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Synthesis of Optically Active Tellurium-Containing Binaphthyls and their Use in the Asymmetric 1,4-Addition Reaction of α,β-Unsaturated Ketones

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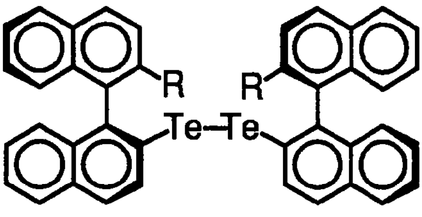
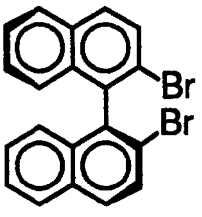
Abstract: Two novel tellurium-containing binaphthyls have been prepared in optically active form and used as chiral inducers in the asymmetric 1,4-addition reactions of α,β-unsaturated ketones with aluminium arenetellurolate.

Although organotellurium compounds have become increasingly important as versatile reagents in modern organic syntheses,[1] no attention has been directed to chiral organotelluriums and their application to asymmetric syntheses. In this regard we have been interested in optically active 1,1'-binaphthyl ditelluride (**1**), because diaryl ditelluride is one of the most useful organotellurium reagents, and 1,1'-binaphthyl compounds possessing axial dissymmetry exhibit high efficiency as chiral auxiliaries in asymmetric syntheses.[2,3] This report describes the synthesis of the parent (**1a**) and the methyl derivative (**1b**) and their application as a chiral source to the asymmetric 1,4-addition reactions of α,β-unsaturated ketones with aluminium arenetellurolate, which is, to the best of our knowledge, the first chiral induction effected by an organotellurium reagent.

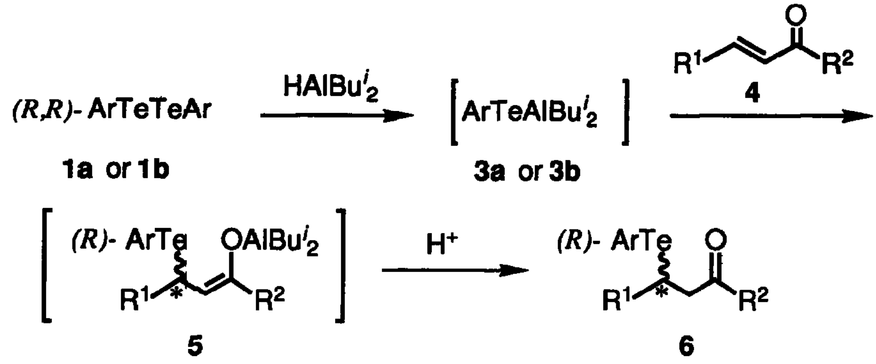


(R,R)-**1a** R=H
(R,R)-**1b** $R=CH_3$



(S)-**2**

Optically active *(R,R)*-bis[1-(1'-naphthyl)-2-naphthyl] ditelluride (**1a**) was prepared in 93% yield by successive treatments of *(S)*-2,2'-dibromo-1,1'-binaphthyl (**2**)[4] with equimolar *t*-butyllithium, elemental tellurium, another equimolar *t*-butyllithium, and methanol followed by air oxidation.[5] *(R,R)*-Bis[1-(2'-methyl-1'-naphthyl)-2-naphthyl] ditelluride (**1b**) was similarly prepared in 78% yield from successive treatments of **2** with *t*-butyllithium, methyl iodide, *t*-butyllithium, and elemental tellurium followed by air oxidation. Use of

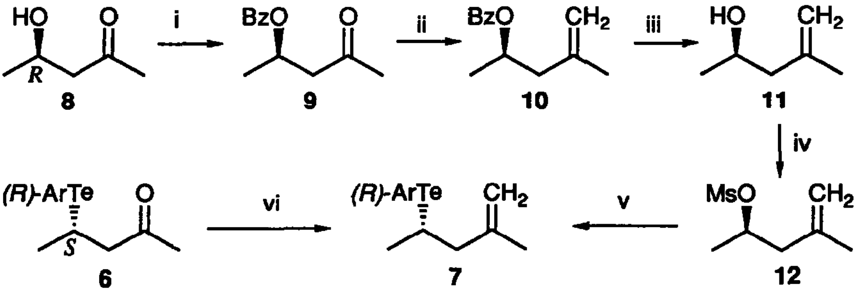


Scheme 1

(R)-2,2'-dibromo-1,1'-binaphthyl (2) as an alternative also gave the corresponding *(S,S)*-enantiomers with the optical rotations of reverse sign.

Since reduction of diaryl ditelluride (1) with diisobutylaluminium hydride readily gives diisobutylaluminium arenetellurolate (3), which undergoes a 1,4-addition reaction towards α,β-unsaturated ketones (4) leading to the formation of functionalized β-aryltelluro ketones,[6] we have examined chiral induction to the β-position using *(R,R)*- (1) (Scheme 1). Thus a solution of **1a** in tetrahydrofuran was mixed with an equivalent amount of diisobutylaluminium hydride (1 mol dm^{-3} hexane solution) to generate **3a**, which was treated in situ with *trans*-3-penten-2-one (**4**, R^1=R^2=Me) at -100 °C under a nitrogen atmosphere. After 3 h, the reaction mixture was quenched with 2*N*-hydrochloric acid, affording a diastereomeric mixture of 4-[1-(1-naphthyl)-2-naphthyltelluro]pentan-2-one (**6**, R^1=R^2=Me) in 74% yield. The diastereomeric excess (d.e.) was determined to be 11% by integration of independent absorptions in the ^{1}H NMR spectrum.[7] On the other hand, use of **3b** as a chiral inducer improved the d.e. up to 64%. The absolute configuration of the asymmetric carbon of the prevailing isomer was determined to be *S* by chemical correlation to *(R)*-4-hydroxy-2-pentanone (**8**)[8] with known absolute configuration (Scheme 2).

As summarized in Table 1, the reactions of other α,β-unsaturated ketones (**4**) with **3b** similarly gave chiral β-aryltelluro ketones (**6**) of predominant *S* configuration. However, the presence of a bulky group at R^1



Scheme 2. i) PhCOCl, pyridine, rt, 9h, 93%; ii) CH_2=PPh_3, THF, 0°C, 6h, 96%; iii) LAH, ether, reflux, 2h, 40%; iv) CH_3SO_2Cl, pyridine, rt, 11h, 83%; v) *(R)*-ArTeLi, THF, rt, 15h, 62%; vi) CH_2=PPh_3, THF, -30 -0°C, 4h, 58%.

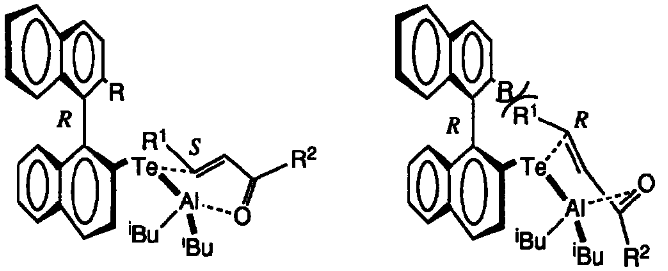
Table 1. Asymmetric addition reactions of α,β-unsaturated ketones (4) with aluminium arenetellurolate (3) in THF at -100°C

Run	R^1	R^2	Reagent	Yield[a]	d.e.	Run	R^1	R^2	Reagent	Yield[a]	d.e.
				%	%					%	%
1	Me	Me	**3a**	74	11	6	*i*-Pr	Me	**3b**	80	49
2	Me	Me	**3b**	83	64	7	*t*-Bu	Me	**3b**	44	32
3	Me	Et	**3b**	87	50	8	*n*-Hex	Me	**3b**	65	64
4	Me	*t*-Bu	**3b**	58	8	9	Cyclohexyl	Me	**3b**	80	58
5	*n*-Pr	Me	**3b**	72	63	10	$PhCH_2$	Me	**3b**	57	70

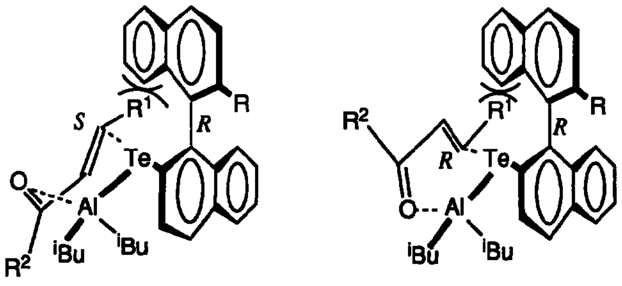
[a] Isolated yield by chromatographic separation.

and R^2 had considerable influence not only on the yield but also on the d.e. In particular, a *t*-butyl group at R^2 drastically reduced the enantioselectivity (Run 4).

A mechanism of the 1,4-addition reaction is assumed to involve a cyclic six-membered ring forming from the two species, which is the transition state of the d.e.-determining key step. There are two approaches to each of the two, *si* and re, faces of *s*-cis conformer of the substrate α,β-unsaturated ketones, leading to the *(R,S)*- and *(R,R)*-diastereomers as shown in Fig. 1. Both approaches to the *re* face suffer from a steric interaction between the R^1 group and the R or benzo moiety of the attached naphthyl skeleton. On the other hand, one of the approaches to the *si* face avoids this. The introduction of a methyl group at the R-position increases the sterical hindrance, resulting in a marked enhancement of the d.e. When 2-cyclopentenone and 2-cyclohexenone were employed as the substrates, the enantioselectivities of the addition products were below



si-face approach (favorable) *re*-face approach (unfavorable)



si-face approach (unfavorable) *re*-face approach (unfavorable)

Fig. 1

6%, though the chemical yields were still high (70%). The cyclic enones cannot participate in such a concerted cyclic transition state occurring from the *s-cis* conformation of acyclic enones, and accordingly their reactions are possibly initiated by cooperative attack by two aluminium arenetellurolates or free ionic species, being responsible for almost no enantioselection.

The present asymmetric 1,4-addition reactions, though not yet attaining sufficient asymmetric induction, indicate that optically active tellurium-containing biphenyls (**1**) have potential as chiral inducers. In order to improve asymmetric induction, further structural modifications of **1** are now in progress.

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References

1. For recent reviews on organotellurium chemistry, see (a) K. J. Irgolic, *Orgnotellurium Compounds;* ed. D. Klaymann, Houben-Weyl, Methods of Organic Chemistry, Georg Thieme Verlag, Stuttgart, 1990; (b) N. Petragnani and J. V. Comasseto, *Synthesis*, 1986, 1; 1991, 793.
2. For recent reviews on the use of 1,1'-binaphthyl derivatives as chiral auxiliaries in asymmetric syntheses, see H. Takaya, T. Ohta, K. Mashima, and R. Noyori, *Pure Appl. Chem.*, 1990, **62**, 1135; R. Noyori and H. Takaya, *Acc. Chem. Res.*, 1990, **23**, 345; S. Otsuka and H. Tani, *Synthesis*, 1991, 665; C. R. Rosini, L. Franzini, A. Raffaelli, and P. Salvadori, *ibid.*, 1992, 503.
3. Similar selenium-containing binaphthyl compounds as a chiral inducer were already studied by Tomoda et al.; S. Tomoda and M. Iwaoka, *J. Chem. Soc., Chem. Commun.* 1988, 1283; *Chem. Lett.* 1988, 1895; S. Tomoda, K. Fujita, and M. Iwaoka, *J. Chem. Soc., Chem. Commun.* 1990, 129; *Phosphorus, Sulfur, Silicon.* 1992, **67**, 247; K. Fujita, M. Iwaoka, and S. Tomoda, *Chem. Lett.*, 1992, 1123.
4. K. J. Brown, M. S. Berry, K. C. Waterman, D. Lingenfelter, and J. R. Murdoch, *J. Am. Chem. Soc.*, 1984, **106**, 4717.
5. Physical and spectroscopic data of *(R,R)*-**1a**: red needles from benzene-hexane; mp 244-245 °C; $[\alpha]_D^{25}$ +104.2 (c 0.45, $CHCl_3$); MS *m/z* 766 (M^+, ^{130}Te); ^1H NMR ($CDCl_3$) δ 7.15-8.10 (m, ArH). *(R,R)*-**1b**: red prisms from benzene-hexane; mp 230-231 °C; $[\alpha]_D^{25}$ +48.9 (c 0.47, $CHCl_3$); MS *m/z* 794 (M^+, ^{130}Te); ^1H NMR ($CDCl_3$) δ 2.10 (s, 6H, Me), 7.05-8.12 (m, 24H, ArH). The optical purity of **1a** and **1b** was estimated to 100%, because a mixture of the *(R,R)*-form and the *(S,S)*-form is in quick equiribrium with the *(R,S)*-form via dissociation to the tellurium radical, and the NMR spectra of **1a** and **1b** showed no signals of the *(R,S)*-form, which absorb at different frequencies.
6. K. Sasaki, Y. Aso, T. Otsubo, and F. Ogura, *Chem. Lett.*, 1989, 607.
7. 4-[1-(1-Naphthyl)-2-naphthyltelluro]pentan-2-one (**6**, R=H, R^1=R^2=Me): yellow glassy oil; HRMS *m/z* 468.076 (M^+), Calcd for $C_{25}H_{22}OTe$ (Te=129.9067) 468.074; , ^1H NMR ($CDCl_3$) δ 1.55, 1.57* (d, Me), 1.96*, 1.99 (s, COMe), 2.67-2.85 (m, CH_2), 3.72-3.79 (m, CH), 7.19-7.96 (m, ArH), in which asterisk peaks refer to the *S*-diastereomer. 4-[1-(2-Methyl-1-naphthyl)-2-naphthyltelluro]pentan-2-one (**6**, R=Me, R^1=R^2=Me): yellow oil; HRMS *m/z* 482.088 (M^+), Calcd for $C_{26}H_{24}OTe$ (Te=129.9067) 482.089; ^1H NMR ($CDCl_3$) δ 1.51, 1.61* (d, Me), 1.93*, 1.96 (s, COMe), 2.07 (s, ArMe), 259-2.84 (m, CH_2), 3.72-3.79 (m, CH), 7.02-7.90 (m, ArH).
8. A. Tai, K. Ito, and T. Harada, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 223.