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A synthon approach to spiro compounds

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Contents

1. Introduction 780
2. Biological activities 780
3. Photochromism 783
4. Synthesis 784
   4.1. Antithetic analysis of spiro unit 785
      4.1.1. Cleavage at branch appendage(s) 785
      4.1.2. Cleavage at ring appendage(s) 786
      4.1.3. Disconnection at both branch and ring appendage(s) 786
   4.2. Synthesis of spiro compounds by using prestruct Ia 787
   4.3. Synthesis of spiro compounds by using prestruct Ib 789
   4.4. Synthesis of spiro compounds by using prestruct Ic 790
   4.5. Synthesis of spiro compounds by using prestruct Id 792
   4.6. Synthesis of spiro compounds by using prestruct Ie 792
   4.7. Synthesis of spiro compounds by using prestruct IIa 792
   4.8. Synthesis of spiro compounds by using prestruct IIb 802
   4.9. Synthesis of spiro compounds by using prestruct IIc 809
   4.10. Synthesis of spiro compounds by using prestruct IId 811
   4.11. Synthesis of spiro compounds by using prestruct IIIa 811
   4.12. Synthesis of spiro compounds by using prestruct IIIb 821
   4.13. Synthesis of spiro compounds by using prestruct IIIc 821
   4.14. Synthesis of spiro compounds by using prestruct IIId 822
   4.15. Synthesis of spiro compounds by using a different type of prestruct 822
Acknowledgements 823
References and notes 823
Biographical sketch 827

Keywords: Photochromism; Synthon; Spiro compounds.
Abbreviations: BINAP, 2,2′-bis(diphenylphospospiro)-1,1′-binaphthalene; Boc, *t*-butoxycarbonyl; CTAB, cetyltrimethylammonium bromide; DEAD, diethylazodicarboxylate; 4-DMAP, 4-(dimethylamino)pyridine; Fmoc, 9-fluorenylmethoxycarbonyl; HMPA, hexamethylphosphoric amide; HMPT, hexamethylphosphorous triamide; KHDMS, potassium hexamethyldisilazide; LAH, lithium aluminium hydride; LDA, lithium diisopropylamide; LiHDMS, lithium hexamethyldisilazide; *m*-CPBA, *m*-chloroperbenzoic acid; NaHMDS, sodium hexamethyldisilazane; NBS, *N*-bromosucinimide; NCS, *N*-chlorosuccinimide; NMO, *N*-methylmorpholine *N*-oxide; PCC, pyridinium chlorochromate; PDC, pyridinium dichromate; Ph, phenyl; PhH, benzene; PhMe, toluene; PLG, L-propyl-leucyl-glycinamide; PMP, 1,2,2,6,6-pentamethylpiperidine; PPTS, pyridinium toluene-4-sulphonate; rt, room temperature; TFA, trifluoro acetic acid; THF, tertrahydrafuran; TMEDA, *N*,*N*,*N*′,*N*′-tetramethylethylene diamine; TMPA, tetramethylene phosphoramide; Tol, *p*-tolyl; TPAP, tetrapropylammonium perruthenate; *p*-TSA, *p*-toluene sulphonic acid; Z, benzyloxycarbonyl.
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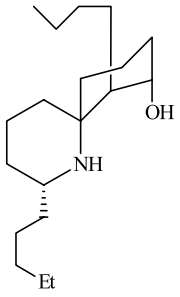
1. Introduction

In 1900, Bayer created the first spiran described as a bicyclic hydrocarbon connected by a single carbon. The term spirocyclanes was used to describe the family of such hydocarbon. Due to the tetrahedral nature of the spiro-linked carbon, the ring planes are nearly perpendicular to each other.

Spiro compounds having cyclic structures fused at a central carbon are of recent interest due to their interesting conformational features and their structural implications on biological systems. The asymmetric characteristic of the molecule due to the chiral spiro carbon is one of the important criteria of the biological activities. The retention of neurotoxic properties of perhydrohistrionicotoxin (**1**), an analogue of a natural product **2**, is clear evidence of the role of the spiro carbon in steering the biological activity.[1]



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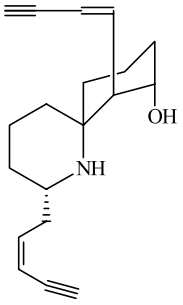


2

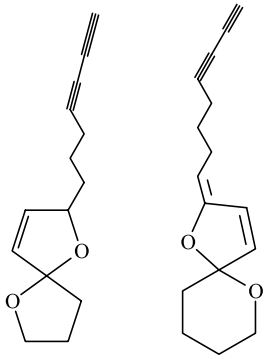
The presence of the sterically constrained spiro structure in various natural products also adds to the interest in the investigations of spiro compounds.[2] Spiro compounds represent an important class of naturally occurring substances characterised by their highly pronounced biological properties.[3–5]

In the arena of photochromism, spiro compounds, due to their steric constraints, equilibrate with the corresponding non-spiro analogue and exhibit various photochemical phenomena. The discovery of the photochromic reactions of spiropyrans[6] (Scheme 1) during 1952 initiated the work in the area of photochemical erasable memory.[7]

Some more related applications based on the equilibrium are self-development photography, actinometry, displays, filters and lenses of variable optical density etc.[8]

2. Biological activities

The spiro functionality has been known for a long time to be present in phytochemicals either in alkaloids, lactones or terpenoids. The spirocyclic alkaloid (−)-histrionicotoxin (**2**), isolated from skin extracts of the poison dart frog, *Dendrobats histrionius*, found in Columbia, is a very potent nicotinic receptor antagonist.[9] Spiroketals are reported to be the sub-units of many naturally occurring substances of biological interest such as insect pheromones, antifeedants and polyether antibiotics.[10] A series of spiroketals (**3–6**) have been isolated from *Chrysanthemum coronanium*, a common vegetable of South China.[11] Some of these compounds are found to have antifeeding activity towards silkworm[12] and spasmolytic and antiphlogistic activity.[13,14] Unsaturated spiroacetals such as 1,6-dioxaspiro[4.4]nona-3,8-diene[15] and 1,6-dioxaspiro[4.5]decane[16] have also been isolated from *Artemisia sp.*



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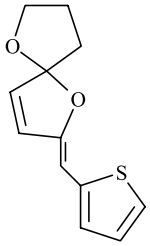

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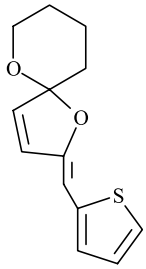

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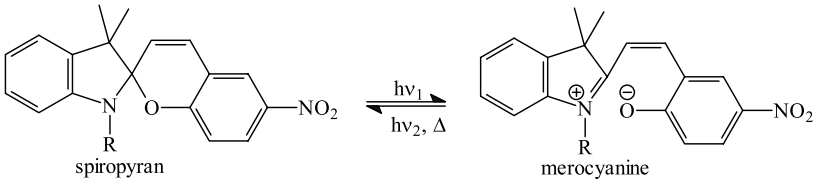
The spiro [pyrrolidin-3,3′-indole] ring system is a recurring structural motif in a number of natural products such as vinblastine and vincristine, that function as cytostatics and are of prime importance in cancer chemotherapy.[17] The derivatives of spiro-oxindole find very wide biological application as antimicrobial, antitumour, and antibiotic agents, and inhibitors of human NK-1 receptor etc.[18–20] Horsfiline (**7**), an oxindole alkaloid containing a spiro-[indole-pyrrolidone] nucleus, has been isolated by Bodo and co-workers[21] from *Horsfieldia superba*, a tree from Malaysia, the extracts of which are commonly employed in local medicine.

The saponaceolides (A–D), **8** are found to possess antitumour activity in 60 human cancer cell lines.[22] Each of these compounds contains a unit of tricyclic trioxaspiroketal.



Scheme 1.

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