Questions

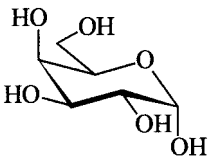
31

How many configurational isomers are there correlated with the constitution expressed in the following names? In those cases where two isomers exist state their relationship to each other.

a) ethanol
b) butan-2-ol
c) glycerol
d) 2,3-dibromobutane
e) acetone oxime
f) pent-3-en-2-ol
g) pentane-2,3-diol
h) pentane-2,4-diol
i) 3-bromobutan-2-ol
j) but-2-enoic acid
k) 4-ethylhepta-2,5-diene
l) hexa-2,3,4-triene

32

Convert the formula of galactose shown below into a Fischer projection formula and state whether it is the α or the β anomer.



33

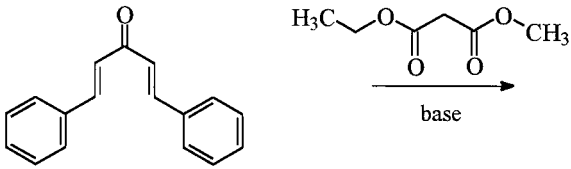
Are there compounds with a constitution where

a) enantiomers but no diastereomers are possible,
b) both enantiomers as well as diastereomers exist,
c) diastereomers but no enantiomers are possible?

Give examples where appropriate.

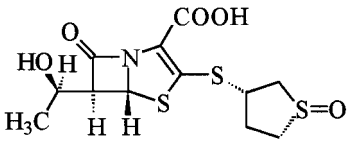
102

Different cyclic products are formed in the double Michael addition of malonic acid ethyl methyl ester to (*E*,*E*)-1,5-diphenylpenta-1,4-dien-3-one under basic conditions. Label the stereogenic units in the reaction products with the appropriate stereodescriptors.



103

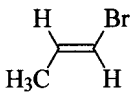
Determine the absolute configuration of the beta-lactam antibiotic sulopenem.



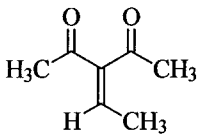
104

Are the two faces of the double bonds in the compounds represented by the following formulae homotopic, enantiotopic or diastereotopic? Give, where appropriate, a suitable descriptor for the face oriented towards you.

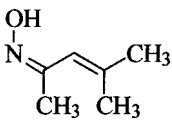
a)



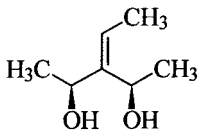
b)



c)

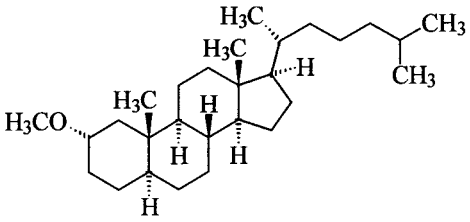


d)



167

Does the methoxy group in the compound shown below occupy an axial or an equatorial position? Use the configuration of the compound to deduce your answer.

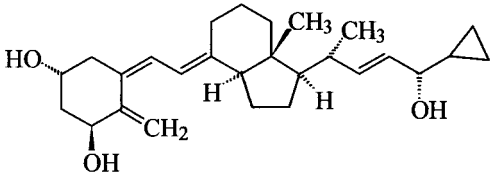


168

What compound would be expected as the major product from a Grignard reaction between (*S*)-2,3,3-trimethylbutanal and propylmagnesium bromide?

169

Deduce the configuration of the stereogenic units of the antipsoriatic calcipotriol and the number of theoretically possible stereoisomers with this constitution.



170

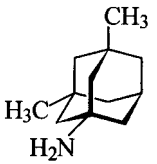
What product is obtained from the reaction of 1-methylcyclopentene with $NaBH_4$ in the presence of acetic acid and subsequent oxidation with an alkaline solution of hydrogen peroxide? Determine also the configuration of the intermediate product.

173

Which symmetry elements are present in *meso*-tartaric acid?

174

Is the NMDA antagonist memantine chiral?

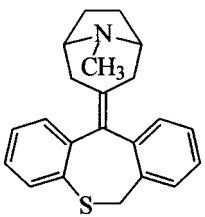


175

The two diastereomers of 1,3,5-trichlorocyclohexane have relative signal intensities of 1:1:1 and 2:2:2:1:1:1 in their ^{1}H NMR spectra, respectively. Which set of signals corresponds to which isomer?

176

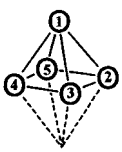
Is tropatepine, a drug used in the treatment of Parkinson's disease, chiral?



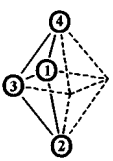
177

Determine the symmetry elements present in the following boranes and hence assign their symmetry point groups. The numbered circles in the polyhedra represent the boron atoms with the corresponding number of attached hydrogen atoms.

a) B_5H_9



b) B_4H_{10}



Answers

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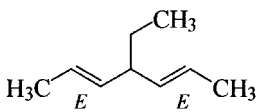
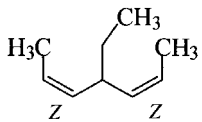
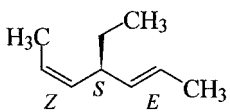
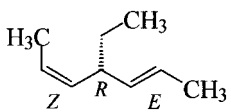
a) Ethanol: no configurational isomers
b) Butan-2-ol: two enantiomers
c) Glycerol: no configurational isomers
d) 2,3-Dibromobutane: three configurational isomers
e) Acetone oxime: no configurational isomers
f) Pent-3-en-2-ol: four configurational isomers
g) Pentane-2,3-diol: four configurational isomers
h) Pentane-2,4-diol: three configurational isomers
i) 3-Bromobutan-2-ol: four configurational isomers
j) But-2-enoic acid: two diastereomers
k) 4-Ethylhepta-2,5-diene: four configurational isomers; Both double bonds here can have the same configuration (*E*,*E* or *Z*,*Z*) or may have a different configuration. In the latter case carbon atom 4 will be a chirality centre and therefore two enantiomers exist. For the determination of the appropriate stereodescriptor by the CIP rules, the *Z*-configured group is ranked higher than the *E*-configured group.





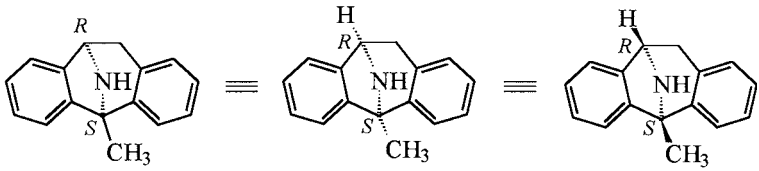




l) Hexa-2,3,4-triene: two diastereomers (*E* and *Z* isomers)

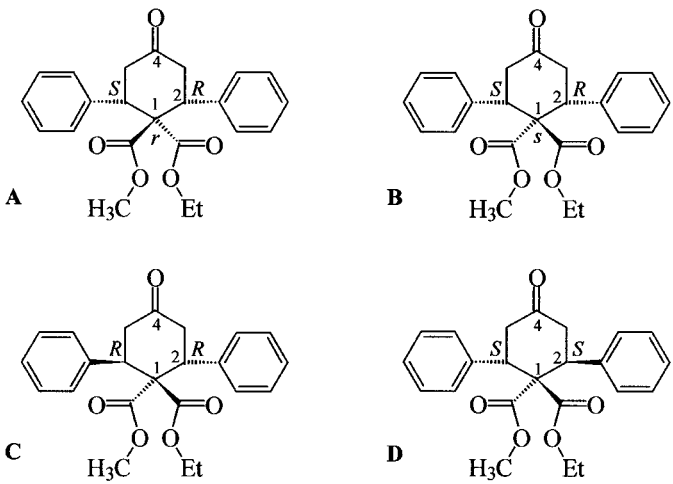
101

Dizocilpine is a chiral compound with two chirality centres. The methylated centre has the *S* configuration, whilst the other bridgehead atom is *R*-configured. For clarification it is helpful to add hydrogen atoms or wedged bonds. Two other possible formulae for the structure are shown below, the last one of which, however, although frequently used is not recommended.



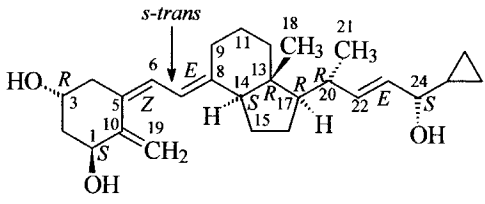
102

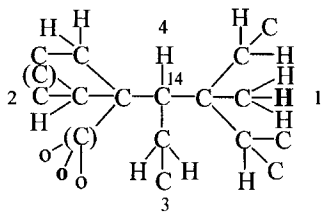
Four stereoisomers can be produced in the reaction. All reaction products have chirality centres at C2 and C6, the absolute configuration of which can be specified by *R* and *S*. Compounds **A** and **B** additionally possess a pseudochirality centre at C1 since there are two constitutionally identical but enantiomorphic groups attached to this position. By applying the CIP rules, C1 in **A** has the stereodescriptor *r*, whilst C1 in **B** has the stereodescriptor *s*. The groups attached to C1 in **C** and **D** are homomorphic, therefore C1 in these compounds is a prochirality centre.



169

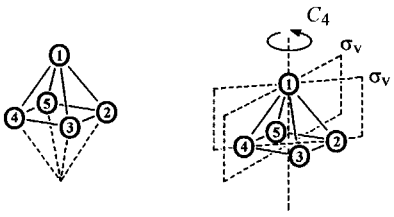
Calcipotriol contains seven chirality centres and three double bonds where isomerism is possible. Since there are two possibilities for the configuration at each of the stereogenic units, there are in theory $2^7 \cdot 2^3 = 2^{10} = 1024$ possible isomers. In addition, the C6-C7 bond has partial double bond character, thus for every isomer there will be an *s-cis* and an *s-trans* conformer. The configuration of the double bonds, determined from the priority order of the substituents, is indicated in the formula shown below. The absolute configuration at C13 is *R*; the priority order of the attached groups can be determined only in the third sphere. For C14 the digraph for determining the priority order is shown below. Again the priority order can only be determined in the third sphere, in particular in the branch of lowest priority. Here the hydrogen atom of the methyl group has priority over the phantom atom (indicator for non-existent groups) at the duplicate representation of the carbon atom. It is possible to deduce the priority order for C17 in the second sphere, i.e. C(C,C,C) > C(C,C,H) > C(C,H,H) > H. The configuration according to the CIP rules of the chirality centres in the side chains attached to C8 and C17 is given in the formula shown below.



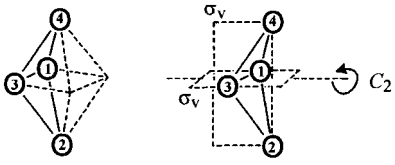


177

a) B_5H_9 has a square pyramidal structure. The compound belongs to the symmetry point group C_{4v}. It has one C_4 axis and four planes of symmetry σ_v two of which pass through opposite corners and two of which bisect opposite edges of the square plane.



b) B_4H_{10} belongs to the symmetry point group C_{2v}. It has one C_2 axis and two planes of symmetry σ_v.



c) B_6H_{10} has a pentagonal pyramidal structure. The compound belongs to the symmetry point group C_{5v}. It has one C_5 axis of symmetry and five vertical planes of symmetry σ_v whose line of intersection is the C_5 axis.