SYNTHESES USING 1-LITHIO 1-SELENO ALKENES

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The synthesis of 1-seleno alkenes by concomitant carbon-carbon bond formation and their transformation to selenium free molecules are disclosed

Several papers ¹ have recently emphasized the synthetic usefulness of functionalized selenides in which the selenenyl molety is attached to an sp^3 carbon atom. The chemistry of their vinylic analogues is however much less known ²,³.

We report herein our preliminary results on the connective synthesis of methyl alkenylselenides which we found particularly valuable to produce a variety of selenium free olefinic compounds including alkenes, alkenyl bromides and allenes.

SCHEME I



l-methylseleno-l-lithio alkenes, chosen as the partner for introducing the selenenyl moiety, were unknown Two phenylseleno analogues were however already prepared by Seebach 4 from l,lbis (phenylseleno) styrene and n-BuLi and by us 3a, by Raucher 3b, and by Reich 3c, d, by metallation of phenylselenoalkenes with metalloamides.

We were unable untill now to exclusively metallate methylseleno alkenes at the vinylic position ⁵ We however observed that the carbon selenium bond, in readily available ⁶ 1,1 bis (methylseleno)-alkenes <u>1</u> is quantitatively cleaved at $-78^{\circ}(0.5hr)$ by n-BuLi in tetrahydrofurane (THF) or t-BuLi if THF is replaced by ether, producing the desired lithic derivative which was trapped by various electrophiles (see Scheme II). The resulting crude products, contaminated with 10-20% of the vinylselenide arising by formal protonation of the carbanion usually consisted in a $\sim 40/60$ mixture of the Z/E stereoisomers

For example, 1-methylselenododecene <u>3a</u>, 1-deutero-1-methylselenododecene <u>3b</u> (soiled with 10-20% of 1-methylseleno-1-dodecene), 2-methyl-seleno-2-tridecene <u>3c</u>, methylseleno substituted - allyl alcohols <u>3d-h</u>, - α,β -unsaturated aldehydes <u>3t</u>, - esters <u>3j</u> and - acids <u>3k</u> were respectively prepared in high yield (see Scheme II) by reacting 1-lithio-1-methylseleno-1-dodecene <u>2</u> used as model respectively with water, deuterated water, methyl iodide, aldehydes and ketones, N,N-dimethylformamide, methyl chloroformate and carbon dioxyde



The selective removal of the selenenyl monety from the vinyl selenides $\underline{3}$ was the next goal to achieve and we first focused our attention on the reduction of the C-Se bond. We found that tributyltin hydride ⁸ (3eq) selectively reduces the selenium-sp² carbon bond of vinylselenides. Thus 2-undecene $\underline{4\ell b}$ (Scheme III), allyl alcohols $\underline{4e \cdot k}$ (Scheme IV) and even the α, α' -allyl alcohol $\underline{4h}$ are readily produced from the corresponding methylseleno vinyl derivatives in the presence of azo-bis-isobutyronitrile (AIBN) [Bu₃SnH(3eq), AIBN(0.leq), toluene, 90°, 3hr].

SCHEME III



SCHEME IV

$nC_{10}H_{21}CH = C \xrightarrow{OH}_{B_1} OH$			Bu ₃ SnH/AIBN	$nC_{10}H_{21}CH = C \xrightarrow{H}_{R_1} \xrightarrow{OH}_{R_2}$	
3	$\frac{R_1}{R_1}$	2 <u>R2</u>		4	Yield
<u>3c</u>	^{nC} 6 ^H 13 ⁻	н		<u>4e</u>	78%
36	с ₆ н ₅ -	сн ₃		46	80%
<u>3</u> g	^{nC} 6 ^H 13 ⁻	сн3		<u>4g</u>	88%
<u>3h</u>	-сн ₂ -сн ₂ -сн ₂ -сн=сн-			<u>4h</u>	80%

Interestingly, the other mode of cleavage [Se - $C sp^3$ bond cleavage , leading to the divinyl diselenide 4La (Scheme III)after work up ⁹, was obtained on reaction with lithium in ethylamine ¹⁰.

We have previously shown ¹¹ that methyl or phenyl alkylselenides can be transformed to alkylbromides on reaction with bromine under various experimental conditions. We found now that in the case of vinylselenides the solvent used has a crucial influence on the nature of the product formed on reaction with bromine. Thus 2-bromo 2-underene 4lc (Schemc III) is produced on reaction of 2-methylseleno-2-undecene with bromine 2a,d,f in aromatic solvents (benzene or chlorobenzene). The same compound and 3-bromo-2-undecanone are formed in methylene chloride in the presence or in the absence of triethylamine, and 2-undecanone is produced in ethanol (Scheme V).

SCHEME V

 $nC_8H_{17}CH = C$ CH_3 CH_3 Br_2 25° , 15hr $nC_8H_{17}CH = C$ CH_3 $H_{17}CH = C$ $H_{17}CH = C$
 CH2C12
 43%

 CH2C12/Et3N
 60%
 4le 24% 24%

We will report in due course the stereochemistry of these reactions which have not yet been determined.

Finally, β -hydroxyselenides in which the selenium atom is linked to an sp³ carbon atom produce high yields of olefins on reaction 1^2 with PI3 or P2I4. The reaction is, as expected, much more difficult to perform in the case of vinylselenides. As a preliminary result we observed that 1-hydroxy-1-phenyl-2-methylseleno 2-tridecene 3d leads to the corresponding allene in 30% yield when reacted at room temperature in methylene chloride with P_2I_4 in the presence of triethylamine (Scheme VI).

SCHEME VI

4d

Generalisation of such transformation is under study in our laboratory.

The authors are grateful to Roussel-Uclaf (France) and to F U.N.D P. (Namur, Belgium) for financial support.

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(Received in UK 24 May 1982)