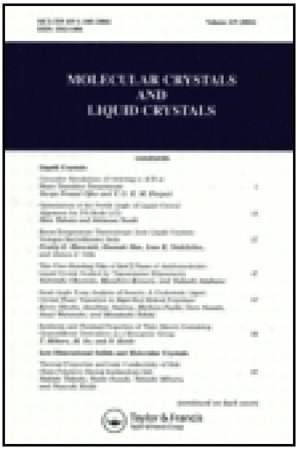

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Absolute Asymmetric Syntheses are Possible from Achiral Reactants by Reaction on One Face of a Single Achiral Crystal

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Absolute Asymmetric Syntheses are Possible from Achiral Reactants by Reaction on One Face of a Single Achiral Crystal

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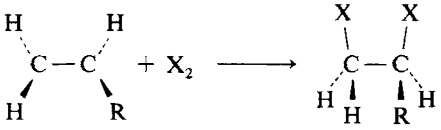
The *syn* addition of X_2 to a single achiral crystal $CH_2{=}CHR$ is examined. A chiral product can be produced provided that (1) reaction occurs on a single surface; (2) the alkene molecular planes are approximately parallel to the surface; and (3) there is no crystallographic mirror or glide plane perpendicular to the surface being attacked.

An exciting area of research is the achievement of stereochemical control of chemical reactions by crystal engineering.[1-6] The solid-state synthesis of chiral molecules from chiral crystals is well-established.[4-6] However, it is not generally recognized that chiral synthesis is possible from achiral crystals. Very recently, Harrison[7] has pointed out that the attachment of a molecule to a surface is a symmetry-destroying process, and Elgavi, Green, and Schmidt[5] have suggested that asymmetric synthesis should be possible from achiral crystals. The conditions which must be met in order to achieve asymmetric synthesis have not been examined previously. In this paper we show that chiral molecules may be synthesized from achiral crystals provided that certain conditions are satisfied: the molecules in the achiral crystal must be aligned in certain ways relative to the symmetry elements in the crystal, and the reaction must occur on only one face of a single crystal.

The method which we use to show that this is so is quite simple. Any crystalline substance must have a molecular packing arrangement describable by one of the 230 crystallographic space groups.[8] Thus one can examine hypothetical packing arrangements for a given molecule and determine which of these are compatible with asymmetric synthesis, given some particular mechanism for the proposed reaction.

Consider, for convenience, the addition reaction between a gaseous halogen X_2 and a crystalline alkene $H_2C{=}CHR$. Assume that the reaction occurs at the surface of the crystal and that addition is *syn*, as has been established for the gas phase chlorination of crystalline *trans*-stilbene.[9] (Eq. 1).



(1)

We now examine packing arrangements generated by two common space group symmetry elements, the center of symmetry (Figure 1) and the glide plane (Figure 2). The presence of either (or both) of these in a crystal means that the crystal is achiral. Figure 1 shows how optically pure R- (or S-) CH_2XCHRX can arise if X_2 attack is confined to one face of a single crystal. The opposite chirality is obtained if X_2 attack occurs on the opposite face. We note that microcrystalline defects on the surface might allow diffusion of the reagents into the interior of the crystal so that attack from within the crystal could occur. If this happens, molecules of both chiralities would be produced in equal amounts from within.

In both Figures 1 and 2, the planes of the alkene molecules are presumed

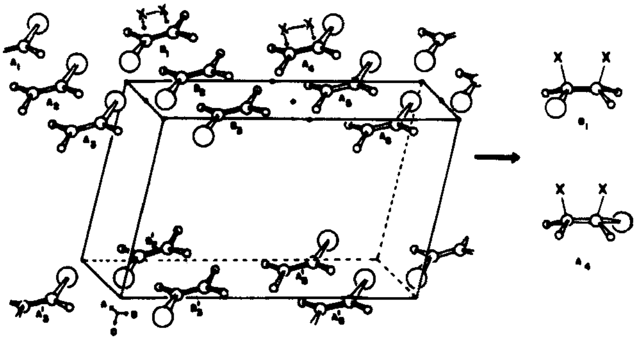


FIGURE 1 Reaction of X_2 with crystalline $CH_2{=}CHR$, in a hypothetical $P\bar{1}$ packing arrangement. The A_n molecules are equivalent to each other by translation in the crystallographic *a* or *b* directions. The B_n molecules are also translationally equivalent. The primed A_n and B_n indicate molecules which are identical to the unprimed ones by translation in the *c* direction, one unit cell below the top surface. The A_n molecules are related to the B_n molecules by inversion through the centres of symmetry, the locations of which are indicated by the small open circles on the top face of the unit cell. The product molecules produced by attack on an A_n molecules and on a B_n molecule are shown on the right; they have identical chiralities.

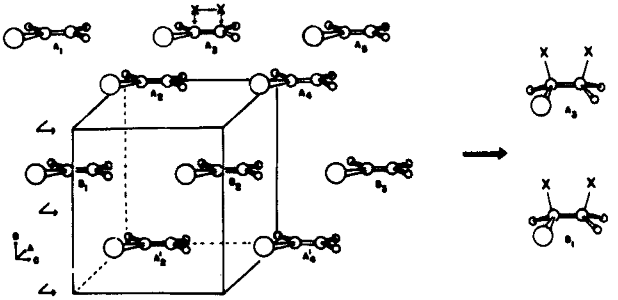


FIGURE 2 Reaction of X_2 with $CH_2{=}CHR$ in a hypothetical Pc packing arrangement. All A_n molecules are translationally equivalent, as are the B_n molecules. The B_n molecules are generated from the A_n molecules by the c-glide planes (indicated by ↳ on the left-hand side of the unit cell). Attack by X_2 from the top surface generated products of the same chirality from A_n and B_n molecules.

to be roughly parallel to the crystal face being attacked. In addition, in Figure 2, the molecules must be aligned parallel to the glide planes if optically pure product is to be generated. It is easily shown that a racemic product will result if the crystal face under attack has a glide or mirror plane perpendicular to it (Figure 3). A racemic product was in fact observed in the gas-phase chlorination of *trans*-stilbene,[9] although no attempt was made to confine the reaction to a single crystal surface. However, the crystal structure of *trans*-stilbene shows that the double bond is almost perpendicular to the glide plane[10] and thus that asymmetric synthesis would not be achievable even in principle in this system.

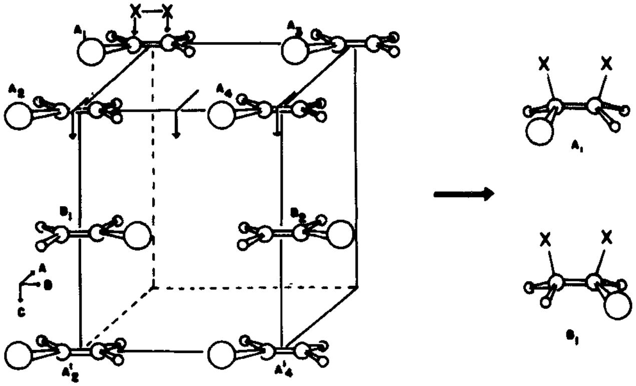


FIGURE 3 Reaction of X_2 with $CH_2{=}CHR$ in a Pc packing arrangement, with the molecular planes perpendicular to the c-glide planes. The A_n molecules are translationally equivalent, as are the B_n molecules. The B_n molecules are generated from the A_n molecules by the c-glide planes (indicated by ∫). The products produced by the A_n and by the B_n molecules are of opposite chiralities.

With these considerations in mind, one can determine that a number of achiral space groups are compatible with asymmetric synthesis. These include triclinic $P\bar{1}$ as well as the common monoclinic groups $P2_1/c$ and $C2/c$, provided that the molecules are aligned approximately parallel to the glide planes in these two cases. On the other hand, the orthorhombic or higher-symmetry groups containing two or three mutually perpendicular glide or mirror planes are generally not compatible with asymmetric syntheses by means of surface reactions.

Thus, if the crystal structure is known of a given compound, it is possible to predict whether reaction at one of the surfaces is capable of producing a chiral molecule. This analysis has far-reaching consequences for many phenomena which involve surface reactions, e.g., catalysis. The idea of producing a catalytically-active surface, such as by epitaxial plating of the active material on a single face of a suitable monocrystalline substrate, needs to be more fully explored. Similarly, chiral polymers can be produced from achiral crystals if initiation can be guaranteed to occur at only one surface, and, of course, if the molecules are suitably oriented both with respect to each other and to the symmetry elements of the crystal.

Finally, it has not escaped our notice that the initial production of optically active substances in the universe could have been brought about by reactions of achiral molecules on a surface of an achiral crystal, by just such a mechanism as we have described herein.

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