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A NEW SYNTHESIS OF DORYANINE AND RELATED ISOCARBOSTYRIL

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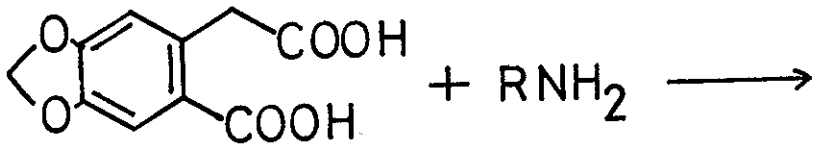
Doryanine was synthesised in one step from 3,4-methylenedioxyhomophthalimide derivative.

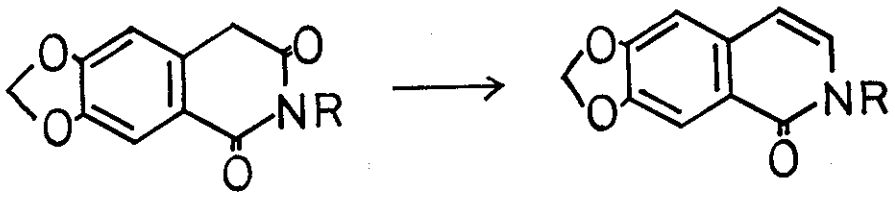
We have briefly reported the reaction of homophthalimides with sodium borohydride followed by treatment with hydrochloric acid afforded the isocarbostyrils[1)]

We now report a synthesis of the isoquinoline alkaloide doryanine[2)] isolated from Doryhora sassafras Endliche.

Reaction of 3,4-methylenedioxyhomophthalic acid[2)] with methylamine at 160° gave 2-methyl-6,7-methylenedioxyhomophthalimide (Ia), m.p.207-209°; ir νmax (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_2O-) and 6.58, 7.55 (2H, s, aromatic Hx2).

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





Ia: R=Me
Ib: R=CH_2Ph

IIa: R=Me
IIb: R=CH_2Ph

the reaction mixture was acidefied with 10% hydrochloric acid to give the doryanine (IIa) in 90% yield, m.p.162-163° (lit., [3] m.p.160-162°) ; ir νmax (nujol) 1650cm^{-1} ; mass m/e 203 (M^+) ; nmr δ($CDCL_3$) 3.58 (3H, S, N-CH_3), 6.01 (2H, s, -OCH_2O-), 6.32 (1H, d, J=8.0Hz, C_3-H), 6.80 (1H, s, C_5-H), 6.90 (1H, d, J=8.0 Hz, C_4-H) and 7.73 (1H, s, C_8-H).

Reaction of 3,4-methylenedioxyhomophthalic acid with benzylamine at 160° gave 2-benzyl-6,7-methylenedioxyhomophthalimide (Ib), m.p.125-127° ; ir νmax (nujol) 1700 and 1650cm^{-1} ; mass m/e 295 (M^+) ; nmr δ($CDCL_3$) 3.92 (2H, s, -CH_2-), 5.12 (2H, s, N-CH_2-), 6.00 (2H, s, -OCH_2O-), 6.60 (1H, s, C_5-H) and 7.52 (1H, s, C_8-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 νmax (nujol) 1650cm^{-1} ; mass m/e 279 (M^+), nmr δ($CDCL_3$) 5.15 (2H, s, N-CH_2-), 6.00 (2H, s, -OCH_2O-), 6.30 (1H, d, J=8.0Hz, C_3-H), 6.81 (1H, s, C_5-H), 6.92 (1H, d, J=8.0Hz, C_4-H) and 7.76 (1H, s, C_8-H).

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