## Solutions to Exercises, Chapter 9

## 9.1



## 9.2



9.3



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**9.4** In the tetrahedral intermediate, the oxygen atoms from the carbonyl and the water cannot be distinguished. Consequently, one of the *different* oxygen atoms of the ethanoic acid (the immediate product of EtO<sup>-</sup> departure) is labelled (either the carbonyl O or the hydroxy O), and one of the two *equivalent* oxygens in the final product (the carboxylate anion) is labelled.

 $H_2^{18}O + HO^ H_2O + H^{18}O^-$ 



**9.5** The product of transesterification in the presence of a base is still an ester, which remains electrophilic, and the base is not consumed in the transformation. Consequently, there is a common reaction path in base-catalysed transesterification which may be followed in forward or reverse directions. In contrast, the alkaline hydrolysis of an ester is irreversible because the carboxylic acid product is deprotonated under the reaction conditions. The resulting carboxylate anion is not electrophilic so it cannot undergo nucleophilic attack and the reverse reaction does take place. The alkaline hydrolysis cannot be catalytic because base is consumed in the neutralization of the carboxylic acid product.

9.6



Carry out the reactions with excesses of the alcohols to maximize the yields of the product esters.



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**9.8** Ethyl benzoate has greater resonance stabilization (positive charge is partially delocalized into the benzene ring) than ethyl ethanoate, but this is lost upon formation of the tetrahedral intermediate. Consequently, it is less reactive (less electrophilic) than the ethanoate.



9.9



9.10



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9.7



9.11



9.12



**9.13** (b) and (d): no reactions

(a)  $CH_3COCCH_3 + NaCI$ (c)  $CH_3CN(CH_3)_2 + C_2H_5OH$ 

9.14





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