Tetrahedron Letters, Vol. 34, No. 31, pp. 4925-4926, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

The Reaction of Electron-deficient Selenoaldehydes with Thiols

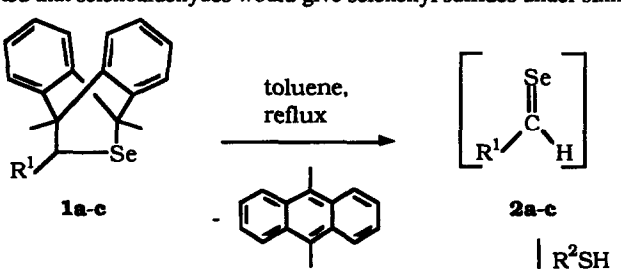
Virginie Duchenet and Yannick Vallée*

Laboratoire de Chimie des Composés Thioorganiques, associé au CNRS,
ISMRA, 14050 Caen, France

Abstract: Electron-poor selenoaldehydes, generated in-situ in refluxing toluene, reacted with thiols in the presence of triethylamine to give selenenyl sulfides, RSeSR'. The formation of a selenodisulfide, RSSeSR, was also evidenced.

Selenenyl sulfides are a relatively rare class of compounds.[1] However, because of their close similitude with disulfides whose biochemical behaviour is of so much importance, it would be of interest to study their chemistry and their biochemistry.

We have recently reported that electron-deficient thioaldehydes react with thiols in the presence of a base to give unsymmetrical disulfides.[2] As the reactivity of selenocarbonyls[3] often parallels the reactivity of thiocarbonyls, it was expected that selenoaldehydes would give selenenyl sulfides under similar conditions.

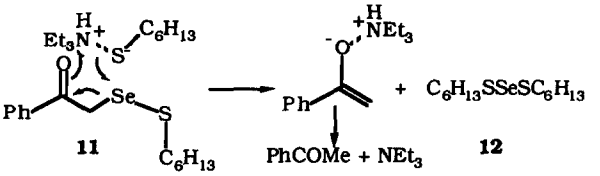


The selenoaldehydes **2a-c** were generated from their 9,10-dimethylanthracene adducts **1a-c**[4] in refluxing toluene (105 min) in the presence of two equivalents of a thiol and triethylamine. In most cases the expected selenenyl sulfide was isolated (see Table). However the yields were only medium with tertiary thiols and poor with primary thiols.[5] Compounds **8** and **11** could not be isolated.

R^1	R^2	Product	Yield %	^1H NMR[5]
CN	t-Bu	**3**	55	1.41 (s), 3.40 (s)
CN	t-Pent	**4**	45	0.96 (t), 1.37 (s), 1.69 (q), 3.38 (s)
CN	n-Oct	**5**	14	1.72 (tt), 3.00 (t), 3.43 (s)
CN	n-Hex	**6**	18	1.71 (tt), 3.02 (t), 3.42 (s)
COMe	t-Bu	**7**	35	1.38 (s), 2.33 (s), 3.59 (s)
COMe	n-Hex	**8**	0	
COPh	t-Bu	**9**	51	1.39 (s), 4.22 (s)
COPh	t-Pent	**10**	46	0.95 (t), 1.32 (s), 1.65 (q), 4.21 (s)
COPh	n-Hex	**11**	0	

Table

We first thought that the cleavage of the sulfur-selenium bond by the excess thiol was the main reason of the low yields. This cleavage will be much easier with primary thiols as it is the case for disulfides.[2] However, the discovery that acetophenone was the main product in the reaction of **2c** with n-hexylthiol (yield estimated by NMR : 83%) clearly indicated that another competitive path had been followed. A thorough search for other products in this particular reaction led to the identification of di-n-hexyl disulfide and of the selenodisulfide **12**.[1,6] This product could arise from a cleavage of the C-Se bond of **12**. Such cleavage would occur *via* a six membered transition state leading to an intermediate ammonium enolate and to **12**.[7]



We thank Profs. P. Beslin and A. Thuillier for a useful discussion concerning the cleavage of the C-Se bond.

References and notes

1. Magnus, P. D. in *Comprehensive Organic Chemistry*, Barton, D. H. R.; Ollis, W. D. Eds; Pergamon Press : Oxford, 1979, vol. 3, pp. 491-538. Selenenyl sulfides are involved in the biochemistry of selenopeptides and selenoproteins such as glutathione peroxidase: Walter, R.; Roy, J. in *Organic Selenium Compounds: Their Chemistry and Biology*, Klayman, D. L.; Günther, W. H. H. Eds.; 1973, pp. 601-627.
2. Duchenet, V.; Vallée, Y. *J. Chem. Soc., Chem. Commun.*, **1993**, 806-807.
3. Guziec, F. S. in *Organoselenium Chemistry*; Liotta, D. Ed.; Wiley : New York, 1987, pp. 277-324.
4. Kirby, G. W.; Trethewey, A. T. *J. Chem. Soc., Perkin Trans. 1*, **1988**, 1913-1922.
5. The experimental conditions are reported in ref.[2]. We used 2 eq. of thiol to minimize the selenoaldehyde oligimerization. The selenenyl sulfides were purified by TLC and characterized by ^1H and ^{13}C NMR and MS. ^1H NMR data are collected in the table. The aliphatic protons in the long chains and the aromatic protons have been omitted. Compounds **3-7**, **9** and **10** were isolated as yellow oils.
6. TLC yielded a *ca.* 1/1 mixture of **12** and the disulfide. **12** was characterized by NMR (SCH_2 : t, 2.93) and MS ($M^{+\cdot}$: 314). Furthermore, when this mixture was treated with PPh_3 (c-C_6H_{12}, reflux, 120 min) no more **12** was detected. The disulfide and $SePPh_3$ (yield from **1c** : 35%) were separated by TLC. The expected yield should be *ca.* 83% (acetophenone yield). However, partial loss of Se from **12** probably occur during the reaction and the extraction process, giving the disulfide. **12** was also detected in the NMR spectra of crude **6** and **8**. Owing to their volatility CH_3CN and acetone were not isolated.
7. The thiolate is more nucleophilic than the thiol itself. However, the thiol could participate in this mechanism, leading to the enol form of acetophenone.

(Received in France 18 May 1993; accepted 10 June 1993)