Solutions to the Problems

Chapter 1

- 1.1. These questions can be answered by comparing the electron-accepting capacity and relative location of the substituents groups. The most acidic compounds are those with the most stabilized anions.
 - a. In (a) the most difficult choice is between nitroethane and dicyanomethane. Table 1.1 indicates that nitroethane (pK = 8.6) is more acidic in hydroxylic solvents, but that the order might be reversed in DMSO, judging from the high pK_{DMSO} (17.2) for nitromethane. For hydroxylic solvents, the order should be CH₁CH₂NO₂ > CH₂(CN)₂ > (CH₃)₂CHC=O(Ph) > CH₃CH₂CN.
 - b. The comparison in (b) is between N-H, O-H, and C-H bonds. This order is dominated by the electronegativity difference, which is O > N > C. Of the two hydrocarbons, the aryl conjugation available to the carbanion of 2-phenylpropane makes it more acidic than propane. (CH₃)₂CHOH > [(CH₃)₂CH]₂NH > (CH₃)₂CHPh > CH₃CH₂CH₃.
 - c. In (c) the two β-dicarbonyl compounds are more acidic, with the diketone being a bit more acidic than the β-ketoester. Of the two monoesters, the phenyl conjugation will enhance the acidity of methyl phenylacetate, whereas the nonconjugated phenyl group in benzyl acetate has little effect on the pK.

d. In (d) the extra stabilization provided by the phenyl ring makes benzyl phenyl ketone the most acidic compound of the group. The cross-conjugation in 1-phenylbutanone has a smaller effect, but makes it more acidic than the aliphatic ketones, 3,3-Dimethyl-2-butanone (methyl r-butyl ketone) is more acidic than 2,2,4-trimethyl-3-pentanone because of the steric destabilization of the enolate of the latter.

Carey Sundberg Solution Manual

Raymond Chang

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