Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS OF STABLE SELENONIUM YLIDES

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(Received March 3rd, 1972)

SUMMARY

Stable selenonium ylides with two electron acceptor groups have been synthesized by the interaction between organic selenide dichlorides and active methylene compounds in the presence of a base. The structure of the synthesized ylides has been confirmed by means of their IR, UV and PMR spectra which in general are little different from the spectra of their sulphonium analogues.

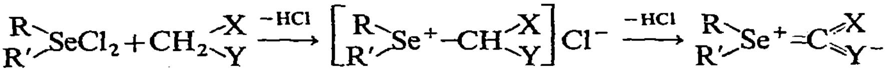
INTRODUCTION

Until recently only two selenonium ylides had been reported in the literature: diphenylselenonium tetraphenylcyclopentadienylide, isolated by Lloyd and Singer[1] as a result of the photochemical decomposition of diazotetraphenylcyclopentadiene in diphenyl selenide, and dimethylselenonium fluorenylide. The latter was obtained as a black precipitate by the action of a base on the dimethylfluorenylselenonium salt[2] and apparently was not a pure substance. The synthesis of stable selenonium ylides is of undoubted interest in view of the possible comparison of their properties with those of the analogous sulphur ylides whose synthesis[3-6] and reactivity have been intensively studied during recent years.

It may be expected that selenonium ylides will be more reactive since participation of the vacant *d*-orbitals in the stabilization of the adjacent carbanion is more likely to occur with the sulphur atom rather than the selenium atom[9,10].

RESULTS AND DISCUSSION

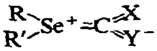
In our previous communication[11] the synthesis of diphenylselenonium dimedoneylide was described. As a development of our previous work we have synthesized a number of stable selenonium ylides (with 2 electron acceptor groups at the ylide atom) by the interaction between dichlorides of organic selenides and active methylene compounds:



$$\overset{R}{\underset{R'}{>}}SeCl_2 + CH_2\overset{X}{\underset{Y}{<}} \xrightarrow{-HCl} \left[\overset{R}{\underset{R'}{>}}Se^+{-}CH\overset{X}{\underset{Y}{<}}\right]Cl^- \xrightarrow{-HCl} \overset{R}{\underset{R'}{>}}Se^+{=}C\overset{X}{\underset{Y^-}{<}}$$

The selenides studied were tetrahydroselenophene (selenolane), methyl phenyl

TABLE 1

SELENONIUM YLIDES OF STRUCTURE 

$R(R')Se^{+}-C^{-}(X)(Y)$

Compound	*R*	*R′*	*X*	*Y*	*Yield (%)*	*M.p. (°C)*	*Empirical formula*	*Analysis: Found (calc (%)*	
								C	*H*
(I)	$-(CH_2)_4-$		$COCH_3$	$-COCH_3$	83	84.5	$C_9H_{14}O_2Se$	46.4 (46.4)	6.1 (6.1)
(II)	$-(CH_2)_4-$		COC_6H_5	COC_6H_5	95	146	$C_{19}H_{18}O_2Se$	63.9 (63.9)	5.2 (5.1)
(III)	$-(CH_2)_4-$		$-COCH_2C(CH_3)_2CH_2CO-$		92	162	$C_{12}H_{18}O_2Se$	52.8 (52.8)	6.3 (6.6)
(IV)	$-(CH_2)_4-$		CN	CN	31	95	$C_7H_8N_2Se$	42.4 (42.3)	4.1 (4.0)
(V)	$-(CH_2)_4-$		CN	CO_2CH_3	82	120	$C_8H_{11}NO_2Se$	41.2 (41.4)	5.0 (4.8)
(VI)	$-(CH_2)_4-$		CN	$CO_2C_2H_5$	50	94–96	$C_9H_{13}NO_2Se$	43.7 (43.9)	5.4 (5.3)
(VII)	$-(CH_2)_4-$		$COCH_3$	$CO_2C_2H_5$	78	Oil	$C_{10}H_{16}O_3Se$	44.7 (45.6)	6.4 (6.1)
(VIII)	CH_3	C_6H_5	$COCH_3$	$COCH_3$	84	62–66	$C_{12}H_{14}O_2Se$	53.6 (53.5)	5.5 (5.2)
(IX)	CH_3	C_6H_5	COC_6H_5	COC_6H_5	37	171.5	$C_{22}H_{18}O_2Se$	67.0 (67.2)	5.0 (4.6)
(X)	CH_3	C_6H_5	$-COCH_2C(CH_3)_2CH_2CO-$		62	132	$C_{15}H_{18}O_2Se$	58.7 (58.3)	5.8 (5.9)
(XI)	CH_3	C_6H_5	CN	CN	34	107–110	$C_{10}H_8N_2Se$	50.5 (51.1)	3.8 (3.4)
(XII)	C_6H_5	C_6H_5	$COCH_3$	$COCH_3$	11.5	125–126	$C_{17}H_{16}O_2Se$	61.9 (61.6)	5.1 (5.5)
(XIII)[a]	C_6H_5	C_6H_5	$-COCH_2C(CH_3)_2CH_2CO-$		58	171–172	$C_{20}H_{20}O_2Se$	64.7 (64.7)	5.7 (5.4)
(XIV)	C_6H_5	C_6H_5	CN	CN	7.5	135 (Dec.)	$C_{15}H_{10}N_2Se$	60.3 (60.6)	3.6 (3.4)

[a] Synthesis reported in Ref. 11.

selenide and diphenyl selenide. The methylene components studied were β-diketones, cyanoacetic, acetoacetic esters and malonic acid dinitrile (see Table 1).

In the absence of a base only the reaction of dichlorides with dimedone (resulting in the elimination of HCl from the corresponding selenonium salt by alumina) gives a high yield of ylides [(III), (X), (XIII)]. In all other experiments only small quantities of ylide were formed. This is possibly due to the fact that the enolic proton of dimedone, in contrast to the enolic proton of acyclic β-dicarbonyl compounds, is not involved in strong intramolecular hydrogen bonding and can promote the polarization of the Se–Cl bond in the transition state[12].

In order to obtain a reasonable yield of ylide it was found necessary to carry out the reaction between dichlorides and compounds containing an active methylene group using a basic solution of methanol as a solvent.

TABLE 2: IR, UV AND PMR SPECTRA OF SELENONIUM YLIDES

Compound	ν^a (cm^{-1})	λ (*nm*)	*log ε*	δ^b (*ppm*)	*Relative weight*	*Assignment*
(I)	1570	278	4.19	3.7–2.9 m	2	$\rangle$Se–CH$_2$–^{c}
	1605			2.9–1.5 m	2	β-CH$_2$–
				2.2 s	3	–COCH$_3$
(II)	1560	232	4.30	4.0–3.0 m	1	$\rangle$Se–CH$_2$–
	1588	290	3.94			
		322	3.98	2.8–1.7 m	1	β-CH$_2$–
(III)	1570	265	4.28	4.0–2.8 m	2	$\rangle$Se–CH$_2$–
				2.8–1.8 m	2	β-CH$_2$–
				2.2 s	2	–COCH$_2$–
				1.0 s	3	–CH$_3$
(IV)	2140	284	3.63	4.0–3.0 m	1	$\rangle$Se–CH$_2$–
	2180			2.8–1.7 m	1	β-CH$_2$–
(V)	1655	228	4.13	4.0–3.0 m	4	$\rangle$Se–CH$_2$–
				3.6 s	3	–O–CH$_3$
	2160	277	3.70	3.0–1.7 m	4	β-CH$_2$
(VI)	1645	227	4.08	4.0 q	2	–O–CH$_2$–
	2155	277	3.68	3.7–3.1 m	4	$\rangle$Se–CH$_2$–
				3.1–1.8 m	4	β-CH$_2$–
				1.3 t	3	–CH$_3$
(VII)	1575	248	4.09	4.0 q	2	–O–CH$_2$–
	1670			5.0–1.5 m	8	$\rangle$Se– and β-CH$_2$–
				1.2 t	3	–CH$_3$
				2.3 s	3	–COCH$_3$
(VIII)	1585	268	4.20	7.4 m	5	–C$_6$H$_5$
	1610			3.0 s	3	$\rangle$Se–CH$_3$
				2.3 s	6	–COCH$_3$
(IX)	1575	287	4.00	8–6.4 m	5	$\rangle$Se–C$_6$H$_5$ and –CO–C$_6$H$_5$
	1595	317	3.96	3.1 s	1	$\rangle$Se–CH$_3$
(X)	1557	261	4.33	7.5 m	5	–C$_6$H$_5$
	1612			3.1 s	3	$\rangle$Se–CH$_3$
				2.2 s	4	–CO–CH$_2$–
				1.0 s	6	–CH$_3$
(XI)	2140	277 (sh)	3.42	7.6 m	5	–C$_6$H$_5$
	2175			2.9 s	3	$\rangle$Se–CH$_3$
(XII)	1577	265	4.21	7.4 m	5	–C$_6$H$_5$
	1592			2.3 s	3	–COCH$_3$
	1617					
(XIII)	1563	257	4.29	7.5 m	5	–C$_6$H$_5$
				2.3 s	2	–COCH$_2$–
				1.0 s	3	–CH$_3$
(XIV)	2157	258 (sh)	3.65	7.5 m		–C$_6$H$_5$
	2190	287 (sh)	3.44			

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[a] Absorption frequencies of CO and CN groups are given. [b] m, multiplet; s, singlet; q, quadruplet; t, triplet. [c] Selenolane β-protons.

From the data in Table 1 it will be seen that the highest yields of ylide were obtained in reactions involving selenolane dichloride which may be attributed to the low degree of hydrolysis exhibited by this compound in comparison to the other dichlorides used in this study. In addition to the hydrolysis of the dichlorides, reduction to the corresponding selenides also occurred, possibly as a result of the decomposition of the selenonium salts formed initially[11]. A similar cleavage has been reported for sulphonium[13] and iodonium[14] salts.

In the reaction of selenolane dichloride with the ethyl ester of cyanoacetic acid in potassium hydroxide/methanol solution, ylide (V) containing a methoxycarbonyl group was isolated rather than the expected ylide (VI). That reesterification had occurred was demonstrated by the elemental analysis of (V) and by its PMR spectrum which exhibited a signal corresponding to a methoxy group.

All the ylides prepared (except for VII) were obtained as crystalline solids, stable at 0° and decomposing slowly at 20°. The most stable ylides were those found from dimedone, the less stable those from dicyanomethane. All the ylides were colourless (with the exception of the ylides (II) and (III), which were yellow).

The structure of the ylides obtained was confirmed by elemental analysis as well as by their UV, IR and PMR spectra (Table 2).

The IR spectra of the selenonium ylides exhibited the characteristic intense absorption bands of "the ylide carbonyl" or of "the ylide nitrile group" in the 1557–1585 cm^{-1} and 2140–2190 cm^{-1} regions of the spectrum respectively. As with the analogous sulphonium ylides[15] these bands are shifted (by ~ 100 cm^{-1}) to lower wavenumbers in comparison with the bands of a "normal" carbonyl and a "normal" nitrile group in the corresponding selenonium (sulphonium) salts. For selenonium as well as for sulphur ylides[3,5,16] the positions of the absorption bands corresponding to carbonyl and nitrile groups are virtually independent of the character of the substituents at the onium atom.

In general the differences between the infrared spectra of the selenonium ylides obtained in this study and those of the analogous sulphonium ylides are insignificant[3,5,16]. Intense absorption bands in the 220–290 nm region of the spectrum were observed both in the UV spectra of the selenonium compounds and in those of the analogous sulphonium ylides[3,16].

The PMR spectra of the ylides obtained in this study exhibited proton signals corresponding to the substituents at the onium atom (R and R′) downfield in comparison to the signals for these protons in the spectra of the corresponding selenides.

EXPERIMENTAL

The IR spectra of the selenonium ylides were recorded on a UR-20 spectrometer [(I)–(VI), (VIII)–(XIV) as suspensions in nujol, (VII) as a liquid film]; UV-spectra of compounds (I)–(XIV) as 0.01 mol solutions in chloroform were measured on a Cary-15 spectrophotometer, while PMR spectra were run on a Varian T-60 spectrometer [(I)–(VII) as chloroform solutions, (VIII)–(XIV) as methylene chloride solutions using hexamethyldisiloxane as an internal standard].

Preparation of selenonium ylides (I)–(X) and (XII)

I. General method

To a three-necked flask fitted with a stirrer and dropping funnel and containing 1.7 g (0.03 mol) of potassium hydroxide in 12.5 ml of methanol at 0° was added 0.01 mol of the methylene component in 12.5 ml of methanol. A 0.01 mol solution of the corresponding dichloride in 25 ml of methylene chloride was then slowly added dropwise. The reaction mixture was stirred for another two hours and then poured into a cooled (0°) solution of potassium carbonate (50 g) in water (200 ml). The organic layer was separated and the aqueous solution extracted with methylene chloride (3 × 50 ml), dried with potassium carbonate and concentrated *in vacuo*. The residue was washed with ether (2 × 15 ml), reprecipitated with ether [with hexane for ylide (I)] from its solution in methylene chloride and dried under reduced pressure.

Ia. Tetramethyleneselenonium dicyanomethylide (IV) obtained according to the general method described above was chromatographed on alumina (l = 30 cm, d = 2 cm; eluant, 40% acetone solution in chloroform).

Ib. Methylphenylselenonium diacetylmethylide (VII) obtained according to the general method described above after being chromatographed on a column with alumina (eluant, 5% methanol solution in chloroform) was recrystallized from ether at low temperature.

Ic. Diphenylselenonium diacetylmethylide (XII) after being treated according to (I) contained diphenylselenium oxide and diphenyl selenide as impurities and was purified on an alumina column, (l = 30 cm, d = 2 cm; eluant, 5% methanol solution in chloroform).

II. Methylphenylselenonium dicyanomethylide (XI)

An attempt to obtain an appreciable yield of (XI) using a methanol solution of potassium hydroxide or a solution of sodium ethylate in absolute ethanol was unsuccessful. The use of pyridine, however, gave satisfactory results. To a solution of 0.66 g (0.01 mol) of dicyanomethane and 2 g (0.025 mol) of pyridine in 25 ml of methylene chloride a solution of 2.4 g (0.01 mol) of methylphenylselenium dichloride in 25 ml of methylene chloride was slowly added dropwise (over 30 min) with stirring (−15°). The reaction mixture was immediately chromatographed on an alumina column (l = 30 cm, d = 3 cm; eluant, 40% acetone solution in chloroform). The ylide ($R_f \approx 0.7$) was eluted with pyridine.

Evaporation of the solvent and treatment with ether (3 × 10 ml) gave 0.79 g (33.6%) of the compound as a brick-red powder. It was purified by absorption filtration through a layer of alumina in 40% acetone/chloroform, the ylide being precipitated by ether from its solution in methylene chloride.

IIa. Diphenylselenonium dicyanomethylide (XIV) was obtained by the same method as described for (II), but after diphenyl selenide dichloride had been added the reaction mixture was filtered through a layer of alumina (l = 2 cm, d = 2 cm) and washed with 20 ml of 40% acetone solution in chloroform. The solution was evaporated to 1 ml and ether was added. The resin-like precipitate was dissolved in 20 ml of 40% acetone/chloroform and subjected to absorption filtration; 0.11 g (5%) of pure ylide XIV was obtained.

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