

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.

- 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 $\text{CH}_3\text{CH}_2\text{NO}_2 > \text{CH}_2(\text{CN})_2 > (\text{CH}_3)_2\text{CHC}=\text{O}(\text{Ph}) > \text{CH}_3\text{CH}_2\text{CN}$.
- 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. $(\text{CH}_3)_2\text{CHOH} > [(\text{CH}_3)_2\text{CH}]_2\text{NH} > (\text{CH}_3)_2\text{CHPh} > \text{CH}_3\text{CH}_2\text{CH}_3$.
- 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 .



- 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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Advanced Organic Chemistry Francis A. Carey, Richard J. Sundberg, 2007-11-24 Since its original appearance in 1977 *Advanced Organic Chemistry* has maintained its place as the premier textbook in the field offering broad coverage of the structure reactivity and synthesis of organic compounds As in the earlier editions the text contains extensive references to both the primary and review literature and provides examples of data and reactions that illustrate and document the generalizations While the text assumes completion of an introductory course in organic chemistry it reviews the fundamental concepts for each topic that is discussed The two part fifth edition has been substantially revised and reorganized for greater clarity Among the changes Updated material reflecting advances in the field since 2001 s Fourth Edition especially in computational chemistry A companion Web site provides digital models for study of structure reaction and selectivity Solutions to the exercises provided to instructors online The control of reactivity to achieve specific syntheses is one of the overarching goals of organic chemistry Part B describes the most general and useful synthetic reactions organized on the basis of reaction type Together with Part A Structure and Mechanisms the two volumes are intended to provide the advanced undergraduate or beginning graduate student in chemistry with a sufficient foundation to comprehend and use the research literature in organic chemistry *Books in Print Supplement* ,1982 Scientific and Technical Books and Serials in Print ,1989 **Core List of Books and Journals in Science and Technology** Russell H. Powell, James R. Powell, 1987-10

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