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Ruthenium–porphyrin-catalyzed carbenoid addition to allylic compounds: application to [2,3]-sigmatropic rearrangements of ylides

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Abstract

The catalytic effectiveness of ruthenium porphyrins for ylide generation in reactions of ethyl diazoacetate and diisopropyl diazomethylphosphonate with allylic amines, sulfides and iodides is described for the first time. These reactions result mainly in products of the [2,3]-sigmatropic rearrangement of intermediate allylic ylides. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Porphyrins; Catalysis; Sigmatropic

1. Introduction

The metal-catalyzed carbene reactions have become one of the most general and efficient methods available to the synthetic organic chemist [1]. There is also considerable interest in the development of effective catalytic systems for the rearrangement of ylides generated from reactions of diazo compounds with allylic substrates [2,3]. The major advances have recently been achieved with various rhodium derivatives. Alternatives to $Rh_2(OAc)_4$, such as copper and to a less extent ruthenium derivatives [4] were also evaluated for their activity in reactions of allylic substrates with ethyl diazoacetate (EDA). Although the accomplishments achieved thus far are quite impressive, cyclopropanation of the double bond competes with sulfonium ylide formation [2] and exploration of new effective catalysts is still essential to extend the scope of these reactions.

Ruthenium porphyrins have been used frequently for oxidation reactions, based on the ruthenium ability to form compounds in various oxidation states, ranging from Ru(II) to Ru(VI) [5,6]. In contrast to these extensive investigations, only a few carbene reactions catalyzed by ruthenium porphyrins have been reported using Ru(II) porphyrins as catalysts [7–11]. This is quite unexpected since iron porphyrin complexes are active catalysts for the cyclopropanation of alkenes by ethyl diazoacetate [15] and osmium porphyrins catalytically convert ethyl diazoacetate to maleate and fumarate esters [16].

Our interest in the chemistry of ruthenium porphyrins prompted us to investigate the ylide generation from diazo compounds. We previously reported cyclopropanation, N–H and S–H insertion reactions [12–14]. We now want to report herein the details of the catalytic reaction of ethyl diazoacetate and diisopropyl diazomethylphosphonate with allylic substrates catalyzed with ruthenium porphyrins. Comparison with rhodium and copper catalyzed reactions with allylic compounds will also be discussed.

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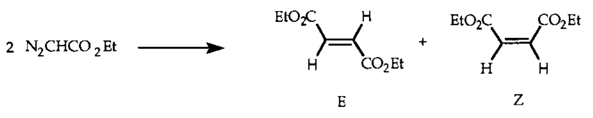
2. Results and discussion

2.1. Reaction of EDA with different allyl sulfides (**1**, **2**, **3**, **4**)

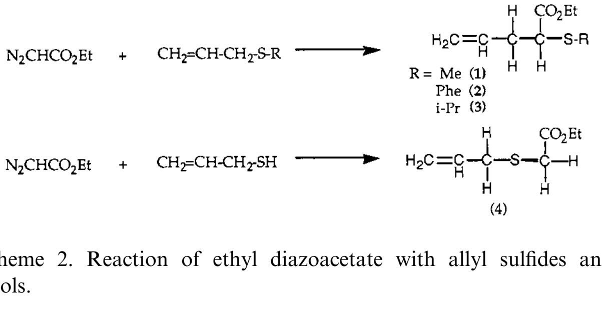
Treatment of allyl methyl sulfide with ethyl diazoacetate at 25°C in the presence of 1 mol% of *meso*-tetraphenylporphyrin carbonyl ruthenium (TPPRuCO) [17] results in the formation of ethyl 2-(methylthio)pent-4-enoate **1** with 96% yield. Table 1 summarizes results obtained from reactions of ethyl diazoacetate with various alkyl allyl sulfides, allylic secondary and tertiary amines and allyl halides. The formation of **1** derives from [2,3]-sigmatropic rearrangement of the sulfur ylide. As previously observed with copper and rhodium catalysts [18], the ruthenium–porphyrin catalytic system is remarkably specific with alkyl allyl sulfides and provides the formal C–S insertion product in nearly quantitative yield. However, reaction with allyl phenyl sulfide provided mainly the coupling products, diethyl maleate and fumarate, and only small amounts of product **2** resulting from ylide rearrangement. Masson et al., using rhodium and copper complexes as catalyst [19] have previously reported such a decrease of reactivity with aromatic sulfide towards diazo derivatives. Due to the conjugation of the sulfur doublet with the aromatic system, the rate of the electrophilic addition of the metal carbene to the sulfide group is probably too low and consequently, the competitive formation of the coupling products, diethyl maleate and fumarate, becomes the major process (Scheme 1). In contrast, the reaction is less influenced by steric effect. Thus, formation of **3** which derives from [2,3]-sigmatropic rearrangement of the isopropylic sulfur ylide is obtained in a fairly good yield (73%).

Table 1
Ratio of insertion product (**P**)/(diethyl fumarate) (**E**)/(diethyl maleate) (**Z**) from (TPP)Ru(CO) catalyzed reactions of ethyl diazoacetate with allyl sulfides, amines and halides

Allyl	Insertion product (**P**)	Ratio of **P**/**E**/**Z**
CH_2=$CHCH_2SMe$	CH_2=$CHCH_2CH(CO_2Et)$-SMe (**1**)	100/0/0
CH_2=$CHCH_2SPh$	CH_2=$CHCH_2CH(CO_2Et)$-SPh (**2**)	8/0/92
CH_2=$CHCH_2SCHMe_2$	CH_2=$CHCH_2CH(CO_2Et)$-$SCHMe_2$ (**3**)	73/0/27
CH_2=$CHCH_2SH$	CH_2=$CHCH_2SCH_2CO_2Et$ (**4**)	100/0/0
CH_2=$CHCH_2NMe_2$	CH_2=$CHCH_2CH(CO_2Et)$-NMe_2 (**5**)	100/0/0
CH_2=$CHCH_2NHMe$	CH_2=$CHCH_2NMe(CH_2$-$CO_2Et)$ (**6**)	95/0/5
CH_2=$CHCH_2Cl$	CH_2=$CHCH_2CH(CO_2Et)$-Cl (**7**)	6/4/90
CH_2=$CHCH_2Br$	CH_2=$CHCH_2CH(CO_2Et)$-Br (**8**)	7/36/57
CH_2vCHCH_2I	CH_2=$CHCH_2CH(CO_2Et)I$ (**9**)	88/0/12



Scheme 1. Dimerization of ethyl diazoacetate.



Scheme 2. Reaction of ethyl diazoacetate with allyl sulfides and thiols.

To complete these data, we also studied the reaction of ethyl diazoacetate with 2-propene-1-thiol. For this substrate, a potential competition between cyclopropanation, ylide rearrangement and the insertion of the diazo compound into a sulfur–hydrogen bond is possible. As previously reported with alkyl and aromatic thiols, we observed complete insertion of the diazo compound into the S–H bond [14] and product **4** was exclusively obtained (Table 1, Scheme 2). It should be noted that a preference for heteroatom–hydrogen insertion has already been observed in the rhodium-catalyzed reaction of diazoesters with unsaturated alcohols [20].

2.2. Reaction of EDA with different allyl amines (**5**, **6**)

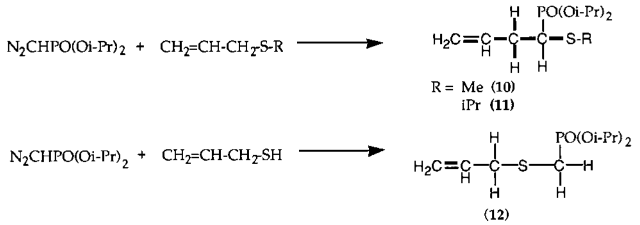
To explore the reactivity profile between secondary and tertiary amines, the reaction between ethyl diazoacetate and alkyl allyl amines was examined. As expected, a tertiary amine such as *N*,*N*-dimethylallylamine, yielded exclusively the product of sigmatropic rearrangement as previously reported with rhodium(II) acetate [18]. Since N–H insertion of metallocarbenoids are widely used in amino acid synthesis [21], secondary allyl amines were also tested as substrates. As expected, the reaction was regioselective yielding mainly N–H insertion with formation of 6 with 95% yield (Table 1).

2.3. Reaction of EDA with different allyl halides (**7**, **8**, **9**)

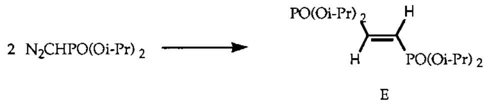
Using rhodium-catalyzed reactions with $Rh_6(CO)_{16}$ or $Rh(OAc)_4$, Doyle et al. have shown that competition between ylide generation and cyclopropanation of the olefin can be manipulated by varying the nucleophilicity of the halogen in the reactant allyl halide [18]. We

Table 2
Ratio of (insertion product, **P**)/(**E**, tetraisopropylethene-1,2-diyl-bis-(phosphonate)) from (TPP)Ru(CO) catalyzed reactions of diisopropyl diazomethylphosphonate with allyl sulfides and amines

Allyl	Insertion product (**P**)	Ratio of **P**/**E**
CH_2=$CHCH_2SMe$	CH_2=$CHCH_2CH[PO(O^iPr)_2]$-SMe (**10**)	100/0
CH_2=$CHCH_2SCHMe_2$	CH_2=$CHCH_2CH[PO(O^iPr)_2]$-$SCHMe_2$ (**11**)	100/0
CH_2=$CHCH_2SH$	CH_2=$CHCH_2SCH_2[PO(O^iPr)_2]$ (**12**)	100/0
CH_2=$CHCH_2NMe_2$	CH_2=$CHCH_2CH[PO(O^iPr)_2]$-NMe_2 (**13**)	0/100
CH_2=$CHCH_2NHMe$	CH_2=$CHCH_2NCH_2[PO(O^iPr)_2]$-Me (**14**)	39/61



Scheme 3. Reaction of diisopropyl diazomethylphosphonate with allyl sulfides.



Scheme 4. Dimerization of diisopropyl diazomethylphosphonate.

observed similar results with reactions catalyzed by the ruthenium catalyst. The product expected from the [2,3]-sigmatropic rearrangement of an intermediate ylide was actually observed with allyl iodide (Table 1). In contrast, reaction of ethyl diazoacetate with allyl chloride or allyl bromide yielded only diethyl maleate and fumarate. The relative proportions of these by-products are variable, but as usually observed, the product of dimerization (maleate) is the main product. This result was not unexpected since the ruthenium catalyst is known to be ineffective for cyclopropanation of electron deficient olefins. It should be underlined that iodides and sulfides are very similar in their ability to intercept carbenoid intermediates [18].

2.4. Reaction of diisopropyl diazomethyl phosphonate with different allyl sulfides (**10**, **11**, **12**)

Since α-phosphoryl sulfides have recently found large application in organic synthesis [19,22,23], we also investigated the reaction of diisopropyl diazomethyl phosphonate with alkyl allyl sulfides, allyl amines and allyl thiols. The results are summarized in Table 2. All the data show that the major reaction with alkyl allyl sulfides is the [2,3]-sigmatropic Wittig rearrangement of the intermediate sulfonium ylide to give the formal C–S insertion as the final compound (compounds **10** and **11**). In contrast, only the S–H insertion is observed with allyl thiol to give the (allylthio)methylphosphonate **12** (Scheme 3).

2.5. Reaction of diisopropyl diazomethyl phosphonate with different allyl amines (**13**, **14**)

Since N–H insertion reactions of carbenoids from diazophosphonates are still rare [24], we next investigated the reaction of the diazophosphonate with a secondary allyl amine as a route to aminophosphonate. Addition of diisopropyl diazomethyl phosphonate to *N*-methyl allyl amine, in the presence of a catalytic amount of TPPRuCO, gave the corresponding phosphonic ester **14** in reasonable yield, but in this case the coupling product was more abondant (Table 2). On the other hand, reaction with *N*,*N*-dimethylallylamine did not lead to the ylide formation (in contrast with the result observed with EDA) but only the carbene dimer tetraisopropyl (*E*)-ethene-1,2-diyl-bis-phosphonate was isolated (Scheme 4) [19].

3. Conclusion

In summary, we have demonstrated that simple ruthenium porphyrins are highly effective catalysts for carbenoid reactions with alkyl allyl sulfides and alkyl allyl amines providing *the formal C–S or C–N* insertion rather than the more classical cyclopropanation. To fully characterize the catalytic properties of the porphyrin compound, we have also shown that in the competition process between ylide generation and the insertion of the diazo compound into heteroatom–hydrogen bond, only the Z–H insertion compound is observed. Future studies will focus on developing stereoselective versions of these [2,3]-sigmatropic rearrangements using chiral ruthenium porphyrins.

4. Experimental

4.1. General data

NMR spectra were recorded in $CDCl_3$ on a Brukner 200 DPX and chemical shifts are referenced to internal TMS. GC/MS analyses were performed on a CE GC8000 coupled with a Finnigan Mat AutomassII. Ethyl diazoacetate and allyl derivatives were purchased from Fluka and Lancaster.

4.2. Insertion reactions of ethyl diazoacetate with allylic amines, sulfides and halides

General procedure for insertion reactions of ethyl diazoacetate: in a typical experiment, the allyl compound (2.4 mmol) and the (TPP)Ru(CO) (1/100 to EDA, 0.005 mmol) were dissolved in 100 μl of dry methylene chloride in a Schlenk flask under argon. Ethyl diazoacetate (52 μl, 0.5 mmol) was added slowly (15 μl in 1 h) at room temperature (r.t.). After 1 day, during which time the reaction was monitored by GC-MS, the product was recovered by vacuum distillation. The product was identified by comparison to literature data [18]. For the amines, the (TPP)Ru(CO) catalyst complex was first dissolved in a minimum of solvent, then amine and EDA were added together dropwise at r.t.

4.3. Insertion reactions of diisopropyl diazomethyl phosphonate with allylic amines and sulfides

General procedures for insertion reactions of diisopropyl diazomethyl phosphonate: in a typical experiment, the allyl compound (2.4 mmol) and the (TPP)Ru(CO) (1/100 to the carbene, 0.005 mmol) were dissolved in 100 μl of dry methylene chloride in a Schlenk flask under argon. Diisopropyl diazomethylphosphonate (100 μl, 0.5 mmol) was added slowly (15 μl in 1 h) at r.t. After 1 day, during which time the reaction was monitored by GC–MS, the product was recovered by vacuum distillation. The product was identified by comparison to literature data [19]. For the amines, the (TPP)Ru(CO) catalyst was dissolved in a minimum of solvent, amine and EDA were added together dropwise at r.t.

Acknowledgements

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