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PUMMERER REARRANGEMENTS USING CHLOROTRIMETHYLSILANE

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Pummerer rearrangements of 3-carbomethoxythian-4-one S-oxide (1) have been investigated and chlorotrimethylsilane found to be the reagent of choice for preparing the corresponding α,β-unsaturated sulphides (2 and 3). Related chlorotrimethylsilane-induced Pummerer rearrangements are also reported.

Miller and McKean recently described the use of iodotrimethylsilane/diisopropylethylamine for the production of α,β-unsaturated sulphides from sulphoxides.[1] We have found that certain sulphoxides undergo the same type of reaction on treatment with chlorotrimethylsilane in the absence of added base. This discovery was made when trying to prepare enones 2 and 3 from 3-carbomethoxythian-4-one S-oxide (1).[2] We first tried to achieve this transformation in boiling acetic anhydride, standard conditions for the Pummerer rearrangement.[3,4] To our surprise, the only products isolated from this reaction were the acetates 4a and 5a (87%, 4a:5a ca. 1:5).[5] Similar rearranged products were also obtained when trifluoroacetic anhydride[6] was employed.

We eventually discovered that enones 2 and 3 could be obtained in high yield using chlorotrimethylsilane in refluxing carbon tetrachloride. To our knowledge this is the first time that this reagent has been employed to effect Pummerer rearrangements. At lower temperatures enones 2 and 3 still predominated but the proportion of rearranged products increased (Table). Surprisingly, in view of the ease with which sulphoxides are reported to undergo deoxygenation on treatment with silyl halides,[7] no 3-carbomethoxythian-4-one was found in the product mixture.

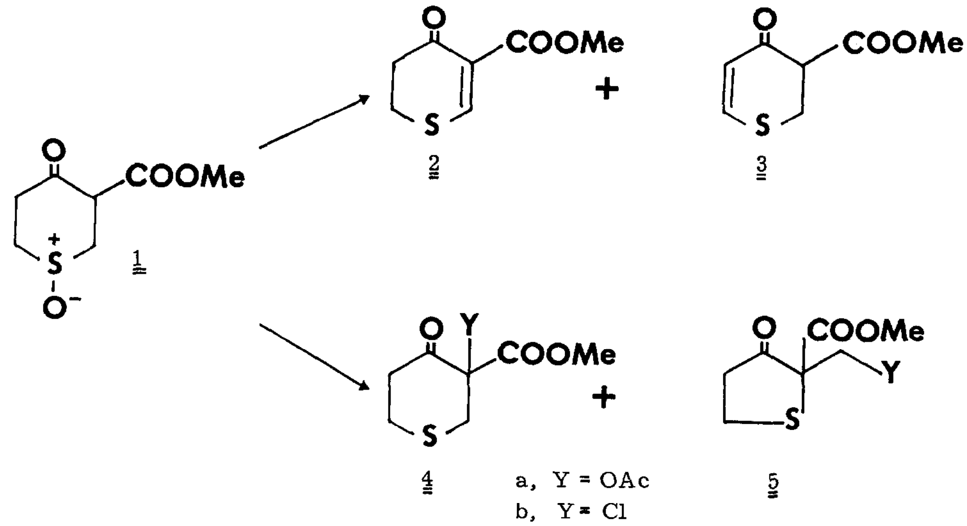


Table Reactions of 1 with $ClSiMe_3$

Conditions[a]	Products[b]		
	2	3	4b/5b[c]
5.0 eq. Me_3SiCl, CCl_4, reflux, 10 min	72%	16%	7%
2.2 eq. Me_3SiCl, CH_2Cl_2, reflux, 10 min	74%	13%	12%
2.2 eq. Me_3SiCl, CH_2Cl_2, r.t., 10 min	54%	4%	40%
2.2 eq. Me_3SiCl, 2.2 eq. $^iPr_2EtN$, CH_2Cl_2, r.t., 60 h	-	-	41%

[a] All reactions were carried out on *ca.* 0.005 mol 1 in *ca.* 35 ml of solvent.

[b] Isolated yields after chromatography.

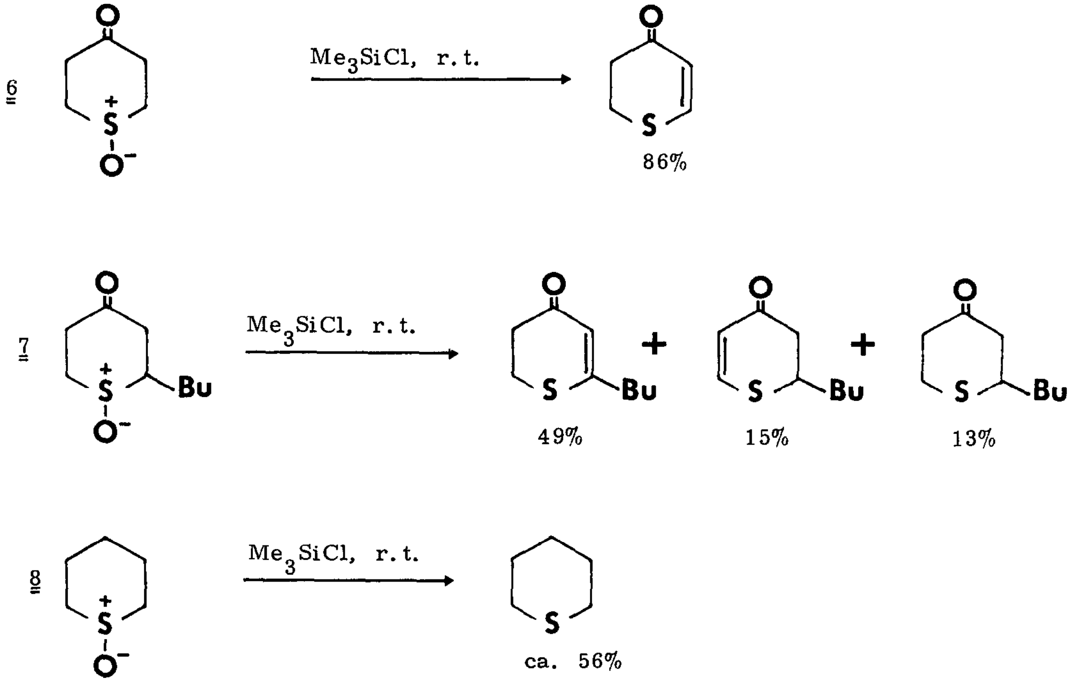
[c] *ca.* 1:5 by ^1H NMR.

In view of Miller and McKeans results[1] it is worth noting that the rearrangement products **4b** and **5b** were still produced in the presence of diisopropylethylamine but under these conditions the reaction was much slower and enones **2** and **3** were not present in the product mixture (Table, last entry).

The reactions of three related sulphoxides **6**-**8** with chlorotrimethylsilane in dichloromethane at r.t. were also investigated (Scheme). Thian-4-one S-oxide (**6**) underwent smooth Pummerer rearrangement whereas a small amount of sulphoxide deoxygenation was observed with the 2-butyl derivative **7**. Deoxygenation became the major pathway in the reaction of thiane S-oxide (**8**), no alkene being present in the crude product according to ^{1}H-NMR.

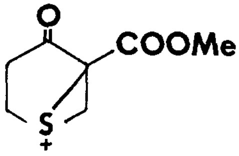
These preliminary studies show that certain sulphoxides[8] undergo efficient Pummerer rearrangement under mild conditions on treatment with chlorotrimethylsilane although simple sulphoxide reduction is sometimes a competing process. Additional synthetic and mechanistic[8] studies are in progress.[9]

SCHEME



References and Notes

1. R.D. Miller and D.R. McKean, *Tetrahedron Lett.*, 1983, **24**, 2619.
2. Prepared by *m*-chloroperbenzoic acid oxidation of the corresponding sulphide (E.A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 1948, **70**, 1813).
3. E. Block, Reactions of Organosulphur Compounds, Academic Press, 1978 (Section 4.6 and references therein).
4. W.E. Parham and L.D. Edwards, *J. Org. Chem.*, 1968, **33**, 4150, and references therein.
5. All new compounds gave satisfactory elemental analyses or high resolution mass spectral data together with consistent ^{1}H-NMR, ^{13}C-NMRand IR spectra.
6. H. Sugihara, R. Tanikaga and A. Kaji, *Synthesis*, 1978, 881.
7. G.A. Olah, B.G.B. Gupta and S.C. Narang, *Synthesis*, 1977, 583; G.A. Olah, S.C. Narang, B.G.B. Gupta and R. Malhotra, *Synthesis*, 1979, 61; K.C. Nicolaou, W.E. Barnette and R.L. Magolda, *J. Amer. Chem. Soc.*, 1978, **100**, 2567; A.H. Schmidt and M. Russ, *Chem. Ber.*, 1981, **114**, 1099.
8. The chlorotrimethylsilane-induced Pummerer reaction appears to be facilitated by γ-carbonyl groups. This suggests that the reactions may proceed *via* the formation, and subsequent deprotonation, of thiiranium intermediates rather than by the conventional sulphocarbonium mechanism.[3] It certainly seems likely that sulphoxide **1** is converted into thiiranium ion **9** to some extent since ring opening with chloride would lead to the observed rearrangement products **4** and **5**.



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