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A STUDY OF THE CONDENSATION BETWEEN *O*-PHENYLENEDIAMINE AND PULVINIC ACID DERIVATIVES

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Abstract—The product (IXb) of the condensation at about 200° of *o*-phenylenediamine with pulvinic acid, vulpinic acid and pulvinic dilactone yields by hydrolytic fission 2-benzylbenziminazole and by ozonolysis 2-benzoylbenziminazole. Vulpinic acid methyl ether also gives IXb as the main product and its N-methyl derivative as minor product, showing that under the basic conditions and high temperature used, demethylation of the enol ether and partial transfer of methyl group to nitrogen occur. Methylation of IXb yields the N-methyl compound; this and its spectral properties show that it is in the keto form. At room temperature, vulpinic and pulvinic acids do not react; however, pulvinic dilactone yields two products: (1) an intermediate amide forming IXb on heating and (2) a product resulting from the condensation of one molecule of diamine with two of the dilactone.

By the reaction of *o*-phenylenediamine with pinastric acid, 4-methoxypulvinic dilactone and iso-pinastric acid, only one product (XXIV) is obtained, indicating the formation of the dilactone as an intermediate stage and explaining the cause of discrepancy in the use of this reagent. The ozonolysis and hydrolysis indicate that in the dilactone, the lactone ring near the substituted phenyl group preferentially reacts in agreement with the theoretical expectation.[a]

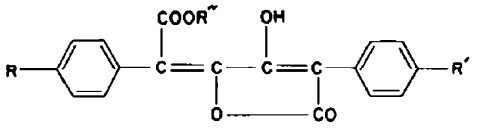
THE condensation of *o*-phenylenediamine with pulvinic acid (I), vulpinic acid (II) and pulvinic dilactone (V) in boiling dimethylaniline was first studied by Schönberg and Sina[1] who obtained the same orange product in each case. As fission with alcoholic alkali yields potassium oxalate and 2-benzylbenziminazole (VII), it was concluded that the amine reacts with the acid or ester group to give the benziminazole (IXa).

Later, this reaction was employed by Seshadri *et al.*[2–6] to determine the position of the substituent in the benzene rings of unsymmetrical derivatives of vulpinic acid, namely leprapinic acid, pinastric acid (III), isopinastric acid (IV) and methyl 4-bromopulvinate and when the condensation product (X) obtained in each case was cleaved with alcoholic alkali, it gave 2-(substituted benzyl)-benziminazole (VIII), thus suggesting that the substituent group in these compounds is attached to the benzene ring close to the ester group. However, results obtained by the reduction[7] and ozonolysis[8] of pinastric acid and isopinastric acid show conclusively that in the former, the methoxyl group is present in the second benzene ring as given in III and that it is a position isomer of isopinastric acid (IV). This indicated the possibility

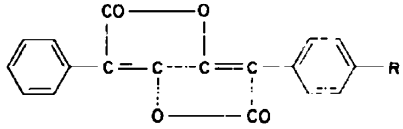
[1] A. Schönberg and A. Sina, *J. Chem. Soc.* 601 (1946).
[2] O. P. Mittal and T. R. Seshadri, *J. Chem. Soc.* 3053 (1955).
[3] O. P. Mittal and T. R. Seshadri, *J. Chem. Soc.* 1734 (1956).
[4] P. K. Grover and T. R. Seshadri, *Tetrahedron* **4**, 105 (1958).
[5] P. K. Grover and T. R. Seshadri, *Tetrahedron* **6**, 312 (1959).
[6] P. K. Grover and T. R. Seshadri, *J. Chem. Soc.* 2134 (1960).
[7] S. C. Agarwal and T. R. Seshadri, *Indian J. Chem.*, in press.
[8] S. C. Agarwal and T. R. Seshadri, *Tetrahedron* **19**, 1965 (1963).

of error in the use of *o*-phenylenediamine reaction and the need to study it in more detail.

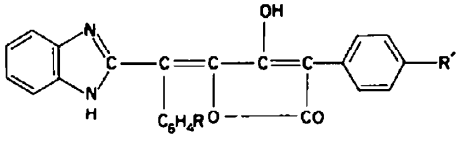
A preliminary investigation was first carried out with vulpinic acid, pulvinic dilactone and vulpinic acid methyl ether (XI) under varying conditions. The condensation of *o*-phenylenediamine with the first two in boiling dimethylaniline yields an orange coloured compound agreeing with the description of IXa by Schönberg and Sina.[1] However, a better yield has now been obtained from the dilactone, the reaction



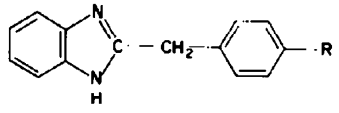
I R, R′, R″ = H
II R, R′ = H; R″ = CH_3
III R = H; R′ = OCH_3; R″ = CH_3
IV R = OCH_3; R′ = H; R″ = CH_3



V R = H
VI R = OCH_3



IXa R, R′ = H
X R, R′ = Substituent

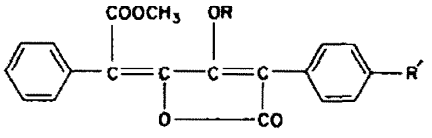


VII R = H
VIII R = Substituent

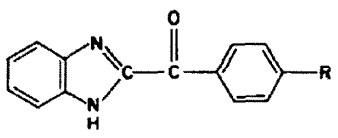
proceeding in less time and even at a lower temperature (180°). Since the usual reaction conditions are fairly vigorous, the above observations raise the possibility of the hydroxy ester yielding the dilactone by elimination of methanol. That this really happens became clear from the fact that vulpinic acid on being heated at about 192°, either alone or with dimethylaniline, changes into pulvinic dilactone. The diamine condensation product (IXa) when subjected to fission with alcoholic potash gives 2-benzylbenziminazole and other products as reported earlier,[1] and its ozonolysis furnishes 2-benzoylbenziminazole (XIII) along with benzoylformic acid and benzoic acid agreeing with the given structure. 2-Benzoylbenziminazole needed for comparison has now been made by the chromium trioxide oxidation of the easily available 2-benzylbenziminazole[9] instead of the α-hydroxy compound used earlier.[10]

The reaction was next studied at room temperature so that dilactone formation would not interfere. Pulvinic acid and vulpinic acid do not undergo any condensation but pulvinic dilactone reacts readily to give two products. The first, an orange compound (m.p. 179–180°) having the composition $C_{24}H_{18}O_4N_2$, gives a green ferric reaction and is similar in its IR spectrum to pulvinic acid anilide (XV), rhizocarpic

[9] J. B. Wright, *Chem. Revs.* **48**, 401 (1951).
[10] A. Bistrzycki and G. Przeworski, *Ber. Dtsch. Chem. Ges.* **45**, 3492 (1912).

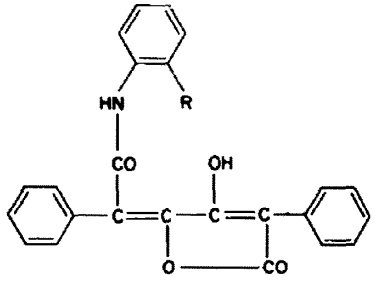


XI R = CH_3; R′ = H
XII R = CH_3; R′ = OCH_3

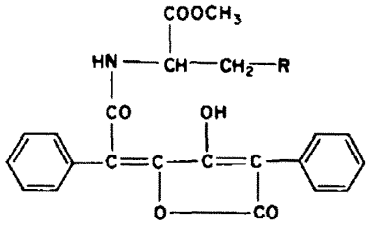


XIII R = H
XIV R = OCH_3

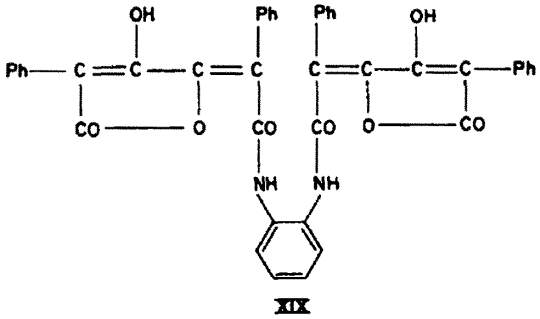
acid (XVII) and epanorin (XVIII).[11] It may, therefore, be concluded that it has the amide structure (XVI) and this was confirmed by its conversion to the final condensation product (IXa) when heated alone or in dimethylaniline at 180°. It thus represents an intermediate stage in the condensation. The second product, a yellow compound (m.p. 256–258°) which does not give any ferric reaction, does not give IXa on heating alone or with dimethylaniline. Its composition and properties suggest the structure XIX resulting from the condensation of one molecule of the diamine with two of pulvinic dilactone.



XV R = H
XVI R = NH_2



XVII R = C_6H_5
XVIII R = $CH(CH_3)_2$



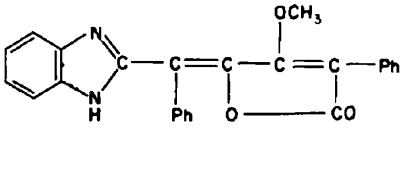
XIX

Another possible method of excluding dilactone formation is the use of vulpinic acid methyl ether (XI); the condensation product could be separated into two fractions. The main fraction was found to be identical with IXa whereas the

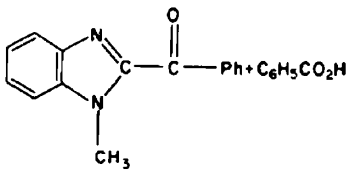
[11] R. L. Frank, S. M. Cohen and J. N. Coker, *J. Amer. Chem. Soc.* 4454 (1950).

other fraction, a yellow compound, agreed in all its properties with the product obtained by methylation of IXa with dimethyl sulphate or diazomethane. Schönberg and Sina[1] earlier recorded that this methylation product has no active hydrogen and considered it to be an O-methyl ether (XX). However, when subjected to ozonolysis, the methylated product affords benzoic acid and a low melting colourless solid which agrees with 1-methyl-2-benzoylbenziminazole (XXI), obtained by the methylation of 2-benzoylbenziminazole. It contains no methoxyl, but has an N-methyl group which proves that the yellow compound is really an N-methyl derivative (XXII) and not an O-methyl ether (XX). Methylation of IXa has therefore taken place as in simple benziminazoles[12] and gives an N-methyl compound.

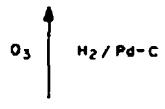
These results would suggest that under the basic conditions of boiling dimethylaniline, demethylation and lactonization of the enol ether first occur and later reaction with *o*-phenylenediamine yields the orange condensation product (IXa) as the main entity, along with a small yield of the yellow N-methyl derivative (XXII) the isolation and preparation of which suggest the following: (i) the methyl group removed from the ether is used for part methylation of the NH group and (ii) that the condensation product is not in the enol form (IXa) but is present in the keto form (IXb). This is supported by its IR spectrum which shows a characteristic carbonyl absorption band at 1724 cm^{-1} besides an inflexion at higher frequency for the lactone carbonyl.

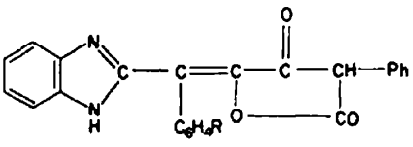


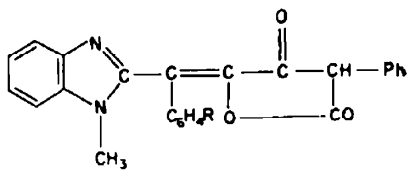
XX



XXI







IX b R = H

XXIV R = OCH_3

XXII R = H

XXIII R = OCH_3

In order to further study this point, vulpinic acid methyl ether was condensed with *o*-phenylenediamine under milder conditions. There is no reaction in dimethylaniline solution at room temperature. However, when the mixture is heated in boiling pyridine solution, demethylation of the enol ether takes place yielding the hydroxy ester i.e., vulpinic acid, and there is no condensation. If the heating is prolonged even the ester group is demethylated.

[18] J. B. Wright, *Chem. Revs.* **48**, 479 (1951).

Condensation of o-*phenylenediamine with pinastric acid* (III), *isopinastric acid* (IV) *and 4-methoxypulvinic dilactone* (VI)

This gives the same condensation product, as reported earlier by Seshadri *et al.*[3,4,5] and the yield is much better with the dilactone than with either of the isomeric esters and it is particularly poor with pinastric acid. The formation of a single condensation product suggests that the dilactone is the intermediate stage thereby eliminating the isomeric differences of pinastric and isopinastric acids. The poor yield from pinastric acid may be due to its more difficult conversion to the corresponding dilactone. Fission of the condensation product with alcoholic potash yields 2-(*p*-methoxybenzyl)-benziminazole (VIII, R = OCH_3) as reported earlier.[5] Phenylacetic acid and *p*-methoxyphenylacetic acid have also been isolated and this indicates that its constitution should be represented by XXIV and that under the conditions of the reaction, the ring near the substituted phenyl opens and the other becomes stable. This is supported by the ozonolysis of the condensation product which yields 2-(*p*-methoxybenzoyl)-benziminazole (XIV) accompanied by anisic and benzoic acids. For comparison, an authentic sample of 2-(*p*-methoxybenzoyl)-benziminazole was prepared by chromium trioxide oxidation of 2-(*p*-methoxybenzyl)-benziminazole.

The results are satisfactorily explained only if the esters, pinastric and isopinastric acids, undergo conversion to the dilactone before entering into condensation with the diamine. The formation of small amount of *p*-methoxyphenylacetic acid during alkali hydrolysis and of anisic acid during the ozonolysis of the condensation product is unusual and may be brought about by the further decomposition of *p*-methoxybenzyl and *p*-methoxybenzoyl benziminazoles respectively.

Condensation of o-*phenylenediamine with pinastric acid methyl ether*

Earlier, the condensation of *o*-phenylenediamine with pinastric acid methyl ether was carried out by Grover and Seshadri[6] and they concluded that the ester group alone reacts and that the lactone ring is not involved because the product obtained has two methoxyl groups. It may be mentioned, that the methoxyl estimation by Zeisel's method repeatedly gave low values unless Zeisel's method was followed by Herzig-Meyer procedure. This was attributed to the possible partial migration of the methyl group to nitrogen. As a result of the present study these observations need correction. The condensation results in the formation of XXIV as the main product together with a yellow compound, identical with the product obtained by the methylation of XXIV. This yellow compound has only one methoxyl group, as shown by Zeisel's method, whereas two methoxyl groups would be expected, if the condensation product is the O-methyl derivative of XXIV. This shows that it is an N-methyl derivative (XXIII) and that in this case also lactone ring closure takes place in the first stage involving demethylation (cf. condensation of *o*-phenylenediamine with vulpinic acid methyl ether).

EXPERIMENTAL

M.ps are uncorrected. UV spectra have been measured with a Hilger spectrophotometer in methanol solution. The IR spectra have been recorded with a Perkin-Elmer Infracord Model 137. Light petroleum had the boiling range 60–80°.

(i) *Condensation of vulpinic acid* (II)

Vulpinic acid (0·5 g; 1 mole) with *o*-phenylenediamine (0·23 g; 1·4 moles) in N,N-dimethylaniline according to Schönberg and Sina[1] gave IXb which crystallized from acetone as orange needles

(0·210 g), m.p. 312–314° (lit.[1] 312–314°); λ max 265 mμ (log ε 4·28); IR (KBr): 3344 (m), 1754 (inf.) 1724 (s), 1592 (s), 1534 (s), 1495 (m), 1447 (m) cm^{-1}. It gave negative ferric reaction.

Pulvinic dilactone (1 g), *o*-phenylenediamine (0·46 g) and dimethylaniline (25 ml) were heated under reflux for 1 hr; on cooling, orange needles of IXb (0·84 g) separated out.

(ii) *Ozonolysis of* (IXb)

A stream of ozonized oxygen (2%; 150 ml/min) was passed through a solution (ca. −15°) of the condensation product (0·75 g) in dry ethyl acetate (270 ml), till the orange colour of the solution almost disappeared (ca. 0·5 hr). The solution was then shaken with hydrogen in the presence of palladized charcoal (5% Pd; 0·7 g) until the rapid absorption ceased. The filtrate was concentrated to 80 ml (red. press.) and extracted repeatedly (5% $NaHCO_3$ Aq.). The residual ethyl acetate solution contained the non-acidic fraction. The bicarbonate extract on working up as mentioned in an earlier publication[8] gave benzoylformic acid and benzoic acid.

The residual ethyl acetate solution was dried ($MgSO_4$) and the solvent removed (red. press.). The brown residue was first crystallized from a mixture of benzene and light petroleum and finally from benzene yielding colourless needles, m.p. 210–211°, undepressed when mixed with 2-benzoyl benziminazole (XIII).

2-Benzoylbenziminazole required for comparison was prepared as follows: A solution of 2-benzyl-benziminazole[18] (0·1 g) in glacial acetic acid (10 ml) was mixed with chromium trioxide (0·4 g) dissolved in glacial acetic acid (10 ml) and the mixture heated at 100° for 10 min. It was kept for 0·5 hr at room temp. and extracted with ether. The residue left on evaporation of the ether extract crystallized from benzene as colourless needles, m.p. 210–212° alone or mixed with the sample obtained by the procedure of Bistrzycki *et al.*[10]; IR (KBr): 2882 (s), 1656 (s), 1600 (m), 1511 (m), 1486 (m), 1429 (s) cm^{-1}.

(iii) *Methylation of* (IXb)

(a) The yellow solid obtained by methylation of the condensation product (IXb) in dilute aqueous alkali using dimethyl sulphate,[1] crystallized from acetone as yellow hexagonal plates (XXII), m.p. 326–328° (lit.[1] 325–326°); it was insoluble in alkali; IR (KBr): 3600 (m), 3106 (m), 1754 (inf.) 1736 (s), 1582 (s), 1499 (s), 1471 (s), 1447 (m) cm^{-1}. (Found: C, 76·3; H, 5·0; N–CH_3, 7·0. Calc. for $C_{28}H_{18}O_3N_2$: C, 76·1; H, 4·6; N–CH_3, 7·4%). Zeisel's method gave no methoxyl value. Ferric reaction was negative.

(b) Methylation of IXb (0·9 g; 1 mole), with dimethyl sulphate (0·1 ml; 1 mole) and potassium carbonate (4 g) in boiling dry acetone (80 ml) for 4 hr gave the same product in better yield.

Ozonolysis of the methylation product (0·5 g) was carried out in dry ethyl acetate (350 ml) and worked up as in (ii). The sodium bicarbonate extract yielded benzoic acid, m.p. 120–121°.

Evaporation of the residual ethyl acetate solution (red. press.) gave a semisolid which was extracted with light petroleum. The extract on concentration (1 ml) and cooling (−20°) deposited colourless needles and the small amount could not be further purified, m.p. (crude) 64–68° unchanged on admixture with an authentic sample of XXI (m.p. 69–71°) which was prepared by refluxing 2-benzoylbenziminazole (1·1 g; 1 mole), ignited potassium carbonate (4 g) and dimethyl sulphate (0·5 ml; 1 mole) in dry acetone for 4 hr. It crystallized from light petroleum as colourless needles, m.p. 69–71°; λ max 265, 306 mμ (log ε 3·98, 4·18); IR (Nujol): 1661 (s), 1577 (w), 1562 (w) cm^{-1}. (Found: C, 75·8; H, 5·3; $C_{15}H_{12}N_2O$ requires: C, 76·3; H, 5·1%).

(v) *Condensation of pulvinic dilactone and o-phenylenediamine at room temperature*

A solution of pulvinic dilactone (1·0 g; 1 mole), *o*-phenylenediamine (0·37 g; 1 mole) and dimethylaniline (15 ml) was kept stirred at room temp. (25°) for 2 hr. An orange coloured compound separated out which was filtered off (filtrate A). The residue (0·7 g) was washed with ice cold dil. HCl followed with water. It crystallized from ethyl acetate–light petroleum as orange rectangular plates, m.p. 179–180° (dec.); λ max 224, 300 mμ (log ε 4·39; 4·46); IR (Nujol): 3268 (sh), 1838 (w), 1761 (m), 1658 (w), 1600 (m) cm^{-1}. (Found: C, 71·6; H, 4·9; N, 6·5. $C_{34}H_{18}O_4N_2$ requires: C, 72·4; H, 4·5; N, 7·0%). It was sparingly soluble in $NaHCO_3$ aq., soluble in Na_2CO_3 and NaOH, difficultly soluble in warm conc HCl and readily soluble in hot alcohol, benzene and ethyl acetate.

[18] R. Walther and T. von Pulawski, *J. prakt. Chem.* **59**, 253 (1899).

It gave a green ferric reaction. When heated to 180° either alone or in dimethylaniline, it was converted to the orange compound (IXb), m.p. 312–314°.

A yellow precipitate (0·3 g) was obtained on addition of cold dil. HCl to the filtrate A. It was treated with ethyl acetate (10 ml) and filtered; the residue crystallized from ethyl acetate–light petroleum as pale yellow plates, m.p. 256–258° (dec.); λ max 231, 299 mμ; IR (Nujol): 3900 (m), 1770 (m), 1658 (w), 1613 (s) cm^{-1}. (Found: C, 73·5; H, 4·6; N, 4·3. $C_{42}H_{28}O_6N_2$ requires: C, 73·2; H, 4·1; N, 4·1%). It was insoluble in $NaHCO_3$ aq., and HCl but dissolved slowly in Na_2CO_3 and readily in NaOH. It gave no ferric reaction.

Pulvinic acid anilide (XV) was prepared from pulvinic dilactone according to Schenck.[14] It crystallized from benzene–light petroleum as yellow plates, m.p. 191–192° (lit.[14] 187–188°); IR (Nujol): 3900 (m), 1779 (m), 1706 (w), 1667 (w), 1618 (m), 1546 (m), 1460 (s) cm^{-1}.

(v) *Condensation of vulpinic acid methyl ether* (XI) *with o-phenylenediamine*

(a) The methyl ether (0·84 g; 1 mole), *o*-phenylenediamine (0·3 g; 1·1 moles) and dimethylaniline (20 ml) were refluxed (ca. 210°) for 2·5 hr. The solution was concentrated (8 ml) under red. press. and ice cold HCl added with stirring. The solid product on fractional crystallization from benzene (charcoal) gave first an orange coloured compound (IXb) which crystallized from ethyl acetate as orange needles (0·25 g). The benzene mother liquor when concentrated and the residue triturated with dry ethyl acetate yielded a yellow solid (XXII) which crystallized from methanol as yellow hexagonal plates (0·08 g), m.p. 327–329° (dec.), undepressed when mixed with the sample obtained in (iii); the IR spectra of the two samples were also identical.

(b) *In pyridine.* A solution of vulpinic acid methyl ether (0·56 g; 1 mole) in dry pyridine (10 ml) was refluxed with or without *o*-phenylenediamine (0·18 g; 1 mole) for 3 hr at 130°. Acidification of the cold solution with dil. HCl gave a precipitate which crystallized from methanol (charcoal) as yellow leaflets, m.p. 148–149° alone or when mixed with an authentic sample of vulpinic acid.

Action of heat on vulpinic acid (II). Vulpinic acid (1·0 g) in dimethylaniline (30 ml) was heated at 210–215° (oil bath) for 3 hr. The solvent was removed (red. press.) and dil. HCl added when a brownish orange solid separated out. It was extracted ($NaHCO_3$ aq.) and filtered. The residue crystallized from benzene (charcoal) as yellow needles (0·7 g), m.p. 221–223° alone or mixed with pulvinic dilactone. Acidification of the sodium bicarbonate solution gave a yellowish orange precipitate which crystallized from benzene–light petroleum as long brownish-orange needles (0·08 g), m.p. 169–170°; IR (KBr): 3600 (w), 3067 (m), 2717 (w), 2577 (w), 1754 (s), 1639 (m), 1608 (s), 1538 (s), 1490 (s), 1451 (s), 1425 (s) cm^{-1}. (Found: C, 74·8; H, 5·3). It gave a faint green ferric reaction. Its nature is not yet clear.

(vi) *Condensation of 4-methoxypulvinic dilactone* (VI)

Condensation of VI (2·0 g; 1 mole) with *o*-phenylenediamine (0·95 g; 1·4 moles) in dimethylaniline (50 ml) as in (i) gave XXIV which crystallized from ethyl acetate as orange red needles (1·38 g), m.p. 303–305° (dec) (lit.[8] 292–294°); more of the compound (0·2 g) was obtained on working up the filtrate; IR (KBr): 3125 (m), 1754 (inf.) 1724 (s), 1587 (s), 1511 (s), 1445 (m) (Found: C, 73·2; H, 4·7. Calc. for $C_{25}H_{18}O_4N_2$: C, 73·2; H, 4·4%). Pinastric acid (III; 0·91 g) and *o*-phenylenediamine (0·52 g) when similarly treated, gave XXIV (0·28 g), m.p. 304–306° (dec). Isopinastric acid (IV; 0·5 g) and *o*-phenylenediamine (0·22 g) also gave the same condensation product (0·2 g), m.p. 302–304° (dec). Their IR spectra were identical in all details.

(vii) *Hydrolysis*

The above product (0·9 g) was heated under reflux with absolute alcoholic potash (50 ml; 15%) for 5 hr. The insoluble potassium salts were filtered off and alcohol removed (red. press.). On addition of cold water to the residue the 2-(*p*-methoxybenzyl)-benziminazole (0·45 g), m.p. 162–164° which separated out[8,5] was filtered off. The filtrate was acidified, extracted with ether (3 × 100 ml) and ether recovered from the dried extract. The oily residue was again extracted with light petroleum and the extract concentrated. Colourless plates (0·02 g) were obtained which were filtered off from the mother liquor (A). The residue had m.p. 81–83°; mixed m.p. with an authentic sample of *p*-methoxyphenylacetic acid (m.p. 85–87°) was undepressed and both the samples had similar IR spectra. The solvent was removed from the mother liquor (A) leaving an oily residue smelling of

[14] R. Schenck, *Liebig's Ann.* **282**, 28 (1894).

phenylacetic acid. Its presence was confirmed by circular paper chromatography, using a buffered solution of bromophenol blue and methyl red as the indicator.

(viii) *Ozonolysis*

A solution of the condensation product (XXIV; 0·5 g) in dry ethyl acetate (120 ml) was treated with ozonized oxygen (3%, 150 ml/min) for 45 min as in (ii). Fractionation of the solution gave the following: The sodium bicarbonate extract was acidified, extracted with ether (4 × 50 ml) and ether recovered from the extract. The residue was sublimed in vacuum; the sublimate was identified as benzoic acid, m.p. 120–121° and the unsublimed portion as anisic acid, m.p. 180–181°.

The residual ethyl acetate solution on evaporation gave a brown residue which on repeated crystallization from benzene (charcoal) furnished colourless needles, m.p. 187–189°; mixed m.p. with an authentic sample of 2-(*p*-methoxybenzoyl)-benziminazole was undepressed; IR spectra were also identical.

2-(p-*Methoxybenzoyl*)-*benziminazole* (XIV). A solution of 2-(*p*-methoxybenzyl)-benziminazole[12] (VIII, R = OCH_3; 0·15 g), chromium trioxide (0·5 g) and glacial acetic acid (20 ml) was heated at 100° for 10 min and then kept for 0·5 hr at room temp. Dilution with water (60 ml) gave a colourless precipitate which crystallized from benzene as shining colourless needles, m.p. 191–192°; IR (KBr): 3333 (s), 1623 (s), 1592 (s), 1558 (m), 1502 (m), 1486 (m) and 1418 (m) $cm.^{-1}$ (Found: C, 70·9; H, 5·4. $C_{15}H_{12}N_2O_3$ requires: C, 71·4; H, 4·8%).

(ix) *Methylation of* (XXIV)

(a) Methylation of the condensation product (0·3 g) in dil. KOH aq. with dimethyl sulphate (3 ml) gave a yellow solid (XXIII) which crystallized from methanol (or acetone) as pale yellow needles, m.p. 328–330° (dec); λ max 233, 274, 284, 299 and 323 mμ (log ε 4·45, 4·35, 4·34, 4·24, 4·39); IR (KBr): 3700 (s), 3450 (s), 1754 (inf.) 1739 (s), 1587 (s), 1495 (s), 1458 (m), 1431 (m) $cm.^{-1}$ (Found: C, 73·8; H, 5·5; OCH_3, 8·8. $C_{35}H_{30}O_4N_2$ requires: C, 74·1; H, 4·7; OCH_3 (one), 7·3%). Methylation with dimethyl sulphate and $NaHCO_3$ in dry acetone also gave the same product in better yield, and when refluxed with ignited K_2CO_3 alone in acetone for 4 hr, XXIV was recovered unchanged.

(x) *Condensation of pinastric acid methyl ether* (XII) *and* o-*phenylenediamine*

The methyl ether (0·75 g; 1 mole), *o*-phenylenediamine (0·25 g; 1·1 moles) and dimethylaniline (20 ml) were heated under reflux at 210–215° for 2·5 hr and worked up as in (v). The brownish-orange solid on fractional crystallization from benzene (charcoal) gave first an orange compound (XXIV) which crystallized from ethyl acetate as orange shining plates, m.p. 301–303° (dec). The mother liquor was concentrated and the residue triturated with light petroleum–ethyl acetate. On keeping overnight, a pale yellow compound (XXIII) separated which crystallized from methanol as pale yellow needles, m.p. 328–330° (dec), undepressed when mixed with the sample obtained in (ix); the IR and UV spectra of the two samples were identical.

Action of heat on isopinastric acid (IV) *and pinastric acid* (III). Isopinastric acid (0·1 g) was heated in a small test tube over a low flame for 15 min. A pale yellow sublimate was deposited on the cooler parts of the tube. Both the sublimed and unsublimed portions were insoluble in $NaHCO_3$ aq., Na_2CO_3 aq. and NaOH (2%) and crystallized from benzene as pale yellow needles, m.p. 197–199° alone or mixed with 4-methoxypulvinic dilactone (VI). In the case of pinastric acid the conversion to the dilactone was less and took longer.

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