Tetrahedron Letters,Vol.22,No.48,pp 4787-4790,1981 0040-4039/81/484787-04$02.00/0
Printed in Great Britain

# SPONTANEOUS [2,3]-SIGMATROPIC REARRANGEMENT OF S-ARYLTHIOSULFONIUM YLIDS FORMED IN THE REACTION OF ARYLSULFENYL CHLORIDES WITH METHYLTHIOMETHYLTRIMETHYLSILANE

Paul G. Gassman* and Takashi Miura

Department of Chemistry, University of
Minnesota, Minneapolis, Minnesota 55455

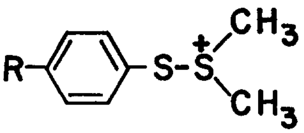
Summary: A new [2,3]-sigmatropic rearrangement of thiosulfonium ylids yields ortho-methylthiomethylthiophenols. The ylids were generated through the cleavage of a C-Si bond with chloride anion.

The use of [2,3]-sigmatropic rearrangements for the exclusive ortho substitution of certain aromatic systems has been widely studied. These rearrangements can be represented by the generalized conversion of **1** into **2**. Among the well characterized general classes of these

**1** **2**

rearrangements are: X = Z = C, Y = N[1]; X = Z = C, Y = S[2]; X = Z = C, Y = Se[3]; X = O, Y = S, Z = C[4]; X = N, Y = S, Z = C[5].[6] In the interest of extending this general concept, we investigated the possibility of X = Y = S, Z = C. We now wish to report the first examples of this rearrangement.

In 1975, Minato and co-workers prepared the thiosulfonium salt, **3**, and subjected it to base treatment.[7] These workers found that base and a variety of nucleophiles selectively

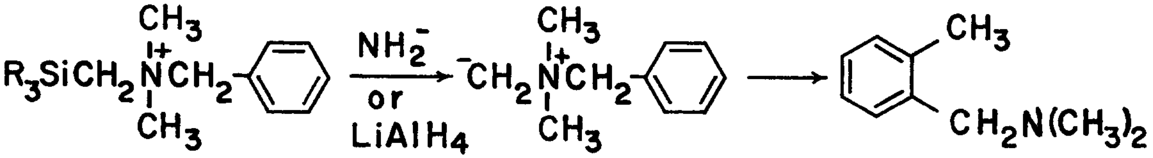


$X^-$ ($X = BF_4$, $ClO_4$)

**3**

attacked the neutral sulfur to displace dimethyl sulfide. This was similar to our observations with certain selenonium salts.[3] With **3**, no evidence was found for the generation or rearrangement of the crucial ylid intermediate. In view of these results, it was evident that we would not be able to generate the desired ylid in a straightforward manner.

A promising approach appeared to be a modification of reactions reported in the literature for the generation of C-N[8] and C-S[9] ylids through the cleavage of a C-Si bond. Of particular relevance was the report of Sato and co-workers[8] who demonstrated that treatment of 4 with either amide anion or with lithium aluminum hydride resulted in the formation of the ylid 5 and subsequent Sommelet-Hauser rearrangement to yield 6. This suggested to us that treatment of arylsulfenyl chlorides (7) with methylthiomethyltrimethylsilane (8)[10] might yield a silyl substituted S-arylthiosulfonium salt, 9, which in turn could be converted to an ylid which would undergo a [2,3]-sigmatropic rearrangement.

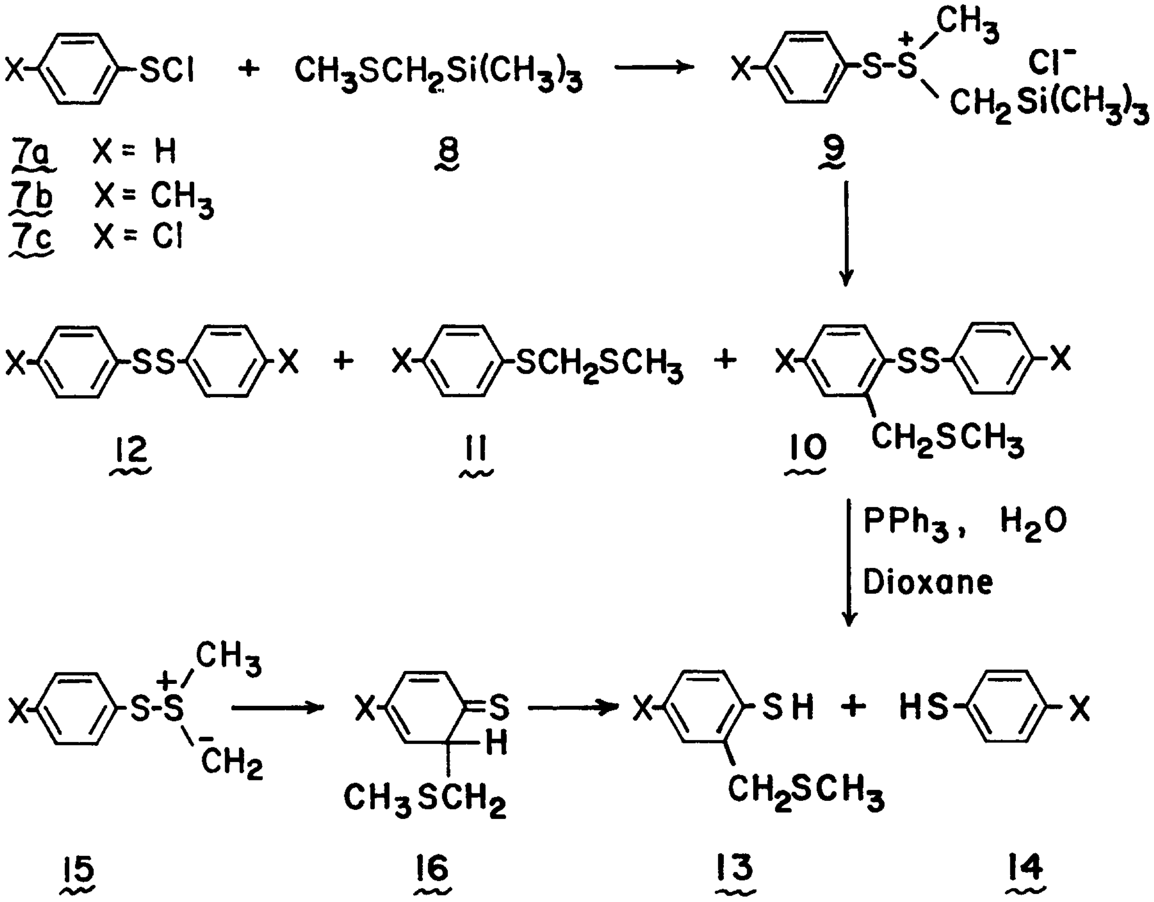


4 5 6

Our initial approach involved the addition of benzenesulfenyl chloride (7a, 1 equiv.) to 1.1 equiv. of 8 in carbon tetrachloride at -20°C, followed by stirring at -20°C for 1 h and then for 10 h at 25°C. This gave 13% of 10a, 29% of 12a and trace amounts (<3%) of the Stevens rearrangement product, 11a.[11] We were surprised to find that chloride ion was sufficiently nucleophilic under our reaction conditions to promote the rearrangement. No other reagent was necessary.

Because we desired the free thiophenol, 13, we modified our reaction conditions in order to allow for a direct reduction of 10 to a mixture of 13 and 14. In a general procedure, 20 mmol of 7 in 20 mL of methylene chloride was added dropwise over a 1-h period to a solution of 10 mmol of 8 at -30°C. The reaction mixture was stirred for 2 h at -30°C and then for 1 h at 25°C. The solvent was removed on a flash evaporator and the small amounts of 11 which were present were removed by fractional distillation. The residue, which contained 10 and 12, was allowed to react with 5-14 mmol of triphenylphosphine in 3:1 dioxane-water containing 1-2 drops of hydrochloric acid for 1 h at 25°C.[12] The reaction mixture was then worked up and 13 and 14 were isolated by fractional distillation. Under these conditions we obtained the following yields: 13a, X = H, 19%; 13b, X= $CH_3$, 20%; 13c, X = Cl, 23%. In addition, the yields of 14 varied from 27 to 39%.

Mechanistically, it would appear that 7 adds to 8 to give 9 in what may be a reversible process. Attack of chloride ion on silicon should then produce 15 and chlorotrimethylsilane (which was isolated).[13] Steven's rearrangement of 15 would give 11 while the desired [2,3]-sigmatropic rearrangement would yield 16. Hydrogen migration and accompanying rearomatization of 16 would produce 13 which in turn could react with 7 to give the observed intermediate 10.



We are continuing to explore the use of the trimethylsilyl group as a leaving group in the generation of ylids for [2,3]-sigmatropic rearrangements.

Acknowledgment. We are indebted to the National Institutes of Health for Grant GM-22346 which supported this investigation.

## References and Footnotes

1. Sommelet, M. *Compt. Rend.* 1937, *205*, 56. Kantor, S.W.; Hauser, C.R. *J. Am. Chem. Soc.* 1951, *73*, 4122. Jones, G.C.; Hauser, C.R. *J. Org. Chem.* 1962, *27*, 3572. Jones, G.C.; Beard, W.Q.; Hauser, C.R. *ibid.* 1963, *28*, 199. See also Fery, L.P.A. *Bull. soc. chim. Belges.* 1962, *71*, 376.

2. Hauser, C.R.; Kantor, S.W.; Brasen, W.R. *J. Am. Chem. Soc.* **1953**, *75*, 2660.

3. Gassman, P.G.; Miura, T.; Mossman, A. *J. Chem. Soc., Chem. Commun.* **1980**, 558.

4. Pfitzner, K.E.; Moffatt, J.G. *J. Am. Chem. Soc.* **1963**, *85*, 3027; *ibid.* **1965**, *87*, 5661, 5670. Burdon, M.G.; Moffatt, J.G. *ibid.* **1965**, *87*, 4656; *ibid.* **1966**, *88*, 5855; *ibid.* **1967**, *89*, 4725. Pfitzner, K.E.; Marino, J.P.; Olofson, R.A. *ibid.* **1965**, *87*, 4658. Marino, J.P.; Pfitzner, K.E.; Olofson, R.A. *Tetrahedron* **1971**, *27*, 4181. Olofson, R.A.; Marino, J.P. *ibid.* **1971**, *27*, 4195. Claus, P. *Monatsh. Chem.* **1971**, *102*, 913. Hayashi, Y.; Oda, R. *J. Org. Chem.* **1967**, *32*, 457. Pettit, G.R.; Brown, T.H. *Can. J. Chem.* **1967**, *45*, 1306. Claus, P. *Monatsh. Chem.* **1968**, *99*, 1034. Claus, P.; Vavra, N.; Schilling, P. *ibid.* **1971**, *102*, 1072. Doucet, J.; Robert, A. *C. R. Acad. Sci., C* **1971**, *272*, 1562. Claus, P.; Rieder, W. *Tetrahedron Lett.* **1972**, 3879. Gassman, P.G.; Amick, D.R. *ibid.* **1974**, 889, 3463. Gassman, P.G.; Amick, D.R. *Syn. Commun.* **1975**, *5*, 325. Gassman, P.G.; Amick, D.R. *J. Am. Chem. Soc.* **1978**, *100*, 7611.

5. Claus, P.; Vycudilik, W. *Monatsh. Chem.* **1970**, *101*, 396. Gassman, P.G.; Huang, C.-T. *J. Chem. Soc., Chem. Commun.* **1974**, 685. Gassman, P.G.; Gruetzmacher, G.D. *J. Am. Chem. Soc.* **1974**, *96*, 5487. Gassman, P.G.; van Bergen, T.J.; Gilbert, D.P.; Cue, B.W., Jr. *ibid.* **1974**, *96*, 5495. Gassman, P.G.; van Bergen, T.J. *ibid.* **1974**, *96*, 5508. Gassman, P.G.; Gruetzmacher, G.D.; van Bergen, T.J. *ibid.* **1974**, *96*, 5512. Gassman, P.G.; Gilbert, D.P.; Luh, T.-Y. *J. Org. Chem.* **1977**, *42*, 1340. Gassman, P.G.; Cue, B.W., Jr.; Luh, T.-Y. *ibid.* **1977**, *42*, 1344. Gassman, P.G.; Parton, R.L. *Tetrahedron Lett.* **1977**, 2055. Gassman, P.G.; Balchunis, R.J. *ibid.* **1977**, 2235. Gassman, P.G.; Schenk, W.N. *J. Org. Chem.* **1977**, *42*, 3240. Gassman, P.G.; Gilbert, D.P.; Cole, S.M. *ibid.* **1977**, *42*, 3233. Gassman, P.G.; Parton, R.L. *J. Chem. Soc., Chem. Commun.* **1977**, 694. Gassman, P.G.; Drewes, H.R. *J. Am. Chem. Soc.* **1978**, *100*, 7600.

6. A 2% conversion for the reaction X = Se, Y = S, Z = C has also been reported: Detty, M.R. *J. Org. Chem.* **1979**, *44*, 4528.

7. Minato, H.; Miura, T.; Kobayashi, M. *Chem. Lett.* **1975**, 1055.

8. Sato, Y.; Sakakibara, H. *J. Organomet. Chem.* **1979**, *166*, 303. See also Sato, Y.; Yagi, Y.; Koto, M. *J. Org. Chem.* **1980**, *45*, 613.

9. Cooke, F.; Magnus, P.; Bundy, G.L. *J. Chem. Soc., Chem. Commun.* **1978**, 714.

10. Peterson, D.J. *J. Org. Chem.* **1967**, *32*, 1717.

11. Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds except for **10b** and **10c** which were not isolated or characterized. In all cases, spectral data was consistent with the assigned structures.

12. Overman, L.E.; Smoot, J.; Overman, J.D. *Synthesis* **1974**, 59.

13. An alternate mechanism would involve the fragmentation of **9** to give chlorotrimethylsilane, thiophenoxide and $CH_3\overset{+}{S}{=}CH_2$ (**17**). Attack of **17** on thiophenoxide or thiophenol could then yield either **11** or **13**. However, the complete absence of any product from the attack of **17** on the para position of thiophenoxide or thiophenol makes **17** an unlikely intermediate in the formation of **13**.

(Received in USA 27 July 1981)