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REGIO AND STEREOSELECTIVE SYNTHESIS OF 1-METHYLSELENO-1-VINYL AND 1-PHENYLSELENO-1-VINYL CYCLOPROPANES

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The Z and E isomers of the title compounds are regioselectively and stereoselectively prepared respectively by reaction of phosphorus ylides with α-selenocyclopropyl aldehydes and by addition of α-lithio seleno-cyclopropanes on α-seleno aldehydes.

In the previous communication we have presented our first approach to 1-methylseleno-1-vinyl and 1-phenylseleno-1-vinyl cyclopropanes 5. Its lack of generality, regio and stereoselectivity leads us to adopt other strategies which will be the subject of this paper and which will meet the desired requirements.

We decided to use a β-elimination of two heteroatomic moieties for the control of the regiochemistry of the π bond formation and to build the required carbon framework from α-selenocyclopropyl moiety by forming one or two new σ bonds.

5

In the first approach, the α-cyclopropyl carbonyl compounds 3 were chosen as building blocks from which the σ and the π bonds (Scheme I) have to be sequentially constructed. This was effectively achieved in one step by reacting phosphorus ylides, or in two steps from α-selenoalkyllithiums.

1-selenocyclopropyl aldehydes 3 were prepared in high yield by reacting α-selenocyclopropyllithium 2 (from bis-selenocyclopropanes 1 and n-BuLi in THF, -78°, 0.5 h [1]) with dimethylformamide [2].

The phenylseleno derivative was also synthesized by reduction of the known [3] phenylselenocyclopropyl nitrile 4 with diisobutylaluminium hydride.

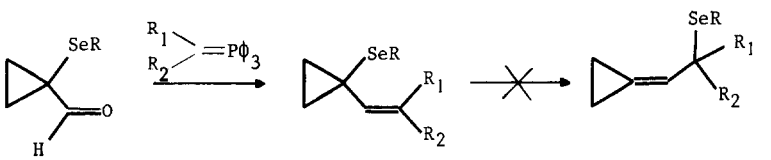
SCHEME I

1 2 3 4

R = Me 80% R = ϕ 74% R = ϕ 66%

The reaction of phosphorus ylides generated from the corresponding phosphonium salts and n-BuLi in THF on selenocyclopropyl aldehydes 3 produces the desired 1-seleno-1-vinyl cyclopropanes 5 in high yield (Table, method C). The regioselectivity of the reaction is complete and the allyl selenide rearrangement which is known [4] to easily occur, is not observed probably due to the strain present in 6.

SCHEME II



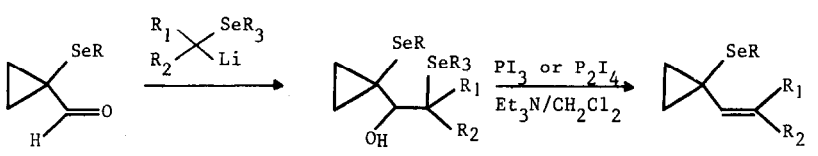
3 5 6

The stereochemistry of the reaction checked on α,β-disubstituted compounds 5 is very high (> 95% from NMR and $|GC|^2$) and favors the Z derivative (see infra for stereochemical determination).

This surprising good selectivity is not usually observed [5] in the synthesis of other disubstituted olefins under these conditions and generally requires salt free reactions conditions [6].

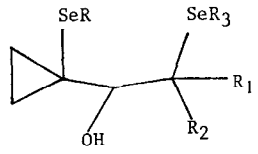
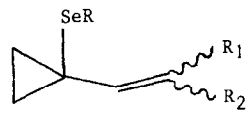
The second approach was achieved by reacting α-selenoalkyllithiums (generated from the corresponding selenoacetal and n-butyllithium in THF) [7] on 3 at -78° (method A). The hydroxy β,β'-diselenides 8 are obtained in high yield and further transformed to the desired 1-seleno-1-vinyl cyclopropanes 5 on reaction with PI_3 or P_2I_4/triethylamine in CH_2Cl_2 at 0° (method A'). The elimination of the hydroxyl group can formally occur with each one of the two seleno groups [8]. It however regioselectively produces the desired 5 by the elimination of the more distant selenyl moiety from the cyclopropane. The strain of the transition state leading to 6 (Scheme II) is again probably responsible of such selectivity.

SCHEME III



3 7 8 5

TABLE

ENTRY												
	R	R_1	R_2	R_3	Method, Yield (%) A	Method, Yield (%) B	R	R_1	R_2	Method used, Yield % ($\frac{Z}{E}$ ratio) A'	Method used, Yield % ($\frac{Z}{E}$ ratio) B'	Method used, Yield % ($\frac{Z}{E}$ ratio) C
a	CH_3	C_6H_{13}	H	CH_3	96	71	CH_3	C_6H_{13}	H	93 ($\frac{45}{55}$)	93 ($\frac{2}{98}$)	89 ($\frac{92}{8}$)
b	CH_3	C_6H_{13}	H	ϕ	63	-	CH_3	C_6H_{13}	H	81 ($\frac{30}{70}$)	-	-
c	ϕ	C_6H_{13}	H	CH_3	86	65	ϕ	C_6H_{13}	H	80 ($\frac{45}{55}$)	86 ($\frac{6}{94}$)	85 ($\frac{90}{10}$)
d	ϕ	C_6H_{13}	H	ϕ	89	-	ϕ	C_6H_{13}	H	91 ($\frac{20}{80}$)	-	-
e	CH_3	ϕ	H	CH_3	95	-	CH_3	ϕ	H	72 ($\frac{32}{68}$)	-	91 ($\frac{98}{2}$)
f	CH_3	ϕ	H	ϕ	75	-	CH_3	ϕ	H	78 ($\frac{25}{75}$)	-	-
g	CH_3	C_9H_{19}	CH_3	CH_3	42	-	CH_3	C_9H_{19}	CH_3	96 ($\frac{45}{55}$)*	-	-
h	CH_3	C_6H_{13}	C_6H_{13}	CH_3	81	-	CH_3	C_6H_{13}	C_6H_{13}	90	-	-
i	ϕ	C_8H_{17}	C_8H_{17}	CH_3	50	-	ϕ	C_8H_{17}	C_8H_{17}	93	-	-
j	ϕ	- $(CH_2)_3$ -		CH_3	72	-	ϕ	- $(CH_2)_3$ -		92	-	-
k	CH_3	CH_3	C_6H_{13}	CH_3	-	81	CH_3	CH_3	C_6H_{13}	-	91 ($\frac{15}{85}$)*	-

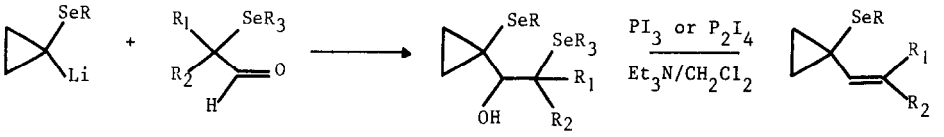
The product 8 obtained by method A is transformed to the olefin 5 by method A'. The one prepared by method B is transformed to 5 by method B'-column C refers to olefin 5 prepared by the Wittig reaction.

* *The stereoisomer assignment has not yet been done.*

As far as the stereochemistry of the C=C bond is concerned the selectivity is much lower (except one case, table, entry d) than the one found in the Wittig reaction and interestingly leads to the predominant formation of the E isomer which was the minor isomer produced in the Wittig reaction.

In order to achieve a higher stereoselective synthesis of the 5E isomer, another approach to 8 was tested [9]. α-lithiocyclopropyl selenides 2 were reacted with α-selenoaldehydes 9 [10] (method B, scheme IV). The hydroxy β,β' diselenides 8 consist in a mixture of stereoisomers in which one largely predominates, and they lead on further reaction [(PI_3, EtN, CH_2Cl_2, 0°, 0.1hr), method B', scheme IV] to a mixture of 5 in which the E isomer is present in more than 94% (NMR, $|GC|^2$).

SCHEME IV



2 9 8 5

The stereochemistry of 8 and consequently of 5 is proposed on the basis of our previous work [9] and related papers about Cram's [11] and Felkin's [12] rules. ^1H NMR spectra of the isomers prepared by the two stereoselective routes also support our assignments (J_{cis} = 11 Hz and J_{Trans} = 16 Hz for the vinylic hydrogens in 5 [13]).

We are currently investigating the missing cases especially the ones of α-seleno ketones (instead of 3 and 9) and we are trying to extend the reactions to the synthesis of allyl selenides different from the cyclopropyl ones.

References and notes

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