

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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Table of Contents Carey Sundberg Solution Manual Part

1. Understanding the eBook Carey Sundberg Solution Manual Part
 - The Rise of Digital Reading Carey Sundberg Solution Manual Part
 - Advantages of eBooks Over Traditional Books
2. Identifying Carey Sundberg Solution Manual Part
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Carey Sundberg Solution Manual Part
 - User-Friendly Interface
4. Exploring eBook Recommendations from Carey Sundberg Solution Manual Part
 - Personalized Recommendations
 - Carey Sundberg Solution Manual Part User Reviews and Ratings
 - Carey Sundberg Solution Manual Part and Bestseller Lists
5. Accessing Carey Sundberg Solution Manual Part Free and Paid eBooks
 - Carey Sundberg Solution Manual Part Public Domain eBooks
 - Carey Sundberg Solution Manual Part eBook Subscription Services
 - Carey Sundberg Solution Manual Part Budget-Friendly Options
6. Navigating Carey Sundberg Solution Manual Part eBook Formats

- ePub, PDF, MOBI, and More
- Carey Sundberg Solution Manual Part Compatibility with Devices
- Carey Sundberg Solution Manual Part Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Carey Sundberg Solution Manual Part
 - Highlighting and Note-Taking Carey Sundberg Solution Manual Part
 - Interactive Elements Carey Sundberg Solution Manual Part
- 8. Staying Engaged with Carey Sundberg Solution Manual Part
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Carey Sundberg Solution Manual Part
- 9. Balancing eBooks and Physical Books Carey Sundberg Solution Manual Part
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Carey Sundberg Solution Manual Part
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine Carey Sundberg Solution Manual Part
 - Setting Reading Goals Carey Sundberg Solution Manual Part
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Carey Sundberg Solution Manual Part
 - Fact-Checking eBook Content of Carey Sundberg Solution Manual Part
 - Distinguishing Credible Sources
- 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
- 14. Embracing eBook Trends
 - Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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