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HYDROLYTIC SELENOXIDE ELIMINATION REACTION FOR THE PREPARATION OF 2-CHLORO-1-OLEFINS

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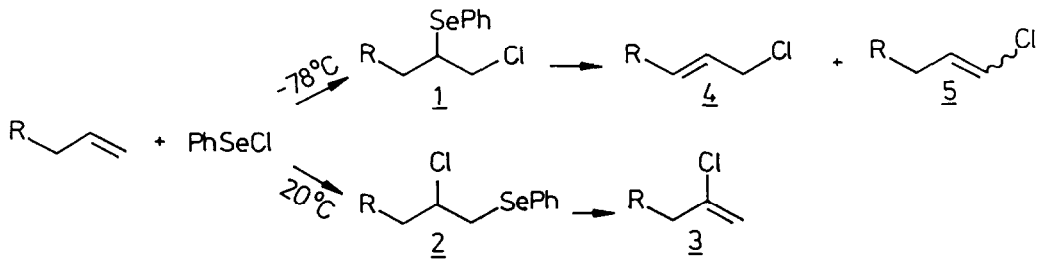
2-Chloro-1-olefins were synthesized in a regiocontrolled way from terminal olefins by a sequence involving Markownikoff-addition of PhSeCl, chlorination of the resulting β-chloroalkyl phenyl selenides with SO_2Cl_2 and, after recrystallization, hydrolysis/selenoxide elimination in a two-phase system.

Vinyl chlorides are becoming increasingly important building blocks for synthetic organic chemists. By Lewis-acid assisted hydrolysis they can be mildly converted to carbonyl compounds.[1] They have also recently been shown to undergo metal promoted homocoupling to give 1,3-dienes.[2] Other interesting applications include the chloro olefin annelation reaction[3] and the preparation of vinylic Grignard reagents.[4]

The inavailability of vinyl chlorides with well-defined stereo- and regiochemistry has been a major restriction to their use in synthesis. This is also true for the 2-chloro-1-olefins. Attempts to prepare these materials from 2-alkanones by treatment with phosphorus pentachloride resulted in complex mixtures containing the 2-chloro-1-olefin together with the 2,2-dichloroalkane and the E- and Z-isomers of the 2-chloro-2-olefin.[5-7] Dehydrochlorination of 1,2-dichloroalkanes[8,9] afforded the 2-chloro-1-olefin together with the E- and Z-1-chloro-1-olefin. 2,2-Dichloroalkanes[5,10] reacted similarly. The addition of hydrochloric acid to terminal acetylenes is also not a synthetically useful reaction giving mixtures of 2,2-dichloroalkanes, 2-chloro-1-olefins as well as cyclobutane derivatives.[11]

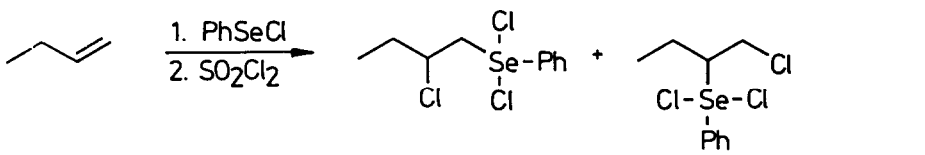
The most promising method so far for the preparation of 2-chloro-1-olefins seems to be the reaction of 2,3-dichloropropene with Grignard reagents[3,7] or arylpalladium salts.[12] $FeCl_3$ has been reported to convert terminal acetylenes in low yields to 2-chloro-1-olefins.[13]

We report here the regiocontrolled preparation of 2-chloro-1-olefins from terminal olefins using selenium methodology. Phenyl selenenyl chloride is known[14] to add reversibly to terminal olefins producing regioselectively 1-chloro-2-phenylselenoalkanes 1 at low temperature (-78 °C, kinetic product) and 2-chloro-1-phenylselenoalkanes 2 at elevated temperature (+20 °C, thermodynamic control) (eq.1). It was our intention to use the newly developed[15] hydrolytic variation of the selenoxide elimination reaction to convert the thermodynamically favoured selenides 2 into 2-chloro-1-olefins 3 (eq.1).

(1) 

This would require an oxidation of the selenide to a selenium dichloride and its subsequent hydrolysis/selenoxide elimination. It would be essential for a completely regiocontrolled synthesis of 2-chloro-1-olefins that the thermodynamic product 2 could be obtained free of its isomer 1. If present, compound 1 would be expected to undergo a non-regiospecific elimination[16] to give a mixture of 1-chloro-2-olefins 4 and 1-chloro-1-olefins 5 (eq.1).

Our initial results with 1-butene are shown below (eq.2). The isomer distribution of the labile β-chloroalkyl phenyl selenides was conveniently "frozen" by a sulfuryl chloride chlorination (a control experiment showed no interconversion of the two selenium(IV) compounds in chloroform solution) and determined by ^1H NMR.

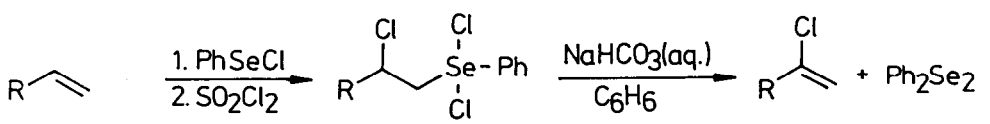
(2) 

(13 : 87) -78°C, CH_2Cl_2

(93 : 7) 20°C / 24 h, $CHCl_3$

Fortunately, the small amount of anti-Markownikoff isomer that was formed under thermodynamic conditions could be efficiently removed by crystallization of the crude reaction mixture from ether/light petroleum (b.p. 40-60 °C). The yields of a number of other representative 2-chloroalkyl phenyl selenium dichlorides are presented in Table 1.

The final hydrolytic selenoxide elimination reaction (eq.3) was performed in a two-phase system containing benzene and aqueous sodium hydrogen carbonate. At ambient temperature the elimination proceeded very slowly but at 100 °C the reaction was usually completed within 4 h as determined by the disappearance of the starting material (TLC). The formation of 2-chloro-1-olefins 7 was always very clean (for yields see Table 1) and diphenyl diselenide was the only observed by-product that had to be separated (diphenyl diselenide is a secondary product of phenylselenenic acid, PhSeOH, which is always formed in the elimination reaction). This was most conveniently performed by shaking of the benzene layer with hydrogen peroxide until the yellow colour faded away. The 2-chloro-1-olefin was then obtained after alkaline extraction, evaporation of the solvent and Kugelrohr-distillation. A representative experimental procedure is given.[17]

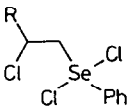
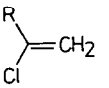
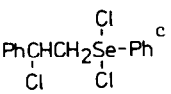
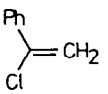
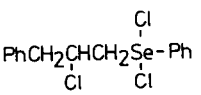
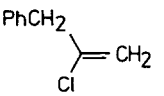
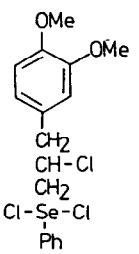
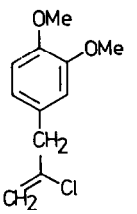
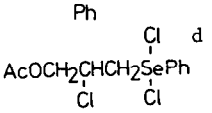
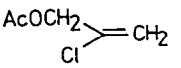
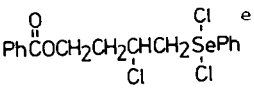
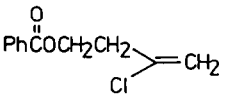
(3) 

6 7

The chlorination/hydrolysis sequence for effecting selenoxide elimination is easily performed and avoids the use of ozone which is otherwise required for the synthesis of vinylic halides using selenium methodology.[18,19] Furthermore, it has the definite advantage of involving an isolable selenium(IV)-intermediate which can be recrystallized to high purity.

Attempts to apply the chlorination/hydrolysis sequence for the preparation of 2-bromo-1-olefins[19] was unsuccesful. The required 2-bromoalkyl phenyl selenium dichlorides could be readily prepared in high yields from terminal olefins and PhSeBr, but their hydrolysis produced only small amounts of the desired vinyl bromides due to competing side-reactions.

TABLE 1. Preparation of 2-chloro-1-olefins via selenoxide elimination

starting material	intermediate Se(IV)-compound	yield(%)	product[a]	yield(%)
	 **6**		 **7**	
1-octene	a R=C_6H_{13}	85	a R=C_6H_{13}	80
1-decene	b R=C_8H_{17}	85	b R=C_8H_{17}	92
1-dodecene	c R=$C_{10}H_{21}$	82	c R=$C_{10}H_{21}$	89
1-tetradecene	d R=$C_{12}H_{25}$	85	d R=$C_{12}H_{25}$	85
1-hexadecene	e R=$C_{14}H_{29}$	78	e R=$C_{14}H_{29}$	96
11-dodecen-1-yl acetate	f R=$(CH_2)_{10}OAc$	77	f R=$(CH_2)_{10}OAc$	94
			g R=$(CH_2)_{10}OH$	89[b]
styrene	 [c]	93		78
allyl benzene		82		79
eugenol methyl ether		78		90
allyl alcohol	 [d]	91		64
3-buten-1-yl benzoate	 [e]	not isolated		83

[a] All new compounds exhibited satisfactory spectroscopic (^{1}H NMR) and analytical and/or exact mass data.

[b] This compound was obtained when the crude reaction product was treated with $NaBH_4$ in EtOH under nitrogen until the yellow colour of diphenyl diselenide had disappeared[4] (reductive work-up). Ethyl ether and water were then added and the organic phase separated by using a syringe through a septum.

[c] This compound was regiospecifically prepared from styrene and phenyl selenium trichloride using dry ether as solvent.

[d] Allyl alcohol was allowed to react for 3 days with PhSeCl in chloroform. After sulfuryl chloride chlorination the product was acetylated in a refluxing mixture of acetyl chloride and chloroform.

[e] The PhSeCl-adduct isomerized very slowly at ambient temperature and was therefore heated at reflux in chloroform for 4 h.

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17. Typical procedure. 2-Chloro-1-dodecene (7c): PhSeCl (1.0 g, 5.2 mmol), was stirred at ambient temperature in dry $CHCl_3$ (5 mL) with 1-dodecene (0.88 g, 5.2 mmol) for 24 h. SO_2Cl_2 (0.80 g, 5.9 mmol) was then added dropwise and the reaction mixture left for 2 h. After evaporation of the solvent and crystallization from ether/light petroleum (b.p. 40-60 °C) 1.85 g (82%) of compound 6c was obtained, m.p. 60-1 °C. Anal. Cald. for $C_{18}H_{29}Cl_3Se$: C, 50.19; H, 6.79. Found: C, 50.11; H, 6.75. ^1H NMR δ: 0.88 (t, 3 H), 1.27 (s, 14 H), 1.95 (m, 2 H), 4.46 (dd, 1 H J = 5.7 Hz and 10.4 Hz), 4.54 (dd, 1 H J = 9.1 Hz and 10.4 Hz), 4.94 (m, 1 H), 7.51-7.55 (several peaks, 3 H), 7.95 (m, 2 H), Compound 6c (7.5 g, 17.4 mmol) was dissolved in benzene (100 mL) and stirred at 100 °C with an aqueous solution (50 mL) of $NaHCO_3$ (4.4 g, 52.3 mmol) in a flask equipped with a reflux condenser. After 4 h the yellow organic phase was separated and shaken with 30% H_2O_2 (40 mL) until the yellow colour had disappeared (5-15 min vigorous shaking). Kugelrohr-distillation afforded 3.10 g (89%) of compound 7c, b.p. 53-4 °C/5.10^{-2} mm Hz. Anal. Calcd. for $C_{12}H_{23}Cl$: C, 71.08; H, 11.43. Found: C, 71.43; H, 11.46, ^1H NMR δ: 0.88 (t, 3 H), 1.27 (s, 14 H), 1.55 (m, 2 H), 2.32 (t, 2 H), 5.09-5.13 (several peaks, 2 H).
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