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Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

A new synthesis of the coumestan ring system

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To cite this Article Kappe, Thomas and Schmidt, Heinrich(1972) 'A new synthesis of the coumestan ring system', *Organic Preparations and Procedures International*, 4: 5, 233 – 236

To link to this Article: DOI: 10.1080/00304947209355551

URL: <http://dx.doi.org/10.1080/00304947209355551>

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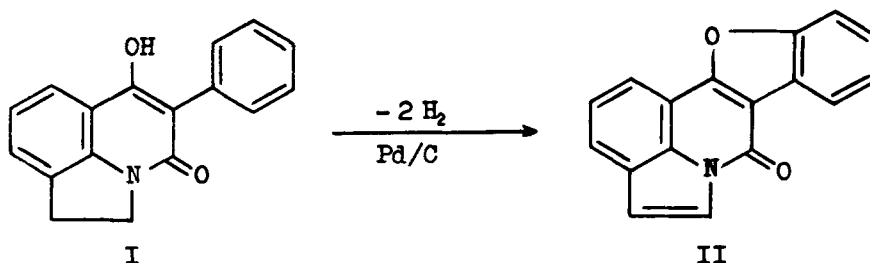
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A NEW SYNTHESIS OF THE COUMESTAN RING SYSTEM

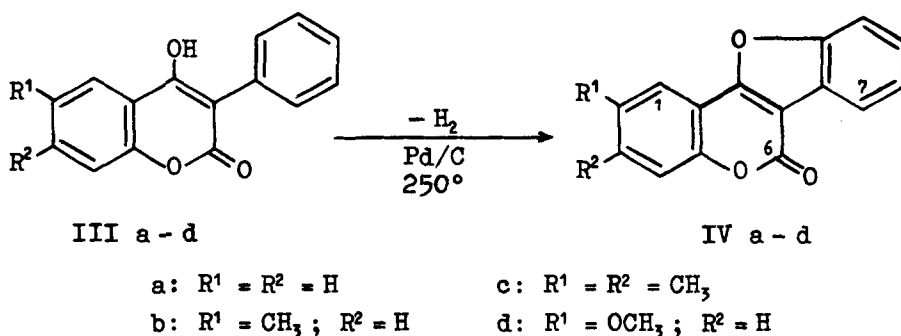
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The catalytic dehydrogenation of some 6-hydroxy-1,2-dihydro-4H-pyrrolo(3,2,1-ij)quinolin-4-ones lead to the corresponding indoles in the presence of Pd/C at about 250°. ¹ However, with the 5-phenyl derivative (I), an interesting secondary reaction occurred, resulting in the formation of 7H-benzofuro(3,2-c)pyrrolo(3,2,1-ij)quinolin-7-one (II).



In order to test the generality of this cyclodehydrogenation of malonyl heterocyclic compounds, we studied the dehydrogenation of some 4-hydroxy-3-phenyl-coumarins (III a-d). We chose compounds of type III because the expected 6H-benzofuro(3,2-c)(1)benzopyran-6-ones (IV) also known as "coumestans", ² have the basic structure of many naturally occurring compounds such as wedelolactone, desmethylwedelolactone, psoralidin, isopsoralidin, erosnin and the estrogenic coumestrol.



Cyclization of the 4-hydroxycoumarins III was achieved in boiling diphenyl ether (b.p. 252°) in the presence of 10% Pd/C catalyst, while air is bubbled through the reaction mixture. The coumestans IVa-d can be easily separated from the starting materials by their insolubility in 0.5 N sodium hydroxide. They show a blue fluorescence on TLC under UV-light. In the nmr spectra the downfield shift of the proton at position 7 to $\delta = 8.0-8.3$ ppm is characteristic for these compounds.

EXPERIMENTAL³

The 4-hydroxy-3-phenyl-coumarins III a-d were prepared according to Ziegler and Junek.⁴

6H-Benzofuro-(3,2-c)(1)benzopyron-6-ones IV.

General procedure. - A solution of 0.005 mole of III in 5-10 ml diphenyl ether containing 1 g of 10% Pd/C was heated to reflux under an air condenser while air is bubbled through the solution at a slow rate (0.5 ml/min). The progress of the dehydrogenation can be followed by tlc inspection of the reaction mixture. The reaction is stopped after about 80% conversion to IV has taken place (in order to minimize decomposition reactions). Compounds IV exhibit a blue fluorescence

and have greater R_f values than the starting materials. Isolation of the reaction products is accomplished by diluting the reaction mixture with 150 ml of hot benzene, filtering the catalyst, washing the resulting solution with 0.5 N NaOH, removing the organic solvents in vacuo, and finally digesting the residue with petroleum ether (b.p. 30-60°).

IVa: 57% yield as needles from methanol, mp. 181-182° (lit.⁵ mp. 181-182°); IR 1735 s (C=O), 1625 m, 1600 m cm^{-1} ; nmr 7.15-7.90 (m, 7, ArH), 7.95-8.15 (m, H at C-7).

IVb: 76% yield as prisms from benzene-cyclohexane or needles from ethanol, mp. 157-158°; IR 1735 s (C=O), 1630 w, 1570 m cm^{-1} ; nmr 2.43 (s, CH₃), 7.2-7.75 (m, 6, ArH), 8.0-8.2 (m, H at C-7).

Anal. Calcd for C₁₆H₁₀O₃: C, 76.79; H, 4.03.

Found: C, 76.53; H, 4.05.

IVc: 80% yield as rods from benzene, mp. 220-222°; IR 1725 s (C=O), 1640 m, 1600 w cm^{-1} ; nmr 2.40 (s, 2, CH₃), 7.20-7.75 (m, 5, ArH), 8.05-8.25 (m, H at C-7).

Anal. Calcd for C₁₇H₁₂O₃: C, 77.26; H, 4.58.

Found: C, 77.06; H, 4.52.

IVd: 69% yield as rods from benzene-cyclohexane, mp. 155-157°; IR 1730 s (C=O), 1570 m cm^{-1} ; nmr 3.95 (s, OCH₃); 7.0-7.8 (m, 6, ArH), 8.05-8.25 (m, H at C-7).

Anal. Calcd for C₁₆H₁₀O₄: C, 72.18; H, 3.78.

Found: C, 72.14; H, 3.77.

7H-Benzofuro(3,2-c)pyrrolo(3,2,1-ij)quinolin-7-one (II): According to the procedure described for compounds IV; however, 2 g Pd/C, 50 ml of diphenyl ether and 300 ml of benzene

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have been used: 58% yield as needles from ethanol, mp. 206-208°; IR 1685 s (C=O), 1605 m cm^{-1} ; nmr 6.86 (d, $J = 3.5$ Hz, H at C-4); 8.04 (d, $J = 3.5$ Hz, H at C-5), 7.20-8.05 (m, 6, ArH); 8.2-8.4 (m, H at C-8).

Anal. Calcd for $\text{C}_{17}\text{H}_9\text{NO}_2$: C, 78.76, H, 3.50, N, 5.40.

Found: C, 78.47, H, 3.61, N, 5.52.

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(Received July 24, 1972; in revised form November 6, 1972)