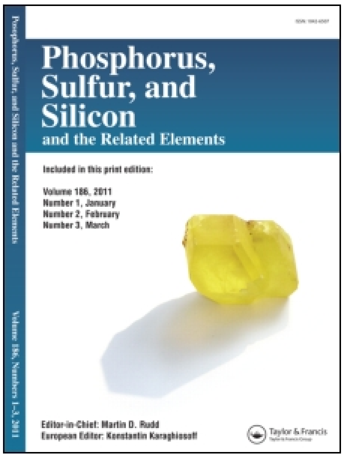

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Chalcogen Chiral Ylides for the Catalytic Asymmetric Epoxidation of Aldehydes: From Sulfur to Selenium and Tellurium

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*The reaction of novel chiral selenonium and telluronium ylides was investigated with aldehydes and compared to the sulfur analogues. (2*R*,5*R*)-2,5-Dimethylselenolane was prepared and reacted as a catalyst for the benzylidenation of aldehydes. Disubstituted epoxides were readily prepared with a (surprising) absence of diastereoselectivity, and with enantiomeric excesses higher than 90%. The reaction of a tellurium analogue, (2*S*,5*S*)-2,5-diethyltellurolane, afforded the oxirane in very moderate yield and e.e.'s in the range of 62–82%. Though this was less productive, it is the first report of a chiral telluronium ylide leading to an asymmetric epoxidation of aldehydes.*

Keywords Asymmetric synthesis; epoxides; selenonium ylide; telluronium ylide

INTRODUCTION

Epoxides are versatile intermediates in organic synthesis,[1–3] as they are easily opened up by a variety of nucleophiles. We have been interested in a straightforward connective route for their access in an enantioenriched fashion: the reaction of chiral sulfur ylides with aldehydes,[4–6] a complementary route to the asymmetric oxidation of alkenes.

We have previously designed and used C_2 symmetric enantioenriched sulfides,[7,8] (2*R*,5*R*)-2,5-dimethylthiolane and (2*R*,5*R*)-2,5-diethylthiolane, as catalysts[9] for the ylide-mediated conversion of aldehydes to oxiranes. A simple one-pot procedure was achieved with excellent yields, good enantio- and diastereo-selectivities, but some limitations were met: modest kinetic rates, scope... This has led us to explore the selenium and tellurium[10–12] chiral congeners with

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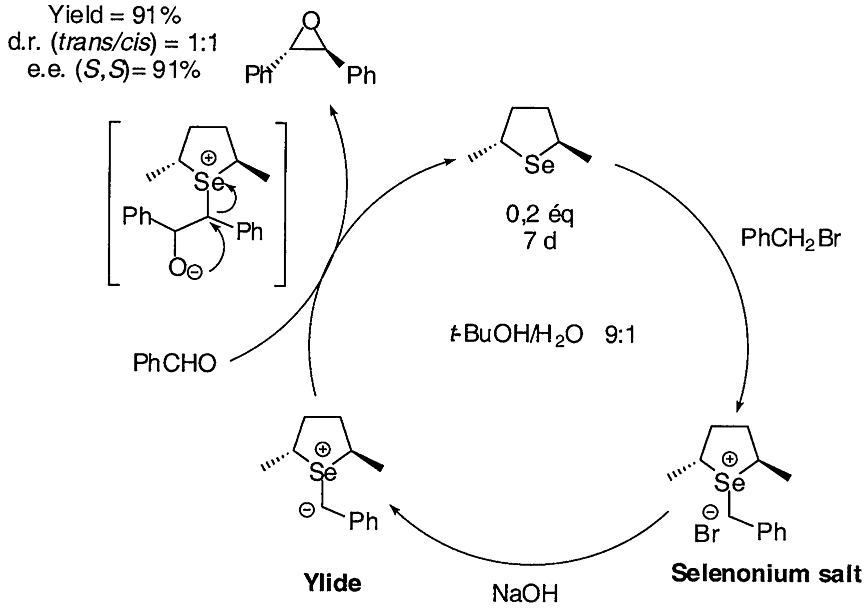
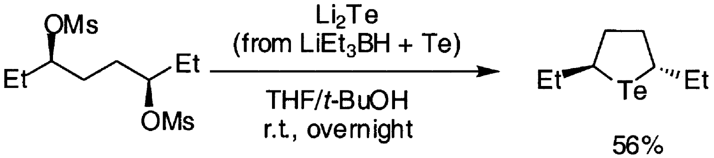
potential advantages: enhanced nucleophilic character for both the initial chalcogenide[13] and the intermediate ylide. Their reaction with aldehydes is much less known than in the sulfur series, but some groups[14–19] have reported that epoxidation is feasible. However, previous to our work, no asymmetric epoxidation was known with these ylides.

(2*R*,5*R*)-2,5-Dimethylselenolane was synthesized in two steps from (2*S*,5*S*)-hexanediol and its hypervalent dibromide adduct was characterized.[20] The selenolane proved to be an efficient catalyst (0.2 equiv) for the benzylidenation of aromatic aldehydes (Scheme 1). The reaction is indeed faster than in the sulfur series. The enantiomer excess is usually higher than 90%. On the other hand, equal amounts of *trans* and *cis* diastereomers were observed. In the sulfur series, the *trans* diastereoisomer is largely predominant for the formation of stilbene oxides. It has been explained[6,21] by a reversible formation of the betaine leading to the *cis* epoxide. We do not have evidence for the origin of the stereochemistry in the selenium series.



SCHEME 1

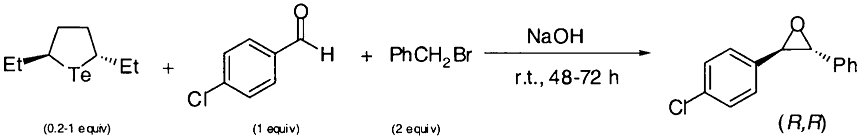
A similar study was launched with tellurium ylides. Reaction of the bis(mesylate) of (2*S*,5*S*)-hexanediol with lithium telluride[22] led to (2*R*,5*R*)-2,5-dimethyltellurolane, but some difficulties were met, including volatility and epimerization. Less volatile (2*S*,5*S*)-2,5-diethyltellurolane (Scheme 2) was then preferred. Though this



SCHEME 2

preparation was more successful than the one with the two methyl groups, it was sometimes not reproducible, and epimerization could also be observed. We suspect a radical cleavage of a C–Te bond by residual Et_3B, and recombination.

A stoichiometric amount of (2*S*,5*S*)-2,5-diethyltellurolane was reacted with benzyl bromide, 4-chlorobenzaldehyde, and sodium hydroxide in a 9:1 *t*-butanol/H_2O mixture (Scheme 3). We were glad to observe that the reaction proceeds but after 48 h the yield was only 35%. The enantiomeric excess was rather moderate: 62%. Under similar conditions, a catalytic amount (20%) of tellurolane was tested. For this solvent system, we were limited to a yield of 24%, with an e.e. of 68%. A higher asymmetric induction was achieved under biphasic conditions, with dichloromethane and concentrated sodium hydroxide. Our highest e.e. was 82%.



SCHEME 3

Thus, tellurium ylides were formed and epoxidation was observed. A competitive olefination pathway[18,23] was also observed, but to a limited extent (<10%). Even if the expected process is not very productive, this is the first report of a chiral telluronium ylide for asymmetric epoxidation.

The diastereoselectivity is in favor of the *trans* isomer. This result is similar to the sulfur series, but surprisingly very different from the selenium series. At this stage, without any further experimental evidence, it appears difficult to rationalize this behavior.

During the course of this study, Tang and co-workers disclosed[24] the use of telluronium ylides, from (2*R*,5*R*)-2,5-dimethyltellurolane, for the asymmetric synthesis of vinyl cyclopropanes.

TABLE I Synthesis of 2-(4-Chlorophenyl),3-Phenyloxirane by Reaction of (2*S*,5*S*)2,5-Diethyltellurolane with Benzyl Bromide and 4-Chlorobenzaldehyde

Equivalent of auxiliary	Solvent	Base	Time (h)	d.r. (*trans*/*cis*)	e.e. (*R*,*R*) (%)	Yield (%)
1	*t*BuOH/H_2O (9/1)	2 NaOH	48	85:15	62	35
0,2	*t*BuOH/H_2O (9/1)	2 NaOH	72	90:10	68	24
0,2	CH_2Cl_2	aq. NaOH (50%) 1 nBu_4NBr	72	97:3	82	28

In conclusion, these are the first reports on the use of enantiopure selenium and telluronium ylides in asymmetric synthesis of epoxides.

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