Pergamon

Tetrahedron Letters, Vol. 36, No. 15, pp. 2627-2630, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)00353-3

Study of the Decomposition of Halo adducts Derived from Propargylic Phenylselenides. Intermediate Formation of Haloallenes

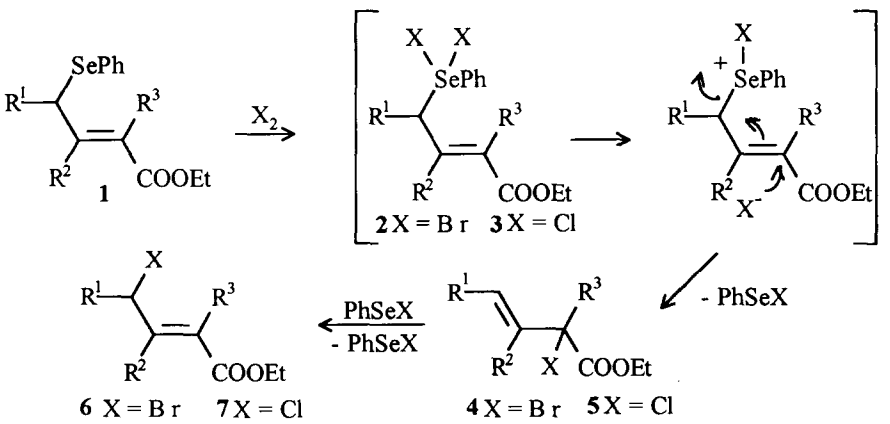
Jean-François Duclos, Francis Outurquin and Claude Paulmier*

Laboratoire de Synthèse Hétéroorganique (I.R.C.O.F.),
Université de Rouen, UFR Sciences, F-76821 Mont Saint Aignan, France

Abstract : The decomposition of bromo- and chloro-adducts, derived from propargylic phenylselenides, leads to 1,3-dihalo 2-phenylseleno propene derivatives through intermediate formation of haloallenes.

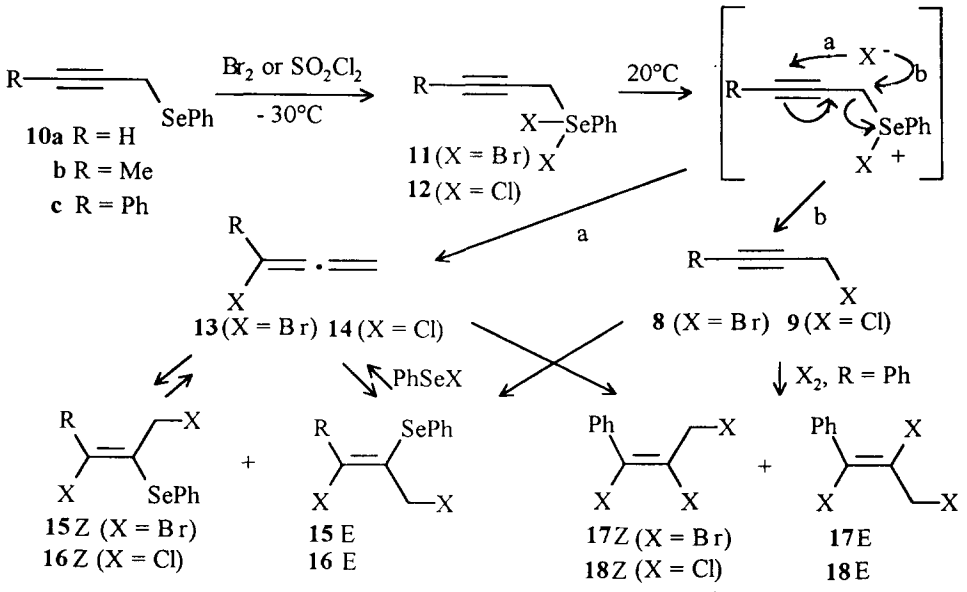
In a previous letter[1] we showed that the decomposition of halo adducts **2** and **3** derived from γ-phenylseleno α,β-unsaturated esters **1** leads to α-halo β,γ-unsaturated esters **4** (X = Br) and **5** (X = Cl) respectively, when benzeneselenenyl halide is trapped. (Scheme 1). Without elimination of PhSeX, γ-halo β,γ-unsaturated esters **6** (X=Br) and **7** (X=Cl) are formed.

Scheme 1



We wish here to present our first results concerning the decomposition of adducts formed by the reaction of bromine or sulfuryl chloride with the propargylic phenylselenides **10** (R = H,[2,3] R = Me,[4] R = Ph[4]) prepared from their corresponding bromides **8**.[4] Isolation of E,Z-mixtures of dihalovinylselenides **15** or **16** results from the intermediate formation of haloallenes **13** or **14** which react with the benzeneselenenyl halide formed (Scheme 2).

Scheme 2



Table

1-Substituted 1,3-dihalo 2-phenylselenopropenes **15**, **16** and 1-substituted 1,2,3-trihalopropenes **17**, **18**.

N°	R	X	Yield %	Z/E ratio	^{1}H NMR (δ, ppm ; J, Hz)			
					Z (methylene)	E	Z (vinyl or methyl)	E
15a	H	Br	90	58/42	3.89	4.17	6.94 J = 1.0	6.68
16a	H	Cl	85	62/38	4.01	4.32	6.73 J = 1.2	6.56
15b	Me	Br	75	60/40	3.88	4.27	2.43	2.61
16b	Me	Cl	80	60/40	4.01	4.36	2.30	2.46
15c	Ph	Br	45	43/57	3.79	4.30		
17	-	-	32	70/30	4.19	4.61		
16c	Ph	Cl	80	45/55	3.93	4.40		
18	-	-	< 5		4.22	4.59		

Treatment of a selenide **10** with bromine or sulfuryl chloride in hexane at - 30°C produces instantaneously the adduct **11** (X = Br) or **12** (X = Cl) with a very good yield.[7] Their decomposition was achieved in dichloromethane at room temperature. In all cases, the vinylic selenides **15** (X = Br) or **16** (X = Cl) were isolated as a mixture of geometric isomers. Adduct **11c** also leads to 1-phenyl 1,2,3-tribromo propene **17**

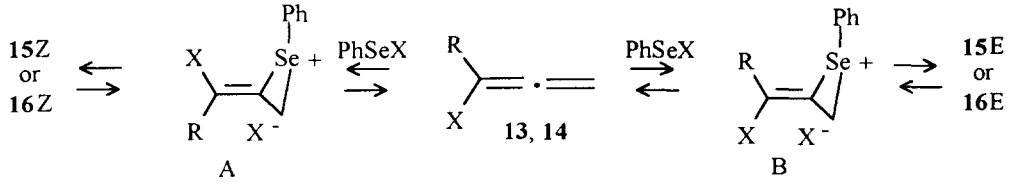
and to the propargylic bromide **8c** as shown by the ^{1}HNMR spectra. Decomposition of **12c** also gave 1,2,3-trichloro propene **18** and the corresponding propargylic chloride **9c** in very small amounts (Table).

The structures of compounds **15-18** were deduced from ^{1}H, ^{13}C NMR and mass spectra analysis. NOE experiments carried out on the dibromoselenide **15a** have allowed the characterization of the two geometric isomers. The decomposition of the adducts **11** and **12** were monitored by ^{1}H NMR in $CDCl_3$. For **11a**, we observed first, the formation of the bromoallene **13a**[8,9] followed by its transformation into the addition product **15a** E, Z. We have verified that bromoallene **13a** reacts with PhSeBr to afford the same E/Z-isomer ratio of **15a** in the same conditions. We have also verified that PhSeBr adds slowly to propargyl bromide **8a**, giving, to begin with, only the E-isomer.[10] Comparable results are observed for the decomposition of **13b**, **14a** and **14b** without identification of the intermediate allene.

PhSeCl[12] and PhSeBr[13] add very easily to allenes. A mixture of regioisomers is generally formed, the phenylseleno group always being linked to the sp-carbon atom. A slow E → Z isomerization could appear and an acid-catalyzed rearrangement of the addition product derived from allene and PhSeBr into E/Z mixture of 1-bromo 2-phenylselenopropene was observed.[13] Nevertheless, no study concerning haloallenes or phenylallene[14] has been reported.

We think that halovinylselenides **15** and **16** are formed through equilibria between haloallenes **13** or **14** and the corresponding halovinylseleniranium halides A and B (Scheme 3). The composition of the isomeric mixtures depends on the reaction conditions and the nature of the substituent.

Scheme 3



In the course of the decomposition of **11c**, bromopropyne **8c** appears after a few minutes beside the vinylselenide **15c** (E/Z : 85/15) and the tribromo derivative **17** (E/Z : 40/60) whose isomer ratio does not change until the adduct **11c** has totally disapeared (≃ 2 h).[16] The E/Z isomer ratio of **15c** changes to attain a value E/Z : 57/43 after four days. The composition becomes : **15c/17/8c** : 52/33/15. Two experiments have shown that paths a and b[17] are competitive in this case. Bromine adds to **8c** giving **17**E as the major product (E/Z : 82/18) after a few minutes.[19] **17**E is formed in a larger amount that for the decomposition of **11c**, and seems to be mainly formed from **13c**. PhSeBr and **8c** give **15c** E exclusively after a slow addition reaction (24 h, R.T.). We think that the formation of the tribromo compound **17** is the result of the equilibrium between PhSeBr and Br_2 :

$$2\ PhSeBr \rightleftarrows PhSeSePh + Br_2$$

It explains the important formation of **17** at the beginning of the decomposition and the presence of **8c** among the final products. The propargylic chloride **9c**[20] appears immediately from **12c** beside **16c** in a E/Z ratio : 4/1 after four days and the total disappearance of **9c**. The presence of trichloropropene **18** (E/Z : 3/1) is observed in the ^{1}H NMR spectra. We have verified that, PhSeCl adds to **9c**, in three hours, with exclusive formation of **16c**E[11] and that SO_2Cl_2 and **9c** lead to **18c** (E/Z : 1/1). These results are explained by initial formations of

allene **14c** and propyne **9c**. The equilibrium between PhSeCl and Cl_2 has here no importance and the vinylselenide **16c** is probably also formed from **9c**.

In summary, we have shown that the halo adducts derived from propargylic phenylselenides rearrange into 1,3-dihalo 2-phenylselenopropene derivatives through the intermediate formation of haloallenes. On some occasions, the corresponding trihalo compounds are also obtained from the isomeric halopropynes which appear in a competitive way. Work is in progress to study different experimental conditions of the adduct decomposition, the isolation of haloallenes and the extension of the reaction to allylic and propargylic phenylselenides with more complex structures.

REFERENCES AND NOTES

1. Duclos, J.F.; Outurquin, F.; Paulmier, C. *Tetrahedron Lett.*, **1993**, *34*, 7417-7420.
2. Saito, S.; Hamano, S.I.; Inaba, M.; Moriwake, T. *Synth. Comm.*, **1984**, *14*, 1105-1110.
3. Fitzner, J.N.; Pratt, D.V.; Hopkins, P.B. *Tetrahedron Lett.*, **1985**, *26*, 1959-1962.
4. The selenide **10a** is prepared as described.[3] **10b** and **10c** are obtained by nucleophilic substitution (PhSeSePh, $NaBH_4$, EtOH, 0°C) achieved on the bromides **8b**[5] and **8c**[6] synthesized from the corresponding alcohols.
5. Rambaud, R. *Bull. Soc. Chim. Fr.*, **1934**, 1342-1355.
6. Clive, D.L.J.; Manning, H.W.; Boivin, T.L.B.; Postema, M.H.D., *J. Org. Chem.*, **1993**, *58*, 6857-6873.
7. Adducts **11** and **12** can be stored at - 10°C for some days. The decomposition was carried out in dichloromethane, with stirring for 24 h at room temperature. After elimination of the solvent, the vinyl selenide **15** (or **16**) was purified by silicagel chromatography (elution : hexane). On some occasions the geometric isomers were separated. The bromo selenides **15aZ** crystallizes (F : 44°C) and slowly isomerizes to reach the equilibrium (Table). The tribromopropene **17** was obtained free of the selenide **15** but in mixture with bromopropynes **8**.
8. Bromoallene **13a** was prepared according to a literature procedure.[9]
9. Jacobs, T.L.; Bull, W.F. *J. Am. Chem. Soc.*, **1953**, *75*, 1314-1307.
10. PhSeBr adds more slowly than PhSeCl to 1,4-dichloro 2-butyne[11].
11. Bridges, A.J.; Fischer, J.W. *J. Org. Chem.*, **1984**, *49*, 2954-2961.
12. Garratt, D.G.; Beaulieu, P.L.; Ryan, M.C. *Tetrahedron*, **1980**, *36*, 1507-1514.
13. Halazy, S.; Hevesi, L. *Tetrahedron Lett.*, **1983**, *24*, 2689-2692.
14. 2,4-Dinitrobenzenesulfenyl chloride adds to phenylallene in acetic acid at room temperature. (Z) 3-Chloro 2-(2,4-dinitrophenylthio) 1-phenylpropene is formed.[15]
15. Izawa, K.; Okuyama, T.; Fueno, T. *J. Am. Chem. Soc.*, **1973**, *95*, 4090-4091.
16. Signals of the methylene protons appear at 5.20 and 5.16 ppm respectively for adducts **11c** and **12c**.
17. 1-Bromo 1-phenylallene **13c** is described but no NMR data were given.[18]
18. Larock, R.C.; Chow, M.S. *Organometalics*, **1986**, *5*, 603-604.
19. Bromine adds immediately to 1,4-dichloro 2-butyne.[11]
20. 3-Chloro 1-phenylpropyne **9c** was prepared according to a known procedure.[21]
21. Nagawa, M.; Ito, H.; Terada, A. *Jap. patent*, 10, 919 (**1973**). C.A., *61*, 13245h (**1964**).

(*Received in France* 16 *January* 1995; *accepted* 20 *February* 1995)