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Principal Investigator		Co- Principal Investigator and Technical Coordinator
Prof. A.K.Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi		**Dr. Vimal Rarh** Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi *Specialised in : e-Learning and Educational Technologies*
Paper Coordinator	**Content Writer**	**Reviewer**
Prof. J M Khurana Professor, Department of Chemistry University of Delhi	**Dr. Vimal Rarh** Asst Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi **Dr. Swarndeep Kaur Sethi** Asst Professor Acharya Narendra Dev College University of Delhi	**Prof. H G Krisnamurty** Professor Emeritus, Department of Chemistry University of Delhi

Anchor Institute : SGTB Khalsa College, University of Delhi

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1. Learning Outcomes

After studying this module, you shall be able to

- Know about spiranes and their basic structure
- Understand the properties of spiranes along with their IUPAC nomenclature.
- Learn about the structural aspects of spiranes.
- Analyse the aspect of chirality in spiranes.
- Study the assignment of correct absolute configuration to spiranes.

2. Introduction and Nomenclature of Spiranes

In the previous modules, we have studied in detail about the stereochemistry of biphenyls and allenes. When one replaces *both* the double bonds in an allene by rings, one obtains a bicyclic ring system in which the two rings have one atom in common. Such bicyclic systems are called “spiranes”.

The root name of spiranes is based on the number of C atoms in the ring structures. The prefix **spiro[x.y]** is added where **x** and **y** are the number of atoms. The size of the rings is indicated in square brackets by counting the number of atoms in the links that make each ring, **x** and **y**, ***excluding* the spirocenter**. The number of atoms in the links is listed smallest first, *i.e.* **spiro[x.y]** where **y** > **x**. For substituted spiroalkanes, the rings are numbered **starting on the smallest ring *adjacent* to the spirocenter**.

Functional group is an alkane, therefore suffix = **-ane**. The ring structure requires the prefix **spiro**. The ring structure is C5 therefore root = **pent**. Excluding the spirocenter, there are two C atoms in each ring = **[2.2]**.

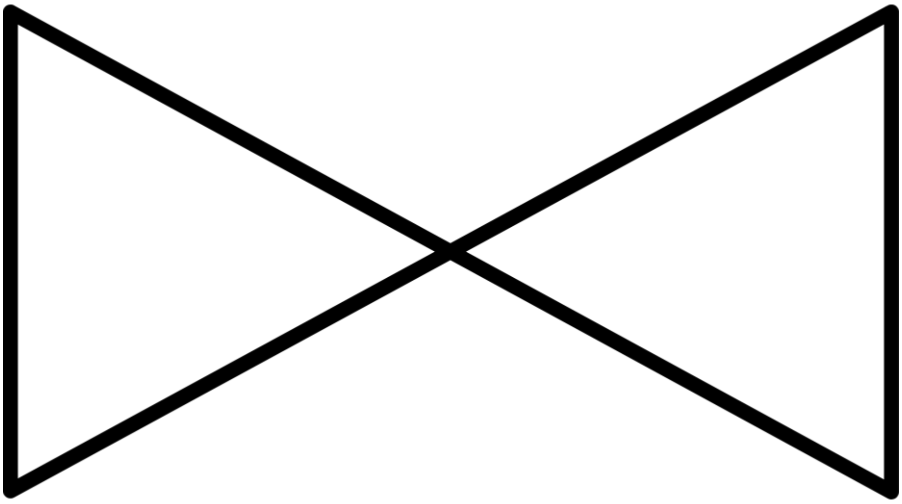


Fig. 1 : spiro[2.2]pentane

Functional group is an alkane, therefore suffix = **-ane**. The ring structure requires the prefix **spiro**. The ring structure is C9 therefore root = **non**. Excluding the spirocenter, one ring has three C atoms and the other has five C atoms = **[3.5]**. There is a C1 substituent = **methyl** group. The lowest locant (first point of difference) = **1**.

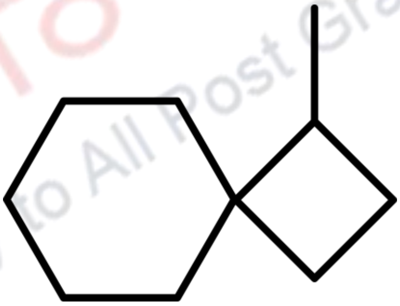


Fig. 2: 1-methylspiro[3.5]nonane

When unsaturation is present, the same enumeration pattern is maintained, but in such a direction around the rings that the double and triple bonds receive numbers as low as possible in accordance with the earlier stated rules.

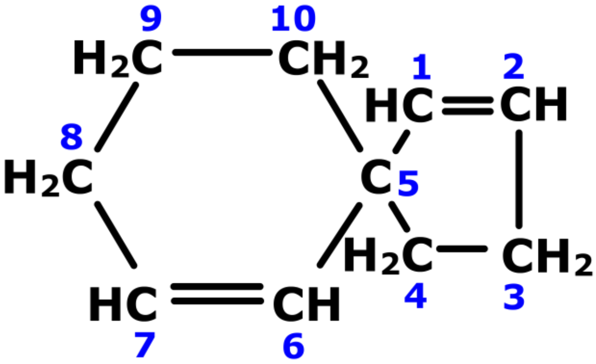


Fig. 3: Spiro[4.5]deca-1,6-diene

If one or both components of the monospiro compound are fused polycyclic systems, "spiro" is placed before the names of the components arranged in alphabetical order and enclosed in brackets. Established numbering of the individual components is retained. The lowest possible number is given to the spiro atom, and the numbers of the second component are marked with primes. The position of the spiro atom is indicated by placing the appropriate numbers between the names of the two components.

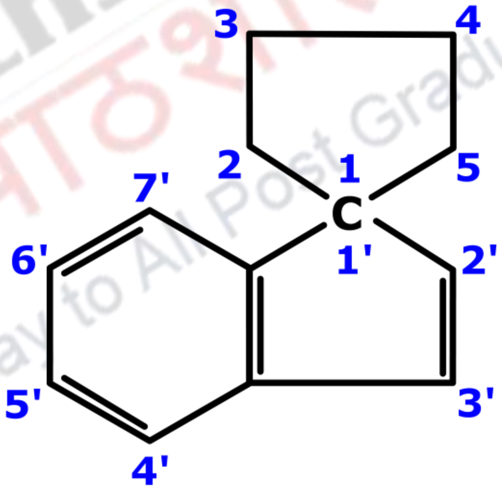


Fig. 4: Spiro[cyclopentane-1,1’-indene]

Monospiro compounds containing two similar polycyclic components are named by placing the prefix "spirobi" before the name of the component ring system. Established enumeration of the polycyclic system is maintained and the numbers of one component are distinguished by primes. The position of the spiro atom is indicated in the name of the spiro compound by placing the appropriate locants before the name.

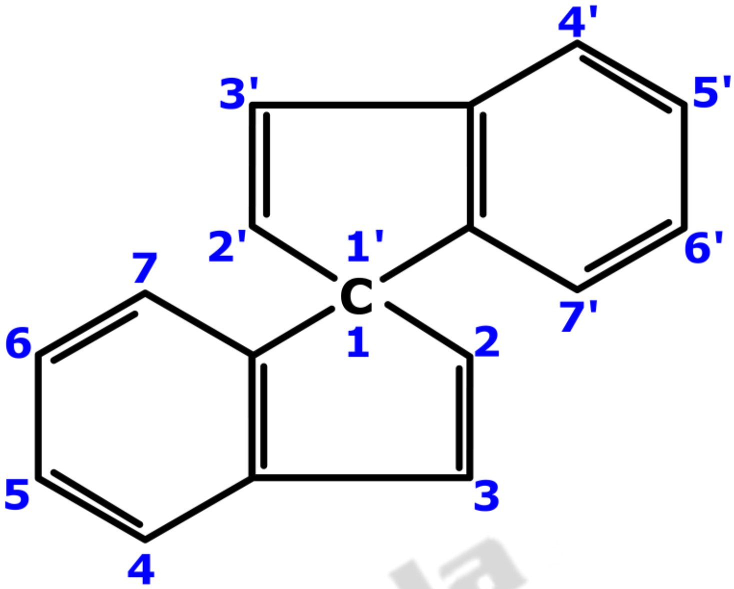
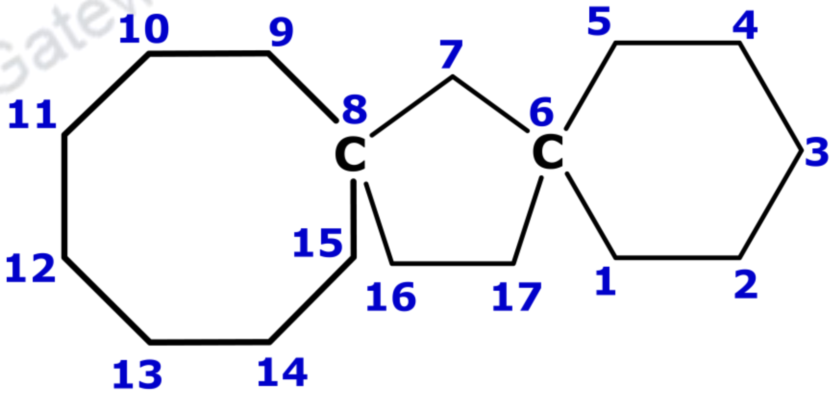


Fig. 5: 1,1’-spirobiindene

Polyspiro compounds consisting of a linear assembly of three or more alicyclic systems are named by placing "dispiro-", "trispiro-", "tetraspiro-", etc., before the name of the unbranched-chain acyclic hydrocarbon of the same total number of carbon atoms. The numbers of carbon atoms linked to the spiro atoms in each ring are indicated in brackets in the same order as the numbering proceeds about the ring. Numbering starts with a ring atom next to a terminal spiro atom and proceeds in such a way as to give the spiro atoms as low numbers as possible after numbering all the carbon atoms of the first ring linked to the terminal spiro atom.



Polycyclic compounds containing more than one spiro atom and at least one fused polycyclic component are named in accordance with earlier part of this rule by replacing "spiro" with "dispiro", "trispiro", etc., and choosing the end components by alphabetical order.

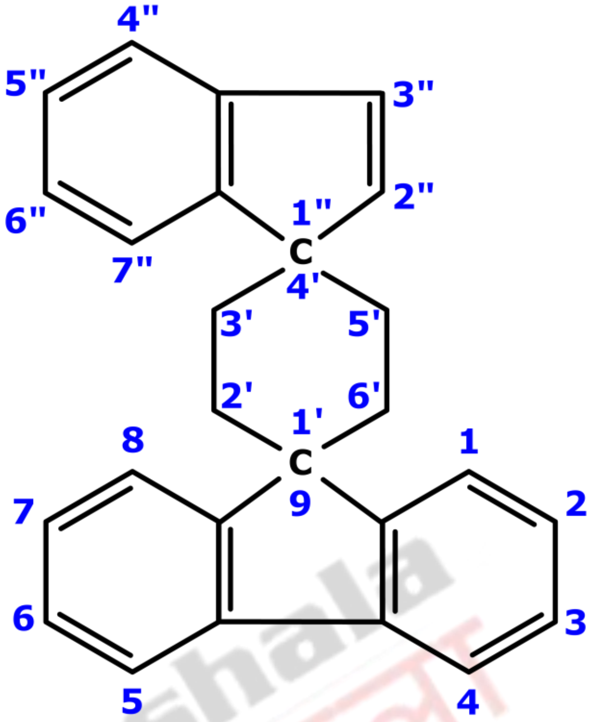


Fig. 6: Dispirofluorene-9,1’-cyclohexane-4’,1’’-indene

In this module we are going discuss about various aspects of spiranes, their stereochemistry and their structural details.

3. Spiranes

It is true that the structure of spiranes is firmly entrenched, the name is somewhat inept. The name "spirane," from the Latin *spira* meaning twist or whorl implies that spiranes are not planar; it is their nonplanarity that gives rise to their chirality. The two rings of the spirane, similar to the pi bonds of the allene are orthogonal and the groups attached to the two ends define planes at right angles to the adjacent and to each other (Figure 7).

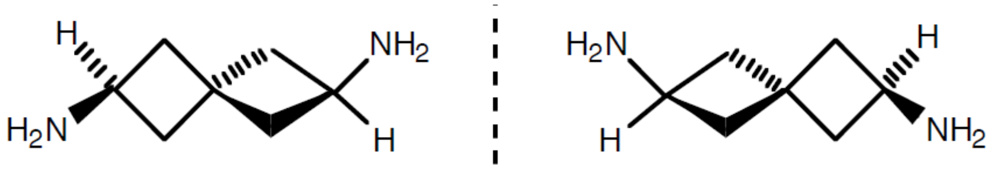
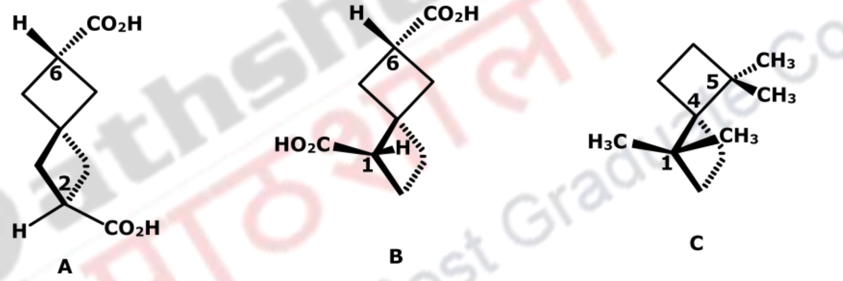


Fig. 7: This figure shows The two rings of the spirane, similar to the pi bonds of the allene are orthogonal and the groups attached to the two ends define planes at right angles to the adjacent and to each other.

Among the chiral spiranes (Figure 8) one may discern three types: A. which definitely displays axial chirality similar to that of allenes and alkylidenecycloalkanes B, which, like corresponding alkylidenecycloalkanes, displays central rather than axial chirality; and C, which conceptually would appear to display axial chirality but, for purposes of nomenclature, is considered to have a chiral centre (Cahn, Ingold and Prelog, 1966). Compound A is described as indicated in Figure 8, the descriptor is a S or P. Compound B has four stereoisomers (2 pairs of enantiomers); C(1) is a chiral centre, whereas C(6) displays cis-trans isomerism and the stereoisomer shown is 1S,6-trans. To name C one arbitrarily gives one ring preference over the other; the more substituted branch in that ring than has priority l and the less substituted has priority 3, whereas the corresponding priorities in the arbitrarily less favoured ring are 2 and 4. The configuration is then 4R; the spiro centre C(4) is considered a chiral center.



(S)-Spiro[3.3]heptane-2,6-dicarboxylic acid "Fecht acid"(P)

(1S,t-6)-Spiro[3.3]heptane-1,6-dicarboxylic acid

(R)-1,1,5,5-Tetramethyl spiro[3.3]heptane

Fig. 8: Types of spiranes

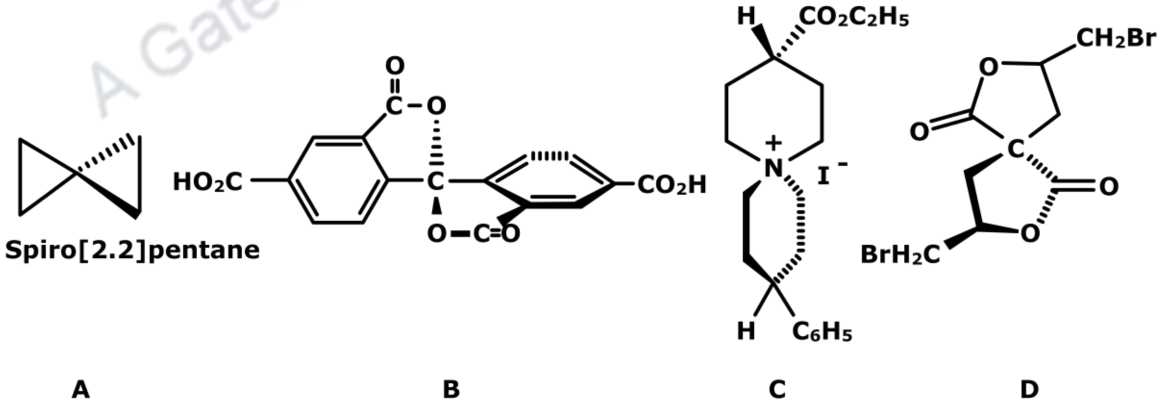


Fig. 9: Examples of spiranes

The most strained saturated spirane, spiro[2.2]pentane (Figure 9, A), was apparently first synthesized in 1896 by Gustavson (q.v.) although it was not then recognized as such. Its strain of 65 kcal mol^{-1} (272 kJ mol^{-1}] is only about 10 kcal mol^{-1} (42 kJ mol^{-1}) greater than that of two isolated cyclopropane rings. Chirality in spiranes, first recognized by Aschan (1902) was demonstrated in 1920 by Mills and Nodder (q.v.) by resolution of a spirodicarboxylic acid (Figure 9, B). This compound is of type C in Figure 8; the central carbon atom can be described as a chiral centre. However, a compound of type A in Figure 8 was resolved 5 years later (Mills and Warren, 1925); it is shown in Figure 9, C. It is of interest that the spiro centre of compound C is a quaternary nitrogen rather than a carbon atom. Compound D in Figure 9 is also interesting; it has a spiro centre and two conventional chiral centres; contemplation of models indicates the existence of three diastereomeric racemates, which have, in fact, been isolated (Leuchs and Giesler, 1912].

Several assignments of absolute configuration of spiranes of type C in Figure 8 have been accomplished. The first correct one, found by Gerlach in 1968) is concerned with the dione shown in Figure 11 and is based on that of its diol precursor shown in the same figure. The relative configuration of this diol had been established by the absence of intramolecular hydrogen bonding and by reductive correlation with a single one of the two diastereomeric mono-ols. The latter result demands **C_2** symmetry, that is, structures **5** and **6** (Figure 10) are excluded. The former result (absence of intramolecular hydrogen bonding) excludes **1** (Figure 10) and its enantiomer **2**. Finally, the absolute configuration of the diol was established by the absence of intramolecular hydrogen bonding and by reductive correlation with a single one of the two diastereomeric mono-ols. Horeau finally established Horeau's rule for assigning absolute configuration of the diol. Oxidation of this diol must lead to the (S)-dione, which, experimentally was found to be laevorotatory.

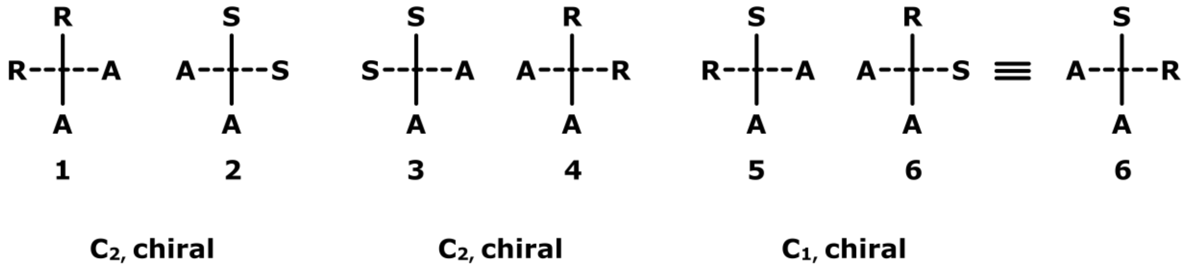


Fig. 10: Combination of spirane and conventional chiral centres

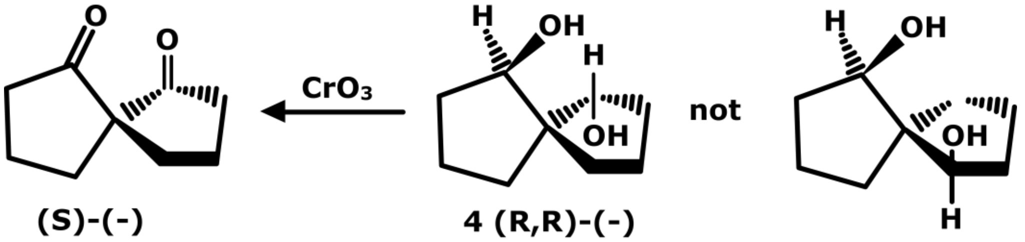


Fig. 11: Configuration of spiro[4.4]nonane-1,6-dione. Intramolecular hydrogen bonding is possible in isomer 1 and in its enantiomer (2, Figure 10)

In 1969, Brewster and Jones correlated the levorotatory quaternary ammonium salt A (Figure 12) by a Stevens rearrangement and considering the rearrangement is superfacial, the configuration at the stereogenic carbon in the product is correlated with that of the starting spirane. The configuration of B is, in turn, correlated chemically with that of (S)-aspartic acid as shown in the figure, i.e., by oxidising the aromatic rings to carboxyl groups. The configuration of laevorotatory spirane is therefore **R**. (Figure 12).

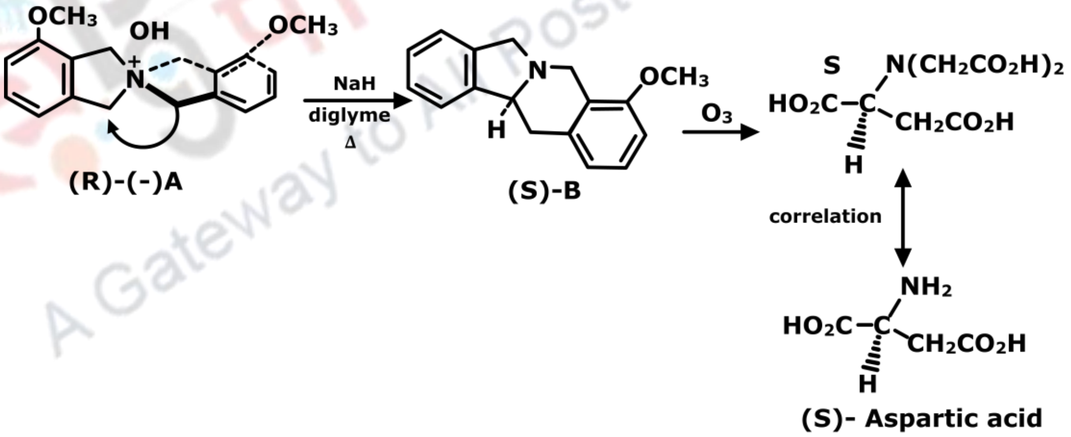


Fig. 12: Correlation of spiroammonium salt with (*S*)-aspartic acid

The third, in principle more direct correlation of configuration of a spirane of the type **C** (Figure 8) by synthesis from a compound with a chiral centre of established configuration at first miscarried because of experimental problems. The correct correlation given by Overberger et al in 1981 is shown in Figure 13. The configuration of the key intermediate, (R)-(-)-**A** was established by conversion of sulphonamide (R)-(+)-**B** whose enantiomer was chemically correlated with (S)-methyethyl succinic acid. The configuration of the latter had been established by Porath in 1951 by the methods of quasiracemates. The compound (R)-(-)-**A** was then converted to a spirane, (+)-**C**, further reduced to diazaspirane (-)-**D** by reduction. The correlation shown in Figure 13 proves that (+)-**C**, (-)-**D** and its derived dextrorotatory have the **R** configuration.

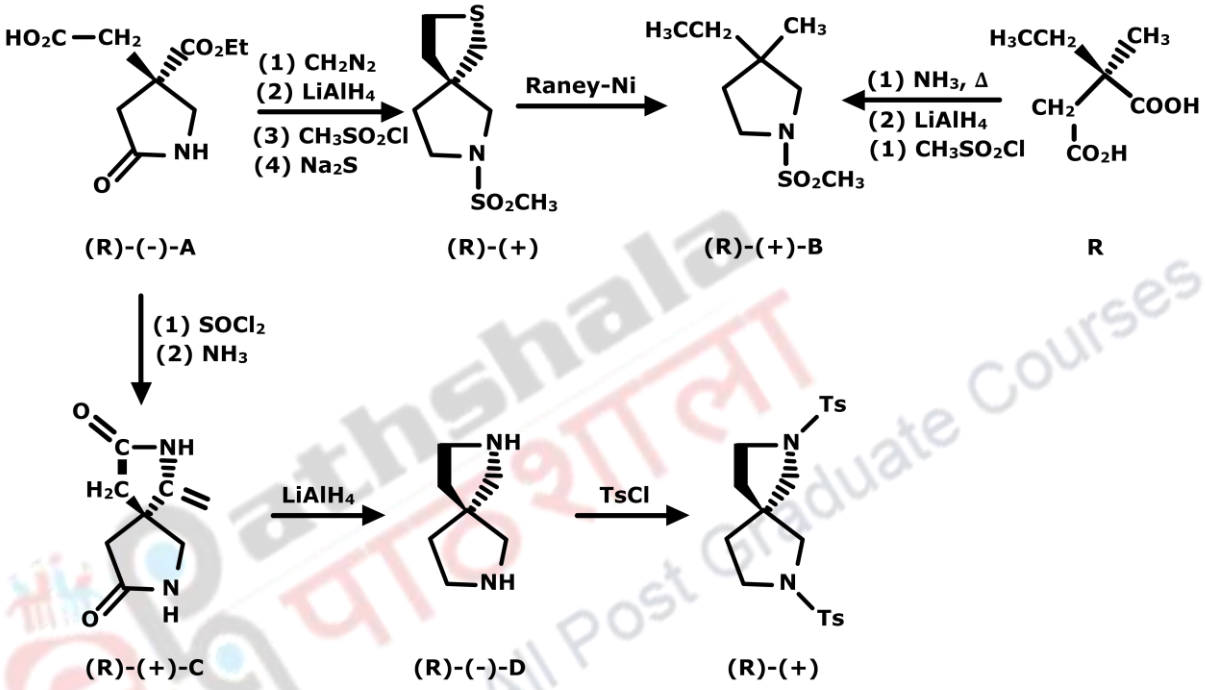
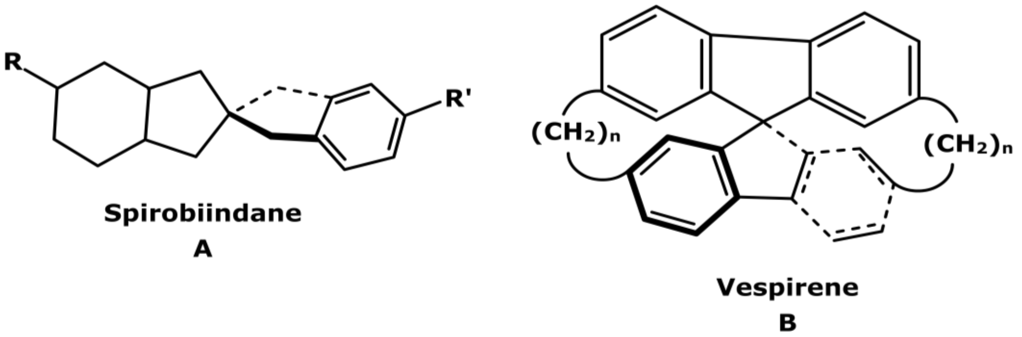


Fig. 13: Configurational assignment of 2,7-diazaspiro[4.4]nonane. The asterisk (*) signifies that the actual experiment was carried out with the *S* acid, which gave (*S*)-(-)-B. the sign of rotation of the acid depends on the concentration as well as on configuration.

Circular dichroism methods have also been used for configurational assignment of the so-called [n, n]-vespirenes (n-6,7,8) shown in Figure 14 B.



Spirobiindane
A

Vespirene
B

Fig. 14: Spirobiindane and vespirene

These chiral compounds are notable in that they display D_2, symmetry and that the four ligands attached to the spiro centre are structurally identical; chirality is enforced by the methylene bridges that cannot lie integrally in the planes of either of the fluorene ring systems.

4. Summary

- When one replaces *both* the double bonds in an allene by rings, one obtains a bicyclic ring system in which the two rings have one atom in common. Such bicyclic systems are called “spiranes”.
- It is true that the structure of spiranes is firmly entrenched, the name is somewhat inept. The name "spirane," from the Latin *spira* meaning twist or whorl implies that spiranes are not planar; it is their nonplanarity that gives rise to their chirality.
- Circular dichroism methods besides correlation methods have also been used for configurational assignment of various spiranes.