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A Convenient Synthesis of Arylselenoacetals and α-Halo-α-(phenylseleno)alkanes

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A CONVENIENT SYNTHESIS OF ARYLSELENOACETALS AND α-HALO-α-(PHENYLSELENO)ALKANES

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Abstract: *α-Halo-α-(phenylseleno)alkanes are prepared by treatment of selenoacetals with halogenating agents. Selenoacetals are produced by heating α-halo-α-(phenylseleno)alkanes on neutral alumina.*

Selenoacetals **1** constitute one of the most important class of selenium compounds, being applied, for example, to generate α-selenoalkyllithiums on reaction with butyllithiums[1,2], and as precursors of α-selenocarbenium ions which reacts with silyl enol ethers[3] and allyl silanes[4]. They can be selectively transformed into vinyl selenides[1] , and suffer hydrolysis to aldehydes and ketones[1] and can be reduced to alkanes[1] by treatment with an appropriate reducing agent.

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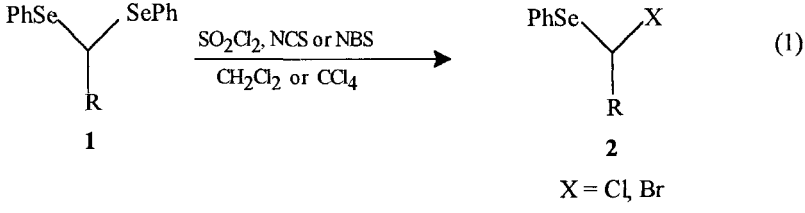
Selenoacetals are most usually prepared from carbonyl compounds by reaction with the appropriate selenol under acidic conditions.[1]

Similarly, α-halogeno alkylselenides **2** are quite useful compounds, since by treatment with a *Lewis acid*, they generate α-seleno alkylcarbenium ions which in turn have been trapped with trimethyl silyl enol ethers[5] or aromatic substrates.[6] In addition, they permit access to α-seleno alkyl lithium compounds by treatment with butyllithiums[7] (X = Br) and α-seleno carbenes by reaction with an appropriate base[8].

α-Halogenoalkyl selenides were prepared by addition of gaseous HCl or HBr to vinyl selenides[7] or by treatment of unpleasant selenophenol and an aldehyde with gaseous HX (X=Cl, Br),[7] which gives in some cases mixtures of α-halo alkyl selenides and seleno acetals. The same mixture is obtained by nucleophylic substitution of dibromomethane by PhSeNa.[9] α-Halo methyl selenides can be conveniently prepared under phase transfer catalysis from the corresponding diselenides.[10] A recent paper describes in detail methods for the preparation of α-halo-α-phenylseleno acetates.[11]

In this communication we wish to describe a convenient preparation of selenoacetals and α-halogenoalkyl selenides. Treatment of selenoacetals **1** with halogenating agents like SO_2Cl_2 , NCS and NBS furnishes the corresponding α-halogenoalkylselenides in acceptable yields (Equation 1, Table I).



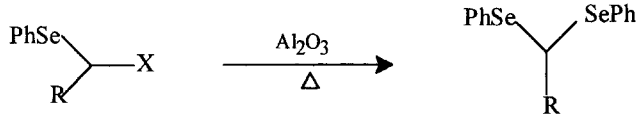
1 **2**

X = Cl, Br

(1)

The above method constitutes a very convenient way to prepare α-halogenoalkylselenides from selenoacetals, since the reactions are easily performed, cleanly furnishing the desired halides. The reactions were carried out by dissolving the selenoacetals (1 mmol) in the appropriate solvent (3 mL) and adding the halogen source (1.2-1.6 mmol) dropwise (SO_2Cl_2 in 1 mL of CH_2Cl_2) or in small portions (NBS/NCS). After stirring the reaction mixture at room temperature or at reflux under the appropriate conditions, the reaction was worked up in the usual way and purified as described on table I (see experimental section).

On the other hand upon heating α-halo-α-(phenylseleno) alkanes on neutral alumina, the corresponding selenoacetals are produced according to equation 2 (Table II).



2 1 (2)

It is quite interesting the case of tris(phenylseleno)methane[12] that upon treatment with sulfuryl chloride furnishes *gem*-dichloro-phenylseleno methane[13] as the only product and in 85% yield. We used this derivative on the preparation of a series of 1-Chloro-1-Arylseleno cyclopropanes.[8] Heating this di-halo compound on alumina without solvent produces tris-(phenylseleno) methane in 70% yield, and again in a very clean reaction (entry 2, Table II).

Recently we described that the reaction of ethyl diazoacetate with phenylselenenyl bromide gives a mixture of ethyl α-bromo-α-phenylseleno acetate and ethyl bis-(phenylseleno) acetate (1.5:1.0 ratio) which is difficult to separate.[6,11] Treatment of this mixture with NBS

Table I - Preparation of α-halogenoalkylselenides

Entry	Starting Material	Halogen Source[d] (equiv.)	Reaction Time(h)	Product	Yield (%)
1	$PhSeCH_2SePh$	SO_2Cl_2 (1.2)	1.0	$PhSeCH_2Cl$[b]	67
2	$PhSeCH_2SePh$	NCS (1.2)	4.8	$PhSeCH_2Cl$[b]	48
3	$PhSeCH_2SePh$	NBS (1.6)	2.0	$PhSeCH_2Br$	f
4	$PhSeCHCH_3SePh$	SO_2Cl_2 (1.2)	1.5	$PhSeCHCH_3Cl$[a]	78
5	$HC(SePh)_3$	SO_2Cl_2 (1.2)	1.0	$PhSeCHCl_2$[a]	85
6	$PhSeCH_2SPh$ [g]	SO_2Cl_2 (1.2)	0.15	$PhSCH_2Cl$[c]	60
7	$PhSeCH_2SPh$	NCS (1.5)	6.5	$PhSCH_2Cl$[c]	58
8	$(PhSe)_2CHCO_2Et$[e]	NBS (1.2)	1.0	$PhSeCHBrCO_2Et$	70

a) PhSeSePh removed by treatment with $NaBH_4$ and basic work-up ;
b) Purified by column chromatography on silica gel;
c) Purified by Kugelrohr distillation;
d) Reactions with SO_2Cl_2 performed under reflux of CH_2Cl_2 and with NBS and NCS in CCl_4 at room temperature;
e) Mixture of $(PhSe)_2CHCO_2Et$ and $PhSeCHBrCO_2Et$ (1 x 1.5 ratio) ; see text. For $(PhSe)_2CHCO_2Et$ bp 174-175°C/1.5 torr and Anal. calcd. for $C_{16}H_{16}O_2Se_2$ C 48.26, H 4.05, found C 49.72, H 4.16.
f) 70% (by NMR of the crude product), obtained as a mixture with diphenyl diselenide, which is difficult to separate in small scale reactions. Column chromatography gives the pure product, but in lower yields, as in contact with silica it decomposes. Higher amounts can be purified by distillation, bp 84-85°C/0.17torr (Lit.[9] 97-99°C/0.25 torr);
g) bp 110-111°C/0.15 torr; Anal. calcd. for $C_{13}H_{12}SeS$ C 55.91, H 4.33, found C 55.98, H 4.44.

Table II - Preparation of selenoacetals

Entry	Starting Material	Temperature °C	Reaction Time (min)	Product	Yield (%)
1	$PhSeCH_2Cl$	90	30	$PhSeCH_2SePh$	87[a]
2	$PhSeCHCl_2$	50	25	$HC(SePh)_3$	70[b]
3	$PhSeCHCH_3Cl$	40	30	$PhSeCHCH_3SePh$	70[c]

a) Purified by column chromatography ;
b) Purified by recristalization from hexane ;
c) Purified by treatment with $NaBH_4$.

furnishes ethyl α-bromo-α-phenylseleno acetate in 70% yield as the only product (entry 8, Table I).

In the same way, treatment of the mixed sulfur and selenium acetals (entries 6 and 7, Table 1), with sulfuryl chloride or NCS gives selectively only the sulfur derivative and diphenyl diselenide. All reactions described here are very easily performed, giving the desired products in good yields. The α-halo selenides can be purified by column chromatography or on the case of compounds that are not stable to purification by column or distillation the treatment with $NaBH_4$ on benzene can be used to remove some diphenyl diselenide .

In summary, we described a convenient way to prepare selenoacetals and their corresponding α-halo selenides from each other, in very simple and clean reactions.

EXPERIMENTAL (Typical procedures)

1. *For the preparation of α-halogenoalkylselenides*

1.a)Preparation of **Dichloromethylphenylselenide** :

To a flask containing a solution of tris(phenylseleno)methane (0,481 g; 1 mmol) in dichloromethane (3 mL) at room temperature was added dropwise a solution of sulfuryl chloride (0,16 g; 1.2 mmol) in dichloromethane (1 mL). The reaction mixture was magnetically stirred and refluxed for 1 hour, then cooled to room temperature, added to a sat. aqueous $NaHCO_3$ solution and extracted with dichloromethane (3 X 20 mL). The solvent was removed under vacuum and the residue was dissolved in benzene (10 mL) and treated with $NaBH_4$ (a 5 % solution in ethanol) until the yellow color of diphenyl diselenide disappear. A sat.

aq. $NaHCO_3$ solution(20 mL) was added, the organic phase was separated and the aqueous extracted with benzene (20 mL). The organic layer dried over magnesium sulfate, and the solvent removed under vacuum to give the pure 1,1-dichloro-1-phenylseleno methane. Additionally, this product can be purified by column chromatography on silicagel, eluting with hexane. Yield : 0,20 g (85 %); bp : 48-50°C/1.2 torr; ^1H NMR(80 MHz, $CDCl_3$): δ 6.73(s, 1H), 7.19-7.75(m, 5H); GC/MS: m/e 240(M+), 205(100%), 169, 157, 125. Anal. calcd. for $C_7H_6Cl_2Se$ C 35.03, H 2.52, found C 35.59, H 2.66.

1.b)Preparation of **Chloromethylphenylselenide**:

To a solution of bis-(phenylseleno)methane (0.326g,; 1 mmol) in dichloro methane (3mL) at room temperature, was added dropwise a solution of sulfuryl chloride(0,16 g; 1.2 mmol) in dichloromethane (1 mL). The reaction mixture was refluxed for 1 hour, then cooled to room temperature, added to a sat. aqueous $NaHCO_3$ solution and extracted with dichloromethane (3 X 20 mL). The solvent was removed under vacuum and the residue purified by column chromatography on silicagel eluting with hexane. Yield : 0.137g (67%). bp: 105°C/1.5 torr (Lit.[8a] 63-65°C/0.1 torr). ^1H NMR(80 MHz, $CDCl_3$) :δ 4.90 (s, 2H), 7.20-7.70(m, 5H); GC/MS: m/e 206(M+), 171, 157, 117, 91, 51(100%).

1.c)Preparation of **Chloromethylphenylsulfide**:

To a solution of phenylseleno phenyltiomethane(0.28g; 1 mmol) in carbon tetrachloride (3 mL) at room was added, in small portions NCS (0.20g; 1.5 mmol). The reaction mixture was stirred at room temperature for 6.5 hours, then filtered to remove succinimide washing with carbon tetrachloride(20 mL). The solvent was removed under vacuum and the residue purified by Kugelrohr distillation. Yield: 0.09g (58 %). bp :80°C/1 torr (Lit.[15] 66-69°C/0.15-0.2 torr). ^1H NMR(80

MHz, $CDCl_3$) : δ 4.93(s, 2H), 7.2-7.6(m, 5H); GC/MS : m/e 158(M+), 123(100%),109.

1.d)**Bromethylphenylselenide**:

Prepared according to procedure 1.c. Yield: 70% ;bp 84-85°C/0.17torr (Lit.[9] 97-99°C/0.25torr; ^1H NMR(80 MHz, $CDCl_3$) : δ 4.72 (s, 2H), 7.2-7.7 (m, 5 H); GC/MS : m/e 250(M^+), 171(100%), 117, 91.

1.e)**1-Chloro-1-Phenylselenoethane**:

Prepared according to procedure 1.a. Yield : 78%, undistillable and quite unstable yellow oil[7]. ^1H NMR(80 MHz, $CDCl_3$) : δ 1.97(d, 3H, J 6.7 Hz), 5.45(q, 1H, J 6.7Hz), 7.2-7.8(m, 5H); GC/MS : m/e 220(M^+,100%), 184, 157, 117, 105.

1.f)**Ethyl α-Bromo-α-phenylseleno acetate**:

Prepared according to procedure 1.c. Yield : 70 %; bp 92-93°C/0.17 torr. ^1H NMR(80 MHz, $CDCl_3$) : δ 1.21(t, 3H, J 7 Hz), 4.15(q, 2H, J 7 Hz), 5.4(s, 1H), 7.1-7.4(m, 3H), 7.5-7.8(m, 2H); GC/MS : m/e 322(M^+), 243, 197, 169(100%), 134, 107, 91, 77; IR : 1736 cm^{-1}.Anal. calcd. for $C_{10}H_{11}BrSeO_2$ C 37.29, H 3.44 found C 36.90, H 3.40.

2.*For the preparation of selenoacetals*

2.a) Preparation of **1,1-bis(Phenylseleno)methane** :

To a round bottom flask equipped with a drying tube was added phenylseleno chloromethane (0,206 g; 1 mmol) and neutral alumina (Merck, Type T, 2 g). The obtained suspension was heated for 30 in at 90°C (oil bath temperature). After the end of reaction, and at room temperature, dichloromethane was added and the alumina removed by filtration. The solvent was

removed and the residue was purified by column chromatography over silicagel eluting with hexane to give a yellow oil at room temperature which crystallize only on freezing. Yield : 0,14 g (87 %). bp 126-127°C/0.015 torr (Lit.[9] 165°C/0.2 torr); ^{1}H NMR($CDCl_3$): δ 4.17(s, 2H), 7.1-7.5 (m, 10H); GC/MS: m/e 328(M^+ +2), 249, 171, 156, 91(100%).

2.b)Preparation of **tris-(Phenylseleno)methane**:

To a round bottom flask was added dichloromethylphenylselenide(0.24g; 1 mmol) and neutral alumina(Merck, Type T, 2 g). The resulting suspension was heated for 25 in at 50°C(oil bath temperature), then cooled to room temperature. Dichloromethane was added and the alumina removed by filtration. The solvent was removed and the remainder solid was purified by recrystallization from hexane. Yield 0.11g(70%). mp 94-96°C (lit.[12] 98-99°C). ^{1}H NMR(80 MHz, $CDCl_3$) : δ 5.28(s, 1H), 7.1-7.3(9H), 7.4-7.6(6H).

2.c)**1,1-bis(Phenylseleno)ethane**:

Prepared according to procedures 2.a or 2.b. Purified by treatment with $NaBH_4$ as in procedure 1.a. Yield 70 %; bp 165°C / 0.2torr (Lit.[9] 110-112/0.0025 torr); ^{1}H NMR(80 MHz, $CDCl_3$) : δ 1.80(d, 3H, J 7.2 Hz), 4.57(q, 1H, 7.2Hz), 7.2-7.4 (m, 6H), 7.5-7.7 (m, 4H); GC/MS : m/e 342 (M^+ +2), 266, 250, 211, 185(100%), 157, 105.

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