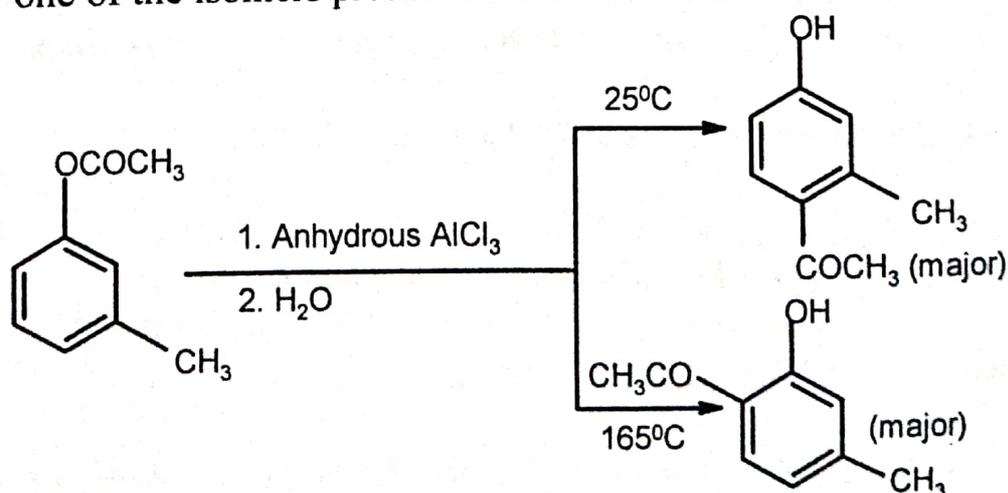


Fries rearrangement is a synthetically useful reaction involving the conversion of phenolic esters to acylated phenols (or may say rearrangement of aryl esters to aryl ketones) in presence of Lewis acid as a catalyst. A phenolic ester when heated with a Lewis acid in an inert solvent, it undergoes a rearrangement reaction to yield a mixture of both *ortho*- and *para*-acylphenols on subsequent hydrolysis. This is usually known as *Fries rearrangement*. Besides Lewis acids, light has also been found to act as catalyst in certain cases.

Catalyst, solvent and reaction temperature

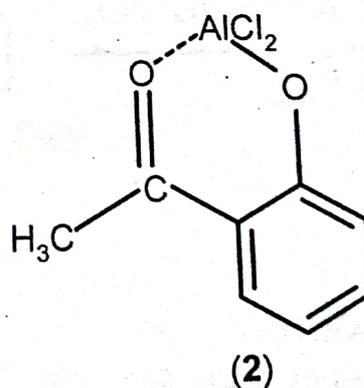
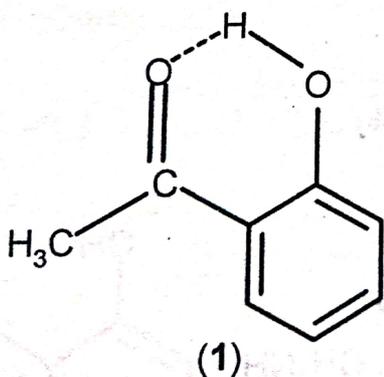
The common Lewis acid used as catalyst in *Fries rearrangement* reaction is anhydrous aluminium chloride/bromide, and the common solvents used are carbondisulphide, nitrobenzene, chlorobenzene, etc. The *ortho*- and *para*-isomers can be separated from their mixture by means of steam distillation or fractional crystallization, as the case may be. However, it is often possible to select conditions so that either one of the isomers predominates.



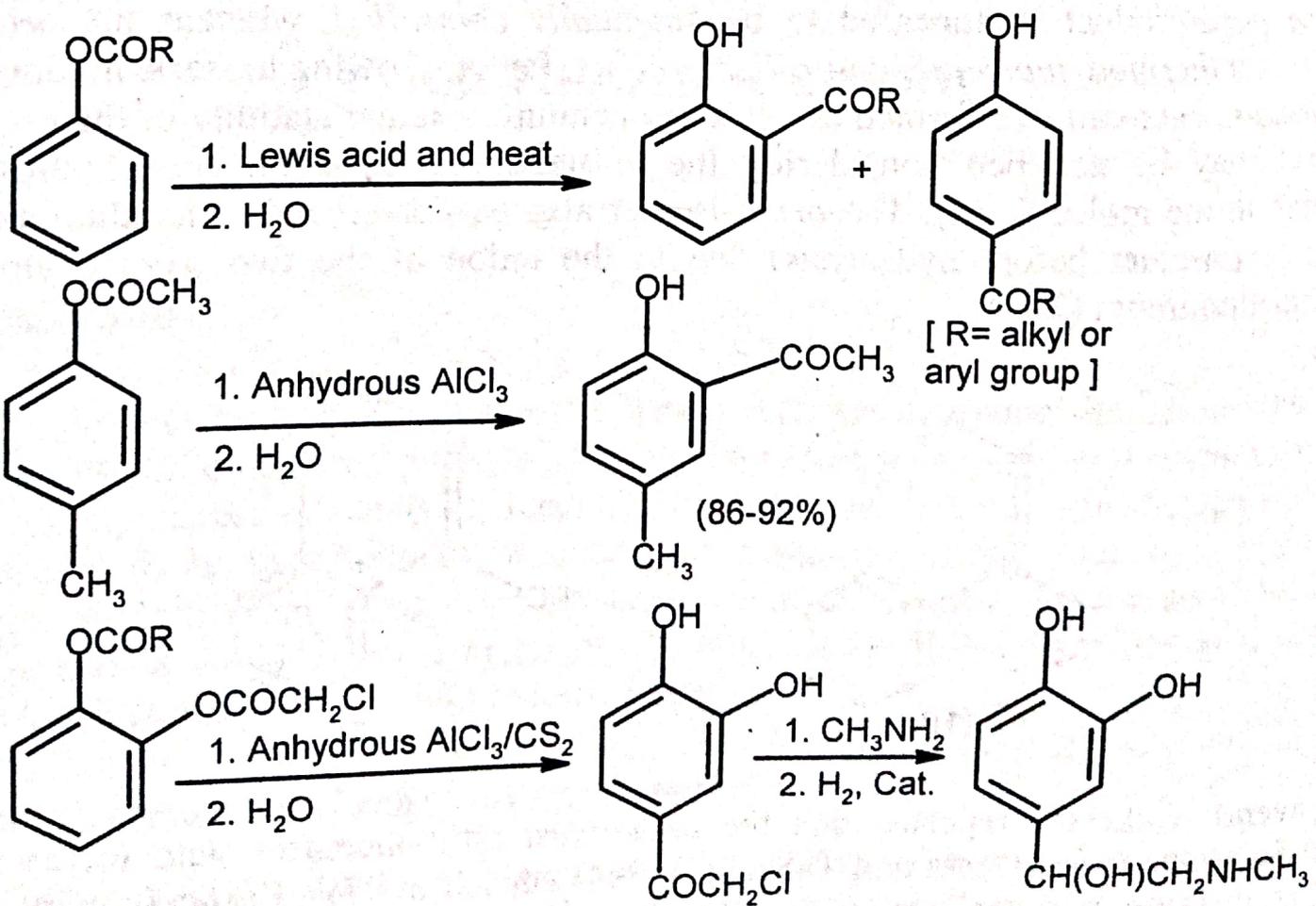
The *ortho/para* ratio is largely dependent on reaction temperature, solvents used and catalyst concentration. Generally, it has been observed that at low temperature

the *para*-isomer predominates, while at higher temperature the *ortho*-isomer becomes the major product.

The *para*-product is appeared to be *kinetically controlled*, whereas the *ortho*-isomer is a *thermodynamically controlled* product. Perhaps, owing to steric hindrance the *ortho*-isomer can't be formed at a low temperature. Greater stability of the *ortho*-product may be ascribed considering the existence of *intramolecular* hydrogen bonding in the molecule (1). The *ortho*-isomer also gets stabilized in its aluminium complex (product before hydrolysis) due to the union of the two oxygen atoms through aluminium (2).

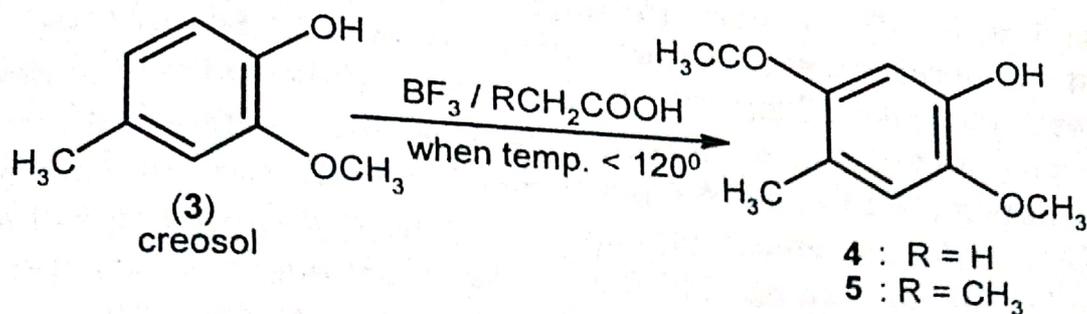


Examples



Abnormalities

Certain abnormal findings relating to *Fries rearrangement* were reported. The most notable exception is the unusual formation of *meta*-product in some cases. T. Reichstein (1927)¹⁶ for the first time recognized the formation of a *meta*-isomer in the rearrangement of acetylguaiacol under *Fries* condition. Latter, in 1961 Paolo and Cimattoribus^{22b} showed that in the acylation of creosol by boron trifluoride/carboxylic acids method involving the *Fries rearrangement*, it is possible to obtain selectively, by varying temperature, *ortho* or *meta* migration of the acyl group. The authors extensively studied the *Fries rearrangement* reaction on acetylcreosol in a varying range of temperatures from 25° to 160°C. Between 25° to 80°, only the *meta*-isomer was obtained with decreasing yield from 90 to 56%, while between 10°-120° the two isomers (*ortho* & *meta*) were formed in a ratio (*ortho/meta*) that varies from 1:4.5 to 4:1. Above 120°, only the *ortho*-isomer was isolated. Thus, by saturating a creosol (3) and acetic or propionic acid mixture (molar ratio 1:2) with boron at ice bath temperature and leaving the reaction mixture at room temperature for two days, the *meta*-migrated products — 2-methyl-4-methoxy-5-hydroxyacetophenone (4) and respectively propiophenone (5) were obtained.

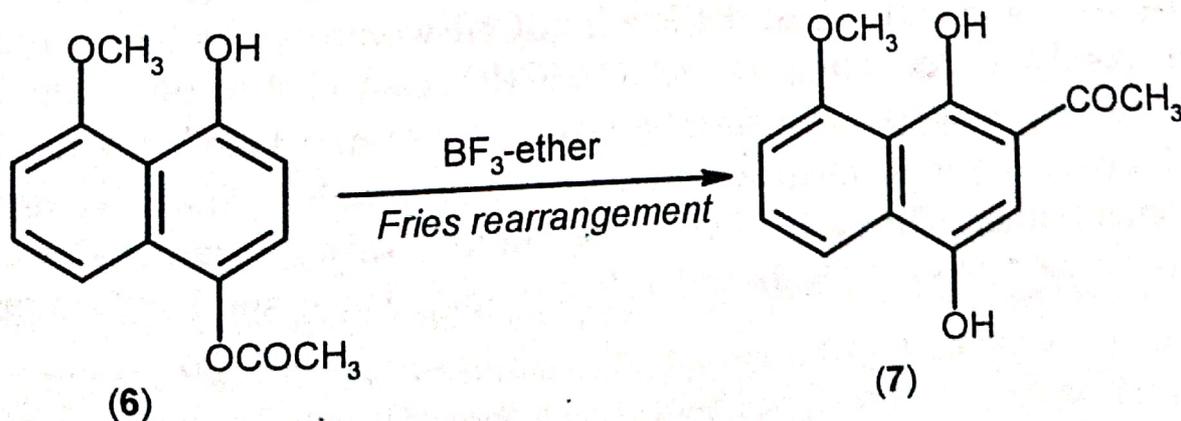


The results as obtained from the experimental observations in carrying out the *Fries rearrangement* of acetylcreosol at varying range of temperatures are summarized below:

Temperature ($^\circ\text{C}$)	<i>ortho</i> -isomer (%)	<i>meta</i> -isomer (%)
25	-	90
40	-	75
60	-	68
80	-	56.6
100	18	40
120	25	10
140	60	-
160	78	-

Hence, it is evident that a temperature of 25°C is sufficient to direct the migrating group exclusively in the *meta*-position with a maximum of 90% yield, while the *ortho*-isomer becomes the exclusive product (maximum of 78% yield) at 160°C .

In 1982, Chorn *et al.*¹⁸ found that 1-acetoxy-4-hydroxy-5-methoxynaphthalene (6) underwent an unusual "*meta-Fries rearrangement*" leading to the formation of 3-acetyl-1,4-dihydroxy-5-methoxynaphthalene (7).



The acetyl group of compound (6) migrates to C-3 (*meta*-position) on treatment with boron trifluoride etherate. The authors supposed that the *abnormal Fries rearrangement* reactions of this type of substrates is induced by the *peri*-methoxyl group and proposed that the *meta*-migration of the migrating moiety proceeds presumably through *intermolecular path*. Besides, in case of arylbenzoates treated with F_3CSO_3H (trifluoromethanesulphonic acid) the reversible *Fries rearrangement* was observed to maintain an equilibrium¹⁹. *Fries rearrangement* has also been found not to work well with *meta*-directing substituents on the aromatic ring.