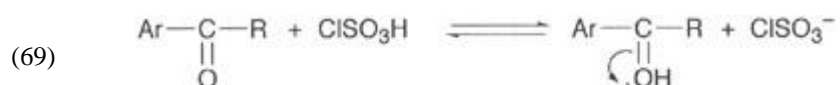
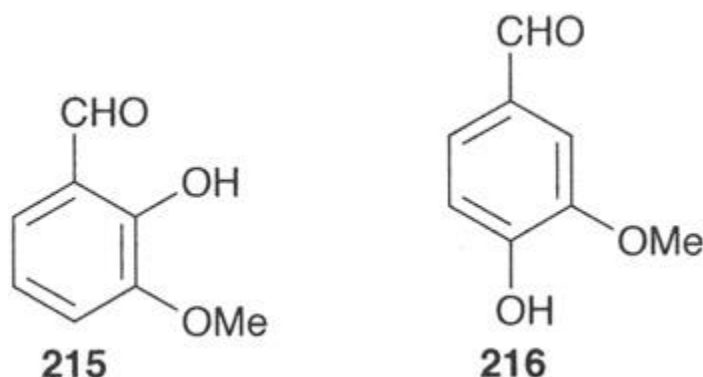


Aromatic carbonyl compounds:

Aromatic carbonyl compounds are protonated in strongly acidic media, like sulfuric and chlorosulfonic acid (Equation 69).⁵ As a consequence, the carbonyl group exerts a powerful electron-withdrawing effect on the attached aromatic nucleus; the sulfonation of aromatic carbonyl compounds is therefore more difficult to achieve than for the parent aromatic hydrocarbons. Comparatively little work has been reported¹⁻³ on the sulfonation of aryl aldehydes and none of these studies involved the use of chlorosulfonic acid.

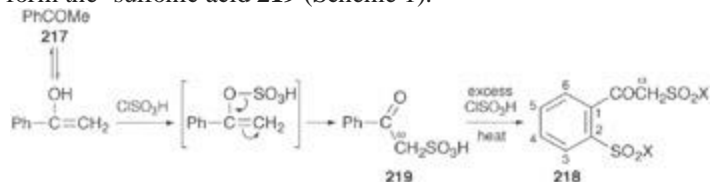


More recent attempts to chlorosulfonate *o*-vanillin **215**, vanillin **216** and 2,5-dimethoxybenzaldehyde with chlorosulfonic acid, under various conditions, were unsuccessful and the reactions only afforded charred products.²³¹ In contrast, aromatic ketones of both the alkyl aryl and diaryl type have been successfully reacted with chlorosulfonic acid.^{1-3,5}



Acetophenone

Acetophenone **217**, by mixing the excess chlorosulfonic acid in the cold followed by heating the mixture at 110 °C (1 hour), gave a disulfonyl chloride which was originally considered to be the 3,5-derivative.²³² However, subsequent work by Suter and Weston²³³ in which acetophenone **217** was treated with the reagent (10 equivalents) in carbon tetrachloride at 0 °C and heated at 110 °C (45 minutes) showed that the product was the 2, 4-disulfonic acid **218** (X = OH); the reaction probably involves initial sulfation of the enolic form of the ketone **217** which then rearranges to form the -sulfonic acid **219** (Scheme 1).



Scheme 1

In support, acetophenone- 2-sulfonic acid