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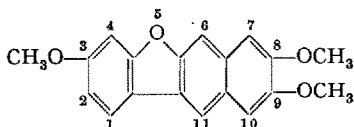
### Summary

The isomerisation of 5-hydroxy-benz(cd)indoline (I) to 5-keto-1,3,4,5-tetrahydro-benz(cd)indole (II) over a palladium catalyst has been studied systematically. Besides (II) varying amounts of the dehydrogenation product (III) are formed. This side reaction does not occur when the isomerisation is carried out in a hydrogen atmosphere.

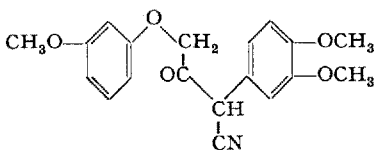
The above isomerisation can be reversed by treatment of (II) with acetanhydride and potassium acetate.

## A Synthesis of Kostanecki's 3:8:9-Trimethoxy- $\beta$ -brazan

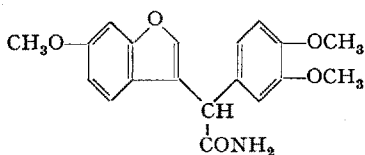
By heating trimethylbrazilone with hydriodic acid for a long period, KOSTANECKI and LLOYD<sup>1</sup> obtained 3:8:9-trihydroxy- $\beta$ -brazan which gave the trimethyl ether (I, m. p. 244–246°C) on methylation. The constitution of (I) was confirmed by converting the above-mentioned hydroxybrazan to  $\beta$ -brazan with the aid of zinc dust. The compound (I) has now been synthesised by an unambiguous method.



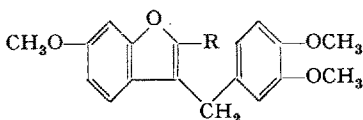
(I)



(II)



(III)



(IV)

The keto-nitrile (II) of PFEIFFER *et al.*<sup>2</sup> gave, on treatment with fuming hydrochloric acid in acetic acid

<sup>1</sup> V. KOSTANECKI and L. LLOYD, Ber. Dtsch. chem. Ges. 36, 2198 (1903).

<sup>2</sup> P. PFEIFFER, K. QUEHL, and F. TAPPERMANN, Ber. Dtsch. chem. Ges. 63, 1304 (1930).

at 30°C, the isomeric amide (III, m. p. 162°C). This on prolonged boiling with 10% hydrochloric acid afforded 6-methoxy-3-(3:4-dimethoxybenzyl)-coumarone (IV, R = H, m. p. 61–62°C; picrate, m. p. 102°C). On Gattermann synthesis with the aid of zinc chloride IV (R = H) gave 6-methoxy-3-(3:4-dimethoxybenzyl)-2-formylcoumarone (IV, R = CHO, m. p. 137°C; 2:4-dinitrophenylhydrazone, m. p. 246–248°C), the orientation of which was established by oxidising it with potassium permanganate in acetone to the known acid<sup>1</sup> (IV, R = CO<sub>2</sub>H, m. p. 196°C). The aldehyde (IV, R = CHO) underwent quantitative cyclodehydration<sup>2</sup> to I (m. p. 244–246°C) with glacial phosphoric acid at 100°C. The correctness of the synthesis was confirmed by typical colour reactions<sup>3</sup> and oxidising (I) with chromic acid to trimethoxy- $\beta$ -brazanquinone (m. p. 261–262°C)<sup>4</sup> which was purified by sublimation in vacuum.

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### Résumé

Une manière non équivoque de synthèse de 3,8,9-triméthoxy- $\beta$ -brazan de KOSTANECKI se décrit dans cet article.

<sup>1</sup> K. W. BENTLEY and R. ROBINSON, J. Chem. Soc. 1950, 1355.

<sup>2</sup> C. K. BRADSHAW, Chem. Rev. 38, 492 (1946).

<sup>3</sup> V. KOSTANECKI and L. LLOYD, Ber. Dtsch. chem. Ges. 36, 2198 (1903).

<sup>4</sup> V. KOSTANECKI and L. LLOYD, Ber. Dtsch. chem. Ges. 36, 2200 (1903).

## 7-Oxo-dehydro-iso-androsterone Acetate

During the purification of technical dehydro-iso-androsterone acetate by crystallization from methanol, the final mother-liquor showed no tendency to crystallization. The residue was dissolved in benzene and this solution subjected to chromatography over Al<sub>2</sub>O<sub>3</sub>. Elution also took place with benzene.

The first fractions contained crystals which could not be identified. From the intermediate fractions crystals have been isolated with a melting range from 160–170°. By recrystallization first from methanol and subsequently from 40% aqueous methanol, the m. p. could be raised to 176–178°. The analysis yielded the following results: C: 73.21 and 73.15%, H: 8.40 and 8.33%. The values, calculated for an oxo-dehydro-iso-androsterone acetate are: C: 73.12%, H: 8.19%. A mixed m. p. with 7-oxo-dehydro-iso-androsterone acetate prepared according to BILLETER and MIESCHER<sup>1</sup> gave no depression. The U. V. absorption spectrum showed a maximum at 235 m $\mu$  with a log  $\epsilon$  of 4.09. A similar maximum is observed in the spectrum of 7-oxo-cholesterol acetate.

The isolation of 7-oxo-dehydro-iso-androsterone acetate from the oxidation products of cholesterol has not yet been described. BILLETER and MIESCHER<sup>2</sup> isolated  $\Delta$ -3,5-androstadienedione-7,17 from the mother-liquors of the dehydro-iso-androsterone semicarbazone and it is not unlikely that this compound has been formed from 7-oxo-dehydro-iso-androsterone acetate during the purification process.

<sup>1</sup> J. R. BILLETER and K. MIESCHER, Helv. chim. acta 31, 629 (1948).