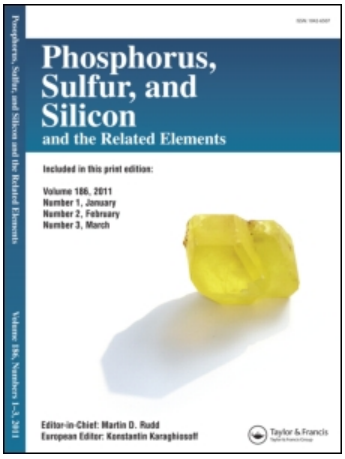

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Novel Synthesis of Tetracyclic Heterogonane Ring Systems

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NOVEL SYNTHESIS OF TETRACYCLIC HETEROGONANE RING SYSTEMS

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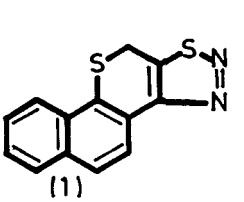
Abstract Total synthesis of tetracyclic heterogonane ring systems(**1**,**2** & **3**) were achieved from 1-oxo-4-thia-1,2,3,4-tetrahydrophenanthrene(**4**) and its oxa analogue(**5**).

INTRODUCTION

In our broad programme[1-3] to develop the novel methods to synthesize newer types of pharmaceutically important sulfur heterocycles, we wish to report the total synthesis of tetracyclic heterogonane ring systems(**1**,**2** & **3**) starting with tricyclic ketones, 1-oxo-4-thia-1,2,3,4-tetrahydrophenanthrene (**4**) and 1-oxo-4-oxa-1,2,3,4-tetrahydrophenanthrene(**5**).



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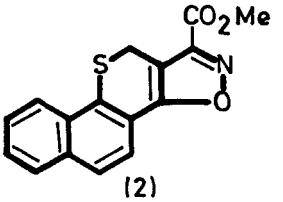

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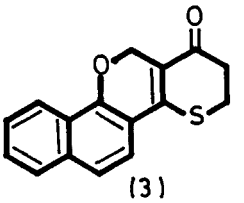

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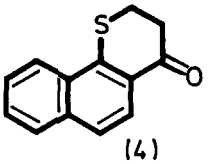

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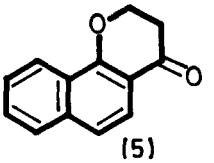

(5)

Treatment of 4-thiatricyclic ketone(**4**)[4] with p-toluenesulfonylhydrazide in ethanol containing few drops of Conc.HCl gave the corresponding tosylhydrazone derivative, as colorless crystalline solid, mp 189-190°C, in 90% yield. Treatment of tosylhydrazone derivative with excess of thionyl chloride in methylene chloride at room temperature for 12 h furnished a dark brown solid, which on chromatographic puri-

fication over silicagel, eluted with hexane-ethyl acetate (8:2) afforded tetracyclic thiadiazole derivative, 11H-naphtho[2',1':5,6]thiopyrano[4,3-d][1,2,3]thiadiazole(**1**), as brown solid, mp 110-112°C, in 50% yield; ^{1}H-NMR($CDCl_3$): δ 4.2 (s, 2H, SCH_2) and 7.0-8.0 (m, 6H, ArH); MS: m/z 256(M^+,56%).

Condensation of 4-thiatricyclic ketone(**4**) with dimethyl oxalate in the presence of sodium methoxide gave the corresponding glyoxalate derivative, as yellow solid, mp 92-94°C, in 80% yield. Condensation of the aforesaid glyoxalate derivative with hydroxylamine hydrochloride in refluxing glacial acetic acid furnished a dark brown solid, which on chromatographic purification over silicagel, gave the tetracyclic isoxazole derivative, 17-methoxycarbonyl-15-oxa-16-aza-11-thiagona-1,3,5(10),6,8,13,16-heptaene(**2**), as brown solid, mp 202-203°C, in 40% yield. IR(KBr): ν_{max} 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.85(s, 3H, OCH_3), 4.2(s, 2H, SCH_2) and 7.1-7.95 (m, 6H, ArH); MS: m/z 297(M^+,10%).

1-Oxo-4-oxa-1,2,3,4-tetrahydrophenanthrene(**5**)[5] was condensed with 3-mercaptopropionic acid in the presence of p-toluenesulfonic acid(PTSA) in refluxing benzene for 20 h afforded dark brown solid, which on chromatographic purification over silicagel, gave from benzene-hexane(1:1) eluates the tetracyclic gonane derivative, D-homo-11-oxa-15-thiagona-1,3,5-(10),6,8,13-hexaen-17a-one(**3**), as yellow solid, mp 157-158°C, in 25% yield. IR(KBr): ν_{max} 1630 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.3-3.3(tt, 4H, SCH_2CH_2CO, J=6 Hz), 4.98(s, 2H, OCH_2) and 6.9-7.9(m, 6H, ArH); MS: m/z 268(M^+,100%). All new compounds mentioned above gave the expected microanalytical results.

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