

Synthesis of Allenes by [2,3]-Sigmatropic Rearrangement of Prop-2-yn-1-yl Oxonium Ylides formed in Rhodium(II) Carboxylate catalysed Reactions of Diazo Compounds

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High oxophilicity of metal carbenes formed in rhodium(II) perfluorobutyrate catalysed decomposition of diazo carbonyl compounds allows selective ylide generation from methyl prop-2-yn-1-yl ethers with resulting allene production through the [2,3]-sigmatropic rearrangement.

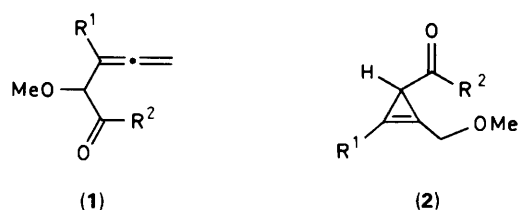
Although prop-2-yn-1-yl oxonium ylides provide a potentially useful pathway to highly-substituted and synthetically versatile allenenes through the symmetry-allowed [2,3]-sigmatropic rearrangement, their generation has received scant attention. Unlike the corresponding ammonium ylides,¹ they are not

amenable to formation by base promoted methodologies, and carbene reactions with alkyl prop-2-yn-1-yl ethers result in a complex mixture of products.^{2,3} Even in rhodium(II) acetate catalysed reactions of diazo esters with methyl prop-2-ynyl ethers,^{4–6} cyclopropene formation, rather than ylide genera-

Table 1. Rhodium(II) carboxylate catalysed reactions of diazo compounds with methyl prop-2-yn-1-yl ethers.^a

| | R ¹ | R ² | Catalyst | Yield ^b (1) + (2)/% | (1) : (2) ^c |
|-----|--------------------|----------------|------------------------------------|-----------------------------------|------------------------|
| (a) | H | Ph | Rh ₂ (pfb) ₄ | 80 | 82 : 18 |
| (a) | H | Ph | Rh ₂ (OAc) ₄ | 32 | 5 : 95 |
| (b) | H | OEt | Rh ₂ (pfb) ₄ | 67 | 61 : 39 |
| (b) | H | OEt | Rh ₂ (OAc) ₄ | 65 | 1 : 99 |
| (c) | Bu | Ph | Rh ₂ (pfb) ₄ | 67 | 90 : 10 |
| (d) | Bu | OEt | Rh ₂ (pfb) ₄ | 83 | 80 : 20 |
| (e) | Me ₃ Si | OEt | Rh ₂ (pfb) ₄ | 80 ^d | 93 : 7 |

^a The diazo compound (2 mmol) in dichloromethane (4 ml) was added over 4 h through a syringe pump to the prop-2-ynyl ether (4 mmol) and rhodium(II) carboxylate (0.02 mmol) in dichloromethane (16 ml).
^b Weight yield of isolated products. ^c Determined by NMR spectroscopy. ^d Analytically pure allene was isolated by fractional distillation in 55% yield.

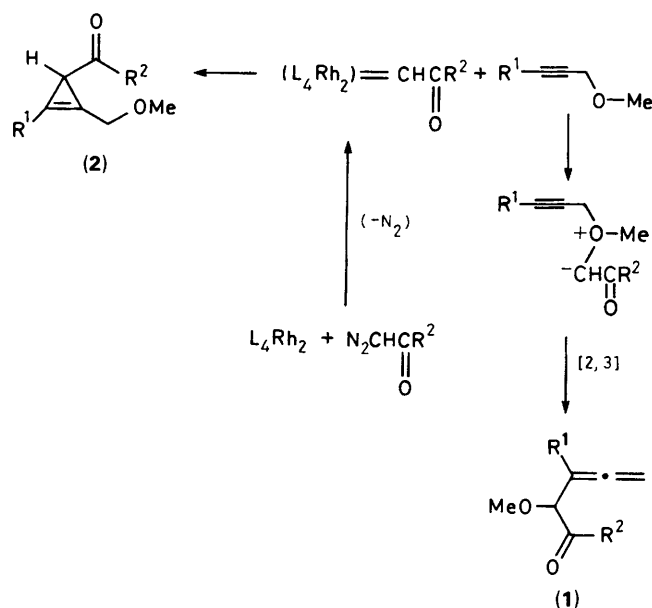
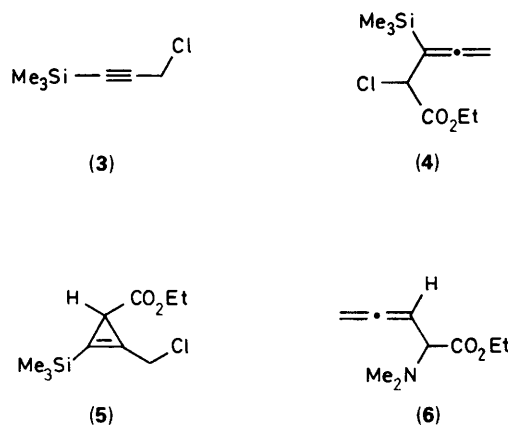


- a; R¹ = H, R² = Ph
 b; R¹ = H, R² = OEt
 c; R¹ = Bu, R² = Ph
 d; R¹ = Bu, R² = OEt
 e; R¹ = Me₃Si, R² = OEt

tion, is by far the dominant process. We now report a new catalytic methodology that optimizes ylide generation and provides convenient access to the functionalized allenes.

Methyl prop-2-ynyl ether and α -diazoacetophenone reacted in the presence of rhodium(II) perfluorobutyrate [Rh₂(pfb)₄]⁷ to form allene (**1a**) and cyclopropene (**2a**) in an 82 : 18 product ratio. In contrast, with [Rh₂(OAc)₄] cyclopropene (**2a**) was produced to the virtual exclusion of (**1a**). Reactions were performed at room temperature in dichloromethane using only a 2-fold molar excess of methyl prop-2-ynyl ether and 1.0 mol% of the rhodium(II) carboxylate catalyst relative to the diazo compound. Similar results were obtained with ethyl diazoacetate, from which a 61 : 39 ratio of (**1b**) : (**2b**) resulted from [Rh₂(pfb)₄] catalysis whereas only (**2b**) was formed in the [Rh₂(OAc)₄] catalysed reaction. Replacement of the acetylenic hydrogen of methyl prop-2-ynyl ether by an alkyl or silyl group resulted in the formation of allene products to the near exclusion of cyclopropenes (Table 1).

The formation of oxonium ylides by intermolecular reactions of catalytically generated metal carbenoid intermediates with allylic and prop-2-ynylic ethers has been elusive.^{4,8} Recently, however, intramolecular oxonium ylide generation resulting in allene-substituted furan-2-ones has been reported to be a facile process in [Rh₂(OAc)₄] catalysed decompositions of appropriately substituted diazoketones.^{9,10} In these cases, cyclopropene formation is not competitive with intramolecular ylide generation. For intermolecular reactions, where cyclopropene formation is directly competitive with ylide generation (Scheme 1), [Rh₂(OAc)₄] catalysis shows a high selectivity for carbenoid addition, although with 3-alkyl or 3-phenyl derivatives of methyl prop-2-en-1-yl ethers, ylide

**Scheme 1.** Competition between ylide formation and cyclopropanation in rhodium(II) carboxylate catalysed reactions of diazo compounds and methyl prop-2-ynyl ethers.

generation occurs in preference to cyclopropanation.¹¹ In contrast, [Rh₂(pfb)₄] catalysis shows a high preference for oxonium ylide generation which can be attributed to the greater oxophilicity of its derivative metal carbene intermediate. In terms of hard and soft acids and bases, the metal carbene derived from [Rh₂(pfb)₄] is a harder acid than that formed from [Rh₂(OAc)₄].

The success achieved by [Rh₂(pfb)₄] catalysis in the generation of prop-2-ynylic oxonium ylides and their [2,3]-sigmatropic rearrangement to allenes can be extended to chlorides which, like ethers, were not previously found to be susceptible to ylide generation.⁸ Thus, treatment of (**3**) with ethyl diazoacetate under conditions identical to those in Table 1 produced an 89 : 11 mixture of (**4**) and (**5**) in 70% yield. Not unexpectedly,¹ dimethyl prop-2-ynyl amine underwent exclusive [Rh₂(OAc)₄] catalysed ylide generation and rearrangement with ethyl diazoacetate to form (**6**) in 85% yield.

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