Tetrahedron Letters,Vol.30,No.32,pp 4237-4240,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

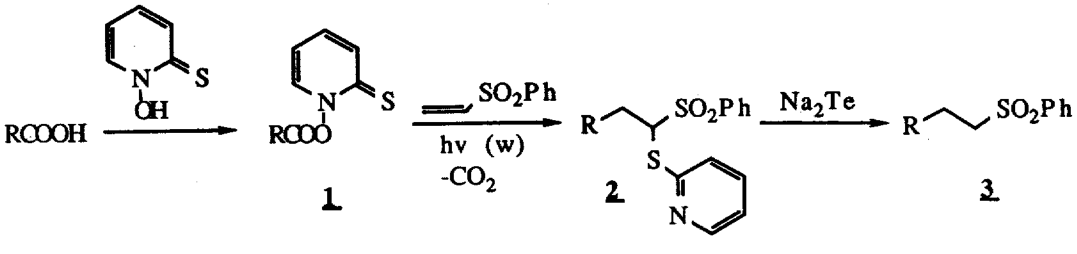
SOME FURTHER NOVEL TRANSFORMATIONS OF GEMINAL (PYRIDINE-2-THIYL) PHENYLSULPHONES

Derek H. R. Barton[a*], Jean Boivin[b], Jadab Sarma[a], Elisabeth da Silva[b,c], and Samir Z. Zard[b*]

a) Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.
b) Laboratoire de synthèse Organique, Ecole Polytechnique, 91128 Palaiseau, France
c) Ministère de la Defense

Summary. Geminal (pyridine-2-thiyl) phenylsulphones, obtained by decarboxylative radical addition of O-acyl derivatives of N-hydroxy- 2-thiopyridone onto phenyl vinyl sulphone, undergo a wide variety of further transformations when subjected to sodium telluride or to organoaluminum reagents.

As part of our study of the radical decarboxylation of carboxylic acids [1], we have recently shown that irradiation with visible light of O-acyl derivatives **1** of N-hydroxy-2-thiopyridone in the presence of phenyl vinyl sulphone gives high yields of addition products **2**[2]. This operation is synthetically quite valuable since, in addition to creating a new carbon-carbon bond, it affords a highly functionalised adduct. In this Letter, we describe some further novel transformations of these derivatives where advantage is taken from the geminal disposition of the sulphide and sulphone groups.



Scheme 1

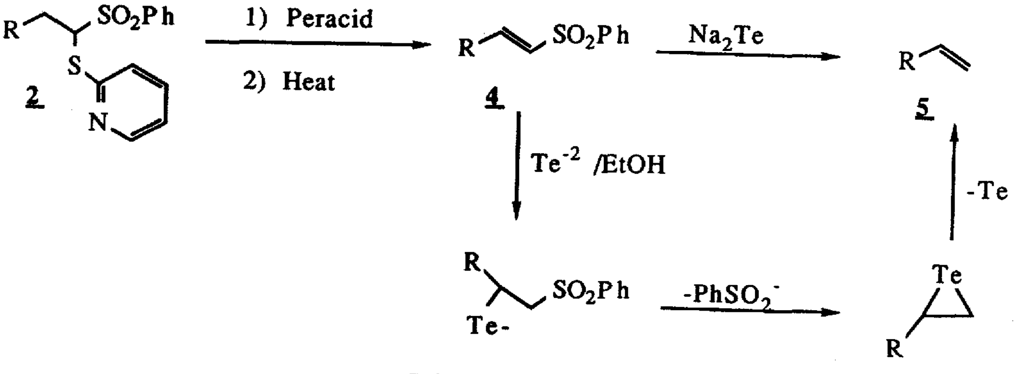
We first considered the possibility of achieving a selective reduction of derivatives **2** using sodium telluride. This easily prepared reagent displays an amazing variety of mechanistic behaviour[3]. In this case, reduction through electron transfer would almost certainly lead to desulphonylation, whereas simple nucleophilic attack at the divalent sulphur would result in the loss of the pyridine sulphide fragment.

In the event, the latter pathway prevailed. Thus, refluxing under an inert atmosphere an ethanolic solution of 2a-f and sodium telluride (prepared *in situ* by reduction of tellurium powder with $NaBH_4$ followed by addition of ethanolic sodium hydroxide until pH 12) gave the corresponding sulphones 3a-f in excellent yield (table). Air is bubbled at the end of the reaction to destroy excess reagent. The tellurium is recovered quantitatively.

TABLE

Entry	**2**	**3** (yield %)	**4** (yield %)	**5** (yield %)
1	**2a**, R= $CH_3(CH_2)_{14}$-	**3a** (95)	**4a** (80)	**5a** (94)
2	**2b**, R= $PhCH_2CH_2$-	**3b** (96)	**4b** (85)	**5b** (75)
3	**2c**, R= 1-adamantyl-	**3c** (96)	**4c** (63)	**5d** (82)
4	**2d**, R= Me_3C-	**3d** (96)	—	—
5	**2e**, R= cyclohexyl-	**3e** (94)	—	—
6	**2f**, R= Me_2CH-	**3f** (94)	—	—
7	**2g**, R= $PhOCH_2$-	—	**4g** (81; by NMR)	**5g** (66)

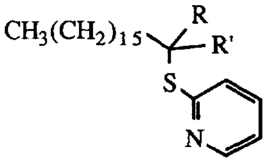
From a synthetic standpoint, perhaps a more useful conversion, also accomplished by this remarkable reducing agent, is the desulphonylation of vinylic sulphones **4** to produce olefins **5** (scheme 2) [4]. The former are easily available from the initial adducts by syn- elimination of the corresponding sulphoxides. As shown by the examples listed in the table, yields are good to excellent. A plausible mechanism for this transformation, which makes use of the exceptional nucleophilicity of the telluride anion, is outlined in the scheme below. Collapse of epitellurides into olefins and elemental tellurium has previously been postulated by Clive and Menchen[5].



Scheme 2

In a parallel series of experiments, we have succeeded in replacing selectively the sulphone moiety with various groups through a Lewis acid catalysed nucleophilic displacement. This is made possible by the presence of the *gem*. pyridine sulphide group which stabilises the incipient carbocation resulting from complexation with the Lewis acid. Previous work on related systems, especially by the group of Trost[6], indicated that this was indeed feasible.

Thus, after some experimentation, we found that ethylaluminum dichloride ($EtAlCl_2$) induced the reaction of **2a** with allyl trimethylsilane[7] to give compound **6** in excellent yield (97%). Other common Lewis acids such as $TiCl_4$ or BF_3 were much less efficient. Moreover, starting the reaction at low temperature was crucial for good and reproducible yields. Oxidation with m-chloroperbenzoic acid of the homo-allylic sulphide thus obtained followed by thermolysis sulphoxide gave terminal diene **7** in 73% overall yield.



2a , R= $-SO_2Ph$; R'= H

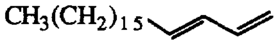
6 , R= allyl; R'= H

8 , R= R'= H

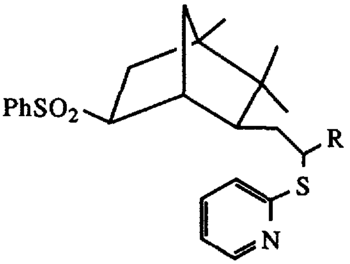
9 , R= $-SO_2Ph$; R'= Me

11 , R= H; R'= Me

13 , R= R'= Me

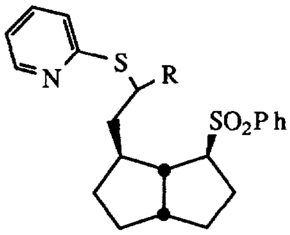


7



15 , R= $-SO_2Ph$

16 , R= Me



10 , R= $-SO_2Ph$

12 , R= H

14 , R= Me

To our initial surprise, a blank experiment, carried out in the absence of allyl trimethylsilane, resulted in the almost quantitative formation of sulphide **8**. To our knowledge, only in one instance is ethylaluminum dichloride reported to act as a reducing agent, causing the reductive opening of certain lactones[8]. The source of hydride is one of the ß-hydrogens of the ethyl group, with concomitant departure of ethylene. This reaction is clearly related to the Meerwein-Pondorff-Verley reduction and to hydride transfers encountered with some organometallic reagents.

This novel reductive desulphonylation was applied to derivatives **9** and **10**. The former is prepared by methylation (MeI) of the anion derived from **2a** and the latter by multiple radical addition onto phenyl vinylsulphone starting from 2-cyclopentenyl acetic acid[9]. The corresponding sulphides **11** and **12** were thus produced in 79% and 73% yield respectively. The second example illustrates the high selectivity of this process and reflects the need to activate the sulphone group for a reduction to take place.

The sulphone group can also be replaced with a methyl group simply by using trimethylaluminum[10] instead of EtAlCl$_2$. In this case no hydride transfer can take place and desulphonative methylation occurs smoothly. This is shown by the following conversions: **2a** --► **11** (94%); **9** --► **13** (80%); **10** --► **14** (80%); and **15** --► **16** (88%). Again high selectivity is achieved in the last two examples.

The novel transformations uncovered in this exploratory study are a consequence of the interplay between the sulphide and the sulphone groups, and underscores the rich chemistry embodied in these systems.

Acknowledgements: We thank Professor J-Y. Lallemand for his interest in this work and the Welch Foundation,the N.I.H., and the Ministère de la Défense for generous financial support.

References

1. Barton, D. H. R., Crich, D., and Motherwell, W. B., *J. Chem. Soc., Chem. Commun.*, 1983, 939. For a review of this work, see: Barton, D. H. R. and Zard, S. Z., *Pure and Appl. Chem.*, 1986, **58**, 675.
2. Barton, D. H. R., Togo, H., and Zard, S. Z., *Tetrahedron Lett.*, 1985, **26**, 6349.
3. Barton, D. H. R., Bohé, L., and Lusinchi, X., *Tetrahedron Lett.*, 1987, **28**, 6609; 1988, **29**, 2571 and references there cited.
4. A similar reaction has been described very recently by Huang, X. and Han-Zong, Z., *Synthesis*, 1989, 42.
5. Clive, D. L. J. and Menchen, S. M. , *J. Chem. Soc., Chem. Commun.*, 1977, 658.
6. Trost, B. M. and Ghadir, M. R., *J. Amer. Chem. Soc.*, 1984, **106**, 7260; 1986, **108**, 1098; Trost, B. M. and Mikhail, G. K., *J. Amer. Chem. Soc.*, 1987, **109**, 4124; Ogura, K., Iihara, T., Kiuchi, S., Kajiki, K., Koshikawa, O., Takahashi, K., and Iida, H., *J. Org. Chem.*, 1986, **51**, 700; Janssen, C. M. and Godefroi, E., *J. Org. Chem.*, 1982, **47**, 3274; Ikegami, S., Torisawa, Y.,and Satoh,Y., *Tetrahedron Lett.*, 1988, **29**, 1729.
7. An analogous desulphonative allylation has been reported very recently by Simpkins, N. S., *Tetrahedron Lett.*, 1988, **29**, 6787.
8. Reinheckel, H., Sonnek, G., and Falk, F., *J. Prak. Chem.*, 1974, **316**, 215; Reinheckel, H., Sonnek, G., and Gensike, R., *ibid.*, 1974, **317**, 273.
9. Barton, D. H. R., da Silva, E., and Zard, S. Z., *J. Chem. Soc., Chem. Commun.*, 1988, 285.
10. For a recent review on organoaluminum chemistry, see: Manuoka, K. and Yamamoto, H., *Tetrahedron*, 1988, **44**, 5001.

(Received in France 23 May 1989)