

THE ADDITION OF CARBOMETHOXY SULFAMOYL CHLORIDE TO TRIMETHYL  
SILYL ENOL ETHERS. AN UNEXPECTED SIDE REACTION.

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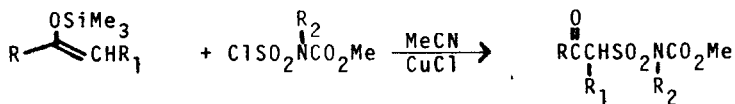
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The recent discovery by Burgess and Williams<sup>1</sup> of the reaction of certain nitriles with the sodium salt of carbomethoxysulfamoyl chloride prompts us to report similar results which we have observed under quite different reaction conditions.

Aryl sulfonyl chlorides have recently been added to trimethylsilyl enol ethers 1 to give  $\beta$ -ketosulfones.<sup>2</sup> This suggested to us a possible route (Scheme 1) to 1,4,3-oxathiazines 4, compounds of opposite regiochemistry from the 1,2,3-

SCHEME 1



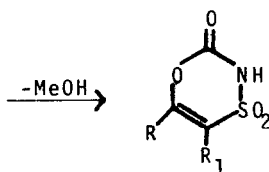
1 a) R=Ph, R<sub>1</sub>=Me

2 a) R<sub>2</sub>=H

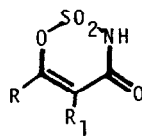
3 a) R=Ph, R<sub>1</sub>=Me, R<sub>2</sub>=H

b) R<sub>2</sub>=D

b) R=Ph, R<sub>1</sub>=Me, R<sub>2</sub>=D

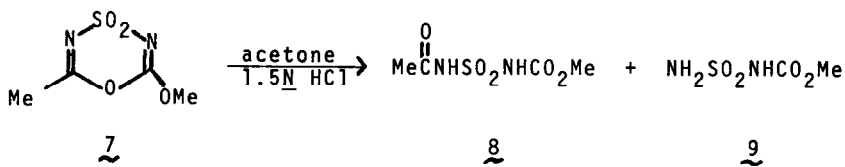


4



5

oxathiazines 5 obtained by reaction of chlorosulfonyl isocyanate (CSI) with ketones.<sup>3</sup> Therefore silyl ether 1a<sup>4</sup> was allowed to react, in the presence of a catalytic amount of cuprous chloride,<sup>2</sup> with carbomethoxysulfamoyl chloride 2a<sup>5</sup> in acetonitrile (2 hr., 25°). Upon anhydrous workup, adduct 3a<sup>6</sup> was indeed obtained but only in 23.6% yield, along with propiophenone 6 (71.0%). In addition, a colorless crystalline compound was produced (54.8%) which displayed properties identical to those reported<sup>1</sup> for 6-methyl-2-methoxy-1,4,3,5-oxathiadiazine-4,4-dioxide 7. Hydrolysis of 7 in acetone/1.5N HCl gave N-acetyl-N'-carbomethoxysulfamide 8 (58.2%),<sup>1</sup> as well as N-carbomethoxysulfamide 9 (33.8%), m.p. 138-39°C



(lit.<sup>5</sup> 139-40°C). Amide 8 could not be converted to 9 under the hydrolysis conditions.

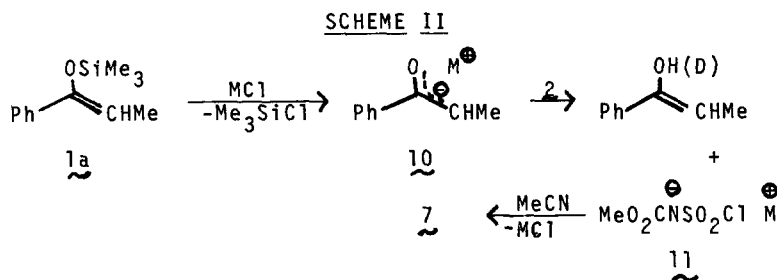
In the absence of silyl ether 1a, CuCl does not catalyze the addition of 2a to acetonitrile. In order to gain more insight into the mechanism of this unusual reaction, it was carried out with N-deuteriocarbomethoxysulfamoyl chloride 2b.<sup>7</sup> Compound 7 was again obtained (15.1%) along with a mixture of 3a and 3b (total 48.7%). The propiophenone isolated in 28.5% yield was shown by NMR to have incorporated 60% deuterium in the  $\alpha$ -position.<sup>8</sup> As a control, propiophenone was stirred with 2b and CuCl under the same reaction conditions as above, except that the silyl ether was omitted--no D-exchange was observed. Other salts have also been found to catalyze the addition of 2a to acetonitrile (Table I). These results indicate that the initial step may be formation of a metal enolate 10 (Scheme II), which acts as a base upon 2, forming the M<sup>+</sup> salt 11. This salt then reacts with acetonitrile to give 7.

Further studies on the reactions outlined are in progress.

TABLE I  
METAL SALTS CATALYZED ADDITION OF CARBOMETHOXYLSULFAMOYL CHLORIDE  
2a TO TRIMETHYLSILYL ENOL ETHER 1a

Catalyst	%7 <sup>a</sup>	%2a	%3a	%6
CuCl	54.8	---	23.6 <sup>a</sup>	71.0 <sup>a</sup>
LiCl	29.2	42.2	13.5	61.7
Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	26.1	26.0	41.7	56.3
NaCl	12.0	55.0	27.6	70.6
None	8.4	37.8	35.1	63.0

<sup>a</sup>Indicates actual isolated yield. Other yields estimated from NMR data.



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### References

1. E. M. Burgess and W. M. Williams, *J. Org. Chem.*, **38**, 1249 (1973).
2. Y. Kuroki, S. Murai, N. Sonoda and S. Tsutsumi, *Organometal. Chem. Syn.*, **1**, 465 (1972).
3. J. K. Rasmussen and A. Hassner, *J. Org. Chem.*, in press.
4. Prepared by the procedure of H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *Ibid.*, **34**, 2324 (1969). 1a was obtained in 82.4% yield, b.p. 86-88°C @ 4.3 mm, and consisted of only one isomer.
5. R. Graf, *Chem. Ber.*, **96**, 56 (1963).
6. M.p. 114.5-115°C;  $\nu_{\max}^{\text{KBr}}$  3280, 1755, 1670, 1365, 1165  $\text{cm}^{-1}$ ;  $\tau_{\text{TMS}}^{\text{CDCl}_3}$  8.24 (d, J = 7, 3), 6.22 (s, 3), 4.28 (g, J = 7, 1), 2.24-2.67 (m, 3), 1.70-2.00 (m, 3); m/e 271; *Anal.* Calcd. for  $\text{C}_{11}\text{H}_{13}\text{NO}_5\text{S}$ : C, 48.71; H, 4.83; N, 5.16. *Found*: C, 48.85; H, 4.82; N, 5.14.
7. Prepared from chlorosulfonyl isocyanate and MeOD by the procedure of Reference 5. The mass spectrum indicated at least 60% D-incorporation.
8. The large differences in product distribution for 2a vs. 2b can perhaps be explained, at least in part, by a kinetic isotope effect. The results were found to be reproducible within a few %.