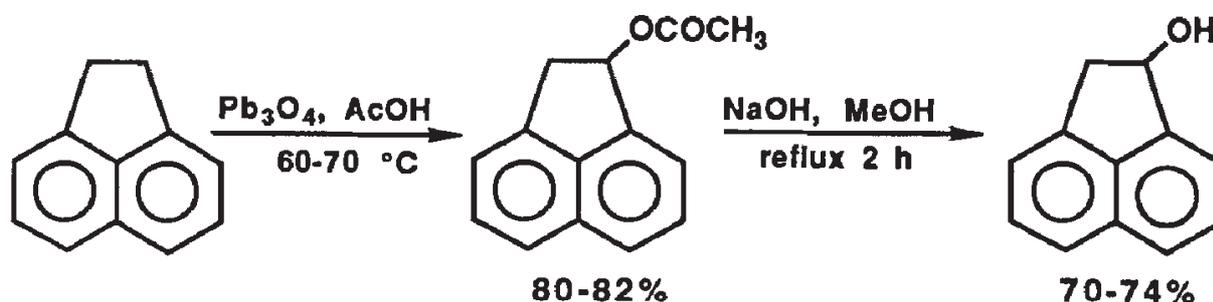


1-acetoxyacenaphthene (equation 167) [434]. Subsequent hydrolysis of the esters with sodium hydroxide yields the corresponding alcohols [434, 435].

[434]

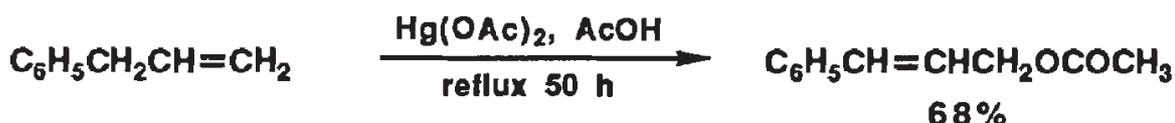
167



In allylbenzene, an easy oxidation at the benzylic, and at the same time allylic, carbon would be expected. However, cinnamyl acetate is formed instead on treatment with mercuric acetate, evidently as a result of an S_N2' reaction at the double bond (equation 168) [404].

[404]

168



OXIDATION TO ALDEHYDES, KETONES, AND THEIR DERIVATIVES

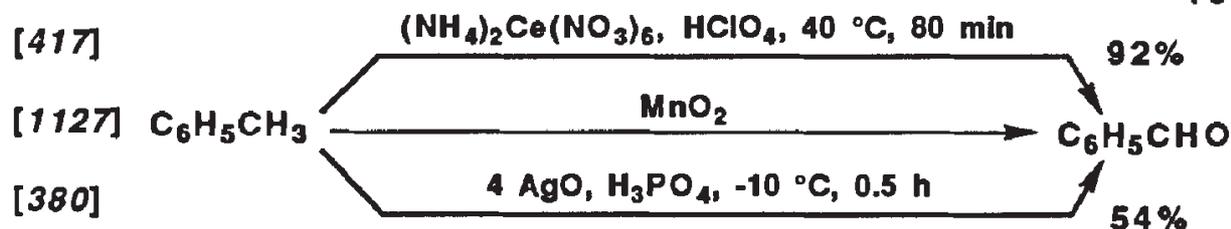
Methyl homologues of aromatic compounds are oxidized to *aldehydes* by silver(II) oxide (argentic oxide) [380], by ceric ammonium nitrate [238, 417, 422], by selenium dioxide [513, 514, 515], by chromyl chloride [477, 667], by periodic acid [760], and by manganese dioxide [1127] (equation 169).

[417]

[1127]

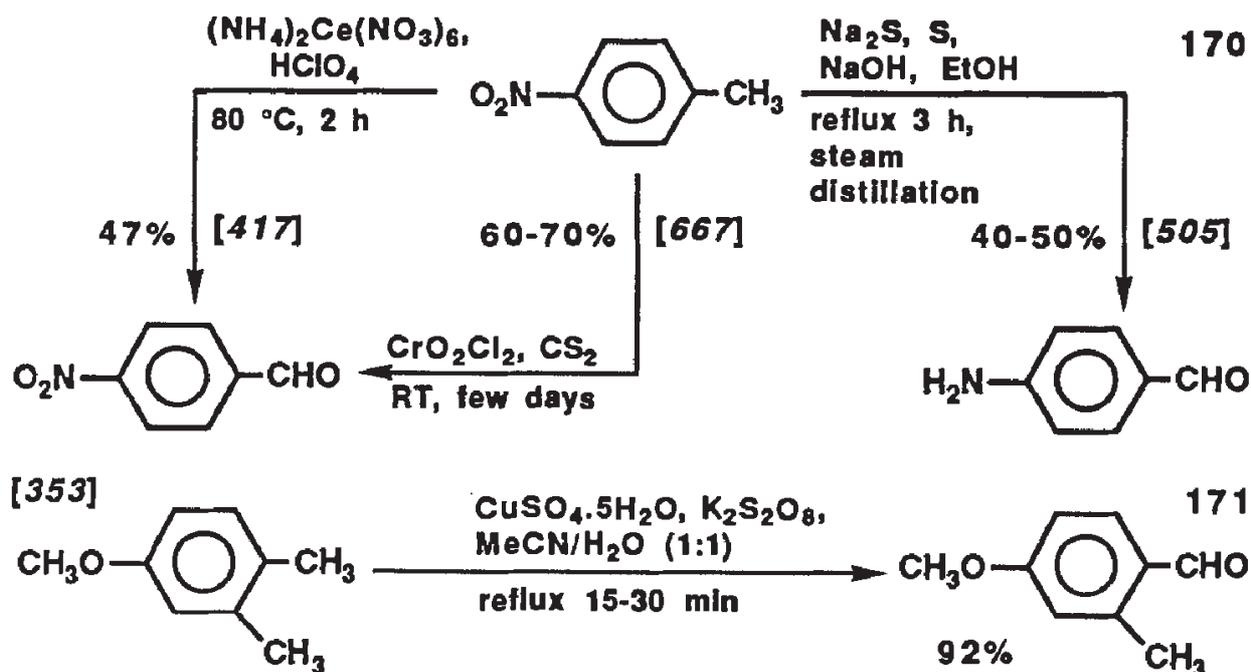
[380]

169

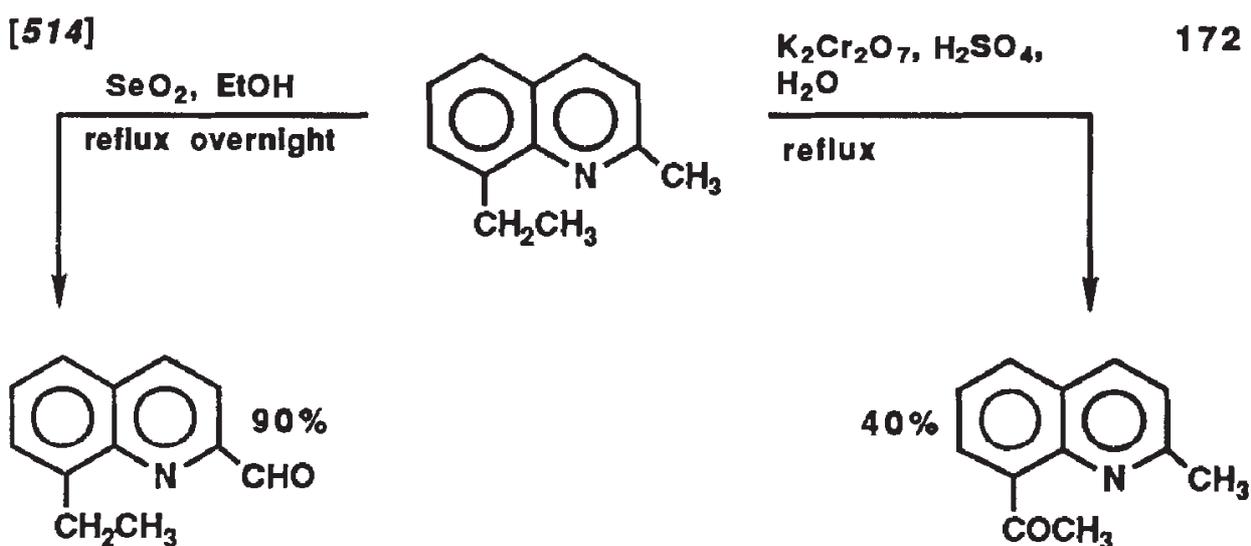


p-Nitrotoluene is oxidized by ceric ammonium nitrate [417] or by chromyl chloride [667] to *p*-nitrobenzaldehyde, whereas refluxing with aqueous alcoholic sodium polysulfide gives *p*-aminobenzaldehyde by an internal redox reaction [505] (equation 170).

The regiospecific oxidation of dimethylanisoles to methoxymethylbenzaldehydes is accomplished with copper sulfate and potassium peroxydisulfate, which oxidize selectively only the methyls in the *ortho* or *para* positions with respect to the methoxy group (equation 171) [353].



In aromatic heterocycles, the methyl groups in α positions with respect to nitrogen are oxidized especially easily. Thus quinaldine gives a 50% yield of quinoline- α -carboxaldehyde on refluxing for 1 h with selenium dioxide in aqueous dioxane [513], and 2,3,8-trimethylquinoline gives an 82% yield of 3,8-dimethylquinoline-2-carboxaldehyde on refluxing for 6 h with selenium dioxide in ethanol [515]. A similar selective oxidation is achieved when 8-ethyl-2-methylquinoline is treated with selenium dioxide or **potassium dichromate** [514]. Treatment with selenium dioxide gives 8-ethyl-2-formylquinoline, whereas treatment with potassium dichromate gives 8-acetyl-2-methylquinoline (equation 172) [514].



Selectivity is also noticed in oxidations of 2,3-dimethylindole. Whereas sodium periodate cleaves the double bond and gives an 85% yield of *o*-acetamidoacetophenone, periodic acid oxidizes the methyl group adjacent to the heterocyclic nitrogen to an aldehyde group in a low yield (equation 173) [760].