

NOVEL REACTIONS OF ORGANIC SULFUR AND SELENIUM COMPOUNDS WITH THALLIUM(III) NITRATE :
SULFOXIDE AND SELENOXIDE FORMATION AND PUMMERER-LIKE REACTION

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Recently, Taylor, McKillop *et al.*¹ have developed several interesting new reactions using thallium(III) nitrate (TTN) as the oxidant. Now, Tl(III), a soft acid, is expected to have a high and selective reactivity with divalent sulfur or selenium atom, a soft base.² Nevertheless, the reactions of organic sulfur or selenium compounds with Tl(III) have little or never been published.³ We wish to report here the new synthetic methods of sulfoxides (3) and selenoxides (4) by the reactions of several aliphatic and aromatic sulfides (1) or selenides (2) with TTN, respectively, and of α -oxoacetals and α -diketones by their Pummerer-like reaction.

Sulfides (1) and selenides (2) were treated with TTN under such mild conditions as stirring at room temperature in suitable solvents to give sulfoxides (3) and selenoxides (4) in high yields, respectively.⁴ (See Scheme I and Table I.)

2,3-Diphenyl-5,6-dihydro-1,4-dithiin prepared from benzoin, ethane dithiol, and BF₃-etherate in CHCl₃ on treatment with 1.2 mol equivalent of TTN in CHCl₃/CH₃OH (1:1) or dimethoxyethane (DME) at room temperature gave sulfoxide 5 in 72% yield within 10-15 min. In this reaction, the solution colored to green, when TTN was added, but lost color within 5 seconds in DME or 30 seconds in CHCl₃/CH₃OH (1:1). This observation suggested a long-lived cation radical 6 and/or a dication 7 as the transient intermediate.⁵ In fact, an intense ESR spectrum shown in Fig. 1 (a) was obtained, when it was measured for a concentrated solution of 2,3-diphenyl-5,6-dihydro-1,4-dithiin and TTN in DME in a degassed tube at -80°.⁶ The g-value of this radical was 2.0070±0.0005, which was close to those of the cation radicals formed from substituted thianthrenes⁷ and diaryl sulfoxides⁸ in concentrated sulfuric acid.

In the ESR spectrum of a diluted radical solution (Fig. 1 (b)), small splittings were observed, which suggested that an unpaired electron spread over the two phenyl groups. The cation radical 6 was thus proved, and this reaction forming 5 is suggested to proceed by a one-

electron oxidation mechanism.⁹ The formation of such a stable cation radical by TTN was first observed by the authors, and an interesting ESR investigation will be further developed.

In the hope of developing to the Pummerer-like reaction, we applied this reaction to several alkylthioacetyl compounds and α -phenylseleno ketones. The alkylthioacetyl compounds were synthesized in high yields by the reaction of the corresponding haloacetyl compounds with the stoichiometric quantity of Tl(I) thiolates¹⁰ at room temperature. These organosulfur compounds on treatment with TTN at room temperature gave the α -oxoacetals in satisfactory yields with the precipitation of Tl(I) nitrate. (See Table II)

ent-17-Nor-15 β -phenylselenokauran-16-one (8) on treatment with TTN (3 mol. equivalents) in CH₃OH or THF for 24 hr afforded α -oxoacetal 10 or α -diketone 11 in 82 or 65% yield, respectively. 3-Phenylselenocamphor (9) on the same treatment for 5 hr gave diketone 12 in 78% yield. The acetal 10 on treatment with perchloric acid gave diketone 11 in 93% yield.

These new reactions provide a convenient synthesis of sulfoxides and selenoxides which are important intermediates¹¹ for the organic synthesis, and furthermore they will be applicable to the syntheses of antitumor active keto aldehydes¹² and of the important compounds relating to the *in vivo* metabolism.

References and Notes

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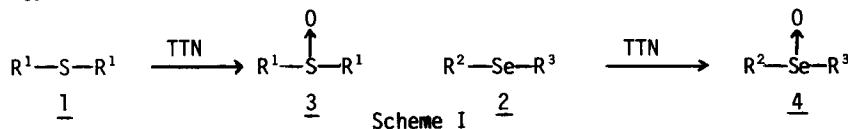


Table I. Reactions of Sulfides (1) and Selenides (2) with TTN

Entry	1 : R ¹	2 : R ²	R ³	TTN (mol.equiv.)	Solvent	Reaction time	Yield(%) ^a	
							3	4
1	C ₂ H ₅			2.2	CHCl ₃ /CH ₃ CO ₂ H ^b (3:1)	5hr	86	
2	C ₃ H ₇			"	"	"	92	
3	C ₄ H ₉			"	"	"	94	
4	C ₆ H ₅			"	"	"	82	
5		C ₆ H ₅	C ₆ H ₅ CH ₂	1.5	THF	20min		87
6		"	"	"	HC(OCH ₃) ₃	5min		98
7		"	C ₆ H ₅	"	THF	24hr		92
8		<i>P</i> -CH ₃ OC ₆ H ₄	<i>P</i> -CH ₃ OC ₆ H ₄	"	"	2hr		100

^a Isolated yield. ^b In CHCl₃/CH₃OH (1:1), the reactions with dialkyl sulfides also took place smoothly, but the reaction with diphenyl sulfide took 65 hr using 4.4 mol. equivalents of TTN. In CHCl₃/(CH₃CO)₂O (3:1), all sulfides gave sulfones in 1.5 hr.

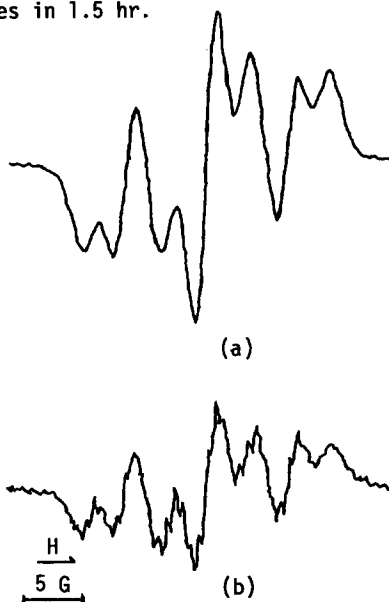
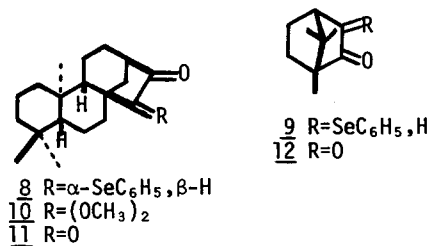
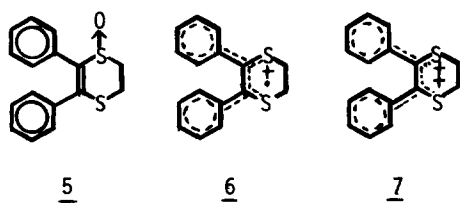


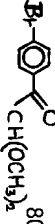
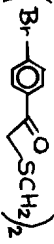

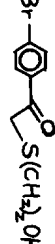
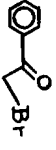

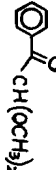

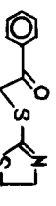
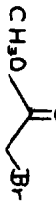
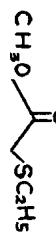
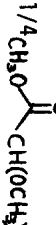
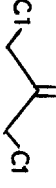
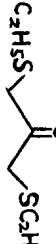



Figure 1. Esr spectra of 2,3-diphenyl-5,6-dihydro-1,4-dithiin cation radical from oxidation with TTN in DME at -80°. (a) In concentrated solution. (b) In diluted solution.

Table II. Preparation of Alkylthioacetyl Compounds and Their Pummerer-like Reaction

Entry	Halooacetyl compound	TT(1) thiolate	Solvent and reaction time(hr)	Alkylthioacetyl compound and yield(%) ^a	Solvent and reaction time ^b (hr)	α -Oxoacetal and yield(%) ^a
1		C ₂ H ₅ ST1	THF	4  91	CH ₃ OH/CHCl ₃ (1 : 1)	1/2  80
2	"	(CH ₂ ST1) ₂	THF/HMP (20 : 1)	24  93	CH ₃ OH/CHCl ₃ (2 : 1)	"
3	"	CH ₂ (CH ₂ ST1) ₂	THF/HMP (20 : 1)	3  83	CH ₃ OH/CHCl ₃ (1 : 1)	"
4	"	HO(CH ₂) ₂ ST1	THF	1  99	CH ₃ OH/CHCl ₃ (2 : 1)	"
5		C ₂ H ₅ ST1	THF	2  94	CH ₃ OH	1/4  89
6	"		THF/HMP (100 : 1)	1  100	CH ₃ OH/CHCl ₃ (4 : 3)	3
7		C ₂ H ₅ ST1	THF	5  73	CH ₃ OH	1/4  53
8		C ₂ H ₅ ST1	THF	3  80	CH ₃ OH	1  55

^a Isolated yield. ^b 2.2 Mol. equivalents of TTN were used, except for entry 6 (6 mol. equivalents) and 8 (4.4 mol. equivalents).