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Polar and Chiral Organic Crystals, Striking Reactivity and Selectivity

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POLAR AND CHIRAL ORGANIC CRYSTALS, STRIKING REACTIVITY AND SELECTIVITY

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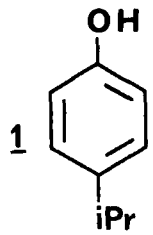
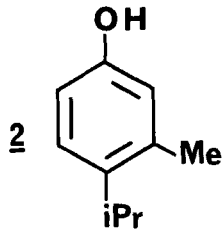
Abstract Polar reactivity differences have been found on the two faces of a slice cut along a polar axis in a 3-methyl 4-isopropyl phenol crystal. A case of absolute asymetric synthesis is noted during the chlorination of the same compound.

It is possible to obtain organic polar crystals *i.e.* crystals in which the disposition of molecules does not present a center of symmetry. The polar axis in such crystals can be but not necessarily, a crystallographic axis[1]. It could be possible with such crystals to observe solid-gas reactions which present selectivities and specificities depending on the absolute direction of the polar axis. In the same way, it is possible to obtain organic chiral crystals *i.e.* crystals in which the disposition of molecules does not present centers of inversion, mirror planes, glide planes and rotation - reflection axis[1-2]. Such crystals exist on both forms depicted in terms of right and left crystals. The corresponding crystalline arrangements may concern both achiral and prochiral molecules. The reactions of such crystals with gases are potentially able to produce mixtures containing one enantiomer in excess, the enantiomeric excess depending on

whether the reaction is performed on a right handed crystal or on a left handed crystal. In both cases one realizes an absolute asymetric synthesis.

We found two phenolic substances crystals of which present a polar axis and moreover are also chiral. They are 4-isopropyl phenol 1 and 3-methyl-4-isopropyl phenol 2.





They have the same crystalline structure and crystallize in $P4_1$ space group. As they are uniaxial it is easy to identify right and left crystals by simple polarized microscopic observations. We have been able to make grow crystals of 18 x 18 x 70 mm dimensions.

The gaseous chlorination of slices cut in such crystals in a direction perpendicular to polar axis shows the reactivity to vary by a factor of 2 as the reaction is performed on one side or the other side of the slices. In addition different selectivities are observed. From a more general point of view, we obtained a *mono*chlorocyclohexadienone which is not produced in solution.

The gaseous chlorination of powdered left or right handed crystals of 3-methyl-4-isopropyl phenol gives liquid mixtures from which the *mono*chlorocyclohexadienone is isolated. This substance in solution presents rotatory power showing that an enantiomeric excess has been produced.

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