chapter - III

synthesis of benzofuroisoflavones

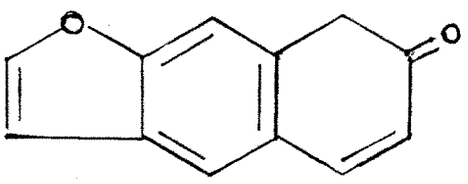
C H A P T E R - III

SYNTHESIS OF BENZOFURO ISOFLAVONE

Isoflavones constitute a group of naturally occuring compounds which are well known for their biological activities. Benzo furan derivatives are known to exhibit diverse physiological properties.[1-3] In view of these reports it was thought of interest to constr uct benzofuran ring on isoflavones. The benzofuroisoflavones thus obtained may have pronounced physiological activities.

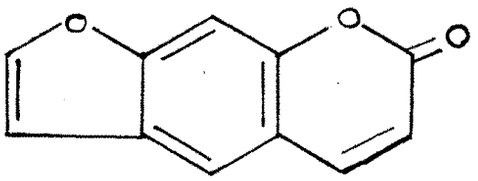
Psoralene (1) and its derivatives have received considerable attention on account of their therapeutic properties. eg. xanthotoxin (2) is a fish poison[4] and possess molluscicidal activity.[5] Musaji and coworkers[6,7] have observed that psoralene derivatives are photodynamicallty active. J.K. Macleod and Worth synthesized linear furocoumarin psoralene by carrying out etherification of 7-hydroxycoumarin (3) with allyl bromide followed by ozonolysis and acidic cyclization. (Scheme-I).

They extended this method to prepare dibenzofuran derivative by condensing 2-bromocyclohexanone with 7-hydroxycoumarin (4) followed by treatment with aqueous KOH under reflux. This product (5) was readily dehydrogenated to 2H-benzofuro (3,2-g)-1-benzopyran (6) (Scheme-II).



Psoralene

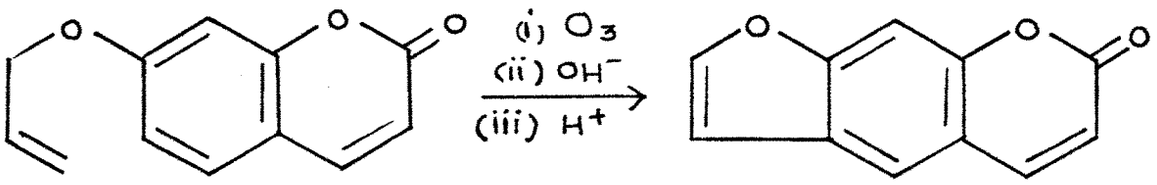
1



Xanthotoxin

2

Scheme I : Macleod and Worth[8]



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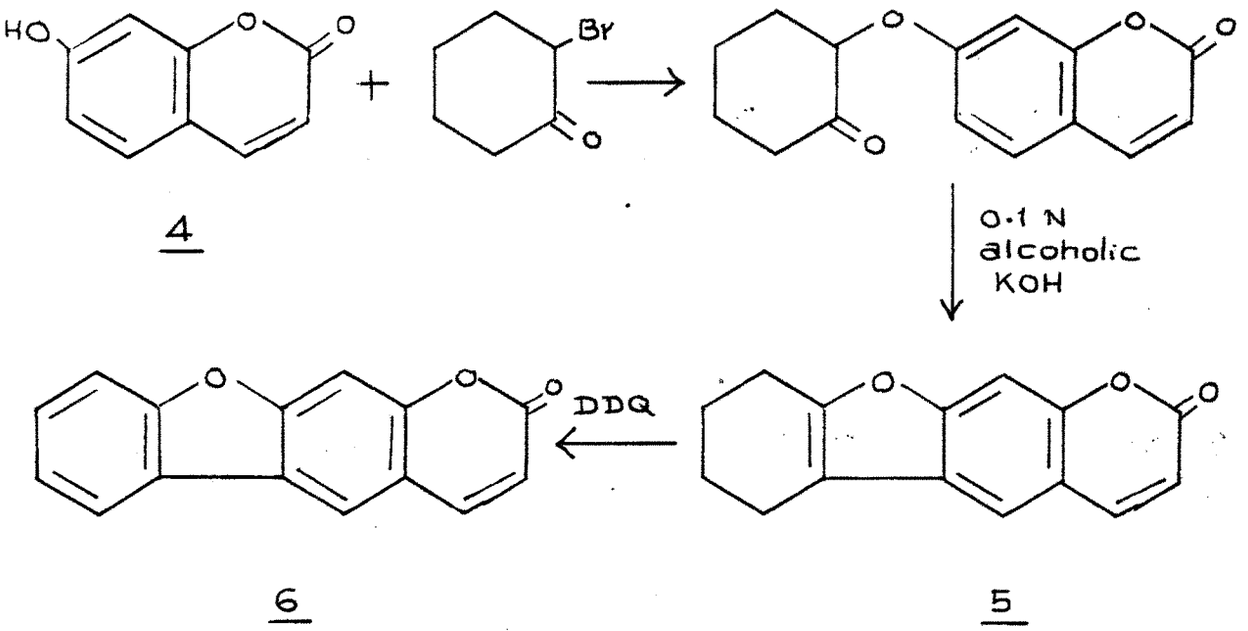
Scheme II : Macleod and Worth[8]



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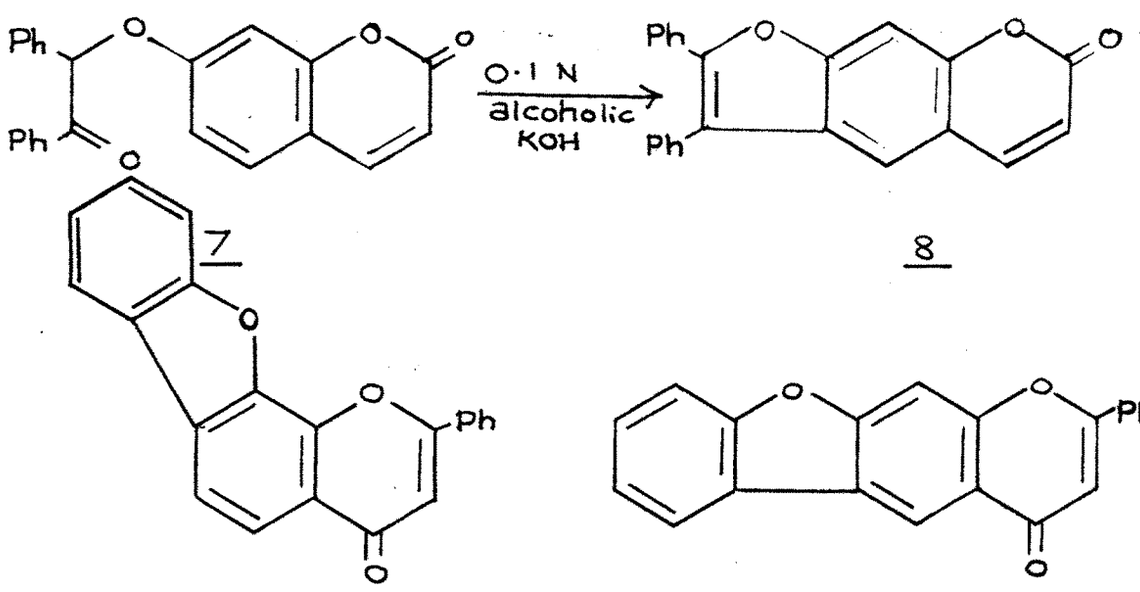
6

5

Scheme III : K. Lingeshwara Rao[9]



7

8

9

10

this procedure K. Lingeshwara Rao[9] prepared (8) from (7). (Scheme-III).

Ahluwalia, Adhikari and Singh[10] carried out similar type of synthesis of benzo-γ-pyrones for the first time. They condensed bromocyclohexanone with 7-hydroxy, 5,7-dihydroxy, 7-hydroxy-8-methyl and 7-hydroxy-5-methoxy flavones and obtained corresponding benzofuroflavones (9), (10).

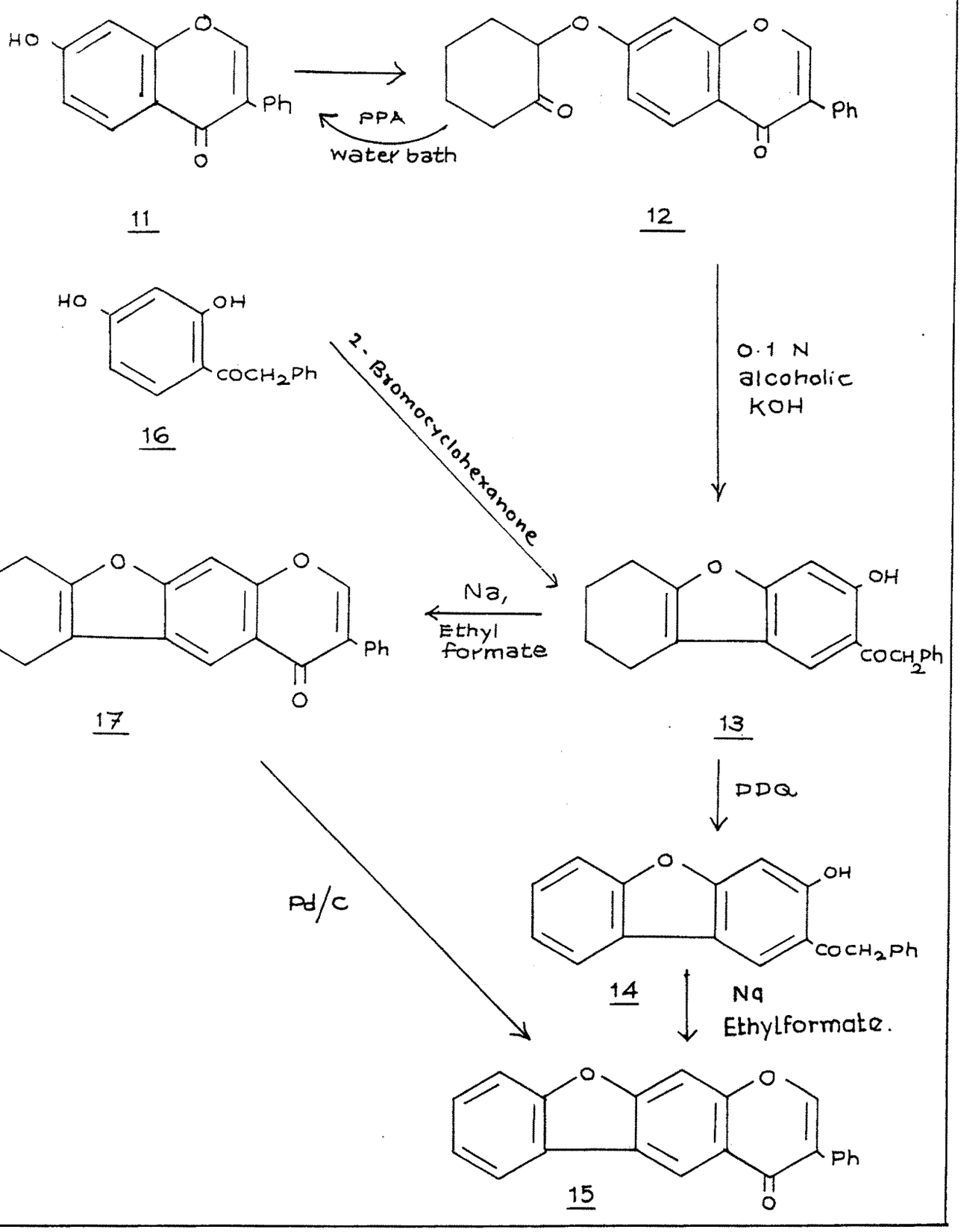
Present work

Desai and Trivedi[11] reported the synthesis of 2-oxo-2H-benzofurano (3,2-g) benzopyran derivatives by condensing the different hydroxy coumarins with 2-bromocyclohexanone followed by cyclization of the ether with mild alkali. This work is now extended to different hydroxy isoflavones to prepare different benzofuro benzo- -pyran derivatives.

Synthesis of 3-phenyl-4H-benzofuro (3,2-g)-[1]-benzopyran -4-one (15)

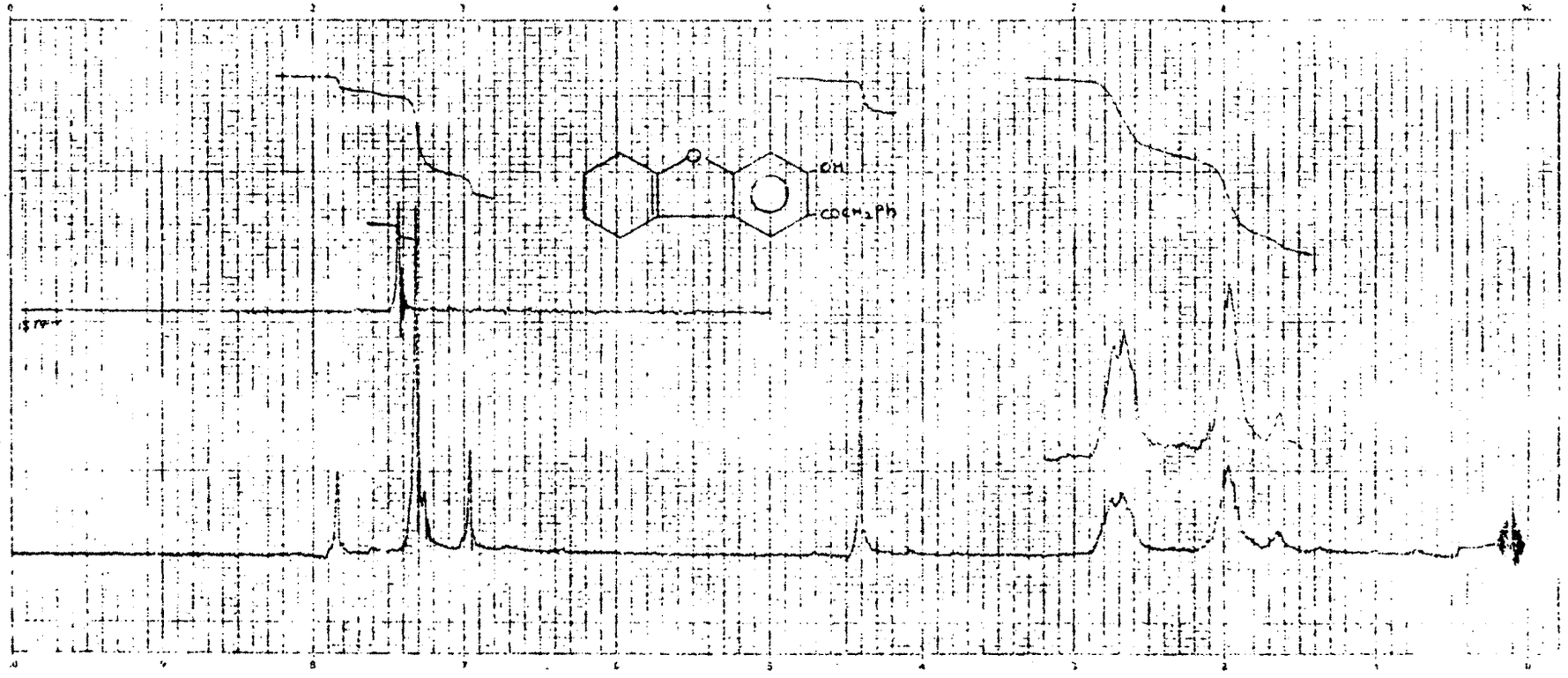
7-Hydroxy isoflavone (11) on condensation with 2-bromocyclohexanone in acetone in presence of anhydrous potassium carbonate gave the ether 7-(cyclohexan-2-onyloxy)-3-phenyl-4H-1-benzopyran-4-one (12) (Scheme-IV). The ether (12) was subjected to cyclization by boiling with

Scheme IV


HO
O
Ph
O
PPA
water bath
O
O
O
Ph
O
11
12
HO
OH
COCH2Ph
16
2-Bromocyclohexanone
0·1 N
alcoholic
KOH
O
O
Ph
O
17
Na,
Ethyl
formate
O
OH
COCH2Ph
13
DDQ
Pd/C
O
OH
COCH2Ph
14
Na
Ethylformate.
O
O
Ph
O
15

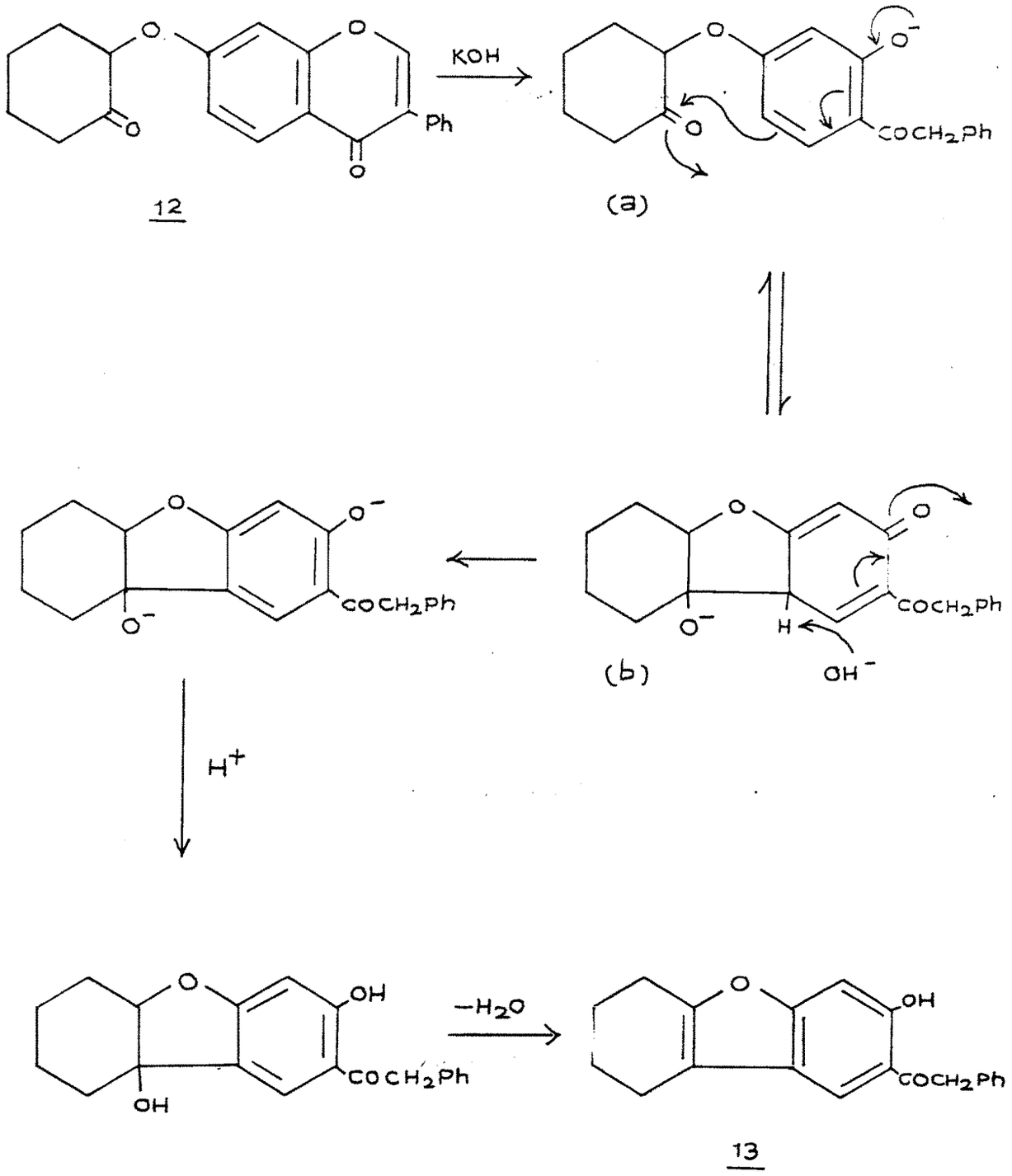
0.1N alcoholic potassium hydroxide solution. The reaction mixture on acidification gave a product which was not the expected benzofurobenzopyran derivative but instead it turned out to be a product with the opening of the pyrone ring with simultaneous cyclization of cyclohexanone ring to give 5,6,7,8-tetrahydro-2-hydroxy-3-phenylacetyl dibenzofuran (13). NMR spectra of (13) exhibited two broad multiplets at δ 1.9 and 2.6 for 4 x 2H methylene protons of cyclohexene ring ; a singlet at 4.3 for methylene group in the side chain $-COCH_2Ph$; singlet at 6.85 for one aromatic proton at C-1 : multiplet for 5 aromatic protons at 7.2; a downfield singlet at 7.78 for one aromatic proton at C-4 which is ortho to the carbonyl group ; the Chelated hydroxyl group appeared at 10.3. (Fig. 1)

Mechanism of this reaction (Scheme-V) can be described as type of intra-molecular aldol condensation in which the phenoxide ion (a) formed by the alkaline hydrolysis of the γ-pyrone ring, which is normally cleaved to o-hydroxyketone, favours the attack at exocyclic carbonyl function through resonance-stabilized carbanion, generated at the para position to the phenoxide ion viz. (a) --- (b). This is irreversidble process because proton at the newly formed ring junction is immediately abstracted by the base to regenerate the phenoxide (c). On acidification the alkoxide ion is protonated, water being eliminated



5,6,7,8-tetrahydro-2-hydroxy-3-phenylacetyl dibenzofuran (13) (Fig 1)

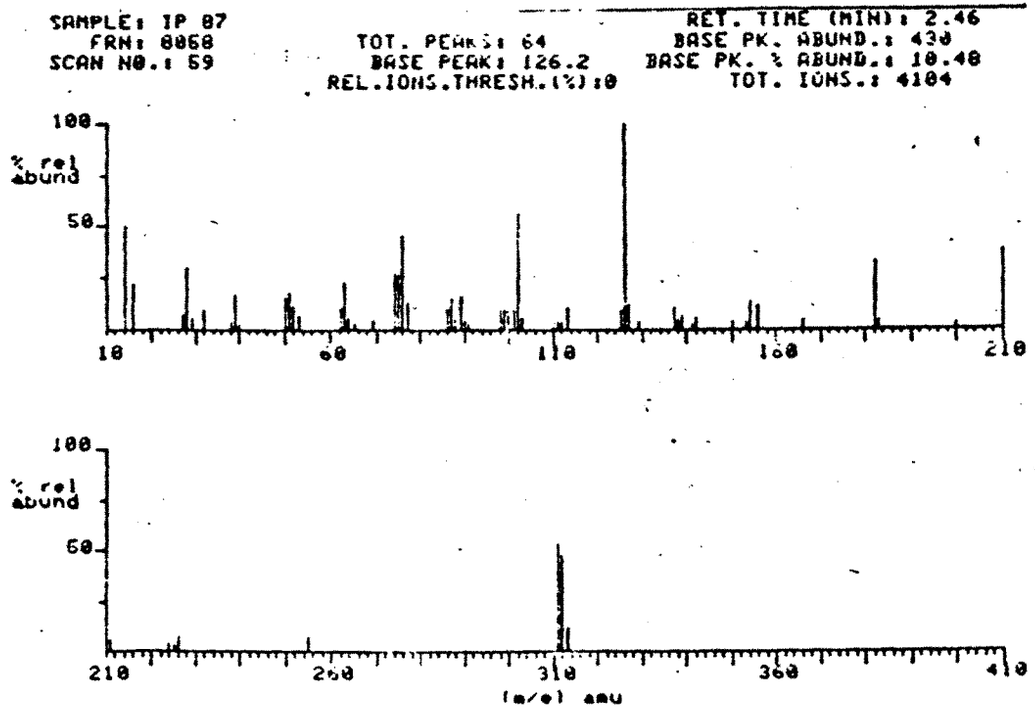
Scheme V



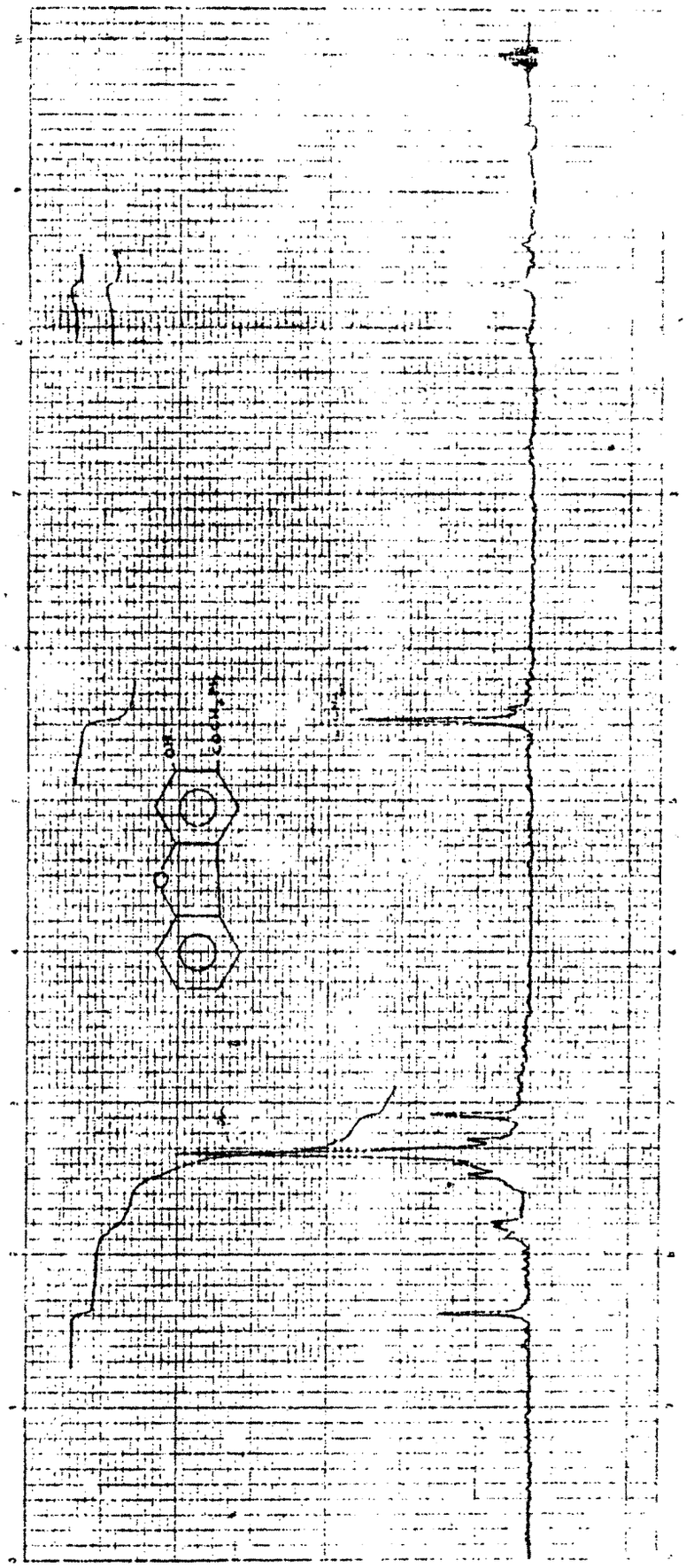
spontenously from the labile 3-hydroxydihydro furan ring system to give (13). (13) was also obtained when 2,4-dihydroxy phenylbenzylketone (16) was condensed with 2-bromocyclohexanone in the presence of anhydrous potassium carbonate and dry DMF as solvent.

Dehydrogenation of (13) was carried out by refluxing it with DDQ in dry benzene. The product was purified by column chromatography on silica gel and was assigned structure (14) and confirmed by pmr spectra which showed singlet at δ 4.45 for two methylene protons in the side chain $-COCH_2Ph$; 7.1 singlet for one proton at C-1 ; multiplet for eight aromatic protons at 7.3 ; 7.8 multiplet for 1H at C-5 in the downfield region and downfield singlet at 8.2 for the proton at C-4.(Fig.2)

3-Phenyl-4H-benzofuro (3,2-g)-1-benzopyran-4-one (15) was finally synthesized by subjecting the above dibenzofuro-ketone (14) to Claisen condensation with sodium and ethyl formate. NMR spectra of (15) could not be recorded as it is insoluble in common organic solvents but its mass spectra showed the following peaks m/e 312(M^+), 210, 182, 102. This is represented in the fragmentation process. (Scheme-VI).(Fig 2A)

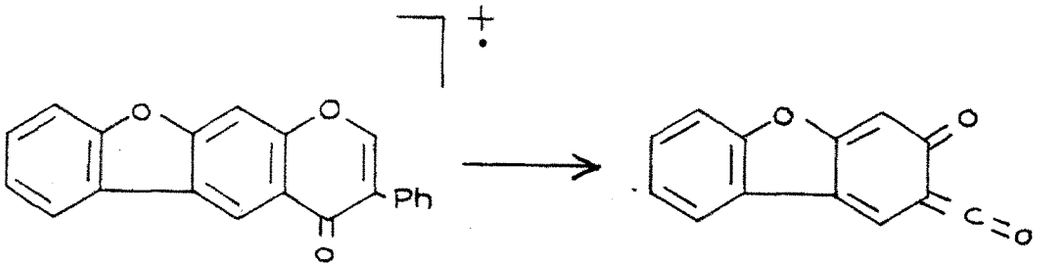


3-Phenyl-[4H]-benzofuro(3,2-g)-1-benzopyran-4-one(15) (fig. 2A)

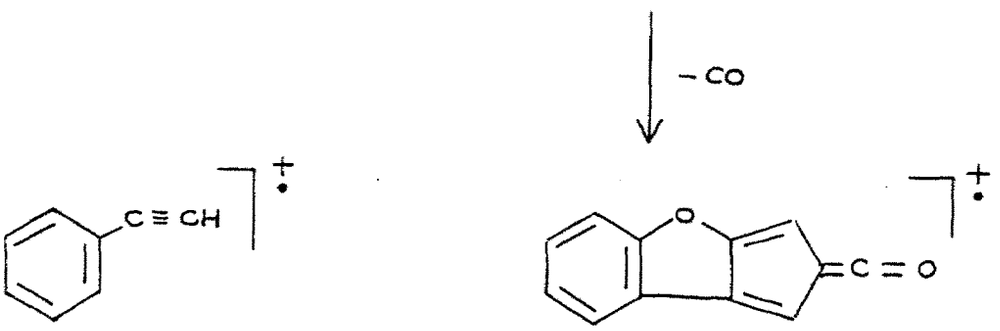


2-Hydroxy-3-phenylacetyldibenzofuran (14) (Fig. 2)

Scheme VI

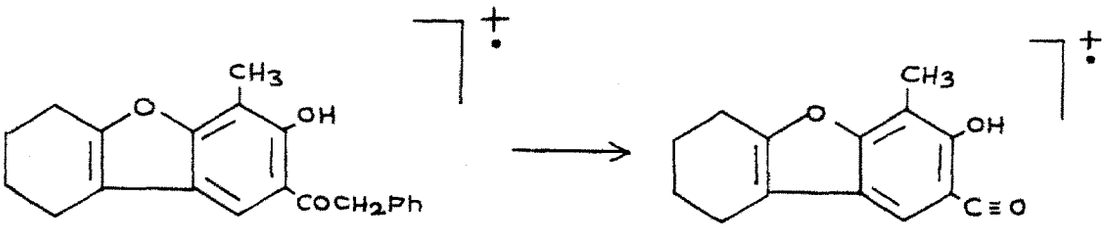


m/e 312 m/e 210

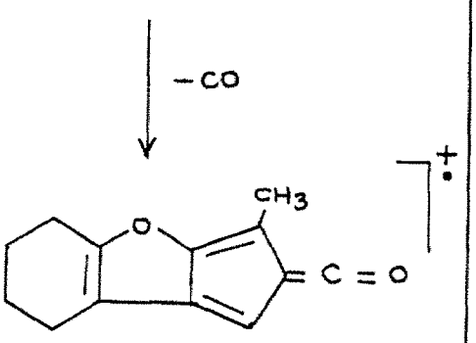


m/e 102 m/e 182

Scheme VII :



m/e 320 m/e 229

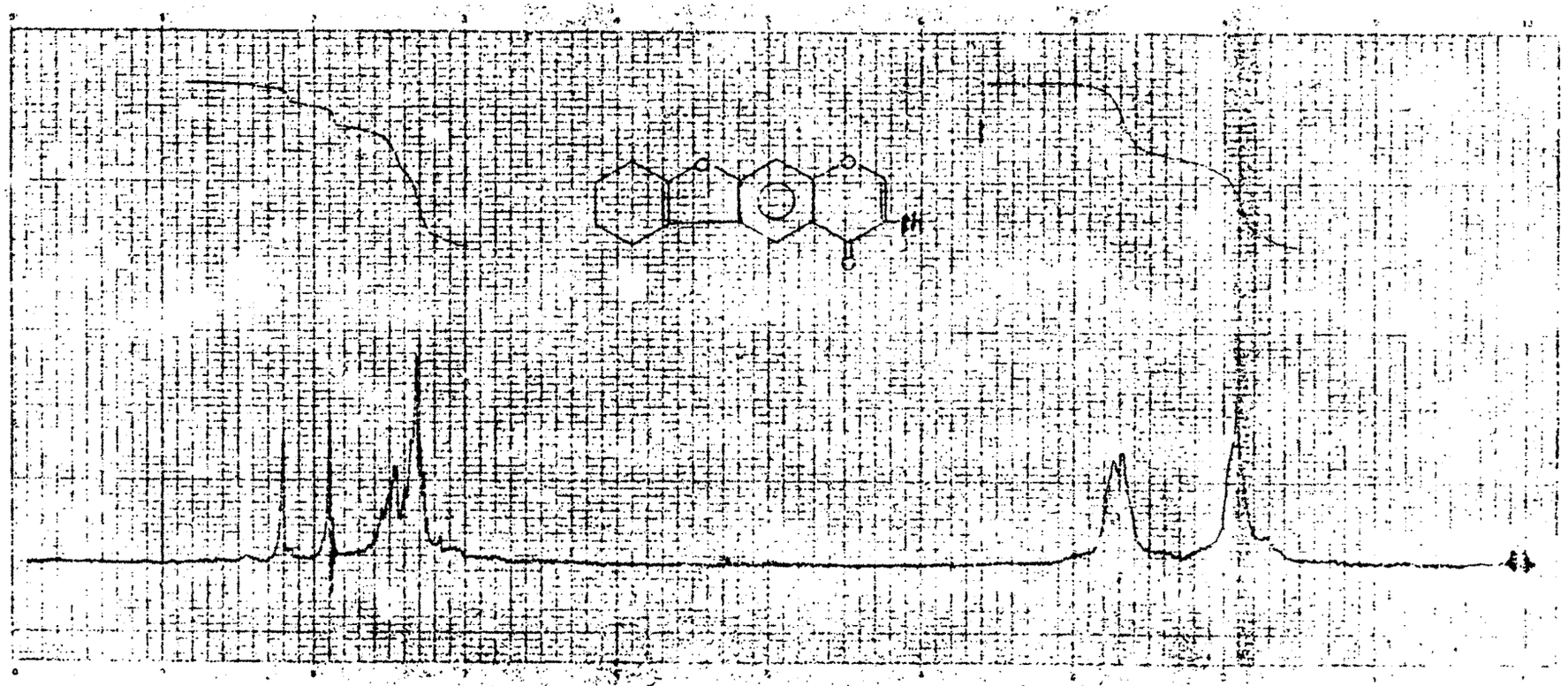


m/e 200

The benzofurobenzopyran (15) was also synthesized by first condensing the o-hydroxyketone (13) with sodium and ethyl formate to obtain 6,7,8,9-tetrahydro-3-phenyl-4H-benzofuro (3,2-g)-1-benzopyran-4-one (17) followed by dehydrogenation. The structure (17) was confirmed by PMR spectra which exhibited following signals δ 1.9 and 2.7, two broad multiplets for four methylene groups of cyclohexene ring 7.3, multiplet for five aromatic protons 7.9, singlet for proton at C-2 and another downfield singlet at 8.2 for proton at C-5. (Fig.3) Dehydrogenation of (17) with Pd/C in refluxing diphenyl ether afforded (15). The compound obtained by both the route were found to be identical by mixed m.p. Co TLC. Synthesis of (17) from (12) was tried by heating the ether (12) with PPA in hot water bath but dealkylation took place giving 7-hydroxy isoflavone (11) and not desired product (17). This series of reactions are shown in (Scheme-IV).

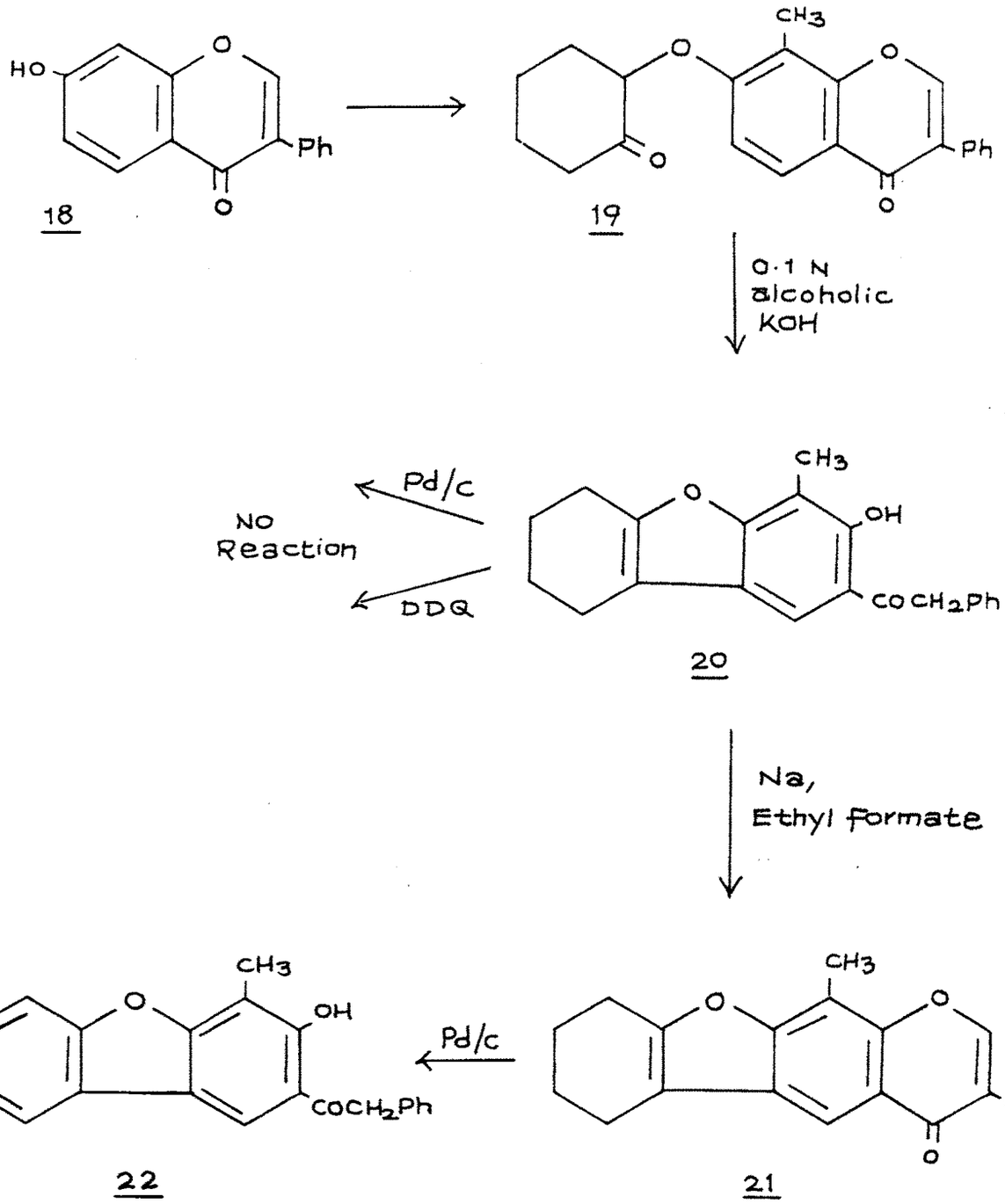
Synthesis of 1-methyl-2-hydroxy-3-phenylacetyl dibenzofuran (22)

7-Hydroxy-8-methyl isoflavone (18) on condensation with 2-bromocyclohexanone in acetone in presence of anhydrous potassium carbonate gave 7-(cyclohexan-2-onyloxy)-8-methyl-3-phenyl-4H-1-benzopyran-4-one (19). The ether (19) was subjected to cyclization by boiling with 0.1N alcoholic KOH solution. The reaction mixture on acidification gave

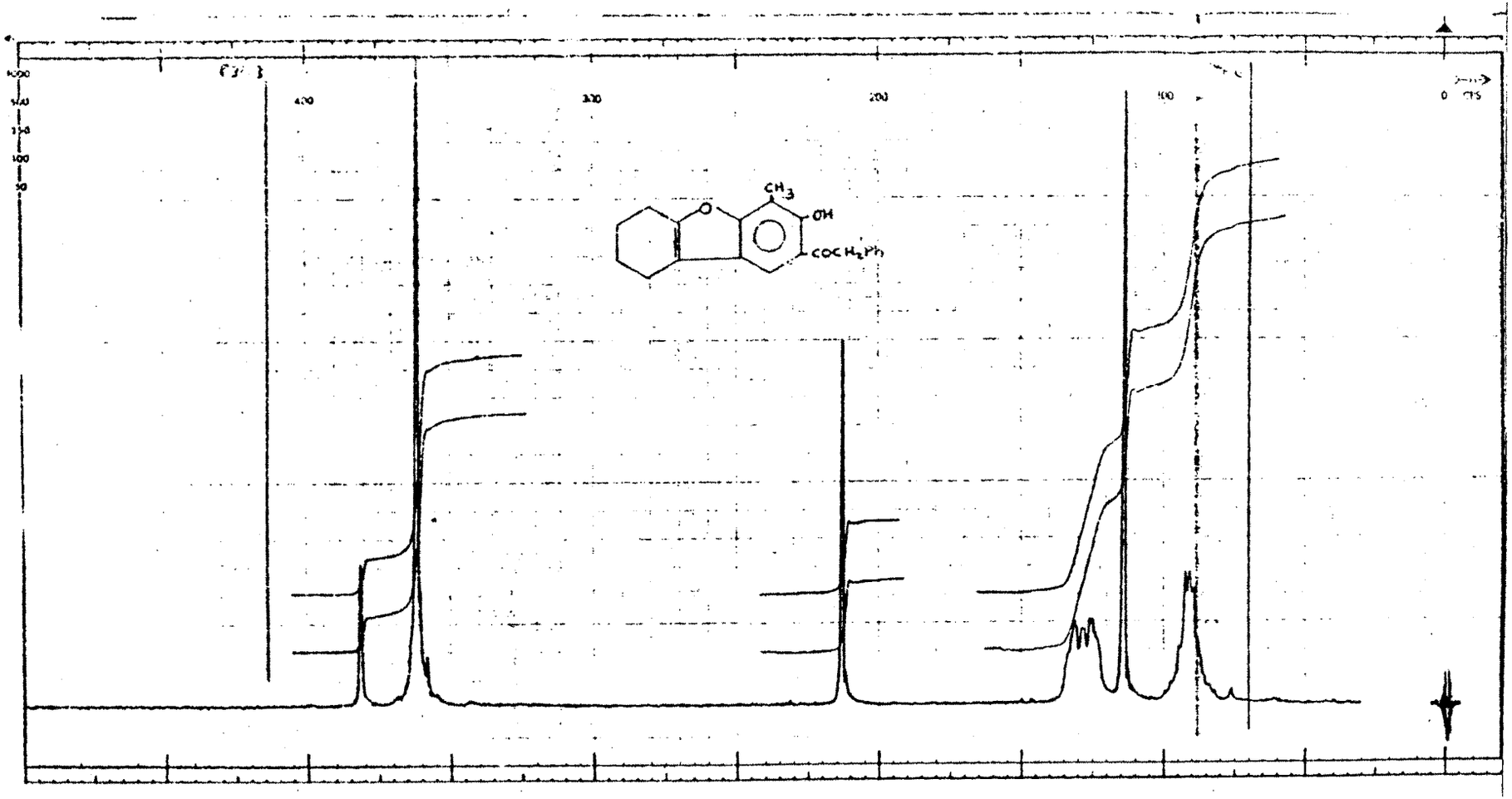


6,7,8,9-Tetrahydro-3-phenyl-(4H)-benzofuro(3,2-g)-1-benzopyran-4-one (17) (Fig.3)

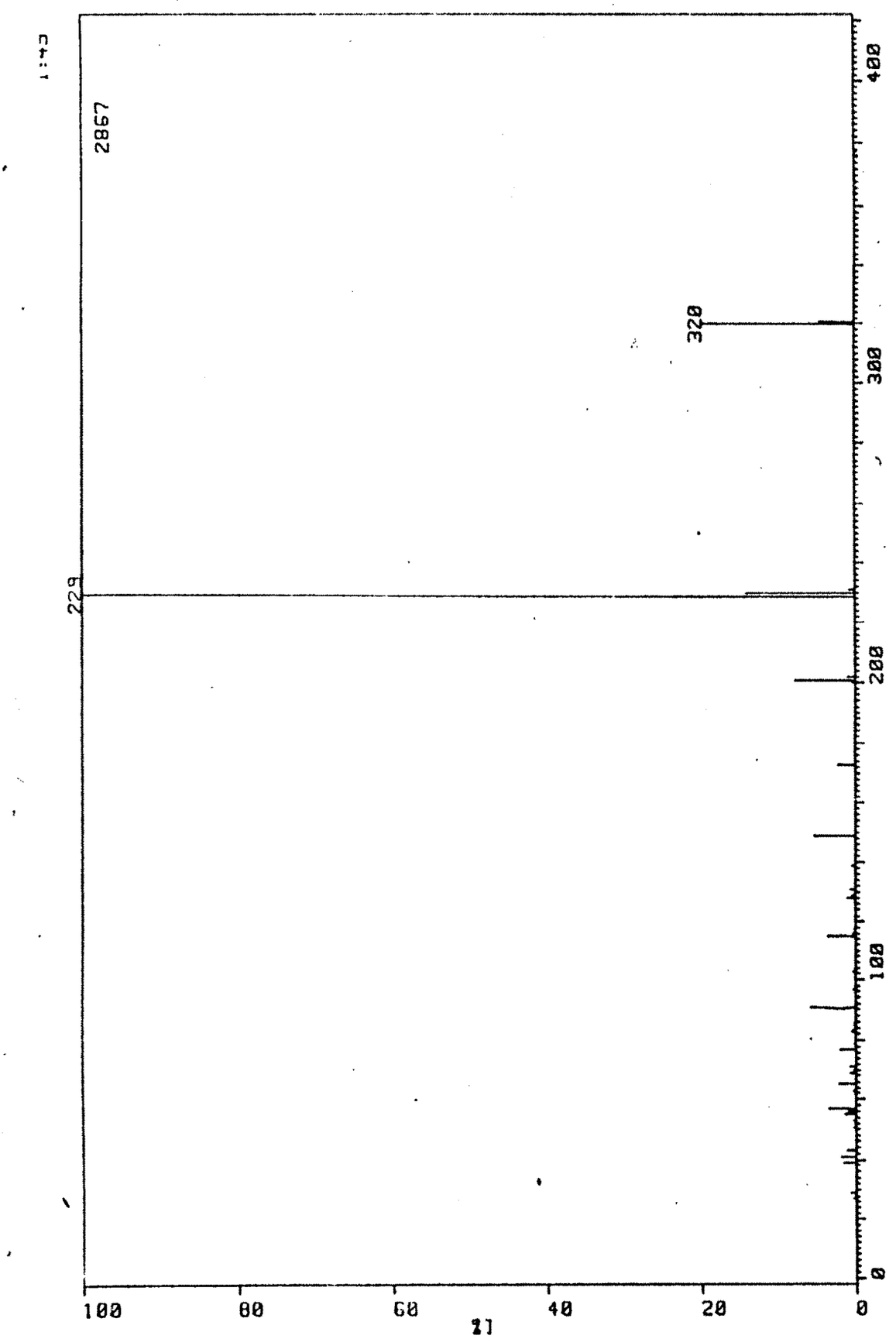
Scheme VIII


HO
O
Ph
O
18
CH3
O
O
O
Ph
O
19
0·1 N
alcoholic
KOH
Pd/c
NO
Reaction
DDQ
CH3
O
OH
COCH2Ph
20
Na,
Ethyl formate
CH3
O
OH
COCH2Ph
22
Pd/c
CH3
O
O
Ph
O
21

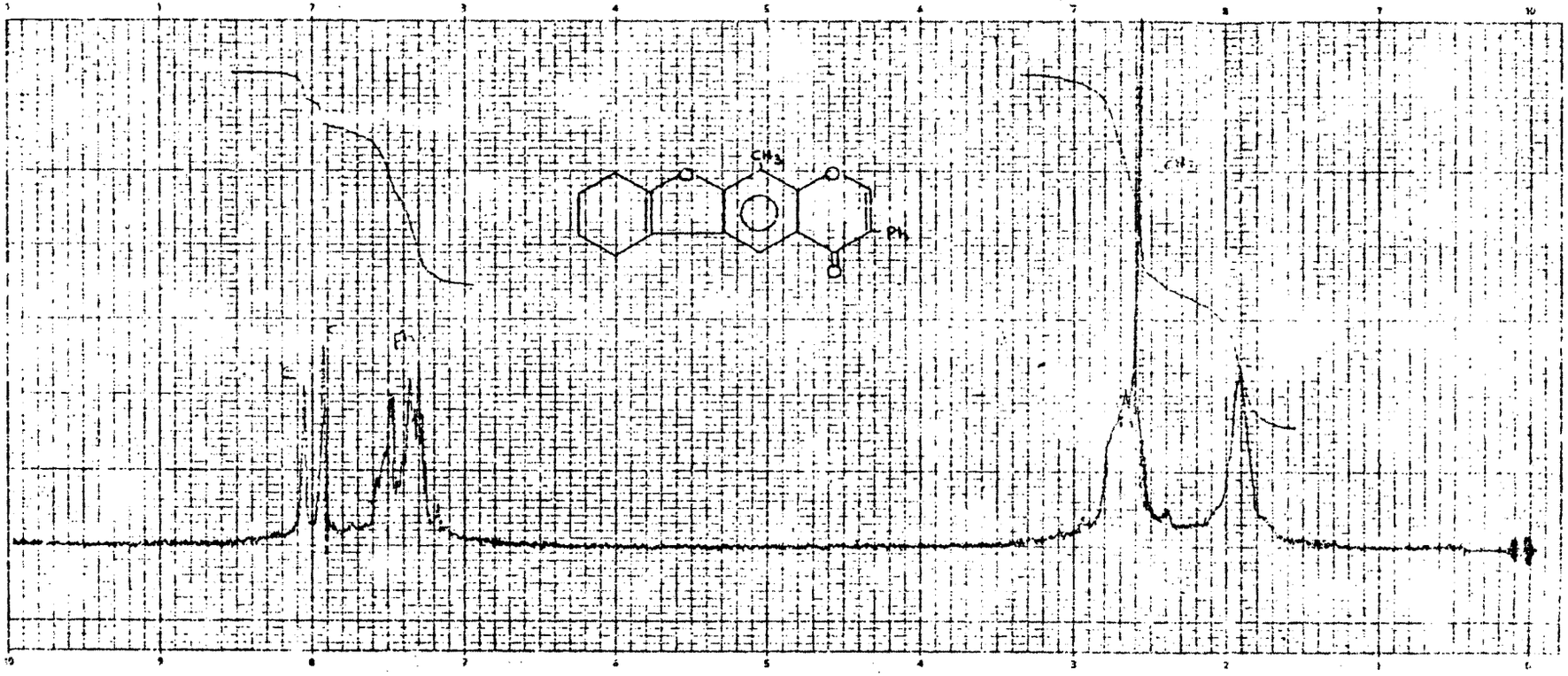
a product which was not the expected benzofurobenzopyran but a derivative of dibenzofuran with simulteneous cyclization of cyclohexanone ring and opening of pyran ring to give 5,6,7,8-tetrahydro-1-methyl-2-hydroxy-3-phenylacetyl dibenzofuran (20). NMR spectra of (20) showed two broad multiplets at δ 1.9 and 2.6 for 2H x 4 methylene protons of cyclohexene ring ; 2.3, singlet for three protons of methyl group at C-1 ; another singlet at 4.3 for methylene protons of side chain $-CO\underline{CH_2}Ph$; five aromatic protons gave multiplet at 7.2 while one aromatic proton at C-5 gave downfield singlet at 7.6. (Fig.4) Its mass spectra exhibited peaks at m/e 320 (M^+), 229, 200. These are represented in the following fragmentation process (Scheme-VII). (Fig 4A) Isoflavone (21) was synthesized by treating solution of ketone (20) in ethyl formate with pulverized sodium. Structure of the product 6,7,8,9-tetrahydro-11-methyl-3-phenyl-4H-benzofuro (3,2-g)-1-benzopyran-4-one (21) was confirmed by pmr spectra giving following signals ($CDCl_3$) : δ 1.9 and 2.7, two broad multiplets, 2H x 4 methylene protons of cyclohexene ring ; 2.6, singlet for three protons by methyl group at C-11 ; five aromatic protons gave downfield multiplet at 7.4 ; one downfield singlet at 7.9 for proton at C-5 and another singlet at 8.05 for proton at C-2. (Fig.5) Dehydrogenation of (21) was carried out by heating it with palladium on charcoal (10%) in



5,6,7,8-Tetrahydro-1-methyl-2-hydroxy-3-phenylacetyl dibenzofuran (20) (Fig 4)



5,6,7,8-tetrahydro-1-methyl-2-hydroxy-3-phenylacetyldibenzofuran (20) (Fig. 4A)



6,7,8,9-Tetrahydro-11-methyl-3-phenyl-(4H)-benzofuro (3,2-g)-1-benzopyran-4-one (21)

(Fig. 5)

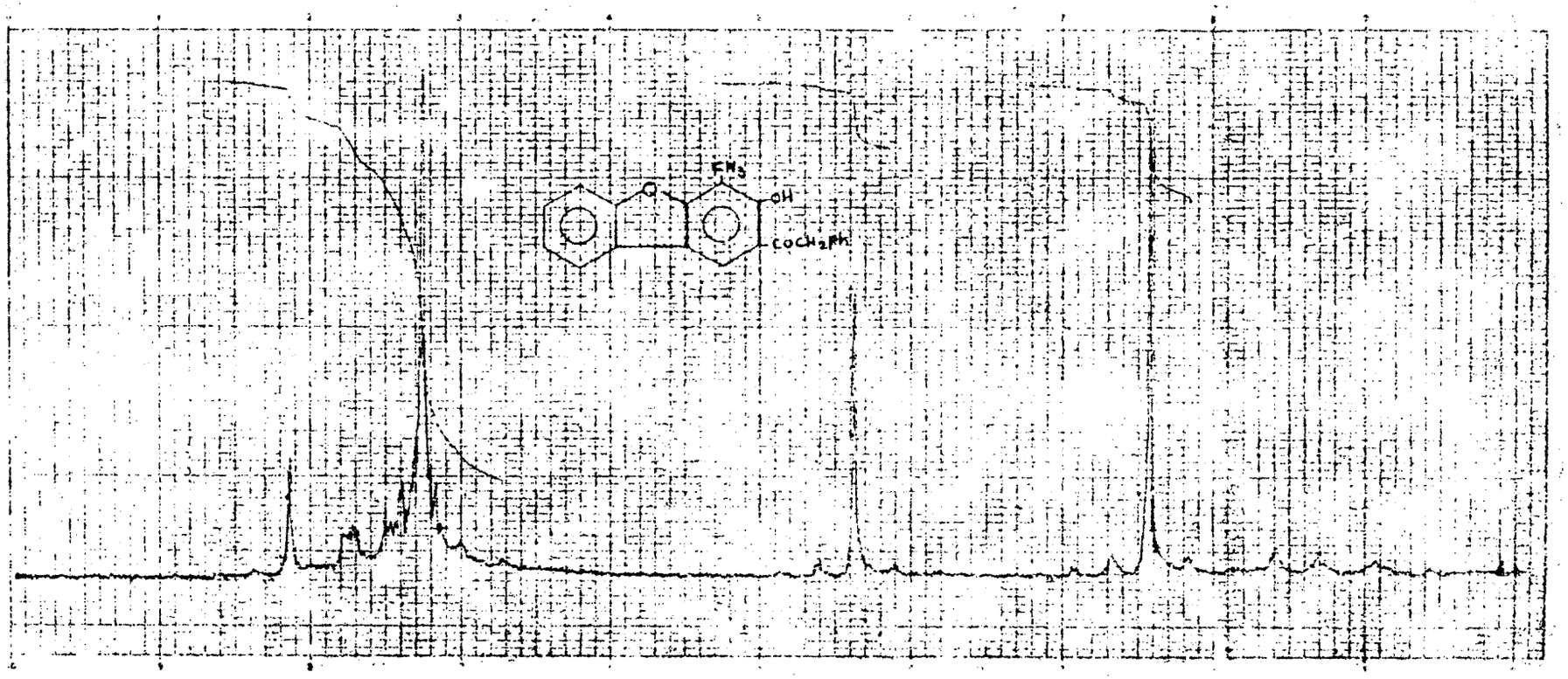
boiling diphenyl ether (Scheme-VIII). The structure of the product obtained is 1-methyl-2-hydroxy-3-phenylacetyl dibenzofuran (22) γ-pyrone ring being opened up during the reaction. As yield at this stage is very poor, building up of isoflavone ring on this nucleus was not possible. PMR ($CDCl_3$) ; δ 2.4, singlet for three protons of methyl group at C-2 ; 4.4, singlet for 2H, methylene protons of the side chain $-COCH_2Ph$; 7.2-7.4, eight aromatic protons gave multiplet, 7.7 multiplet, 1H at C-5 ; and one aromatic proton at C-4 gave downfield singlet at 8.1.(Fig.6)

Dehydrogenation of ketone (20) with Pd/C or DDQ met with failure.

Direct cyclization of (19) to (21) in PPA was tried but it gave dealkylated product (18) instead of (21). Series of these reaction is shown in (Scheme-VIII).

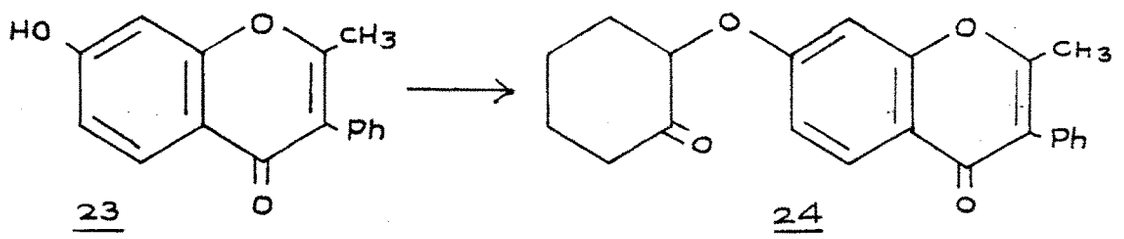
Synthesis of 2-methyl-3-phenyl-[4H]-benzofuro (3,2-g)-1-benzopyran-4-one (26)

7-Hydroxy-2-methylisoflavone (23) on condensation with 2-bromocyclohexanone in acetone in presence of anhydrous potassium carbonate gave ether 7-(cyclohexan-2-onyloxy) 2-methyl-3-phenyl-[4H]-1-benzopyran-4-one (24). The ether (24) was subjected to cyclization by boiling with 0.1N alcoholic potassium hydroxide solution. The reaction

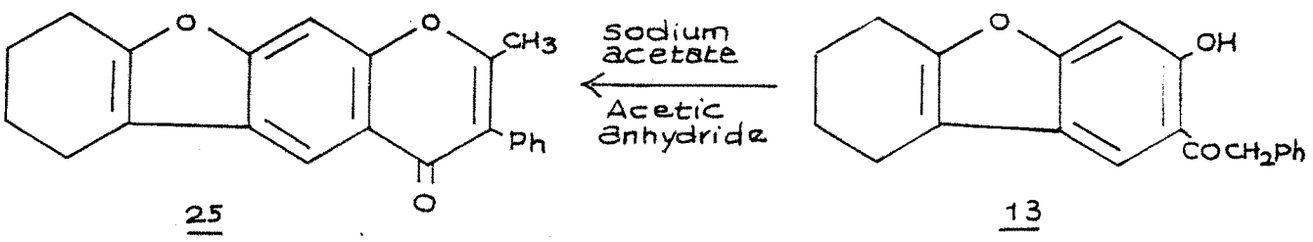


2-Hydroxy-1-methyl-3-phenylacetyl dibenzofuran (22) (Fig.6)

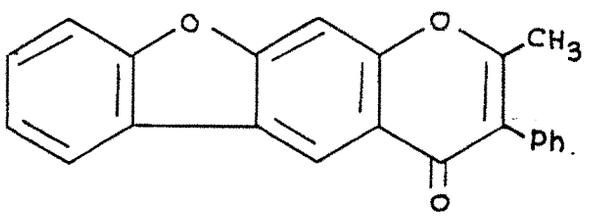
Scheme IX



0·1 N alcoholic KOH



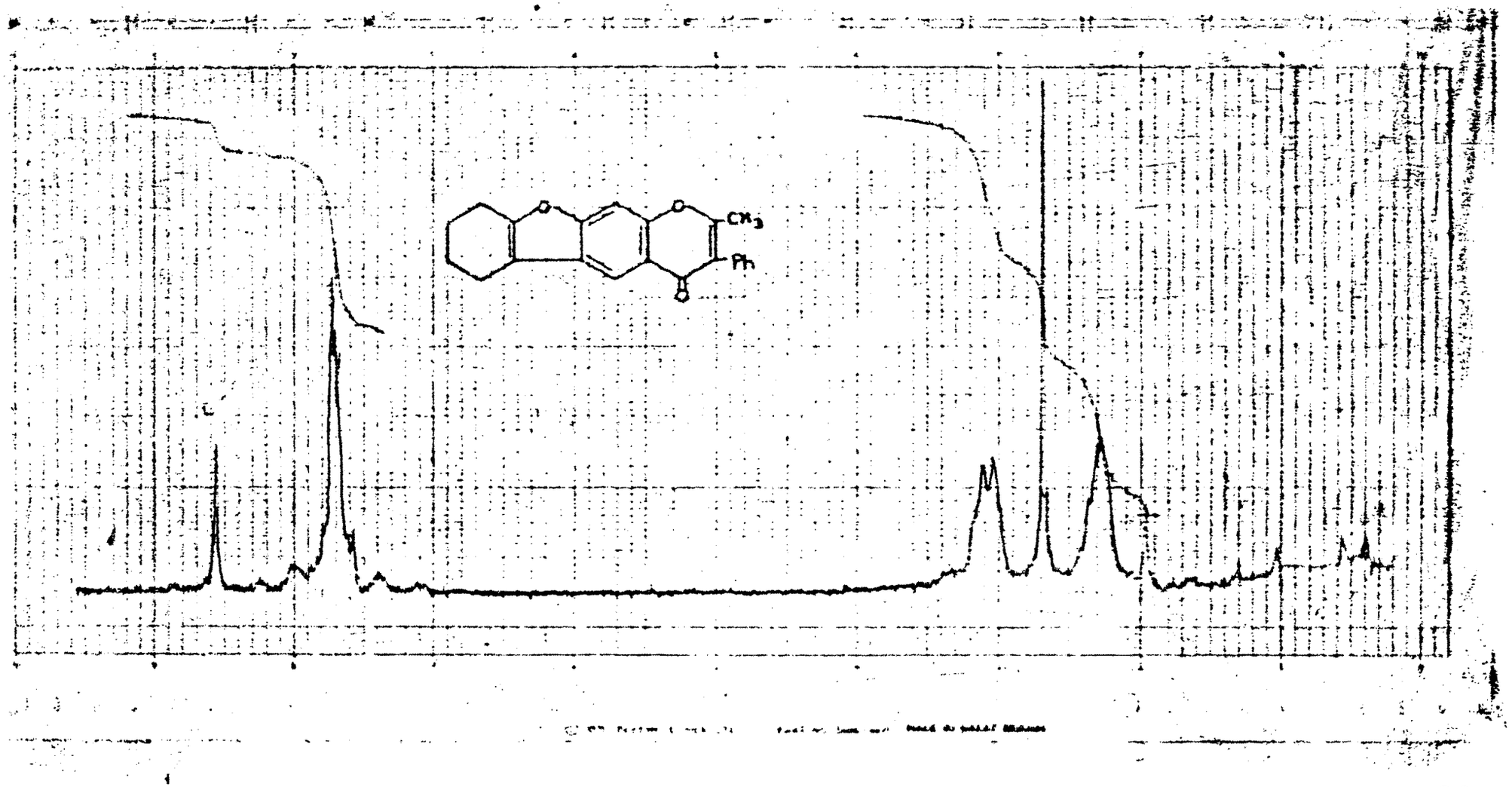
Pd/C



mixture on acidification gave a product which is identical with 5,6,7,8-tetrahydro-2-hydroxy-3-phenylacetyldibenzofuran (13). (13) was refluxed with acetic anhydride in the presence of anhydrous sodium acetate. The reaction mixture was worked up as before to gave 6,7,8,9-tetrahydro-2-methyl-3-phenyl-[4H]-benzofuro (3,2-g)-1-benzopyran-4-one (25). The structure (25) was established by pmr spectrum giving following signals : 1.9 and 2.7, two broad multiplets for four methylene groups 2H x 4 of cyclohexene ring ; 2.3, 3H, singlet for methyl group at C-2 ; 7.3, multiplet for 5H, aromatic protons ; 8.15, singlet, 1H, C-5 proton. (Fig.7) (25) was refluxed with Pd/C in diphenylether for 12 hrs. The product obtained on working up the reaction mixture was 2-Methyl-3-phenyl-[4H]-benzofuro (3,2-g)-1-benzopyran-4-ene (26). The structure was established from nmr spectrum. ($CDCl_3$) : δ 2.3, singlet for methyl protons at C-2 ; nine aromatic protons exhibited multiplet in the region from 7.2 to 7.5 ; another multiplet for proton at C-6 appeared at 7.95 ; proton at C-5 showed singlet at 8.7. (Scheme-IX) (Fig.8)

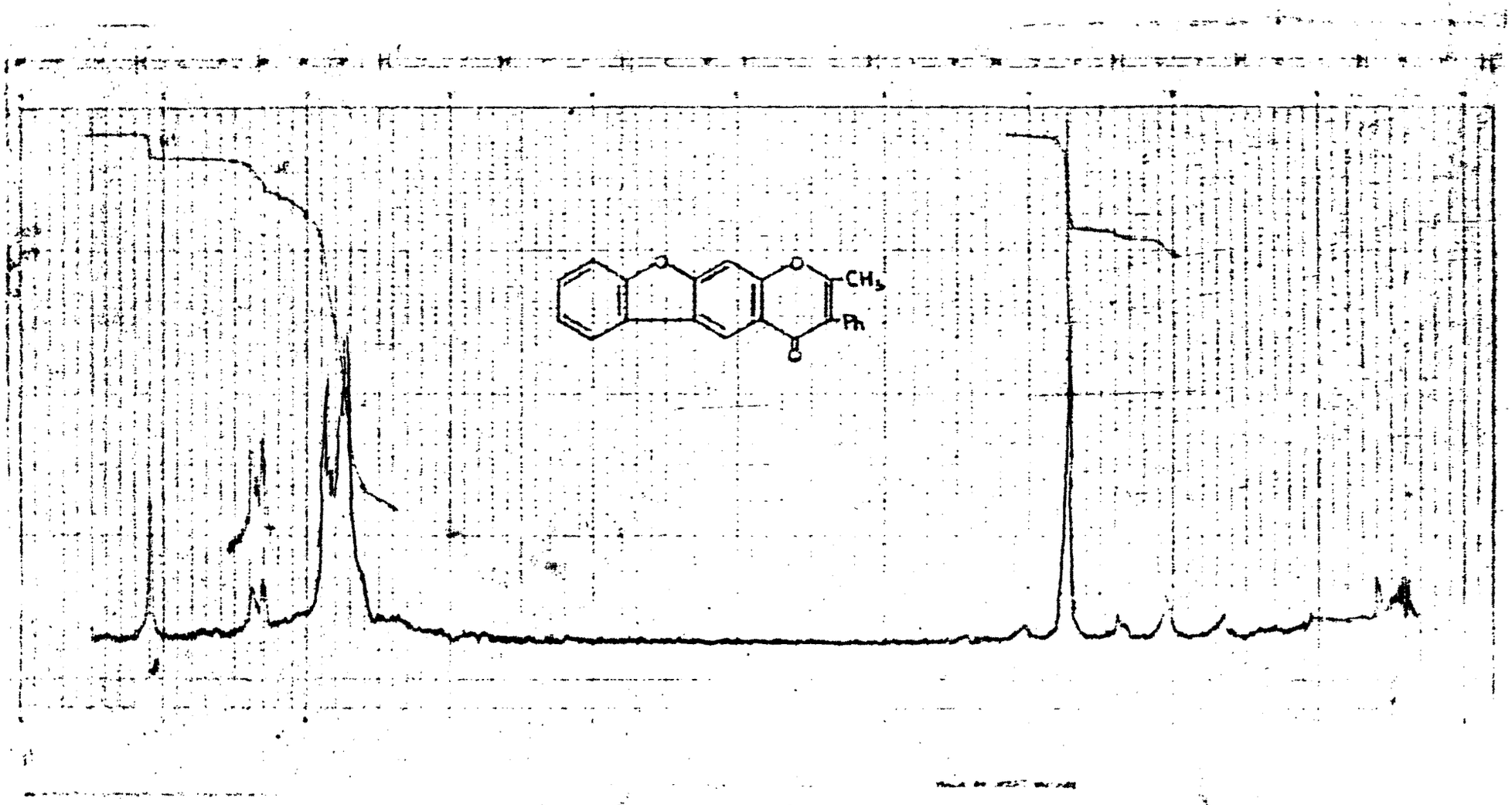
6-Hydroxy-7-methyl-5-phenylacetyl 2,3-diphenylbenzofuran (28)

2,4-Dihydroxy-3-methyl phenylbenzylketone (27) was condensed with desylchloride in the presence of anhydrous potassium carbonate and few crystals of potassium iodide in dry acetone as solvent. Reaction mixture worked up



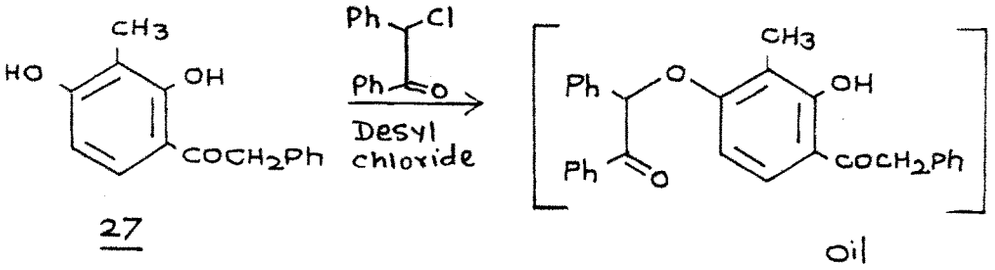
6,7,8,9-Tetrahydro-2-methyl-3-phenyl- 4H -benzofuro(3,2-g)-1-benzopyran-4-one (25)

(Fig. 7)



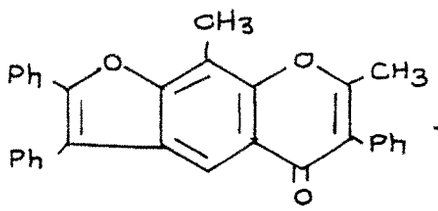
2-Methyl-3-phenyl -4H -benzofuro(3,2-g)-1-benzopyran-4-one (26) (Fig. 8)

Scheme X



27

Oil



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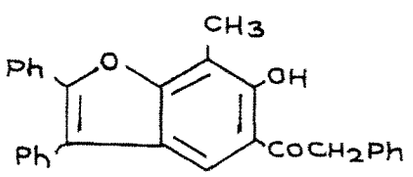
Sodium acetate

Acetic anhydride



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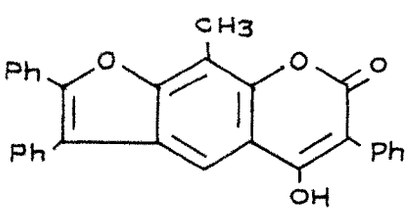
Na

Diethyl carbonate



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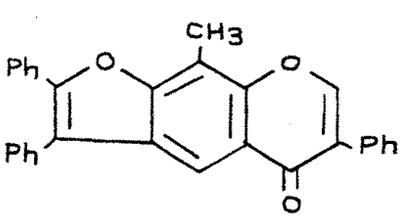
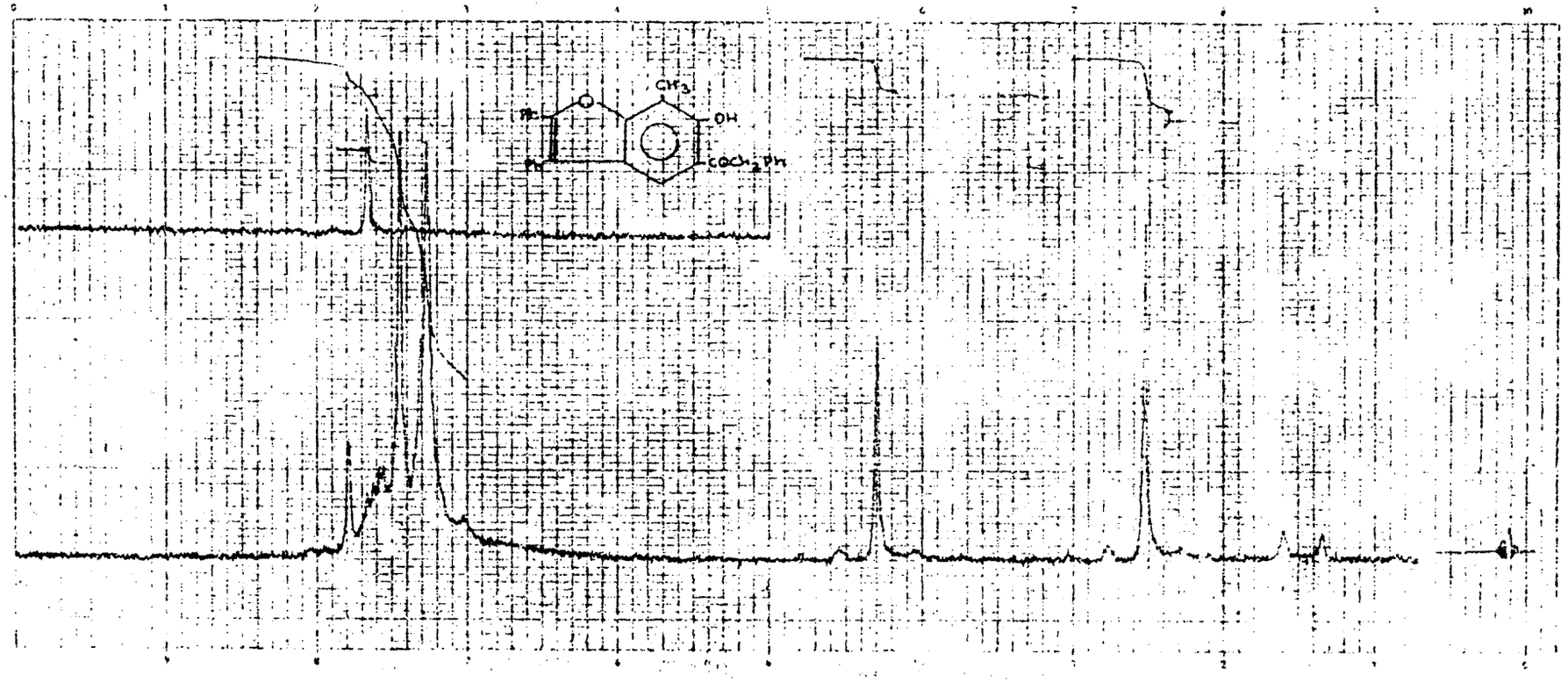
Na,
Ethyl Formate

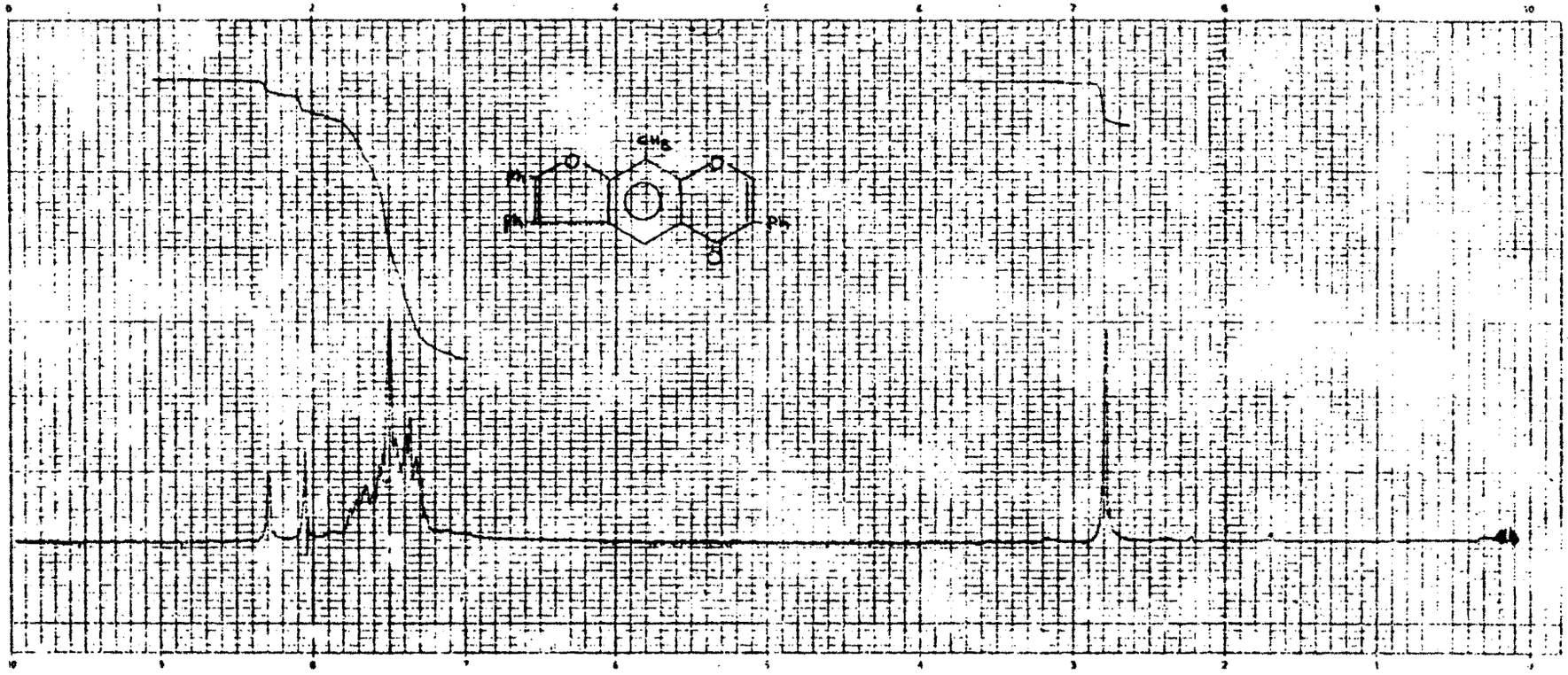


29

as usual to obtain 2-hydroxy-3-methyl-4-desyloxy phenyl benzylketone, in the form of crude oil. This oil without further purification was directly dissolved into O.1N alcoholic KOH solution and refluxed. Excess of solvent was distilled off and reaction mixture acidified to obtain 2,3-diphenyl-6-hydroxy-7-methyl-5-phenylacetyl-benzofuran (28). Structure (28) was confirmed by pmr spectrum giving following signals ($CDCl_3$) : δ 2.4, singlet for 3 protons of methyl group at C-2 ; another singlet at 4.2 for methylene protons of the side chain $ArCOCH_2Ph$; multiplet in the downfield region at 7.3 for 15 aromatic protons singlet for proton at C-5 appeared at 7.7 and other singlet at 12.6 for hydroxyl proton. (Fig.9) Corresponding isoflavone of (29) was synthesized by dissolving it in freshly distilled ethyl formate and solution poured over pulverized sodium. Vigorous reaction took place charging colour of the reaction mixture from yellow to brown. It was poured over crushed ice and next day solid separated. It was crystallized to obtain 2,3,6-triphenyl-9-methyl-furo (3,2-g) (1)-5H-benzopyran-5-one (29). It exhibited following signals in pmr. ($CDCl_3$) ; δ 2.7, singlet for three protons of methyl group at C-9 ; 7.4, multiplet in the downfield region for 15 aromatic protons ; 7.95, singlet for proton at C-2 and another singlet at 8.2 for proton at C-5.(Fig.10)



2-Methyl-3-hydroxy-4-phenylacetyl-6,7-diphenyl benzofuran (28) (Fig.9)

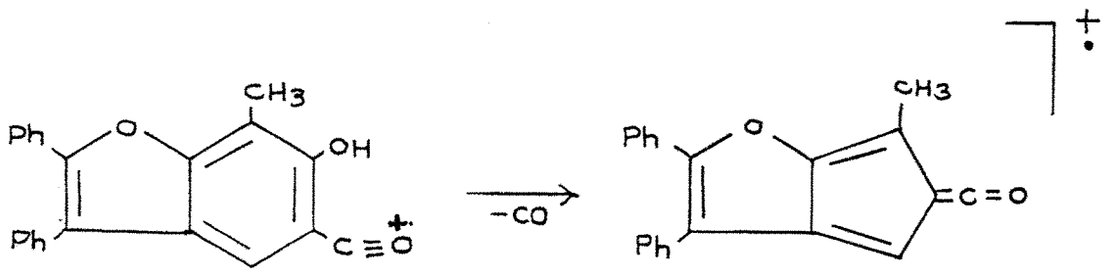


2,3,6-Triphenyl-9-methyl fu..(3,2-g)-1-benzopyran-(5H)-one (29)(Fig 10)

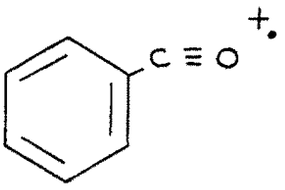
The ketone (28) was thoroughly mixed with anhydrous sodium acetate & refluxed in acetic anhydride. The product was boiled with dilute sodium carbonate solution to hydrolyse acetyl derivative, giving rise to 2,3,6-triphenyl-7,9-dimethyl furo (3,2-g) (1)-5H-benzopyran-5-one (30). (Scheme-X) This compound has high melting point and non-volatile hence no fragmentation is shown in mass spectra thus giving no helpful information. It was crystallized from large quantity of dimethylformamide solvent. It was not soluble in common organic solvents used in NMR studies.

The ketone (28) on condensation with diethyl carbonate and sodium gave 2,3,6-triphenyl-5-hydroxy-9-methyl furo(3,2-g) (1)-7H-benzopyran-7-one (31). Structure (31) was confirmed by mass spectra. m/e : (444) M , 327, 298, 105 (Scheme-XI) (Fig-10A)

Scheme XI :



m/e 327 m/e 298



m/e 105

FILENAME:RL3051.01
COMMENT:SCJ-107

MODE: EI
EV: 70 GAIN: 3.0
IS TEMP: 250 SCAN SPEED: 8
DI TEMP: 140

DATA	R.T.	PEAK	MASS RANGE	BASE PEAK	TOTAL	RAW-	B.G.
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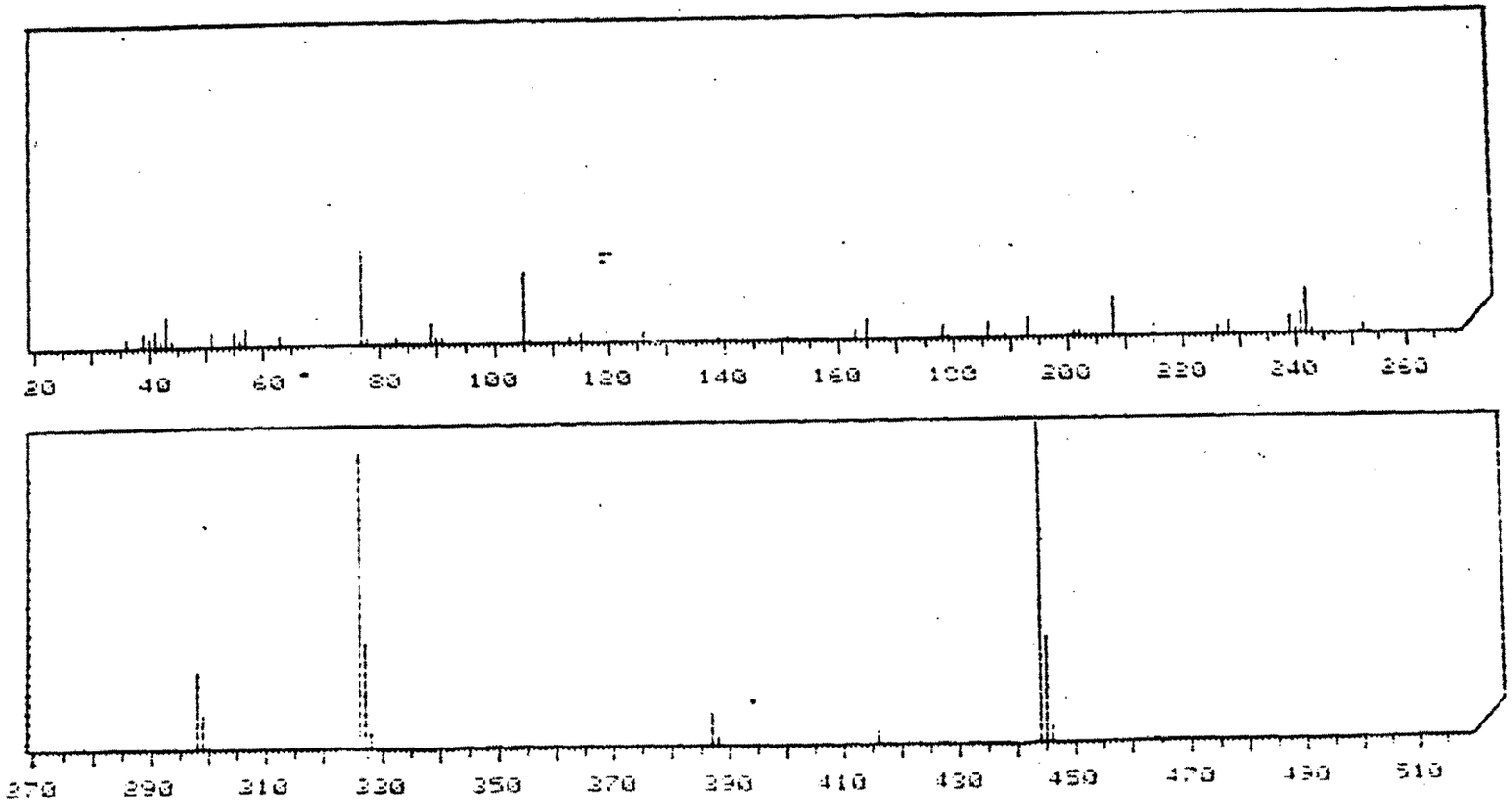
		83	36- 446	400900(444)	2364860	0-	0



2,3,6-triphonyl-5-hydroxy-9-methylfuro(3,2-g)-1- 7H -benzopyran-7-one(31) (Fig. 10A)

experimental

EXPERIMENTAL

All melting points are uncorrected. PMR spectrum recorded on Perkin-Elmer (R-32) (90 MHz) Spectrometer, using TMS as internal standard. Silica-gel used for column chromatography with mesh size 60-120.

7-(cyclohexan-2-onyloxy)-3-phenyl-[4H]-1-benzopyran-4-one (12)

A mixture of 7-hydroxyisoflavone (3.5 g) (11), 2-bromocyclohexanone (2.5 g) and freshly ignited potassium carbonate (12 g) was refluxed in dry acetone (200 ml) on waterbath for 10 h. Reaction mixture was cooled and filtered. Excess of solvent was removed to obtain 7-(cyclohexan-2-onyloxy)-3-phenyl-[4H]-1-benzopyran-4-one (12). It crystallised from benzene. M.p. 216°,yield 3 g.

Analysis : Found : C, 75.9 ; H, 4.9

$C_{21}H_{18}O_4$: requires : C, 75.4 ; H, 5.4%

5,6,7,8-tetrahydro-2-hydroxy-3-phenyl acetyl dibenzofuran (13)

7-(cyclohexan-2-onyloxy)-3-phenyl-[4H]-1-benzopyran-4-one (12) (1 g) was treated with alcoholic potassium hydroxide solution (0.1N, 400 ml) and refluxed for 6 h. Excess of solvent was removed and product separated on acidification

with dilute HCl solution. Product crystallized from light petroleum ether (40-60°). M.p. 140°, yield 600 mg.

Analysis : Found : C, 78.4 ; H, 5.8

$C_{20}H_{18}O_3$: requires : C, 78.4 ; H, 5.9%

2-Hydroxy-3-phenylacetyldibenzofuran (14)

(13) (600 mg) was mixed with DDQ (600 mg) and the mixture was refluxed in dry benzene (100 ml) for 45 min. Excess of solvent was removed and crude product purified by passing through the column of silica gel with benzene as eluent. It crystallized from benzene + light petroleum ether to furnish 2-hydroxy-3-phenylacetyl dibenzofuran (14). M.p. 175°, yield 400 mg.

Analysis : Found : C, 79.1 ; H, 4.4

$C_{20}H_{14}O_3$: requires : C, 79.5 ; H, 4.6%

3-Phenyl-[4H]-benzofuro (3,2-g)-1-benzopyran-4-one (15)

On finely pulerised sodium (400 mg) a solution of (14) (400 mg) in freshly distilled ethyl formate (15 ml) was added slowly in portions. The reaction was allowed to keep at room temperature for 4 h. Reaction mixture was added over crushed ice and separated product crystallized from benzene + ethanol mixture. M.p. 265°, yield 150 mg.

Analysis : Found : C, 80.3 ; H, 3.9

$C_{21}H_{12}O_3$: requires : C, 80.8 ; H, 3.8%

6,7,8,9-Tetrahydro-3-phenyl-4H-benzofuro (3,2-g)-1-benzopyran-4-one (17)

On finely pulverized sodium (1 g), a solution of 5,6,7,8-tetrahydro-2-hydroxy-3-phenylacetyl-dibenzofuran (13) (1 g) in freshly distilled ethylformate (30 ml) was added slowly and cautiously at room temperature. After 4 h, it was added over crushed ice, solid separated and crystallized from benzene to obtain (17). M.p. 180°, yield 300 mg.

Analysis : Found : C, 79.8 ; H, 5.0

$C_{21}H_{16}O_3$: requires : C, 79.7 ; H, 5.0%

3-Phenyl-[4H]-benzofuro (3,2-g)-1-benzopyran-4-ene (15)

(300 mg) of 6,7,8,9-tetrahydro-3-phenyl-[4H]-benzofuro (3,2-g)-1-benzopyran-4-one (17) and palladized charcoal (300 mg) were refluxed togather in boiling diphenylether solvent for 10 h. Excess of solvent was removed by steam distillation and product crystallized from methanol. M.p. 265°, yield 70 mg. M.p. and m.m.p. with authentic sample (15) are identical.

7-(Cyclohexan-2-onyloxy)-8-methyl-3-phenyl-[4H]-1-benzopyran-4-one (19)

A mixture of 7-hydroxy-8-methylisoflavone (18)(2.5g), 2-bromocyclohexanone (1.7 g) and fused potassium carbonate (8 g) was refluxed in dry acetone (200 ml) for 8 h. Reaction

mixture worked up as usual and product crystallized from benzene. M.p. 165°, yield 1 g.

Analysis : Found : C, 75.8 ; H, 6.1

$C_{22}H_{20}O_4$: requires : C, 75.9 ; H, 5.7%

5,6,7,8-Tetrahydro-2-hydroxy-1-methyl-3-phenylacetyl dibenzofuran (20)

(19) (1 g) was treated with alcoholic potassium hydroxide solution (0.1N, 400 ml) and refluxed for 6 h. Excess of solvent was removed and product separated on acidification. It crystallised from benzene to furnish 5,6,7,8-tetrahydro-2-hydroxy-1-methyl-3-phenylacetyl dibenzofuran (20). M.p. 170°, yield 600 mg.

Analysis : Found : C, 79.1 ; H, 6.2

$C_{21}H_{20}O_3$: requires : C, 78.1 ; H, 6.2%

6,7,8,9-Tetrahydro-11-methyl-3-phenyl-[4H]-benzofuro (3,2-g) -1-benzopyran-4-one (21)

On finely pulverized sodium (1 g), a solution of 5,6,7,8-tetrahydro-2-hydroxy-1-methyl-3-phenylacetyl dibenzofuran (20) (1 g) in ethylformate (30 ml) was added slowly and cautiously. Vigorous reaction allowed to subside and after 4 h., reaction mixture poured over crushed ice. The solid product crystallized from benzene. M.p. 215°, yield, 300 mg.

Analysis : Found : C, 79.9 ; H, 5.5

$C_{22}H_{18}O_3$: requires : C, 80.0 ; H, 5.4%

1-Methyl-2-hydroxy-3-phenylacetyl dibenzofuran (22)

(21) (300 mg) was mixed with palladized charcoal (300 mg) in diphenyl ether solvent and refluxed for 10h Excess of solvent was removed by steam distillation and crude product crystallized from benzene to furnish 1-methyl -2-hydroxy-3-phenylacetyl dibenzofuran (22).M.p. 170-72°, yield 70 mg.

Analysis : Found : C, 80.0 ; H, 5.0

$C_{21}H_{16}O_3$: requires : C, 79.9 ; H, 5.0%

7-(Cyclohexan-2-onyloxy)-2-methyl-3-phenyl-[4H]-1-benzopyran-4-one (24)

A mixture of 7-hydroxy-2-methylisoflavone (23) (2.5g) 2-bromocyclohexanone (1.7 g) and fused potassium carbonate (8 g) was refluxed in dry acetone (200 ml) for 10 h. Reaction mixture worked up as usual and product crystallized from benzene M.p. 140°, yield, 1.8g.

Analysis : Found : C, 75.8 ; H, 6.0

$C_{22}H_{20}O_4$: requires : C, 75.9 ; H, 5.7%

5,6,7,8-Tetrahydro-2-hydroxy-3-phenylacetyl dibenzofuran (13)

Above ether (24) (1 g) was treated with alcoholic potassium hydroxide solution (0.1N, 400 ml) and refluxed for 6 h. Excess of solvent distilled off and reaction mixture acidified to furnish the product. It crystallised fromlight petroleum ether. It shows yellow fluorescence in UV light and Rf value identical to (13). M.p. and m.m.p. with authentic sample are similar. Yield, 500 mg.

6,7,8,9-Tetrahydro-2-methyl-3-phenyl-[4H]-benzofuro (3,2-g) -1-benzopyran-4-one (25)

A mixture of 5,6,7,8-tetrahydro-2-hydroxy-3-phenyl acetyl dibenzofuran (13) (1 g), fused sodium acetate (1g) fused sodium acetate (1 g) and acetic anhydride (15 ml) was heated together in oil bath at 170-80° for 10 h. Reaction mixture poured over crushed ice and left overnight. Next day solid was separated, filtered and dried. It crystallised from benzene. M.p. 170-73°, yield, 800 mg.

Analysis : Found : C, 79.8 ; H, 5.6

$C_{22}H_{18}O_3$: requires : C, 80.0 ; H, 5.5%

2-Methyl-3-phenyl-[4H]-benzofuro (3,2-g)-1-benzopyran-4-one (26)

(700 mg) of above isoflavone (25) and palladised

charcoal (700 mg) were refluxed together for 12 h. in boiling diphenylether solvent. Excess of solvent removed and product separated. It crystallized from benzene. M.p. 236-7°, yield 150 mg.

Analysis : Found : C, 81.4 ; H, 4.5

$C_{22}H_{14}O_3$: requires : C, 81.0 ; H, 4.3%

2,3-Diphenyl-6-hydroxy-7-methyl-5-phenylacetyl benzofuran (28)

2,4-Dihydroxy-3-methylphenyl benzylketone (27) (2.42g) desylchloride (2.3 g) fused potassium carbonate (10 g) and few crystals of potassium iodide were mixed and refluxed in dry acetone (200 ml) for 10 h. Reaction mixture filtered and excess of solvent removed by distillation. Brown coloured oily compound was obtained which dissolved in 0.1N alcoholic potassium hydroxide solution (400 ml) and refluxed for 6 h. Excess of solvent ether distilled off and product separated on acidification. It was filtered, dried and crystallized from benzene. M.p. 178-80°, yield 1 g.

Analysis : Found : C, 83.4 ; H, 5.2

$C_{29}H_{22}O_3$: requires : C, 83.2 ; H, 5.3%

2,3,6-Triphenyl-9-methylfuro (3,2-g)-1-benzopyran-5H-one (29)

A solution of above ketone (28) (1 g) in redistilled

ethylformate (30 ml) was added slowly and cautiously on finely pulverized sodium (1 g). Vigorous reaction took place with colour change from yellow to brown. Reaction mixture kept at room temperature for 4 h. It poured over crushed ice and next day solid product separated. It crystallised from benzene to obtain 2,3,6-triphenyl-9-methylfuro (3,2-g)-1-benzopyran-[5H]-one (29). M.p. 205°, yield 400 mg.

Analysis : Found : C, 84.3 ; H, 4.9

$C_{30}H_{20}O_3$: requires : C, 84.1 ; H, 4.7%

2,3,6-Triphenyl-7,9-dimethylfuro (3,2-g) benzopyran-5H-one (30)

A mixture of 6,7-diphenyl-2-hydroxy-1-methyl-3-phenyl-acetylbenzofuran (28) (1 g), fused sodium acetate (1 g) and acetic anhydride (15 ml) was heated togather in oil bath at 170-80° for 10 h. Reaction mixture was added over crushed ice and left overnight. Next day solid separated was filtered and dried. It crystallised from N,N-dimethylformamide solvent to furnish pure (30), M.p. 285-6°, yield 550 mg.

Analysis : Found : C, 83.8 ; H, 4.9

$C_{31}H_{22}O_3$: requires : C, 84.2 ; H, 4.9%

2,3,6-Triphenyl-5-hydroxy-9-methylfuro (3,2-g) benzopyran-7H-one (31)

A solution of 6,7-diphenyl-2-hydroxy-1-methyl-3-phenylacetylbenzofuran (28) (1 g) in diethyl carbonate (30 ml) was added slowly over finely pulverized sodium metal (1 g). Reaction mixture heated in water bath for 5h. Then it poured over crushed ice and left overnight. Next day solid separated was filtered and dried. It crystallised from benzene + light petroleum ether mixture. M.p. 270°, yield 500 mg.

Analysis : Found : C, 80.6 ; H, 4.6

$C_{30}H_{20}O_4$: requires : C, 81.0 ; H, 4.5%

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