Interzooidal pores present. Zooecial chamber circular to subcircular in cross-section. Diaphragms—basal diaphragms numerous, closely spaced and convex aborally.

Remarks : It occurs in abundance in the drk grey, hard, arenaceous, fossiliferous, oolitic limestone of the Upper Tals and in the Coralline Limestone Bagh Beds. It resembles *Ceriocava corymbosa* (Lamouroux) in outline but differs from later in having thin endozone.

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SYNTHESIS OF HETEROCYCLES *VIA* LACTONES

A New Route to Nitrogen-sulphur Heterocycles[1]. A Novel Synthesis of N-(2-benzo [b] then-3-yl) Isoindole[1]

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ABSTRACT

A novel synthesis of N-(2-benzo [b] then-3-yl) ioindole (5) has been described starting from the condensation of 2-benzo [b] then-3-yl ethylamine (3) with ethyl 2-bromomethyl benzoate (2).

INTRODUCTION

A good number of derivatives of benzo [b] thiophenes possess remarkable biological activity[2]. They have been reported to have anti amino acid, anti histaminic pesticidal, analgetic, local anaesthetic and anticancerous activity[2]. Keeping in view the remarkable biological activity of the sulphur containing heterocycles, it was aimed to utilize the phthalide (1) for the synthesis of the sulphur containing isoindole derivative (5).

Following our own methodology[3,4] the phthalide (1) was converted to ethyl 2-bromomethyl benzoate (2) and condensed with 2-benzo [b] then-3-yl ethylamine[5] (3) in presence of potassium carbonate and catalytic amounts of potassium iodide in refluxing ethanol to get the tetracyclic lactam, N-(2-benzo [b] then-3-yl ethyl) isoindolin-1-one (4). The IR and NMR spectra for the idolin-1-one-(4) are in complete agreement with the proposed structure; IR (KBr) 1680 cm^{-1} [$\geq C=O$; 5 membered lactam; NMR (CCl_4) δ : 7·1 (s, S–CH), 5·06 (s, N—CH —Ar), 3·79 (t, $J = 8$ Hz; CH_2—CH_2—N), 3·10 (t, $J = 8$ Hz; CH_2—CH_2—N)]. The hydrochloride of the isoindolin-1-one (4) exhibited IR peaks at 2560, 1685 cm^{-1} ($\bar{N} = C—OH \leftrightarrow \overset{+}{N}—C=OH$). The NMR spectrum has a blurred signal at δ 9·1 (OH).

Lithium aluminium hydride reduction of the tetracyclic lactam (4) in refluxing tetrahydrofuran gave the title compound (5) which has been assigned the structure N-(2-benzo [b] then-3-yl) isoindole based on spectroscopic data; IR (KBr) 2380 cm^{-1} ($\overset{+}{N}H$, broad); NMR ($CDCl_3$) δ : 7·31 (s, aromatic H of isoindoline), 7·29 (*s*, S—CH), 5·26–4·85 and 4·49–4·08 (each a broad signal for N—CH_2—Ar), 3·62 (*s*, broad, CH_2—CH_2—$\bar{N}$) (*Scheme* 1).

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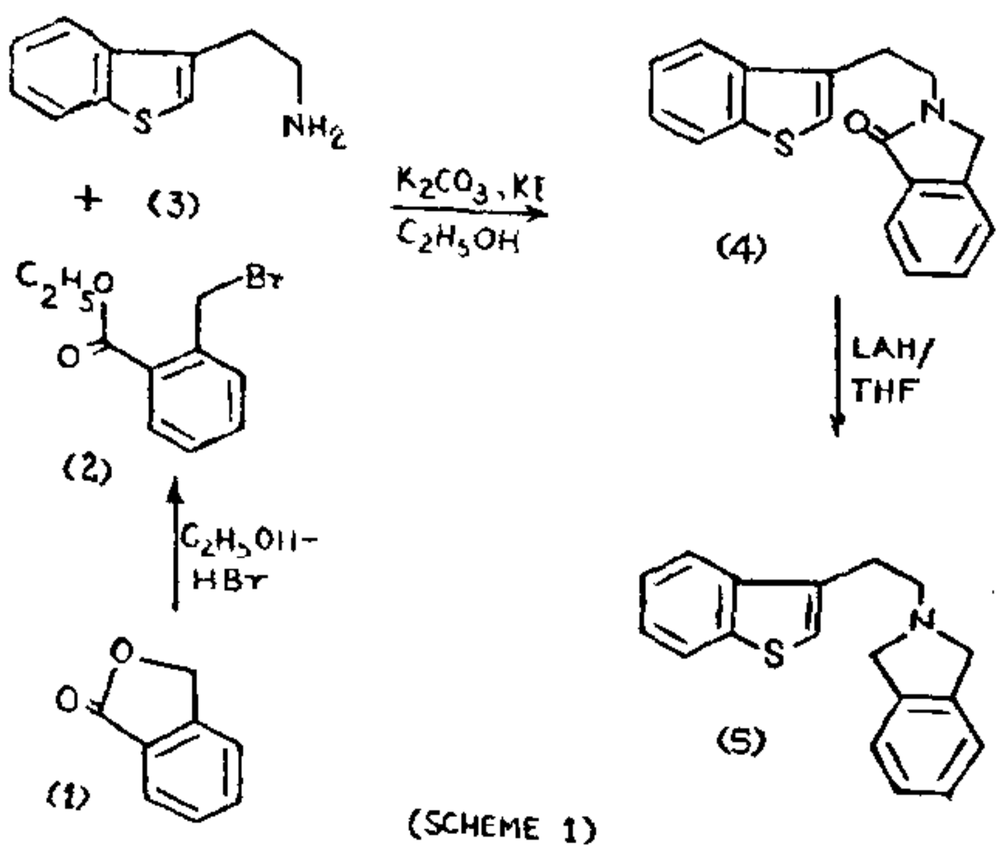

(SCHEME 1)

EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were recorded either on a Hitachi EPI-G_3 or a JASCO model IRS spectrophotometer. NMR spectra were recorded with a Varian T-60 spectrometer using TMS as internal standard.

Ethyl 2-bromomethyl benzoate (2)

1·35 g of phthalide (1) was added in portions to a solution of hydrogenbromide (2·50 g) in absolute ethanol (10 ml), cooled to 0° C with constant stirring. The lactone dissolved as the reaction mixture was allowed to reach 20°. The stirring was then stopped and the mixture set aside for 24 hrs. at 20°. The solvent and excess reagent were removed at reduced pressure to get the bromo ester (2) as an oil, 2·10 g (86%); IR ($CHCl_3$) 1716, 1460, 1400, 838 cm^{-1}. (Found: C, 49·15; H, 4·5; O, 11·0; $C_{10}H_{11}O_2$ Br requires C, 49·3; H, 4·4; O, 11·1%.

N-(2 Benzo [b] then-3-yl ethyl) isoindolin-1-one (4)

To a well stirred solution of ethyl 2-bromomethyl benzoate (2) (240 mg) in absolute ethanol (10 ml) containing anhydrous K_2CO_3 (100 mg) and potassium iodide (25 mg) was added, benzo [b] then-3-yl ethylamine (3) (260 mg). The solution was refluxed at 100° for 72 hrs. The cooled solution was diluted with an excess of water and extracted with $CHCl_3$ (30 ml) washed with water (2 × 40 ml) and dried (Na_2SO_4). Removal of the solvent *in vacuo* gave a syrup which recrystallized from isopropanol to give (4) 200 mg (66·6%) m.p. 106–107°.

(Found : C, 73·39; H, 5·06; N, 4·85, $C_{18}H_{15}NOS$ requires C, 73·69; H, 5·15; N, 4·78%).

The hydrochloride of (4) was obtained as plates from ethanol-ether, m.p. 141–142°.

(Found : C, 65·43; H, 4·96, Cl, 10·20; $C_{18}H_{16}ClNOS$ requires C, 65·54; H, 4·89, Cl, 10·75%).

N-(2-Benzo [b] then-3-yl ethyl) isoindoliniumchloride (5)

145 mg of the foregoing anhydrous lactam (4) was added in portions to a suspension of 375 mg of lithium aluminium hydride in 12·0 ml of anhydrous tetrahydrofuran and the reaction mixture stirred and refluxed for 4 hrs. The excess of hydride was decomposed at 0° with moist ethyl acetate and the reaction mixture was made alkaline with 0·1 N aqueous sodium hydroxide solution. The organic layer which separated was extracted repeatedly with dilute HCl and the combined acid extracts when made alkaline gave a solid which was dissolved in ether, washed well with water, dried (Na_2SO_4) and treated with dry hydrogen chloride to get the hydrochloride (5), 120 mg (74%), m.p. 189°. Recrystallization from ethanol-ether gave (5), m.p. 191–194° (sublimed 160°).

(Found : C, 68·06; H, 5·60; Cl, 11·25; N, 4·23; $C_{18}H_{18}ClNS$ requires C, 68·45; H, 5·74; Cl, 11·23; N, 4·43%).

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