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SYNTHESIS OF 1-PHENYLSELENO-1-VINYL AND 1-METHYLSELENO-1-VINYL CYCLOPROPANES BY FORMAL DEHYDRATION OF β-HYDROXYCYCLOPROPYL SELENIDES

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Unknown 1-phenylseleno-1-vinyl and 1-methylseleno-1-vinyl cyclopropanes are readily available from β-hydroxycyclopropyl selenides using (carboxysulfamoyl) triethylammonium hydroxide inner salt methyl ester. Limitations of the method are presented.

We felt that 1-phenylseleno-1-vinyl and 1-methylseleno-1-vinyl cyclopropanes, unknown compounds, could be valuable for the synthesis of various cyclopropane derivatives.

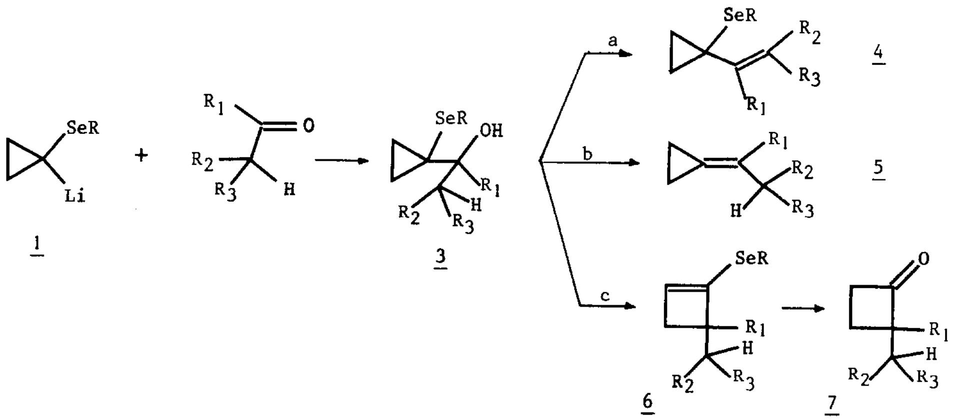
This communication presents our first approach for the synthesis of such molecules.

β-hydroxycyclopropyl selenides 3 [1] readily available from 1-lithio-1-cyclopropylselenides 1 and aldehydes or ketones (see table) were choosen as candidates on which a dehydration reaction must be performed (Scheme I, route a). The reagents used for that purpose must avoid at least two competing reactions :

a) the formal elimination of the hydroxyl and the selenyl moieties which leads to alkylidene cyclopropanes 5 (Scheme I, route b) ;

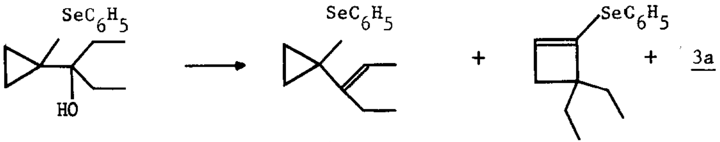
b) the ring enlargement reaction which can produce selenocyclobutenes 6 (Scheme I, route c). Both reactions have been observed when the hydroxyl group is activated to a better leaving group with PI_3 or carbonyldiimidazole for olefin synthesis [2], with p-toluene sulfonic acid in benzene for the cyclobutane ring formation [2].

SCHEME I



During our previous work on alkylidenecyclopropane synthesis, we had the occasion to test the reaction of thionylchloride/triethylamine with β-hydroxyselenides which usually produces olefins [3]. We observed (Scheme II) in case of β-hydroxycyclopropyl selenides 3 in which the hydroxyl group is attached to a fully substituted carbon atom a 40% yield of desired allylselenide 4a [4]. Other conditions such as thionyl chloride in pyridine [5] (reflux, 12 hr) or thionyl chloride in HMPT followed by reaction of t-BuOK in DMSO lead to 35-45% yield of 4a,to some starting material recovered and to a small amount of 6a (Scheme I).

SCHEME II



3a	4a	6a	
$SOCl_2,Et_3N$	40	-	-
$SOCl_2$,py,80°,12h	35	-	50%
$SOCl_2$,HMPT,t-BuOK,DMSO	45	5%	-

β-hydroxyselenides in which the hydroxyl group is attached to a secondary carbon atom lead to unidentified products under similar conditions.

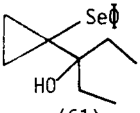
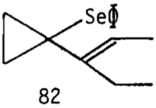
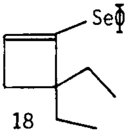
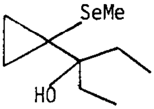
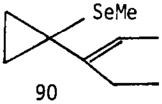
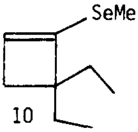
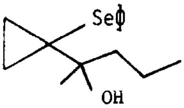
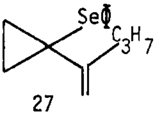
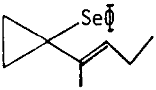
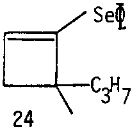
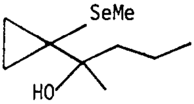
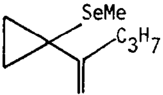
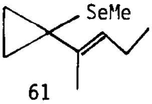
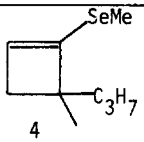
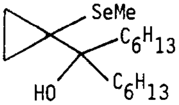
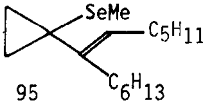
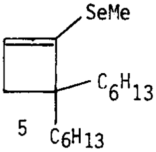
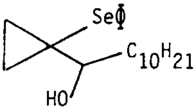
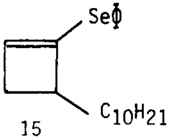
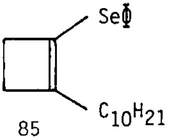
We also tried the Burgess method [6] ($CH_3O_2CN^-SO_2N^+(C_2H_5)_3$, toluene, 110°) which is known to produce vinylcyclopropanes from cyclopropyl carbinols [6] and which allowed B.M. Trost [5,7] to synthesize some analogous 1-phenylthio-1-vinyl cyclopropanes from β-hydroxyphenylthiocyclopropanes in which the hydroxyl group is attached to a tertiary carbon atom. The results concerning the dehydration of selenium derivatives by the Burgess method ($CH_3O_2CN^-SO_2N^+(C_2H_5)_3$, toluene, 110°, 2-38 hrs) (Scheme I, route a) are summarized in the Table.

1-seleno-1-vinyl cyclopropanes were obtained in good to moderate yields in the cases of β-hydroxycyclopropyl selenides in which the alcohol is attached to a tertiary carbon atom. The desired compounds 4 ,which are the more conveniently obtained from the selenomethyl derivatives, are always contaminated with some selenocyclobutene 6.

Unfortunately, all attemps to produce the desired selenides 4 from compounds 3 bearing a secondary alcohol fonction were unsuccessful. For example, in the case of selenophenyl derivative (Table, entry f), a mixture of regioisomeric selenocyclobutenes 6 is obtained.

The method just described requires further comments : if two olefinic regioisomers can be formed, the more substituted is the major one and a mixture of stereoisomers is usually obtained.

TABLE

3 (yield in 3 %)	Products obtained (relative yield %)	Overall yield % (time required in hours)
3a  (61)	 82  18	80 (3)
3b  (60)	 90  10	60 (2,5)
3c  (85)	 27  49  24	77 (2,5)
3d  (60)	 35  61  4	65 (38)
3e  (93)	 95  5	90 (15)
3f  (72)	 15  85	60 (4)

$\phi = C_6H_5$

Experimental. The (carboxysulfamoyl) triethylammonium hydroxide inner salt methylester (430 mgr, 2 mmoles) is added at once to a solution of the β-hydroxyselenide in 5 ml of toluene. The mixture is heated at 110°C during the time indicated ; hydrolysis with aqueous $NaHCO_3$ *and usual work up leads to products which have been purified by PLC [* SiO_2 *(Merck, pentane)] . The cyclopropyl and cyclobutyl derivatives are not separated from each other except in one case (Table, entry a).*

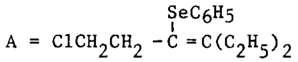
References and notes

1) S. Halazy, J. Lucchetti and A. Krief, Tet. Lett., 3971 (1978).

2) S. Halazy and A. Krief, J.C.S. Chem. Comm., 1136 (1979).

3) J. Rémion and A. Krief, Tet. Lett., 3743 (1976).

4) We have also isolated 30% of a compound to which we tentatively assign the structure A. Work is in progress to confirm this assignment.



$$A = ClCH_2CH_2-\overset{\overset{\displaystyle SeC_6H_5}{|}}{C}=C(C_2H_5)_2$$

5) This reagent was used by B.M. Trost for the dehydration of some β-hydroxycyclopropyl sulfides.

B.M. Trost, D.E. Keeley, J. Amer. Chem. Soc., 98, 249 (1976).

6) E.M. Burgess, H.R. Penton and E.A. Taylor, J. Org. Chem., 38, 26 (1968).

7) B.M. Trost, D.E. Keeley, H.C. Arndt and M.J. Bogdanowicz, J. Amer. Chem. Soc., 99, 3088 (1977).

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