

Formation of Dimeric Acetylenes: an Unexpected Reaction of Acetylenic Selenides

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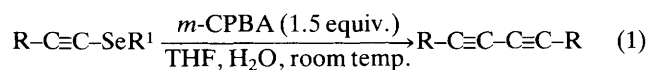
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1-Selenoalk-1-yne react with *m*-chloroperoxybenzoic acid in tetrahydrofuran–water furnishing 1,4-disubstituted 1,3-diynes free of selenium in high yield.

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-yne 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-yne 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).



Acetylenic selenoxides are presumed to be intermediates in

this reaction. When R¹ 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–H₂O (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-yne is a mild and efficient procedure for the dimerization of terminal acetylenes.¹⁰

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- 10 For previous syntheses of symmetrically 1,4-disubstituted 1,3-diynes see: R. Rossi, A. Carpita, and C. Bigelli, *Tetrahedron Lett.*, 1985, **26**, 523 and references therein.

Table 1. Oxidation of 1-selenoalk-1-yne^a to 1,4-disubstituted buta-1,3-diynes.^b

R	R ¹	Reaction time/h	Yield ^d /%
Ph	Ph	6	86
<i>p</i> -MeC ₆ H ₄	Ph	8	80
Ph	Et	12	60 ^c
Cyclohex-1-enyl	Ph	12	79
Cyclohex-1-enyl	<i>m</i> -CF ₃ C ₆ H ₄	12	81
<i>n</i> -C ₄ H ₉	Ph	12	No reaction
<i>n</i> -C ₄ H ₉	<i>m</i> -CF ₃ C ₆ H 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.