Pergamon

Tetrahedron Letters, Vol. 37, No. 1, pp. 119-122, 1996
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4039/96 $15.00 + 0.00

0040-4039(95)02088-8

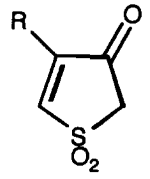
Michael Additions to 3(2H)-Thiophenone 1,1-dioxide.

Nini Hofsløkken, Solveig Flock, Lars Skattebøl*
Department of Chemistry, University of Oslo, POB 1033, 0315 Oslo, Norway.

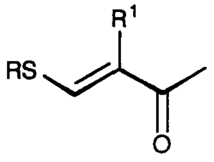
Abstract: The addition of thiols and amines to 3(2H)thiophenone 1,1-dioxide takes place with extrusion of sulfur dioxide,furnishing in high yields the corresponding vinyl sulfides and enamines. Addition of dithiols afforded the corresponding thioacetals.The rates of the the Michael addition and the extrusion reaction are strongly influenced by the solvent employed. In ethanol, sulfur dioxide extrusion took place even at room temperature.

The thermally induced, orbital symmetry controlled extrusion of sulfur dioxide from 2,5-dihydrothiophene 1,1-dioxide derivatives is a synthetically valuable method for the preparation of 1,3-butadienes.[1,2] We have studied Michael additions of thiols and amines to the 3(2H)-thiophenone 1,1-dioxides 1 and the subsequent sulfur dioxide extrusion which in some cases took place even at room temperature.

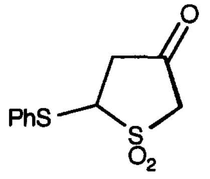
The ketone 1a was available from 2,5-dihydrothiophene1,1-dioxide through three consecutive steps in 40% overall yield,[3,4] and the homologue 1b was prepared in a similar yield from 3,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide.[5] Reaction of 1a with benzenethiol in THF under reflux, in the presence of pyridine, proceeded with extrusion of sulfur dioxide and formation of a 7 : 2 mixture of (E)- and (Z)-4-phenylsulfinyl-3-buten-2-one (2a)[6] in 80% isolated yield. Quenching the reaction after 30 min. gave 5-phenylsulfinyl-2,5-dihydro-3-thiophenone 1,1-dioxide(3), in almost quantitative yield. The rate of this Michael addition was strongly influenced by the base and solvent employed. While no reaction of 1a took place after 20 hours in refluxing THF without added base, an ethanol solution in the presence of triethylamine was completely converted to a mixture of 2a and 3 after 10 min. at room temperature; apparantly these conditions strongly enhanced the rate of sulfur dioxide rusion as well.[7] Heating an ethanol solution of 3 under reflux for 40 min. in the presence of triethylamine gave E-2a as sole product in practically quantitative yield; a separate experiment showed no equilibration of an isomer mixture of 2a under the reaction conditions, indicating that the extrusion reaction takes place preferentially by an outward rotation of the phenylsulfinyl group. Further addition of benzenethiol to 2a occurs as well; depending on the reaction conditions, a small amount[8] of the acetal 4 was occasionally present in the product.



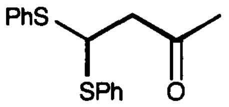
1 **a** R = H
b R = Me



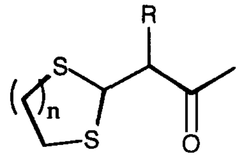
2 **a** R = Ph; R^1 = H
b R = Ph; R^1 = Me
c R = Bu; R^1 = H
d R = $(CH_2)_2CO_2Me$; R^1 = H



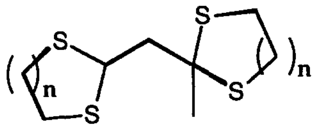
3



4



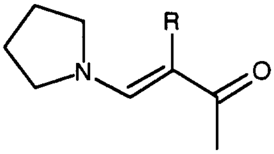
5 **a** R = H; n = 1
b R = H; n = 2
c R = Me; n = 2

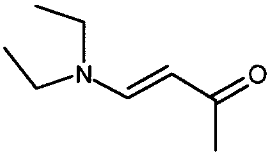


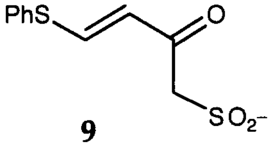
6 **a** n = 1
b n = 2

Similarly, reactions of an ethanol solution of **1a** with 1-butanethiol and methyl 3-mercaptopropionate in the presence of pyridine furnished the ketones **2c**[9] and **2d** in 88 and 92% yields, respectively, as almost pure E-isomers.[10] Furthermore, the addition of one equivalent of 1,2-ethanedithiol and 1,3-propanedithiol to **1a** under the same conditions provided the thioacetals **5a**[11] and **5b**[11] in 93 and 88% yields, respectively; however, using two equivalents of the dithiols and *p*-toluenesulphonic acid as catalyst the bis-thioacetals **6a**[11] and **6b**[11] were formed in 93 and 91% yields. The methyl-substituted derivative **1b** was much less reactive; with benzenethiol (*E*)-3-methyl-4-phenylsulfinyl-3-buten-2-one (**2b**)[12] was obtained in 99% yield after 2.5 hours of reflux in ethanol-triethylamine, and with 1,3-propanedithiol the thioacetal **5c** was obtained in 85% yield after 56 hours of reflux in ethanol-pyridine. On the other hand, a reaction of **1b** and 1,3-propanedithiol in toluene-pyridine was incomplete even after several days under reflux.

The addition of pyrrolidine to a THF solution of **1a** at room temperature afforded as sole product the E-isomer of the enaminone **7a**[13] in 92% yield, and a similar yield of **8** was obtained using diethylamine. The reactions of the amines were also slower in the case of **1b**; pyrollidine furnished the enaminone **7b**[13] as the E-isomer in 73% yield after 24 hours of reflux in toluene.


7 **a** R = H
b R = Me


8


9

It is known that five-membered cyclic sulfones react with base by cleavage of the carbon-sulfur bond forming sulfinate anions which may lose sulfur dioxide.[14] Such a two-step mechanism may account for our products and the effects of both solvent and base as well; however, using the sulfolene 3 as a model compound, we were unable to trap an intermediate sulfinate anion 9 by methyl iodide.[15] Hence, for our reactions we favour a concerted ring opening and sulfur dioxide extrusion from an enolate intermediate, the rate of which must be strongly influenced by substituent effects; while the sulfur dioxide extrusion from 3 was finished in less than one hour, the reaction of 3-tetrahydrothiophenone 1,1-dioxide under the same conditions, yielding 4-phenylsulfinylbutan-2-one,[16] was incomplete after 91 hours of reflux.

The thioacetals 5 a and b may prove synthetically interesting, particularly since they are easily obtained in high yields by transacetalization of commercially available 4,4-dimethoxybutan-2-one with 1,2-ethanedithiol and 1,3-propanedithiol, respecti-vely.[11] The synthetic use of these compounds is being explored.

Acknowledgement. Financial assistance from Norsk Hydro and The Norwegian Research Council is gratefully acknowledged.

References and Notes:

1. Mock, W. L. *J. Am. Chem. Soc.*, (1975) 97, 3666, 3673

2. Simpkins, N. S., *Sulphones in Organic Chemistry*, Pergamon Press, Oxford 1993.

3. Prochazka, M., Horak, V., *Coll. Czech. Chem. Commun.*, (1959) 24, 1509.

4. Tostikov, G. A., Kazakov, V. P., Shul´ts, E. E., Bulgakov, R. G. Kantyukova, R. G., *Zh. Org. Khim.*, (1984) 20, 313.

5. Houge-Frydrych, C. S. V., Motherwell, W. B., O´Shea, D. M., *J. Chem. Soc., Chem. Commun.*, (1987)1819.

6. Haynes, R. K., Vonwiller, S. C,. Stokes, J. P., Merlino, L. M., *Aust J. Chem.* (1988) 41, 881 .
7. A solvent effect has been reported previously;[1] the sulfur dioxide extrusion from 2-vinyl-substituted tetrahydrothiophene 1,1- dioxides took place in ethanol at 60 °C.[17] Relatively little is known about the effect of substituents on this reaction; the 2-methyl derivative extrudes sulfur dioxide 5 x faster than the parent 3-sulfolene.[1]
8. The compound was generally formed in barely detectable amounts, except in the product from the reaction of 1a with benzenethiol in ethanol-pyridine , which furnished 13% of the acetal; it was identified from the ^1H NMR spectrum of the crude product, particularly by the triplet at δ 4.92 , due to the acetal proton.

9. Akiyama, S., Nakatsuji, S., Hamamura, T., Kataoka, M., Nakagawa, M., *Tetrahedron Lett.* (1979) 2809.

10 Novel compounds were characterised spectroscopically including high resolution MS. Less than 5% of (Z)-2d was formed based on ^1H NMR spectrum of the crude product.

11. Coffen, D. L., Bank, K. C., Garrett, P. E., *J. Org. Chem.* (1969) 34, 605.

12. The configuration was assigned by comparing the chemical shift of the olefinic proton with those of (E)- and (Z)-2a.

13. Maggiulli, C. A., Tang, P-W., *Org. Prep. Proc. Int.* (1984)16, 31.

14. de Souza Gomes, A., Joullié, M. M., *J. Heterocyclic Chem.* (1969) 6, 729; Ishikawa, Y., Kurebayashi, Y, Suzuki, K., Terao, Y., Sekiya, M., *Chem. Pharm. Bull.* (1981) 29, 2496.

15. Crumbie, R. L., Ridley, D. D., *Aust. J. Chem.* (1981) 34, 1017; Näf, F., Decorzant, R., Escher, S. D., *Tetrahedron Lett.* (1982) 23, 5043.

16. Ahlbrecht, H., Ibe, M., *Synthesis* (1988) 210.

17. Takayama, H, Suzuki, T., *J. Chem. Soc., Chem. Commun.*, (1988) 1044.

(*Received in UK* 9 *October* 1995; *revised* 30 *October* 1995; *accepted* 3 *November* 1995)