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Metathetical cyclization of dienes containing P, O, S or Si heteroatoms by a cyclometallated aryloxy-carbene of tungsten. Inhibition effects and steric constraints: A review

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Abstract

Intramolecular metathesis of various diallyl compounds containing the O, S, Si or P hetero element was achieved with good yields by using the cyclometallated carbene complex

$$\overline{\mathrm{W(OAr)}}$$

(OAr)($CHMe_3$)Cl(OEt_2). Unsubstituted diallyl ether is converted into 2,5-dihydrofuran; diallyl sulfide is converted into 2,5-dihydrothiophen; diallyl-phenyl phosphine is converted into phenyl-2,5-phospholen and diallyl dimethyl- or diphenyl-silanes are converted into the corresponding silacyclopentenes. Metathesis reaction of methyl-substituted diallyl-sulfides shows that steric effects are very important. These steric effects are also well seen by addition of di-*n*-propyl or di-*i*-propyl sulfides during the metathesis reaction of diallyl sulfide. Indeed, only the former compound inhibit the reaction, showing that there is an important steric crowding around the tungsten atom.

Keywords: Olefin metathesis; Diallyl compounds; Functional olefins; Steric crowding

1. Introduction

The olefin metathesis process represents a powerful tool in carbon–carbon bond formation reactions [1]. In particular, during recent years ADMET has been the focus of great interest in applied organic synthesis. The metathesis of diene compounds can be used to prepare functionalized polymer materials or unsaturated cyclized products. Up to very recently only some examples of the metathesis of dialkenyl ethers [2], amines [3], carbonates [4], ketones [5] and sulfides [6] were described in the literature, opening novel fields of application. In most cases the catalyst was the Schrock molybdenum carbene $Mo(=NAr)(=CHCMe_2Ph)(OR)_2$ [7] or the Grubbs ruthenium carbene (see for example Refs. [2,3]).

In some previous papers we reported the synthesis of a well defined *o,o′*-diphenyl ary-

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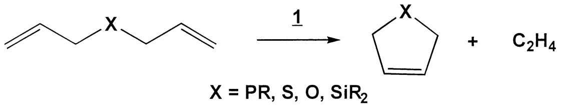


Scheme 1.

loxo(chloro)neopentylidene tungsten complex which displays the formula

$$\overline{\mathrm{W(OA}}\mathrm{r)}$$

(OAr)(CHCMe$_3$)Cl(OEt$_2$) **1** [9,10]. **1** is probably one of the most active and stereoselective system for the metathesis of *cis*-2-pentene (conversion of 1000 equivalents at room temperature in 3 min with 95% of *cis* products even near to the thermodynamic equilibrium [8]). Catalyst **1** can also achieve the metathesis of functionalized olefins such as esters [9], sulfides [10,11], phosphanes [12] and unsaturated carbohydrates [13]. The high tolerance of **1** towards functional groups and its enhanced stereoselectivity are probably due to two important features: (i) the bulkiness of the *o,o′*-diphenyl aryloxo ligands and (ii) the orthometallation which renders the structure extraordinarily rigid and crowded.

In this work we wish to widen the concept of the ADMET reaction and to better understand the behavior of this complex by studying its activity towards various diallylic substrates, i.e., diallyl ether, diallyl silanes, diallyl phosphane, diallyl sulfide and some of its methylated derivatives (see Scheme 1). It must be pointed out that, in these compounds, in contrast to previously reported works, the heteroatom is not ‘masked’ and so it could easily coordinate the metal center and deactivate the alkylidene species.

2. Experimental

All experiments were carried out using classical Schlenk techniques, under dried and deoxygenated argon. Chlorobenzene was distilled over phosphorus pentoxide under nitrogen and kept over molecular sieves. Most of the diallyl compounds (diallyl sulfide, diallyl ether, diallyl silanes and diallyl phenyl phosphane) were commercial compounds which were purchased by Aldrich. All products (except phosphanes) were purified by distillation and treatment over activated alumina. Their purity was checked by carbon-13 NMR. Mono- or disubstituted diallyl sulfides were prepared as described in the literature [14,15]. They were characterized by mass spectroscopy, carbon-13 NMR and chemical analysis. They were also kept over activated alumina.

All catalytic experiments (except those with the phosphorous compounds) were made as follows: 4 ml of chlorobenzene, 0.1 ml of *n*-octane (used as an internal standard in the liquid phase) and the desired amount of the diallyl compound were introduced into a 50 ml Schlenk reactor previously purged with argon. The solution was then kept at 80°C under vigorous stirring and the catalyst (20 mg, 2.35×10^{-5} mol), in solution in 1 ml of chlorobenzene, was added. The conversion of the substrate was monitored by GC of the liquid phase (determination of the disparition of the substrate and of the evolved cyclization product). No polymeric materials were detected by GC or NMR and the mole balance between reagents and products was always near 100%.

A slightly different procedure was used for phosphanes, these products being not easily determined by GC. In this case, the conversion rate was determined by measuring the evolution (in the gas phase) of ethylene with propane as an internal standard. In a typical experiment 4.68×10^{-4} mol of diallyl phosphane (89 mg), 1 ml of chlorobenzene and 1 ml of propane were introduced in a Schlenk tube previously purged with argon. The reaction was then performed as above but the conversion was monitored by determination of the evolved ethylene. After 12 h of reaction, the solvent was removed by evaporation at room temperature under reduced pressure (1 Torr). The residue was then distilled at 100°C and condensed in a liquid nitrogen trap. It was characterized by chemical analysis, ^{1}H, ^{13}C and ^{31}P NMR and mass spectroscopy.

3. Results and discussion

Despite the presence of heteroatoms in the substrates (oxygen, phosphorous, sulfur, . . .), the metathesis cyclisation of the diallyl compounds was achieved easily by using **1** and led always to the expected cyclization product without formation of polymeric species. The results are summarized in Tables 1 and 2. Diallyl sulfide leads to dihydrothiophene, diallyl ether to dihydrofuran, diallyl silanes to the corresponding cyclization products and diallyl phenyl phosphane to the desired phospholen. The conversion is often very high, showing the high activity of **1** for the metathesis of functional olefins. Indeed, even in the presence of highly inhibiting molecules such as phosphanes, the metathesis reaction occurs. A simple comparison between the results of Table 1 shows that the highest conversion is achieved with sulfur compounds (more than 350 equivalents) while with the phosphane compounds only 20 equivalents could be converted into the corresponding phosphane. This reactivity order is in agreement with the liganding properties of the substrates, phosphanes inhibiting more easily than sulfur compounds. This inhibition effect can be regarded as a coordination of the substrate to the metal center by its heteroatom. More strongly this coordination, lowest will be the conversion. In order to confirm this hypothesis, we have performed kinetic studies of the metathesis reaction of diallyl sulfide and we have determined the reaction orders vs. the catalyst and the substrate. The initial rate depends linearly on the catalyst concentration but the order vs. the olefin is -1, in agreement with an inhibiting effect due to the presence of the sulfur atom.

Table 1
Metathesis reaction of various diallyl compounds

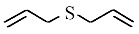
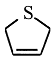
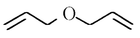
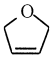
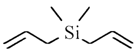
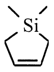
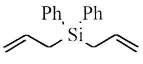
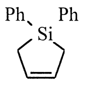
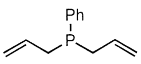
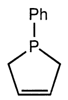
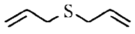
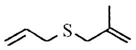
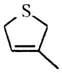
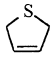
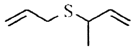
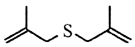
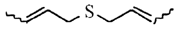
Substrate	Olefin/W	Product	Time (min)	Yield
	500 250		60 60	75 100
	200 100 40		120 120 120	30 75 100
	100 50		20 20	70 100
	100		60	8
	20		300	95

Table 2
Metathesis of substituted diallyl sulfides

Substrate	Olefin/W	Product	Time (min)	Yield (%)
	500 250		60 60	75 100
	100		60	100
	100		60	90
	100	-	60	0
	100	-	60	0
	100	-	60	0

In order to have further proof that the inhibition occurred via the coordination of the sulfur atom, we studied the effect of the addition of sulfur compounds on the reaction rate. The reaction was performed at 60°C with a substrate/catalyst ratio of 300, the other conditions being the same than above (a lower reaction temperature was chosen in order to better determine the conversion variations). Various amounts of di-*n*-propyl or di-*i*-propyl sulfide (which have the same number of carbon atoms than diallyl sulfide and so quite similar steric hindering and liganding properties) were added to the reaction mixture prior introduction of the catalyst and the conversion was determined after 10 min reaction. The results are shown in Fig. 1. It can be seen that addition of di-*n*-propyl sulfide results in a decrease of the conversion of diallyl sulfide, in agreement with a coordination by the sulfur atom inhibiting the reaction.

Most surprising is the result obtained with di-*i*-propyl sulfide as addition of this sulfide compound has no significant effect on the reaction rate. The only one explanation to such an effect is that in this case the sulfur atom cannot coordinate the metal atom and so there is no inhibition by this molecule. Due to the great analogy between the di-*n*-propyl and di-*i*-propyl sulfides, the difference of reactivity of these two molecules can only be explained by steric effects avoiding coordination of the sulfur atom in the case of the *iso* isomer. This result shows also that there is a strong steric crowding around the tungsten atom in catalyst **1** and so that this catalyst will have unexpected properties depending greatly on the steric hindering of the substrates. Examples of such properties are given in Tables 1 and 2: Steric effects are very important in the ADMET reaction of diallyl silanes, diallyl dimethyl silane being converted much more rapidly than diallyl diphenyl silane. The data of Table 2 show that the catalytic activity of **1** for the ADMET reaction of substituted diallyl sulfides depends greatly on the number and position of the substituents on the chains. If the two allyl chains are substituted by methyl groups, no reaction occurs, whatever the position of the methyl group. In contrast, if only one chain is substituted, the reaction proceeds as rapidly than with unsubstituted di-allyl sulfide, with only one exception when there is a methyl group on the α carbon atom of the chain. These results suggest strongly that the first propagating carbene species can only be generated by coordination of the unsubstituted allyl group. In this case the corresponding tungstacyclobutane has only two substituents in the 1–3 positions and should be favored [16]. The absence of reaction with the two symmetrically substituted sulfides can also be rationalized on the basis of the stability of the corresponding tungstacyclobutane. Indeed, in this case the metallacyclobutane has three substituents in 1–2–3 positions, a situation which is not favorable [16]. The next step of the catalytic cycle is the intramolecular coordination of the remaining unsaturated fragment to complete the cyclization with elimination of ethylene. The absence of reaction of the diallyl sulfide monosubstituted on the α carbon atom shows that this step is also probably driven by steric interactions.

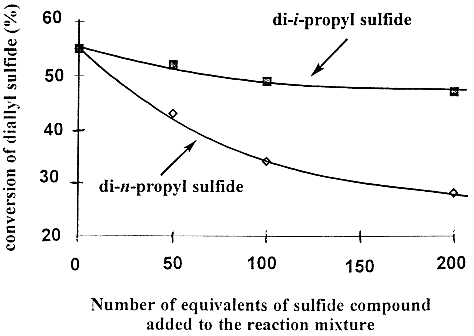


Fig. 1. Conversion of diallyl sulfide after 10 min reaction as a function of the amount of di-*n*-propyl or di-*i*-propyl sulfides added to the reaction mixture.

4. Conclusion

We have shown that catalyst **1** is able to realize the metathesis cyclization of various diallyl compounds containing heteroatoms such as oxygen, silicon, sulfur or even phosphorus. These results show the great possibilities of this catalyst for the metathesis of functional olefins.

In this compound there is an important steric crowding around the tungsten center, as shown by the absence of coordination of di-*iso*-propyl sulfide or the absence of reaction of some substituted diallyl suldides. This steric crowding could lead to very interesting stereoselective properties of this catalyst.

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