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Synthesis of chalcogenol esters from chalcogenoacetylenes

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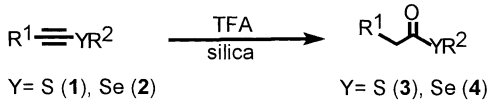
Abstract—Thiol and selenol esters were conveniently prepared in good yields by reacting chalcogenoacetylenes with trifluoroacetic acid in dichloromethane in the presence of silica.

1. Introduction

Thiol and selenol esters are important intermediates in organic synthesis. They have been used as precursors of acyl radicals,[1] as mild acyl transfer reagents,[2] as intermediates in the synthesis of ketones[3] and for asymmetric aldol reactions.[4] Recently, applications of this functional group have expanded into the synthesis of proteins by chemical ligation of benzyl thiol esters[5] as well as substrates to undergo facile and efficient radical decarbonylation in the synthesis of (+)-geissoschizine.[6]

In spite of the growing interest in new organic transformations of these compounds, preparative methods available for their synthesis are still limited, with few exceptions,[7] to those based on conventional methodology (i.e. formal substitution at the carbonyl carbon of carboxylic acids and their derivatives or addition to nitriles).[8] In this context, we have shown that chalcogenol esters can be prepared by the reaction of bis-(organochalcogeno)mercurials with acid chlorides in the presence of tetrabutylammonium halides as catalyst in good yields.[9] Additionally, we found that hydrolysis of thioacetylenes with acid in the presence of silica gel leads to thiol esters in good yields (Scheme 1).[10]



Scheme 1.

In this paper, we give a full account of our efforts toward the synthesis of chalcogenol esters by means of the hydrolysis of chalcogenoacetylenes.

2. Results and discussion

The study of the reaction of 1-(methylthio)-2-phenylethyne **1a** and its selenium analog **2a** with various acids was undertaken (Table 1). To study the efficiency of the acid on the hydrolysis of **1a** and **2a**, dichloromethane was the solvent of choice. The first experiments were performed with several acids (Table 1). From these, trifluoroacetic acid (TFA) proved to be the most effective acid for the hydrolysis of both chalcogenoacetylenes, providing the

Table 1. Chalcogenol esters **3a** and **4a** formation in various acids

Chalcogenoacetylenes **1a** and **2a**	Chalcogenol esters **3a** and **4a**	Acid	Time (h)		Yield[a] (%)	
			Y=S	Y=Se	Y=S	Y=Se
Ph≡YCH3	Ph, O, YCH3	TFA	2	48	86	92
		p-TsOH	10	70	86	88
		$ClSO_3H$	6	56	85	48
		$HClO_4$	140	96	80	70
		HCl	15	96	80	40
		AcOH	140	140	–	5

[a] Refer to isolated yields by column chromatography.

Keywords: selenol esters; selenoacetylenes; thiol esters; thioacetylenes; chalcogenol esters; hydrolysis.
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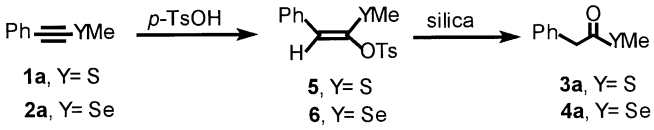


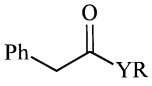
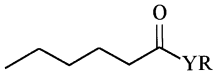
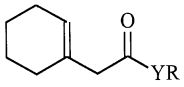
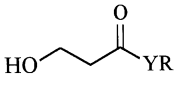
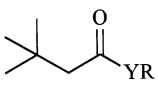
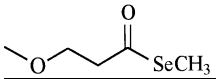
Scheme 2.

corresponding chalcogenol ester in very good yields. For thioacetylenes, both TFA and *p*-TsOH promoted the hydrolysis with the same efficiency. With other acids, such as $ClSO_3H$, $HClO_4$, or HCl, **3a** and **4a** were obtained in lower yields. In acetic acid, no reaction was observed for the thioacetylene **3a** and very low yields for the selenoacetylene **4a**.

We also examined the behavior of other solvent systems (DMF, chloroform, benzene, ether, THF, 1,2-dichloroethane) under the same experimental conditions. Dichloromethane was the only one to promote the hydrolysis efficiently. Also, the reaction did not proceed satisfactorily in the absence of silica with its natural water content. The use of additional amounts of water neither improve the yields nor increase the rates of the reactions.

The reactions can be monitored by NMR and the two stages of the process (Scheme 2) can be observed. For example, for 1-(methylthio)-2-phenylethyne **1a**,[11] within 10 min of the addition of *p*-TsOH, no methyl signal attributable by NMR to the starting alkynyl sulfide was observed [expected signal at δ ($CDCl_3$) 2.33], but a new signal appeared at δ 6.49 as a singlet and a weak signal at δ 3.79 as a singlet. We assign the former to the vinylic sulfide **5** and the latter to thiol ester **3a**. The signal due to **3a** gradually increases in intensity at the expense of the signals representing the vinylic sulfide **5**. Analogous compounds with selenium, like **6**, were observed to react by a similar path upon the addition of *p*-TsOH to selenoacetylenes.[12]

Table 2. Synthesis of chalcogenol esters by reaction of chalcogenoacetylenes with TFA (according to Scheme 1)

Chalcogenol ester		YR	Time (h)	Yield[a] (%)
	**3a**	SCH_3	2	86
	4a	$SeCH_3$	48	92
	3b	SPh	15	80
	4b	SePh	64	88
	3c	SCH_2Cl	20	86
	4c	$SeCH_2Cl$	72	82
	3d	SBu-*t*	96	81
	**3e**	SCH_3	52	90
	3f	SPh	49	80
	4d	$SeCH_3$	54	86
	**3g**	SPh	25	85
	4g	$SeCH_3$	48	86
	**3h**	SCH_3	20	60
	4h	$SeCH_3$	12	54
	**3i**	SCH_3	16	85
	4i	$SeCH_3$	54	65
	**4j**		16	65

[a] Refer to isolated yields by column chromatography.

The reactions described here are performed very easily by simply mixing all reagents at 40°C. The chalcogenol esters are obtained in good yields (Table 2). The most evident difference between sulfur and selenium analogs was their hydrolysis reaction time. We have observed that the rate of hydrolysis to prepare selenol esters is very slow compared to the sulfur counterparts. In fact, we observe by NMR experiments that the first step (addition of the acid to the chalcogenoacetylenes) have comparable rates. But the rate of the second step (hydrolysis to the chalcogenol esters) is slower in the case of the selenium analogs. At present, we do not have an explanation for this difference.

In this way, several types of chalcogenol esters were obtained and a good chemoselectivity was observed in some cases. For example, in the case of compounds **1h** and **2h**, it was not necessary to protect the hydroxyl group. In all cases studied, only the regioisomer shown in Scheme 2 was obtained. This result can be rationalized in terms of a carbocation stabilization by the chalcogen atom.[13] This procedure is especially useful since the starting chalcogenoacetylenes are readily available by various efficient methods.[14]

3. Conclusions

The present procedure nicely complements other methods, offering several advantages such as the greater availability of the starting materials, compatibility with various functional groups, and avoiding the use of the very toxic reagents such as heavy metal thiolates and selenolates or phenyl dichlorophosphate. Most importantly, the isolation of pure material is easily achieved.

4. Experimental

4.1. General information

IR spectra of neat compounds were obtained using a Perkin–Elmer 1310 IR spectrophotometer and Bruker IFS 28; peaks are reported as ν_{max} in cm^{-1}. Microanalyses were performed on Vario EL and Perkin–Elmer CHN 2400. ^1H and ^{13}C NMR spectra were recorded with Bruker DPX-200 (200 MHz) or DPX-400 (400 MHz) spectrometers; chemical shifts are reported in ppm using tetramethylsilane as an internal standard and $CDCl_3$ as solvent. Mass spectra were obtained using CG-MS HP 5090–5890 and INCOS-50 Finigan (IQ-USP). Melting points were determined on a Reichert Thermovar apparatus. Boiling points are uncorrected, determined on a Büchi GKR-50 (Kugelrohrofen). Purification of products by column chromatography and

the hydrolysis reactions were performed using Merck Silica Gel-60 (230–400 mesh).

4.2. Synthesis of the chalcogenol esters 3 and 4: general procedure

Typical procedure for thiol ester **3a**: To a round flask was added 1-(methylthio)-2-phenylethyne **1a** (0.148 g; 1 mmol), 5 mL of dichloromethane, *p*-TsOH (0.19 g; 1.1 mmol) and 1 g of silica. The resulting suspension was heated at 40°C. After 10 h, 5.0 mL of dichoromethane was added and the silica removed by filtration. The solvent was removed and the residue was purified by column chromatography over silica eluting with hexane.

Typical procedure for selenol ester **4a**: To a round flask was added 1-(methylseleno)-2-phenylethyne **2a** (0.195 g; 1.0 mmol), 5 mL of dichloromethane, TFA (0.171 g; 1.5 mmol) and 1 g of silica. The resulting suspension was heated at 40°C. After 48 h, dichloromethane was added and the silica removed by filtration. The solvent was removed and the residue was purified by column chromatography over silica eluting with hexane.

4.2.1. S-Methyl phenylthioacetate 3a. Bp 50°C/0.9 mmHg; IR (neat) 3010, 2910, 1670 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 7.32–7.24 (m, 5H), 3.80 (s, 2H), 2.25 (s, 3H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 197.7, 133.6, 129.5, 128.6, 127.3, 50.3, 11.8; MS *m/z* 166 (13%), 138, 119, 91 (100%). Anal. calcd for $C_9H_{10}OS$: C, 65.03; H, 6.06. Found: C, 64.91; H, 6.12.

4.2.2. Se-Methyl phenylselenoacetate 4a. Bp 65°C/0.5 mmHg; IR (neat) 3027, 2931, 1699, 1599, 1493 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 7.28–7.17 (m, 5H), 3.76 (s, 2H), 2.10 (s, 3H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 200.2, 133.1, 129.9, 128.6, 127.6, 53.9, 5.2; MS *m/z* 214 (25%), 119, 91 (100%).

4.2.3. S-Phenyl phenylthioacetate 3b. Mp 62°C; IR (neat) 3023, 1685, 1493, 1453 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 7.46–7.26 (m, 10H), 3.88 (s, 2H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 195.1, 134.3, 133.2, 129.5, 129.3, 129.0, 128.4, 128.0, 127.4, 50.0. Anal. calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30. Found: C, 73.91; H, 5.39.

4.2.4. Se-Phenyl phenylselenoacetate 4b. Mp 42.5–42.7°C; IR (KBr) 3059, 3029, 2875, 1709, 1579, 1494, 1476, 1438 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 7.40–7.15 (m, 10H), 3.83 (s, 2H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 198.6, 135.7, 132.6, 130.0, 129.2, 128.8, 128.7, 127.8, 126.6, 53.6; MS *m/z* 276 (10%), 157, 118, 91 (100%). Anal. calcd for $C_{14}H_{12}OSe$: C, 61.10; H, 4.39. Found: C, 61.17; H, 4.01.

4.2.5. S-Chloromethyl phenylthioacetate 3c. IR (neat) 3028, 1702, 1495, 1454, 1235, 1180, 1016 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 7.34–7.23 (m, 5H), 4.83 (s, 2H), 3.86 (s, 2H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 193.8, 132.24, 129.7, 128.7, 127.8, 50.2, 41.8. Anal. calcd for C_9H_9OSCl: C, 53.87; H, 4.52. Found: C, 54.12; H, 4.66.

4.2.6. Se-Chloromethyl phenylselenoacetate 4c. Bp 68°C/0.3 mmHg; IR (neat) 3062, 3029, 2924, 1711, 1495, 1453, 1206, 1175, 1032, 968, 700, 560 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 7.37–7.25 (m, 5H), 4.87 (s, 2H), 3.89 (s, 2H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 197.3, 131.7, 130.2, 128.8, 128.2, 53.6, 35.9. Anal. calcd for C_9H_9OSeCl: C, 43.66; H, 3.66. Found: C, 43.11; H, 3.36.

4.2.7. S-Methyl thiohexanoate 3d. Bp 40–45°C/0.5 mmHg; IR (neat) 2954, 2927, 2858, 1693, 1465 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 2.55 (t, J=7.0 Hz, 2H), 2.29 (s, 3H), 1.66 (qui, J=7.0 Hz, 2H), 1.34–1.30 (m, 4H), 0.89 (t, J=7.0 Hz, 3H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 199.9, 43.8, 31.0, 25.3, 22.2, 13.7, 11.4. Anal. calcd for $C_7H_{14}OS$: C, 57.49; H, 9.65. Found: C, 57.11; H, 9.69.

4.2.8. S-Phenyl thiohexanoate 3e. Bp 95–100°C/1.1 mmHg; IR (neat) 2956, 2929, 2859, 1708, 1477 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 7.39–7.34 (m, 5H), 2.63 (t, J=7.0 Hz, 2H), 1.69 (qui, J=7.0 Hz, 2H), 1.35–1.32 (m, 4H), 0.89 (t, J=7.0 Hz, 3H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 197.3, 134.3, 129.2, 129.1, 127.8, 43.5, 30.8, 24.9, 22.0, 13.7. Anal. calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74. Found: C, 68.81; H, 7.54.

4.2.9. Se-Methyl hexaneselenoate 4d. Bp 85°C/0.5 mmHg; IR (neat) 2937, 2926, 2870, 1710, 1458 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 2.62 (t, J=7.2 Hz, 2H), 2.21 (s, 2H), 1.66 (m, 2H), 1.37–1.29 (m, 4H), 0.91 (t, J=6.4 Hz, 3H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 201.9, 47.9, 30.9, 25.2, 22.3, 13.8, 4.7; MS *m/z* 194 (12%), 123, 99, 71, 57 (100%). Anal. calcd for $C_7H_{14}OSe$: C, 43.53; H, 7.31. Found: C, 43.18; H, 6.98.

4.2.10. S-Phenyl 2-(1-cyclohexenyl)thioacetate 3f. IR (neat) 3058, 2929, 1710, 1581, 1476 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 7.41–7.33 (m, 5H), 5.45 (m, 1H), 3.23 (s, 2H), 1.83–1.79 (m, 4H), 1.48–1.33 (m, 4H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 195.7, 134.3, 130.6, 129.0, 128.9, 128.1, 127.6, 52.4, 28.6, 25.3, 22.6, 21.7. Anal. calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.02; H, 6.71.

4.2.11. Se-Methyl 2-(1-cyclohexenyl)selenoacetate 4g. Bp 55°C/0.5 mmHg; IR (neat) 3391, 2931, 1704, 1435, 1268 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 5.69 (m, 1H), 3.16 (s, 2H), 2.17 (s, 3H), 2.06–1.90 (m, 4H), 1.66–1.56 (m, 4H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 201.3, 130.6, 128.6, 56.3, 28.5, 25.5, 22.7, 21.7, 4.7; MS *m/z* 218 (5%), 123, 95, 67, 55 (100%). Anal. calcd for $C_9H_{14}OSe$: C, 49.78; H, 6.50. Found: C, 49.25; H, 6.41.

4.2.12. S-Methyl 3-hydroxythiopropanoate 3h. Bp 45°C/0.2 mmHg; IR (neat) 3380, 2930, 1681, 1412, 1049 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 3.83 (t, J=5.6 Hz, 2H), 2.84 (t, J=5.6 Hz, 2H), 2.54 (s, 1H), 2.35 (s, 3H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 199.5, 58.7, 45.9, 11.5. Anal. calcd for $C_4H_8O_2S$: C, 39.98; H, 6.71. Found: C, 39.55; H, 6.33.

4.2.13. Se-Methyl 3-hydroxypropaneselenoate 4h. Bp 55°C/0.3 mmHg; IR (neat) 3400, 2930, 1697 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 3.83 (t, J=5.6 Hz, 2H), 2.84 (t, J=5.6 Hz, 2H), 2.18 (s, 3H), 2.14 (s, 1H); ^{13}C NMR δ

(50 MHz, $CDCl_3$): 201.6, 58.5, 50.2, 5.0; MS *m/z* 168 (5%), 93, 73 (100%). Anal. calcd for $C_4H_8O_2Se$: C, 28.76; H, 4.83. Found: C, 28.40; H, 4.51.

4.2.14. S-Methyl 3,3-dimethylthiobutanoate 3i. Bp 25–30°C/0.5 mmHg; IR (neat) 2957, 2927, 2869, 1690, 1464, 1366 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 2.40 (s, 2H), 2.24 (s, 3H), 1.0 (s, 9H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 197.4, 56.0, 30.8, 29.0, 11.0. Anal. calcd for $C_7H_{14}OS$: C, 57.49; H, 9.65. Found: C, 57.07; H, 9.45.

4.2.15. Se-Methyl 3,3-dimethylbutaneselenoate 4i. Bp 45°C/0.5 mmHg; IR (neat) 2956, 2907, 1710, 1465, 1366, 1003 cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$): 2.53 (s, 2H), 2.20 (s, 3H), 1.04 (s, 9H); ^{13}C NMR δ (100 MHz, $CDCl_3$): 200.4, 60.6, 31.5, 29.6, 5.3. Anal. calcd for $C_7H_{14}OSe$: C, 43.53; H, 7.31. Found: C, 43.11; H, 6.91.

4.2.16. Se-Methyl 3-methoxypropaneselenoate 4j. IR (neat) 2930, 2885, 2815, 1701, 1450, 1385, 1115 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$): 3.68 (t, J=6.2 Hz, 2H), 3.35 (s, 3H), 2.88 (t, J=6.2 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR δ (50 MHz, $CDCl_3$): 199.7, 67.7, 58.7, 47.8, 4.8; MS *m/z* 182 (5%), 94, 87, 59 (100%). Anal. calcd for $C_5H_{10}O_2Se$: C, 33.16; H, 5.57. Found: C, 32.79; H, 5.12.

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