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STEREOSELECTIVE ISOMERISATIONS OF DISUBSTITUTED OLEFINS VIA SELENIRANES AND THIIRANES (1)

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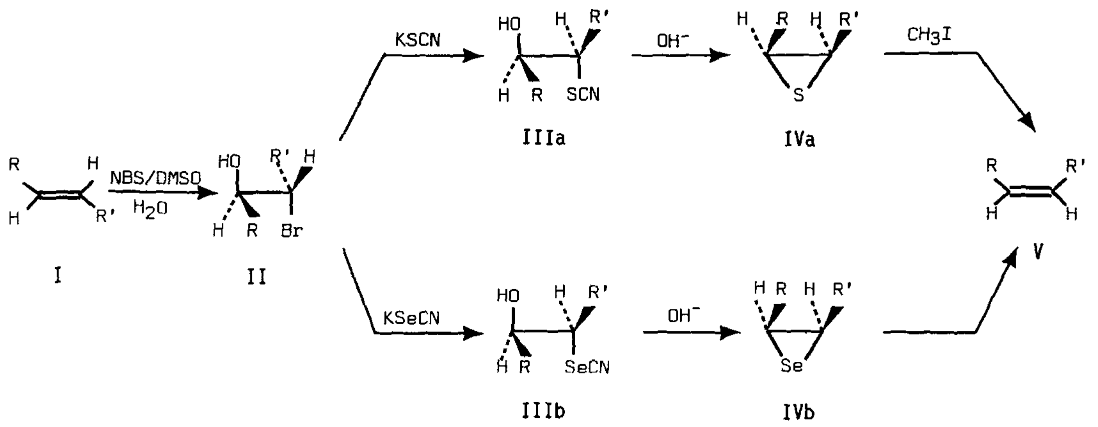
During the last decade several methods (2-5) of stereospecific isomerisation of olefins have appeared in the literature. Corey has shown the potential of this transformation by synthesizing pure optically active cis cyclooctene (3).

This communication reports an original (9) application of synthons which allow the (Z/E or E/Z) isomerisation of disubstituted olefins. These two routes take advantage of new stereoselective routes to thiiranes and seleniranes starting from β-halogenohydrins.

Both proposed pathways (scheme I) include the well known trans addition of Br and OH moieties to an olefin I (DMSO/NBS/H_2O) (6).

SCHEME I



We found that treatment of the bromohydrin II (7), formed in high yield, with a fourfold excess of potassium sulfocyanate or potassium selenocyanate in DMF (60° C, 24 - 48 hrs) produces the β-hydroxy sulfocyanate IIIa or the β-hydroxy selenocyanate IIIb in high yield. Usually these compounds (10) are used in the next step without further purification.

β-hydroxy sulfocyanate IIIa when treated with potassium carbonate (4 eq., in DMF/H_2O) produces a thiirane (11) IVa (70 % yield) which is in turn transformed to an olefin (70 % yield) by one of the known procedures (CH_3I, 45° C, 2 hrs) (12).

When β-hydroxy selenocyanate IIIb is subjected to similar treatment with base, an olefin is directly formed (40-58 % yield). This can be explained by analogy with sulphur, via the formation of a selenirane IVb which is not stable under our experimental conditions and which is known to expel easily the selenium atom leading to an olefin (13).

The stereochemistry of the olefin formed in our synthons (table I), should reflect the stereochemistry of the reaction between the bromohydrin and the potassium sulfocyanate or selenocyanate. Indeed the others steps are described to be highly stereoselective. For instance it is known (11a) that the conversion of the potassium salt of a β-hydroxy sulfocyanate to a thiirane proceeds with an inversion of configuration at the carbon atom bearing the oxygen and that a cis (trans) olefin is stereospecifically formed when a cis (trans) thiirane is reacted with methyl iodide (12). Likewise, the extrusion of the selenium atom from a cis (trans) selenirane leads stereospecifically to a cis (trans) olefin (13).

We found that the time (14) required for these reactions and the stereochemistry of the β-hydroxy sulfocyanate IIIa or the β-hydroxy selenocyanate IIIb formed are very dependent of the choice of the solvent and of the temperature. The best results were obtained when the substitution reactions are carried out in DMF at 60° C.

TABLE I

Starting olefin		Sulphur route (19)*			Selenium route (19)*	
	II%*	IIIa%	(I + V)% from IIIa	$(\frac{V}{I + V})$%	(I + V)% from II	$(\frac{V}{I + V})$%
2-Octene E	94	65	30 (73)+	75	(40)+	92
2-Octene Z	87	70	(80)+	88	(40)+	98
4-Octene E	55	72		70	(47)+	90
1-methoxy 9-octadecene Z	73	60	57	85	58	88
2-Decene E	94	74	40 (78)+	72	(60)+	92
5-Decene E	88	87	57 (76)+	70	(40)+	91

*Yield of purified products.

+Refer to the yield of the corresponding dibromo compound.

The high percentage of Walden inversion in these transformations (see Table I) and the fact that potassium selenocyanate which is a better nucleophile than potassium sulfocyanate (15) leads to the best percentage of inverted compounds III, suggests an S_N2 mechanism predominates. The fo mation of the diastereoisomers III' can be explained by an S_N1 mechanism [favoured by the neopentylic ressemblance of our bromo compounds] or in terms of neighbouring hydroxyl group participatio [i.e. by two S_N2 processes (16)].

To our knowledge little is known about the reactivity of bromohydrins with nucleophiles (18) except the epoxide formation which proceeds via an S_N2 process and in which the nucleophile acts as a base. Nevertheless Winstein has described some reactions of bromohydrins with nucleophiles in acetic acid (18); the yield of the substituted products was rather low (10 ∿ 20 %) but the substitution reactions occurred mainly with retention of configuration, attributed to a neighbouring oxygen interaction (18).

Work is in progress in order to explain these differences. The stereochemistry of the reaction of β-bromoacetate with potassium sulfo (seleno) cyanate is under study in our laboratory.

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1) In the case of selenocyanato compounds IIIb, gray metallic selenium deposits during this treatment.
2) In the case of sulphur analog IIIa, the thiirane is obtained at this stage, and is subjected to the reaction with methyl iodide (6) to lead to the olefin.

The Z/E isomer's percentage of volatile olefins is determined by VPC (20). For 1-methoxy-9-octadecene, the isomer ratio is determined by NMR on the corresponding thionocarbonate. [Olefin → diol (Osmium tetroxide) → cyclic thionocarbonate (Thiocarbonyl diimidazole)].

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