

Catalytic Aldehyde Olefinations

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Abstract: Several efficient catalytic aldehyde olefination reactions reported, since the late 1980s, are described. This paper deals with the results obtained with several metals. The reaction conditions, selectivities and the yields obtained are presented. Furthermore, the mechanisms suggested by the different authors are discussed in some detail.

Keywords: olefination, catalytic, aldehyde, transition-metal, carbene, ylide.

INTRODUCTION

The olefination of aldehydes and ketones is a very important transformation in organic synthesis. Although the Wittig reaction [1] (Eq. (1)) as well as its modified versions, such as the Horner-Wadsworth-Emmons reaction, the Peterson reaction, the Kocienski-Julia reaction etc. provide highly effective and general methods, they still have several drawbacks such as the low selectivity for some ylides, the possible epimerization of base-sensitive substrates and the fact that multi-step processes are usual [2]. Several systems employing organometallic stoichiometric reagents based on tantalum, titanium, zirconium, molybdenum, tungsten, zinc and other metals have been developed to overcome these problems [3]. Some of them, such as those based on titanium and zinc provide efficient methylation of numerous carbonyl substrates [3j]. However, the use of stoichiometric amounts of usually expensive and, in some cases even pyrophoric compounds, as well as the competitive reductive coupling of aldehydes observed with such reagents [3i], are undesired factors indicating that there is still a significant need to develop new reagents to carry out Wittig type reactions. A particularly favorable way to utilize organometallic reagents to improve or enable aldehyde or ketone olefination reactions is the use of these reagents as catalysts. Therefore, the intention of this review is to give an overview on the catalysts available to date to promote aldehyde olefination reactions and to give an insight into the mechanistic examinations, which are supposed to elucidate the role of the catalyst in order to get to even more active catalysts, employable in even lower quantities as their previously applied congeners.

MOLYBDENUM BASED CATALYTIC ALDEHYDE OLEFINATION

The interest on developing new, practicable organometallic methodologies for generalized olefin synthesis has prompted Schwartz *et al.* about 25 years ago

to investigate several transition metal systems. Simple phosphoranes and $\text{Cp}_2\text{Mo}(\text{PR}_3)$ analogs react readily, however, the resulting product condenses rapidly with another equivalent of phosphorus ylide to give only the symmetrical olefin. These results led to a more detailed investigation of the potential of molybdenum-based systems for this type of reactions. In contrast to phosphoranes, diazoalkanes react rapidly and in high yield with simple molybdenum complexes to give "metalloazine" adducts, which demonstrate susceptibility to nucleophilic attack on the carbon atom bound to the diazo unit. Phosphoranes react with these adducts to give olefins in an organometallic variation of the Wittig reaction, this process resulting in the regeneration of the free phosphine starting material as well as of the molybdenum compound. A particularly successful system was found to consist of $\text{MoO}(\text{S}_2\text{CNR}_2)_2$ ($\text{R} = \text{Me}, \text{Et}$) and N_2CHR ($\text{R} = \text{t-butyl}, \text{propyl}, \text{phenyl}, \text{etc.}$). Olefin yields of 90% with ($\text{Z/E} = 1.25$) were obtained [4].



Equation 1. The Wittig reaction

Although in this case no aldehyde is involved in the formation of the olefin (the "metalloazine" adduct can be regarded as a carbonyl group derivative), this work has paved the way for further research on organometallic complexes as catalysts for aldehyde olefination.

A direct follow-up of this work was presented in 1989 by Lu *et al.* [5], using $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$ in the presence of triphenylphosphine and diazoacetate as aldehyde olefination catalyst. Several aldehydes were converted to olefins using 10 mol% of catalyst, being that aromatic aldehydes showed better yields than aliphatic, and in the aromatic aldehydes, the presence of electron donating groups on the benzene ring had a positive effect on the yield, in contrast to the reactivity pattern of the Wittig reaction. Olefin yields of up to 83 % were reached at 80 °C reaction temperature within 5 h, the E-isomer being by far the main product, in some cases (with varying aldehyde) the only product. Without catalyst, the corresponding azine was formed in high yields. The two mechanistic pathways conceived for this reaction are shown in Fig.(1) and (2).

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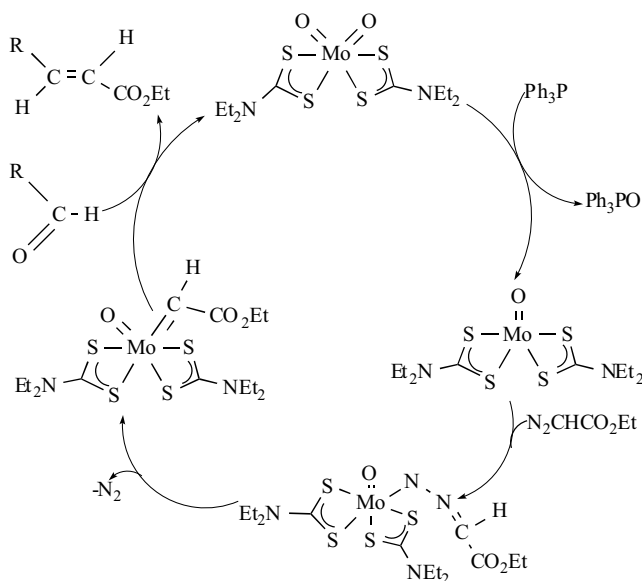


Fig. (1). Catalytic aldehyde olefination according to Lu *et al.* [5] involving a hypothetical metallacarbene intermediate.

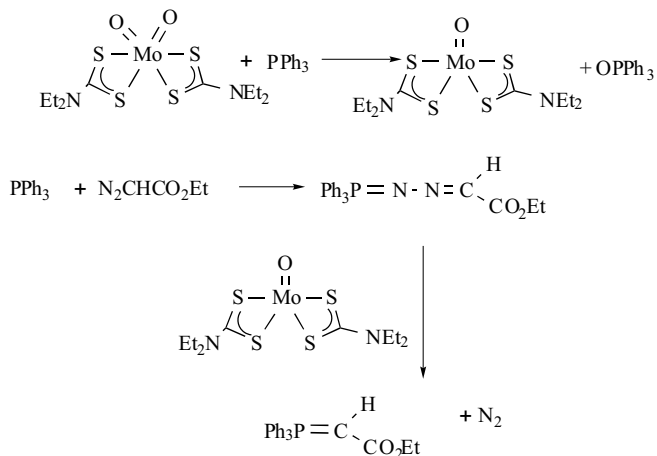


Fig. (2). Catalytic aldehyde olefination according to Lu *et al.* generating an ylide.

The second pathway, creating catalytically a phosphorus ylide was considered to be the main pathway of this reaction. However, the first involving a (hypothetical) metal carbene intermediate could not be excluded, since the stoichiometric reaction of MoO₂(S₂CNEt₂)₂, aldehyde and diazoacetate, leads to the formation of olefin in the absence of triphenylphosphine. The reactivity pattern of the different aldehydes could be then explained in the following way: for the more reactive aldehydes (aldehydes with an electron-withdrawing group on the benzene ring), the attack of the nitrogen atom on the carbonyl group would be faster than the evolution of dinitrogen and azines are obtained as main products, whereas for the less reactive aldehydes (with an electron-donating group on the benzene ring), the dinitrogen is evolved first, a phosphorus ylide is formed and as a result of attack by the ylide carbon atom on the carbonyl group, olefins are obtained as the main product. The main difference between the two mechanisms considered by Lu *et al.*, however, is the creation of a metal carbene intermediate in the first case and the catalytic formation of an ylide, undergoing then a Wittig type reaction in the second.

RHENIUM BASED CATALYTIC ALDEHYDE OLEFINATION

In 1991 W. A. Herrmann *et al.* reported on an aldehyde olefination catalyzed by Methyltrioxorhenium(VII), CH₃ReO₃ [6a], a compound already successfully applied in several other catalytic reactions, among them olefin metathesis, and, most notably a broad variety of oxidation reactions, such as the olefin epoxidation [7]. The aldehyde olefination reaction with CH₃ReO₃, nowadays usually abbreviated as "MTO" (MethylTriOxorhenium), was carried out at room temperature by adding diazoalkane dissolved in benzene or tetrahydrofuran (THF) dropwise to a solution of stoichiometric amounts of aldehyde and triphenylphosphine and a catalytic amount of MTO (1-10 mol %) in the same solvent. The reaction temperature (-20 - + 80 °C) has little effect on the product distribution. Ethyldiazoacetate and diazomalonate have been applied together with both saturated and α,β-unsaturated aldehydes and triphenylphosphine or tri-*n*-butylphosphine. Depending on the aldehyde used, yields up to 98 % and E:Z ratios of up to 97:3 could be reached within 20 min reaction time at 20 °C. The more catalyst is present, the worse is the selectivity towards *trans* product and the less azines, RCH=N-N=CHR are produced. Electron withdrawing substituents on the aldehyde favor the olefination in contrast to the Mo-based catalytic system established by Schwartz *et al.* [4] and Lu *et al.* [5] (see above). Another important difference is that olefins derived from diazomalonate are obtained with MTO as a catalyst but not with [MoO₂{S₂CN(C₂H₅)₂}₂]. Instead a stable phosphorus ylide, (C₆H₅)₃P=C(CO₂CH₃)₂, is formed in the latter case, which does not react with aldehydes in a Wittig reaction. Therefore, a significant advantage of the MTO catalyzed system is that the synthesis of olefins from otherwise unreactive precursor compounds is possible. The mechanistic implications of this observation are discussed below in some detail. Some cyclic ketones also undergo the olefination reaction with MTO as the catalyst. However, the yields and activities are in this case considerably lower. The predominant side reaction here is a metal catalyzed formation of the symmetric olefin from the diazoalkane.

Since it was already known that MTO reacts readily with phosphines, it was assumed that in a first step of the catalytic reaction one of the terminal oxo atoms originally bound to the rhenium center is abstracted by the phosphine, forming a compound of the composition CH₃ReO₂•OPPh₃, which then would react in a further step with the diazo acetate under liberation of both phosphine and dinitrogen [6a].

A follow up work showed that the catalytically active species really was a rhenium(V) complex based on methyldioxorhenium(V), nowadays known as "MDO" (MethylDiOxorhenium) [6b]. This compound is formed, as it has been previously anticipated, *via* reduction of MTO with the phosphine under formation of phosphine oxide. It was assumed that in the catalytic cycle, after the formation of the Re(V) species, in a second step a rhenium carbene complex is formed by the reaction of MDO with the diazocomplex under extrusion of dinitrogen gas. The carbene would then react with the aldehyde and form a metallacycle, which finally reforms MTO (with oxygen from the aldehyde)

and olefin [6]. The whole reaction cycle is shown in Fig. (3). However, neither the rhenium carbene nor the metallacycle could be directly observed. However, rhenium(VII) carbenes could be generated independently already before, but have never been applied as catalysts or carbene transfer reagents for the aldehyde olefination [8,9]. Therefore, based on the work of Espenson *et al.* [10] another mechanistic suggestion was made for the MTO/MDO based olefination of aldehydes by Abu-Omar *et al.* (Fig. 4) [11]. However, a closer examination of the different steps of this alternative mechanism shows that the decisive steps of this mechanism - despite being all plausible in itself and some of them being observed under different reaction conditions - would be too slow under the conditions applied for the aldehyde olefination with the MTO/MDO system to play a major role.

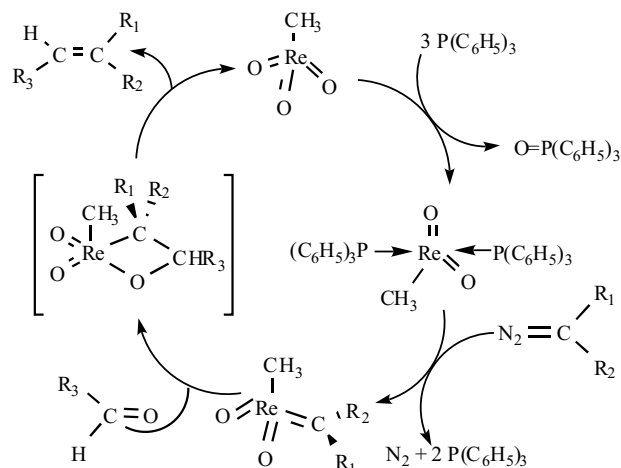


Fig. (3). Catalytic aldehyde olefination with MTO as catalyst as proposed by Herrmann *et al.* [6].

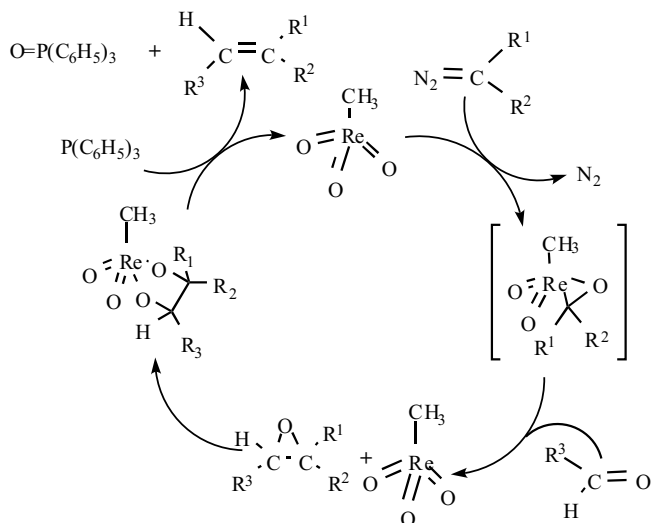


Fig. (4). Mechanism of the catalytic aldehyde olefination with MTO as catalyst as suggested by Abu-Omar *et al.* [11].

Recently, two studies with other Re catalyst systems performed independently by Romão, Kühn *et al.* [12] and by Chen *et al.* [13] proved the presence of Re carbenes under the applied reaction conditions by NMR and MS techniques. The first group used several stable derivatives of MDO, such as CH₃ReO₂(PhC≡CPh) [14] as catalysts for the aldehyde olefination. It was found that the formation of a phosphazine

prior to the reaction with the Re(V) catalyst is a decisive step of the reaction. Abstraction of an oxygen from the MDO moiety by the positively polarized phosphine (observed by ¹⁷O-NMR spectroscopy) leads to the formation of a labile Re(V) carbene complex (observed by ¹³C-NMR) and phosphine oxide (Fig. 5). Addition of excess alkyne leads to a significant slowing down of the reaction, probably due to a competition between phosphazine and alkyne for the coordination to the MDO moiety [12]. In the work of Chen *et al.* ionic catalyst systems based on Lewis-base adducts of dirheniumheptoxide (Re₂O₇) were used [13a]. In the gas phase evidence for Re carbene species has been found by ESI-MS spectroscopy. First indications for a "rhenaoxethane" as intermediate have also been reported [13b]. However, Chen *et al.* also observed Re bound ylides in the gas phase and by NMR spectroscopy in solution and assumed the Re catalyzed formation of ylides (Fig. 6). Since the observed E/Z-relationships are dependent on the phosphine used, it is assumed that PR₃ cannot only be a deoxygenation agent [13a].

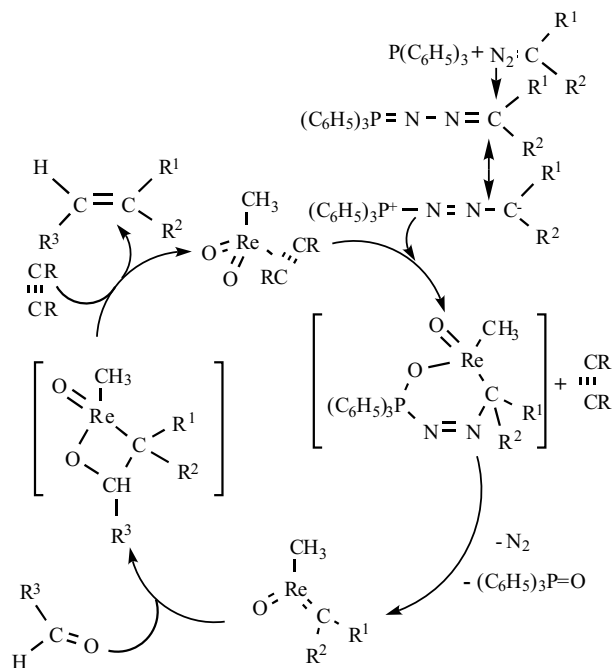


Fig. (5). Mechanism of the catalytic aldehyde olefination with CH₃ReO₂(PhC≡CPh) as catalyst precursor according to Romão, Kühn *et al.* [12].

It has been assumed by several groups that the catalytic formation of ylides is the most important role played by the catalysts in aldehyde olefination. This topic will be discussed below in some detail for other elements than Re. However, an interesting detail in the context of the Re catalyzed aldehyde olefination is the following observation: While the stable phosphorus ylide (C₆H₅)₃P=C(CO₂CH₃)₂ does not even react with aldehydes in boiling benzene, the reaction takes place at room temperature in the presence of MTO. Under these conditions olefins of the formula RCH=C(CO₂CH₃)₂ are formed. MTO in benzene does not catalyze olefin formation from ylides and phosphazines (without aldehyde being present) at room temperature [6a]. MTO therefore, implements the Wittig olefination of aldehydes with otherwise unreactive phosphorus ylides. With respect to the mechanism, this latter observation may

indicate that MTO either catalyzes the aldehyde olefination according to Fig. (3) or catalyzes the formation of ylides in a similar way as suggested by Chen *et al.* for ReO_3^+ derivatives [13a] and afterwards, in a second step, catalyzes the classical Wittig reaction with the previously formed ylide and the aldehyde. This question still remains unsettled.

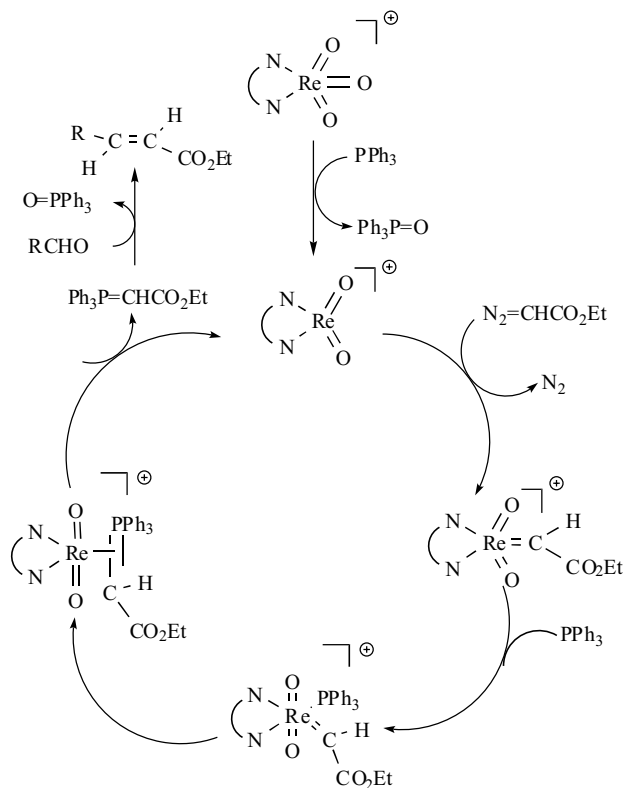


Fig. (6). Aldehyde olefination catalyzed by Lewis-base adducts of Re_2O_7 according to Chen *et al.* [13a].

Another Re(V) complex, $\text{Cl}_3(\text{O})\text{Re}(\text{PPh}_3)_2$, was also found to catalyze the aldehyde olefination showing higher *cis/trans* selectivity than the MTO/MDO based system [6b]. However, several derivatives of MTO, namely $(\text{C}_5\text{H}_5)\text{ReO}_3$ [16a], $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$ [16b], and $(t\text{-bu}_2\text{bipy})(\text{CH}_3)\text{ReO}_3$ [16c] show low activity [6b]. $(\text{C}_5(\text{CH}_3)_5)\text{Re}(\text{CO})_3$, $\text{BrRe}(\text{CO})_5$, $\text{Re}_2(\text{CO})_{10}$, and both ionic and covalent perhenates, such as $[\text{NH}_4]\text{ReO}_3$ and $\text{Me}_3\text{SnOReO}_3$ are completely inactive as catalysts in the aldehyde olefination [6b]. The reason for the low activity of CpReO_3 and its derivatives is the different $\text{Re}=\text{O}$ bond strength in comparison to MTO. In MTO the $\text{Re}=\text{O}$ bond is so strong that an oxygen can not be totally abstracted by PR_3 as is the case for $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$. As outlined above, in MTO the $\text{Re}-\text{O}$ bond is activated through a phosphine base, resulting in $\text{CH}_3\text{ReO}_2 \cdot \text{OPR}_3$ or the isolated $\text{CH}_3\text{ReO}_2(\text{PR}_3)_2 \cdot (\text{O}=\text{Re}(\text{CH}_3)\text{O}_2)$ [6b]. In $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$ OPR_3 is extruded, the resulting $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_2$ is stabilized by dimerization to $((\text{C}_5(\text{CH}_3)_5)\text{ReO}_2)_2(\mu\text{-O}_2)$ [17]. DFT-calculations indicate that dimer-formation is exothermic for $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$ and $(\text{C}_5\text{H}_5)\text{ReO}_2$, but endothermic for $\text{CH}_3\text{ReO}_2 \cdot \text{OPR}_3$ [18]. The OPR_3 , however, can be easily abstracted when surface fixed phosphine is used in the presence of alkyne to generate $\text{CH}_3\text{ReO}_2(\text{PhC}\equiv\text{CPh})$ [14], which is also an aldehyde olefination catalyst, as mentioned

above [12]. The chemistry of $(t\text{-bu}_2\text{bipy})(\text{CH}_3)\text{ReO}_3$ [16c] and other closely related bidentate Lewis base adducts of MTO resembles more that of $(\text{C}_5(\text{CH}_3)_5)\text{ReO}_3$ than the chemistry of free MTO [19], explaining their low activity in the aldehyde olefination reaction.

The use of MTO as aldehyde olefination catalyst as described by Herrmann *et al.* has, according to some other authors [13, 20] – non withstanding the mechanistic debate – some practical drawbacks, among them being the use of dry solvents, the formation of OPPh_3 as co-product, which can often complicate product isolation and purification, and the catalyst itself, which had to be prepared from expensive Re_2O_7 [21]. Carreira *et al.* therefore, set out to develop a variation based on $\text{Cl}_3(\text{O})\text{Re}(\text{PPh}_3)_2$ as catalyst (1 mol %), which could be performed in reagent grade solvents without purification of any reagent prior to use [20]. Good yields (ca. 85 %) and diastereoselectivities of 20:1 have been reached by replacing PPh_3 by $\text{P}(\text{OEt})_3$. The by product $\text{OP}(\text{OEt})_3$ can be easily removed by aqueous work up [20]. Since then the synthesis of MTO has also been significantly modified, so that it can be directly synthesized from Re powder [22]. This is a particularly easy and inexpensive way to get to this stable and easy to handle compound. From the cost, stability and preparative point of view, no other Re(VII) compound is nowadays a match for MTO [22a]. However, in the meantime some other, not Re based aldehyde olefination catalysts have been described, which rival the Re based systems both in selectivity and activity. They are described in more details in the next chapters.

CATALYTIC FORMATION OF YLIDES

Independently of the work of Schwarz *et al.* and Lu *et al.* a work of Shi, Huang *et al.* appeared, claiming to have found the first example of a catalytic Wittig type reaction [23]. A tri-*n*-butylarsine catalyzed olefination of aldehydes with methyl bromoacetate or *o*-bromoacetophenone in the presence of triphenyl phosphite as oxygen acceptor was described. At room temperature olefin yields of up to 87 % could be reached within 18 h, the *E/Z* ratio usually being higher than 98:2. Fig.(7) depicts the proposed mechanism, describing the formation of an arsonium ylide as a key intermediate, which is formed in the presence of potassium carbonate. The mechanism was based on plausibility, but no direct experimental evidence was provided.

One year later, Huang *et al.* presented a one pot reaction of tributylstibine, diazocompounds, carbonyl compounds (including both aldehydes and ketones) and a catalytic amount of Cu(I) , leading to olefins in yields of up to 98 % within 4 h reaction time at 40 – 80 °C. 5 – 20 mol % catalyst have been used for the reactions. Stibonium ylides are formed as intermediates. Several Cu compounds representing formal Cu oxidation states between 0 and II have been examined. The most efficient catalyst found was Cu(I) . Tributylstibine proved to be more efficient as mediator than Bu_3P , Bu_3As and Bu_3Bi [24].

In a further continuation of this work Huang *et al.* could demonstrate that a one pot reaction of diorganyl telluride, diazocompounds and carbonyl compounds (including again both aldehydes and ketones) and a catalytic amount of Cu(I) affords the olefination products in yields of up to 95 %, in

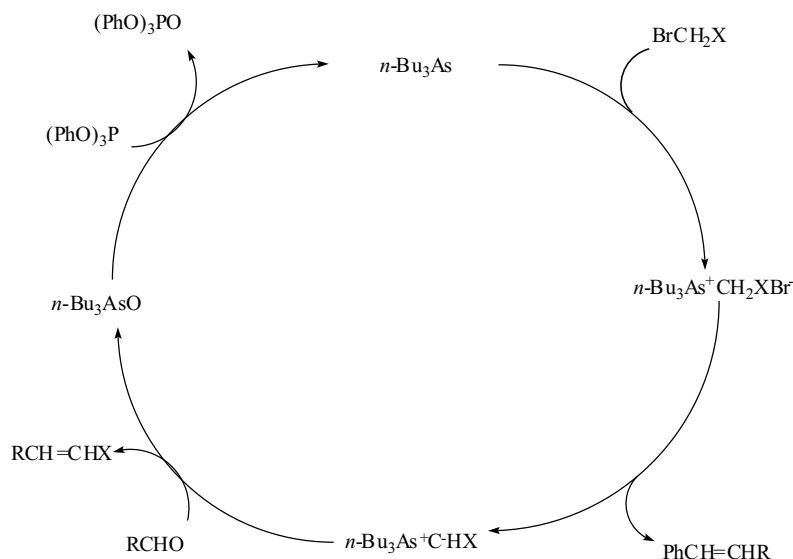
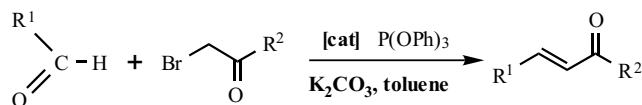


Fig. (7). Mechanism of the catalytic aldehyde olefination with $n\text{-Bu}_3\text{As}$ as catalyst as proposed by Shi, Huang *et al.* [23].

E-configuration, at a reaction temperature of 100 °C within 5 h. The CuI catalyst was used in an amount of 30 mol %. Other Cu complexes lead to lower product yields [25]. It has been assumed that the reaction proceeds *via* highly stabilized telluronium ylide with two strong electron withdrawing substituents. These ylides are reactive towards carbonyl compounds due to their high nucleophilicity. While all attempts to isolate these telluronium ylides by chromatography failed, they could be identified via ^1H NMR spectroscopy. Although some telluronium ylides had been described before in the literature, their reactivity towards carbonyl compounds had not been examined [26].

In an extension of the work of Huang *et al.* Tang *et al.* reported on $(\text{Br}(\text{Bu})_2\text{Te})_2\text{O}$ as a novel catalyst for Wittig type reactions. In the presence of triphenyl phosphite and K_2CO_3 a variety of aldehydes could react with α -bromoacetates to afford α,β -unsaturated esters or ketones in yields between 80 and 100 % and E/Z ratios of usually higher than 99/1 in reaction times of 18 – 72 h at 80 °C when 1 – 2 mol % $(\text{Br}(\text{Bu})_2\text{Te})_2\text{O}$ are used (Eq. (2)) [27]. On the basis of the mechanism proposed by Huang *et al.* [23–25] (see Fig. (7)) and additional reactions performed in their laboratory, Tang *et al.* suggested a mechanism for their catalytic reaction. This mechanism is presented in Fig. (8) [27].



Equation 2. Catalytic aldehyde olefination catalyzed by $(\text{Br}(\text{Bu})_2\text{Te})_2\text{O}$ according to Tang *et al.* [27].

Fujimura *et al.* reported on the transformation of aldehydes and ethyl diazo acetate with PPh_3 in the presence of 0.5 – 2.5 mol % $\text{RuCl}_2(\text{PPh}_3)_3$ as the catalyst at 50 °C to olefins within 4 – 24 h and yields between 82 and 92 % and E/Z ratios of up to >99/1 [28]. Since it is known that ruthenium carbene species are generated from $\text{RuCl}_2(\text{PPh}_3)_3$ and diazo compounds by carbene transfer [29], it was assumed that the carbene moiety could be further transferred

from ruthenium to phosphorus, which is capable of olefinating aldehydes [30]. The olefination did not take place without triphenylphosphine. Therefore, a phosphorus ylide was considered being formed. In the case the reaction was performed in the absence of the ruthenium catalyst, azine was obtained as the only product [28].

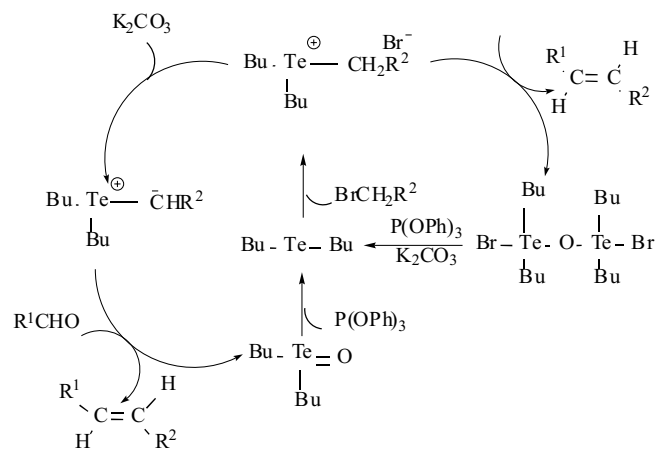


Fig. (8). Catalytic formation of olefins according to experiments performed by Tang *et al.* [27] with Te based catalysts.

Lebel *et al.* also applied Ru and Rh catalysts for the aldehyde olefination [31]. They found that among several examined Ru and Rh compounds $\text{RhCl}(\text{PPh}_3)_3$, usually known as "Wilkinson's catalyst" is the most efficient one. Catalyst amounts of 2.5 – 5 mol % were applied and conversions of > 98 % were reached when cinnamaldehyde was reacted with diazo compounds (either $\text{EtO}(\text{O})\text{C}(\text{H})\text{CN}_2$ or CH_2N_2 or $(\text{CH}_3)_3\text{SiCHN}_2$) and PPh_3 . The best results were obtained with $(\text{CH}_3)_3\text{SiCHN}_2$, where the reaction was virtually completed after 30 min reaction time at room temperature with 2.5 mol% of catalyst. The reaction conditions do not require the use of a base and are mild enough to be compatible with sensitive and enolizable substrates. However, a reaction of cinnamaldehyde with the preformed metal carbene $\text{CH}_2=\text{RuCl}(\text{NO})(\text{PPh}_3)_2$, obtained from the reaction between CH_2N_2 and $\text{RuCl}(\text{NO})(\text{PPh}_3)_2$

was not observed. Furthermore, no carbene was detected by spectroscopic methods, when $(\text{CH}_3)_3\text{SiCHN}_2$ and 2-propanol were added to $\text{RuCl}(\text{NO})(\text{PPh}_3)_2$. Moreover, Rhodium(II) acetate, known for producing metal carbenes with diazo compounds, was inefficient at catalyzing the olefination reaction at room temperature. Based on these observations and the fact that it has been known that diazo compounds react with Rh(I) through nitrogen complexation and the adduct does not produce carbene species [32], Lebel *et al.* concluded that no carbene intermediate is involved in the catalytic aldehyde olefination [31].

Instead they assumed that the catalytic cycle would involve the activation of the diazo compound, e. g. $(\text{CH}_3)_3\text{SiCHN}_2$ by $\text{RhCl}(\text{PPh}_3)_3$ through nitrogen complexation. Nucleophilic attack by PPh_3 followed by desilylation (mediated by 2-propanol) and nitrogen extrusion leads to the formation of a phosphorous ylide (in this case $\text{H}_2\text{C}=\text{PPh}_3$) and regeneration of the catalyst. The formation of the ylide was confirmed by ^{31}P NMR spectroscopy [31].

Chen *et al.* compared the behavior of their Re(VII) based system, where carbene intermediates have been observed in the gas phase, with Lebel's Ru systems, employing seemingly no carbene intermediate, by DFT-calculations (B3LYP/LACVP-level) [13a]. According to those model calculations, they found that phosphorane formation from a carbene precursor is favorable in the case of the Re complex. Formation of a phosphorane ligand for a model ruthenium complex with both carbene and phosphine ligands, however, is strongly endothermic. Even the expected dimerization of the coordinatively unsaturated product makes the overall transformation only approximately thermoneutral. Without the large exothermicity of the Re system, it may be expected that phosphorane formation by ruthenium complexes may be strongly dependent on the particular phosphine, substitution of the carbene moiety, and even the concentration of the complex [13a].

When in $\text{ClRh}(\text{PPh}_3)_3$ one of the PPh_3 ligands is replaced by the bulky *N*-heterocyclic carbene bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene) (IMes), the catalytic activity of the resulting Rh complex $\text{ClRh}(\text{IMes})(\text{PPh}_3)_2$ in the aldehyde olefination is significantly reduced at room temperature, due to the lowering of the ease of displacement of the remaining triphenylphosphines [33]. Mechanistic examinations performed by Lebel *et al.* imply that the rhodium catalyzed olefination cycle involves the coordination of the diazo component to the rhodium catalyst through nitrogen coordination, following the dissociation of a PPh_3 ligand. Since $\text{ClRh}(\text{IMes})(\text{PPh}_3)_2$ is thermally more stable than $\text{ClRh}(\text{PPh}_3)_3$ it was shown that the former complex could be used as olefination catalyst with better yields at 50 °C than at room temperature. Yields of up to 98 % could be reached in the olefination of certain aldehydes at 50 °C after 2 h reaction time [33]. Considering the already well studied behavior of *N*-heterocyclic carbenes as ligands in comparison to phosphine ligands, these observations fit well with the expectations [34].

Utilizing 2.5 mol % of $\text{RhCl}(\text{PPh}_3)_3$ as the catalyst also enabled the methylenation of functionalized fluorinated ketones utilizing $(\text{CH}_3)_3\text{SiCHN}_2$ to give the corresponding fluoromethylalkenes in yields of 61 – 90 % at room temperature. The reaction is highly chemoselective: only

traces of the diene were observed in the methylenation of the keto-monofluoromethylketone [35]. For not fluorinated substrates only very low yields are obtained under the same reaction conditions. The higher the fluorine content of the substrate, the higher the product yield, being the biggest yield difference found between a not fluorinated and a monofluorinated substrate. This observation might indicate that the electron density of the carbonyl moiety is of decisive importance for the olefination reaction. Such an observation may also explain why aldehydes, and particularly the more electron deficient aldehydes, have been found to be significantly more reactive than ketones in most of the described catalytic reactions, employing non-fluorinated substrates.

The application of an Iron(II) porphyrin complex ($\text{Fe}(\text{TPP})$) as catalyst for the aldehyde olefination with ethyl diazoacetate has been described by Woo *et al.* [36]. After reaction times of 3 – 23 h at room temperature with 1 – 2 mol % catalyst olefin yields between 85 and 99 % and E/Z ratios of 10/1 – 49/1 have been reached. Electron poor aldehydes were found to be more readily transformed than electron rich ones. Turnover numbers (TON) of 64 – 128 were observed. In the absence of catalyst azine formation was formed as main product when the reaction mixture was allowed to react for two days.

Lowering the catalyst loading with reactive substrates lead only to a slight slowdown of the reaction velocity, but to a higher E/Z selectivity, favoring even more the *trans* (E) product. With less reactive substrates a lowering of the catalyst loading led to an increased formation of azine, finally becoming the main reaction product [36b].

With respect to the solvent applied it was found that non coordinating solvents (such as toluene) lead to a higher product yield within a given time than coordinating solvents (such as THF) [36b].

Reactions of ketones were substantially slower than the aldehyde reactions. Large excesses of ketone were necessary to yield acceptable amounts of olefination products. Typical reaction conditions were 10 equiv. of ketone, 1.1 equiv. of triphenylphosphine, one equiv. of ethyl diazoacetate and 1 mol % $\text{Fe}(\text{TPP})$ catalyst versus diazoacetate. After 2 – 4 days of reaction time 64 – 89 % of olefin (yield given versus diazoacetate) with a *cis/trans* selectivity of maximum 2.8:1 could be isolated [36b]. Without using a significant ketone excess EDA dimerization was the only reaction observed after 2 days of stirring at room temperature. At 50 °C also only maleates and fumarates were found by GC analysis of the reaction mixture after 2 days [36b].

Woo *et al.* performed detailed experiments to elucidate the mechanism of the Fe(II) catalyzed reaction [36b]. They came to the conclusion, that the catalytic cycle does not proceed in a way that would be analogous to that suggested by Herrmann *et al.* [6] for MTO as the catalyst (precursor) (see Fig. (3)). Such a reaction cycle for the Fe(II) catalyst, as considered by Woo *et al.* is depicted in Fig. (9). The existence of a carbene seems likely according to the authors, although (*meso*-tetratoluyloxy)porphyrin $\text{Fe}=\text{C}(\text{H})\text{C}(\text{O})\text{OEt}$ is very reactive and has never been isolated or detected spectroscopically. Nevertheless, related compounds have been observed spectroscopically or even been isolated [37].

The formation of an intermediate with a Fe=O bond, however, is considered as unlikely, since control experimental evidence indicates otherwise. Oxygen atom acceptors do not react as they should do with an oxoiron(IV) complex. For example, epoxidation reactions do not occur when cyclohexene is added instead of PPh₃. Epoxidation, however, should readily proceed under the conditions applied if a oxoiron(IV) porphyrin would be present [38]. Woo *et al.* assumed that the catalytic cycle should not proceed according to Fig. (9) but according to Fig. (10) with phosphorus ylides being formed, which could be detected by ¹H- and ³¹P-NMR spectroscopy [36b]. For ketones and electron rich aldehydes the selectivities, reaction rates and yields were in accordance with the expectations if the mechanism given in Fig. (10) would be correct [36b].

For more reactive, electron deficient aldehydes, however, the experimental results did not match the expectations solely based on Fig.(10). More *cis*-product was found, particularly with higher catalyst loadings, than would be expected. Woo *et al.* therefore assumed, based on UV-Vis studies, that a π -complex between Fe(TPP) and electron poor aldehydes, such as 4-nitrobenzaldehyde forms and changes the *cis/trans* selectivity in favor of the *cis* product. The reason for such a change is that the Lewis acidic iron(II) porphyrin will activate the carbonyl group toward nucleophilic attack by the phosphorane and the transition state for oxethane formation occurs earlier than without the metal complex. In the earlier transition state, steric factors are not as important as in the late transition state and consequently, a larger fraction of *cis*-oxethane is produced

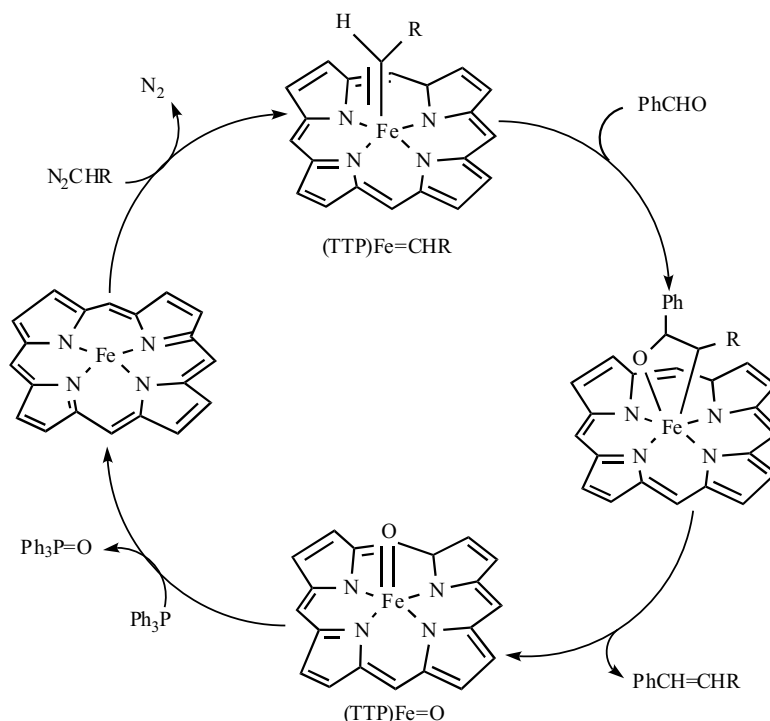


Fig. (9). Catalytic aldehyde olefination cycle for the Fe(TTP) system, analogous to the MTO catalyzed reaction as proposed by Herrmann *et al.* [6], according to Woo *et al.* [36].

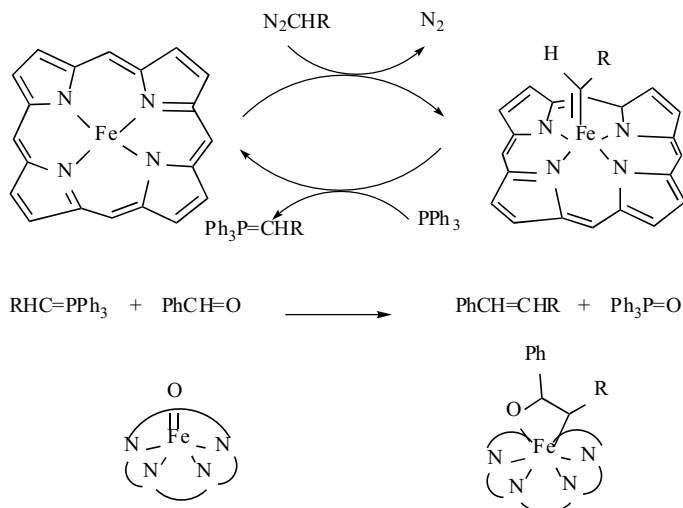


Fig. (10). Most likely mechanism of the Fe(TTP) catalyzed aldehyde olefination as suggested by Woo *et al.* [36].

[36b]. These considerations also bring new light on the question discussed in the previous chapter, whether the Re catalyzed aldehyde olefination would lead to a phosphorus ylide, which subsequently would react in a Wittig type reaction with an aldehyde. Since even phosphorus ylides, which do not undergo the Wittig reaction in the presence of aldehydes are reactive in the presence of MTO [6a], this strongly indicates that also in the MTO catalyzed reaction an interaction as described by Woo *et al.* for the Fe(II) system [36b] might take place. Whether or not this is the only reaction pathway, excluding the cyclic "rhena-oxethane" intermediate [6a], however, is not yet clear.

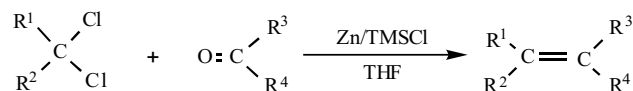
The reactivity profile of the Fe(TTP) catalyzed olefination reaction differs significantly from that of the MoO(S₂CNEt₂)₂-mediated process [36]. The catalytic cycle for the Mo systems involves metalloazines of the type (Et₂NCS₂)₂OMo=N=N=CHCO₂Et and phosphazines as described by Schwartz *et al.* [4] and Lu *et al.* [5] (see above). The phosphazine may be responsible for the formation of the considerable amounts of azines when electron-poor aldehydes are applied.

Based on the above discussed results of Woo *et al.* [36], Zhang *et al.* described the commercially available Fe(III) and Ru(II) porphyrin complexes Fe(TPP)Cl and Ru(TPP)(CO) as efficient catalysts for the selective olefination of a variety of aldehydes with ethyl diazoacetate in the presence of triphenylphosphine [39]. Yields of usually more than 90 % and E/Z-selectivities of > 90:10 were obtained with a broad variety of aldehydes at reaction temperatures of usually 80 °C within one hour or less with a catalyst loading of 0.01 – 2.0 mol%. Air, as the reaction atmosphere was tolerated. A broad variety of first row transition metal TPP catalysts have been investigated, including V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Ru, but except the above mentioned Fe and Ru complexes only Co(TPP) gave a significant amount of olefin. The highest yields, however, were obtained with Fe(TPP)Cl and Ru(TPP)(CO).

OTHER METAL MEDIATED ALDEHYDE OLEFINATION REACTIONS

A combination of excess zinc metal and a catalytic amount of chlorotrimethylsilane (10 mol % with respect to

the carbonyl compound) was found to promote the transformation of various aldehydes and ketones with gem-dichloro compounds, such as methyldichloro acetate and benzylidene dichloride according to Eq. (3) [40]. The corresponding cross coupling products, such as methyl acrylates and substituted styrene are obtained in yields of 60 – 95 % at 50 °C after 3 h reaction time. The E/Z selectivity is high in the case of the reaction of aldehydes, in some cases only the E product is obtained. Aromatic aldehydes react more smoothly than aliphatic aldehydes, ketones do not react with benzylidene dichloride under the conditions applied. The mechanism has not been examined in detail, but the authors assume that the reaction may proceed through organometallic zinc intermediates, such as zinc-carbenoids or geminal dizinc compounds [40].



Equation 3. Catalytic aldehyde/ketone olefination with gem-dichloro-compounds according to Ishino, Nishiguchi *et al.* [40].

Nenajdenko *et al.* reported in a series of papers on a related catalytic olefination reaction of aromatic aldehydes and ketones [41]. They found that *N*-unsubstituted hydrazones of aromatic carbonyl compounds could be transformed into the corresponding substituted alkenes by treatment with polyhalogenated alkanes in the presence of catalytic amounts (10 mol %) of CuCl. This approach was expanded to the synthesis of dichloroalkenes, dibromoalkenes, vinylbromides, vinyliodides, and fluoroalkenes from aromatic and heteroaromatic carbonyl precursors. The general formula of the olefination agents is described as C(Hal)₂XY, among them CCl₄, CHBr₃, CBr₄, CF₃CCl₃, and CF₂ClCFCl₂, being used as C₁ and C₂-building blocks in the syntheses of the corresponding alkenes. The olefination of carbonyl compounds via hydrazones, prepared *in situ*, by treatment with CBr₄, for example, leads to dibromalkenes with product yields between 43 and 97 %, dependent on the carbonyl precursor compound. 1,1-dibromolefins are important reagents in organic synthesis, being synthetic precursors of terminal and asymmetric acetylenes and bromoacetylenes [42].

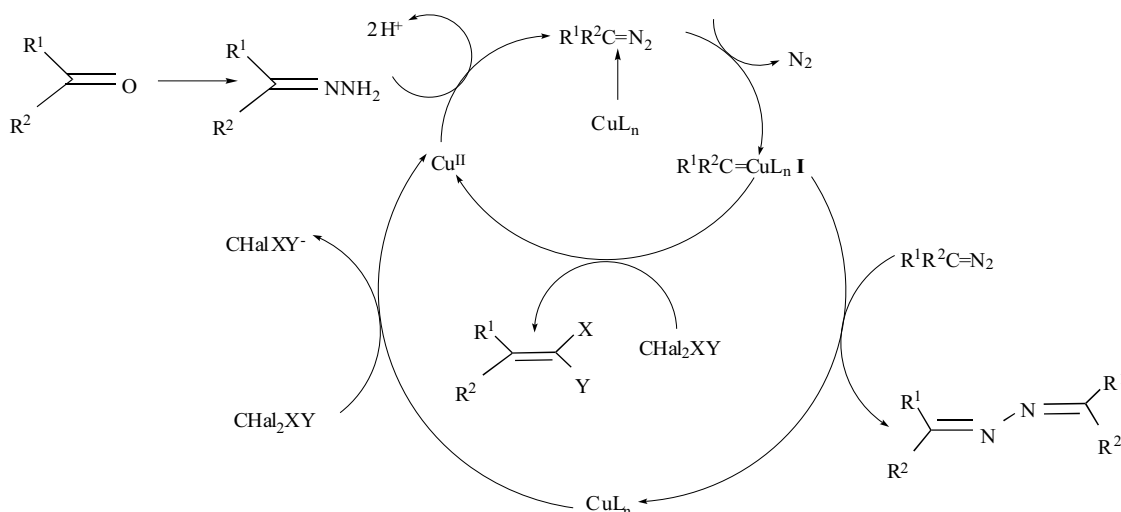


Fig. (11). Mechanism of the Cu-catalyzed olefination of carbonyl compounds as described by Nenajdenko *et al.* [41h].

Furthermore, methods for the stereoselective reduction of dibromoalkanes into E- and Z-isomers of terminal vinyl bromides as well as cross-coupling reactions with dibromoalkanes have been described [43]. The same carbonyl-dibromoalkyl conversion, using a non catalytic Wittig-type reaction with CBr_4 and PPh_3 has been reported for both aldehydes and ketones [44]. However, the necessity of large amounts of PPh_3 is a significant disadvantage of this latter approach.

In the catalytic reaction, which is assumed to be mechanistically equivalent to the olefination of hydrazones of arylalkyl ketones and aromatic hydrazones, Cu(I) is oxidized to Cu(II) in the initial step. The formed Cu(II) species is assumed to oxidize the hydrazone into the corresponding diazoalkane. A copper-carbene is considered as the key intermediate of the olefination reaction. The copper-carbene is formed after the Cu-catalyzed decomposition of the diazoalkane, reacting subsequently with $\text{C}(\text{Hal})_2\text{XY}$ to the product alkene [41h]. The stability of the intermediate diazoalkanes is the main factor determining the direction of the reaction. In the case of sufficiently stable diazoalkanes, other products can be formed under the reaction conditions along with the products of the catalytic olefination [41h]. The mechanism is summarized in Fig. (11).

SUMMARY

A variety of efficient catalytic aldehyde olefination reactions have been reported since the late 1980ies. Starting with Mo catalysts, several other metals, among them Re, Ru, Rh, and Fe have been established as useful catalysts, partially under very mild conditions (room temperature), short reaction times (even below one hour until nearly quantitative yields are reached), and high selectivities. However, the mechanism of the catalytic reaction is under close examination and debate. Some authors assume that the different catalytic systems go through closely related intermediates. While the key role of carbene complexes has been firmly established for the Re- and Fe systems under investigation during the recent years, the existence of metallacycle-type intermediates, however, is not yet settled. In several cases, however, catalytic ylide formation has been demonstrated and the catalysts seem to promote both ylide formation and its reaction with electron poor aldehydes and fluorinated ketones. It is rather likely that the research on the catalytic aldehyde olefination will lead to even more active and broadly applicable catalyst systems in the years to come and closer insight into the mechanisms of the reactions will help to find and tailor make the improved or novel catalysts.

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