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Hypervalent Iodine in Synthesis XXV: An Effective Synthesis of Acetylenic Selenides via Alkynylphenyliodonium Tosylates

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HYPERVALENT IODINE IN SYNTHESIS XXV: AN EFFECTIVE SYNTHESIS OF ACETYLENIC SELENIDES VIA ALKYNYLPHENYLIODONIUM TOSYLATES

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Abstract: Acetylenic selenides have been prepared by the reaction of sodium areneselenolates with alkynylphenyliodonium tosylates in DMF.

Acetylenic selenides are well-known useful intermediates in organic synthesis.[1-10] They are convenient precursors for the synthesis of stereodefined trisubstituted alkenes and several classes of vinylic selenides. Moreover, selenium free acetylenes are obtained in high yields by oxidation of acetylenic selenides with MCPBA and subsequent treatment with aqueous sodium hydroxide, but selenium free dimeric acetylenes are obtained when the base treatment is omitted.

According to the importance of acetylenic selenides in organic synthesis, much attention has been devoted to their preparation and there are available for their preparation including the reaction of terminal acetylenes with n-butyllithium followed by reaction with arylselenides bromides,[11] or with phenylselenenyl bromide in the presence of silver nitrite[12], or with phenyl selenenyl bromide in

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the presence of copper (I) iodide[13], reaction of alkynyl bromides with lithium selenolates or with diorganoyl diselenides in the assisting of copper(I) iodide[14,15]. Pyrolsis of stabilized selenophosphoranes[6] and reaction of terminal alkynes with iodobenzene diacetate and diphenyl diselenides in methylene chloride[16].

However, these methods are defient in some respects, such as low yields, expensive, toxic or not readily available reagent, unattractive reaction conditions. It is necessary to develop a new effective method for the synthesis of acetylenic selenides.

Our recent interest[17] in tricoordinate iodine species and their renaissance in organic synthesis, coupled with the ready availability and high reactivity[18] of alkynylphenyliodonium tosylates (1), prompted us to examine their use as direct alkynylating agents in the formation of acetylenic selenides (3) from sodium areneselenolates. Hence, in this paper we report an effective synthesis of acetylenic selenides via alkynylphenyliodonium tosylates, Analogous to S-alkynylation,[19,20] the sodium areneselenolates prepared by reduction of diaryl diselenides with sodium borohydride, with alkynylphenyliodonium tosylates readily occurred in a single step to afford acetylenic selenides, stirring the sodium areneselenolates (2) with alkynylphenyliodonium tosylates in dimethylformamide at 70—80°C gave, after work up, the desired products, acetylenic selenides (3) in good yields as given in Table 1.

The products were characterized by ^{1}H NMR, IR, MS spectra and m. p. as summarized in the Table 1.

The present method has the advantages of accessible starting materials, mild reaction conditions, convenient manipulation and moderate yield. Furthermore, the range of useful applications of alkynylphenyliodonium tosylates as alkynylating agents in organic chemistry has been extended.

Table 1 Acetylenic selenides (3) prepared

Product	Reaction Time(hr)	Yield (%)	m. p(°C)	^{1}H-NMR δ(ppm) (CCl_4/TMS)	IR, ν(cm^{-1})	MS(M^+)or elemental analysis [found(calcd.)]%
3a	2	65%	oil	7. 07-7. 50 (m, 10H)	3080, 2940, 2170, 1588, 1485, 1448, 1070, 1020, 735,690	258
3b	2	60%	50—51°C	7. 10-7. 33(m,9H) 2. 23(s,3H)	3040, 2942, 2170, 1450, 1068,1017,800,753,690	272
3c	1. 5	71%	44°C	7. 33-7. 46(m,9H)	3080, 2930, 2170, 1480, 1450, 1090, 1010, 810, 755,690	292
3d	2. 5	58%	oil	7. 00-7. 23(m,9H) 2. 30(s,3H)	3090, 2940, 2163, 1600, 1470,1385,1030,740,690	272
3e	4	55%	oil	7. 00-7. 50(m,5H) 1. 23(s,9H)	3081, 2990, 2179, 1335, 1089,730,690	C:60. 59(60. 76) H:5. 86(5. 95)
3f	4	56%	oil	7. 10-7. 45(m,5H) 1. 25(s,9H)	3080, 2990, 2175, 1338, 1089,1011,752,686	C:53. 00(53. 06) H:4. 91(4. 82)

$$RC{\equiv}CI^{+}Ph^{-}OTs + ArSeNa \xrightarrow[70-80\,^{\circ}C]{DMF} ArSeC{\equiv}CR$$

(1)	(2)	(3)	
R = Ph-	Ar = Ph-	Ar	R
t-Bu-	p-$CH_3C_6H_4$	a: Ph	Ph
	p-ClC_6H_4	b: p-$CH_3C_6H_4$	Ph
	o-$CH_3C_6H_4$	c: p-ClC_6H_4	Ph
		d: o-$CH_3C_6H_4$	Ph
		e: Ph	t-Bu
		f: p-ClC_6H_4	t-Bu

General procedure for preparation of acetylenic selenides (3): A mixture of the appropriate diaryl diselenide (1 mmol)[21] and $NaBH_4$ (2.2 mmol) in DMF (10 ml) was stirred under an N_2 atmosphere at 80—90 °C until the solution was clear, then the temperature was raised to 110 °C for five minutes. The mixture was allowed to cool to room temperature and an appropriate alkynylphenyliodonium tosylates (1) (2 mmol) was added. The mixture was heated at 70—80 °C with stirring for the time given in the Table. After being cooled, the mixture was diluted with water (15 ml) and the product was extracted with petroleum ether and dried with $MgSO_4$. After removal of the solvent, the residue was chromatographed on a column of silica gel using n-hexane as eluent to give the acetylenic selenide. All relevant data are summarized in the Table.

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