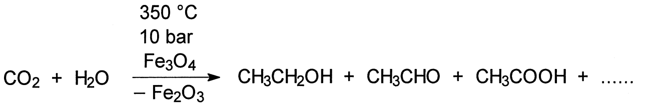

$$CO_2 + H_2O \xrightarrow[-\ Fe_2O_3]{350\ °C,\ 10\ bar,\ Fe_3O_4} CH_3CH_2OH + CH_3CHO + CH_3COOH + \ldots\ldots$$

Scheme 3. Carbon fixation of CO_2 in the presence of magnetite.

organic compounds can be produced from inorganic gases is significantly expanded. Given the fact that iron oxides are common in the crust, this could be a more important source for organic substances than was previously thought.

The work described above proves that a prebiotic organic chemistry with CO and CO_2 as C_1 building blocks could have occurred in hydrothermal or volcanic settings. Remarkably, even chemically inert N_2 can be converted under such conditions. This was shown by Brandes et al.[8] Likewise with the help of magnetite the reduction of N_2, NO_2^-, and NO_3^- to NH_3 is possible at elevated temperatures (300–800 °C) and pressures (0.1–0.4 GPa). In the presence of pyrite instead of magnetite the reduction of NO_2^- and NO_3^- is even faster. This shows that certain areas of the crust as well as hydrothermal vents represent a possible source for NH_3, a molecule with relevance for the production of amino acids as described above. Given that the ammonia produced this way finally makes its way into the atmosphere, a connection between the chemistry at hot minerals and the chemistry of a primordial soup begins to emerge.[9]

Exogenous sources for organic molecules have also been discussed extensively.[3, 10] Nevertheless, compounds with extraterrestial origin have to have been produced sometime somewhere. Possibly, the underlying chemical reactions are the same as on earth. In this case, the model reactions described above are also important for a deeper understanding.

The prebiotic synthesis of organic molecules of low complexity was an important first step for the origin of life. In view of the results presented the origin of these compounds appears to be less mysterious. But crucial further steps have not (or insufficiently) been simulated in the laboratory so far. How were long information-carrying biopolymers produced although the hydrolysis of such compounds is fast on the geological time scale? Did minerals[11] or metal ions[12] act as a catalyst? How and at which stage did the break of symmetry occur, which is manifested in the homochirality of present day biomolecules?[10, 13] And what were the first molecules which were able to self-replicate[14] and which were subsequently subjected to molecular evolution? There is plenty of room for new hypotheses and especially for new experiments.

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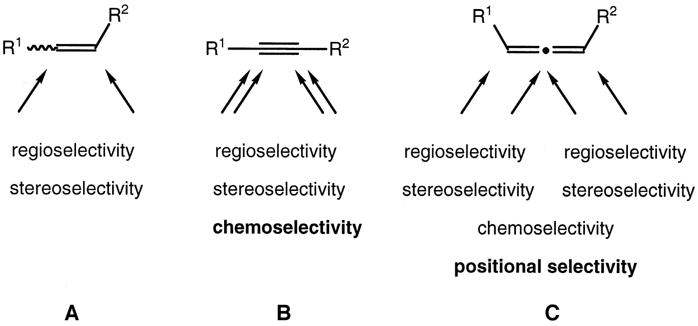
New and Selective Transition Metal Catalyzed Reactions of Allenes

A. Stephen K. Hashmi*

Among the most popular organic substrates for transition metal catalyzed reactions are alkenes **A** and alkynes **B** (Scheme 1). Allenes **C** have received much less attention. This is easily explained by increasing selectivity problems when we proceed from **A** to **C**. While in **A** we face the question of regioselectivity (Markovnikov versus anti-Markovnikov ori-



Scheme 1. Selectivity problems in different types of unsaturated substrates **A**–**C**.

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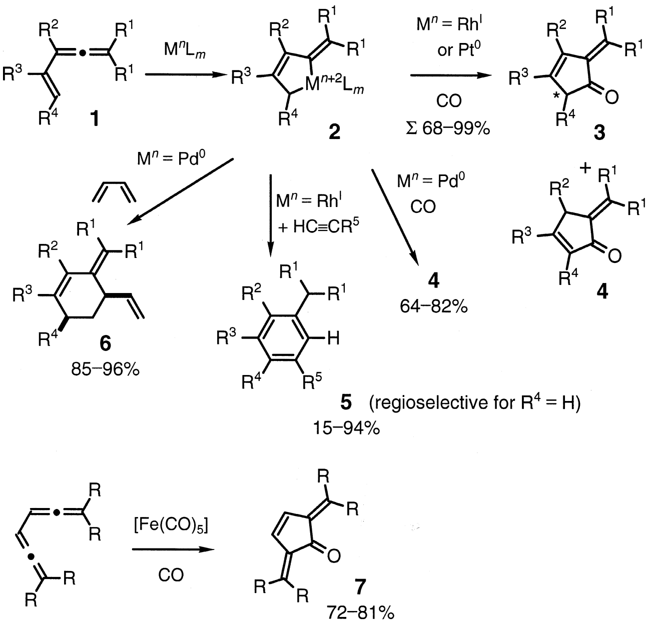
entation leading to constitutional isomers) and stereoselectivity of an addition reaction (*cis*- or *trans*-addition at possibly enantiotopic or diastereotopic faces of the double bond, leading to stereoisomers), in **B** we have to cope with the problem of chemoselectivity (single or double addition leading to different products) and for each addition the regio- and stereoselectivity problems apply as discussed for **A**. In **C** the situation is even more complicated: as with the alkynes chemo-, regio-, and stereoselectivity are significant, but furthermore we face the question of positional selectivity (which of the two orthogonal double bonds will react in the case of a single addition, thus again leading to constitutional isomers).

In early investigations of the reactions of allenes with transition metals the conversions proceeded quite unselectively, due to the *enhanced reactivity* of the allenes.[1] This observation led to the neglect of allenes as substrates in such reactions for a long time. In the past decade allenes have reemerged as interesting compounds for scientists working in the field of transition metal catalysis. Three major principles were used to overcome the selectivity problem: 1) In intermolecular reactions, the positional selectivity was often controlled by steric hindrance, that is, by substituents on only one of the double bonds. 2) Intramolecularization of the reactions, usually by placing the groups at such a distance that five- or six-membered rings are formed, automatically solved the positional selectivity problem. 3) Allenes bearing functional groups on the carbon atom next to the allene unit allowed the control of the selectivity by both geometrical restrictions and electronic differentiation of the two cumulated double bonds of the allene, not only in intramolecular but also in intermolecular reactions.

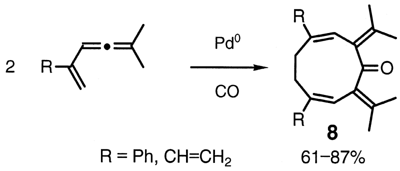
While principle 1 has allowed some very interesting transformations and numerous mechanistic details could be investigated,[2] the substituents used to provide steric hindrance also limited the synthetic potential. Principle 2 seems to have a higher potential for organic synthesis.[3] Principle 3, in particular, seems to provide some interesting and truly new transformations, which shall be summarized here. The following section is organized in terms of the different types of substrates that all belong to the type of principle 3. If not otherwise stated, the reactions proceed with 0.5–5 mol% of catalyst.

a) Vinyl Allenes

As mentioned in the introduction,[1c] no selectivity was observed in early dimerization experiments of **1**. But when other partners were offered, the corresponding cross-dimerizations were quite selective. Probably methylene metallacyclopentenes **2**,[4] which could be isolated, are intermediates that then react with the other partners (Scheme 2). Generally, the related 1,3-dienes are less reactive than **1** with its reactive allenic double bond and do not react in a similar manner.[4a] Rh-catalyzed [4+1] cycloadditions with CO as a second reaction partner led to alkylidene cyclopentenones **3** and **4**,[4, 5] while in Pd-catalyzed reactions where **1** was generated in situ and a base was present, only **4**[6] was formed. When Pt^0 was used instead of Rh^I in the carbonylation reaction, both in the presence of the (*R*,*R*)-DuPHOS ligand, opposite enantiomers of **3** were obtained.[5b] This observation still needs a precise explanation. [Fe(CO)$_5$]-mediated reactions of diallenes form dialkylidene cyclopentenones **7** (Scheme 2, here 10 mol% of catalyst are needed).[7] Other partners like alkynes in Rh- or 1,3-dienes in Pd-catalyzed reactions led to arenes **5**[8] or vinyl alkylidene cyclohexenes **6**.[9] Since these [4+2] cycloadditions take place between two electronically quite similar partners, a direct Diels–Alder reaction is not feasible. With a certain substitution pattern even [4+4+1] cycloadditions that deliver nine-membered rings **8**[10] could be achieved (Scheme 3). With Rh^I the same substrate delivers **3**.



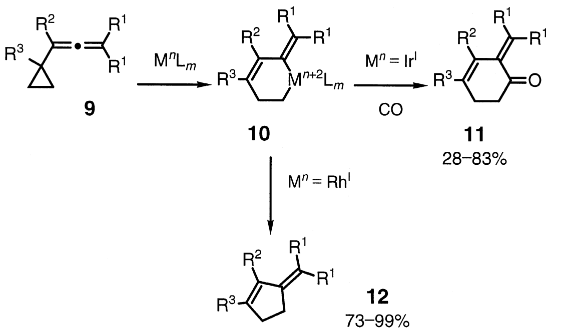
Scheme 2. Reactions of vinyl allenes **1**.



Scheme 3. Formation of nine-membered rings from vinyl allenes and CO.

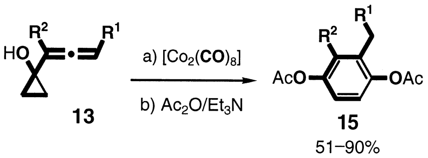
b) Cyclopropyl Allenes

Substrates **9** can be regarded as homoolefinic derivatives of **1** (Scheme 4). Here also the analogous vinyl cyclopropanes do not react similarly to **9**; the allenic unit makes **9** more reactive.[11] In Ir^I-catalzed reactions with CO the six-membered analogues of **3**, the cyclohexenones **11**,[11] were formed in a [5+1] cycloaddition (Scheme 4). On the other hand, Rh^I in the absence of CO leads to **12**[12] formed by a vinyl cylopropane/cyclopentene rearrangement. Such a rearrangement without a catalyst would require temperatures between 300 and 400 °C! Again one suspects metallacycles **10** as intermediates that either insert CO or undergo a reductive elimination immediately. With [Co$_2$CO$_8$] 1-hydroxycycloprop-



Scheme 4. Reactions of cyclopropyl allenes **9**.

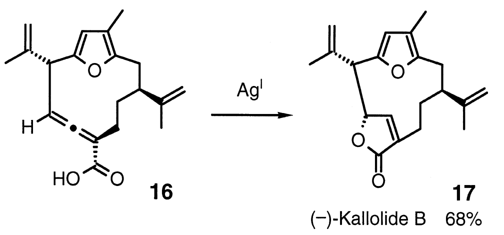
yl allenes **13** can be transformed into hydroquinones **14** and the corresponding diacetates **15**, respectively, under mild conditions (Scheme 5).[13] This methodology can be used in the synthesis of vitamin E and K analogues .



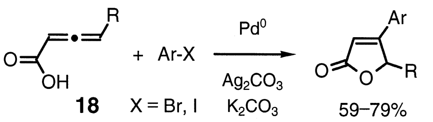
Scheme 5. Formation of dihydroquinones from cyclopropyl allenes **13**.

c) Allenes with Neighboring OH or NH Groups

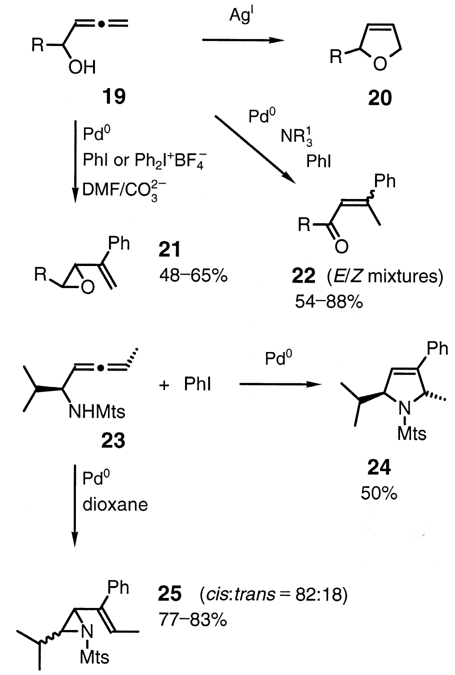
The addition of hydroxy groups to the distal double bond of the allene, mediated by Hg^{II} or Ag^{I} and leading to dihydrofurans, has been known for some time.[14] Marshall very successfully applied this principle to the synthesis of natural products and extended it to allenyl carboxylic acids like **16**,[15] which can lead to lactones like **17** (Scheme 6). With substrates **18** additional C–C bonds can be formed in Pd-catalyzed reactions with aryl halides as reaction partners (Scheme 7).[16] In the case of Pd-catalyzed reactions of aryl halides with allenyl carbinols **19**, enones **22**[17] were obtained (Scheme 8). Interestingly, in DMF as solvent and with CO_3^{2-}, for **19** a cyclization leading to the corresponding vinyl epoxides **21**[18] could be achieved! Simple treatment of **19** with Ag^{I} delivers **20**. The silver(I) catalysts show significant lower reactivity, thus usually 20 mol% or even more are applied. Similar developmentswere possible for the amines **23**, which either formed dihydropyrroles **24** or vinyl aziridines **25** (Scheme 8).[19] Here also the reaction heavily depends on the solvent, but no explanation has been provided so far. On the other hand in the presence of a Pd catalyst and CO, tertiary amines **26**, which cannot form another C–N bond, gave α-vinylacrylamides **27** (Scheme 9).[20]



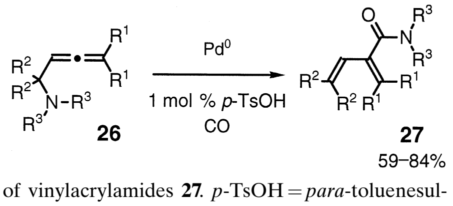
Scheme 6. Silver-catalyzed lactonization in Marshall's synthesis of (−)-kallolide B (**17**).



Scheme 7. Combination of C–C bond formation and lactonization.



Scheme 8. Reactions of allenyl carbinols **19** and related amines **23**. Mts = 2,4,6-trimethylbenzenesulfonyl.

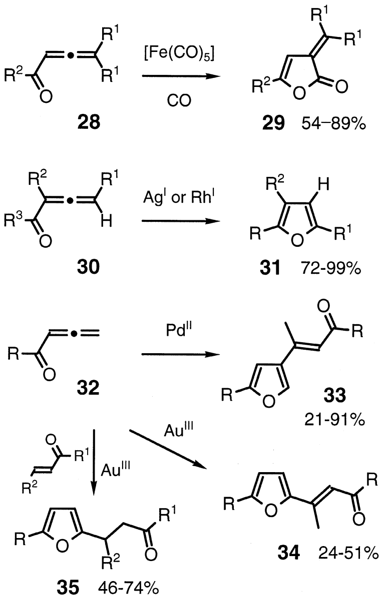


Scheme 9. Formation of vinylacrylamides **27**. *p*-TsOH = *para*-toluenesulfonate.

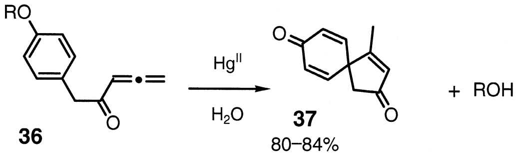
d) Allenyl Ketones

Here also a diversity of reactions was developed. With γ,γ-disubstituted derivatives **28** and $[Fe(CO)_5]$ (again 10 mol%), the lactones **29** were formed (Scheme 10).[21] Rh^{I} or Ag^{I} cause the cycloisomerization of **30** to the corresponding furan **31**.[22] Even greater is the diversity of substrates **32**. Pd^{II} leads to the formation of the dimer **33**,[23] Au^{III} to a constitutional isomer of **33**, the dimer **34**. When the latter reaction was performed in the presence of Michael acceptors, the mixed dimers **35** were formed.[24] Finally, in the case of alkoxy-substituted allenyl benzyl ketones **36**, the spirocycles **37** are obtained (Scheme 11).[25]

Today many selective and synthetically interesting transformations of allenes are known but sometimes the unique chemoselectivity still lacks explanation. A deeper mechanistic understanding of these selectivities might be the key for the future development of even more exciting reactions.



Scheme 10. Transition metal catalyzed reactions of allenyl ketones **28**, **30**, and **32**.



Scheme 11. Hg^{II}-catalyzed formation of spiro[4.5]decanes **37** from *p*-alkoxy allenyl ketones **36**.

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