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Design, Properties and Preparing Through Elimination Reactions: A Case Study of Alkenes

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Abstract – Alkene carboxylation's represent a major technology for the production of value-added bulk and fine chemicals. Nowadays, all industrial carboxylation processes make use of highly toxic and flammable carbon monoxide. Here we show the application of abundantly available carbon dioxide as C1 building block for the alkoxy carboxylation's of industrially important olefins in the presence of a convenient and inexpensive ruthenium catalyst system. In our system, carbon dioxide works much better than the traditional combination of carbon monoxide and alcohols.

INTRODUCTION

Alkenes are the unsaturated hydrocarbons having one or more carbon – carbon double bond. These are also termed as olefins since ethene (or ethylene – common name), the simplest alkene forms an oily liquid when treated with chlorine.



ethylene (substitutive name: ethene)

Because compounds containing double or triple bonds have fewer hydrogens than the corresponding alkanes, they are classified as unsaturated hydrocarbons, in contrast to alkanes, which are classified as saturated hydrocarbons.

In this paper, we will explore another type of reaction, called *elimination*, commonly observed for compounds with leaving groups. Although elimination reactions occur in a variety of different contexts, for now we will examine them as a method for forming alkenes. Consider the difference between substitution and elimination reactions (Figure 2). In a substitution reaction, the leaving group is replaced with a nucleophile. In an elimination reaction, a proton from the beta position is removed together with the leaving group, forming a double bond. This type of reaction is called a beta elimination, or 1,2-elimination, and can be accomplished with any good leaving group. Specific classes of beta eliminations were characterized before chemists understood they had a common set of mechanisms. Thus, some types of beta elimination reactions are named on the basis of the leaving group.



FIGURE 2 : The products of substitution and elimination reactions.

DESIGN

The double bond geometry of alkenes is typical of that found in ethene. Each of the double bonded carbon atom is Sp² hybridized, molecular geometry of which requires it to have trigonal planar geometry i.e. all the atoms surrounding each carbon atom lie in the same plane with bond angles approximating 120°. Of the three hybrid orbitals formed by Sp² hybridization two overlap with s orbital of each hydrogen forming sigma bond. The third hybrid orbital overlapps with the Sp² hybrid orbital of adjacent carbon atom forming another sigma bond. Pure p orbital on each of the two adjacent carbon atoms undergoes sideways overlap to form a pi bond. As a result of the double bond the carbon bond length is shorter for alkenes in comparison to the alkanes (also because in Sp² hybrid orbitals there is large amount of s character (33%)and therefore density with in Sp² orbitals is concentrated closer to the nucleus). e.g. C₂H₂



Another feature of alkene design is apparent from a comparison of the structures of propene and propane. Notice that the carbon-carbon single bond of propene (1.501 Å) is shorter than the carbon-carbon single bonds of propane (1.54 Å). The shortening of all these bonds is a consequence of the particular way that carbon atoms are hybridized in alkenes.

ALKENE STABILITY

In general, a cis alkene will be less stable than its stereoisomeric trans alkene. The source of this instability is attributed to steric strain exhibited by the cis isomer. This steric strain can be visualized by comparing space-filling models of dx-2-butene and trans-2-butene. The methyl groups are only able to avoid a steric interaction when they occupy a trans configuration.



The difference in energy between stereoisomeric alkenes can be quantified by comparing their heats of combustion:

\checkmark	+	6 O ₂	\longrightarrow	4 CO ₂	+	4 H ₂ O	$\Delta H^\circ = -2682 \text{ kJ/mol}$
$/= \setminus$	+	6 O ₂	\longrightarrow	4 CO ₂	+	4 H ₂ O	$\Delta H^\circ = -2686 \text{ kJ/mol}$

Both reactions yield the same products. Therefore, we can use heats of combustion to compare the relative energy levels of the starting materials (Figure 3). This analysis suggests that the trans isomer is 4 kj/mol more stable than the *cis* isomer.



FIGURE 3 : Heats of combustion of the stereoisomers of 2-butene.

When comparing the stability of alkenes, another factor must be taken into account, in addition to steric effects. We must also consider the degree of substitution. By comparing heats of combustion for isomeric alkenes (all with the same molecular formula. CgH[^]), the trend in Figure 4 emerges. Alkenes are more stable when they are highly substituted. Tetrasubstituted alkenes are more stable than trisubstituted alkenes. The reason for this trend is not a steric effect (through space), but rather an electronic effect (through bonds). Recall that alkyl groups are electron donating via hyperconjligation. Specifically, we saw that alkyl groups can donate electron density to the neighboring sp^2 -hybridized carbon atom of a carbocation. In a similar way, alkyl groups can also donate electron density to the neighboring sp^2 -

hybridized carbon atoms of a^{π} bond. The resulting derealization of electron density is a stabilizing effect.



FIGURE 4 : The relative stability of isomeric alkenes with varying degrees of substitution.

ALKENES NOMENCLATURE

The IUPAC substitutive nomenclature of alkenes is derived by modifying alkane nomenclature in a simple way. An unbranched alkene is named by replacing the ane suffix in the name of the corresponding alkane with the ending ene. The carbons are numbered from one end of the chain to the other so that the double bond receives the lowest number.

$$H_{2}C = CH - CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}$$

hexame + ene = hexene position of double bond

The IUPAC recognizes an exception to this rule for the name of the simplest alkene, H2CACH2, which is usually called ethylene rather than ethene. (Chemical Abstracts (Sec. 2.4D, p. 61), however, uses the substitutive name ethene.) The names of alkenes with branched chains are, like those of alkanes, derived from their *principal chains*. In an alkene, the principal chain is defined as the carbon chain containing the greatest number of double bonds, even if this is not the longest chain. If more than one candidate for the principal chain has equal numbers of double bonds, the principal chain is the longest of these. The principal chain is numbered from the end that results in the lowest numbers for the carbons of the double bonds.

When the alkene contains an alkyl substituent, the position of the double bond, not the position of the branch, determines the numbering of the chain. However, the position of the double bond is cited in the name after the name of the alkyl group. The

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following study problem shows how these principles are implemented. Nomenclature of alkenes can be derived by simply modifying the alkane nomeclature.

1. An unbranched alkene is named by replacing the "ane" suffix in the corresponding alkane with "ene".

2. Carbon atoms are numbered from one end of the chain to other so that the double bond receives the lowest number.

3. For the branched alkenes, the principal chain is defined as the carbon chain containing the greatest number of double bonds even if it is not the longest (if more than one chain with equal numbers of double bonds then the longer one is the principal chain).

4. The principal chain is numbered from the end that results in the lowest numbers for the carbon of the double bond.

5. Alkene containing the alkyl substituent the position of the double bond and not the position of branch determines the numbering of the chain.

6. Position of the double bond is cited in the name after the name of the alkyl group.

7. If the compound contains more than one double bond, the "ane" ending of the corresponding alkane is replaced by "adiene" or "atriene" and so on for two three or more double bonds.

SYSTEMS FOR ELIMINATION

Alkenes can be prepared via elimination reactions, in which a proton and a leaving group are removed to form a π bond:



As we begin to explore the possible mechanisms for elimination reactions, that ionic mechanisms are comprised of only four types of fundamental arrowpushing patterns (Figure 1). Ail four of these steps will appear in this research, so it might be wise to review SkillBuilders 6.3 and 6.4.



FIGURE 1 : The four fundamental electron transfer steps for ionic processes.

All elimination reactions exhibit at least two of the four patterns: (1) proton transfer and (2) loss of a leaving group:



Every elimination reaction features a proton transfer as well as loss of a leaving group. But consider the order of events of these two steps. In the figure above, they occur simultaneously (in a concerted fashion). Alternatively, we can imagine them occurring separately, in a stepwise fashion:



In this stepwise mechanism the leaving group leaves, generating an intermediate carbocation (much like the Sj^l reaction), which is then deprotonated by a base to produce an alkene. The key difference between these two mechanisms is summarized below:

- In a *concerted process*, a base abstracts a proton and the leaving group leaves simultaneously.
- In a *stepwise process*, first the leaving group leaves, and then the base abstracts a proton.

POLYMERIZATION OF ALKENES

Large number of monomer molecules with double or triple bond joins together to form high molecular weight molecules called polymers. These are of two types addition polymerization and condensation polymerization.

Ionic Polymerization		Initiation
Addition polymerization	proceeds by	Propagation
Radical Polymerization		termination

lonic Polymerization: lonic catalyst like lewis acids, eg. H_2SO_4 , HF, AlCl₃ etc. catalyse the reaction. For example.

(i) Initiation.

$$\begin{array}{c} C H_{3} \\ H_{3} - C = C H_{2} \end{array} \xrightarrow{H^{+}} C H_{3} - C - C H_{3} \end{array}$$

(ii) Propagation

$$\begin{array}{c} \begin{array}{c} CH_3 & CH_3 & CH_3 & CH_3 & CH_3 & CH_3 \\ I & I & I \\ CH_3-C-CH_3+CH_2=C-CH_3 \longrightarrow CH_3-C-C & CH_2 \\ \odot & & I \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 & CH_3 \\ I & I & I \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-C-CH_3 & CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-C-CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-C-CH_3 & CH_3 \\ \end{array} \xrightarrow{} \begin{array}{c} CH_3-C-C-CH_3 \\ \end{array}$$

(iii)Termination

Free Radical polymerization: This is brought about by the catalyst that generate free radicals eg. organic or inorganic peroxides or salts of the peracids eg. Benzoyl peroxide.

Initiation:

$$\begin{array}{c} O & O & O \\ R' - C - O \xrightarrow{?} O - C - R' \longrightarrow R' - C - O \xrightarrow{\parallel} R' + C O_2 \\ R' + R - CH = CH - R \longrightarrow R - CH = CH - R \\ R' \end{array}$$

Propagation:

Termination:

i) By combination of two chains.

$$2\left(\begin{array}{c} R'-CH-\dot{CH}\\ R\\ R\\ R\\ R\end{array}\right)^{n} \xrightarrow{R'-\left(\begin{array}{c} R-CH-CH\\ I\\ R\\ R\\ R\end{array}\right)^{n}} R$$

ii) By disproportionation.

$$2\mathbf{R} \stackrel{\frown}{\leftarrow} \underbrace{C\mathbf{H} - C\mathbf{H}}_{\mathbf{R}} \stackrel{\frown}{\rightarrow} \underbrace{C\mathbf{H} - C\mathbf{H}}_{\mathbf{R}} \stackrel{\bullet}{\rightarrow} \underbrace{\mathbf{R} - C\mathbf{H} - C\mathbf{H} - C\mathbf{H} - C\mathbf{H}}_{\mathbf{R}} \stackrel{\bullet}{\rightarrow} \underbrace{\mathbf{R} - C\mathbf{H} - C\mathbf{H} - C\mathbf{H}}_{\mathbf{R}} \stackrel{\bullet}{\rightarrow} \underbrace{\mathbf{R} - C\mathbf$$

CONCLUSION

Alkenes have a carbon-carbon double bond. Each carbon of a double bond is trigonal, and connected to only three other atoms, all of which lie in a plane with bond angles of 120o. Ordinarily, rotation around double bonds is restricted. All six atoms of ethylene lie in a single plane. The C=C bond length is 1.34 Å, shorter than a C—C bond (1.54 Å). These facts can be explained by an orbital model with three sp^2 hybrid orbitals (one electron in each) and one p orbital

perpendicular to these (containing the fourth electron). The double bond is formed by end-on overlap of sp^2 orbitals to form a \mathbf{O} bond and lateral overlap of aligned p orbitals to form a π bond. Since rotation around the double bond is restricted, cis-trans isomerism is possible if each carbon atom of the double bond has two different groups attached to it.

Alkenes react mainly by addition. Typical reagents that add to the double bond are halogens, hydrogen (metal catalyst required), water (acid catalyst required), and various acids. If either the alkene or the reagent is symmetrical, only one product is possible. If both the alkene and reagent are unsymmetrical, however, two products are possible, in principle. In this case, Markovnikov's rule allows us to predict the product obtained.

REFERENCES

- A.I. Vogel, 'Practical Organic Chemistry' 4th Edn, Longmans, London, 1978, p. 1112; L.M. Harwood and C.J. Moody 'Experimental Organic Chemistry', Blackwell, 1989, p.260; 2nd. ed, 1999, p. 254.
- Astruc, D. in Organometallic Chemistry and Catalysis Ch. 19, 395-408 (Springer, 2007).
- Bertleff, W. inUllmann's Encyclopedia of Industrial Chemistry Wiley-VCH Verlag GmbH & Co. KGaA (2000).
- Diebolt, O., Müller, C. & Vogt, D. 'On-water' rhodium-catalysed hydroformylation for the production of linear alcohols. Catal. Sci. Technol. 2, 773-777 (2012).
- Hebrard, F. & Kalck, P. Cobalt-catalyzed hydroformylation of alkenes: generation and recycling of the carbonyl species, and catalytic cycle. Chem. Rev. 109, 4272-4282 (2009).
- Jimenez Rodriguez, C., Foster, D. F., Eastham, G. R. & Cole-Hamilton, D. J. Highly selective formation of linear esters from terminal and internal alkenes catalysed by palladium complexes of bis-(di-tert-butylphosphinomethyl)benzene. Chem. Commun. 1720-1721 (2004).
- Keii, T. & Soga, K. E. d. Catalytic Olefin Polymerization Elsevier (2007).
- L.F. Fieser and M. Fieser, 'Reagents for Organic Synthesis', John Wiley, New York, vols, 1-15; P.S. Bailey, Chem. Rev., 1958, 58, 925; P.R. Story, et al., J. Am. Chem. Soc., 1965, 87, 737.

R. Criegee, Angew. Chem. Int. Ed. Engl., 1975, 14, 745.

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• Tominaga, K.-i. & Sasaki, Y. Rutheniumcatalyzed one-pot hydroformylation of alkenes using carbon dioxide as a reactant. J. Mol. Catal. A: Chem. 220, 159–165 (2004).

• Van Leeuwen, P. W. N. M. & Claver, C. Rhodium Catalyzed Hydroformylation (Catalysis by Metal Complexes) Kluwer Academic Publishers (2000).