SYNTHESIS OF DECARINE

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Abstract - The amine (IX), obtained by sodium borohydride reduction of the Schiff base derived from 1-amino-6,7-methylenedioxy naphthalene (VIII) and 3-benzyloxy-5-bromo-2-methoxy benzaldehyde (VII), on treatment with potassium amide in liquid ammonia gave decarine (Ia).

For confirming the position of the free phenolic group in decarine (Ia), Ishii et al. synthesized the compound (Ib) and showed it to be different from the ethoxy derivative of the alkaloid (Ic). Synthesis of decarine itself does not seem to have been achieved so far, probably because of the difficulty in obtaining a synthon with appropriate substitution pattern. In the present synthesis the requisite regioselectivity has been achieved by carrying out O-benzylation of the catechol II through its dianion and by exploiting the meta directing influence of the ester group in bromination of aldehyde IV.

Reaction of the catechol II with benzyl chloride (one mole) in the presence of sodium hydride (2 mole) in DMSO gave (50%) the phenol III (C14H12O3, mp 84-85°C). It was converted (98%) into the ethyl carbonate IV (C17H16O5, mp 58-59°C) and treated with bromine (1 mole) in water containing potassium bromide. The crude product (V) was hydrolysed (aq NaOH, CH3OH) to get (35%) the phenol VI (C14H11BrO3, mp 61-62°C); 1H NMR (CDCl3) δ 5.20 (2H, s, OCH2C6H5), 6.95, 7.10 (1H each, d, J = 9 Hz, ArH), 7.30-7.65 (5H, m, ArH), 10.40 (1H, s, CHO), 12.40 (1H, s, OH). Methylation led to VII (C15H13BrO3, mp 74-75°C) in which the nuclear position of the bromine atom was confirmed by the downfield position of the aldehydic resonance (δ 10.40) in the 1H NMR spectrum.

The naphthylamine VIII was obtained from piperonal in 5 steps and condensed with VII. The crude product on reduction with sodium borohydride in ethanol gave the amine IX (C26H22BrN04, mp 141-143°C) which was subjected to a benzyne cyclisation reaction with KNH2 in liquid ammonia (40 min). The usual work
up and crystallisation (CH$_3$OH/CHC$_3$) afforded Id (62%, C$_{26}$H$_{19}$NO$_4$, mp 210-211$^\circ$C). Debenzylation (CH$_3$COOH/HCl) furnished decarine (Ia, C$_{19}$H$_{13}$NO$_4$, mp 242-243$^\circ$C; lit.,$^9$ mp 243$^\circ$C), the identity of which was confirmed by comparison with an authentic sample$^{10}$ (mixture mp, t.l.c. and $^1$H NMR).

![Chemical structures](image)

REFERENCES AND NOTES
2. Reaction of the monoanion gave the isomeric product arising from benzylation at the more acidic phenolic site.
10. We are very grateful to Professor H.Ishii of Chiba University, Japan for an authentic sample of decarine.

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