Tetrahedron Letters, Vol.32, No.45, pp 6653-6654, 1991
Printed in Great Britain

0040-4039/91 \$3.00 + .00
Pergamon Press plc

An Interesting Rearrangement of Unsaturated Sulphonate and Thiosulphonate Esters

Arménio C. Serra and Carlos M. M. da Silva Corrêa*

Centro de Investigação em Química (INIC)
Laboratório de Química - Faculdade de Ciências - 4000 Porto - PORTUGAL

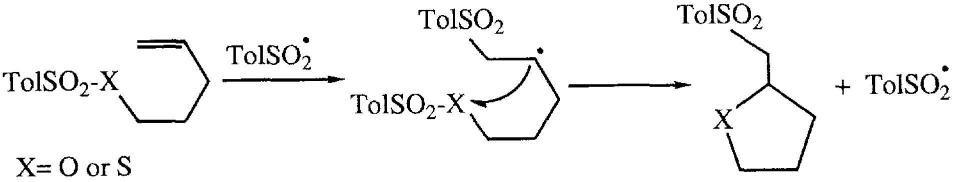
Abstract: *Alkenyl tosylates and thiotosylates, in the presence of radical initiators, undergo radical rearrangements to the corresponding tetrahydofuran and tetrahydrothiophen derivatives.*

The free radical displacemement at divalente sulphur is well known. Sulphides,[1] disulphides,[1] polysulphides,[1] sulphoxides,[1] sulphinyl esters,[2] thiosulphonates,[3] and thioesters[4] are attacked at the divalent sulphur and several kinds of free radicals are displaced.

Radical displacements at oxygen are usual in peroxocompounds[1] but examples of reactions at nonperoxidic oxygen are relatively rare except for carbonyl oxygen.

In this communication we report a radical chain intramolecular displacement at nonterminal oxygen in alkenyl tosylates and at sulphur in thiotosylates (**Scheme 1**) to yield cyclic products through a reaction similar to the Whitham rearrangement.[5]

Scheme 1



(**3**) : X=O ; (**4**) : X=S

In a typical experiment a solution of 4-pentenyl tosylate (**1**) (300 mg; 1.3 mmol), or 4-pentenyl thiotosylate (**2**), in carbon tetrachloride (1.0 mL) was heated for 16 hours (72 hours in the case of the thiotosylate) in a degassed closed tube at 80-90 °C in the presence/absence of benzoyl peroxide (10 mg). The tosylate was completely converted into the cyclic sulphone (**3**) but it did not reacted in the absence of the initiator. The thiotosylate rerranged into (**4**) even in the absence of initiator.

N.M.R. characteristics of the reaction products are in Table 2. The starting reagents were prepared according to the **Scheme 2**. Studies of the effect of the leaving radical, of the ring size , of the heteroatom and of the substituents are in course in this laboratory.

We thank the Instituto Nacional de Investigação Científica (INIC) for financial support.

Scheme 2

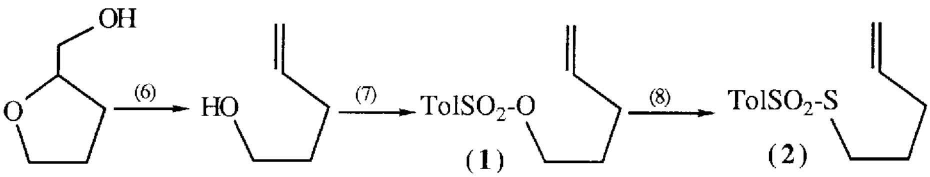


Table 2-n.m.r. (200 MHz) characteristics of the rearranged products.

Product (% yield)	^{1}H n.m.r.(∂,$CDCl_3$,TMS)	^{13}C n.m.r.(∂,$CDCl_3$,TMS)
3 (100)	7.78 (d, 2H, J=8.3 Hz, Ar), 7.35 (d, 2H, J=8.3 Hz, Ar), 4.43-4.06 (m, 3H, OCH_2, OCH), 3.28-3.01(m, 2H, CH_2SO_2), 2.45 (s, 3H, CH_3), 2.15-1.70 (m, 4H, CH_2)	144.77 (Ar), 132.73 (Ar), 129.77 (Ar), 127.63 (Ar), 69.29 (OCH_2) 61.77 (CH_2SO_2), 56.65 (OCH), 34.65 (CH_2), 25.45 (CH_2), 21.45 (CH_3)
4 (90)	7.78 (d, 2H, J=8.3 Hz, Ar), 7.36 (d, 2H, J=8.0 Hz, Ar), 3.67(m, 1H, J=6.5 Hz, SCH) 3.33 (d, 2H, J=6.7 Hz, CH_2SO_2), 2.91-2.60 (m, 2H, SCH_2), 2.45 (s, 3H, CH_3) 2.35-1.70 (m, 4H, CH_2)	144.72 (Ar), 136.08 (Ar), 129.77 (Ar), 127.93 (Ar), 62.61(CH_2SO_2) 41.17 (SCH), 36.61 (SCH_2), 32.34 (CH_2), 29.91(CH_2), 21.43 (CH_3)

REFERENCES and NOTES

1- Ingold, K. U. and Roberts, B. P.,"Free Radical Substitution Reactions," Wiley-Interscience, New York, 1971.

2- Albetazzi, A.; Leardini, R.; Pedulli,G. F.; Tundo, A. and Zanardi,G.,*J. Org. Chem.*,**1984**, *49*, 4482; Beckwitth, A. L. J.; Hong, B. P. and Williams, G. W., *J. Chem. Soc., Chem. Comm.*,**1989**,1202.

3- Degani, J.; Ghersetti, S. and Tundo, A., *Ann. Chim.*(Italy), **1961**, *51*, 461.

4- Tada, M.; Uetake, T. and Matsumoto, M., *J. Chem. Soc., Chem. Comm.*, **1990**,1408..

5- Smith, T. A. K. and Whitham, G.H., *J. Chem. Soc., Chem. Comm.*, **1985**, 897 and following papers.

6- Brooks, L. A. and Snyder, H. R., *Org. Synth.*, **1962**, Coll. Vol. 3, 698

7- Tipson, R. S., *J. Org. Chem.*, **1944**, *9*, 238.

8- $TolSO_2SK$ in acetone, refluxing for 16 hours.

(Received in UK 9 September 1991)