Objective

After completing this section, you should be able to draw the structures and construct molecular models of cis- and trans-decalin and of norbornane.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- bridgehead carbon atom (see the “Study Notes,” below)
- polycyclic molecule

Study Notes

A bridgehead carbon atom is a carbon atom which is shared by at least two rings. The hydrogen atom which is attached to a bridgehead carbon may be referred to as a bridgehead hydrogen. Make models of cis- and trans-decalin. You should have enough “carbon” balls in your model set to enable you to construct a model of the testosterone molecule shown at the bottom of page 130 of the textbook. Molecules of this type are biologically very important. You need not be concerned over the IUPAC name of norbornane. The nomenclature of compounds of this type is beyond the scope of this course.

The strain in polycyclic molecules just like the small ring cyclo alkanes are brought about by the angle and eclipsing strain, although, these strains would become still more important in going from cyclobutane to bicyclo[1.1.0]butane or from cyclooctane to pentacyclo[4.2.0.0^2.5.0^3.8.0^4.7]octane (cubane). This expectation is borne out by the data in Table 4.9.1, which gives the properties of several illustrative small-ring polycyclic molecules that have been synthesized only in recent years.

The extraordinary strain energy of cubane (~ 142 kcal mole^-1) is worthy of special note. It is roughly equal to six times the strain energy of a single cyclobutane ring (~ 26 kcal mole^-1) as befits a molecule made up of six cyclobutane rings as faces. Despite this, cubane is surprisingly stable to spontaneous decomposition processes, although it will rearrange under the influence of metal or acid catalysts.

Another extraordinarily strained polycyclic hydrocarbon that has been prepared is prismane (the Ladenburg structure for benzene, see Exercise 1-6).

This substance is a liquid that decomposes explosively when heated. In dilute solution at 100°, it is converted slowly to benzene.
One of the most interesting types of polycyclic carbon compounds prepared in recent years is the group of tricyclic substances known as "propellanes." A typical example is tricyclo [3.2.2.01.5]nonane, which sometimes is called [3.2.2]propellane, 12. The physical properties of several of these are included in Table 4.9.1. A quick look at formula 12 probably does not suggest any great structural difference from the bicyclic compounds we have discussed previously. However, if one tries to construct a ball-and-stick model of 12, one soon concludes that the propellanes are truly extraordinary substances in that all four carbon bonds at the bridgehead carbons extend, not to the corners of a tetrahedron, or even a distorted tetrahedron as for a cyclopropane ring, but away from the carbon on the same side of a plane through the carbon as in 13:

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Heat of Formation (ΔH) (kcal/mol)</th>
<th>Strain Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bicyclo[1.1.0] butane</td>
<td><img src="image1" alt="Structure" /></td>
<td>-</td>
<td>8</td>
<td>51.9</td>
<td>59</td>
</tr>
<tr>
<td>spiro[2.2]pentane</td>
<td><img src="image2" alt="Structure" /></td>
<td>-107</td>
<td>39</td>
<td>44.2</td>
<td>56</td>
</tr>
<tr>
<td>bicyclo[2.1.0]pentane</td>
<td><img src="image3" alt="Structure" /></td>
<td>-</td>
<td>45.5</td>
<td>37.6</td>
<td>50</td>
</tr>
<tr>
<td>cubane</td>
<td><img src="image4" alt="Structure" /></td>
<td>130-131</td>
<td>-</td>
<td>148.7</td>
<td>143</td>
</tr>
<tr>
<td>tricyclo[4.2.2.]</td>
<td><img src="image5" alt="Structure" /></td>
<td>32</td>
<td>109</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>tricyclo[3.2.2.0]nonane</td>
<td><img src="image6" alt="Structure" /></td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Angle strain is severe. Accordingly, [3.2.1]propellane reacts rapidly with bromine at -60° and with hydrogen over palladium at room temperature:

Still another way to torture the valence angles of carbon is to twist a double bond by connecting it to the bridgehead carbon of a bicyclic system with reasonably small rings, as in bicyclo[3.3.1]l-nonene, 14:
As with 12, it might appear that there is nothing unusual about 14. But a ball-and-stick model of 14 reveals that the carbon-carbon double bond is in a strained configuration like 15. Some of the properties of 14 are given in Table 4.9.1. That compounds with a double bond to a bridgehead carbon, such as 14, should be highly strained is known as “Bredt’s Rule.” The most spectacular example of this form of molecular distortion reported so far is bicyclo[2.2.1]-l-heptene, 16, for which evidence has been adduced that it is an unstable reaction intermediate:

![Image of 16]

**Bicyclic Ring Systems**

**Decalin ring system (6/6)**

Decalins can come in two diastereomers, the *trans*- or *cis*- diastereomer. The *trans*-diastereomer is a rigid structure which cannot undergo a ring flip. The *cis*-diastereomer is mobile and can ring flip to allow substituents to sit in the equatorial position.

![Images of trans-decalin and cis-decalin]

**Steroids**

Steroids include such well known compounds as cholesterol, sex hormones, birth control pills, cortisone, and anabolic steroids.
Cholesterol

The best known and most abundant steroid in the body is cholesterol. Cholesterol is formed in brain tissue, nerve tissue, and the bloodstream. It is the major compound found in gallstones and bile salts. Cholesterol also contributes to the formation of deposits on the inner walls of blood vessels. These deposits harden and obstruct the flow of blood. This condition, known as atherosclerosis, results in various heart diseases, strokes, and high blood pressure.

Much research is currently underway to determine if a correlation exists between cholesterol levels in the blood and diet. Not only does cholesterol come from the diet, but cholesterol is synthesized in the body from carbohydrates and proteins as well as fat. Therefore, the elimination of cholesterol rich foods from the diet does not necessarily lower blood cholesterol levels. Some studies have found that if certain unsaturated fats and oils are substituted for saturated fats, the blood cholesterol level decreases. The research is incomplete on this problem.

Structures of Sex Hormones

Sex hormones are also steroids. The primary male hormone, testosterone, is responsible for the development of secondary sex characteristics. Two female sex hormones, progesterone and estrogen or estradiol control the ovulation
cycle. Notice that the male and female hormones have only slight differences in structures, but yet have very different physiological effects.

Testosterone promotes the normal development of male genital organs and is synthesized from cholesterol in the testes. It also promotes secondary male sexual characteristics such as deep voice, facial and body hair.

Estrogen, along with progesterone regulates changes occurring in the uterus and ovaries known as the menstrual cycle. For more details see Birth Control. Estrogen is synthesized from testosterone by making the first ring aromatic which results in more double bonds, the loss of a methyl group and formation of an alcohol group.

Contributors