STUDIES IN ALICYCLIC SYSTEMS

PART III

Synthesis of Polyesters based on p-Hydoxybenzoic acid

In connection with some other work in our faculty, we were requested to prepare some compounds with thermotropic properties. The importance of these compounds in industry is too well known.

In this section we present in brief the synthesis of 1,2-bis(p-carboxyphenoxy)ethane (I) and 1,4-bis-(p-carboxy)-phenoxybutane[1] (II).

Though aryl esters of p-alkoxybenzoic acids are known to exhibit thermotropism, not much work seems to have been done on polyesters based on p-hydroxybenzoic acid with terminal mesogenic units and a central spacer. Only recently these compounds have been reported to exhibit thermotropic properties.[2]

The required bis-benzoic acids have been reported in as their ethyl or methyl esters mostly in patent literature.[3] These compounds have been prepared by condensing p-hydroxy-benzoates with appropriate dihaloalkanes. In view of the

importance of these compounds, we investigated alternative routes to these compounds.

Condensation of phenol with 1,2-dibromoethane and 1,4-dibromobutane yielded 1,2-diphenoxyethane[4] (III) [m.p. 97°] and 1,4-diphenoxybutane[5] (IV) [m.p. 99°] respectively in appreciable yields.

It has been reported that aryl ethers are extremely sensitive to acylation and that acylation may occur in presence of less powerful catalysts than anhydrous aluminium chloride; even free carboxylic acids have been used as acylating agents. Kosolapoff[6] has reported that anisole can be acetylated by refluxing it with a mixture of glacial acetic acid and phosphoric acid in presence of calcium carbonate. In view of the extreme simplicity of this procedure and the reported very high yields, we attempted the acetylation of diphenoxyethane and diphenoxybutane by this procedure. A mixture of diphenoxyalkane, glacial acetic acid and phosphoric acid anhydride was refluxed in presence of calcium carbonate for two hours. The acyl compounds (V & VI) could be isolated in approximately 10% yields.** Increasing the time of reflux

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** Diacetyldiphenoxybutane (VI) prepared by either method had correct molecular weight (m/e 326) but in the PMR only one $COCH_3$ could be accounted for. It appears that the monoacetyl compound (VII) is formed in major quantity withthe diacetyl compound in only a minor amount. As we had to

(contd on p 150)

or using varying proportions of the reactants had no marked effect on the overall yields.

Friedel Craft's acylation procedure using acetic anhydride and anhydrous chloride gave the diacetyl compounds in excellent yields. (see foot-note).

Oxidation of the diacetyl compounds with alkaline potassium permanganate[7] or sodium hypobromite gave 1,2-bis-(p-carboxy)-phenoxyethane (I) and 1,4-bis-(p-carboxy)-butane (II) as high melting compounds. They were identified as their ethyl esters by comparing with authentic samples prepared by condensing ethyl p-hydroxybenzoate with dibromoethane or dibromobutane.

The conversion of the diacetyl compounds to 1,2-bis-(p.aminophenoxy)ethane and 1,4-bis-(p-aminophenoxy)-butane is in progress. The investigation of the thermotropic properties of these compounds is being done by a separate group

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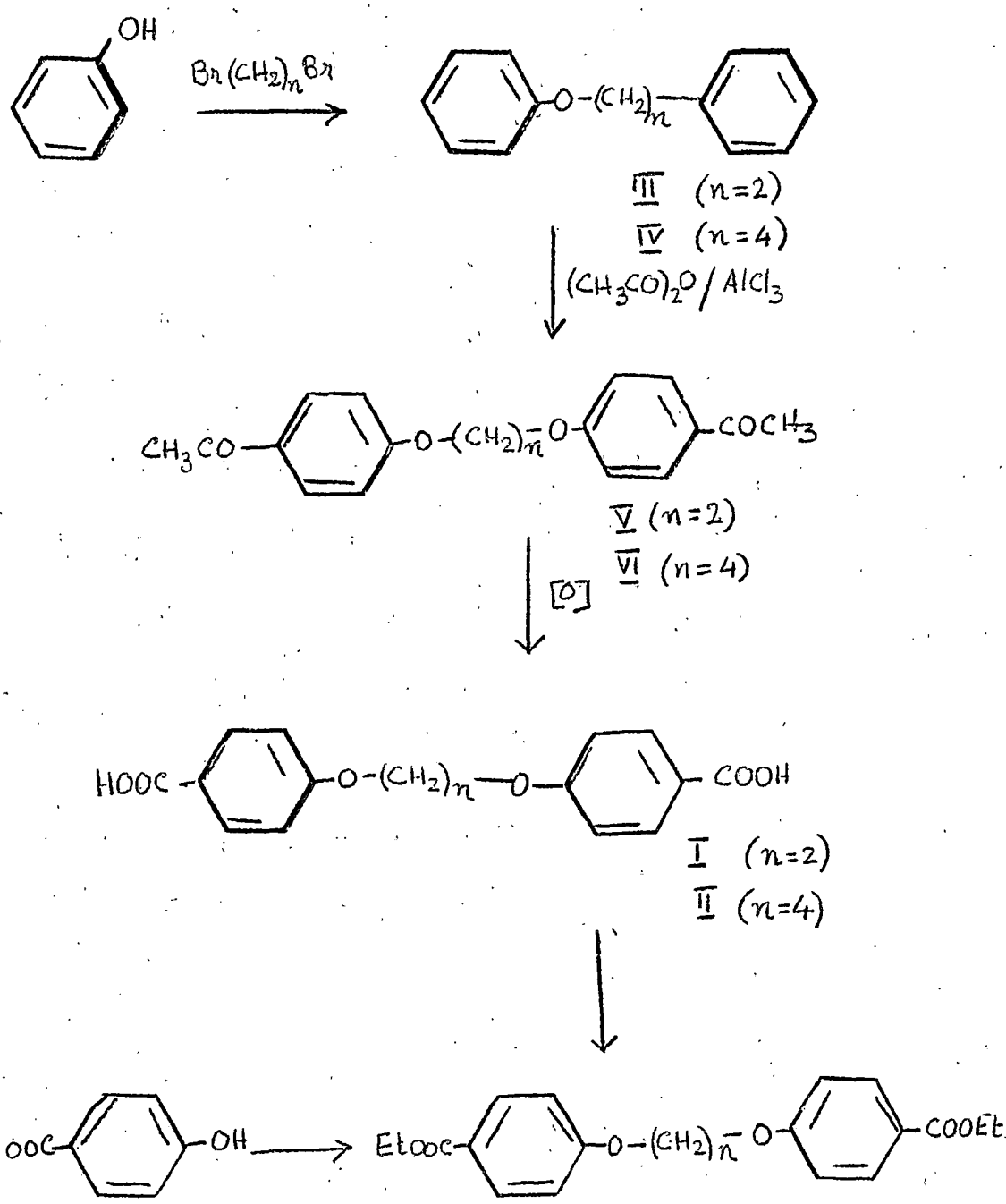
depend on outstation research institutions for Mass and PMR spectra, we made what appeared to us to be a reasonable assumption that the diacetyl compound was formed (as in the case of diphenoxyethane) and proceeded with the next step. Interestingly, the derived diacid was found to be the desired dicarboxylic acid (q.v.)


OH
Br(CH2)nBr
O-(CH2)n
III (n=2)
IV (n=4)
(CH3CO)2O / AlCl3
CH3CO
O-(CH2)n-O
COCH3
V (n=2)
VI (n=4)
[O]
HOOC
O-(CH2)n-O
COOH
I (n=2)
II (n=4)
EtOOC
OH
EtOOC
O-(CH2)n-O
COOEt

of workers in the Department of Physics of our University.

STUDIES IN ALICYCLIC SYSTEMS

PART III

EXPERIMENTAL SECTION

Diphenoxyethane (III) and Diphenoxybutane (IV)

A mixture of phenol (0.2 mole), dibromoalkane (0.1 mole) 10% aqueous sodium hydroxide solution and sufficient rectified spirit to make the solution homogeneous was refluxed for a period of five hours. The reaction mixture was cooled and diluted with water to afford the diphenoxyalkanes.

Diphenoxyethane (III) m.p. 97° (Lit[4] 97°)

IR (nujol) (In cm^{-1}) (Spectrum 36)

1600, 1490, 1450, 1380, 1290, 1250, 1170, 1080, 1050, 920, 880, 790

Diphenoxybutane (IV) m.p. 99° (Lit[5] 98°)

IR (nujol, in cm^{-1}) (Spectrum 37)

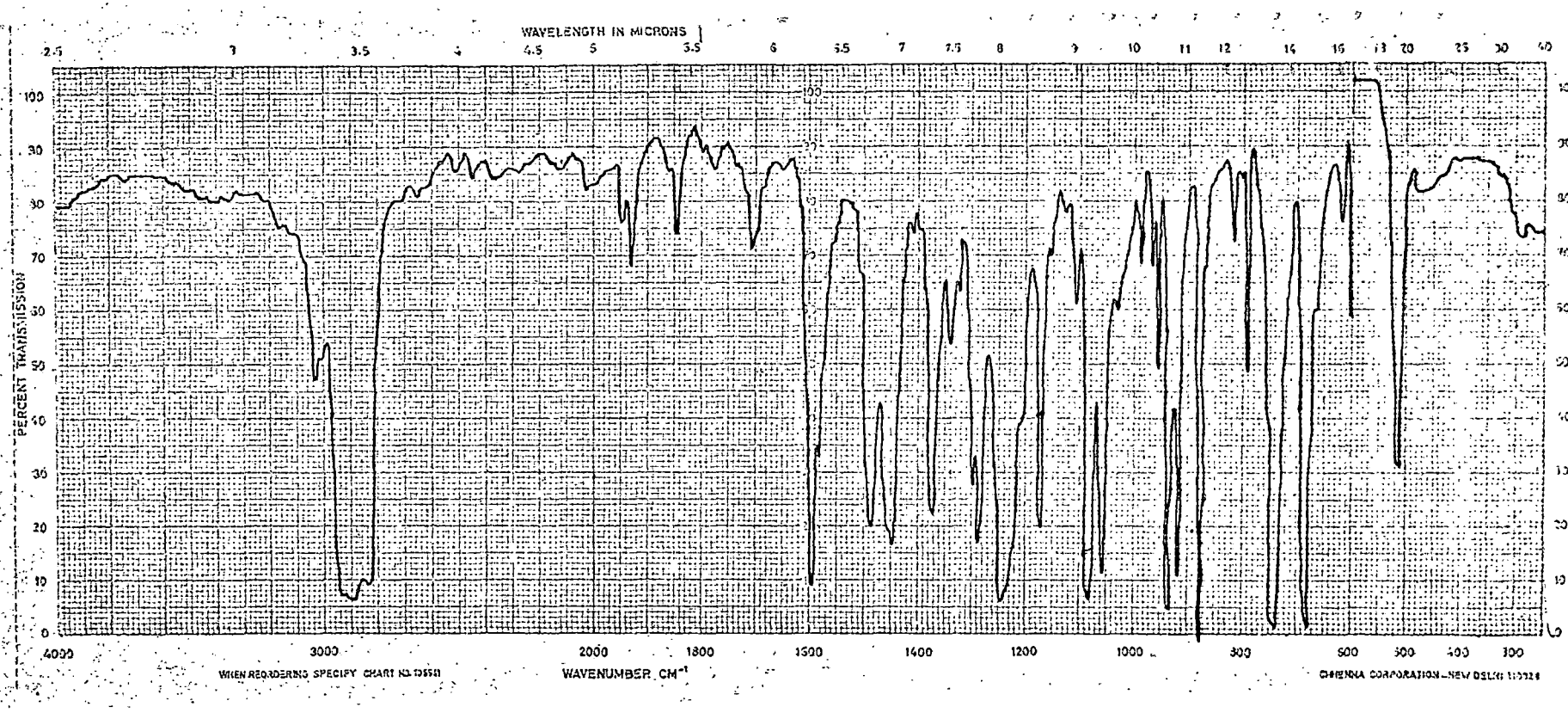
1600, 1490, 1460, 1450, 1380, 1310, 1290, 1250, 1200, 1170, 1080, 1050, 970, 870, 850, 750, 680, 600, 530

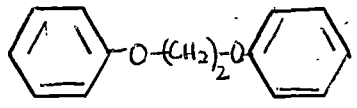
Acetylation of the phenoxyalkanes: Formation of the acetyl compounds (V) and (VI)

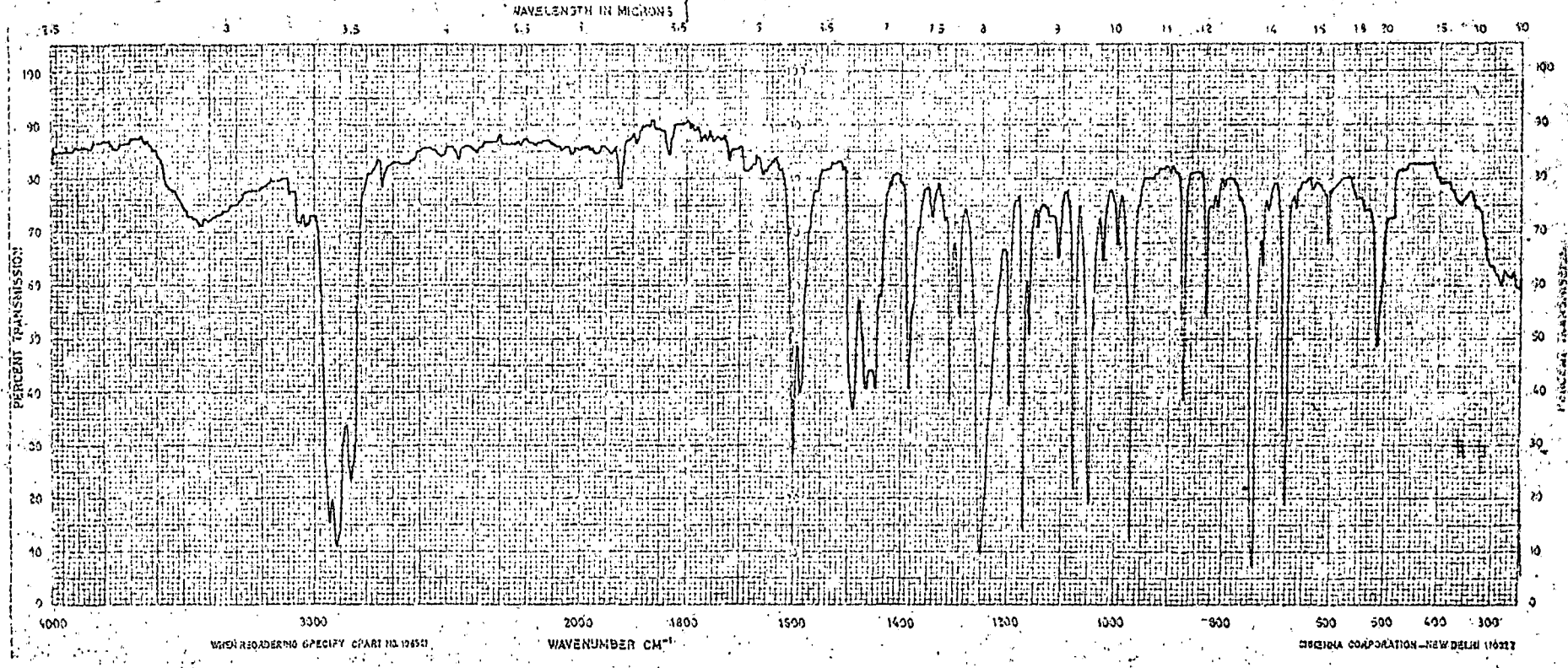
Konalopoff's[6] procedure

A mixture of diphenoxyalkane (0.01 mole), phosphoric anhydride (0.02 mole) and calcium carbonate (1.0 g) in anhydrous benzene (100 ml) was refluxed with glacial acetic

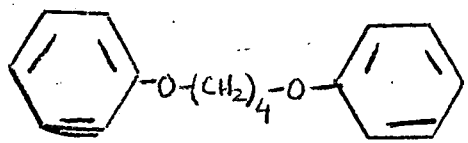
SPECTRUM # 36


WAVELENGTH IN MICRONS
PERCENT TRANSMISSION
WAVENUMBER CM⁻¹
WHEN REORDERING SPECIFY CHART NO. D5501
CHEMNA CORPORATION - NEW DELHI


O-(CH2)2-O


WAVELENGTH IN MICRONS
PERCENT TRANSMISSION
WAVENUMBER CM⁻¹
4000
3300
2000
1800
1600
1400
1200
1000
900
600
500
400
300

SPECTRUM 57


-O-(CH2)4-O-

(0.02 mole) with continuous sitrring for two hours. Usual working up afforded the diacetyl compounds (V) and (VI)*** in approximately 10 % yields.

Diacetyldiphenoxyethane (V) m.p. 159°

IR (nujol, in cm^{-1}) (Spectrum 38)

1680, 1600, 1365, 1310, 1260, 1180, 1120, 1080, 960, 840 820.

PMR (ppm) (Spectrum 39)

2.48 (6H,S), 4.44 (4H,S), 6.8 - 8.0 (8H, m)

Mass (Spectrum 40) (m/e)

298, 283, 256, 214, 163, 121, 120

Diacetyldiphenoxybutane (VI) m.p. 133°

IR (nujol, in cm^{-1}) (Spectrum 41)

1680, 1600, 1365, 1330, 1290, 1260, 1180, 990, 870

PMR (ppm) (Spectrum 42)***

2.45 (3H, S), 3.8 - 4.2 (3H, multiplet), 7.0-8.0 (8H, m)

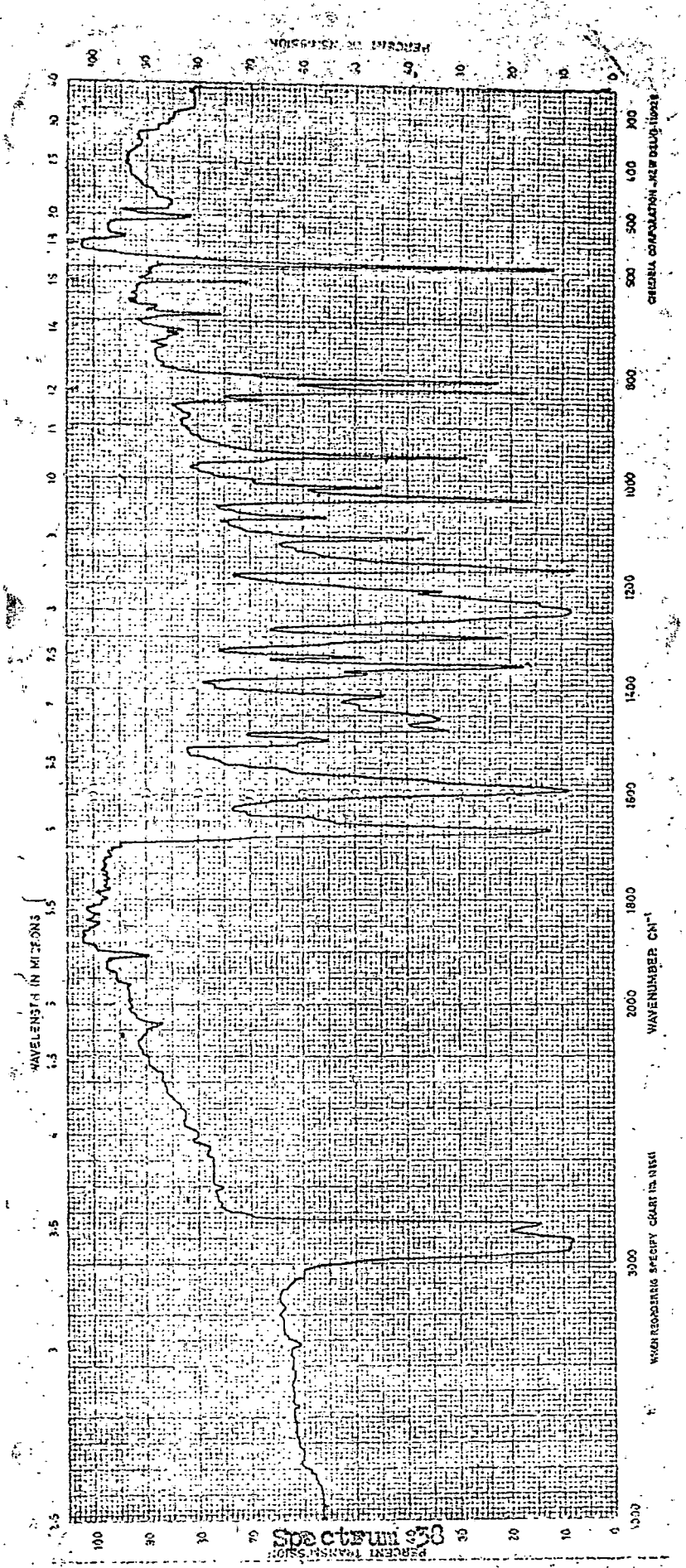
Mass (m/e) (Spectrum 43)

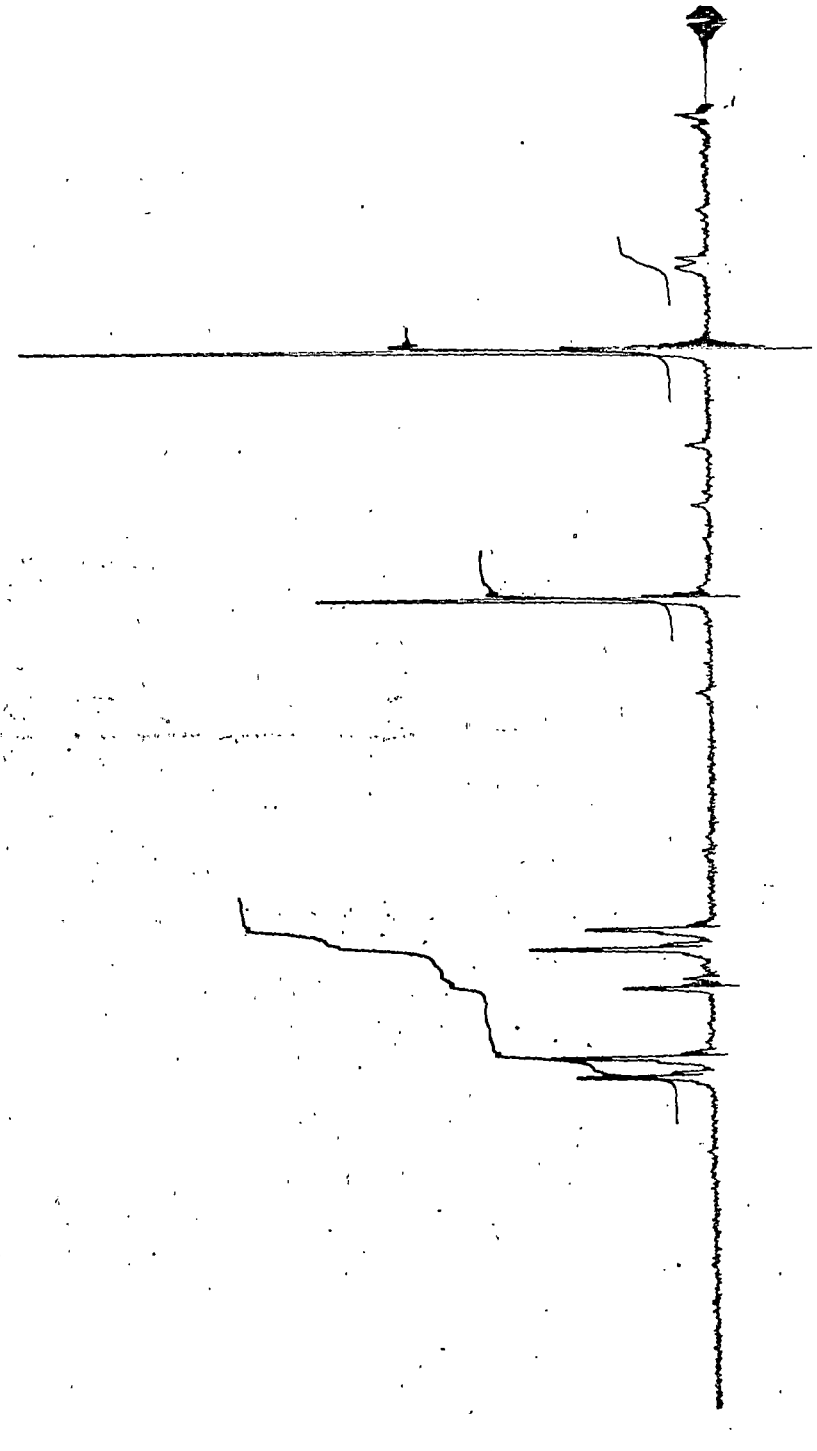
326, 192, 149, 121, 119, 107

Friedel Craft's acylation procedure:

To a mixture of diphenoxyalkane (0.05 mole) and acetic

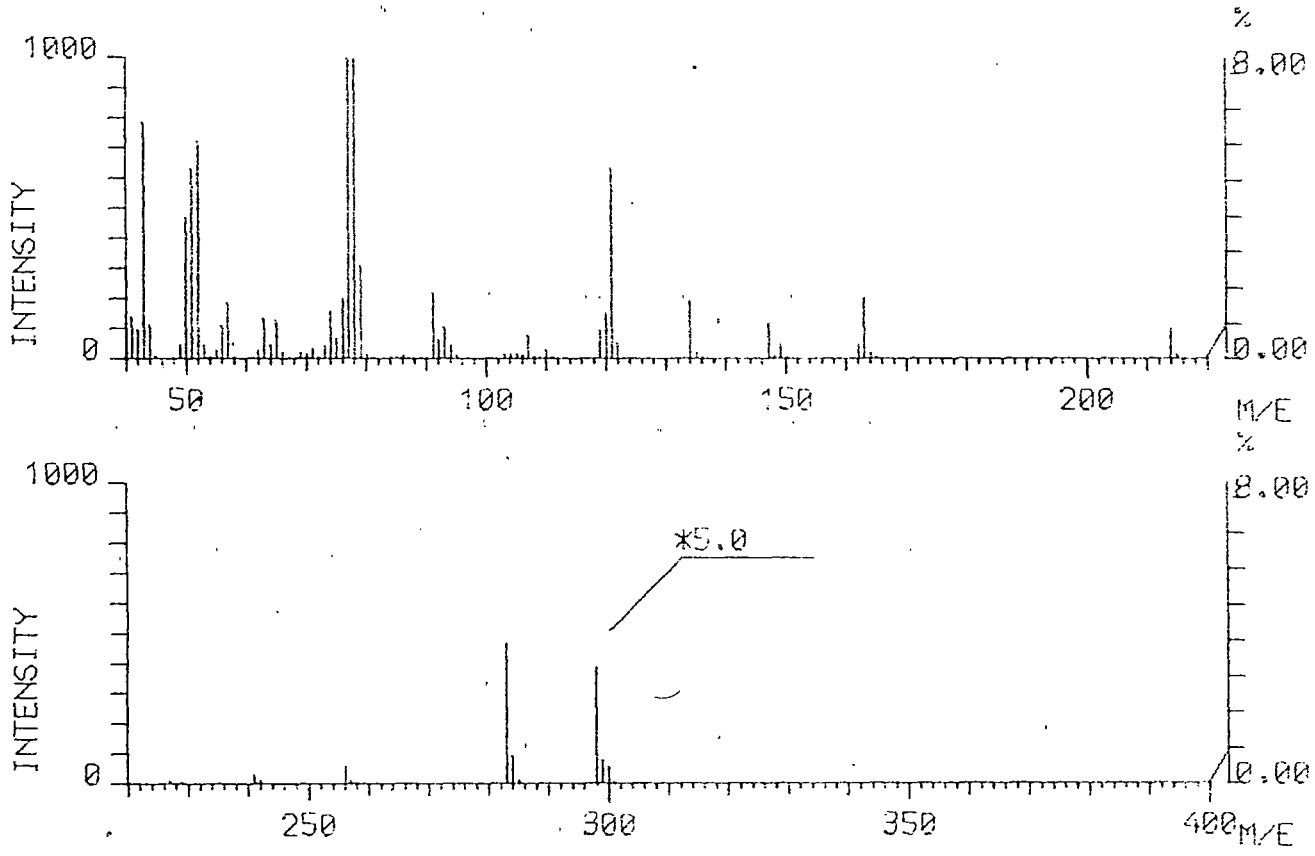
*** Please see the foot note on p- 149.


Spectrum 450
WAVELENGTH IN MICRONS
WAVENUMBER CM⁻¹
PERCENT TRANSMISSION
PERCENT TRANSMISSION

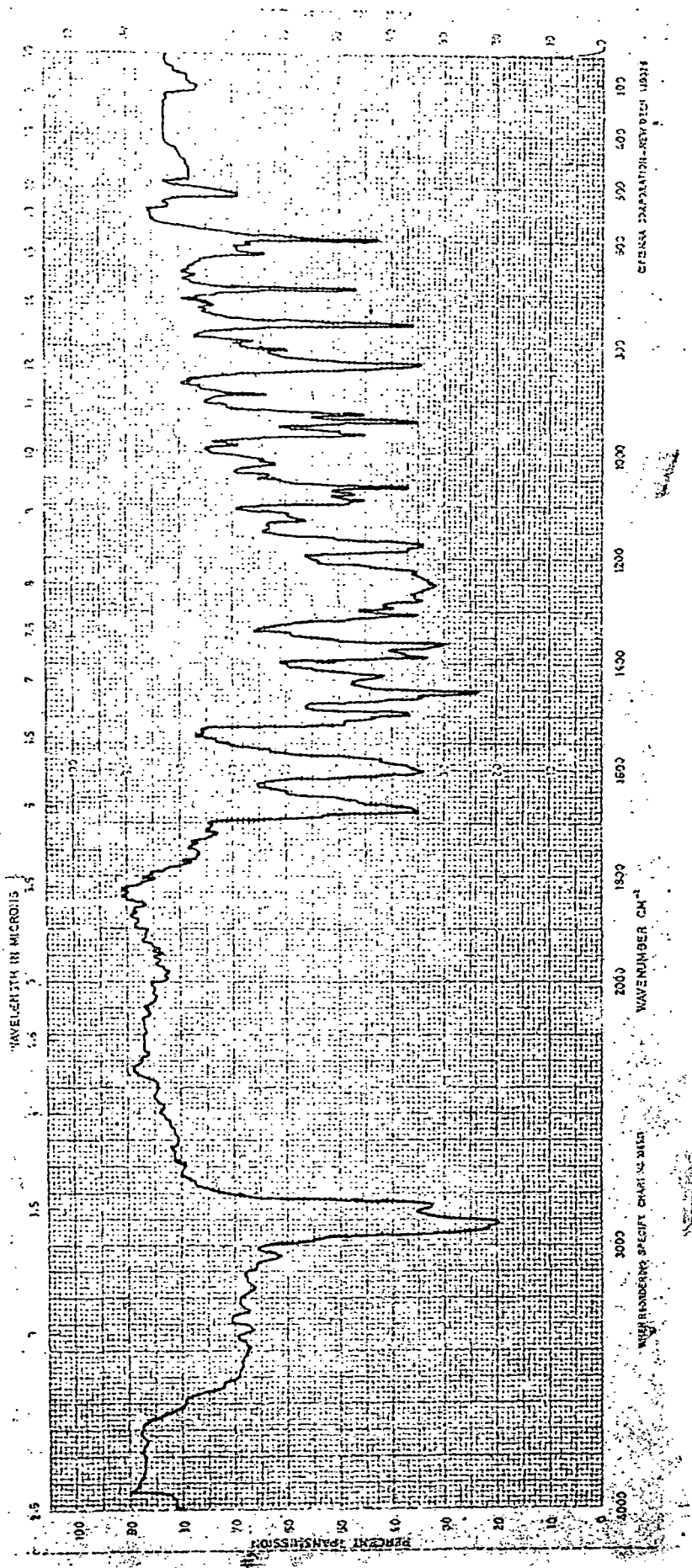


Spectrum 39

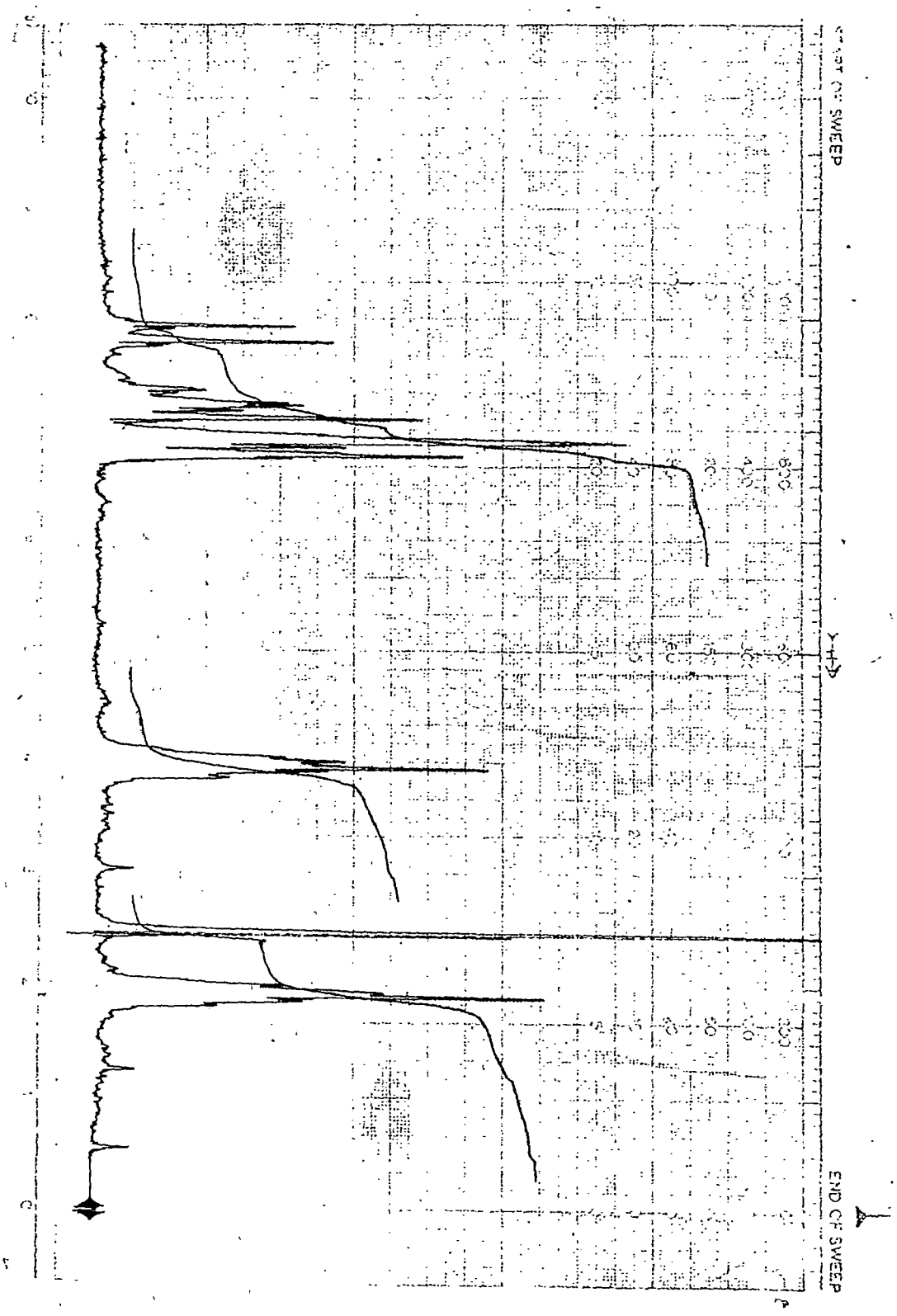
MASS SPECTRUM : (6 TO 7)
SAMPLE:MM-1,DR.P.K.GHOSH,N.W.UNIVERSITY.
NOTE :2ND,AUG.,1982
BASE PEAK . M/E 77.0 INT. 563.0



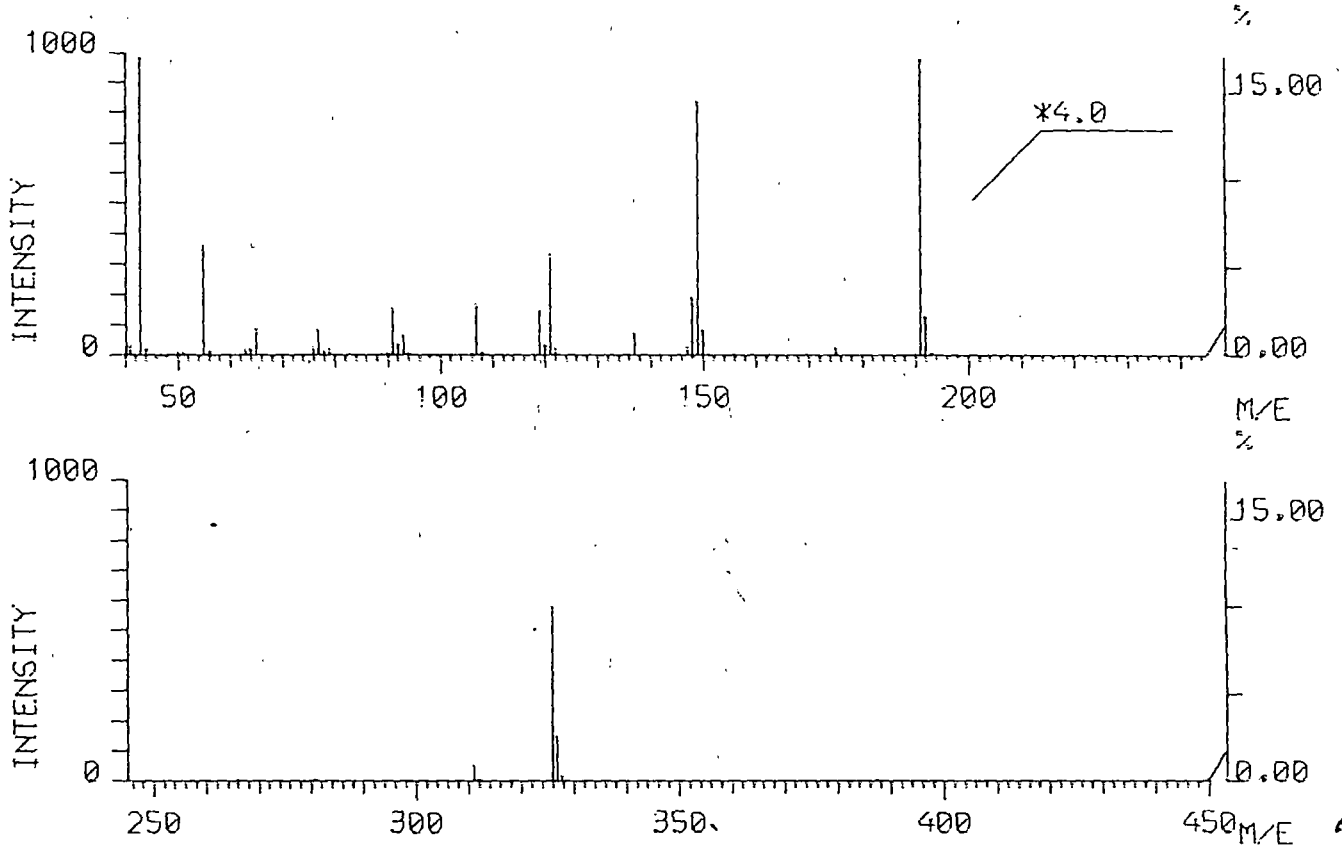
Spectrum 40


WAVELENGTH IN MICRONS
WAVENUMBER CM⁻¹
PERCENT TRANSMISSION

SPECTRUM 41



(Spectrum 42)


1000
INTENSITY
0
50
100
150
200
%
15.00
*4.0
0.00
M/E
1000
INTENSITY
0
250
300
350
400
450
%
15.00
0.00
M/E

Spectrum 43

anhydride (0.1 mole) in carbon disulphide (100 ml) was added with cooling and stirring anhydrous aluminium chloride (0.3 mole) in small lots. After the addition, the reaction mixture was stirred for a period of three hours and left overnight at room temperature. Usual working up gave the acetyl compounds in nearly 80% yields. They were found to be identical with the ones obtained from the previous method.

Dicarboxydiphenoxy alkanes (I) and (II)

Oxidation of the acetyl compounds with alkaline potassium permanganate

The acetyl compound (500 mg) was refluxed with 10% potassium permanganate in 10% aqueous potassium hydroxide solution for two hours. Acidification of the reaction mixture gave the crude diphenoxy acids which were redissolved in sodium carbonate solution and filtered to remove suspended impurities. Acidification gave the acids (I) and (II) as very high melting solids.

1,2-Bis-(p-carboxyphenoxy)-ethane m.p. >250

Mass spectrum 44

m/e 302, 298, 283, 211, 210

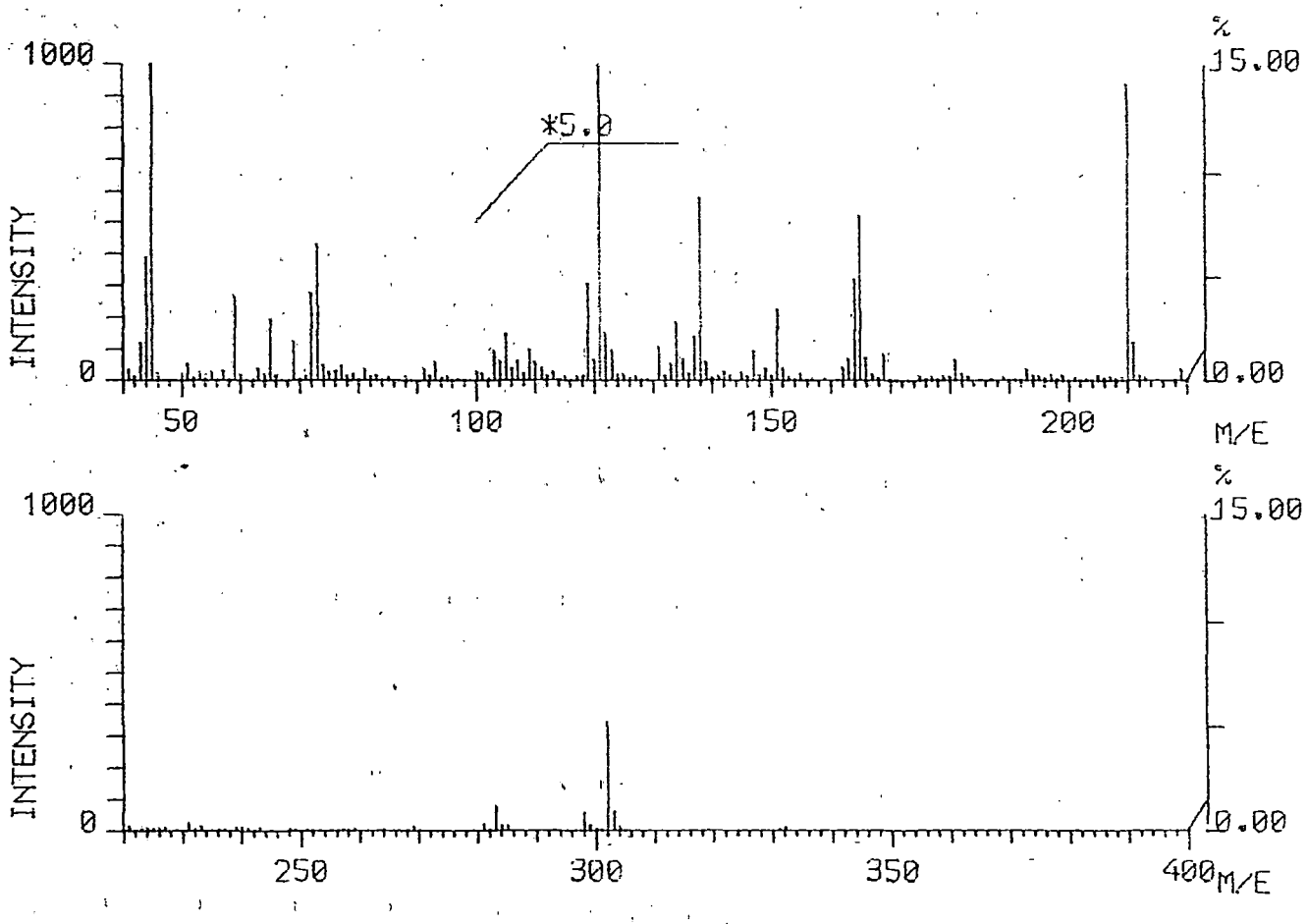
PMR Spectrum 45

1,2-Bis(p-carboxyphenoxy)-butane m.p. >250

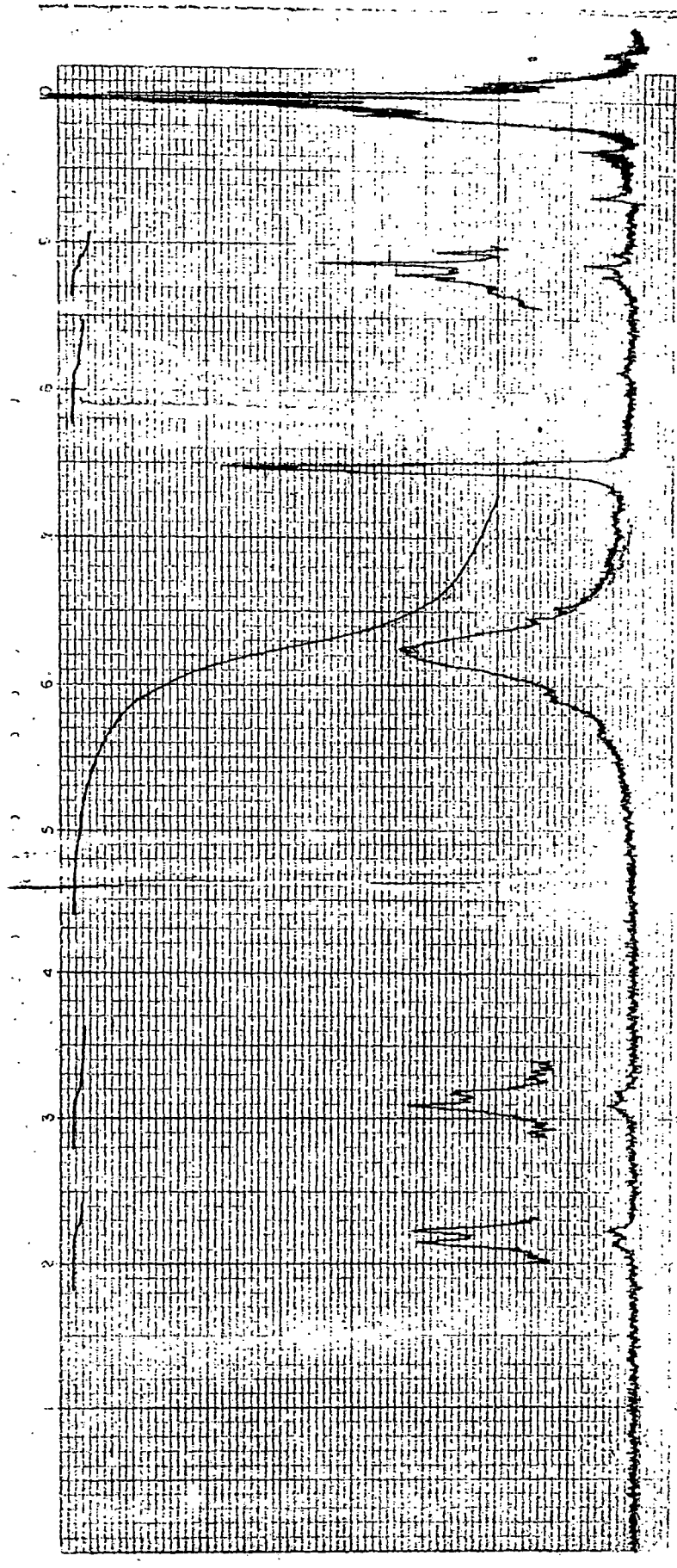
Mass Spectrum 46

m/e 330, 238, 221

MASS SPECTRUM : (9 TO 10)
SAMPLE:MM-3,DR.A.K.KHOSH,N.W.UNIVERSITY
NOTE :2ND AUG.82
BASE PEAK : M/E 45.0 INT. 315.0

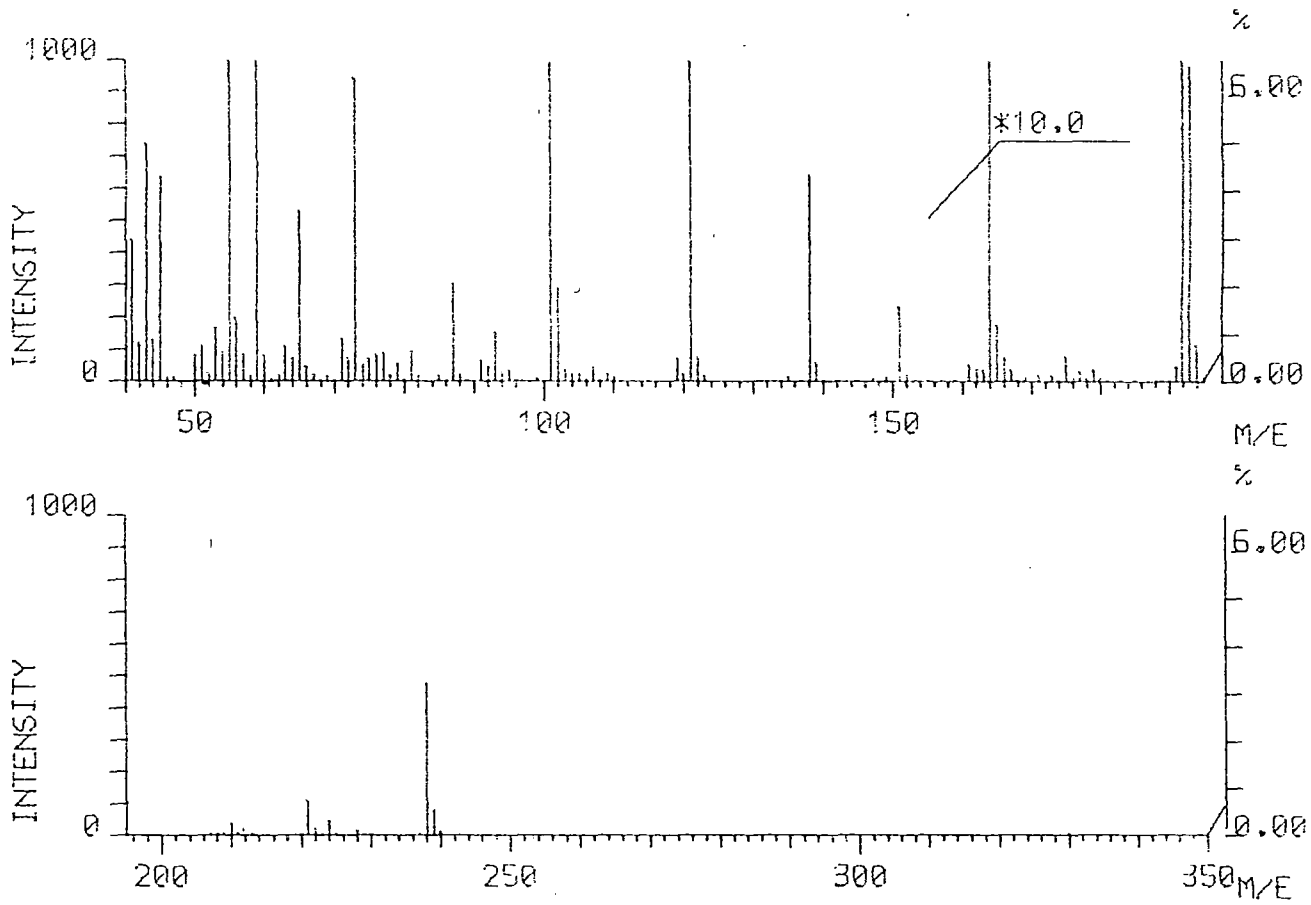


Spectrum 44



SPECTRUM 45

MASS SPECTRUM : (3 TO 4)
SAMPLE.MM-4,DR.A.K.GHOSH,N.U.UNIVERSITY
NOTE .2ND AUG.82
BASE PEAK : M/E 121.0 INT. 633.8



SPECTRUM 46

Oxidation with sodium hypobromite

To a cooled solution of sodium hydroxide (20 g) in water (175 ml) was added bromine (9.5 ml) with stirring. Into this was introduced a solution of the diacetyl compound (0.05 mole) in dioxane with stirring and cooling over a period of one hour. The stirring was continued for a further period of two hours. Usual working up gave the dicarboxylic acids in approximately 30% yields.

The acids were converted into their ethyl esters by standard procedure

1,2-Bis-(p-ethoxycarbonylphenoxy)-ethane m.p. 70°

1,4-Bis-(p-ethoxycarbonylphenoxy)-butane m.p. 85°

The esters showed no depression in melting point on admixture with authentic samples prepared by condensing ethyl p-hydroxybenzoate (0.1 mole) with dibromoalkane (0.08 mole) in presence of sodium carbonate (0.5 g) in methanol (50 ml) containing a little diglyme.

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