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SYNTHETIC ROUTES TO CYCLOPROPYLIDENECARBINOLS AND TO CYCLOPROPYLIDIENES

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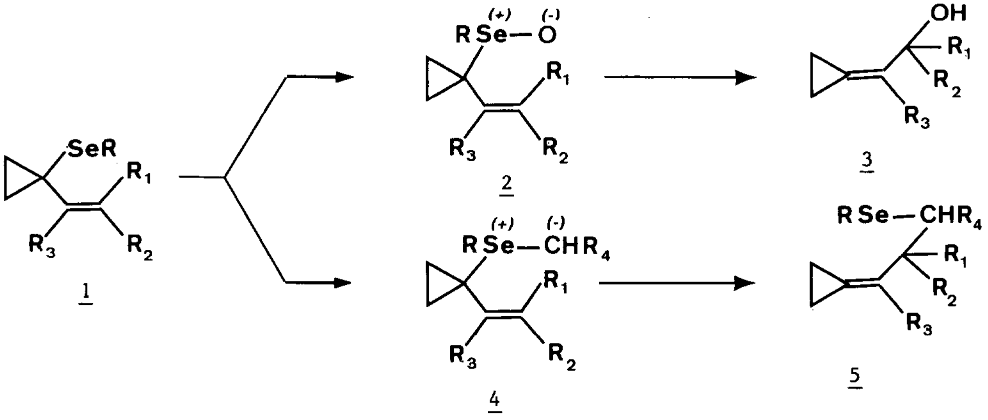
Functionalized alkylidene cyclopropanes have been prepared from 1-seleno 1-vinyl cyclopropanes using [2,3] sigmatropic rearrangements of their corresponding selenoxides or selenonium ylides. A comparison with sulphur analogues is presented.

In previous papers [1], we have presented four synthetic routes to 1-seleno-1-vinyl cyclopropanes. In this letter, we disclose our first results concerning their reactivity namely their conversion to selenium free derivatives. The variety of compounds prepared and their availability open a new dimension to the chemistry of cyclopropyl compounds.

This paper deals with the thermal and base induced rearrangement respectively of selenoxides 2 and selenonium ylides 4 both readily available from the corresponding 1-seleno-1-vinylcyclopropanes 1 [1].

SCHEME 1



The [2,3] sigmatropic rearrangement of straight chain allyl phenylselenoxides to allyl alcohols readily occurs [2] on treatment of allyl phenylselenides with hydrogen peroxide[(THF/H_2O or methanol, 20°) (method A)] [2a] and is much easier than the one performed on thio analogues [3] which usually requires a thiophilic agent.

In the course of this study, we found that methylseleno analogues are much more difficult to rearrange under similar conditions (method A). The rearranged alcohol 7 (Scheme II) was however formed in high yield when pyridine is present in the medium (H_2O_2, 5 eq., pyridine 2 eq., CH_2Cl_2, 20°) (method B)[2b] or when the reaction is performed with $NaIO_4$ (1,05 eq) in methanol/water at 20°, 3h (method C).

SCHEME II

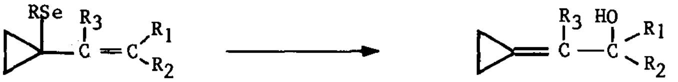
$$C_6H_{13}-CH=CH-CH_2SeR \longrightarrow C_6H_{13}-\overset{OH}{\overset{|}{C}}H-CH=CH_2$$

6 7

R	Method	Yield
$R=CH_3$	Method A	28%
$R=CH_3$	Method B	84%
$R=C_6H_5$	Method C	84%
$R=CH_3$	Method C	82%

Phenylseleno- and methylseleno derivatives 1 are, as it can be expected, much reluctant to rearrange probably due to the strain introduced in the transition state and in the alkylidene cyclopropanes 3. No allyl alcohol was found under conditions A-C, but in the last case, the corresponding selenoxides 2 are quantitatively extracted with chloroform after 3 hrs reaction. The desired transformation 1 → 2 → 3 was successfully achieved by simply reacting the phenylselenoxides 2 (20°, 20h) with piperidine (5 eq) as selenophilic agent in a solvent of low polarity [4] (cyclohexane) (method D). See table I. Neither the corresponding methylselenoxides, nor the phenylsulphoxides analogues [5] of 2 rearrange under similar conditions [6].

TABLE I

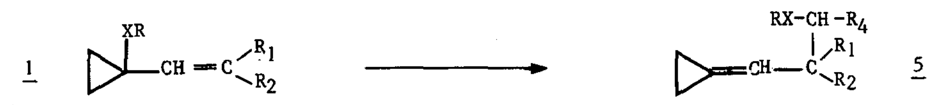
1  3					
R	R_1	R_2	R_3	Method	Yield in 3 (%)
φ	H	C_6H_{13}	H	C then D	75
φ	H	φ	H	C then D	70
φ	C_8H_{17}	C_8H_{17}	H	C then D	75
φ	$-(CH_2)_3-$		H	C then D	80[7]
φ	H	C_5H_{11}	H	C then D	77
φ	H	C_5H_{11}	C_6H_{13}	C then D	92
φ	H	C_5H_{11}	H	A	0
φ	H	C_5H_{11}	C_6H_{13}	B	33
Me	H	C_5H_{11}	H	C then D	16

The cyclopropylidene carbinols 3 have been previously prepared by Conia [7] and Bertrand [8]. Our method appears to successfully compete with the published ones.

We further turned our attention towards a closely related reaction which involves the [2,3] sigmatropic rearrangement of allylic selenonium ylides[9] and the application of the rearrangement to cyclopropyl derivatives : this should produce functionalized alkylidenecyclopropanes 5. Closely related rearrangements have been described in the case of allylic sulphur ylides[10] ; nevertheless they have never been applied to the synthesis of alkylidenecyclopropanes.

The selenonium and sulphonium salts have been easily prepared by alkylation of the corresponding 1-seleno-1-vinyl cyclopropanes 1 or 1-thio-1-vinyl cyclopropanes[5] [CH_3SO_3F in ether, (method E) or in dichloromethane (method F) or alkyliodide/$AgBF_4$ in dichloromethane (method G)] and lead to the rearranged alkylidenecyclopropanes on reaction with base [t-BuOK, DMSO, 20°, 15 hrs (method H)] ; see table II.

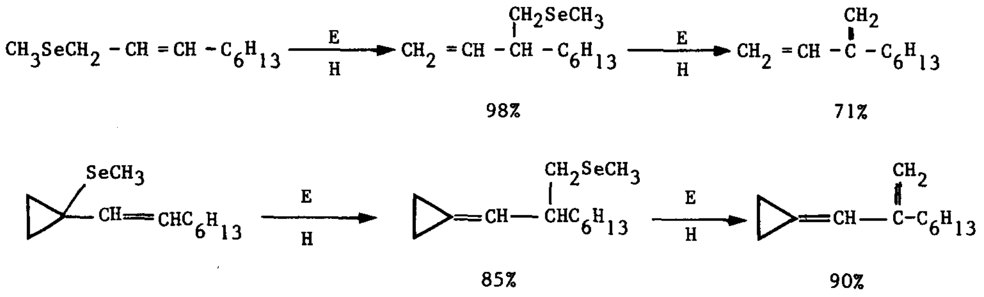
TABLE II

1  5

X	R	R_1	R_2	Methods	R_4	Yields (%)
Se	CH_3	H	C_6H_{13}	E then H	H	85
Se	CH_3	H	C_6H_{13}	G(CH_3I) then H	H	53
Se	C_6H_5	H	H	G(CH_3I) then H	H	60
Se	C_6H_5	H	C_6H_{13}	G(CH_3I) then H	H	56
Se	C_6H_5	H	C_6H_{13}	F then H	H	67
Se	CH_3	CH_3	C_6H_{13}	E then H	H	85
S	C_6H_5	H	C_6H_{13}	G(EtI) then H	CH_3	71
S	C_6H_5	H	C_6H_{13}	G(CH_3I) then H	H	77

The homoallyl selenides were found good precursors of dienes. Alkylation of the selenium atom (method E) followed by treatment with t-BuOK/DMSO (method H) regioselectively produces the dienes by an elimination reaction[11] (Scheme III).

SCHEME III



$$CH_3SeCH_2-CH=CH-C_6H_{13} \xrightarrow[H]{E} CH_2=CH-\overset{CH_2SeCH_3}{\overset{|}{CH}}-C_6H_{13} \xrightarrow[H]{E} CH_2=CH-\overset{CH_2}{\overset{\|}{C}}-C_6H_{13}$$

To our knowledge, only one synthesis of cyclopropylidiene has been so far described [12]. We are currently investigating the scope of these reactions and the reactivity of cyclopropylidienes in Diels-Alder reactions.

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