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NOVEL SYNTHESIS OF TETRACYCLIC HETEROGONANE RING SYSTEMS

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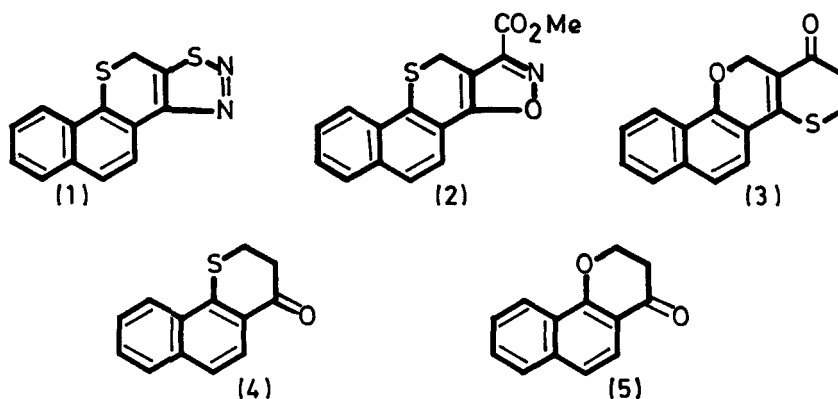
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Abstract Total synthesis of tetracyclic heterogonane ring systems(1,2 & 3) were achieved from 1-oxo-4-thia-1,2,3,4-tetrahydrophenanthrene(4) and its oxa analogue(5).

INTRODUCTION

In our broad programme¹⁻³ 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).



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; $^1\text{H-NMR}(\text{CDCl}_3)$: 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} ; $^1\text{H-NMR}(\text{CDCl}_3)$: 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} ; $^1\text{H-NMR}(\text{CDCl}_3)$: δ 2.3-3.3(tt, 4H, $\text{SCH}_2\text{CH}_2\text{CO}$, 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.

REFERENCES

1. B. Ramesh Babu, D.V. Ramana and S.R. Ramadas; Phosphorus, Sulfur and Silicon, **60**, 175 (1991)
2. B. Ramesh Babu, D.V. Ramana and S.R. Ramadas; Sulfur Letters, **7**, 225 (1988)
3. B. Ramesh Babu, D.V. Ramana and S.R. Ramadas; Steroids, **56**, 388 (1991)
4. S.R. Ramadas and M. Vijayakrishna; Indian J. Chem, **22**, 1093 (1983)
5. S.D. Sharma and S. Kaur; Indian J. Chem, **23**, 518 (1984)