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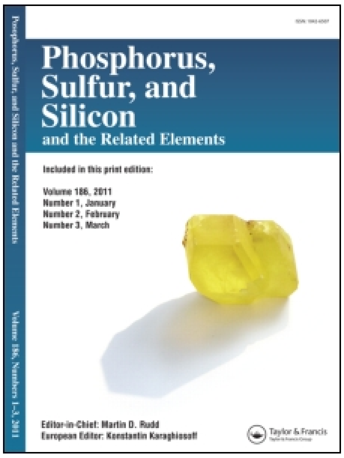

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REACTIONS OF SELENOBENZOPHENONES WITH OLEFINS

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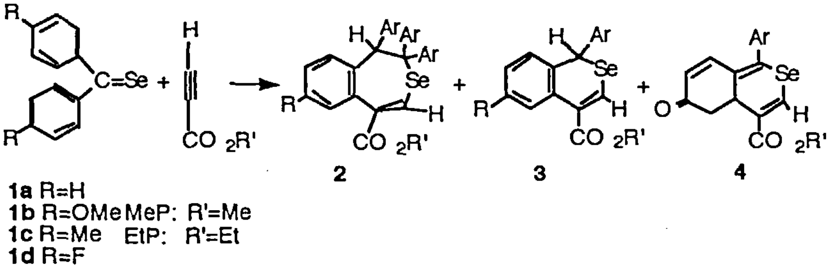
Reactions of selenobenzophenones with methyl propiolate afforded two types of cycloadducts regioselectively. The reaction with tetracyanoethylene gave selenophene derivatives. Mechanisms of these reactions were discussed.

Keywords: selenobenzophenone; acetylene; tetracyanoethylene

The chemistry of the carbon selenium double bond is of current interest.[1] We have reported that selenobenzophenone (**1a**) reacted with dienes to afford several types of cycloadducts. For example, the reaction of **1a** with cyclopentadiene gave [4+2] type cycloadducts, which further reacted with elemental selenium to give cyclic diselenides.[2] However, there are relatively few reports on the reaction of **1** with olefins. The reaction of **1a** with dimethyl acetylenedicarboxylate afforded the unusual 7-membered cyclic adducts.[2,3] In view of this anomalous reactivity, we have reacted **1** with other acetylenic compounds.

The reaction of selenobenzophenone (**1a**) with methyl propiolate (MeP) gave benzoselenepin (**2**) regiospecifically. On the other hand, reaction of 4,4'-dimethoxyselenobenzophenone (**1b**) with MeP gave methyl 4*H*-3-selena-4-*p*-methoxyphenyl-7-methoxynaphthalenecarboxylate (**3**) and methyl 3,7,8,8a-tetrahydro-3-selena-4-*p*-methoxyphenyl-7-oxonaphthalenecarboxylate (**4**) (Scheme 1, Table 1).

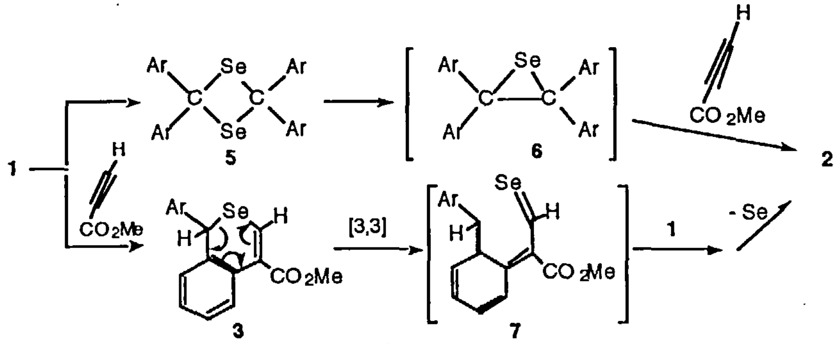


Scheme 1.

TABLE 1 Reaction of 1 with Methyl Propiolate.

1	Acetylene	Conditions		Products (Yield/%)		
		Temp./°C	Solvent	2	3	4
1a	MeP	reflux	Toluene	36	0	0
1b	MeP	reflux	Benzene	0	35	28
1c	MeP	reflux	Toluene	30	13	0

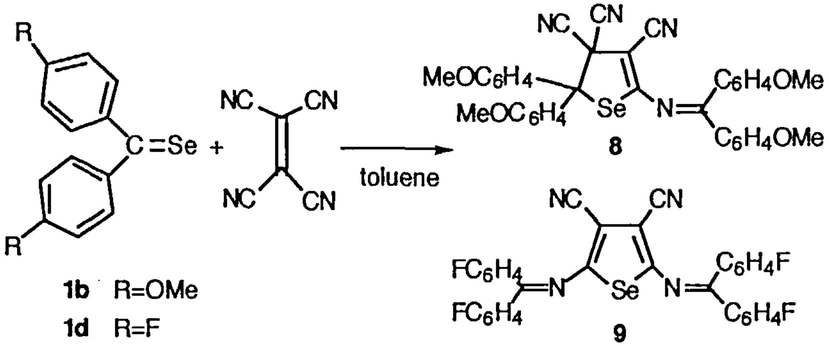
There are two plausible mechanisms to explain the formation of benzoselenepin **2**. First, selone **1** dimerized to afford diselenetane (**5**), Monodeselenation changed this compound into selenerane (**6**), which further reacted with acetylenes via a [4+2] manner to give **2**. The other route is a sequential reaction of selenobenzophenone; preferential formation of normal [4+2] type cycloadduct **3** rearranged to give the intermediate **7**, which further reacted with selone **1** (or diphenylcarbene) to give **2** (Scheme 2). At present, we do not have any evidence to substantiate the exact mechanism.



Scheme 2.

The benzoquinone derivative **4** might be formed as follows: initial [4+2] cyclization of selenobenzophenone afforded the corresponding **3**, which was demethylated by the attack of a trace of acid to give **3**. Actually, the reaction of **1b** with propiolic acid gave 3,7,8,8a-tetrahydro-3-selena-4-*p*-methoxyphenyl-7-oxonaphthalenecarboxylic acid (**4b**) in much better yield. Recently, we have reported the reaction of 4,4'-dimethoxythiobenzophenone with norbornadiene, the reaction product of which is a similar benzoquinone derivative.[4] Thus, demethylation is a general tendency in the case of methoxy substituted thio- and selenobenzophenones.

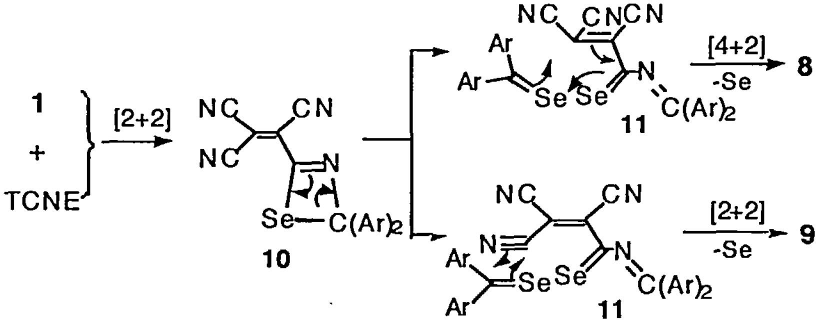
Quinodimethanes and cyanoethylenes are intriguing molecules and have attracted attention from synthetic and structural points of view. Tetracyanoethylene (TCNE) reacts with 2 mole equivalent of **1b** to give a novel type of cycloadduct (2,3-dihydroselenophene, **8**).[5] On the other hand, the reaction of TCNE with **1d** affords a selenophene derivative (**9**) (Scheme 3). These results are quite different from those obtained with thiobenzophenones.



Scheme 3.

Huisgen *et al.* suggested that the reaction of thiobenzophenone with TCNE proceeded through the initial attack of thiocarbonyl sulfur on nitrile *via* a [2 + 2] manner, followed by the attack of another thiobenzophenone on the same side of the nitrile to yield thioamide derivatives, and the final sulfur extrusion formed five-membered cyclic thiophene derivatives.[6]

A similar initial attack would occur in the reaction of selenobenzophenones with TCNE. However, a four-membered intermediate (**10**) is more hindered than that from thiobenzophenone, and is easily converted into ring-opened selenoamide (**11**). Another selenobenzophenone reacted with **11** *via* a [4 + 2] manner to afford the six-membered cyclic diselenide, which finally extruded selenium to give **8**. The more reactive **1d** would react with the nitrile group of **11** to give **9**.



Scheme 4.

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