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1,3-DITHIANE-1-p-TOSYLSULFIMIDE: PREPARATION, REACTIONS & ^{13}C NMR

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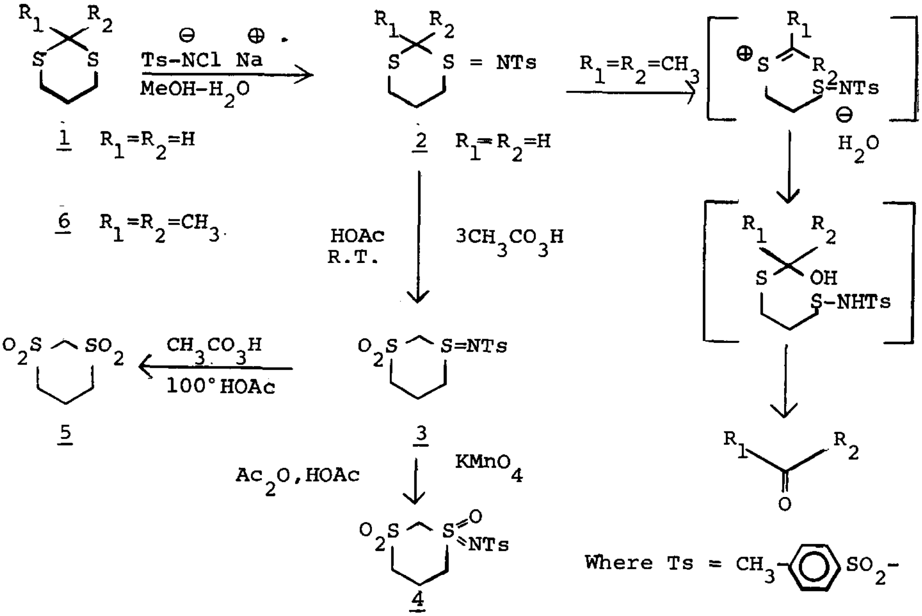
Two recent communications[1,2] reported the facile cleavage of 2-substituted 1,3-dithianes and related compounds with N-chloro-p-toluene-sulfonamide sodium salt (chloramine-T) under mild conditions, thus making these systems useful as carbonyl protecting functions. It was postulated[1] that the mono-N-tosylsulfimides of various 2-alkyl substituted dithio and oxathio heterocycles open to produce a stabilized carbonium ion which subsequently undergoes fragmentation leading to a carbonyl compound.

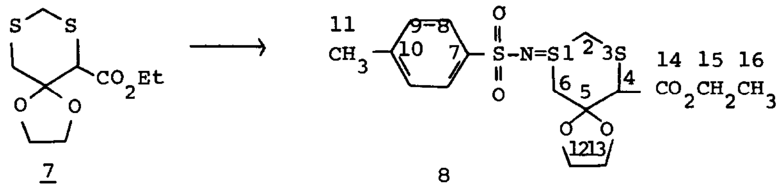
We have now isolated and characterized such a mono-N-tosylsulfimide thereby giving more credence to the earlier speculations[1,2]. Thus, reaction of 1,3-dithiane (1) with one or two equivalents of chloramine-T in 95% methanol-water at ambient temperatures led to the isolation of the mono-N-tosylsulfimide (2) as a stable crystalline solid (mp 164-5°) in a 60% yield[3]. No indications were found for the formation of the bis-N-tosylsulfimide (9), even when large excesses of chloramine-T were employed and the reaction mixture was subject to prolonged reflux. Apparently there is insufficient stabilization of the intermediate carbonium ion which would result from ring fission of 2 to promote the breakdown of the 2-unsubstituted 1,3-dithiane system. This supposition was supported when acetone was isolated (as the 2,4-dinitrophenylhydrazone) from the complex reaction mixture produced by the treatment of 2,2-dimethyl-1,3-dithiane[4] with chloramine-T under the same conditions employed for the preparation of 2.

Selective oxidation of the unfunctionalized sulfur of 2 was performed at room temperature using three eqts. of 40% peracetic acid to give 3 (mp 187-188°) in 60% crude yield. Attempts to further oxidize 3 with peracid at room temperature were unsuccessful, while at elevated temperatures



only the disulfone 5 was isolated. Complete oxidation of 3 to 4 (mp 219-221°) could be accomplished in 60% yield in an acetic acid-acetic anhydride solvent system using 2.2 molar eqts. of KMnO$_4$. Alternatively, 4 was also obtained by KMnO$_4$ oxidation of 2 using 6.5 molar eqts. of oxidant. Other 2-unsubstituted 1,3-dithianes were found to react analogously to 1; e.g., 7[5] gave in *ca.* 50% yield a *single* N-tosylsulfimide (8, mp 153-155°), the structure of which was assigned on the basis of its ^{13}C nmr spectrum.

Table 2 shows the deviations ($\Delta\delta$'s) obtained by comparing the observed and calculated ^{13}CMR shifts for 8 and 8a. Calculated shifts were obtained by additivity of substituents (see eq. Table 2) of the model compounds 1, 2 and 7. This method has been shown to have general success in predicting the ^{13}CMR shifts of unknown compounds[6,7,8]. The temperature independence of the ^{13}CMR spectrum of 2 (Table 1) indicates that the NTs group is essentially in one conformation which is expected to be equatorial in 2[9,10,11]. Since the equatorial NTs conformation is expected[9] also in 8 and 8a, the deviations in Table 2 are largely independent of conformational equilibria.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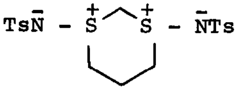
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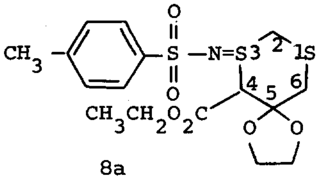
8a

Table 1 - ^{13}CMR Data of Dithiane Derivatives*

	Compound			
C Atom	1	2	7	8
2	30.9	46.5(48.8)**	31.5(32.2)	50.4
4	28.9	26.5(28.9)	45.2(45.2)	43.3
5	26.3	26.2(27.7)	99.5(100.0)	105.3
6	28.9	46.4(48.2)	25.6(26.4)	41.2
7		142.0(142.7)		141.5
8		125.5(126.2)		125.6
9		129.2(129.8)		129.3
10		141.0(140.5)		141.4
11		20.7(21.8)		20.7
12			64.9(66.2)	65.8
13			64.9(66.2)	65.6
14			169.2(169.9)	168.3
15			60.7(62.2)	61.5
16			13.7(14.1)	13.2

* Cmr shifts are reported in ppm downfield (+) from TMS in DMSO-d_6 and were recorded on a Varian CFT-20 spectrometer.

** Parenthetic values are cmr shifts relative to TMS in CD_2Cl_2 and they were relatively constant through the temperature range 35 to -90°C. Only slight broadening of the signals of C^2 - C^6 in 2 and of all the C atoms in 7 was observed at -90°C.

The small deviations between the calculated and observed ^{13}CMR shifts of 8 vs. 8a clearly establish 8 as the correct structure. The deviations of C^2(+3.2) and C^5(+5.8) are related to steric and/or electronic interactions of the substituents. We are presently studying this and similar 1,3 interactions in a series of dithiane derivatives and will report on this in detail in a future publication.

Table 2 - Comparison of the ^{13}CMR Shifts(PPM) Observed with Those Calculated for Ring Carbon Atoms

C-Atom	Calculated Shifts*		Obs. Shifts	Deviation	
	8	8a	8	8	8a
2	47.2	47.2	50.4	+3.2	+3.2
4	42.8	62.7	43.3	+0.5	-19.4
5	99.5	99.5	105.3	+5.8	+5.8
6	43.1	23.2	41.5	-1.6	+18.3

*Calc. from the equation:

$$\delta^{Cn}(\underline{8}) = \delta^{Cn}(\underline{1}) + \left[\delta^{Cn}(\underline{2}) - \delta^{Cn}(\underline{1})\right] + \left[\delta^{Cn}(\underline{7}) - \delta^{Cn}(\underline{1})\right]$$

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