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Allegato n. 2 – Verbale n. 4

Scheda n. 2

Candidato

Firma. ....

1) Spettroscopia UV-Vis: aspetti teorici e pratica
2) Estrazione acido/base: aspetti teorico-pratici

Prova di inglese:
Si veda allegato al verbale

Prova di informatica:
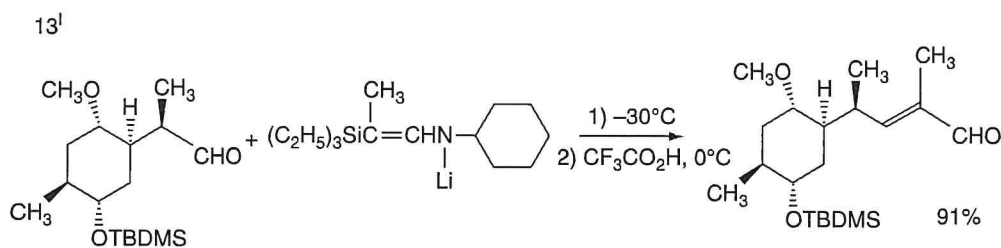Redazione retta di calibrazione su foglio di calcolo excel

BUSTA 2

DOMANDA 1

Spettroscopia UV-Vis: aspetti teorici e pratici

DOMANDA 2

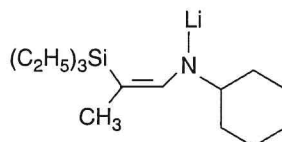Estrazione acido/base: aspetti teorico-pratici

13^l

a. K. Shimoji, H. Taguchi, H. Yamamoto, K. Oshima, and H. Hozaki, *J. Am. Chem. Soc.*, **96**, 1620 (1974).
b. P. A. Grieco, C. L. J. Wang, and S. D. Burke, *J. Chem. Soc. Chem. Commun.*, 537 (1975).
c. I. Matsuda, S. Murata, and Y. Ishii, *J. Chem. Soc., Perkin Trans. 1*, 26 (1979).
d. F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 939 (1972).
e. F. A. Carey and O. Hernandez, *J. Org. Chem.*, **38**, 2670 (1973).
f. D. Seebach, M. Kolb, and B.-T. Grobel, *Chem. Ber.*, **106**, 2277 (1973).
g. B. T. Grobel and D. Seebach, *Chem. Ber.*, **110**, 852 (1977).
h. P. Magnus and G. Roy, *Organometallics*, **1**, 553 (1982).
i. W. Adam and C. M. Ortega-Schulte, *Synlett*, 414 (2003).
j. L. F. van Staden, B. Bartels-Rahm, J. S. Field, and N. D. Emslie, *Tetrahedron*, **54**, 3255 (1998).
k. J.-M. Galano, G. Audran, and H. Monti, *Tetrahedron Lett.*, **42**, 6125 (2001).
l. S. F. Martin, J. A. Dodge, L. E. Burgess, and M. Hartmann, *J. Org. Chem.*, **57**, 1070 (1992).

unstable olefins. Entries 1 to 8 show the use of lithio silanes having a range of anion-stabilizing groups. The anions are prepared using alkyllithium reagents or lithium amides. Entries 9 to 11 illustrate the utility of the reaction to prepare relatively unstable substituted alkenes. The silyl anions are typically more reactive than stabilized Wittig ylides, and in the case of Entry 12 good results were obtained while the triphenylphosphonium ylide was unreactive. Entry 13 shows the use of Peterson olefination for chain extension with an α-methyl-α, β-unsaturated aldehyde. The preferred reagent for this transformation is a lithio β-trialkylsilylenamine.[276]

2.4.3. The Julia Olefination Reaction

The *Julia olefination* involves the addition of a sulfonyl-stabilized carbanion to a carbonyl compound, followed by elimination to form an alkene.[277] In the initial versions of the reaction, the elimination was done under *reductive conditions*. More recently, a modified version that avoids this step was developed. The former version is sometimes referred to as the *Julia-Lythgoe olefination*, whereas the latter is called the *Julia-Kocienski olefination*. In the reductive variant, the adduct is usually acylated and then treated with a reducing agent, such as sodium amalgam or samarium diiodide.[278]

[276.] R. Desmond, S. G. Mills, R. P. Volante, and I. Shinkai, *Tetrahedron Lett.*, **29**, 3895 (1988).
[277.] P. R. Blakemore, *J. Chem. Soc., Perkin Trans. 1*, 2563 (2002).
[278.] A. S. Kende and J. Mendoza, *Tetrahedron Lett.*, **31**, 7105 (1990); G. E. Keck, K. A. Savin, and M. A. Weglarz, *J. Org. Chem.*, **60**, 3194 (1995); K. Fukumoto, M. Ihara, S. Suzuki, T. Taniguchi, and Y. Yokunaga, *Synlett*, 895 (1994); I. E. Marko, F. Murphy, and S. Dolan, *Tetrahedron Lett.*, **37**, 2089 (1996); I. E. Marko, F. Murphy, L. Kumps, A. Ates, R. Touillaux, D. Craig, S. Carballares, and S. Dolan, *Tetrahedron*, **57**, 2609 (2001).

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<center>Allegato n. 3 – Verbale n. 4</center>

Scheda n. 1

Candidato ███████████

Firma ███████████ ....

1) Spettroscopia IR: aspetti teorici e pratici
2) Tecnica di cristallizzazione: aspetti teorico-pratici

Prova di inglese:
Si veda allegato al verbale

Prova di informatica:
Redazione retta di calibrazione su foglio di calcolo excel
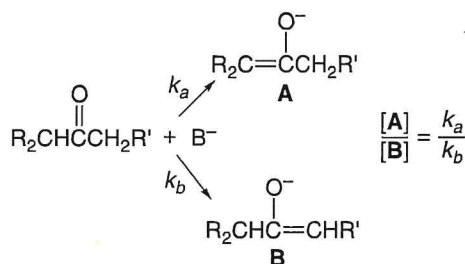
BUSTA 1

DOMANDA 1

Spettroscopia IR: aspetti teorici e pratici

DOMANDA 2

Tecnica di cristallizzazione: aspetti teorico-pratici

by *kinetic control* when the product composition is determined by the *relative rates of the competing proton abstraction reactions.*

$$R_2CHCCH_2R' + B^- \xrightarrow[k_b]{k_a} \begin{array}{c} R_2C=CCH_2R' \quad \textbf{A} \\ \\ R_2CHC=CHR' \quad \textbf{B} \end{array} \qquad \frac{[A]}{[B]} = \frac{k_a}{k_b}$$

Kinetic control of isomeric enolate composition

By adjusting the conditions of enolate formation, it is possible to establish either kinetic or thermodynamic control. *Conditions for kinetic control of enolate formation are those in which deprotonation is rapid, quantitative, and irreversible.*[8] This requirement is met experimentally by using a very strong base such as LDA or LiHMDS in an aprotic solvent in the absence of excess ketone. Lithium is a better counterion than sodium or potassium for regioselective generation of the kinetic enolate, as it maintains a tighter coordination at oxygen and reduces the rate of proton exchange. Use of an aprotic solvent is essential because protic solvents permit enolate equilibration by reversible protonation-deprotonation, which gives rise to the thermodynamically controlled enolate composition. Excess ketone also catalyzes the equilibration by proton exchange.

Scheme 1.1 shows data for the regioselectivity of enolate formation for several ketones under various reaction conditions. A consistent relationship is found in these and related data. *Conditions of kinetic control usually favor formation of the less-substituted enolate*, especially for methyl ketones. The main reason for this result is that removal of a less hindered hydrogen is faster, for steric reasons, than removal of a more hindered hydrogen. Steric factors in ketone deprotonation are accentuated by using bulky bases. The most widely used bases are LDA, LiHMDS, and NaHMDS. Still more hindered disilylamides such as hexaethyldisilylamide[9] and *bis*-(dimethylphenylsilyl)amide[10] may be useful for specific cases.

The equilibrium ratios of enolates for several ketone-enolate systems are also shown in Scheme 1.1. Equilibrium among the various enolates of a ketone can be established by the presence of an excess of ketone, which permits reversible proton transfer. Equilibration is also favored by the presence of dissociating additives such as HMPA. The composition of the equilibrium enolate mixture is usually more closely balanced than for kinetically controlled conditions. In general, the more highly substituted enolate is the preferred isomer, but if the alkyl groups are sufficiently branched as to interfere with solvation, there can be exceptions. This factor, along with CH_3/CH_3 steric repulsion, presumably accounts for the stability of the less-substituted enolate from 3-methyl-2-butanone (Entry 3).

[8] For reviews, see J. d'Angelo, *Tetrahedron*, **32**, 2979 (1976); C. H. Heathcock, *Modern Synthetic Methods*, **6**, 1 (1992).

[9] S. Masamune, J. W. Ellingboe, and W. Choy, *J. Am. Chem. Soc.*, **104**, 5526 (1982).

[10] S. R. Angle, J. M. Fevig, S. D. Knight, R. W. Marquis, Jr., and L. E. Overman, *J. Am. Chem. Soc.*, **115**, 3966 (1993).

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<div align="center">Allegato n. 4 – Verbale n. 4</div>

Scheda n. 3

Candidato /

Firma...

1) Tecniche di caratterizzazione di composti inorganici
2) Cromatografia su colonna: aspetti teorico-pratici

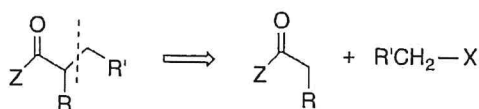**Prova di inglese:**
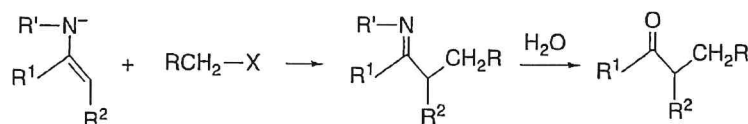**Si veda allegato al verbale**

Prova di informatica:
Redazione retta di calibrazione su foglio di calcolo excel

$$Z \overset{O}{\underset{R}{\bigcup}} R' \implies Z \overset{O}{\underset{R}{\bigcup}} + R'CH_2{-}X$$

There are similar reactions involving nitrogen analogs called *imine anions*. The alkylated imines can be hydrolyzed to the corresponding ketone, and this reaction is discussed in Section 1.3.

$$R' {-} \overset{N^-}{\underset{R^1 \diagdown \atop R^2}{\bigg|}} + RCH_2{-}X \longrightarrow R^1 \overset{R'{-}N}{\underset{R^2}{\bigg|}} CH_2R \xrightarrow{H_2O} R^1 \overset{O}{\underset{R^2}{\bigg|}} CH_2R$$

Either enolate or imine anions can be used to introduce alkyl α-substituents to a carbonyl group. Because the reaction involves a nucleophilic substitution, primary groups are the best alkylating agents, with methyl, allyl, and benzyl compounds being particularly reactive. Secondary groups are less reactive and are likely to give lower yields because of competing elimination. Tertiary and aryl groups cannot be introduced by an S_N2 mechanism.

1.1. Generation and Properties of Enolates and Other Stabilized Carbanions

1.1.1. Generation of Enolates by Deprotonation

The fundamental aspects of the structure and stability of carbanions were discussed in Chapter 6 of Part A. In the present chapter we relate the properties and reactivity of carbanions stabilized by carbonyl and other EWG substituents to their application as nucleophiles in synthesis. As discussed in Section 6.3 of Part A, there is a fundamental relationship between the stabilizing functional group and the acidity of the C−H groups, as illustrated by the pK data summarized in Table 6.7 in Part A. These pK data provide a basis for assessing the stability and reactivity of carbanions. The acidity of the reactant determines which bases can be used for generation of the anion. Another crucial factor is the distinction between *kinetic or thermodynamic control of enolate formation by deprotonation* (Part A, Section 6.3), which determines the enolate composition. Fundamental mechanisms of S_N2 alkylation reactions of carbanions are discussed in Section 6.5 of Part A. A review of this material may prove helpful.

A primary consideration in the generation of an enolate or other stabilized carbanion by deprotonation is the choice of base. In general, reactions can be carried out under conditions in which the enolate is *in equilibrium* with its conjugate acid or under which the reactant is *completely converted* to its conjugate base. The key determinant is the amount and strength of the base. For complete conversion, the base must be derived from a substantially weaker acid than the reactant. Stated another way, the reagent must be a stronger base than the anion of the reactant. Most current procedures for alkylation of enolates and other carbanions involve complete conversion to the anion. Such procedures are generally more amenable to both regiochemical and stereochemical control than those in which there is only a small equilibrium concentration of the enolate. The solvent and other coordinating or chelating additives also have strong effects on the structure and reactivity of carbanions formed by