Formation of Dimeric Acetylenes: an Unexpected Reaction of Acetylenic Selenides

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1-Selenoalk-1-ynes react with *m*-chloroperoxybenzoic acid in tetrahydrofuran–water furnishing 1,4-disubstituted 1,3-diynes free of selenium in high yield.

Acetylenic selenides are compounds that have not been widely investigated.[1—6] Recently we have developed methods for the synthesis of this class of compounds and have demonstrated that they can be conveniently transformed into vinylic selenides[3,7] or into mono- and di-substituted acetylenes free of selenium.[4] In this communication, we report a new and unexpected reaction of this class of organoselenium compounds.

Previously we found that oxidation of 1-selenoalk-1-ynes with *m*-chloroperoxybenzoic acid (*m*-CPBA) in a mixture of tetrahydrofuran (THF)–water, followed by immediate treatment of the reaction mixture with 1 M sodium hydroxide, leads to alk-1-ynes free of selenium.[8] Surprisingly, when a mixture of the 1-selenoalk-1-yne and *m*-chloroperoxybenzoic acid is maintained at room temperature for a prolonged time (4.5—12 h) symmetrically 1,4-disubstituted buta-1,3-diynes are formed in high yield (equation 1).

$$\text{R–C}\equiv\text{C–SeR}^1 \xrightarrow[\text{THF, H}_2\text{O, room temp.}]{m\text{-CPBA (1.5 equiv.)}} \text{R–C}\equiv\text{C–C}\equiv\text{C–R} \qquad (1)$$

Acetylenic selenoxides are presumed to be intermediates in this reaction. When R^1 is an ethyl group, the reaction is slower than when it is a phenyl group. This is in accord with published data concerning selenoxide elimination.[9] No reaction was observed in the cases where R was a saturated alkyl group. However, the diyne was obtained in good yield when R was the cyclohex-1-enyl group. These results indicate that the reaction is sensitive to electronic factors.

The dimerization reaction was carried out by adding *m*-chloroperoxybenzoic acid to a solution of 1-selenoalk-1-yne in a mixture of THF–H_2O (10 : 1) at 0 °C and then stirring the reaction mixture at room temperature (Table 1). Treatment with 1 M sodium hydroxide and column chromatography of the residue provided the 1,4-disubstituted buta-1,3-diynes in the yields indicated in Table 1.

The results reported in this communication show that the oxidation of 1-selenoalk-1-ynes is a mild and efficient procedure for the dimerization of terminal acetylenes.[10]

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Table 1. Oxidation of 1-selenoalk-1-ynes[a] to 1,4-disubstituted buta-1,3-diynes.[b]

R	R^1	Reaction time/h	Yield[d]/%
Ph	Ph	6	86
p-MeC_6H_4	Ph	8	80
Ph	Et	12	60[c]
Cyclohex-1-enyl	Ph	12	79
Cyclohex-1-enyl	*m*-$CF_3C_6H_4$	12	81
n-C_4H_9	Ph	12	No reaction
n-C_4H_9	*m*-$CF_3C_6H_4$	12	No reaction

[a] For the preparation of the acetylenic selenides see ref. 8. [b] The spectral and combustion data are in accordance with the proposed structures. [c] Phenylacetylene was isolated as by-product. [d] Yield of the isolated products purified by column chromatography eluting with hexane.

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