Tetrahedron Letters No. 13, pp 1141 - 1144, 1978. Pergamon Press. Printed in Great Britain.

OLEFIN SYNTHESIS FROM SELENIDES AND SELENOXIDES

t.BUTYLHYDROPEROXIDE-ALUMINA, A POWERFUL REAGENT FOR SELENIDE OXIDATION-ELIMINATION

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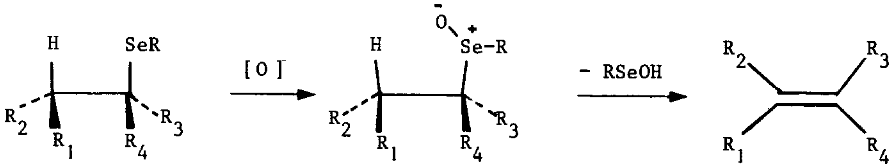
(Received in UK 26 January 1978; accepted for publication 3 February 1978)

Since the more extensive work of Sharpless [1], Clive [2] and Reich [3] on selenoxide formation and its mild transformation to olefins [4,5], these reactions have attracted much interest in organic synthesis especially in the field of natural products[4,5,7].

In the usual conditions [(30% H_2O_2/THF, 25°C, 5hrs), (O_3,CH_2Cl_2, -78°C then 25°C, 5 hrs) ($NaIO_4$, Ethanol, 25°C) or RCO_3H], olefins are rapidly formed from selenides (through the selenoxides).



Since the first publications several reports have dealt with the difficulties encountered in selenoxide eliminations. For example, in one of the first publications , Sharpless noticed the low elimination rate of primary alkylphenyl selenoxides [1b] and has later described [8] the easier elimination of such selenoxides bearing an electron withdrawing group on the benzene ring.

In the course of our earlier work, we pointed out the reluctance of the methyl selenoxide analogs [9,10] to undergo elimination even in the most favorable cases, especially with 30% H_2O_2, THF, 25°C or 60°C [9], with ozone (O_3,CH_2Cl_2, -78°C then 40°C) or with singlet oxygen ($^1O_2$, CH_3OH 20°C then 50°C). Besides the desired olefinic product, always obtained in low yield, we have observed in the two latter reactions (O_3 or $^1O_2$) a quite large reduction of the selenoxide back to the starting selenide. Thus 1-decene is obtained in 30% yield from 1-decyl phenyl selenoxide and in trace amount from 1-decyl methyl selenoxide (O_3,CH_2Cl_2,-78°C then 40° C, 24 hrs).

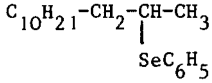
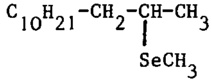
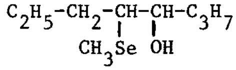
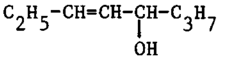
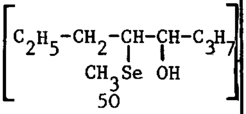
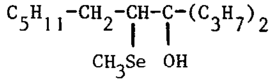
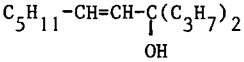
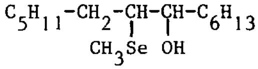
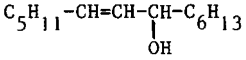
Under the same experimental conditions, the secondary derivatives (2-tridecyl phenyl- and 2-tridecyl methyl selenoxides) are transformed respectively into mixtures of olefins in 85% and 30% overall yield.

It is the purpose of this letter to present two new powerful procedures to improve the yield in olefin from primary alkyl phenyl and alkyl methyl selenoxides as well as from secondary alkyl methyl selenoxides. At the same time these methods prevent the formation of the starting selenide during elimination.

1. We found that selenoxides, obtained quantitatively and pure by reaction of ozone on the corresponding selenides, can be transformed to olefins in high yield when heated in methylene chloride for 1-4 hours in the presence of 1-3 equivalents of triethylamine [11]. The only exceptions to this are primary alkyl methyl selenoxides which are converted in low yield (∿20%) to the terminal olefin along with the corresponding selenide (∿10%) even after prolonged reaction times.
   We found that the triethylamine catalyzed eliminations on 2-tridecyl phenyl and methyl selenoxides lead to the same ratio of regioisomers 1-tridecene (65%) and 2-tridecene (35%). *Interestingly this ratio is reversed in the purely thermal elimination of 2-tridecyl methyl selenoxides (Table - entry 3 and 4).*

2. In order to suppress the formation of the starting selenide in the course of the elimination reactions, we tried to perform them in the presence of the oxidizing agent. The results were disappointing : neither the H_2O_2/THF method (presence or absence of triethylamine, at 25° or at reflux) nor t-butylhydroperoxide/THF gave satisfactory results.
   However, when t-butylhydroperoxide, Al_2O_3 (basic alumina woelm grade I) and the selenides were stirred at 55° in THF, the olefins were formed in excellent yield [12] and no selenoxide was detected in solution (by TLC). Besides its basic nature, aluminium oxide should exert a surface effect, maybe in a similar fashion as has been suggested recently for glass surfaces in ester pyrolyses [13]. When 2-tridecyl methyl selenoxide (prepared by ozone in THF) was allowed to react in the presence of Al_2O_3, the yield in olefin was somewhat lower (68% overall and 26% of 2-tridecyl methyl selenide recovered) but the ratio of regioisomers was the same as in the triethylamine catalyzed reactions. In none of the reactions described with Al_2O_3, did we observe epoxidation of the olefin formed, as has been reported recently, with or without silica gel [14]. Although it is not clear whether or not a carbonium ion tightly adsorbed to the surface of aluminum oxide is involved in these reactions, this simple procedure should reinforce the synthetic utility of selenoxides for olefin formation.

Our efforts are presently directed to discover more about the scope and limitations of our reaction , its intimate mechanism and to determine the stereochemistry of the olefins produced. We are also looking at the applicability of our reagent systems to reactions like the sigmatropic rearrangement of allylic selenoxides.

Starting selenide	Method	Product Yield (%)		
		Olefins	Composition	
1. $C_8H_{17}\text{-}CH_2\text{-}CH_2\text{-}Se\text{-}C_6H_5$			$C_8H_{17}\text{-}CH{=}CH_2$	
	A (24hrs)	30	30	
	B (24hrs) (3eq.amine)	75	75	
	C (3hrs)	86	86	
2. $C_8H_{17}\text{-}CH_2\text{-}CH_2\text{-}Se\text{-}CH_3$			$C_8H_{17}\text{-}CH{=}CH_2$	
	A (24hrs)	<1	<1	
	B (26hrs) (3eq.amine)	23	23	
	C (3hrs)	83	83	
3.  $C_{10}H_{21}\text{-}CH_2\text{-}\underset{SeC_6H_5}{\underset{\vert}{CH}}\text{-}CH_3$			$C_{10}H_{21}\text{-}CH_2\text{-}CH{=}CH_2$	$C_{10}H_{21}\text{-}CH{=}CH\text{-}CH_3$
	A (6hrs)	64	65	35
	A (15hrs)	80	65	35
	B (1hr)	91	65	35
	C (4.5hrs)	86	65	35
4.  $C_{10}H_{21}\text{-}CH_2\text{-}\underset{SeCH_3}{\underset{\vert}{CH}}\text{-}CH_3$			$C_{10}H_{21}\text{-}CH_2\text{-}CH{=}CH_2$	$C_{10}H_{21}\text{-}CH{=}CH\text{-}CH_3$
	A (16hrs)	33	40	60
	B (4hrs)	70	65	35
	C (6hrs)	84	65	35
5.  $C_2H_5\text{-}CH_2\text{-}\underset{CH_3Se}{\underset{\vert}{CH}}\text{-}\underset{OH}{\underset{\vert}{CH}}\text{-}C_3H_7$	$O_3/CDCl_3$ 60°-2hrs	50	 $C_2H_5\text{-}CH{=}CH\text{-}\underset{OH}{\underset{\vert}{CH}}\text{-}C_3H_7$ + 50	 $\left[C_2H_5\text{-}CH_2\text{-}\underset{CH_3Se}{\underset{\vert}{CH}}\text{-}\underset{OH}{\underset{\vert}{CH}}\text{-}C_3H_7\right]$ 50
6.  $C_5H_{11}\text{-}CH_2\text{-}\underset{CH_3Se}{\underset{\vert}{CH}}\text{-}\underset{OH}{\underset{\vert}{C}}\text{-}(C_3H_7)_2$	B (2eq.amine) (1.5hrs)	96	 $C_5H_{11}\text{-}CH{=}CH\text{-}\underset{OH}{\underset{\vert}{C}}(C_3H_7)_2$	
7.  $C_5H_{11}\text{-}CH_2\text{-}\underset{CH_3Se}{\underset{\vert}{CH}}\text{-}\underset{OH}{\underset{\vert}{CH}}\text{-}C_6H_{13}$	B (2eq.amine) (3 hrs)	66	 $C_5H_{11}\text{-}CH{=}CH\text{-}\underset{OH}{\underset{\vert}{CH}}\text{-}C_6H_{13}$	

All the yields quoted are given for pure products in hand (NMR and IR spectra agree with the proposed structures)

Method A : The selenide is oxidized quantitatively with ozone in methylene chloride after removal of the excess of ozone.The reaction mixture is heated for the time shown in the table.

Method B : Identical to the method A except that triethylamine (1 eq. or more as noted in the table) is added just prior heating.

Method C : The selenide(1 eq.), the t-butyl hydroperoxide (4 eq.) and alumina (basic grade I) (8 eq.) are mixed in THF and heated for the time stated in the table.

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11. Secondary amines have been used previously (see H.J. Reich, J.M. Renga and I.L. Reich, J. Amer. Chem. Soc., 97, 5434 (1975); S. Raucher, Tet. Lett., 3909 (1977) but care must be taken to avoid side reactions (see H.J. Reich and J.M. Renga, J. Org. Chem., 40, 3313 (1975)). We also observed a relatively easy conversion of 2-tridecylmethyl selenoxide into mixtures of olefines in t-butylOH/t-butylOK/55°/5hrs or in DMSO/KOH/55°/4hrs but in lower overall yields (61% and 60% respectively).

12. In a typical experiment 236 mg (10^{-3}M) of n-decylmethyl selenide, 360 mg (4×10^{-3}M) of t-butylhydroperoxide and 916 mg (8×10^{-3}M)of Al_2O_3 (basic, grade I) were stirred in 6 ml THF at 55°. The reaction was monitored by VPC (decalin as internal standard). After 4 hrs the yield in olefin was 83% and the reaction did not proceed further even after addition of further portions of t-butylO_2H.

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