

Homogeneous Metathesis of Functionalized Alkynes

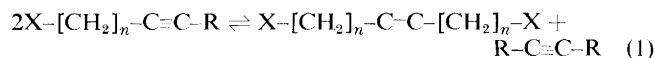
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Various functionalized disubstituted acetylenes, including esters, are prepared metathetically with high selectivity on molybdenum based homogeneous catalytic systems; this procedure is a useful tool for the synthesis of acetylenes, which can provide *cis*- or *trans*-olefins by further selective hydrogenation.

The metathesis of functionalized olefins has been the subject of thorough investigations¹ owing to their potential synthetic applications.

However, this reaction suffers from both a lack of activity and of selectivity where a *Z* or *E* enantiomer is required, for example in the synthesis of pheromones.^{2,3} Recent results from the metathesis of alkynes have shown that this catalytic reaction carried out with dialkylalkynes $2 \text{RC}\equiv\text{CR}' \rightleftharpoons \text{RC}\equiv\text{CR} + \text{R}'\text{C}\equiv\text{CR}'$ on tungsten carbyne complexes⁴ or on $\text{MoO}_2(\text{acac})_2\text{-AlEt}_3\text{-PhOH}$ ($\text{Hacac} = \text{acetylacetonate}$) combinations⁵ is much more efficient than the same reaction with olefins over conventional catalysts. Such a high reactivity combined with the unusual selectivity observed for alkynes[†] suggests that a corresponding result could be obtained for functionalized alkynes and hence, in contrast with olefins, that they would undergo efficiently the reaction shown in equation (1).



In this study, we report the results obtained for acetylenic compounds bearing functional groups such as double bonds, halogens, and esters, over molybdenum based catalysts.

The homogeneous reactions were carried out in refluxing toluene in a glass reactor under nitrogen with stirring. The $\text{MoO}_2(\text{acac})_2\text{-AlEt}_3$ catalyst was prepared as described earlier.⁵ After 15 min at room temperature, the catalytic solution was introduced into the reactor, containing the acetylenic substrate and the phenolic cocatalyst. The products were formed immediately, according to reaction (1). The conversion and selectivity were followed by gas chromatography using the internal standard method. After the reaction was complete (reaction time 1–24 h, based on the substrate), the catalytic solution was treated with an NaOH solution in order to eliminate phenol. The products were either carefully distilled on a Nester and Faust spinning band column or separated by preparative gas chromatography (VARIAN Aerograph A 700). The pure products were identified by n.m.r. spec-

[†] Selectivities were found to be up to 95% for all the efficient homogeneous catalytic systems used (tungsten carbyne complex or molybdenum reduced combinations).

Table 1. Metathesis of functionalized alkynes catalysed by molybdenum in toluene at 110 °C; [Mo] = 10⁻³ M; Al: Mo = 6:1.

Substrate (A)	Products (B + C)	[C≡C]: [Mo]	[PhOH]/M	TR/h ⁻¹ ^a
Bu-C≡C-Pr	Bu-C≡C-Bu + Pr-C≡C-Pr	2000	0.1	144 000
Ph-C≡C-C ₆ H ₄ Me	Ph-C≡C-Ph + C ₆ H ₄ Me-C≡C-C ₆ H ₄ Me	100	1.0	383
R-C≡C-Bu R = CH ₂ =CH-CH ₂	R-C≡C-R Bu-C≡C-Bu	1000	0.1	1680
Cl[CH ₂] ₃ -C≡C-Et	Cl[CH ₂] ₃ -C≡C-[CH ₂] ₃ Cl + Et-C≡C-Et	1000	0.1	60 900
R-C≡C-Bu ^b R = MeCO ₂ [CH ₂] ₂	R-C≡C-R + Bu-C≡C-Bu	100	1.0	13

^a TR = initial turnover rate. All reactions have selectivities up to 95% and attain a statistical equilibrium 2A ⇌ B + C 50:25:25. ^b Mo(CO)₆ as catalytic precursor.

troscopy. All the products obtained had selectivities up to 95%, which indicates that little or no triple bond isomerization had taken place. Examples of the reactions of various alkynes are given in Table 1.

It appears that the reaction rate depends strongly upon the nature of the substituents. In particular, as found previously,⁶ the metathesis of aryl-disubstituted alkynes is very slow compared with that of dialkylalkynes and chlorine-containing acetylenes. It is also noteworthy that the metathesis of non-1-en-4-yne occurs selectively at the triple bond, in contrast with the use of heterogeneous MoO₃-SiO₂ catalysts, where both double bond and triple bond metatheses occur simultaneously on the same substrate.⁷ The MoO₃(acac)₂-AlEt₃ combination did not give good results with esters under our experimental conditions and the original Mo(CO)₆-PhOH catalyst⁸ has been used to convert selectively this type of substrate, but with a lower activity, as expected. However, this reaction is complete within 12 h, giving rise to equimolar amounts of the symmetrical products.

Apart from the metathesis reaction of esters on the Mo(CO)₆-PhOH catalyst, which has an activity similar to that observed with ethylenic esters on WCl₆-SnMe₄ catalysts,¹ the main advantages of these systems are that the observed selectivities and activities are very high, and that no isomerization of the substrate and products occurs, even at equilibrium. This general behaviour, as well as the availability of the catalytic

components, offers new routes to difunctional compounds of technological interest. In particular, such reactions could lead to functionalized alkynes by cross metathesis or to analogous olefinic compounds by further selective hydrogenation of the triple bond, thereby achieving the synthesis of specifically Z or E olefins,^{9,10} which can be used for pheromone synthesis.

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