C, 66.26 ; H, 5.81 %.

8,8'-Bichromanonyl methane :

2,2'-Di-(β-carboxyethoxy)diphenyl methane (0.5 g.), was heated with polyphosphoric acid (20 g. P_2O_5 ; 10 ml. o-phosphoric acid) on a steam bath for 7 hr. The product obtained on addition of ice cold water to the reaction mixture was washed with sodium bicarbonate solution and crystallised from alcohol in pale yellow needles (0.15 g.), m.p. 146-47°.

Analysis : Found : C, 73.89 ; H, 4.88 %.
$C_{19}H_{16}O_4$: requires : C, 74.01 ; H, 5.19 %.

8,8'-Bichromonyl methane :

8,8'-Bichromanonyl methane (0.5 g.) in diphenyl ether (5 ml.) was refluxed with palladised charcoal (10 %; 0.25 g.) for 8 hr. The reaction mixture was filtered hot, cooled and petroleum ether was added. The separated precipitates crystallised from toluene-petroleum ether mixture in orange buds (0.2 g.), m.p. 222-23°.

Analysis : Found : C, 75.44 ; H, 4.01 %.
$C_{19}H_{12}O_4$: requires : C, 74.99 ; H, 3.95 %.

2,2'-Dihydroxy-3,3'-diacetyldiphenyl methane :

8,8'-Bichromonyl methane (50 mg.) was refluxed with sodium hydroxide solution (10 ml. ; 10 %) for 20 minutes. The clear alkaline solution was acidified with conc. hydrochloric acid and the separated product crystallised from dilute alcohol in pale yellow needles, m.p. 108-09°. It gave a violet colouration with alcoholic ferric chloride solution.

Analysis : Found : C, 72.04 ; H, 5.33 %.
$C_{17}H_{16}O_4$: requires : C, 71.83 ; H, 5.55 %.

The di-(2,4-dinitrophenyl hydrazone) :

The above ketone was dissolved in alcohol and 2,4-dinitrophenyl hydrazine in alcohol was added . The separated product crystallised from glacial acetic acid. M.p. 277-78° (decomp.).

Analysis : Found : N, 17.05 %.

$C_{29}H_{24}N_8O_{10}$ requires : N, 17.40 %.

Cyanoethylation of 4,4'-dihydroxydiphenyl methane :

4,4'-Di-(β-cyanoethoxy)diphenyl methane :

A mixture of 4,4'-dihydroxydiphenyl methane (2 g.), acrylonitrile (5 ml.) and cupric oxide (0.2 g.) was refluxed on a steam bath for 30 hr. The product obtained on working up the reaction mixture as before crystallised from alcohol in brown shining needles (2.2 g.), m.p. 115-16°.

Analysis : Found : C, 74.40; H, 5.54; N, 9.00 %.

$C_{19}H_{18}N_2O_2$ requires : C, 74.50; H, 5.88; N, 9.15 %.

4,4'-Di-(β-carboxyethoxy)diphenyl methane :

The above cyano derivative (1 g.) was refluxed with conc. hydrochloric acid (50 ml.) for 7 hr. The product obtained was purified by sodium bicarbonate extraction. It crystallised from dilute alcohol in white shining plates (0.5 g.), m.p. 188-89°.

Analysis : Found : C, 66.33 ; H, 5.53 %.

$C_{19}H_{20}O_6$ requires : C, 66.26 ; H, 5.81 %.

6,6'-Bichromanonyl methane :

4,4'-Di-(β-carboxyethoxy)diphenyl methane (1 g.) was refluxed with thionyl chloride (3 ml.) for 1 hr. Excess thionyl chloride was removed by distillation and the acid chloride was mixed with anhydrous aluminium chloride (2 g.) in dry nitrobenzene (5 ml.). The reaction mixture was kept overnight, decomposed with ice cold hydrochloric acid and the nitrobenzene was removed by steam distillation. The product obtained crystallised from butyl alcohol-petroleum ether mixture in white buds (0.2 g.), m.p. 131-32°.

Analysis : Found : C, 73.91 ; H, 5.16 %.
$C_{19}H_{16}O_4$ requires : C, 74.01 ; H, 5.19 %.

6,6'-Bichromonyl methane :

6,6'-Bichromanonyl methane (0.5 g.) in diphenyl ether (5 ml.) was refluxed with palladised charcoal (10 %; 0.25 g.) for 8 hr. The reaction mixture was filtered hot and cooled. The separated product crystallised from absolute alcohol in pale brown plates (0.1 g.), m.p. 193-94°.

Analysis : Found : C, 74.80 ; H, 4.08 %.
$C_{19}H_{12}O_4$ requires : C, 74.99 ; H, 3.95 %.

Hydrolysis :

6,6'-Bichromonyl methane (50 mg.) was refluxed with sodium hydroxide solution (10 ml.; 10 %) for 30 minutes. The product obtained on acidification of the clear alkaline solution crystallised from alcohol in light brown plates.

M.P. and mixed m.p. with 3,3'-diacetyl-4,4'-dihydroxydiphenyl methane, prepared previously by the Fries migration of 4,4'-diacetoxy diphenyl methane, was 155-56°.

Cyanoethylation of 4,4'-dihydroxybenzophenone : 4,4'-Di-(β-cyanoethoxy)benzophenone :

A mixture of 4,4'-dihydroxybenzophenone (2 g.), acrylonitrile (10 ml.) and cupric oxide (0.2 g.) was refluxed on a steam bath for 30 hr. and the reaction mixture was worked up as before. The product obtained crystallised from alcohol in white shining plates (1.5 g.), m.p. 136-37°.

Analysis : Found : C, 71.06; H, 4.96; N, 9.12 %.
$C_{19}H_{16}N_2O_3$ requires : C, 71.25; H, 5.00; N, 8.75 %.

4,4'-Di-(β-carboxyethoxy)benzophenone :

4,4'-Di-(β-cyanoethoxy)benzophenone (1 g.) was refluxed with sulfuric acid (20 ml.; 80 %) for 1 hr. and worked up as before. The product obtained crystallised from dilute alcohol in white shining plates (0.5 g.), m.p. 203-04°.

Analysis : Found : C, 63.92; H, 5.00 %.
$C_{19}H_{18}O_7$ requires : C, 63.70; H, 5.03 %.

6,6'-Bichromanonyl ketone :

A mixture of the above dicarboxylic acid (0.5 g.) and polyphosphoric acid (20 g. P_2O_5; 10 ml. o-phosphoric acid) was heated on a steam bath for 7 hr. The product obtained on dilution of the reaction mixture with water crystallised from alcohol in white needles (0.2 g.), m.p. 193°.

Analysis : Found : C, 70.76 ; H, 4.48 %.

$C_{19}H_{14}O_5$ requires : C, 70.80 ; H, 4.35 %.

6,6'-Bichromonyl ketone :

A mixture of 6,6'-bichromanomyl ketone (0.5 g.) in diphenyl ether (5 ml.) and palladised charcoal (10 % ; 0.25 g.) was refluxed for 7 hr. The product obtained on dilution of the filtrate with petroleum ether crystallised from alcohol in white needles (0.1 g.), m.p. 249-50°.

Analysis : Found : C, 71.69 ; H, 3.29 %.

$C_{19}H_{10}O_5$ requires : C, 71.70 ; H, 3.15 %.

Hydrolysis :

6,6'-Bichromonyl ketone (50 mg.) was refluxed with sodium hydroxide solution (10 ml.; 10 %) for 30 minutes. The product obtained on acidification of the clear alkaline solution was crystallised from acetic acid. M.p. and mixed m.p. with an authentic sample prepared according to Balani and Sethna[63] was 180-81°.

Cyanoethylation of 4,4'-dihydroxydiphenyl sulfone : 4,4'-Di-(β-cyanoethoxy)diphenyl sulfone :

A mixture of 4,4'-dihydroxydiphenyl sulfone (2 g.), acrylonitrile (10 ml.) and cupric oxide (0.2 g.) was refluxed on a steam bath for 30 hr. The reaction mixture was worked up as before and the product was crystallised from alcohol in white needles (0.8 g.), m.p. 155-56°.

Analysis : Found : C, 60.53; H, 4.03; N, 7.51 %.

$C_{18}H_{16}N_2O_4S$ requires : C, 60.70; H, 4.49; N, 7.87 %.

4,4'-Di-(β-carboxyethoxy)diphenyl sulfone :

The above cyano derivative (1 g.) was refluxed with sulfuric acid (20 ml.; 80 %) for 20 minutes. The reaction mixture was cooled and diluted with water. The separated product was filtered and purified by extraction with sodium bicarbonate solution. The product obtained on acidification of the bicarbonate extract was crystallised from dilute acetic acid in white shining needles (0.4 g.), m.p. 198-99°.

Analysis : Found : C, 55.04; H, 4.65 %.

$C_{18}H_{18}O_8S$ requires : C, 54.82; H, 4.57 %.

6,6'-Bichromanonyl sulfone :

A mixture of the above dicarboxylic acid (0.5 g.) and polyphosphoric acid (20 g. P_2O_5 ; 10 ml. o-phosphoric acid) was heated on a steam bath for 6 hr. The product obtained on working up the reaction mixture as before crystallised from alcohol in white shining plates (0.2 g.), m.p. 177-79°.

Analysis . : Found : C, 60.40; H, 3.64 %.

$C_{18}H_{14}O_6S$ requires : C, 60.34; H, 3.91 %.

6,6'-Bichromonyl sulfone :

6,6'-Bichromanonyl sulfone (0.5 g.) in diphenyl ether (5 ml.) was refluxed with palladised charcoal

(10 % ; 0.25 g.) for 8 hr. and filtered hot. The product obtained on addition of excess petroleum ether to the filtrate was crystallised from xylene-petroleum ether mixture in yellowish-orange plates (0.1 g.), m.p. 266-68°.

Analysis : Found : C, 60.82; H, 3.23 %.

$C_{18}H_{10}O_6S$ requires : C, 61.03; H, 2.82 %.

Hydrolysis :

6,6'-Bichromonyl sulfone (5o mg.) was refluxed with sodium hydroxide solution (10 ml. ; 10 %) for 30 minutes. The product obtained on acidification of the clear alkaline solution crystallised from acetic acid in pale brown needles. M.p. and mixed m.p. with an authentic sample of 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfone according to Kulkarni[64] was 187-88°.

Attempted cyanoethylation of 2,2'-dihydroxybenzophenone :

A mixture of 2,2'-dihydroxybenzophenone (2 g.), acrylonitrile (5 ml.) and cuprous chloride (0.2 g.) was refluxed on a steam bath for 30 hr. The reaction mixture was worked up as before. Original alkali soluble 2,2'-dihydroxybenzophenone was recovered unchanged. Condensation did not take place when different condensing agents such as cupric oxide, sodium hydroxide, sodium methoxide, metallic sodium and a mixture of cuprous chloride and sodium hydroxide were used. In all cases either the original

2,2'-dihydroxybenzophenone was obtained back or xanthone was obtained. M.p. and mixed m.p. with the xanthone prepared according to Holleman[70] by the distillation of salol was 169°.

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