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OLEFINS SYNTHESES FROM β-HYDROXYSULFIDES

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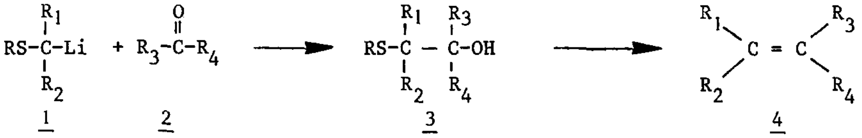
Di-,tri-,tetrasubstituted β-hydroxysulfides readily prepared from α-thioalkyllithiums and carbonyl compounds are easily transformed to di- and trisubstituted olefins on reaction with P_2I_4 or PI_3, and to tetrasubstituted ones with $SOCl_2$.

The synthesis of olefins from β-hydroxysulfides is a valuable transformation particularly difficult to perform, which was till recently [1] confined to β-hydroxy primary alkylmethyl or phenylsulfides [2] and which usually requires metals as reducing agents.

We now show that diphosphorus tetraiodide (method A) and phosphorus triiodide (method B) in the case of di- and trisubstituted β-hydroxysulfides, thionylchloride (method C) in the case of tetrasubstituted ones,allow the high yield synthesis of the corresponding olefins. The reactions are usually performed in methylene chloride at reflux and in the presence of triethylamine for 2 to 6 hrs (Scheme I).

SCHEME I

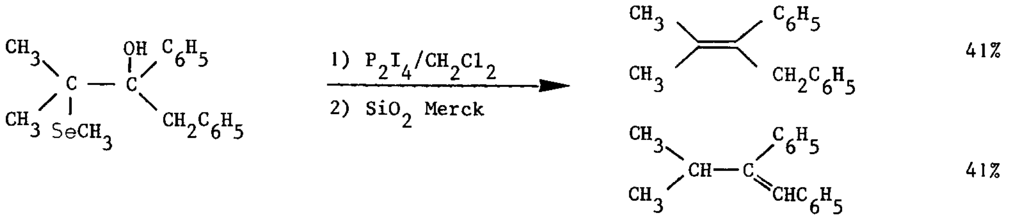


R	R_1	R_2	R_3	R_4	Yield in 3 % (method)	Yield in 4 % (time, method)
CH_3	CH_3	H	$C_{10}H_{21}$	H	73(E)	88(3,A) ; 71(2,B)
C_6H_5	CH_3	H	$C_{10}H_{21}$	H	71(E) ; 67(D)	85(3,A) ; 71(2,B)
CH_3	$C_{10}H_{21}$	H	CH_3	CH_3	72(F)	80(2,A)
CH_3	CH_3	CH_3	$C_{10}H_{21}$	H	70(E)	79(2,A)
CH_3	CH_3	CH_3	C_6H_5	$C_6H_5CH_2$	75(E)	78(6,C)

The reactions described on Scheme I are completely regiospecific. 1,2-diphenyl-2-hydroxy-3-methylseleno-3-methylbutane reacts very slowly with P_2I_4/NEt_3 (method A). The reaction is easier if triethylamine is omitted. However, a mixture of the expected olefin and the corresponding iodoalkane are obtained which on purification by PLC (SiO_2) affords a 1:1 mixture of two regioisomeric olefins (Scheme II).

The stereochemistry of the reaction was studied on couples of two diastereoisomeric disubstituted β-hydroxyphenyl and methylsulfides stereospecifically prepared from cis and trans 9,10-oxidooctadecene and methyl- or phenylthiol (RSH, KOH, ethanol; 90°, 1.5-3 hr, 90% yield).

SCHEME II



On reaction with P_2I_4 or PI_3 (method A or B) the erythro isomers produce stereochemically pure 9E-octadecene (93% yield). The threo isomers for their part lead to 9Z-octadecene (90% yield) polluted with a few percent of its 9E isomer (Z:E ∿ 94:6) in the methylthio series whereas isomerization is much more important in the phenylthio one (Z:E ∿ 75:25).

Thus the reaction formally occurs by anti-elimination of the hydroxyl and the sulfenyl moieties. Thiiranium ion is a possible intermediate. PI_3 and P_2I_4 are the choice reagents since they transform the hydroxyl group on a better living group and produce a iodine ion known for its ability to attack thiiranium salts on the sulfur atom[3].

The interest of the transformations just disclosed arises from the great availability of the reagents[4], the mildness of the reaction conditions and the availability of the β-hydroxysulfides from α-thioalkyllithiums. Those described in Scheme I were prepared by bromine-metal exchange in α-bromophenylsulfides[6] (nBuLi, THF,-78°, method D) or from α-thio α-methylselenoalkanes[6] by cleavage of the C-Se bond (nBuLi, THF,-78°, method E).

Typical experiment :
Method,A : a solution of erythro 9-hydroxy-10-phenylthiooctadecane (378 mg, 1 mmole) and triethylamine (252 mg, 2.5 mmole) in CH_2Cl_2 *(2 ml) is added at 20° on a suspension of* P_2I_4 *(313mg, 0.55 mmole) in* CH_2Cl_2 *(4 ml). The mixture is then refluxed at 50° for 1.5 hr, the solution is cooled to 0°, hydrolysed and extracted with ether. The ether extracts are washed with an aqueous solution of thiosulfate and dried over* $MgSO_4$*. Removal of the solvants leads to an oily material (370 mg) which on purification by PLC (*SiO_2*;pentane) affords 9E-octadecene (240 mg, 95% yield).*

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