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NEW SYNTHETIC ROUTES TO β-HYDROXYSELENIDES AND β-AZIDOSELENIDES.

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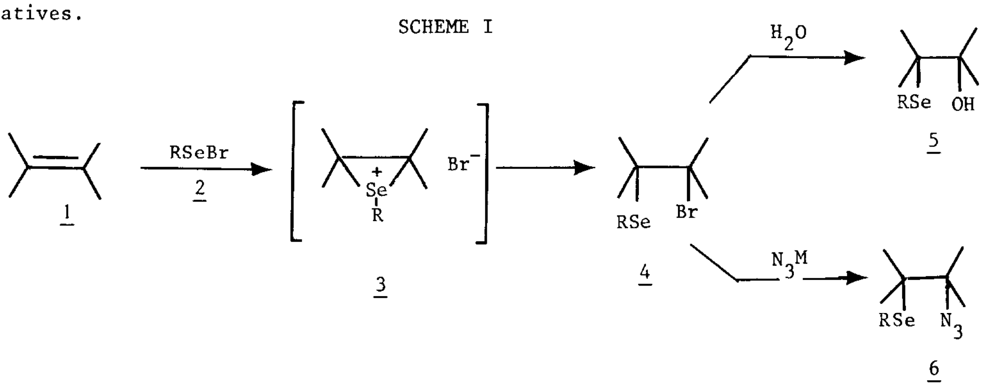
β-hydroxy and yet unknown β-azidoselenides are prepared from β-bromophenyl and yet unknown β-bromomethylselenides. First evidence of selective reaction of selenenylbromides with the less substituted double bonds of polyolefins, is disclosed.

Addition of pseudohalides containing a selenyl moiety[2] to olefins has attracted wide interest in organic synthesis and allowed the synthesis of selenides substituted in the β positi by an halogen atom[3,4], an alkoxy[3c,5], an acetyl[3a,de,6], an hydroxyl[7] or an amino group [8,9].

Some of these derivatives were prepared from β-halogenoselenides via a substitution reaction which take advantage of neighbouring group participation of the selenyl moiety. As expected the reactivity of β-halogenoselenides should be modulated by the nature of the other group (R) attached to the selenium atom and β-bromomethylselenides are expected to be more reactive than phenylseleno analogues although the nucleophilic attack also can occur on the selenium atom leading back to the olefin[10].

This letter presents our preliminary observations concerning the addition of phenyl 2' and methyl 2" selenenyl bromides to olefins, the transformation of the resulting adduct 4 to β-hydroxyselenides 5 and β-azidoselenides 6 which are further transformed to selenium free derivatives.

SCHEME I



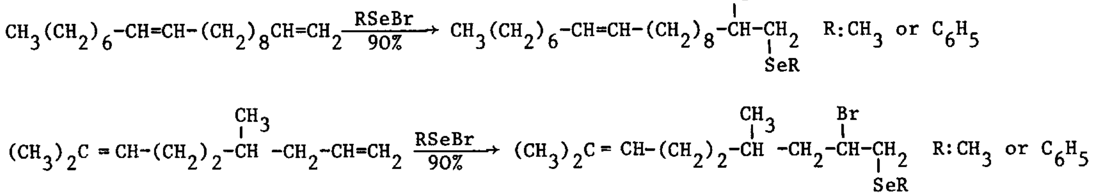
Methylselenenyl bromide was readily prepared (0.1 hr) by mixing together at -10°, bromine in CH_2Cl_2 (1 eq mol) to dimethyl diselenide (1 eq) in the same solvent to get a 1M final black red solution which discloses a major peak at 3.16 ppm by NMR (TMS as standard). This solution was further used with olefins.

Phenylselenenyl bromide was prepared as already described[3] and reacted with olefins in CH_2Cl_2 or in CH_3CN [3f].

Whatever the reagent used, the reaction occurs readily at -10° with terminal olefins such as 1-octene or 1-dodecene and with cyclohexene producing the corresponding β bromomethylselenides[11] 4'' and known β bromophenylselenides[3] 4' in high yield (∿ 90% of crude product) but is more difficult with straight chain olefins especially when methylselenenyl bromide is used. Thus 2E, 2Z and 4Z octenes lead quantitatively to β-bromophenylselenides whereas methylseleno-analogues are obtained in ∿40% yield and 9E octadecene is reluctant to the addition of both reagents.

Related to these observations is the finding that both reagents add selectively (100%) and quantitatively on the less substituted double bond of polyolefins[12,13] as examplified in Scheme II.

SCHEME II.



$$CH_3(CH_2)_6\text{-}CH{=}CH\text{-}(CH_2)_8CH{=}CH_2 \xrightarrow[90\%]{RSeBr} CH_3(CH_2)_6\text{-}CH{=}CH\text{-}(CH_2)_8\text{-}\overset{\displaystyle Br}{\overset{|}{C}H}\text{-}\underset{\displaystyle SeR}{\underset{|}{CH_2}} \quad R{:}\,CH_3 \text{ or } C_6H_5$$

$$(CH_3)_2C{=}CH\text{-}(CH_2)_2\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow[90\%]{RSeBr} (CH_3)_2C{=}CH\text{-}(CH_2)_2\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{-}CH_2\text{-}\overset{\displaystyle Br}{\overset{|}{C}H}\text{-}\underset{\displaystyle SeR}{\underset{|}{CH_2}} \quad R{:}\,CH_3 \text{ or } C_6H_5$$

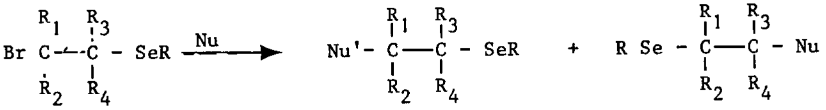
This selectivity, which is the reverse of the one observed when polyolefins are reacted with electrophilic reagents, should be very important in organic synthesis especially if the β bromoselenide formed can be further transformed.

The second part of this report discloses our preliminary results directed toward this objective using saturated β-bromoselenides 4 as models. We found that they can be transformed (Scheme III) in high yield to β-hydroxyselenides 5 and as yet unknown β-azidoselenides 6 when reacted with water (method A) or sodium azide (method B) in trifluoroethanol . This solvent is the best among those used and moreover allows the selective (>99%) formation of 2-hydroxy-selenides 5 from 2-bromoselenides 4 (scheme III). Unfortunately such selectivity is not observed in β-azidoselenides 6.

Other solvents such as DMF or HMPT are much less valuable. The reactions are much slower, especially with long chain derivative and lead to a mixture of regioisomers in cases of 2-bromo-selenides [DMF/H_2O(method C) ; DMF/LiN_3 (method D)].

During the course of this research, we interestingly found that β-bromophenylselenides are transformed to β-hydroxyselenides when simply stirred with silicagel (Merck 7747) in CH_2Cl_2 (method E).

SCHEME III



$$Br\,\underset{\displaystyle R_2}{\overset{\displaystyle R_1}{C}}\text{—}\underset{\displaystyle R_4}{\overset{\displaystyle R_3}{C}}\text{ - }SeR \xrightarrow{Nu} Nu'\text{- }\underset{\displaystyle R_2}{\overset{\displaystyle R_1}{C}}\text{—}\underset{\displaystyle R_4}{\overset{\displaystyle R_3}{C}}\text{ - }SeR \quad + \quad R\,Se\text{ - }\underset{\displaystyle R_2}{\overset{\displaystyle R_1}{C}}\text{—}\underset{\displaystyle R_4}{\overset{\displaystyle R_3}{C}}\text{ - }Nu$$

Nu' : OH 5a 5b

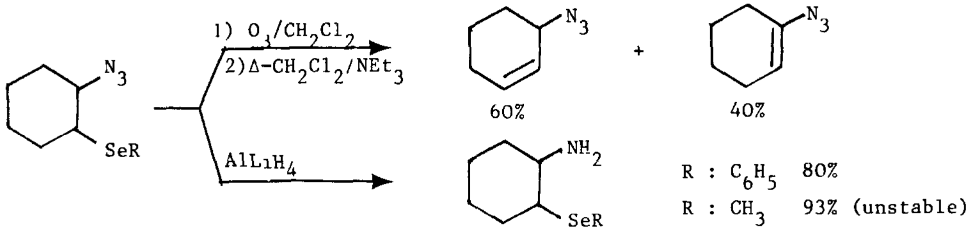
Nu' : N_3 6a 6b

4					Overall yield in 5(5a %)			Overall yield in 6 (6a %)	
R	R_1	R_2	R_3	R_4	method A	method C	method E	method B	method D
CH_3	C_6H_{13}	H	H	H	-	63(69) 74hr	15(-)	65^+(50) 10hr	-
C_6H_5	C_6H_{13}	H	H	H	74(99) 2hr	68(91) 72hr	72(-) 18hr	76^+ 6hr	-
CH_3	$C_{10}H_{21}$	H	H	H	74(99) 4hr	15(-)	-	66(57) 3.5hr	70(40) 5hr
C_6H_5	$C_{10}H_{21}$	H	H	H	-	-	77 16hr	92(43) 10hr	-
CH_3	$CH_2(CH_2)_2$	CH_2	H	H	80 3hr	78 5hr	-	80 1.9hr	80 3hr
C_6H_5	$CH_2(CH_2)_2$	CH_2	H	H	-	70 17hr	70 15hr	84 3hr	72 1hr
C_6H_5	C_5H_{11}	H	H	CH_3*	-	90 3hr	-	77^+ 16hr	-
C_6H_5	C_5H_{11}	CH_3	H	H**	-	75 17hr	-	60^+ 18hr	-

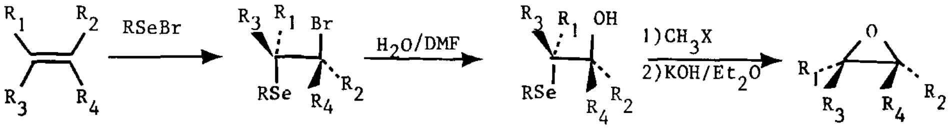
* obtained from 2E octene ** obtained from 2Z octene + performed in methanol

Finally, we present in the last section examples of selective activation on some of the above products. Thus, 1-azido-2-phenylseleno-cyclohexane is oxidized to the corresponding selenoxide with ozone in CH_2Cl_2 and further decomposed by heating at reflux of the solvent in the presence of triethyl amine, to a mixture of 3-azido (60%) and unknown [14] 1-azidocyclohexene (40%) which are obtained in 50% overall yield and which are quantitatively separated.

1-Azido 2-phenylseleno and methylseleno cyclohexane are quantatively reduced to the corresponding amine when reacted with lithium aluminium hydride in ether (the methylseleno) derivative is unstable).



On the other hand β-hydroxyselenides are transformed to the corresponding epoxides [15] and when 2E and 2Z octenes are subjected to the reactions disclosed in the following scheme, trans and cis epoxides are stereoselectively (>95%) obtained. These results suggest that the substitution reaction on β-bromoselenides occurs, at least for these cases, with retention of configuration.



Work is actually in progress to perform substitution reaction with other nucleophiles, to transform β-azidoselenides selectively to the corresponding amines or aziridines and to allow the selective formation of epoxides and aziridines on the less substituted carbon carbon double bond of a polyolefin.

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