

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 $\text{CH}_3\text{CH}_2\text{NO}_2 > \text{CH}_2(\text{CN})_2 > (\text{CH}_3)_2\text{CHC}=\text{O}(\text{Ph}) > \text{CH}_3\text{CH}_2\text{CN}$.
- 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 $\text{O} > \text{N} > \text{C}$. Of the two hydrocarbons, the aryl conjugation available to the carbanion of 2-phenylpropane makes it more acidic than propane. $(\text{CH}_3)_2\text{CHOH} > [(\text{CH}_3)_2\text{CH}]_2\text{NH} > (\text{CH}_3)_2\text{CHPh} > \text{CH}_3\text{CH}_2\text{CH}_3$.
- 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 *t*-butyl ketone) is more acidic than 2,2,4-trimethyl-3-pentanone because of the steric destabilization of the enolate of the latter.



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