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NEW SYNTHETIC ROUTES TO VINYL SULFIDES, KETENE THIOACETALS AND THEIR SELENO ANALOGUES FROM CARBONYL COMPOUNDS

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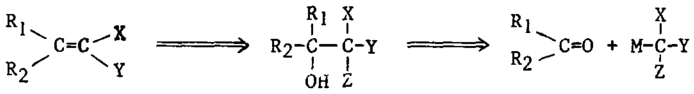
Title compounds have been prepared from carbonyl compounds by formal removal of hydroxyl and sulfenyl or hydroxyl and selenyl moieties from the corresponding functionalized β-hydroxysulfides or β-hydroxyselenides.

The β-elimination of two heteroatomic moieties is a method of choice for the regioselective formation of carbon-carbon double bonds.

The reaction is particularly valuable if one of the two leaving groups is an hydroxyl group since the starting material can be formally prepared from readily available aldehydes or ketones and α-heterosubstituted organometallics [1].

SCHEME I



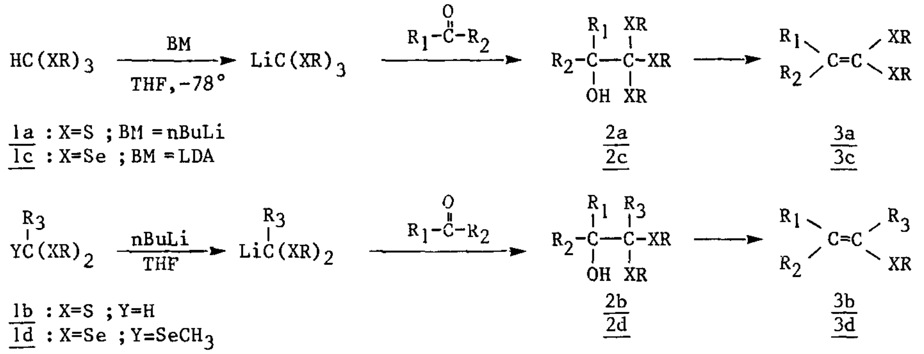
Ketene thioacetals 3a, vinyl sulfides 3b and their seleno analogues 3c and 3d have been already prepared along these lines by elimination of the hydroxyl group with a silyl [2,3] [Scheme I, $Z=Si(R)_3$] or a phosphoryl [4,5] moiety [Scheme I, $Z=\overset{+}{P}R_3$, $\overset{+}{P}(OMe)_3$].

The transformation however requires the use of α-heterosubstituted organometallics bearing different heteroatoms on the carbanionic center.

Identically heterosubstituted organometallics should be more suitable since they are usually more easily prepared [6].

We found that β-hydroxyorthothioesters 2a, β-hydroxythioacetals 2b and their seleno analogues 2c and 2d, easily prepared from carbonyl compounds and orthothioesters [1b,7], thioacetals [1b,8] and orthoselenoesters [9] respectively according to described methods[1,2,7-9] are cleanly transform to olefinic products [6] on reaction with P_2I_4 or PI_3 (1 mol.eq/NEt_3/CH_2Cl_2, 0°C, 0.5-0.75hr).

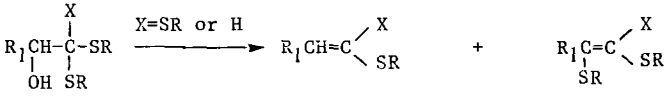
SCHEME II



The reaction, which is reminiscent of the synthesis of olefins from β-hydroxysulfides [10] and β-hydroxyselenides [11], leads to the desired products 3a, 3b, 3c and 3d in good to excellent yield (Scheme II, Table) by removal of the hydroxyl and sulfenyl or selenyl moieties.

A major change in the course of the reaction is seen to occur whenever a secondary alcohol is present in the thio derivatives 2a and 2b (Scheme III, Table) : variable amounts of rearranged products 4a and 4b are formed [14] besides the expected thioacetals 3a and 3b.

SCHEME III



2a,b 3a,b 4a,b

Rearranged products of this type were not detected when the alcohols 2a were tertiary nor with secondary or tertiary alcohols in the selenium series.

It is interesting to point out a significant increase in the extent of the reaction on going from β-alkyl to β-cyclopropyl to β-aryl β-hydroxyorthothioesters 2a. This trend suggests the importance of the stabilization of the initial carbenium ion like intermediate.

During this work, we also had the occasion to use $SOCl_2$ [12,13] in place of P_2I_4 ; we observed that the rearranged products 4 are quite exclusively formed whenever they were present even as a by-product in the reaction with PI_3 and P_2I_4 (see Table).
These migrations are connected to the ones observed by Warren [15] in closely related compounds ; however, the alternative pathways available in the previous study [15] are not available in our case. Interpretation of these results is not quite straightforward and needs more detailed investigations.

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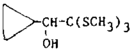
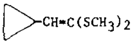
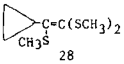
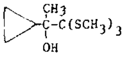
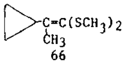
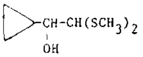
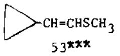
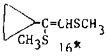
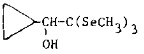
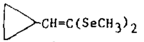
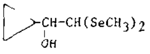
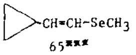
TABLE

Starting 2	Prepared from () yield		Reagent used	Products formed (yield %)	
$nC_5H_{11}\underset{OH}{CH}-C(SCH_3)_3$	(1a)	80%		$nC_5H_{11}CH=C(SCH_3)_2$	$nC_5H_{11}\underset{CH_3S}{C}=C(SCH_3)_2$
			P_2I_4	47	13
			PI_3*	63	13
			$SOCl_2$	00	85
	(1a)	66%			
			P_2I_4	31	28
			$SOCl_2$	00	90
$C_6H_5\underset{OH}{CH}-C(SR)_3$	(1a)			$C_6H_5CH=C(SR)_2$	$C_6H_5\underset{RS}{C}=C(SR)_2$
R=CH_3		85%	P_2I_4	10	60
			PI_3	7	68
R=C_6H_5		73%	P_2I_4	31	41
	(1a)	83%			
			P_2I_4	66	
			PI_3	69	
			$SOCl_2$	69	
$C_6H_5\overset{CH_3}{\underset{OH}{C}}-C(SCH_3)_3$	(1a)	66%		$C_6H_5-\overset{CH_3}{C}=C(SCH_3)_2$	
			P_2I_4	64	
	(1b)	76%			
			P_2I_4	53***	16*
			$SOCl_2$	trace	50***
$nC_7H_{15}\underset{OH}{CH}-CH(SC_6H_5)_2$	(1b)	77%		$nC_7H_{15}CH=CHSC_6H_5$	$nC_7H_{15}\underset{C_6H_5S}{C}=CHSC_6H_5$
			P_2I_4**	73***	8***
$nC_{10}H_{21}\underset{OH}{CH}-C(SeCH_3)_3$	(1c)	63%		$nC_{10}H_{21}CH=C(SeCH_3)_2$	
			P_2I_4	85	
			PI_3	70	
			$SOCl_2$	18	
	(1c)	62%			
			P_2I_4	85	
$C_6H_5\underset{OH}{CH}-C(SeR)_3$	(1c)			$C_6H_5CH=C(SeR)_2$	
R=CH_3		80%	P_2I_4	70	
R=C_6H_5		79%	P_2I_4	74(3a)	
			PI_3	86	
	(1c)				
		46%	P_2I_4	65***	
$nC_{10}H_{21}\underset{OH}{CH}-\underset{CH_3}{C}(SeCH_3)_2$	(1c)			$nC_{10}H_{21}CH=\underset{CH_3}{C}-SeCH_3$	
		35%	P_2I_4	90***	

* DMF was used as the solvent instead of NEt_3/CH_2Cl_2

** Refluxing for 1hr at 55° is required for this reaction to occur

*** Obtained as a mixture of Z and E stereoisomers

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Experimental

Synthesis of 1,1-bis(methylseleno)-1-dodecene

1,1,1-tri(methylseleno)-2-hydroxydodecane (0.35g, 0.75 mmol.) and triethylamine (0.18g, 1.76mmol) in CH_2Cl_2 (1ml) are added at 0°C to a stirred suspension of P_2I_4 (0.23g, 0.40 mmol) in CH_2Cl_2 (2ml). The resulting mixture is stirred at 0°C for 0.5hr, hydrolysed with water and extracted with ether. After usual work up,the crude product is purified by Preparative Layer Chromatography (PLC) (SiO_2, pentane, rf=0.44) leading to the corresponding ketene selenoacetal (0.29g, 85% yield).

Synthesis of 1,1,2-tri(methylthio)-2-cyclopropyl etnylene

$SOCl_2$ (0.24g, 2mmol) in CH_2Cl_2 (2ml) is added at 20°C to a solution of 1,1,1-tri(methylthio)-2-hydroxy-2-cyclopropyl ethane (0.22g,1 mmol) and triethylamine (0.61g, 6 mmol) in CH_2Cl_2 (3ml). The resulting dark-brown mixture is stirred for 0.5hr then quenched with solid K_2CO_3 (excess). K_2CO_3 (saturated solution) is added and the mixture extracted with ether. After usual work up, the crude product is purified by PLC (SiO_2, pentane/ether : 98/2, rf=0.42). 1,1,2-tri(methylthio)-2-cyclopropyl ethylene is isolated in 90% yield (0.185g).

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