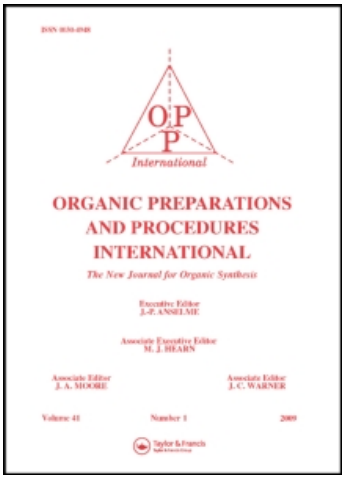

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PREPARATION OF 4-THIAZOLIDINONE-1-OXIDES

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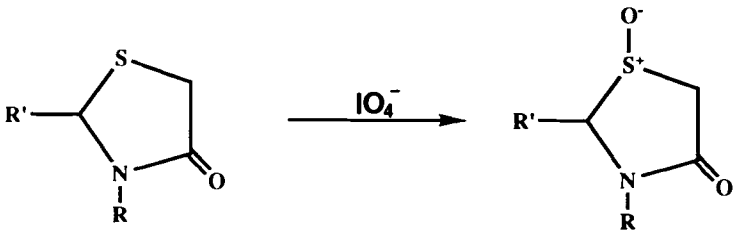
The somewhat increased stability of α-ketocarbanions bearing a β-sulfoxide group has been utilized in a variety of synthetic processes, but no study seems to have been made of cyclic β-ketosulfoxides. Cyclic β-ketosulfones in contrast have been known for some time.[1] Since the acidity of the methylene group of thiazolidin-4-ones has been used extensively for carbanion condensations, it was of interest to compare the reactivity of the sulfoxide analogues, in order to examine the effect of the sulfoxide group upon the ease of production, stability and reactivity of the carbanion and to compare the β-carboxamido sulfoxide and β-ketosulfoxide reactivity.

Since the first recorded sulfoxide synthesis in 1865,[2] numerous methods have been examined for the conversion of sulfides to sulfoxides. Thus, treatment of sulfides with iodobenzene dichloride in aqueous pyridine at temperatures between -40° and 20° was claimed to provide sulfoxide free of sulfone[3] and oxidation of thioxanone with iodobenzene diacetate gave thioxanone sulfoxide in 78% yield, whilst other oxidants gave mainly the sulfone.[4] In contrast, other workers report that sulfoxides are selectively formed in good yield from sulfides by treatment with m-chloroperbenzoic acid.[5] Johnson and McCants describe[6] the conversion of 4-substituted thianes exclusively to the cis oxide by treatment with tert-butyl hypochlorite. They also report high yield conversions of sulfides to sulfoxides by treatment with N-chlorobenzotriazole;[7] no sulfone was detected. However, oxidation with this type of reagent also gives at least partial chlorination of α-methylene groups.[8] It is claimed that treatment of sulfides with N-bromo- or N-chlorosuccinimide led, in controlled fashion, to either the sulfoxides or the sulfones.[9] Leonard and Johnson introduced sodium metaperiodate as a selective reagent for sulfoxide preparation.[10]



1 2

Previous attempts to prepare thiazolidinone sulfoxides by use of hydrogen peroxide[11] or permanganate[12] led mainly to sulfone production. Although theoretically[13] selectivity should be achieved with peracids, in practice we found it difficult to stop the oxidation at the sulfoxide stage with peracetic, performic, perbenzoic, perphthalic, or m-chloroperbenzoic acids. Similarly, clean reactions were not observed either with the N-halocompounds or with most of the other oxidants mentioned above. Since preliminary oxidation of tetrahydrothiophene with sodium metaperiodate showed that a good yield of the sulfoxide could be obtained, we investigated the use of this reagent in the thiazolidinone series and found that treatment of thiazolidin-4-ones in aqueous methanol with sodium metaperiodate at 15° was a suitable method. Monitoring of the reaction by tlc indicated that reaction had gone to completion overnight, and in most cases no appreciable overoxidation to sulfone had occurred.

TABLE 1. Yields, mps, ^1H nmr and Analyses of 4-Thiazolidinone-1-oxides

R	R'	Yield[a] (%)	mp. (°C)	C_2-H (δ)	C_5-H (δ)	Elemental Analyses C	H	N
						(Calcd)		
4-MeC_6H_4	C_6H_5	73	180-181	6.42	3.71	67.44	5.32	4.53
						(67.37	5.26	4.91)
C_6H_5	C_6H_5	58	192-194	6.39	3.72	66.40	4.84	5.23
						(66.42	4.80	5.17)
4-$MeOC_6H_4$	C_6H_5	80	161-162	6.45	3.65	64.01	5.04	4.71
						(63.79	4.98	4.65)
4-ClC_6H_4	C_6H_5	78	170-171	6.39	3.74	59.03	4.02	4.86
						(58.91	3.93	4.58)
4-$NO_2C_6H_4$	C_6H_5	84[c]	196-198	6.17	3.71	56.94	3.62	8.95
						(56.96	3.80	8.86)
C_6H_5	4-FC_6H_4	38	198-199	6.17	3.73	62.60	4.23	4.61
						(62.28	4.15	4.84)
C_6H_5	4-$EtOC_6H_4$	85[c]	185-187	6.44	3.68	65.37	5.86	4.83
						(64.76	5.40	4.44)
C_6H_5	4-$NO_2C_6H_4$	93[c]	183-184	6.30	3.70	57.61	4.14	8.90
						(56.96	3.80	8.86)
C_6H_5	4-$MeOC_6H_4$	87[c]	107-109	6.41	3.70	64.34	5.42	5.36
						(63.79	4.98	4.65)
C_6H_5	4-ClC_6H_4	84[c]	142-145	6.31	3.69	58.24	4.14	4.22
						(58.91	3.93	4.58)
C_6H_5	4-MeC_6H_4	63	137-139	6.40	3.73	67.38	5.37	4.94
						(67.37	5.26	4.91)
C_6H_5	$C_6H_5CH_2$	57	150-151	5.35	3.65	67.46	5.32	5.23
						(67.37	5.26	4.91)
3,4-$CH_2O_2C_6H_4$	4-$AcNHC_6H_4$	62	184-186	6.08	3.81	57.81	4.54	7.23
						(58.06	4.30	7.53)

a) Yield of recrystallised product (from methanol) unless otherwise noted. b) Centre of doublet of doublets. c) Crude product; use directly in further reactions.

The thiazolidin-4-one-1-oxides (2) were obtained in good yield as highly crystalline solids showing bands at ~ 1700 cm^{-1} and 1060 cm^{-1}. Apart from the expected ^1H nmr signals for the R and R^1 substituents, they all showed a pair of doublets centered at δ 3.75 for the ring methylene group, the two hydrogens being non-equivalent with a geminal coupling of 18 Hz. The chemical shift of the methine hydrogen (a singlet) varies with substituent (δ 3.6-4.7) but only very approximately in correlation with the expected (Hammett) sustituent effect.

EXPERIMENTAL SECTION

General Oxidation Procedure.- To a stirred solution of the 2,3-disubstituted thiazolidin-4-one (4 mmoles) in aqueous methanol (60 ml) was added a solution of sodium metaperiodate (4 mmoles) in 75% aqueous methanol (70 ml). The mixture was kept at room temperature overnight. The precipitate of sodium iodate was separated and the filtrate evaporated to dryness. The residue was extracted with chloroform, the extracts washed, dried and evaporated to yield the 2,3-disubstituted thiazolidin-4-one-1-oxide (Table 1) which was recrystallized (if necessary), usually from methanol.

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