

A NEW SYNTHESIS OF
DORYANINE AND RELATED ISOCARBOSTYRIL

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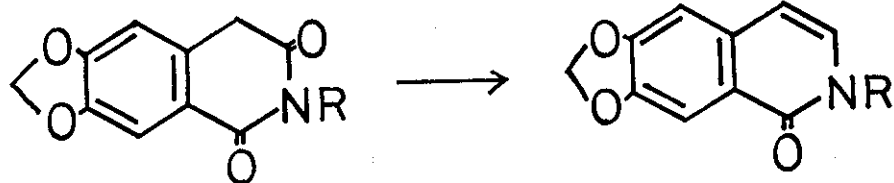
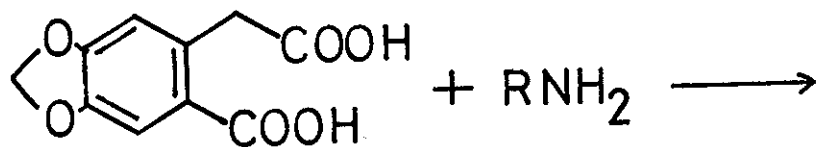
Doryanine was synthesised in one step from
3,4-methylenedioxyhomophthalimide derivative.

We have briefly reported the reaction of homophthalimides
with sodium borohydride followed by treatment with hydrochloric
acid afforded the isocarbostyrils¹⁾

We now report a synthesis of the isoquinoline alkaloid
doryanine²⁾ isolated from Doryhora sassafras Endliche.

Reaction of 3,4-methylenedioxyhomophthalic acid²⁾ with
methylamine at 160° gave 2-methyl-6,7-methylenedioxyhomo-
phthalimide (Ia), m.p. 207-209°; ir ν_{\max} (nujol) 1700 and
1650 cm^{-1} ; mass m/e 219 (M^+); nmr δ (CDCl_3) 3.30 (3H, s,
N- CH_3), 3.90 (2H, s, - CH_2 -), 6.04 (2H, s, - OCH_2 -) and 6.58,
7.55 (2H, s, aromatic Hx2).

After treatment of the imide (Ia) with sodium borohydride,



Ia: R=Me
Ib: R=CH₂Ph

IIa: R=Me
IIb: R=CH₂Ph

the reaction mixture was acidified with 10% hydrochloric acid to give the doryanine (IIa) in 90% yield, m.p.162-163° (lit., 3) m.p.160-162°); ir ν_{\max} (nujol) 1650cm^{-1} ; mass m/e 203 (M^+); nmr $\delta(\text{CDCl}_3)$ 3.58 (3H, s, N-CH₃), 6.01 (2H, s, -OCH₂O-), 6.32 (1H, d, J=8.0Hz, C₃-H), 6.80 (1H, s, C₅-H), 6.90 (1H, d, J=8.0 Hz, C₄-H) and 7.73 (1H, s, C₈-H).

Reaction of 3,4-methylenedioxyhomophthalic acid with benzylamine at 160° gave 2-benzyl-6,7-methylenedioxyhomophthalimide (Ib), m.p.125-127°; ir ν_{\max} (nujol) 1700 and 1650cm^{-1} ; mass m/e 295 (M^+); nmr $\delta(\text{CDCl}_3)$ 3.92 (2H, s, -CH₂-), 5.12 (2H, s, N-CH₂-), 6.00 (2H, s, -OCH₂O-), 6.60 (1H, s, C₅-H) and 7.52 (1H, s, C₈-H).

2-Benzyl-6,7-methylenedioxy-1(2H)-isoquinolone (IIb) was prepared by the above method from 2-benzyl-6,7-methylenedioxyhomophthalimide (Ib) in 90% yield, m.p.127-129°; ir ν_{\max} (nujol) 1650cm^{-1} ; mass m/e 279 (M^+), nmr $\delta(\text{CDCl}_3)$ 5.15 (2H, s, N-CH₂-), 6.00 (2H, s, -OCH₂O-), 6.30 (1H, d, J=8.0Hz, C₃-H), 6.81 (1H, s, C₅-H), 6.92 (1H, d, J=8.0Hz, C₄-H) and 7.76 (1H, s, C₈-H).

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