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SYNTHETIC CONNECTIVE ROUTE TO ALLYL ALCOHOLS FROM CARBONYL COMPOUNDS

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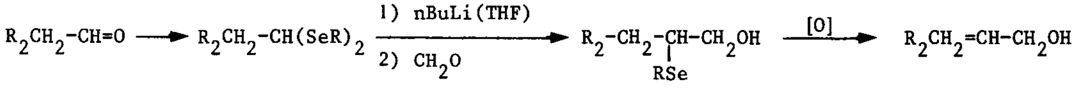
During the past few years, several methods [1-7] have appeared in the literature for allyl alcohol synthesis using β-hydroxyselenides [1-9], among them those which form a new carbon-carbon bond [4-7]. However, no report deals with the synthesis of primary allyl alcohols, which are found in several natural products. This is due in part to the limitation of the existing methods [1,4]. Therefore we have directed our effort to solve this problem by a route which has proved to be powerful namely by reaction of a suitable α-selenocarbanion on a carbonyl compound [5-8] (here formaldehyde) followed by oxidation of the resulting β-hydroxyselenide 1 (Scheme I).

SCHEME I



$$R_2CH_2\text{-}CH{=}O \longrightarrow R_2CH_2\text{-}CH(SeR)_2 \xrightarrow[2)\ CH_2O]{1)\ nBuLi(THF)} R_2\text{-}CH_2\text{-}\underset{RSe}{\underset{|}{C}}H\text{-}CH_2OH \xrightarrow{[O]} R_2CH_2{=}CH\text{-}CH_2OH$$

1

TABLE I

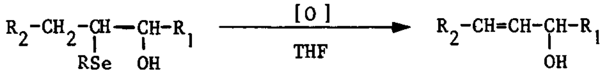
R	R_2	aldehyde	yield(%) in 1
C_6H_5	C_5H_{11}	CH_2O(gas)	78
C_6H_5	C_5H_{11}	$n(CH_2O)$	50
CH_3	C_5H_{11}	CH_2O(gas)	58
CH_3	C_5H_{11}	$n(CH_2O)$	33
CH_3	C_7H_{13}	CH_2O(gas)	69

The best yields are obtained when primary selenophenyl carbanions are reacted with an excess of gaseous formaldehyde in THF (-78°;0.25 - 1 hr,then hydrolysis with NH_4Cl). The yields were lowered by 10-20% in the case of selenomethyl analogs or by use of paraformaldehyde.

The yields are very low (20%) when secondary selenocarbanions are used and we are trying to improve them (Table I).

As to the subsequent oxidation-elimination reaction (Scheme II), we were rather surprised to find that the usual method (30% H_2O_2/THF/20° giving excellent yields [1,5,6] in secondary and tertiary allyl alcohols from β-hydroxyphenyl selenides) is quite ineffective (35% at 25°/16hrs) for the primary allylalcohol synthesis. Neither was it effective for the transformation of β-hydroxymethyl selenides to allylalcohols whatever the substitution around the alcohol function (table II) Several reaction conditions were tried for this latter transformation with little success : H_2O_2/THF/20° prolonged times; higher temperature (55°) or addition of triethylamine. Although addition of alumina to the reaction mixture (30% H_2O_2/THF/55°/Al_2O_3) improved the yield, the best results were undoubtedly obtained with the t-butyl O_2H/THF/Al_2O_3/55° procedure presented in the accompanying paper[10]. By this method the less reactive primary β-hydroxymethylselenide was converted to allyl alcohol in more than 80% yield (Table II).

SCHEME II



$$R_2\text{-}CH_2\text{-}\underset{RSe}{CH}\text{-}\underset{OH}{CH}\text{-}R_1 \xrightarrow[THF]{[O]} R_2\text{-}CH{=}CH\text{-}\underset{OH}{CH}\text{-}R_1$$

2

TABLE II

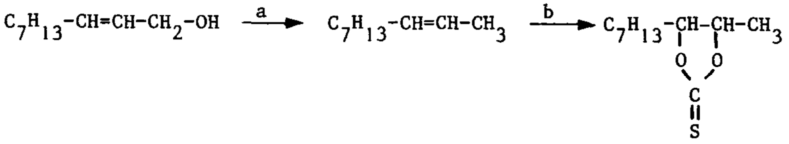
R	R_1	R_2	Yield in 2 % (*)	Method
C_6H_5	H	nC_5H_{11}	35(16)	H_2O_2(20°)
			74(3)	H_2O_2-Al_2O_3(55°)
			78(4)	t-butylOOH-Al_2O_3 (55°)
CH_3	H	nC_5H_{11}	47(6)	H_2O_2-Al_2O_3(55°)
			80(5)	t-butylOOH-Al_2O_3 (55°)
CH_3	H	nC_7H_{11}	96(5,3)	t-butylOOH-Al_2O_3 (55°)
CH_3[8]	nC_2H_5	nC_3H_7	14(4)	H_2O_2 (20°)
			27(5)	H_2O_2 (55°)
			43(6)	H_2O_2-Al_2O_3(20°)
			39(2,4)	t-butylOOH-Al_2O_3 (55°)
			63(3)	H_2O_2-Al_2O_3(55°)
			73(2,5)	t-butylOOH-Al_2O_3 (55°)
CH_3[8]	nC_6H_{13}	nC_5H_{11}	50(7)	t-butylOOH-Al_2O_3 (55°)**

(*) reaction time in hours

(**) in this case we also isolated 12% of the enone arising from the oxidation of 2. The same hydroxyselenide gave 66% of 2 by the O_3/CH_2Cl_2/NEt_3 method (see entry 7, Table, accompanying paper).

Finally, the stereochemistry of the 2-dodecene-1 ol (arising from 1-hydroxy-2(methylselenyl)-dodecane by the tbuOOH-Al_2O_3, THF, 55° procedure) was determined [12] by the sequence outlined in Scheme III to be 75% E; 25% Z.

SCHEME III



$$C_7H_{13}\text{-CH=CH-CH}_2\text{-OH} \xrightarrow{a} C_7H_{13}\text{-CH=CH-CH}_3 \xrightarrow{b} C_7H_{13}\text{-}\underset{|}{CH}\text{-}\underset{|}{CH}\text{-CH}_3 \; (\text{O, O} \text{ joined by } C{=}S)$$

E:75 , Z:25

a) 1. SO_3 - pyridine (20°-4hrs) [11]
   2. $LiAlH_4$ THF(0°-3hrs) [11]

b) 1. OsO_4 - pyridine (20°-3hrs)
   2. $NaHSO_3$ (20°-12hrs)
   3. thiocarbonyl diimidazole - toluene (110°-3hrs)

(overall yield 86%)

Work is in progress to determine the stereochemistry of the allylalcohols described in this paper and this will be published in the full paper.

References

1. K.B. Sharpless, R.F. Lauer and A.Y. Teranishi, J. Amer. Chem. Soc., 95, 2697 (1973)
2. K.B. Sharpless and R.F. Lauer, J. Org. Chem., 39, 429 (1974)
3. H.J. Reich, J. Org. Chem., 39, 428 (1974)
4. D.L. Clive, J.C.S. Chem. Soc., 100 (1974)
5. H.J. Reich and S.K. Shah, J. Amer. Chem. Soc., 97, 3250 (1975)
6. W. Dumont, P. Bayet and A. Krief, Angew. Chem. Int. Ed., 13, 804 (1974)
7. D. Seebach and A.K. Beck, Angew. Chem. Int. Ed., 13, 806 (1974)
8. D. Van Ende, W. Dumont and A. Krief, Angew. Chem. Int. Ed., 14, 700 (1975)
9. A.M. Leonard-Coppens and A. Krief, Tet. Lett., 3227 (1976)
10. D. Labar, L. Hevesi, W. Dumont and A. Krief, previous communication
11. E.J. Corey and K. Achiwa, J. Org. Chem., 34, 3667 (1969)
12. A. Krief, L. Hevesi, J. B.Nagy and E.G. Derouane, Angew. Chem. Int. Ed., 16, 100 (1977)