Synthesis of Vinyl Sulphides, Azido Sulphides, and Olefins from β-Hydroxy-sulphides

By WILLY DUMONT and ALAIN KRIEF
(*Department of Chemistry, Facultes Universitaires N.D. de la Paix*, 61, *rue de Bruxelles, Namur, Belgium*)

Summary Vinyl sulphides, azido sulphides, and olefins have been prepared from β-hydroxy-sulphides *via* β-chloro-sulphides; the regio- and stereo-chemistry of these reactions is discussed.

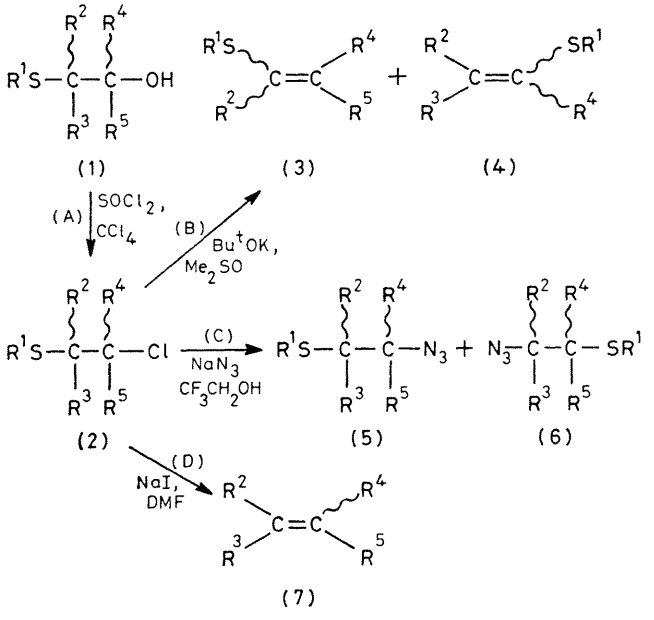
β-CHLORO-SULPHIDES (**2**) may be prepared stereoselectively from olefins and sulphenyl chlorides,[1] or by the reaction of thionyl chloride with β-hydroxy-sulphides (**1**)[2] ($SOCl_2$, 1·5 equiv., CCl_4, 20 °C, 3–5 h, method A, Scheme 1) (**5**) and (**6**) with sodium azide in trifluoroethanol (20 °C, 3 h, method C), and (iii) the olefins (**7**) on heating with 1 equiv. of sodium iodide in dimethylformamide (DMF) (80 °C, 2—3 h, method D)[7]

TABLE 1 Reactions (B)–(D), Scheme 1 [a]

					% Yield		
					Reaction (B)	Reaction (C)	Reaction (D)
R^1	R^2	R^3	R^4	R^5	(**3**)/(**4**)	(**5**)/(**6**)	(**7**)
Me	H	H	$C_{10}H_{21}$	H	12/30	—	53
Me	Me	H	$C_{10}H_{21}$	H	35/35	32/32	—
Me	$C_{10}H_{21}$	H	Me	Me	62/0	60/5	73
Me	Me	Me	$C_{10}H_{21}$	H	—	50/7	—
Ph	H	H	$C_{10}H_{21}$	H	8/32	—	—

[a] The β-hydroxy-sulphides (**1**) were prepared from thioalkyl-lithium compounds, obtained by cleavage of the C–Se bond of mixed thioseleno-acetals (ref. 3)

The hydroxy-sulphides (**1**) can, in turn, be prepared regioselectively, but as a mixture of stereoisomers, from α-thioalkyl-lithium reagents[3] and carbonyl compounds, or stereoselectively from the reaction of epoxides with thiols in basic media



SCHEME 1.

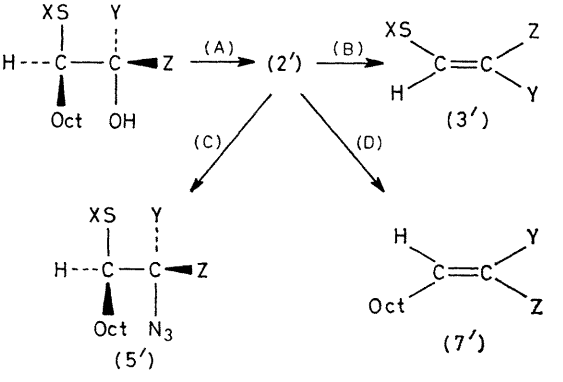
We report here preliminary results (Tables 1 and 2) on the reactions of β-chloro-sulphides (**2**) with nucleophilic/basic reagents which lead to (i) the vinyl sulphides† (**3**) and (**4**) on reaction[1,2] with potassium t-butoxide in dimethyl sulphoxide (20 °C, 1 h, method B), (ii) the β-azido-sulphides

TABLE 2 Reactions of stereoisomerically pure β-chloro-sulphides (2′) (Scheme 2) [a]

			% Yield			
X	Y	Z	(**3′**)	(**5′**)	(**7′**)	(*cis*/*trans*)
Me	H	C_8H_{17}	80	80	80	(95/5)
Me	C_8H_{17}	H	84	88	88	(2/98)
Ph	H	C_8H_{17}	60	75	62	(80/20)
Ph	C_8H_{17}	H	76	70	64	(5/95)

[a] The β-hydroxy-sulphides (**1′**) were prepared stereospecifically from reactions of epoxides with thiolates (ref. 4)

The transformations (A)—(D) are highly stereoselective‡ (Table 2) Reaction (A)§ occurs with complete retention of configuration and the vinyl sulphides (**3**) and (**4**)[8] result from the *anti*-elimination of HCl and R^1SCl or XSCl, respectively Although highly stereoselective, the synthesis of β-chloro-sulphides and consequently of the β-azido-sulphides and vinyl sulphides from β-hydroxy-sulphides is not regioselective (Table 1)



SCHEME 2 Oct = C_8H_{17} See Scheme 1 for (A)—(D)

† To the best of our knowledge, there are only a few reports dealing with the stereochemistry of the elimination reaction which leads to the synthesis of vinyl sulphides, and these are restricted mainly to the phenylthio-derivatives (ref. 5) For other syntheses of vinyl sulphides see ref. 6

‡ As shown by ^1H and ^{13}C n.m.r. spectra and the stereochemistry of further reactions

§ Work is in progress to assess unambiguously the stereochemistry of transformation (B)

We suggest that these results, as well as the stereochemistry observed in all cases, may be explained by the intermediate formation of thiironium salts.[9]

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