

251. Ru-Catalyzed Oxidation of Acetylenes to α -Diketones with Iodosylbenzene

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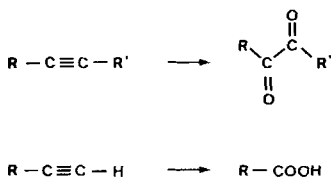
(25.VIII.81)

Summary

Disubstituted acetylenes are oxidized with PhIO in presence of Ru-catalysts to afford α -diketones in 65–85% yield. Under the same conditions terminal acetylenes are cleaved to carboxylic acids.

Iodosylbenzene, PhIO, in conjugation with Ru-catalysts is an efficient oxidant of alcohols to aldehydes, ketones or carboxylic acids [1]. We now report that this combination also oxidizes disubstituted acetylenes to α -diketones and terminal acetylenes to carboxylic acids (*Scheme 1*). The experimental procedure is simple.

Scheme 1



In a typical example the catalyst ($\text{RuCl}_2(\text{PPh}_3)_3$, 96 mg) in 20 ml of CH_2Cl_2 was added to PhIO (6.6 g, 30 mmol) suspended in 40 ml of CH_2Cl_2 . To this was added at once diphenylacetylene (1.78 g, 10 mmol) in 20 ml of CH_2Cl_2 . An exothermic reaction started immediately. After 15 min with magnetic stirring the solution was transparent. The solvent was evaporated and the product separated from PhI by chromatography. Yield 1.81 g (86%) of benzil.

Table 1 summarizes the results with some representative substrates. The best yield was obtained with diphenylacetylene. The resulting diketone is stable towards PhIO/ $\text{RuCl}_2(\text{PPh}_3)_3$ (no reaction in 2 h). Acetylenes with aliphatic substituents showed a marked tendency for cleavage to carboxylic acids. This could be somewhat improved by lowering the excess of PhIO. Oxidation of terminal acetylenes proceeded rapidly to carboxylic acids. No α -ketoaldehydes were isolated even if only 2 mol-equiv. of PhIO were used.

Among the various catalysts tried, only Ru-complexes were really effective although slow oxidation of diphenylacetylene to benzil was also observed with

Table 1. *Oxidation of alkynes with iodosylbenzene/RuCl₂(PPh₃)₃^a*

Substrate	of Mol.-equiv. PhIO	Time	Isolated yield ^{b)}
Diphenylacetylene	3	15 min	86% diketone
1-Phenyl-1-heptyne	2.6	15 min	72% diketone
1-Phenyl-1-propyne	2.6	15 min	65% diketone
2-Pentyne	2.1	15 min	70% ^{c)} diketone
Phenylacetylene	3.2	5 min	69% acid
1-Octyne	3.2	5 min	81% ^{d)} acid
1-Pentyne	3.2	5 min	71% ^{d)} acid

^{a)} 10 mmol scale, conditions as described above. ^{b)} By chromatography on silica gel. ^{c)} By NMR.: isolated yield 42%, owing to evaporation during work-up. ^{d)} By extraction with 2N NaOH.

Table 2. *Oxidation of diphenylacetylene with various catalysts^{a)}*

Catalyst	Yield of benzil ^{b)}
RuCl ₂ (PPh ₃) ₃	98%
Ru ₃ (CO) ₁₂	79%
RuCl ₂ (CO) ₂ (PPh ₃) ₂	96%
RuCl ₃ aq. ^{c)}	96%
Ruthenocene ^{d)}	84%
None ^{e)}	0%

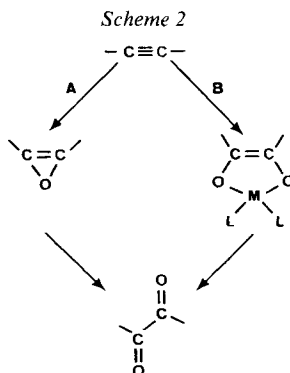
^{a)} Conditions: 1 mmol of alkyne in 8 ml of solvent, 3 mol-equiv. of PhIO, 1% catalyst, 15 min, RT.

^{b)} By GC. ^{c)} In acetone. ^{d)} [2]. ^{e)} After 3 h.

Co(acac)₂, Cr(acac)₃ and Zr(acac)₄. There is little variation in yield upon changing the ligands of the complexed ion (Table 2). This could indicate that in all cases the same Ru-species is involved, the role of PhIO being to regenerate this active species. An analogous oxidation of acetylenes to diketones uses sodium hypochlorite or sodium metaperiodate in a two-phase system to reoxidize the consumed ruthenium [3]. Yields and C, C-cleavage reactions in the two-phase system are comparable to the PhIO-catalyzed procedure. However the latter is experimentally simpler and conditions are milder.

The combination *N*-methylmorpholine-*N*-oxide/RuCl₂(PPh₃)₃, efficient for oxidation of alcohols [4], does not attack acetylenes. Similarly, *t*-butylhydroperoxide/Mo(CO)₆ or VO(acac) gave no reaction, while iodylbenzene, PhIO₂ [5] or (diacetoxyiodo)benzene [6] with Ru-catalysts afforded diketones but at much lower rate than PhIO.

The oxidation of acetylenes to diketones by PhIO consists formally in two O-transfer reactions from oxidant to substrate. Such reactions have been reported for uncatalyzed systems involving PhIO and ketenes, α -ketocarboxylic acids and ketones [7] as well as sulfides [8]. Oxygen transfer from PhIO to organic substrates is catalyzed by metalloporphyrins containing Fe [9], Cr [10] or Mn [11]. These transformations are believed to proceed *via* intermediate metal/oxo complexes or porphyrin/PhIO adducts which are capable of transferring an O-atom to olefins. With acetylenic substrates this would lead to intermediate formation of an oxirene



[12] (path A), *Scheme 2*. The analogy with the Ru-catalyzed reactions has yet to be established. However, the observation that chlorotetraphenylporphinato iron (III) [9] does not catalyze acetylene oxidation with PhIO does not support this view and a mechanism involving cyclic intermediates as proposed for acetylene oxidation with OsO₄ [13], KMnO₄ [14], RuO₄ [15] and thallic nitrate [16] (path B, *Scheme 2*) is as likely.

We are indebted to the *Swiss National Science Foundation* for financial support.

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