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OLEFIN SYNTHESIS BY REDUCTIVE ELIMINATION OF β-HETEROSUBSTITUTED ALKYLHALIDES

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Terminal and disubstituted olefins are formed on reaction of methyl-or phenylselenolate with vic-dibromides, β-halogenoselenides, β-iodo-and β-bromo-alkylchlorides and vic-dichlorides. The reaction occurs stereoselectively by formal anti elimination in the three first cases and by formal syn elimination in the last one.

The presence of a β heteroatom in an alkylhalide clearly influences the nature and the stereochemistry of the product formed on reaction with nucleophiles [1,2,3].
We report here our preliminary results concerning the reaction of sodium phenyl- or methylselenolate in THF/HMPT : 3/1 (method A) or in ethanol (method B) on a series of alkylhalides 1 bearing on the β carbon a hydroxy, sulfo, halogeno or a seleno group.

We observed in the two first cases the respective formation of β-hydroxy- and β-sulfo-selenides [4] 2 resulting from the substitution of the halogen atom on the starting derivatives (scheme I)

Scheme I

$$R_1\text{-}\underset{X}{\underset{|}{CH}}\text{-}\underset{Y}{\underset{|}{CH}}\text{-}R_2 + RSeNa \longrightarrow R_1\text{-}\underset{RSe}{\underset{|}{CH}}\text{-}\underset{Y}{\underset{|}{CH}}\text{-}R_2 + NaX$$

X	Y	1 R_1	R_2	2 Method(°C,hr)	Yield of 2%
Br	OH	CH_3(or C_5H_{11})	C_5H_{11}(or CH_3)	B (40,4)	92
Cl	SC_6H_5	C_8H_{17}	C_8H_{17}	A (60,2)	67

Vic-dihalides and β-halogenoselenides do not lead to substitution products on reaction with selenolates (method A or B)[5] but olefins are instead formed in high yields (scheme II, table).

Scheme II

$$R_1\text{-}\underset{X}{\underset{|}{CH}}\text{-}\underset{Y}{\underset{|}{CH}}\text{-}R_2 + nRSeNa \longrightarrow R_1\text{-}CH{=}CH\text{-}R_2 + \frac{n}{2}\ RSe\text{-}SeR$$

1 3

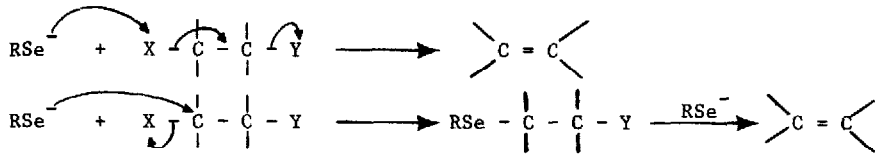
The reaction is usually rapid (< 6hr) and occurs at room temperature (method A) for all the cases studied except for the dichlorides which require heating at 80°. Only one equivalent[6a] of selenolate is required when β halogeno selenides are concerned whereas two equivalents[6b] are needed for *vic*-dihalides.

We tried to trap the hypothetical β-halogenoselenides in the cases of *vic*-bromides and *vic*-dichlorides by performing the reaction with only one equivalent of phenylselenolate (method A,

20° or -78°). Our efforts were unsuccessful since every time 50% of the starting material was recovered along with the olefin 3 (although obtained in low yield at -78°)[7].

We have carefully investigated the stereochemistry[8] of the disubstituted olefins obtained form pure erythro 1a and threo 1b derivatives. In all the cases, the reaction is highly bi stereoselective (∿ 98%). It occurs by formal anti elimination of the two heteroatomic moieties for dibromides, for β-halogenoselenides, and for β-chloro alkyliodides. Formal syn elimination reaction is however observed with *vic*-dichlorides and surprisingly vinyl chloride is formed in appreciable amount (42% yield) along with the Z olefin in the case of the erythro isomer 1b (entry 20). The stereochemical differences observed between *vic*-dibromides and *vic*-dichlorides are preceeded by the recent results of Sonnet and Oliver[1] on reaction of these derivatives with sodium iodide and speculative interpretation, already given on that occasion can of course apply to our results. The reaction could imply the direct attack of the selenolate on the halogen atom followed by concerted elimination of the second heteroatomic moiety (scheme III, route I).

Scheme III



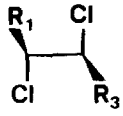
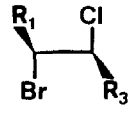
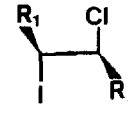
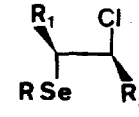
The selenolate could also react on the carbon bearing the halogen atom (scheme III, route II) leading thus to a β-halogenoselenide, by a substitution reaction, which could in turn be transformed to the olefin by formal anti elimination of the two heteroatomic moieties as described in the table.

The reaction of β-halogenoselenides with different nucleophiles is reported to produce, depending on the nature of the nucleophile, either the substitution product (with retention of the configuration at the substituted carbon atom)[3] or the olefin[9] (by formal anti elimination reaction of the two heteroatomic moieties).

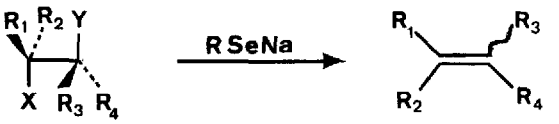
Vic-diselenides which can be postulated as intermediate to explain the reactions described here, are to our knowledge unknown. They have been proposed as intermediates in the copper iodide promoted olefin synthesis[10] from α-selenoalkyllithiums and in the coupling reaction[11] of α-phenylselenoacrylate and α-phenylselenoacrylonitrile promoted by azabisisobutyronitrile. We were not yet able to prepare them.

Finally, we like to bring attention to the following order of selectivity observed in the case of some threo isomers 1b (scheme IV).

Scheme IV

1b				
3 E	95	63	00	00
3 Z	05	37	100	100

TABLE



1 3

Entries	R_1	R_2	R_3	R_4	X	Y	R	Yield(time,temp°,method;cis/trans) in purified products except *
1	$C_{10}H_{21}$	H	H	H	Br	Br	C_6H_5	89 (0.5,25,A)
2	$C_{10}H_{21}$	H	H	H	Br	Br	C_6H_5	77 (2,25,B)
3	$C_{10}H_{21}$	H	H	H	Br	Br	CH_3	83 (2,25,B)
4	C_8H_{17}	H	C_8H_{17}	H	Br	Br	CH_3	95 (2,25,B ; 96/04)
5	C_8H_{17}	H	C_8H_{17}	H	Br	Br	C_6H_5	87 (2,40,B ; 98/02)
6	C_8H_{17}	H	H	C_8H_{17}	Br	Br	CH_3	96 (2,25,B ; 00/100)
7	C_8H_{17}	H	H	C_8H_{17}	Br	Br	CH_3	95 (2,25,A ; 00/100)
8	C_8H_{17}	H	H	C_8H_{17}	Br	Br	C_6H_5	96 (0.5,40,B ; 00/100)
9	C_5H_{11}	H	H	CH_3	Br	Cl	C_6H_5	97*(3,25,A ; 47/53)
10	C_5H_{11}	H	H	CH_3	Br	Cl	CH_3	91*(3,25,A ; 06/94)
11	C_5H_{11}	H	CH_3	H	Br	Cl	C_6H_5	90*(0.5,25,A ; 37/63)
12	$C_{10}H_{21}$	H	H	H	Br	SeC_6H_5	C_6H_5	79 (2,25,B)
13	C_5H_{11}	H	CH_3	H	Br	SeC_6H_5	C_6H_5	95 (1,25,A ; 100/00)
14	$C_{10}H_{21}$	H	H	H	Cl	SeC_6H_5	C_6H_5	60 (3,25,B)
15	C_5H_{11}	H	H	CH_3	Cl	SeC_6H_5	C_6H_5	97*(6,25,A ; 00/100)
16	C_5H_{11}	H	CH_3	H	Cl	SeC_6H_5	C_6H_5	95*(1,25,A ; 100/00)
17	C_5H_{11}	H	H	CH_3	Cl	I	C_6H_5	86*(1,25,A ; 00/100)
18	C_5H_{11}	H	CH_3	H	Cl	I	C_6H_5	92*(0.5,25,A ; 97/03)
19	$C_{10}H_{21}$	H	H	H	Cl	Cl	C_6H_5	90 (3,25,A)
20	C_8H_{17}	H	H	C_8H_{17}	Cl	Cl	C_6H_5	36**(12,80,A ; 100/00)
21	C_8H_{17}	H	C_8H_{17}	H	Cl	Cl	C_6H_5	92 (4,80,A ; 05/95)
22	C_5H_{11}	H	H	CH_3	Cl	Cl	C_6H_5	77*(2,80,A ; 100/00)

* Yield determined by $|GC|^2$ using an internal standard

** 9-chloro 9-octadecene is also obtained in 42% yield

Whatever is the interpretation of the elimination reaction, the transformations described here should be valuable for the synthetic chemist : they can advantageously be compared to the NaI promoted elimination reaction of *vic*-dihalides [1] (10 fold excess of NaI, high temperature). They only need stoichiometric amount of selenolate and occur at 20° (method A).
The solution is pale yellow at the end of the reaction due to the presence of a diselenide formed as a by-product, which is easily separated from the olefin and can be reused for synthesizing the selenolate ($RSeSeR + 2Na \longrightarrow 2RSeNa$).

References and notes

1. P.E. Sonnet and J.E. Oliver, J. Org. Chem., 41, 3284 (1976) and references cited.
2. D. Van Ende and A. Krief, Tet. Letters, 2709 (1975).
3. J.N. Denis, J. Vicens and A. Krief, Tet. Letters, 2697 (1979) and references cited.
4. The stereochemistry of these products will be disclosed in the full paper.
5. Experimental procedure :

   METHOD A.

   Erythro 9,10-dibromo octadecane (4.1 g - 10^{-2}m) in THF (10 mℓ) is added to a red solution of sodium methylselenolate (2.5 10^{-2}m) [from CH_3SeH (1.48 mℓ - 2.5 10^{-2}m) and NaH (0.8 g - 2.5 10^{-2}m)] in anhydrous THF-HMPT (20.10 mℓ) at 20°C. A white precipitate is immediatly formed. After stirring for 2hr more, the suspension is hydrolysed (H_2O - 5 mℓ), extracted and dried. The crude mixture is purified by preparative dry column chromatography (SiO_2, pentane). The trans 9-octadecene (2.4 g) is obtained in 95% yield (Rf=0.98, pentane) (cis/trans :00/100).

   METHOD B.

   An ethanolic solution of sodium phenylselenolate (5 mℓ - 5.10^{-3} m) is added to threo 9,10-dibromo-octadecane (0.820 g - 2.10^{-3} m) in ethanol (1 mℓ). The mixture is stirred for 0.2 hr at 40°C, hydrolysed with water (2 mℓ) extracted and dried over magnesium sulfate.
   The crude mixture is purified by preparative thick layer chromatography (SiO_2 ; 2mm, pentane Rf = 0.98). The cis 9-octadecene (0.435 g) is obtained in 87% yield (cis/trans : 98/02).
6. For synthetic purposes (scheme II, table) we use a small excess of selenolate a) 1.25 eq ; b) 2.5 eq.
7. We ensured that β-halogenoselenides [3] are stable in this medium under these conditions.
8. By comparison of the crude mixtures with authentic samples by $|GC|$ [2].
9. The reaction of thionylchloride in CH_2Cl_2 with a β-hydroxyselenide produces a β-chloroselenide [9a] whereas an olefin is formed when the reaction is performed in the presence of triethylamine [9b].

   9a) J.N. Denis and A. Krief, unpublished.

   9b) J. Rémion and A. Krief, Tet. Letters, 3743 (1976).
10. J. Lucchetti, J. Rémion and A. Krief, C.R. Acad. Sci., 288, 553 (1979).
11. *Captodative Substituent Effect in Synthesis with radical and radicophiles*, H.G. Viehe, R. Merenyi, L. Stella and Z. Janousek, Angew. Chem., in press, reference 32.
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