Method B.—Working as described for I, 3 g. of II yielded, after crystallization from ethanol, 1.8 g. (87%) of needles, m. p. 156°, $[\alpha]^{20}D$ −139° (in chloroform). The tetranitromethane test was positive and the sulfur test negative.

Anal. Calcd. for $C_{19}H_{28}O$: C, 83.76; H, 10.35. Found: C, 83.79; H, 10.40.

This is the $\Delta^{3,5}$-androstadien-17(β)-ol previously described by Butenandt[28] and also by Kuwada and Miyasaki[25] who report m. p. 153–155°.

The acetate, prepared in the usual manner, melted at 128°. Kuwada and Miyasaki[25] report m. p. 126°, $[\alpha]^{20}D$ −155° (in chloroform).

Anal. Calcd. for $C_{21}H_{30}O_2$: C, 80.20; H, 9.61. Found: C, 80.26; H, 9.64.

In order to obtain an authentic specimen for comparison, we also prepared $\Delta^{3,5}$-androstadien-17-ol by the following method, which is essentially the one followed by Butenandt[28] but with some modifications: one gram of testosterone was dissolved in 200 cc. of anhydrous ether. This solution was added dropwise to a boiling solution of 0.8 g. of lithium aluminum hydride in 200 cc. of anhydrous ether. After working up the reaction mixture as described in previous examples, a residue was obtained which was a mixture of isomeric androstenediols. These were dissolved in 300 cc. of ethanol and after addition of 10 cc. of hydrochloric acid, refluxed for two hours. The product was poured into water and worked up as usual. By crystallization from ether–hexane, 0.5 g. of $\Delta^{3,5}$-androstadien-17(β)-ol, m. p. 158° was obtained.

When mixed with a sample of the product obtained by method B (see above) the mixture melted at 156–158°.

Hydrogenolysis of the 3-(β-Hydroxyethyl)-thioenol Ether of Δ^4-Androstene-3,17-dione (VII). Method A.—Proceeding as described for I, 4 g. of VII yielded a crude reaction product of 2.7 g. (85%). After treatment with Girard reagent T, 0.7 g. (22%) of androstan-17(β)-ol, m. p. and mixed m. p. 162–164°, was obtained from the non-ketone fraction. The tetranitromethane test and the sulfur test were negative. The ketone fraction yielded 1 g. (32%) of $\Delta^{3,5}$-androstadien-17-one, m. p. 85–87°, $[\alpha]^{20}D$ −22° (in chloroform). The tetranitromethane test was positive; the sulfur test negative.

Method B.—Working as above, from 2 g. of VII, 1.3 g. (83%) of white plates of $\Delta^{3,5}$-androstadien-17-one, m. p. and mixed m. p. 87–88°, $[\alpha]^{20}D$ −21.5° (in chloroform) was obtained. The tetranitromethane test was positive; the sulfur test negative.

Hydrogenolysis of the 3-(β-Hydroxyethyl)-thioenol Ether of Testosterone (X). Method A.—Working as in previous examples, 2 g. of X yielded 1.3 g. (82%) of androstan-17(β)-ol, m. p. and mixed m. p. 164–166°. The tetranitromethane test and the sulfur test were negative.

The acetates prepared from this androstan-17(β)-ol and from the one obtained by hydrogenolysis of II were identical.

Androstan-17(β)-ol (0.5 g., 0.002 mole) was dissolved in 30 cc. of acetic acid. A solution of 1.5 g. (0.015 mole) of chromic anhydride in 10 cc. of 80% acetic acid was added. The mixture was left standing at room temperature for three hours, then poured into water and extracted with ether. After the usual workup and crystallization from methanol, 0.2 g. of white plates of androstan-17-one, m. p. 122°, $[\alpha]^{20}D$ + 103° (in chloroform) was obtained. The tetranitromethane test was negative.

Method B.—Working as in previous examples, 2 g. of X yielded 1.4 g. (90%) of needles of $\Delta^{3,5}$-androstadien-17-(β)-ol, m. p. and mixed m. p. 154–155°. The tetranitromethane test was positive, the sulfur test negative.

Hydrogenolysis of the 3-Benzylthioenol Ether of Δ^4-Cholestenone (XIII). Method A.—Working as in previous examples, 4 g. of XIII yielded after crystallization from methanol–ether, 2.5 g. (82%) of cholestane, m. p. 78–79°, $[\alpha]^{20}D$ + 23.7° (in chloroform). The tetranitromethane test and the sulfur test were negative.

Anal. Calcd. for $C_{27}H_{48}$: C, 87.01; H, 12.98. Found: C, 87.16; H, 12.72.

Method B.—Working as described above, 1.5 g. of XIII yielded 1 g. (88%) of crystals of $\Delta^{3,5}$-cholestadiene, m. p. 78–79°, $[\alpha]^{20}D$ −101° (in chloroform). The tetranitromethane test was positive and the sulfur test negative.

Anal. Calcd. for $C_{27}H_{44}$: C, 87.96; H, 12.03. Found: C, 87.82; H, 12.23.

The mixed melting point of the reaction products of method A and method B showed a marked depression.

Summary

1. Several thioenol ethers of Δ^4-3-keto steroids have been prepared.

2. The conversion of the thioenol ethers of Δ^4-androstene-3,17-dione and its esters to the corresponding testosterone derivatives has been accomplished by treatment with lithium aluminum hydride.

3. Evidence for the structure of the 3-thioenol ethers of Δ^4-3-ketosteroids has been given.

MEXICO CITY, MEXICO RECEIVED APRIL 5, 1949

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF SZEGED, HUNGARY]

Synthetic and Degradative Studies in the Isoquinoline Series. IV

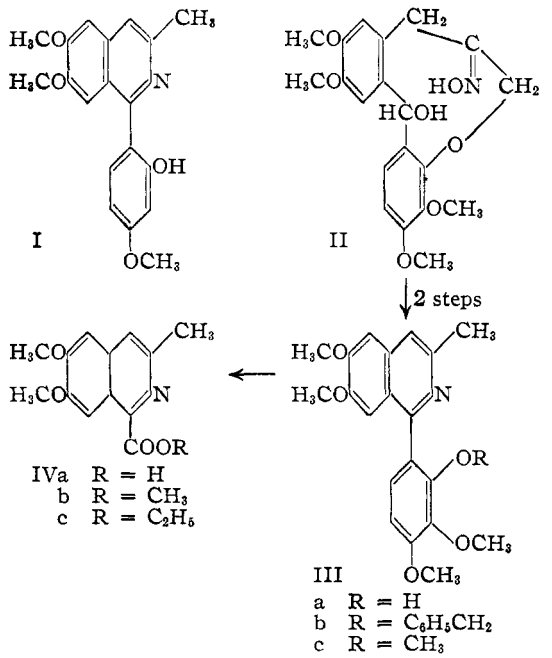
BY G. FODOR, V. BRUCKNER, J. KISS AND J. KOVÁCS

In our recent communication of this series[1] an unequivocal synthesis of I and the proof of its structure by oxidative degradation was described. This compound was isomeric, but not identical, with that prepared by Pfeiffer, *et al.*,[2] from brasilin and formulated as I; consequently the structure of their compound became doubtful.[1]

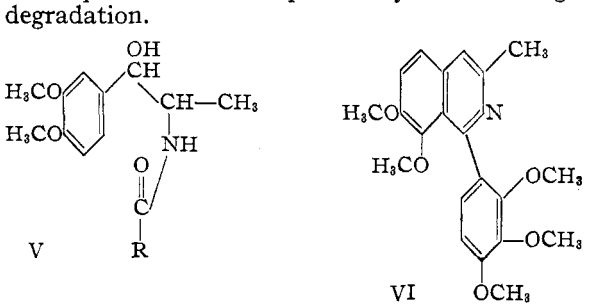
Tetramethyl hematoxylonol oxime (II) was converted by the same authors[2] in two steps into an amphoteric compound to which we will refer below as "H." Oxidation of "H" with permanganate yielded metahemipinic acid (3,4-dimethoxyphthalic acid). Degradation with nitric acid furnished an acid ("A") only isolated as picrate. Acid "A" reacted with diazomethane under formation of a monomethyl derivative, which was again only isolated as picrate. On the basis of these facts Pfeiffer, *et al.*,[2] suggested for "H" structure IIIa and for acid "A" formula IVa. These structures were not confirmed by synthesis. Although the synthesis of the methyl ether of "H" from amide Vb was attempted, the obtained synthetic

(1) Bruckner, Fodor, Kovács and Kiss, THIS JOURNAL **70**, 2697 (1948).

(2) Pfeiffer, Breitbach and Scholl, *J. prakt. Chem.*, **2**, 154, 157 (1940).



product was not identical with the methyl ether of "H," but only isomeric with it. Because of this failure Pfeiffer, *et al.*,[2] concluded that the intramolecular condensation of Vb, due to an unusual (o. m.) ring closure, led to the isoquinoline derivative (VI). However, this structure for the synthetic product was not proved by them through degradation.



The present publication deals with the synthesis and degradation of isoquinoline (IIIa) and with that of 3-methyl-6,7-dimethoxyisoquinoline-1-carboxylic acid (IVa).

The isoquinoline derivative (IIIa) was prepared by reaction of α-(3,4-dimethoxyphenyl)-β-aminopropanol with 2'-hydroxy-3,4-dimethoxybenzoyl chloride via the compound Va which was then benzylated to give Vc.[3]

This was then condensed to give the crystalline isoquinoline (IIIb). The latter was debenzylated by hydrogenolysis giving IIIa whose properties differed from "H," but which gave on treatment with diazomethane the methyl ether (IIIc) already obtained by Pfeiffer, *et al.*[2] The same compound was also obtained by us from the stereoisomeric form of Vb.[4]

The direction of the ring closure was elucidated by oxidative degradation of IIIa, leading to metahemipinic acid, so that there could be no further doubt as to the structure of the synthetic product. Obviously, the sole fact observed by Pfeiffer, *et al.*,[2] of "H" also giving an oxidative degradation metahemipinic acid, is no adequate proof for "H" possessing structure III, but only indicates the maintenance of the two carbon atoms, attached in *m*, *p* position to the methoxy groups of oxime II, during the two steps conversion into "H."

It remains to be decided whether the existing difference between IIIa and "H" is to be sought for in the different positions of the substituents in the aryl radical attached to carbon atom 1 of the isoquinoline system, or in the structure of the hetero ring. In the first case, both compounds ought to give on oxidation the same carboxylic acid (IVa). As we did not succeed in isolating on oxidation of IIIa with nitric acid either acid "A" or its picrate,[2] we attempted to approach the problem by a straightforward synthesis of IVa.

For this purpose the trichloroacetyl amide (Vd) was prepared which on condensation should yield a trichloromethylisoquinoline which on hydrolysis would be expected to give the desired acid (IVa) and on hydrogenolysis would give the known[5] 1,3-dimethyl-6,7-dimethoxyisoquinoline. Unfortunately, all attempts to form an isoquinoline derivative from Vd failed. Accordingly, we adopted another line of synthesis starting with the ethoxalyl derivative (Ve) preparable in good yield. Its intramolecular condensation by means of $POCl_3$ gave the 1-carbethoxyisoquinoline (IVc) and subsequent hydrolysis the crystalline acid (IVa). This acid, under the conditions reported by Pfeiffer, *et al.*,[2] did not give any precipitate with picric acid; moreover, on evaporating the solution only the picrate of 3-methyl-6,7-dimethoxyisoquinoline could be isolated, indicating the loss of the carboxylic group during the reaction. The identity of this unexpected product was shown by synthesis from the formamido compound (Vf).

Acid IVa gave with diazomethane a crystalline methyl ester (IVb, m. p. 151–153°), the picrate of which showed m. p. 168–170°. As Pfeiffer, *et al.*,[2] recorded for the picrate of their methyl ester, obtained from "A," m. p. 216°, IVa cannot be identical with "A." Furthermore, as structure IVa for our synthetic acid could be confirmed by its oxidative degradation leading to metahemipinic acid, "A" must have another structure, remaining still to be elucidated.

(3) Condensation of 2-benzyloxy-3,4-dimethoxybenzoyl chloride with the aminopropanol, in an analogous manner as described previously, did not go smoothly.

(4) The stereoisomer forms of acylamide (Vb) are in the same relation as ephedrine and ψ-ephedrine. Compare Bruckner, Fodor, Kiss and Kovács, *J. Chem. Soc.*, 885 (1948).

(5) Bruckner, Kovács and Kovács, *Ber.*, **77**, 610 (1944).

It is evident from the above facts that the difference between "H" and IIIa is not to be sought for in the difference of the aryl radicals attached to the carbon atom 1 of the isoquinoline ring, but perhaps in the difference of the position of both substituents of the hetero ring, or even in the structure of the entire hetero ring system of "H." To reach a decision in this matter the structure of "H" must be fully investigated.

Experimental

2-Benzyloxy-3,4-dimethoxybenzoic Acid.—Ten grams of methyl 2-hydroxy-3,4-dimethoxybenzoate, 1.1 g. of sodium and 6 ml. of benzyl chloride were condensed in 50 ml. of absolute ethanol[1] to yield colorless needles of the acid, melting at 95–96° after recrystallization from ethanol.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.60. Found: C, 66.62; H, 5.30.

The acid was converted to the oily acid chloride by means of thionyl chloride.

α-(3,4-Dimethoxyphenyl)-β-(2-hydroxy-3,4-dimethoxybenzoylamino)-propanol (Va).—2-Hydroxy-3,4-dimethoxybenzoyl chloride, prepared from 11.5 g. of the acid was condensed in the usual manner[1] with 27 g. of α-(3,4-dimethoxyphenyl)-β-aminopropanol[6] to yield 18 g. of Va, m. p. 87–88°. Va, treated with ethereal diazomethane, was converted to Vb, melting at 107–108°, after recrystallization from toluene. Vb was also prepared by treating 2.2 g. of the aminopropanol with 1.06 g. of 2,3,4-trimethoxybenzoyl chloride.

Anal. Calcd. for $C_{21}H_{27}O_7N$ (Vb): C, 62.21; H, 6.71. Found: C, 62.26; H, 6.65.

Vb is stereoisomeric with the compound of Pfeiffer, m. p. 127–128°, obtained from the stereoisomeric aminopropanol.

1-(2'-Benzyloxy-3',4'-dimethoxyphenyl)-3-methyl-6,7-dimethoxyisoquinoline (IIIb).—To a solution of 18 g. of Va in 500 ml. of absolute ethanol was added a solution of 1.05 g. (0.046 mole) of sodium in 50 ml. of absolute alcohol. To this mixture was added 8 ml. (0.04 mole) of benzyl chloride and the solution refluxed for eight hours. The reaction mixture was filtered, the alcohol evaporated and the residue dissolved in 500 ml. of hot toluene. Addition of 25 ml. of phosphorus oxychloride yielded 8 g. of VIb, prisms melting at 147–148° after recrystallization from 50% ethanol.

Anal. Calcd for $C_{27}H_{27}O_5N$: C, 72.79; H, 6.09. Found: C, 72.91, 72.45; H, 6.41, 6.11.

1-(2'-Hydroxy-3',4'-dimethoxyphenyl)-3-methyl-6,7-dimethoxyisoquinoline (IIIa).—A solution of 6.5 g. of IIIb in 280 ml. of ethanol was subjected to hydrogenolysis using 2.5 g. palladium–charcoal (7% palladium). Absorption of hydrogen was quantitative in seventeen minutes and there was produced, as yellowish prisms, m. p. 158–60.5°, 5.1 g. (95.6% theoretical) of III, isolated by precipitation from alkaline solution by carbon dioxide. Recrystallization from ethanol afforded nearly colorless prisms, m. p. 168–169°.

Anal. Calcd. for $C_{20}H_{21}O_5N$: C, 67.57; H, 5.96. Found: C, 67.19; H, 6.41.

Pfeiffer[2] recorded for "H" m. p. 174°.

The **picrate** of IIIa was obtained as yellow crystals, m. p. 238–239° from ethanol.

Anal. Calcd. for $C_{26}H_{24}O_{12}N_4$: C, 53.40; H, 4.14. Found: C, 53.17; H, 4.35.

Pfeiffer[2] recorded for the picrate of "H" m. p. 210°.

The **methyl ether IIIc**, m. p. 105–107°, was obtained by treating a methanol solution of IIIa with ethereal diazomethane. Pfeiffer reported[2] the same melting point for the synthetic product from his Vb. We have obtained in the usual manner 0.76 g. of IIIc from 1 g. of our Vb (m. p. 109–110°) which is stereoisomeric with that of Pfeiffer.

The **picrate** of IIIc is obtained from methanol as yellow crystals, m. p. 184–185°.[2]

Anal. Calcd. for $C_{27}H_{26}O_{12}N_4$: C, 54.16; H, 4.38. Found: C, 54.15; H, 4.52.

Degradation of IIIa to 3,4-Dimethoxyphthalic Acid.—Three and seven-tenths grams (0.0107 mole) of IIIa dissolved in 525 ml. of hot 0.03% aqueous sodium hydroxide was treated with 23.7 g. of potassium permanganate dissolved in 475 ml. of hot water to obtain 3,4-dimethoxyphthalic acid.[1] The product weighed 200 mg. after recrystallization from water and melted at 175–177°[7] alone and when mixed with an authentic sample. The 3,4-dimethoxyphthalic acid was further characterized by converting it to metahemipinic ethylimide, m. p. 228–229°.[7]

Anal. Calcd. for $C_{12}H_{13}O_4N$: C, 61.25; H, 5.57. Found: C, 60.90; H, 5.57. Hemipinic ethylimide melts at 93°.[8]

α-(3,4-Dimethoxyphenyl)-β-N-ethoxalylaminopropanol (Ve).—Twenty-one and one-tenth grams (0.1 mole) of the corresponding aminopropanol[6] was dissolved in 100 ml. of hot chloroform, 6.8 g. (0.05 mole) of ethoxalyl chloride was added and the mixture allowed to stand overnight. The amino-propanol hydrochloride was collected, the filtrate washed with a total of 30 ml. of water, dried, the solvent blown off and the residue recrystallized from toluene; yield, 6.5 g.; m. p. 92–93°.

Anal. Calcd. for $C_{15}H_{20}O_6N$: C, 58.06; H, 6.50. Found: C, 57.93; H, 7.05.

α-(3,4-Dimethoxyphenyl)-β-N-trichloro-acetylamino-propanol (Vd).—From 2.11 g. of the amino-propanol[6] and 0.82 g. of trichloroacetyl chloride in 40 ml. of toluene, 0.8 g. of recrystallized amide (Vd) was obtained; needles from benzene–ligroin, m. p. 115–116°.

Anal. Calcd. for $C_{13}H_{16}O_4NCl_3$: C, 43.75; H, 4.52. Found: C, 43.89; H, 4.08.

3-Methyl-6,7-dimethoxyisoquinoline-1-carboxylic Acid (IVa).—To 0.94 g. of the amide Ve in 15 ml. of anhydrous toluene, 0.8 ml. of phosphorus oxychloride was added and the mixture refluxed for one hour. Then ice was added until phosphorus oxychloride decomposed, and the separated aqueous layer was made alkaline with ammonia and extracted with ether. The material recovered from the ether weighed 183 mg. and was hydrolyzed by boiling with 4 ml. of 10% sodium hydroxide solution and with 5 ml. of methanol for ninety minutes. The methanol was then evaporated, the alkaline aqueous solution extracted with ether, decolorized and acidified to congo red paper. The acid separated forming yellowish crystals; yield 57 mg., m. p. 203–204° (dec.). Recrystallized from water containing a drop of hydrochloric acid, its hydrate could be obtained (free of chlorine); from methanol the anhydrous acid could be obtained.

Anal. Calcd. for $C_{13}H_{13}O_4N \cdot H_2O$: C, 58.84; H, 5.70. Found: C, 58.80; H, 5.40. Calcd. for $C_{13}H_{13}O_4N$: C, 63.13; H, 5.30. Found: C, 62.80; H, 5.20.

Picrate.—By adding an aqueous solution of the acid to an alcoholic solution of picric acid, as reported by Pfeiffer,[2] the above acid did not give any precipitation. When a solution of 25 mg. of IVa and 23 mg. of picric acid in 1.5 ml. of methanol was heated and then allowed to stand, crystallization could not be observed. By evaporation of the solvent yellow crystals separated, m. p. 269–270° (shrinking from 200°). The analytical data showed that decarboxylation had taken place, yielding the picrate of 3-methyl-6,7-dimethoxyisoquinoline.

Anal. Calcd. for $C_{18}H_{16}O_9N_4$: C, 50.50; H, 3.76. Found: C, 50.30; H, 3.97.

3-Methyl-6,7-dimethoxyisoquinoline.—A solution of 4.5 g. of the aminopropanol[6] in 80 ml. of anhydrous formic

(6) Iwamoto and Hartung, *J. Org. Chem.*, **9**, 511 (1944).

(7) Goldschmiedt, *Monatsh.*, **9**, 722 (1888).

(8) Freund and Heim, *Ber.*, **23**, 2906 (1890).

acid was refluxed for forty-eight hours. Formic acid was then removed in a vacuum and the brownish glassy formamido compound (Vf) treated with 10 ml. of phosphorus oxychloride in 100 ml. of toluene in the usual manner. The isoquinoline was purified by repeated distillation under 1 mm. pressure; yield 1.2 g., m. p. 135–136°.

Anal. Calcd. for $C_{12}H_{13}O_2N$: C, 70.92; H, 6.45. Found: C, 71.21; H, 6.60.

Hydrochloride.—Long needles from ethanol–ether, m. p. 237–238°.

Picrate.—It is very poorly soluble in hot alcohol, m. p. 270°, and is identical with the picrate obtained from the acid (IVa).

Anal. Calcd. for $C_{18}H_{16}O_9N_4$: C, 50.5; H, 3.76. Found: C, 50.30; H, 4.02.

Decarboxylation of IVa.—Twenty-two mg. of the acid was heated under 1 mm. pressure in a Spaeth tube to 200° and the solid distillate converted into a picrate; crystals from methanol, m. p. 270°. It was identical with the picrate of the crystalline 3-methyl-6,7-dimethoxy-isoquinoline, obtained from the formamido compound, as described above.

Methyl Ester (IVb).—Five millimoles (123 mg.) of the acid (IVa) was dissolved in 23 ml. of methanol and 3 ml. of an ethereal diazomethane solution added. The solvent was evaporated under reduced pressure, the solid residue (53 mg.) treated with 10 ml. of ether and filtered. The filtrate was shaken with a dilute sodium bicarbonate solution, dried and the ether removed. The residue was 48 mg., m. p. after recrystallization from benzene–petroleum ether, m. p. 151–153°.

Anal. Calcd. for $C_{14}H_{15}O_4N$: C, 63.70; H, 5.98. Found: C, 63.80; H, 6.03.

Picrate.—Yellow needles from methanol, m. p. 168–170°. Pfeiffer recorded for the picrate of the methyl ester of the acid a melting point of 216°.

Anal. Calcd. for $C_{20}H_{18}O_8N_4$: OCH_3, 18.94. Found: OCH_3, 18.67.

1-Carbethoxy-3-methyl-6,7-dimethoxyisoquinoline (IVc).—This ester could be isolated by decomposing with absolute ethanol (instead of water) the excess of phosphoryl chloride in the mixture obtained on ring closure of the amide (Ve); yield 2.1 g. from 9.5 g. of ethoxyalylamide (Ve). Repeated distillation from a Spaeth tube under 1 mm. pressure afforded yellowish needles, m. p. 86–87°.

Anal. Calcd. for $C_{15}H_{17}O_4N$: N, 9.1. Found: N, 9.3.

Picrate.—Glistening gold-yellow needles (from 96% ethanol), m. p. 176–177°.

Anal. Calcd. for $C_{21}H_{20}O_{11}N_4$: C, 50.0; H, 4.0. Found: C, 50.1, 50.1; H, 4.4, 4.45.

Degradation of 1-Carboxy-3-methyl-6,7-dimethoxyisoquinoline (IVa) to 3,4-Dimethoxyphthalic Acid.—Two hundred and ten milligrams of potassium permanganate dissolved in 10 ml. of water was added to a solution of 247 mg. of 1-carboxy-3-methyl-6,7-dimethoxyisoquinoline in 40 ml. of dilute sodium hydroxide in fifteen minutes. The residue of evaporation (350 mg.) was extracted as described in previous degradation procedures and 144 mg. of crude crystals was obtained. Purification through the lead salt yielded 27 mg. of metahemipinic acid, m. p. after recrystallization from 0.5 ml. of water 176°, alone and mixed with an authentic specimen. The product was converted in the usual manner into its ethylimide which after sublimation and recrystallization showed m. p. 229° under the microscope.

Summary

The synthesis of 1-(2′-hydroxy-3′,4′-dimethoxyphenyl) - 3 - methyl - 6,7 - dimethoxyisoquinoline (IIIa) is described. Its structure has been confirmed by oxidative degradation. It differs from a compound obtained from hematoxyline, incorrectly assigned the same structure in the literature. The synthesis of 3-methyl-6,7-dimethoxyisoquinoline-1-carboxylic acid (IVa) and its methyl ester (IVb) was accomplished in a straightforward manner. They were found to be different from the compounds described earlier.

The recent results proved, in accordance with previous investigations, that the intramolecular condensation of acylamides of type V lead in every case to 6,7-dialkoxy isoquinoline derivatives and in no case to 7,8-dialkoxyisoquinolines, the latter possibility being assumed by earlier investigators.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF FURMAN UNIVERSITY]

Formation of Bromine Addition Compounds with Some Condensed Ring Hydrocarbons

BY JOHN R. SAMPEY, JESSIE M. COX AND ANNE B. KING

The formation of intermediate addition compounds plays a prominent role in current theories on the mechanism of bromination.[1] Crystalline dibromide addition products of phenanthrene and anthracene have been isolated,[2] while more than fifty years ago Orndorff and Moyer[3] prepared a crystalline naphthalene tetrabromide in 3% yield. In the present study we increased the yield of the latter compound to 30% by photobromination, and we found all the above and other addition compounds stable when shaken with sodium sulfite solution to remove unreacted bromine, but each readily gave a test for active bromine when treated with an acetone solution of sodium iodide.

(1) Price, *Chem. Revs.*, **29**, 37-67 (1941); Kharasch, White and Mayo, *J. Org. Chem.*, **2**, 574-576 (1938).

(2) Price, THIS JOURNAL, **58**, 1834-1838 (1936).

(3) Orndorff and Moyer, *Am. Chem. J.*, **19**, 262-270 (1897).

Experimental

Preparation of Naphthalene Tetrabromide.—12.8 grams of pure naphthalene in 100 ml. of carbon tetrachloride was brominated under anhydrous conditions at 0° with one mole of bromine in 100 ml. of the same solvent during two hours with a 2″ arc at the distance of 2″; the solvent was evaporated and the product extracted with 95% alcohol and crystallized from chloroform; yield 30% of naphthalene tetrabromide, melting 111° and giving four atoms of bromine on a Rosanoff analysis. A sodium