It is significant that when *p*-bromoacetanilide and *p*-nitroacetanilide were subjected to a similar photo-oxygenation, they did not give any *ortho* substituted product and starting materials were recovered unchanged.

Further investigations on the reaction of other acylamines, the nature and mechanism of the reaction and energy transfer process during rearrangement are in progress.

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SYNTHESIS OF HETROCYCLES *VIA* LACTONES[1]—A NOVEL SYNTHESIS OF SULPHUR *CONTAINING HETEROCYCLES*[2]—SYNTHESIS OF 1-DESAZA-1-THIA-15, 16, 17, 18, 19, 20-HEXADEHYDROYOHIMBANE

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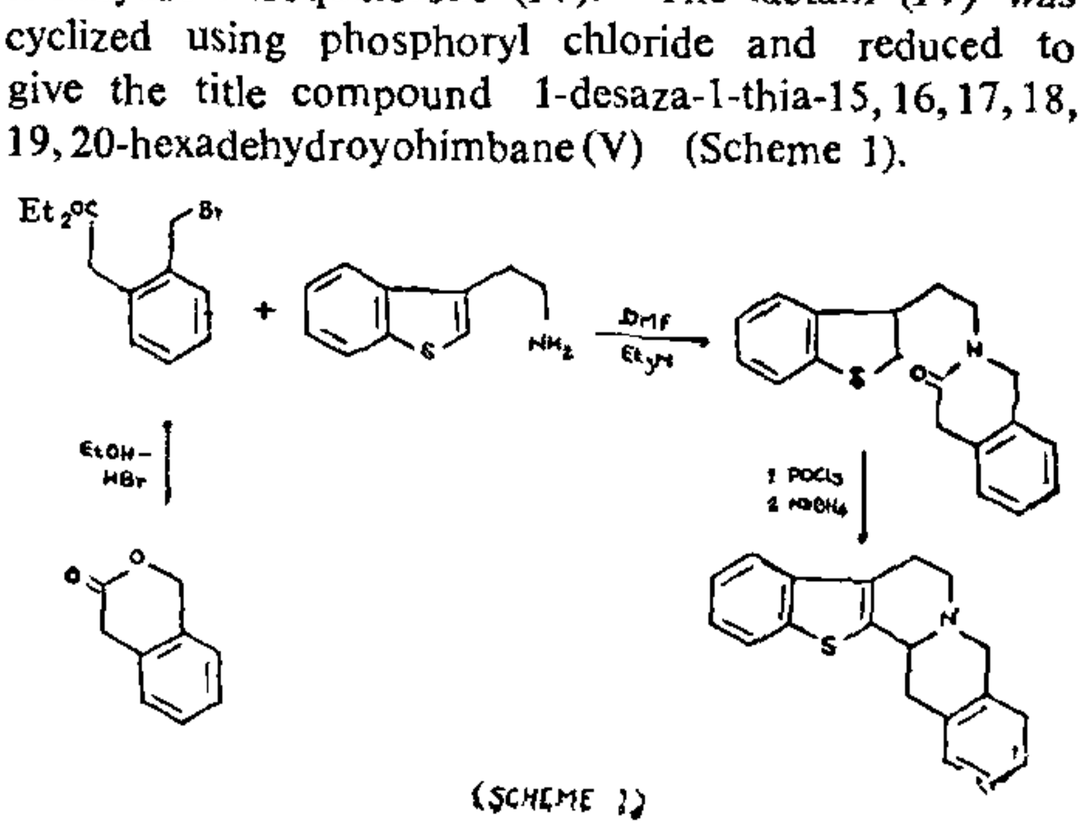
ABSTRACT

Recently we reported some convenient syntheses of the isoquinoline alkaloids using 3-isochromanones and the bromo esters derived from them. Now, a new synthesis of a sulphur-heterocycle, *viz.*, 1-desaza-1-thia-15, 16, 17, 18, 19, 20-hexadehydroyohimbane(V) is being described using the 3-isochromanone.

INTRODUCTION

RECENTLY some new syntheses of 1,2,3,4-tetrahydroisoquinoline[3], N-benzyl-1,2,3,4-tetrahydroisoquinoline[4], N-phenethyl-1,2,3,4-tetrahydroisoquinoline, and berbine[5] alkaloids have been reported from this laboratory using the 3-isochromanones and the bromo esters derived from them as the potential tools. Our continuing experiments on synthesis of heterocycles have led us to successful utilization of the bromo ester (II) for the sulphur containing heterocycle synthesis and we report the results in the present paper.

3-Isochromanone (I) was prepared by the method of Swan[6]. This on dissolution in cooled ethanolic-hydrobromic acid gave the bromo ester (II). The ester (II) was condensed with benzo (b) then-3-ylethylamine[7] (III) in dimethylformamide under basic conditions to give N-(*β*-benzo (b) then-3-yl)ethyl-1,2,3,4-tetrahydro-3-isoquinolone (IV). The lactam (IV) was cyclized using phosphoryl chloride and reduced to give the title compound 1-desaza-1-thia-15, 16, 17, 18, 19, 20-hexadehydroyohimbane (V) (Scheme 1).



(SCHEME 1)

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Experimental

M.p.s are incorrected and were recorded on a 'Toshniwal' m.p. apparatus. IR spectra were recorded on a Perkin Elmer 337 spectrophotometer. NMR spectra were recorded on a Varian Associates A–60 spectrometer using TMS as an internal standard. All solutions were dried over anhydrous sodium sulphate.

Ethyl 2-bromomethylphenyl acetate (II)

3-Isochromanone (I) (450 mg) was added in portions to a solution of hydrogen bromide (800 mg) in abs. ethanol (6 ml) cooled to 0° with constant stirring. The lactone dissolved as the reaction mixture was allowed to reach room temperature. The mixture was then set aside for 24 h. The solvent and excess reagent were then removed at reduced pressure to give the ester (II) as a clear oil, 700 mg (90·9%); IR ($CHCl_3$) 1717, 1460, 1400, 840 cm^{-1} (Found : C, 51·5; H, 4·90; Br, 31·6. $C_{11}H_{13}O_2$ Br requires C, 51·3; H, 5·05; Br, 31·1%).

N-(β-benzo (b) then-3-yl) ethyl-1,2,3,4-tetrahydro-3-isoquinolone (IV)

To a well-stirred solution of ethyl 2-bromomethylphenyl acetate (II) (520 mg) in dimethylformamide (5 ml) containing triethylamine (0·6 ml) was added benzo (b) then-3-yl ethyl amine (III) (330 mg). The mixture was refluxed at 100° for 60 hr. The cooled solution was diluted with water and extracted with methylene dichloride to leave a syrupy residue. Recrystallization from ethanol gave (IV), 480 mg (66%), IR (KBr) 1635 cm^{-1} (six membered lactam) (Found : C, 74·2; H, 5·61; N, 4·83. $C_{19}H_{17}ONS$ requires C, 74·0; H, 5·84; N, 4·54%).

1-Desaza-1-thia-15,16,17,18,19,20-hexadehydroyohimbane (V)

Freshly dsistilled phosphoryl chloride (1·5 ml) was added to a solution of the foregoing lactam (IV) (250 mg) in dry toluene (6 ml). The solution was heated at 95° for 2 hr. The residue left after evaporation of the reagent and solvent was treated with ice, the organic materials extracted with chloroform (2 × 15 ml) and solvent distilled *in vacuo* to leave a residue. The residue was dissolved in methanol (10 ml) and water (1 ml) and treated with sodium borohydride (70 mg). The mixture was refluxed at 100° for 1·5 hr. Evaporation of the solvent, dilution with water (10 ml) and extraction with ether (10 × 3 ml) gave a syrup after *in vacuo* removal of the solvent which recrystallized from ethanol to give (V), 160 mg (65%), m.p. 176–178°).(lit.[8], m.p. 177–179°); IR (KBr) 2900, 2825, 2740 cm^{-1}; NMR ($CDCl_3$) δ: 4·4–3·62 (*m*, –CH–N–CH_2–Ar), 3·59–2·69 (*m*, Ar–CH_2–CH_2–N–CH–CH_2–Ar) (Found : C, 78·4; H, 5·71; N, 4·72. $C_{19}H_{17}NS$ requires C, 78·3; H, 5·84; N, 4·81%).

The hydrochloride of (V) melted at 208–209° (dec.).

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