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AZASTEROIDS IV. SYNTHESIS OF 13-AZA-18-NOREQUILENIN METHYL ETHER

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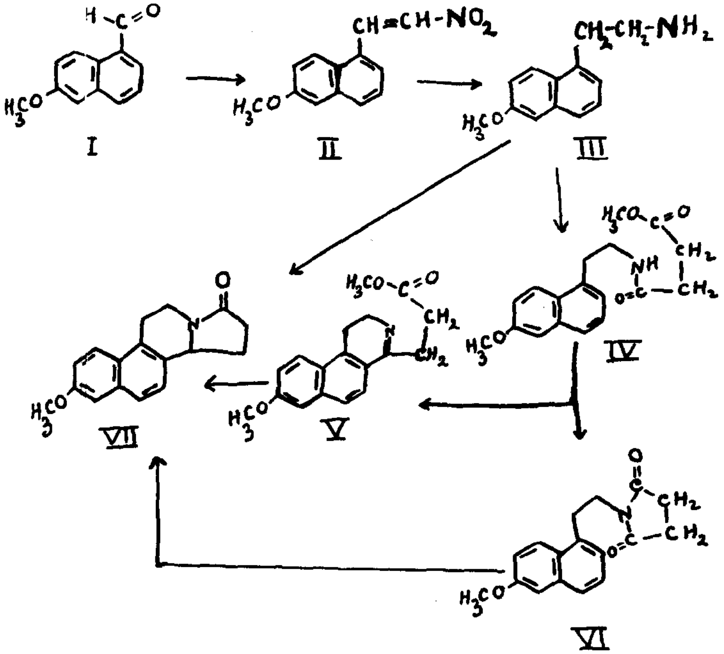
In continuation of our work on total synthesis (1) of nitrogen analogues of steroids of biological interest we report the synthesis of the title compound.

Grignard reaction (2) of 1-iodo-6-methoxynaphthalene (3) with ethylorthoformate furnished the aldehyde I ($C_{12}H_{10}O_2$, b.p. 160-162°/4 mm.) which was condensed with nitromethane in acetic acid and the product II ($C_{13}H_{11}NO_3$, m.p. 106-107°) was reduced with lithium aluminium hydride to obtain the amine III (b.p. 186-188°/5 mm.; picrate $C_{19}H_{18}N_4O_8$, m.p. 195-196°)

The amine III when condensed with β-carbomethoxypropionyl chloride yielded the amide IV ($C_{18}H_{21}NO_4$, m.p. 108-110°, λ_{max} 5.75, 6.06, 6.43 μ) which was cyclised (phosphorous oxychloride, 120 hours, room temperature) to obtain a basic and a neutral fraction.

The basic material (V) on hydrogenation (platinum and acetic acid) followed by thermal cyclisation afforded (±)-13-aza-18-norequilenin ($C_{17}H_{17}NO_2$, m.p.162-165°,λ_{max} 5.91,6.17, 6.25,6.61 μ).The neutral fraction on crystallisation furnished



the imide VI ($C_{17}H_{17}NO_3$, m.p. 130-131°, λ_{max} 5.89, 6.16,6.59 μ). Attempted cyclisation of VI (polyphosphoric acid, 1 hour,135-145°) resulted in the formation of a bluish green product (λ_{max} 6.0, 6.41, 8.0, 11.8, 12.1 μ) which was not investigated further(4).

The amide VII could also be isolated (low yield) from a single step condensation of the amine III with α-ketoglutaric acid (5) in refluxing acetic acid.

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