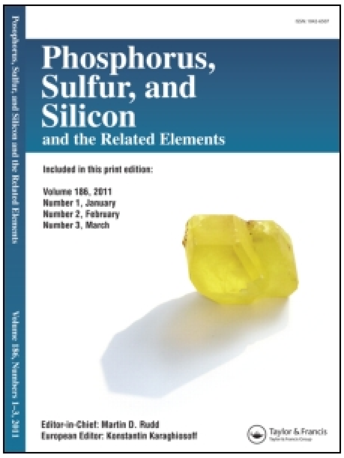


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Sulfinate-Sulfone Pummerer Rearrangement

Kurt Schank[a]; Stefan Buegler[a]; Norbert Schott[a]
[a] FR 11.2 Organische Chemie, Universität, Saarbrücken

To cite this Article Schank, Kurt , Buegler, Stefan and Schott, Norbert(1994) 'The Sulfinate-Sulfone Pummerer Rearrangement', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 435 — 436
To link to this Article: DOI: 10.1080/10426509408034266
URL: http://dx.doi.org/10.1080/10426509408034266

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95–96, pp. 435–436
Reprints available directly from the publisher
Photocopying permitted by license only

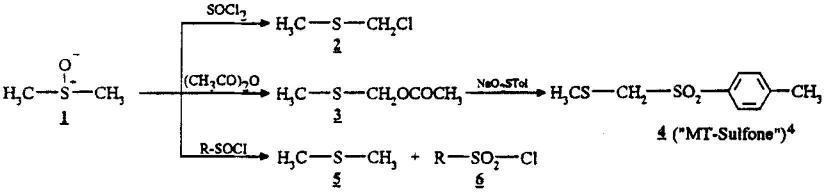
THE SULFINATE-SULFONE PUMMERER REARRANGEMENT

KURT SCHANK*, STEFAN BUEGLER, AND NORBERT SCHOTT
FR 11.2 Organische Chemie, Universität D-66041 Saarbrücken

Abstract: α-CH acidic sulfoxides with additional electron-withdrawing substitution at C-α afford generation of α sulfonyl thioethers during reaction with sulfinyl chlorides. Some reaction details as well as a mechanistic proposal are presented.

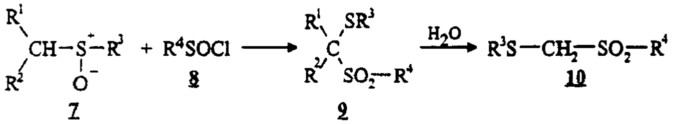
Introduction

The PUMMERER rearrangement is an acid catalyzed intramolecular redox reaction of CH acidic sulfoxides which leads to reduction at sulfur and to oxidation of α carbon[1]. A suchlike formed OH-group can be easily replaced by other nucleophilic groups. Thus, conversion of DMSO (1) i.e. with acyl chlorides leads to acyloxy sulfonium chlorides which are in equilibrium with chloro sulfonium carboxylates presumably via tetracovalent sulfur intermediates[2]. Since on the one hand conversion of DMSO with thionyl chloride yields directly chloromethyl methyl sulfide[3] (2), and MT-sulfone 4 is easily available from DMSO, acetic acid anhydride and sodium 4-toluene sulfinate[4] via Pummerer reaction, sulfinyl chlorides on the other hand are oxygenated to sulfonyl chlorides 6 by sulfoxides[5] :



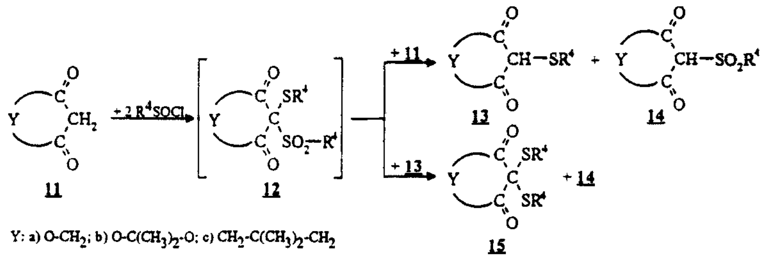
Results

Additional enhancement of sulfoxide α-CH acidity by electron withdrawing groups rendered possible sulfone formation via sulfinate-sulfone Pummerer rearrangement[6]:



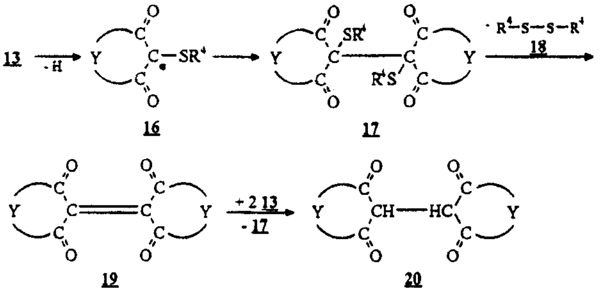
R^1= acyl; R^2= H or acyl

Because of high CH acidity of open-chain 1.3-dicarbonyl compounds application of the aforementioned scheme by use of two mols of sulfinyl chloride 8 yields the corresponding α sulfonyl thioethers 10[6,7]. This reaction sequence, however, fails with particularly strong acidic cyclic 1.3-dicarbonyl compounds 11 because their bis-sulfur substituted derivatives 12 represent very efficient sulfenylating agents which attack all suitable nucleophiles present in the reaction mixture[8]:

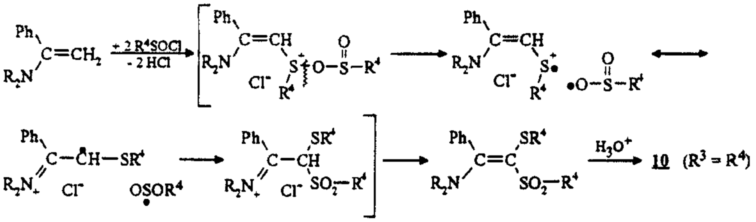


Y: a) O-CH$_2$; b) O-C(CH$_3$)$_2$-O; c) CH$_2$-C(CH$_3$)$_2$-CH$_2$

Additionally, intermediacy of 13 gives rise to formation of capto-dative substituted radicals 16 which dimerize to give dimers 17 and subsequent products (18-20):



The related geminal ß-dithiofunctionalization of α-morpholino styrene[9] is of particular importance for mechanistic interpretation of this type of Pummerer rearrangement because it suggests sulfonyl radical migration within an radical cation-radical-pair rather than sulfinate formation:



In these cases a one-pot procedure affords directly i.e. MT-sulfone.

References

1. S.W. Schneller, Int. J. Sulfur Chem. 8 (4), 579 (1976), p. 583.
2. N.E. Hester, Int. J. Sulfur Chem. 8 (1), 119 (1973).
3. F.G. Bordwell, B.M. Pitt, J. Am. Chem. Soc. 77, 572 (1955).
4. K. Ogura, Pure & Appl. Chem. 59, 1033 (1987).
5. a) A. Senning, Chem. Commun. 1967, 64;
   b) T. Numata, K. Ikura, Y. Shimano, S. Oae, Org. Prep. Proced. Int. 8, 119 (1976).
6. G.A. Russell, E.T. Sabourin, J. Org. Chem. 34, 2336 (1969).
7. a) E.M. Philbin, E.R. Stuart, R.F. Timoney, T.S. Wheeler, J. Chem. Soc. 1957, 2338;
   b) K. Schank, S. Bügler, Sulfur Lett. 1, 63 (1982).
8. N. Schott, Ph. D. Dissertation, Saarbrücken 1992.
9. S. Bügler, Ph. D. Dissertation, Saarbrücken 1983.