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REACTIVITY OF MIXED SULFO-SELENO ACETALS AND OXO-SELENO ACETALS WITH N-BUTYLLITHIUM : A NEW ROUTE TO SUBSTITUTED EPOXIDES (1).

A. Anciaux, A. Eman, W. Dumont and A. Krief*
Department of Chemistry, Facultés de Namur,
61, rue de Bruxelles, B-5000 Namur (Belgium).

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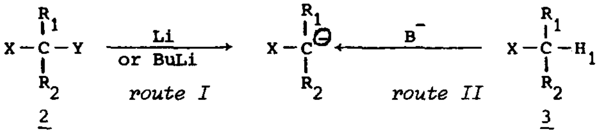
α-Heterosubstituted carbanions 1 are highly reactive intermediates in organic synthesis as carbenoïds or carbenes. These reagent 1 are well known if $R_1 = R_2 = H$ and are generally prepared via halogen-metal exchange from -hetero substituted alkyl halides 2 : *route I* or by action of a suitable base on compounds 3 : *route II (Scheme I).*

Scheme I

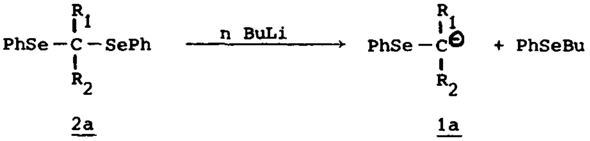


X = F, Cl, Br, R_2N, RS, RO, RSe, R_3Si, R_3P.

Nevertheless higher homologs of 1 (R_1 = H, Alkyl ; R_2 = Alkyl) are much less well known (2) due to the low acidity of H_1 in 3 which makes *route II* difficult and attempted application of *route I* leads to an olefin by β elimination reaction or to other side reactions.

We (3) and others (4) recently achieved the first synthesis of highly substituted α-selenonio carbanions 1a via the easy cleavage of the C-Se bond in selenoacetals 2a with n-butyllithium *(Scheme II).*

Scheme II



The present communication reports the behaviour of mixed, sulfo-selenoacetals 2b and oxo-selenoacetals 2c with n-butyllithium. The generation of unknown highly substituted α-sulfocarbanion 1b (1-4) is described, as well as their use for a convenient synthesis of epoxide (5,6).

For instance the sulfo-selenoacetals 2b (7) are readily cleaved by n-butyllithium in THF (- 78° C, 1 hr) to give butyl phenyl selenide and α-sulfo-carbanions 1b. The highly nucleophilic α-sulfo-carbanion 1b adds a variety of carbonyl compounds, even highly enolisable ones such as deoxybenzoine, producing the β-hydroxysulfides 5 in fair yield*(scheme III, table I)*.

Scheme III

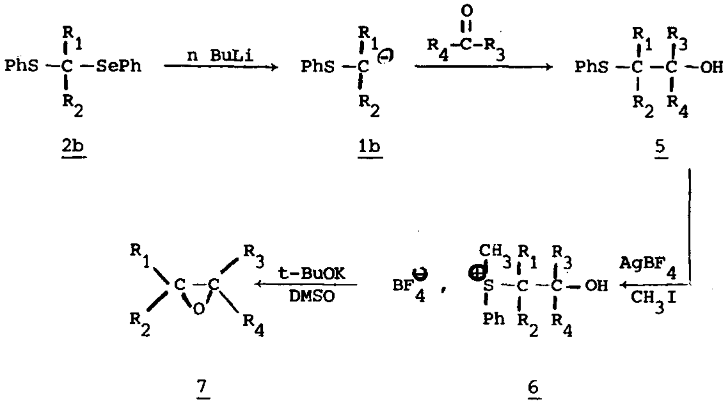


Table I

R_1	R_2	R_3	R_4	β-hydroxysulfide 5	Epoxide 7
H	H	H	C_6H_5	94 %	55 %
H	H	H	nC_6H_{13}	84	50
H	H	$-(CH_2)_2-CH(tC_4H_9)-(CH_2)_2-$		58	60
H	CH_3	C_6H_5	$CH_2-C_6H_5$	92	60
H	CH_3	$-CH_2-(CH_2)_3-CH_2-$		56	60
H	CH_3	H	C_6H_5	86	45
H	CH_3	H	nC_6H_{13}	45	34
CH_3	CH_3	H	nC_6H_{13}	57	
CH_3	CH_3	C_6H_5	$CH_2-C_6H_5$	30	
CH_3	CH_3	$-CH_2-(CH_2)_3-CH_2-$		51	

yields of 5 and 6 refer to purified products and spectroscopic data are in accord with the proposed structures.

It should be mentioned that the parent α-sulfo-carbanion (R_1-R_2=H) was previously prepared from methyl phenyl sulfide by hydrogen abstraction with n-butyllithium (6,8). However the same procedure cannot be applied to higher homologue (R_1 = alkyl) due to metalation of the phenyl sulfide in the ortho-position (9).

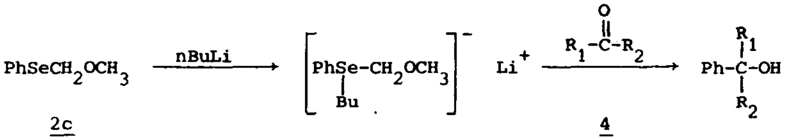
As synthetic application of the C-Se bond cleavage in mixed sulfo selenoacetals we describe the connective (7) synthesis *(Scheme III, table I)* of epoxides, including some of them which cannot be produced by conventional connective methods (6,10) such as 1-benzyl-1-phenyl-2-methyloxirane.

β-Hydroxysulfonium salts 6 are readily formed when β-hydroxysulfides 5 are treated with methyl iodide in the presence of silver tetrafluoroborate (neat 25° C, 2 hrs); subsequent treatment of the crude salt with base (tBuOK-DMSO, 25° C, 2 hrs) produces the desired epoxide 7 and thioanisole.

Unfortunately, rearranged carbonyl compounds and unidentified products (11) are obtained when β-hydroxysulfides (R_1, R_2=alkyl) are treated under our conditions (CH_3I-$AgBF_4$) and tetrasubstituted epoxides are not yet accessible by this way.

Finally, we studied the reaction of n-butyllithium with the oxo-seleno acetal 2c (THF, -78° C, 1 hr). In this case, we observe the preponderant cleavage of the Se-C bond leading to phenyllithium rather than to the α-alkoxy carbanion 1c as shown by the phenylated products obtained by adding carbonyl compounds in the medium *(Scheme IV)*.

Scheme IV

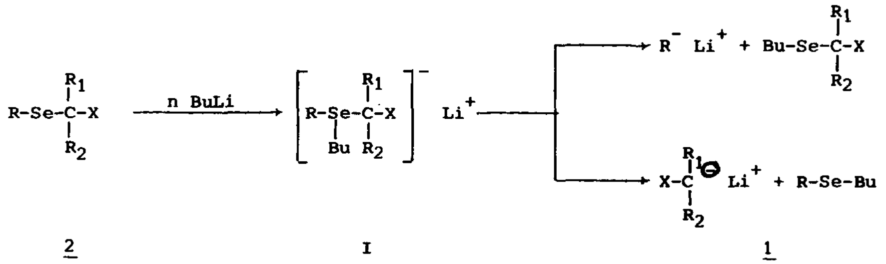


R_1 = H ; R_2 = Ph 70% yield

R_1 = H ; R_2 = nC_6H_{13} 85 "

R_1, R_2 = $-(CH_2)_5-$ 60 "

We are not yet able to determine the factors which decide the mode of cleavage of the selenides 2 by n-butyllithium; following an hypothesis the complex I decomposes to give the best stabilised carbanion. The *d* orbital stabilisation should be of great importance.



Work is actually in progress to determine these modes of cleavage in compound 2 (Y = RSe; X = SiR_3, NR_2, PR_2 and halogens). Nevertheless the C-Se bond cleavage should provide an original and potent way of carbanion generation.

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