OBTAINING OF ALKENES BY REDUCTIVE COUPLING OF CARBONYLIC COMPOUNDS; SYNTHESIS OF Z,E-6-DODECENE, SYNTHESSES OF FLEXIBILENE AND ISOARYOPHYLLENE, MECHANISTIC VIEWS; THE ORGANIC CHEMISTRY NOTEBOOK, Nº 14

OBTENCIÓN DE ALQUENOS POR ACOPLAMIENTO REDUCTIVO DE COMPUESTOS CARBONÍLICOS; SÍNTESIS DE Z,E-6-DODECENO, SÍNTESIS DE FLEXIBILENO Y ISOARYOPHYLLENE, VISTAS MECANICISTAS; EL CUADERNO DE QUÍMICA ORGÁNICA, Nº 14

Short review

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ABSTRACT

The Organic Chemistry Notebook Series, a Didactical Approach, is the series designed with educational purposes in the organic synthesis field. With the present paper we add to a total of fourteen contributions so far in the series.

This series of studies is designed to help students when getting started in the synthesis subject. The method of learning includes many fully and explicitly designed reactions step by step. The best manner to understand a synthesis is by means of graphical views which have been proposed by the authors of the series, and when they are accompanied in most of the cases by illustrative comments by the authors that describe de graphical mechanistic proposals and add some criteria deduced from the different mechanistic steps. We have taken a series of reactions compiled by W. Carruthers in ‘Some modern methods of organic synthesis’, and we have proposed didactical and mechanistic views for them. This theme is included in the chapter “Formation of carbon-carbon double bonds” in the mentioned text.
Carbonyl compounds can be reduced until alkenes by reductive dimerization, this is the so called Intermolecular Carbonyl Coupling InterMolCC. For aldehydes and ketones is feasible the obtaining of alkenes on reductive dimerization by using a reductive agent based on Ti(III) 3Cl and LiAlH₄ or Zn(Cu) or active metallic Ti. The InterMolCC also includes the Intermolecular Mixed Carbonyl Coupling InterMolMCC. Also, we described in a mechanistic manner what has been exposed by diverse other authors with regard to a variant of InterMolMCC, the Intramolecular Mixed (or not) Carbonyl Coupling IntraMolMCC.

RESUMEN

"La serie de cuadernos de química orgánica, un enfoque didáctico", es la serie diseñada con fines educativos en el campo de la síntesis orgánica. Con el presente documento, sumamos un total de catorce contribuciones hasta ahora en la serie.

Esta serie de estudios está diseñada para ayudar a los estudiantes cuando se inician en el tema de síntesis. El método de aprendizaje incluye muchas reacciones diseñadas completa y explícitamente paso a paso. La mejor manera de entender una síntesis es por medio de vistas gráficas que han sido propuestas por los autores de la serie y cuando en la mayoría de los casos están acompañadas por comentarios ilustrativos de los autores que describen propuestas mecanicistas gráficas y agregan algunos criterios deducidos de los diferentes pasos mecanicistas. Hemos tomado una serie de reacciones compiladas por W. Carruthers en "Algunos métodos modernos de síntesis orgánica", y hemos propuesto puntos de vista didácticos y mecanicistas para ellos. Este tema se incluye en el capítulo "Formación de dobles enlaces carbono-carbono" en el texto mencionado.

Los compuestos carbonílicos se pueden reducir hasta alquenos por dimerización reductiva. Para los aldehídos y las cetonas es factible la obtención de alquenos en la dimerización reductora utilizando un agente reductor basado en Ti (III) 3Cl y LiAlH₄ o Zn (Cu) o Ti metálico activado.

INTRODUCTION

Due to lack of knowledge of classical mechanisms, students experiment emptiness when comprehending a determined synthesis found in the literature. Since a mechanistic proposal is naturally mandatory for a rational explanation of products emerging from a synthesis, we offer the present series theming on mechanistic approaches on several published syntheses. As academics we are committed with the didactics and we have designed a series of articles exposing mechanistic theoretical proposals, articles have a character of short review. The present contribution: Obtaining of alkenes by reductive dimerization of carbonylic compounds; mechanistic views; the organic chemistry notebook, nº 14, is the fourteenth study in the series: “The Organic Chemistry Notebook Series, a Didactical Approach” [1-13].

REVIEW OF REACTIONS, MECHANISTIC THEORETICAL PROPOSALS, DISCUSSION

Reductive coupling of carbonyl compounds [14]

Aldehydes and ketones are appropriate substrates for transformation to afford alkenes [14]. The method includes reductive dimerization of substrates by means of carbonyl coupling; the employ of TiCl₃ and LiAlH₄ or Zn(Cu) couple as reductive agents, is mandatory [14]. Alternatively, an active titanium metal species can be applied, the later can be formed by reducing TiCl₃ with K or Li [14-17]. This reaction was widely used, however its utility is limited since when the intermolecular reaction occurs, this lacks selectivity and affords mixtures of the E and Z isomers. See the example in in Figure 1.

\[
\begin{align*}
\text{CHO} & \xrightarrow{\text{TiCl₃, K}} \text{THF, reflux} \quad \begin{array}{c}
\text{58} \\
(77\% ; 70\% \ E, 30\% \ Z)
\end{array} \\
\text{59}
\end{align*}
\]

Figure 1. Reductive dimerization of carbonyl compounds in the synthesis of 6-dodecene, reviewed by W. Carruthers [14]

The reaction requires a surface of active titanium particles for interactions [14]. Reaction occurs in two stages. In the first step a pinacol reduction happens to conduct the reaction to the apparition of a new C-C bond by mediating a
monomeric coupling or dimerization [14]. Carbonyl is reduced into ketyl by means of receiving an electron from the donor titanium; ketyl dimerizes to pinacol [14]. Pinacols have been proposed as intermediates since they convert into alkenes in smooth conditions when titanium is employed [14]. Subsequently, in the second step of the reaction, deoxygenation occurs, because of coordination of pinacol to titanium particle [14]. Excision of the two bonds O-C comes about, yielding the alkene along with the oxidized titanium surface [14]. See Figure 2 for an explanatory scheme of this reaction [14]. See figure 3 for a mechanistic view of reaction of Figure 1.

Figure 2. Carbonylic compound reduction until pinacol by dimerization; conversion of pinacol into alkene by action of titanium; titanium is responsible of de-oxygenation of pinacol by coordinating of titanium with the diol substrate; oxygen atoms are freed from the diol and attached to the titanium surface and thus the alkene is formed. Reviewed by W. Carruthers [14]

Figure 3. Carbonylic compound reduction of 58 (hexanal) until pinacol by dimerization; conversion of pinacol into alkene (6-dodecene) by action of titanium; titanium is responsible of de-oxygenation of pinacol by coordinating of titanium with the diol substrate; oxygen atoms are freed from the diol and attached to the titanium surface and thus 6-dodecene 59 is formed. Titanium exerts a coordination interaction at all stages of the reaction. Reviewed by W. Carruthers [14]. Theoretical mechanistic proposals by the authors
The dimerization and reduction of aldehydes into alkenes containing as double number of carbons in comparison to the aldehyde, can be achieved by the coupling of 2 molecules of aldehyde. In Figure 3 the two molecules of hexanal (58) are coplanar in the same plane one faced to the other in proximity enough to make possible coupling of the carbonyl groups but with oxygen of carbonyls placed as far as possible one from another. The pentyl moiety of the two hexanal molecules are very close each other because of the similarity of their polarity (these moieties are non-polar and they mix easily), this alkyl characteristic of hexanal makes possible the monomeric coupling. The current method under analysis is the one employing reduced titanium from TiCl₃, and excludes the utilization of any reducing agent, namely LiAlH₄ [14]. It is meant by that we are in a surface catalysis process, which implies a radicals’ mechanism, whereas hydride using implies a Sₜ₂ ionic mechanism [14-17]. Hence, in Figure 3, the π electrons of both carbonyl groups of the aldehydes delocalize onto the extremes of the ancient double bond forming a di-radical. This di-radical is stabilized by pairing the unpaired oxygen electron with an electron on the Ti(0) which becomes thus a “prêt à porter” electron. The departure of such electron from the surface of Ti(0) occurs by oxidizing to Ti(I) and increasing thus the electron richness of the electron-receiver oxygen. The whole process runs under the auspicious covalent bond establishment between oxygen from aldehyde and the titanium atoms, represented by segmented traces in Figure 3. Once the oxygen received the metallic electron, the former becomes an anion alkoxy, which converts to alcohol by interaction with water equilibrium, taking the aqueous proton. Titanium is now a Ti⁺ species, always imbibed in the Ti(0) surface. According to Figure 3, carbonyl has been reduced so far and sequentially to ketyl, alkoxy and presently to alcohol. Next step contemplates the reduction of alcohol to alkene by means of extracting oxygen from alcohol by eliminating gas hydrogen first followed by homolysis of the C-O, leading to an unsaturated hydrocarbon (E and Z alkenes 59) and oxidized Ti⁺ coordinated to neutral oxygen atoms. Highly unstable due to its atom condition, or an only atom of oxygen with a double radical character (diradical), and because its high electronegativity, oxygen provokes an oxidation of Ti⁺ to Ti²⁺.

The preparation of alkenes of increased number of carbons is also feasible by combination of two different carbonyl compounds, ketone and aldehyde for instance [14]; mixtures of compounds are produced reducing its effectiveness and interest in synthesis [14]. One example of alkenes from condensation of two different carbonyl groups is an intramolecular reaction of a di-carbonyl compound to form a cyclic alkene [14]. Thus, alkenes of 4 to 16 atoms of carbon have been prepared by this method [14]. In this route, compound 60 (a keto-aldehyde) was employed to produce compound 61 named flexibilene [18], a cyclic polylene (52%) [14]. See Figure 4 for the scheme of the reaction [14], and Figures 11 and 12 for a mechanistic explanation.

![Diagram](http://www.bolivianchemistryjournal.org)

**Figure 4.** Synthesis of flexibilene [18], a naturally occurring 15-membered-ring diterpene, 61, by titanium-induced intramolecular reductive coupling of 3,3,7,11-tetramethyl-15-oxohexadeca-4E,7B,11E-trienal (60); reviewed by W. Carruthers [14]

**Comments**

The mechanistic approaches for reductive couplings of carbonyls are scarce. The fundamental differences between approaches lie in the nature of the process, ionic, by radicals or mixed. According to the literature, it has been established that carbonyl mixed couplings are effected by means of the conversion of carbonyl into alcohol to afford a pinacol after condensation [19,20]. It has also been proposed and it is widely accepted that pinacol dimerization occurs via anion radicals [21]. It has been proposed that the mixed carbonyl coupling of diaryl ketones with acetone happens in such a way that diaryl ketone reduces to a dianion whose carbamion realizes a nucleophilic attack over carbonyl of acetone to afford the pinacolate dianion [16]. Figure 5 shows this feature [16], this is the beginning of any further mechanistic proposal [16]. Figures 6, 7 and 9 show four of many possible mechanistic routes for mixed carbonyl reductive coupling [16]. Figures 6, 7 and 9 are schemes for dimerization of carbonyl compounds to afford.
olefins which present paths A1, A2, B and C as possible mechanisms [16]. The initial or first step (Fig. 5) is the
 carbonyl coupling to form the pinacolate after reduction by Ti(0) [16]. In Path A1 pinacolate forms a five
 membered ring between oxygen atoms and the same titanium atom. Homolytic C-O bonds excision follows to form a
 hydrocarbon the alkene C=C bond and the diradical [TiO₂]. Titanium (II) further oxidizes into Ti(IV) by providing
 two electrons to form the π bonds Ti(IV)=O₂. The principal feature of path A1 is the fact that it is a concerted
 process where homolysis, metal oxidation and new bonds formation are simultaneous. The proposition of an only
 titanium atom bonding to two oxygen atoms makes the reaction regioselective. Figure 3 which is a dimerization of
 hexanal, clearly shows in the products that the reaction is not regioselective which means that A1 is not a likely
 mechanism in this case. However, a hypothesis for the observed mixture of cis and trans products backed by reports
 on pinacol reverse reaction could justify the stereoisomers mixture found as products [22,23]. The non-concerted
 mechanistic alternative is path A2 (Figure 6, [16]).

\[
\begin{align*}
\text{Redox processes} & \\
\text{TiCl}_3 & \rightarrow \text{\textit{RBQ} + 3Cl}^- \\
3\text{K}^0 & \rightarrow 3\text{K}^+ + 3\text{e}^- \\
\text{TiCl}_3 + 3\text{K}^0 & \rightarrow \text{Ti}^0 + 3\text{Cl}^- + 3\text{K}^+ \\
& \\
\text{Ar}_2\text{C}=\text{O} + \text{Ti}^0 & \rightarrow \text{Ar}_2\text{C}=\text{O} + \text{Ti}^{2+} + 2\text{e}^- \\
& \rightarrow \text{Ar}_2\text{C}=\text{O} + 2\text{e}^- \\
& \rightarrow \text{O}^- \\
& \rightarrow \text{Ar}_2\text{C}=\text{O}\text{CH}_3_2
\end{align*}
\]

Figure 5. First step for any mechanism involving mixed carbonyl reductive coupling. The diarylketone becomes a diradical
carbonyl compound which is reduced by one atom of Ti⁰ towards the obtaining of the pinacolate, the Ti(0) species come from the
redox processes [16]

Such a fact has been proved experimentally by the reducing of meso- and dl-5,6-dihydroxydecane with TiCl₃/K to
obtain Z- and E-5-decene [16]. Another mechanistic possibility is depicted in path B of Figure 7 [16]. Path B shows
the absence of the five-membered ring, and the presence of two titanium atoms instead of one as shown in paths A1
and A2, involved in the reductive process [16]. The process is supposed to not to be concerted [16]. An experiment
has been designed to prove that path B is not the more appropriate mechanism, at least in the case where cis- and
trans-9,10-decadiol (62 and 63) was reduced to 1,2,3,4,5,6,7,8-octahyronaphthalene (64) [16]. In such experiment
the cis isomer afforded the naphthalene derivative suggesting a concerted reaction pathway but the trans isomer gave
no alkene [16]. These empiric conclusions seem to point a concerted reaction pathway as A1 instead of a non-
concerted one or B [16]. See Figure 8.

The last considered likely mechanism in the reference 16 is pathway C [16] (Figure 9). This implies the use of
Ti(0) but in a heterogeneous catalysis process. The difference between paths C and A is that the two oxygens are
linked to a Ti surface (path C) instead of a common Ti atom (path A) [16]. Both mechanisms are compatible with the
results of the isomeric decadiol reactions [16]. There has been designed an experiment mentioned by McMurry et
al. [16] to establish the presence or the absence of a five-membered ring intermediate that showed a much faster
reaction of cis-diol 65 than trans-diols 66 and 67 with various reagents assumed to form five-membered rings like
lead tetraacetate for instance. The kinetic studies carried out demonstrated the easy (rapid) way for glycol 65 to form
a five-membered lead alkoxide and the hard, even impossible way (too slow to be kinetically monitored) to form it
for 66 and 67 [16]. The reason is simple, on the one hand, the close to position, of hydroxyls of 65 with regard to the
metal surface, and on the other hand, the far away from position, of hydroxyls toward the metallic surface in 66 and
67. Thus, a five-membered ring is not feasible for 66 and 67 under the interaction with lead tetraacetate [16]. Let us
return to the interaction with titanium now. Similar kinetic studies, employing titanium in place of lead tetraacetate,
have been done by McMurry et al. [16]. The results are conclusive. The employ of cis- (65) and trans-camphanediols
(66 and 67) conducted to the reduced 2-bornene [16] (Figure 10).

Literally we reproduced a fragment as an excerpt that better explains the conclusions of McMurry and
collaborators about the choice of path C in place of path A for proposing a mechanism for the reactions under current
survey: “If the titanium deoxygenation reaction also proceeds through a five-membered ring (path A), we would
expect cis diol 7 (65) to reduce at a much faster rate than trans diols 8 (66) and 9 (67). If, however, the hydroxyls
need only approach a common broad surface (path C), both cis and trans diols should reduce. Treatment of cis diol 7
(65) and a 70:30 mixture of trans diols 8 (66) and 9 (67) in side by side experiments gave the results shown in Table IX. Aliquots were periodically removed, and yields of 2-bornene were determined by GLC. The table clearly shows that both cis- and trans-camphanediols were reduced at approximately the same rate and were complete after 5 h. These results strongly suggest to us that the deoxygenation of diols does not require the formation of a five-membered ring intermediate. We therefore conclude that the reaction occurs by the route shown in path C of Scheme II; i.e., the deoxygenation of diols occurs in a heterogeneous process on the surface of an active titanium particle (see Scheme III)” (reproduced from [16]).

**Figure 6.** Four hypothetical mechanisms involving mixed carbonyl reductive coupling. Paths A1 and A2 [16]

Our own approach to the problematic includes mechanistic proposals as the ones showed in Figure 3 and Figures 11 and 12, that correspond to the synthesis of flexibilene [14] (Figs. 12 and 13) and of Z- and E-6-dodecene [14] (Figure 3), which were not studied by McMurry and col. in reference 16. In this article we tried to give complementary ideas on the path C, now collectively accepted as the most appropriate mechanism for carbonyl couplings, with some, so far missing concepts, regarding the process itself. However, our focus is strictly theoretical, but it adds in some cases, and replaces in others, to what was already established by McMurry and col. [16]. Our mechanisms (Fig. 3, 11 and 12) propose, instead of the radical-anionic initial step as exposed in Figures 5-7 and 9 and in reference 16, a purely radical initial process. Figure 9 shows some missing explanation with respect to the cation Ti$^{2+}$, which seems not to be equaled in a strict stoichiometrical sense. Another feature of mechanisms in Fig. 3, 11 and 12, is the fact of considering two or more atoms of Ti(0) involved, a fact not specified in path C by McMurry and col. In this way, we
propose that the carbonyls’ coupling just before reduction into olefins occurs on the metal surface itself and not before intervention of the surface as showed by McMurry and col. in Figure 5 [16]. A missing explanation in path C (Figure 9) is about the number of titanium atoms in the surface involved in coupling with hydroxyls in the carbonyls’ reduction [16]. We propose two superficial atoms of Ti(0) that oxidize later when going toward products. Also a missing explanation in [16] is the manner how titanium atoms interact with oxygen of pinacol; is it a covalent bonding or a coordination bonding? Questions that remain unanswered. Thus, we propose covalent bonding.

![Initial step](image)

**Figure 7.** Four hypothetical mechanisms involving mixed carbonyl reductive coupling. Path B [16]

**Figure 8.** An experiment (reduction of cis-9,10-decalindiol into 1,2,3,4,5,6,7,8-octahydonaphthalene) demonstrating the concerted way of deoxygenation in contrast with de non-concerted route, reducing of glycol into alkenes, Path B, reproduced from [16]

In Figure 3 we propose essentially that the metallic surface keeps reduced except for a couple of titanium atoms that oxidize by giving one electron each to an oxygen in the substrate to afterward quit the surface at any moment under the form of Ti(I). But we believe that these oxidized titanium atoms, belong still for a while to the conglomerate of the surface, in a continuous interaction with the substrate in the formation of the σ bond first, and until deoxygenation to form the Π bond of the final olefinic product. Once these cations of Ti⁺, bonded to an oxygen, have abandoned the metallic platform, they oxidize to Ti²⁺ by giving one electron to oxygen which becomes an anion (O⁻). A third titanium atom is involved by temporarily coupling the two radicals of the intermediate with available electrons in the titanium atom. Such interaction lasts in the way of a surface catalysis, until the formation of the sigma bond between the oxymethylene groups in the synthesis of compound 59, and between the methylenecarboxy and the oxymethylene groups
in the synthesis of 61. In the synthesis of flexibilene (61, Figures 11 and 12), we apply the same succession of steps as the one described for the synthesis of 6-dodecene.

Figure 11 is a first approach to the proposal of a mechanism for the synthesis of compound 61. As already mentioned, we apply the same steps developed for the mechanism of 59. This supposes the interaction between the substrate the ketoaldehyde 60 and a surface of Ti(0). Thus, the surface interacts with the substrate throughout three titanium atoms (Fig. 11 A), whose highly directional atomic orbital (hybrid or not) should overlap with a sp³ orbital of radical oxygen (or a sp² of radical carbon) containing a single electron. This interaction constitutes a covalence or a covalent Ti-O (or Ti-C) bonding containing a couple of electrons one from titanium and the other from radical oxygen (or the radical carbon). Let us signal at this point that the interaction Ti-C requires two highly directional atomic orbitals of titanium, each containing an unpaired electron (Fig. 11 A B).

Following steps in Figure 11, when titanium (0) transfers its covalent bonding electron to oxygen (Fig. 11 C), the covalence becomes an ionic bond.

Path C
Initial step

![Path C diagram]

**Figure 9.** Four hypothetical mechanisms involving mixed carbonyl reductive coupling. Path C [16]

**Figure 10.** An experiment [cis- (65) and trans-camphanediols (66 and 67) were reduced to 2-bornene (68)] demonstrating the pathway C as the correct mechanism instead of mechanism A. Reproduced from [16]
Titanium atoms are now cations and oxygen atoms are anions and they’re still linked as an ionic pair or an ionic bond (Fig. 11 D). In Figure 11 E when the alkoxides RO\(^-\) become a secondary and a tertiary alcohol by protonation from...
water, the interaction of titanium in the surface (as Ti⁺) and oxygen in the substrate passes by the overlapping of the very same titanium atomic orbital originally used in the covalences with carbonyl’s oxygens, but empty of electrons and a sp³ orbital with two electrons available of oxygen who shares partially the cationic charge of titanium⁺ which reduces to Ti(0) in equilibrium (HO-Ti⁺⇌HO⁺-Ti) with the equilibrium displaced toward the cationic Ti⁺ ion (HO-Ti⁺). This is the driving force that provokes deoxygenation of the substrate by homolysis of C-O bonds. The interaction surface-substrate ends in Fig. 11 F when deoxygenation occurs and the alkene is formed.

The inconvenient in Figure 11 is that that disposition of titanium atoms (cis-diol), side by side in the metallic surface, conducts to the cis H-1/CH₂-16 isomer which is not the diterpene flexibilene (61), but its geometric isomer, whereas the trans H-1/CH₂-16 isomer explained mechanistically in Figure 12 fits well the structure of flexibilene (61) and it’s obtained from titanium atoms in mutual remote position (trans-diol). This last statement is supported by what is explained in Figure 10 regarding the surface catalysis, a mechanism currently accepted as the more adequate one in carbonyls’ coupling to form olefins [16].

To end this contribution, we’ll discuss the formation of cyclic ketones starting from keto-esters [14]. For example, isocaryophyllene (70) is synthesized from the keto-ester (69) followed by Wittig methylation [14], Figure 13. The corresponding mechanism is exposed in Figure 14.

Figure 13. Synthesis of isocaryophyllene 70, by titanium-induced intramolecular reductive coupling of carbonyls; reviewed by W. Carruthers [14]

Mechanism for 69 → 70

Redox processes

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TiCl₃ → Ti⁺³ + 3Cl⁻
2LiAlH₄ → Li⁻ + 2MgH₂
2LiH → 2Li⁻ + 3H⁻
3e⁻ + 3e⁻ → Li⁻ Li⁻
3e⁻ + 3e⁻ → Ti⁰
TiCl₃ + 2LiAlH₄ → 2AlH₃ + Ti⁺³ + 3Cl⁻ + Li⁻ + 2H⁻ + Li⁻
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Figure 14. Synthesis of isocaryophyllene 70, by titanium-induced intramolecular reductive coupling of carbonyls; reviewed by W. Carruthers [14]; mechanistic views proposals by authors
Figure 14.(Cont.) Synthesis of isocaryophyllene 70, by titanium-induced intramolecular reductive coupling of carbonyls; reviewed by W. Carruthers [14]; mechanistic views proposals by authors

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