Tetrahedron Letters, Vol.22, No.43, pp 4341 - 4344, 1981
Printed in Great Britain

0040-4039/81/434341-04\$02.00/0

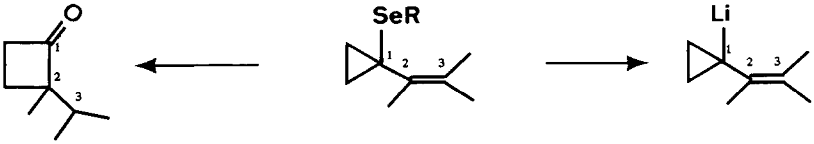
NEW REACTIONS OF 1-SELENO-1-VINYL CYCLOPROPANES

S. Halazy and A. Krief*
Facultés Universitaires Notre-Dame de la Paix
Department of Chemistry
61,rue de Bruxelles, B-5000 - Namur, Belgium

1-lithio-1-vinyl-cyclopropanes and cyclobutanones are obtained in high yield from the readily available title compounds.

We recently disclosed several synthetic routes to 1-seleno-1-vinyl cyclopropanes[1,2] which allow for some of them [2] the stereoselective synthesis of the Z and E isomers. These previously unknown polyfunctionalized molecules were already found [3] to be valuable precursor of functionalized alkylidene cyclopropane including cyclopropylidiene.

We now present the scope and limitation of some new reactions which take place when 1-seleno-1-vinyl cyclopropanes are reacted respectively with alkyllithiums and with p-toluene sulfonic acid and which allow the respective synthesis of 1-lithio-1-vinyl cyclopropanes and cyclobutanones.



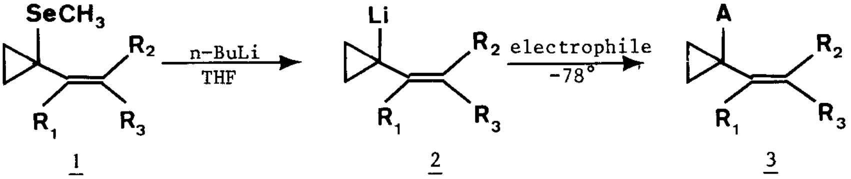
6 1 2

Thus, 1-methylseleno-1-vinyl cyclopropanes [1,2] react with one equivalent of nBuLi in THF to produce 1-lithio-1-vinyl cyclopropanes 2 in quite quantitative yield. The ease of the reaction is directly related to the nature and to the number of substituents present on the carbon carbon double bond. It occurs at appreciable rate [monitored by ^{77}Se-NMR] [4] respectively at -78°, -60° and -45°C when a phenyl group, an alkyl group or two alkyl groups are respectively attached at the C_3 carbon atom of 1. These organometallics 2 have been further trapped by several electrophiles including water, alkylhalides and carbonic anhydride.

The regio and stereochemistry of the resulting cyclopropyl derivatives is of both theoretical and synthetic interest.

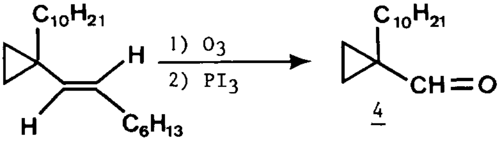
As a general trends the electrophile (H_2O,RX,CO_2) exclusively react on the cyclopropyl ring producing functionalized vinylcyclopropanes in good to high yield (see scheme II).

SCHEME II



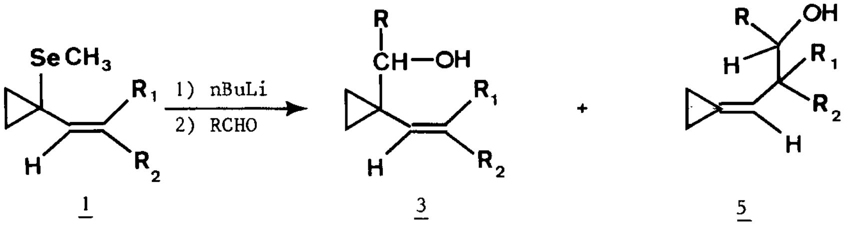
Entry	R_1	R_2	R_3	Z/E	Electrophile	A	Rdt (%)
1	H	H	C_6H_{13}	20/80	H_2O	H	80
2	H	C_6H_{13}	H	90/10	H_2O	H	84
3	C_6H_{13}	C_5H_{11}	H	-	H_2O	H	80
4	H	H	C_6H_{13}	2/98	CH_3I	CH_3	82
5	H	C_6H_{13}	H	90/10	CH_3I	CH_3	77
6	H	H	C_6H_{13}	2/98	$n\text{-}C_{10}H_{21}Br$	$n\text{-}C_{10}H_{21}$	75
7	H	C_6H_{13}	H	90/10	$n\text{-}C_{10}H_{21}Br$	$n\text{-}C_{10}H_{21}$	94
8	H	H	C_6H_{13}	2/98	CO_2	COOH	60
9	H	C_6H_{13}	H	90/10	CO_2	COOH	65
10	H	H	ϕ	5/95	H_2O	H	76
11	H	ϕ	H	98/2	H_2O	H	80[*5]

In one case (see below), we have subjected the alkylated product (entry 6) to the reaction of ozone (O_3-CH_2Cl_2,-78°) followed by in situ reduction[6] of the resulting ozonide with PI_3 at -78°. The formation of aldehyde 4 (87%) fully supports our structural assignement.



A mixture of alkylidene cyclopropanes 5 and vinyl cyclopropanes 3 is however found on reaction of 2 with aldehydes (Scheme 3). At present, we are unable to direct the reaction exclusively at the C_1 or at the C_3 site of 2. For example, the ratio of alcohols 3 is not obviously changed if the hydroxy alkylation is performed in the presence of TMEDA (see scheme 3) entry 4) and various unidentified compounds were observed if the reaction is conducted in the presence of HMPT.

SCHEME III



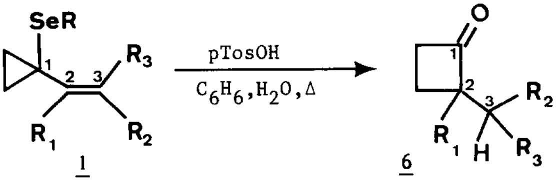
Entry	R_1	R_2	R	Reaction conditions	Rdt (%)	% 3	% 4
1	C_6H_{13}	H	CH_3	THF, -78°C	55	50	50
2	H	C_6H_{13}	CH_3	THF, -78°C	68	80	20
3	C_6H_{13}	H	ϕ	THF, -78°C	90	25	75
4	C_6H_{13}	H	ϕ	THF,TMEDA,-78°C	88	20	80
5	H	C_6H_{13}	ϕ	THF, -78°C	96	46	54

The reactions presented in scheme II and III are highly bistereoselectives. At the exclusion of 1-seleno-1-styryl cyclopropanes which both (Z or E isomers) exclusively produce the E styryl cyclopropane, all other 1-seleno-1-vinyl cyclopropanes were found to retain the stereochemistry of the starting olefin.

1-phenylseleno-1-vinyl cyclopropanes behave differently than their methylselenoanalogues. Under closely related experimental conditions (nBuLi, 1 eq/THF/0°) the two possible modes of cleavage occur producing a mixture of phenyl lithium and 1-lithio-1-vinyl cyclopropane. 1-Butylseleno-1-vinylcyclopropanesand butyl phenyl selenide are also formed. Phenyllithium and 1-lithio-vinylcyclopropane are however quantitatively prepared if the reaction is conducted with two equivalent of nBuLi. More detailled informations will be presented in the full paper.

The synthetic new route to 1-lithio-1-vinylcyclopropanes outlined in this paper is highly potent one. Only few 1-metallo-1-vinyl cyclopropanes have been so far described [7,8]. Kobrich [7] reported that they cannot be prepared by metallation of vinylcyclopropanes. He however reported the synthesis of one 1-lithio-1-vinyl cyclopropane from the corresponding 1-bromo-1-vinyl cyclopropane and alkyllithiums. We recently found a new synthetic route to such derivatives and were able to prepare the corresponding 1-lithio cyclopropane by reaction with alkyllithiums. However side reactions occur which make it less attractive than the route we just report. Detailled informations on that topic will soon appear.

Finally, some 1-seleno-1-vinyl cyclopropanes[9] were reacted with equimolecular amounts of p-toluene sulfonic acid/H_2O (benzene/80°, 3 to 15hr). Cyclobutanones were formed in high yield every time the carbon 3 in 1 is identically or less substituted than carbon 2 (Scheme). If it is not the case, a mixture of starting material and isomerized 1-seleno-1-allyl cyclopropane is formed, along with a trace amount of cyclobutanone[10] and presumably cyclopentanone.



R	R_1	R_2	R_3	Yield in 6
CH_3	H	C_6H_{13}	H	80%
C_6H_5	H	C_6H_{13}	H	63%
CH_3	C_6H_{13}	C_5H_{11}	H	92%
C_6H_5	C_6H_{13}	H	H	90%
CH_3	H	C_9H_{19}	CH_3	< 5%

References and notes

1. S. Halazy, A. Krief, Tet. Lett., 1829 (1981).
2. S. Halazy, A. Krief, Tet. Lett., 1833 (1981).
3. S. Halazy, A. Krief, Tet. Lett., 2135 (1981).
4. JEOL. FX. 90Q multiprobe.
5. Only the E isomer is obtained. For other synthesis of such derivatives, see E.E. Schweizer, J.G. Thompson and A. Ulrich, J. Org. Chem., 33, 3082 (1968).
6. Several other reduction of ozonides, with PI_3 and P_2I_4 have been performed in our laboratory A report on that topic will appear in due course.
7. A. Schmidt, G. Köbrich, Tet. Lett., 2561 (1974).
8. R.A. Moss, R.C. Munjal, Synthesis, 425 (1979).
9. Related (1,3-diseleno-2-hydroxy) cyclopropanes also produce cyclobutanone on reaction with pTosOH. Detailled informations will be reported in the full paper.
10. We are trying at present to direct the reaction toward the formation of these compounds.

(Received in UK 21 July 1981)

Acknowledgements

The authors are grateful to I.R.S.I.A. (Belgium) for a fellowship to S.H. and acknowledge F.N.R.S. (Belgium) for financial support.