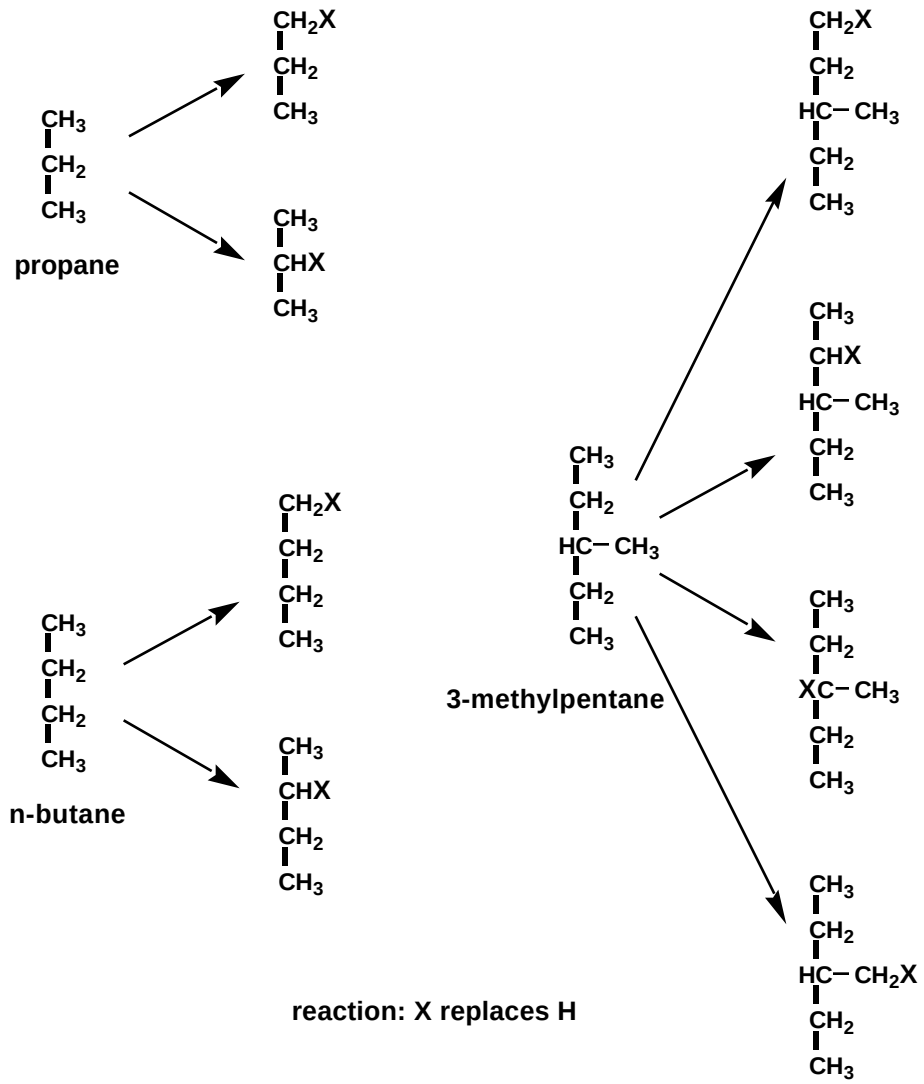
Text Related to Segment 6.01 ©2002 Claude E. Wintner

There remains a final concept to be examined as part of our consideration of stereochemistry, particularly because of its importance for an understanding of the course of many enzymatic reactions. At a given ambient energy we wish to be clear, for example, about whether two molecules are distinguishable or not, or whether a single molecule is achiral or chiral. For such purposes it is sufficient to treat molecules as objects in their entirety, as we have until this point in our discussion of stereochemical characteristics. However, chemists are interested in chemical transformation as well as in structure *per se.* In this connection, groups that are themselves constitutionally identical, but reside in *constitutionally distinct environments* within a molecule, should be — in principle if not always so easily in practice! — *chemically* distinguishable. Given a proper set of reaction conditions, a reaction involving one such group within a molecule should occur at a rate different from the rate of the same reaction involving the identical group residing in a constitutionally distinct environment in the same molecule, and it should be capable of producing a constitutionally distinct product as well. The figure outlines how reaction of propane with reagent X to replace a hydrogen atom by X will lead to constitutionally distinct products, depending upon whether the reaction occurs at a methyl hydrogen or at a methylene hydrogen. The same is true for the methyl and methylene hydrogens of n-butane. For 3-methylpentane, four products are possible, all differing in constitution, again as demonstrated in the figure.



chemical reaction of constitutionally identical groups residing in constitutionally distinct environments in a molecule leading to products differing in constitution

One's first instinct might be to extend this idea, to the effect that reaction of groups which are themselves constitutionally identical, *and which also reside in constitutionally identical environments in a molecule,* should not be able to lead to products that are distinguishable in any way. *This extension is incorrect; the stereochemical environment of the groups must be taken into account.* We shall see that while in *some* such cases the products will not be distinguishable, in others they

may be enantiomers; or, they may be diastereoisomers. In the ensuing segments we shall develop a simple test to differentiate among these possibilities.