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First Enantioselective Synthesis of Vinyl Oxiranes from Aldehydes and Ylides Generated from Allyl Halides and Chiral Sulfides

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Received June 20, 2002

Abstract: Asymmetric allylidenation of aldehydes with sulfur ylides is possible with proper substitution of the initial sulfide, to avoid the [2,3] sigmatropic rearrangement of the unsaturated ylides. One-pot reaction of (2*R*,5*R*)-dimethylthiolane with allyl halides, aldehydes, and sodium hydroxide in *tert*-butyl alcohol affords vinyl oxiranes in good yields. Enantiomeric excesses up to 90% and trans selectivities have been achieved with methallyl-type halides.

The reaction of sulfonium ylides with aldehydes, disclosed[1−3] in the 1960s, has recently been revisited to devise an enantioselective synthesis of oxiranes.[4,5] A number of chiral sulfur compounds have been designed and successful versions have been reported using oxathianes, derived from pulegone,[6−8] and camphor[5,9] as well as sulfides, derived from 1,4-diols,[10−12] camphor,[13,14] and other sources.[15−18] The model example involved benzylidene transfer from the ylide to an aldehyde, typically an aromatic one.

We wished to extend the scope of this reaction to the use of allyl halides. Subsequent deprotonation of allylsulfonium salts **1** with an appropriate base would lead to a conjugated ylide **2** and reaction with an aldehyde would potentially furnish a vinyl oxirane **3** (Scheme 1, path a). To our knowledge, no asymmetric example has been reported so far. We have been intrigued by the absence of such a method.[4] Two possible limits are the γ attack of the conjugated ylide, or the competition with a [2,3] sigmatropic shift[19−24] (path b) of the regioisomeric ylide **4**, leading to sulfide **5**. To avoid the latter pathway, arsine[22,25,26] and tellurium ylides[27−30] have been employed (in the racemic series). A key point in the sulfur series appears[20−22] to be the regioselectivity of the sulfonium salt deprotonation (α versus α'). We have assumed that a proper design of the sulfide could favor the α proton abstraction, necessary for oxirane formation (path a). A higher degree of substitution on the α' position (path b) could kinetically inhibit the abstraction of its proton. This aspect seems to have been overlooked, and we have indeed found[23,31,32] very few precedents of vinyl oxiranes (racemic) synthesized by such a route. To achieve success with chiral sulfides, the challenges will then be enantio- and diastereoselectivities. We have previously shown that the simple (2*R*,5*R*)-dimethylthiolane is a source of chiral sulfur ylides for enantioselective conversion of aldehydes into oxiranes (87−93% yields, 66−96% ee).[10,11] This C_2 symmetric auxiliary has provided the key points: formation of a single diastereomeric sulfonium salt, generation of a favored conformation of the sulfur ylide, and high face selectivity. We now wish to report the first asymmetric allylidene transfer starting from an allyl halide.

Very recently, an enantioselective synthesis of vinyl cyclopropanes was reported using a stoichiometric chiral sulfur ylide.[24] We have attempted allylidenation of aldehydes under similar conditions as for benzyl halides and found[10,11] that they can indeed be used without any modification. A one-pot reaction of (2*R*,5*R*)-2,5-dimethylthiolane **6** or (2*R*,5*R*)-2,5-diethylthiolane **7**, an allyl iodide or bromide **8**, substituted or not, an aromatic aldehyde **9**, and sodium hydroxide was carried out in a 9:1 mixture of *t*-BuOH/H_2O, at ambient temperature, for

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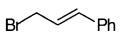
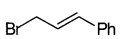
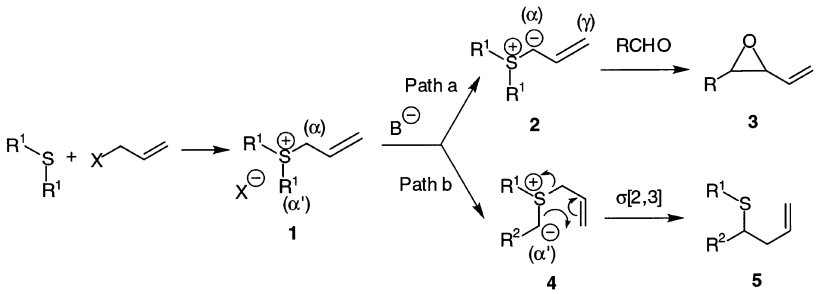
10.1021/jo026085z CCC: $22.00
Published on Web 11/09/2002

TABLE 1. Asymmetric Conversion of Aldehydes into Oxiranes Using Sulfur Ylides

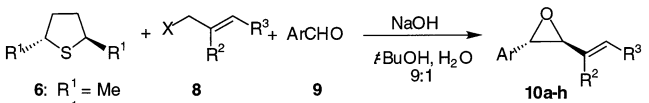
entry	thio-lane	8	9 Ar	time	Oxirane	Yield (%)	dr[a] *trans: cis*	ee *trans* (*S,S*) (%)	ee *cis* (%)
1	**6**		Ph	2 d	**10a**	85	2.3:1	37[b]	3[b]
2	**6**		Ph	15 h	**10b**	76	2.2:1	50[b]	15[b]
3	**7**		Ph	15 h	**10b**	81	2.8:1	53[b]	22[b]
4	**6**		Ph	4 d	**10c**	55	24:1	85[b]	40[b]
5	**6**		Ph	2 d	**10c**	60	≥50:1	84[b]	n.a.
6	**6**		Ph	6 d	**10d**	60	2.3:1	90[b]	n.a.
7	**6**		Ph	5 d	**10e**	72	≥50:1	45[c]	n.a.
8	**6**		2–Naphthyl	3 d	**10f**	70	≥50:1	70[c]	n.a.
9	**6**		4–Cl–C_6H_4	3 d	**10g**	64	≥50:1	78[c]	n.a.
10	**6**		2–Thienyl	2 d	**10h**	[d]	≥50:1	77[c]	n.a.
11	***(S,S)***		Ph	2 d	**10c**	65	≥50:1	77[b] *(R,R)*	n.a.

[a] Diastereoisomeric excess determined on the ^{1}H NMR of the crude product. [b] Enantiomeric excess determined by chiral HPLC using a Daicel AD column. [c] Enantiomeric excess determined by chiral HPLC using a Chirosebond no. 2 C1 column. [d] Unstable product on silica gel. Analysis of the crude material.

SCHEME 1



SCHEME 2

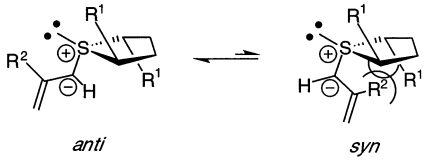


a few days. Vinyloxiranes **10** were obtained in good yields, even though their acidic sensitivity required rapid purification on silica gel (Scheme 2). Thus, the first element of control was secured: substitution of both α′ carbons led to selective abstraction of the α proton (Scheme 1).

With benzaldehyde, a variety of allyl halides were tested (Table 1), which revealed that the enantio- and diastereoselectivities are largely dependent upon the allyl framework of the halide. Unsubstituted allyl iodide (entry 1) led to a rather modest level of ee: 37% for the trans oxirane **10a** and 3% for the cis isomer. The reaction with cinnamyl bromide was also chemically efficient and brought some improvement (50−53% ee for trans, 15−22% for cis) with both thiolanes **6** and **7** (entries 2 and 3).

At this stage, we reasoned that the vinyl chain of the ylide is too small a substituent to provide differentiation (Scheme 3) between the two possible anti and syn conformers of the ylide (planar carbon and tetrahedral sulfur, with the sulfur lone pair lying in the plane of the ylide carbon substituents[10]). Indeed, an ethenyl group, with sp^2 centers only, is a small group according to the conformational energy scale.[33] So, we wished to increase

SCHEME 3



the steric hindrance and thought to introduce a methyl group on the nearest sp^2 carbon.

Replacement of the allyl by a methallyl chain (entry 4) provided a delightful observation: ee raised to 85% (entry 4). The diastereoselectivity, which was previously around 3:1, jumped to 24:1. Reaction with methallyl iodide (entry 5) was faster and provided similar high selectivity (84% ee). The cis isomer was not detected by NMR. The strong effect of the introduction of an alkyl group on the double bond was further exploited by preparing cyclohexen-1-ylmethyl iodide (entry 6). Again, a high degree of control was observed with 90% ee. More surprising is the increase of the cis isomer, for this case (2.3:1 dr). Another unsaturated chain was explored: 2-phenyl-2-propenyl iodide, leading to a modest enantioselectivity but a high diastereoselectivity (entry 7).

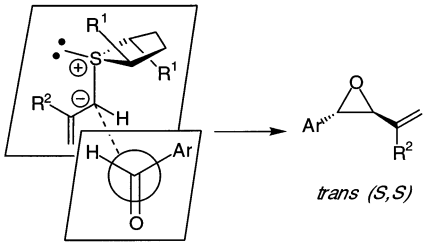
Asymmetric allylidene transfer was extended to some aromatic aldehydes (entries 8−10): 2-naphthaldehyde, 4-chlorobenzaldehyde, and 2-thienylcarboxaldehyde. Efficient conversion to methylethenyl oxiranes was achieved, with 70−78% enantioselectivity, and high diastereocontrol in favor of the trans isomer.

The (*S*,*S*)-antipode of thiolane **6** can be used as well (entry 11). The slight erosion of excess is attributed to a lower enantiopurity of the thiolane.

The absolute stereochemistry of 3-ethenyl-2-phenyloxirane **10a** (entry 1) was assigned by chemical correlation.[34] (2*S*,3*S*)-*trans*-3-Phenyloxirane-2-methanol, a product from Sharpless epoxidation,[35] was submitted[34] to a Swern oxidation and the resulting epoxyaldehyde was reacted with triphenylmethylenephosphorane to give the Wittig product **10a**. No change of diastereopurity (NMR) was observed along the sequence. The resulting (2*S*,3*S*)-3-ethenyl-2-phenyloxirane was analyzed by HPLC (Chiral-Pak AD Daicel column) and compared with both the racemic compound ($\alpha = 1.48$) and our product (entry 1), demonstrating that the major enantiomer from sulfur ylide chemistry has the same (2*S*,3*S*) stereochemistry as that from the independent synthesis. For the other oxiranes **10b**−**h** (entries 2−10), the HPLC order of elution of the major/minor enantiomers is homogeneous and by analogy we tentatively assign them the same configurations.

This (*S*,*S*) configuration can be rationalized as in Scheme 4. The C_2 symmetry of our initial sulfide dictates the formation of a single sulfonium salt by reaction with allyl halides. Out of the two possible conformations for the ylide, the anti one is favored as the vinyl group (made bulky) is away from the thiolane ring (Scheme 3). A classical[36] anti 109° approach of the aldehyde is considered (Scheme 4), avoiding the gauche interaction between the ylide and aldehyde aryl groups.[37] Facial selectivity of the ylide will be simply controlled by the methyl groups of the thiolane ring. Approach of the electrophile will occur on the face bearing the hydrogen atom down, as shown, and lead to the *trans*-(*S*,*S*)-enantiomer.

SCHEME 4



As far as diastereoselectivity was concerned, noteworthy observations were made. A modest control in favor of the trans oxirane was observed with the unsubstituted allyl iodide with a 2.3:1 dr. The introduction of a methyl group with methallyl iodide afforded only the trans oxirane. Other examples also showed important variations. Thus, steric effects appear to play a key role. It is not straightforward to explain these changes. The formation of the syn ylide is clearly disfavored. Another point is that steric hindrance slows down the closure of the betaine leading to the cis oxirane and favors reversibility to the starting material and subsequent increased formation of the trans oxirane.[37,38]

Though thiolane **6** is easily available in two steps from a commercial diol,[10,11] a catalytic version would be appreciated. With methallyl iodide and benzaldehyde and 0.1 equiv of thiolane **6**, at room temperature for one month, we were able to achieve a catalytic cycle leading to **10a** with a 60% chemical yield, dr≥ 50:1, and an ee of 86%. We are now searching to increase the kinetics of this epoxidation. The previous reported[12] addition of *n*-Bu_4I did not lead to an acceptable yield, probably in connection with a poor compatibility of this additive with the produced oxirane.

In conclusion, we have reported the first example of asymmetric allylidenation of aldehydes mediated by chalcogen ylides. C_2 symmetric 2,5-dialkylthiolanes are efficient chiral auxiliaries, which are prepared in two steps from commercially available diols.[11,10,39] The readily available allyl iodides or bromides provided a source of chiral allylidene ylides, for the first time. Extremely simple reaction conditions led to good yields. The allyl framework dramatically influences the enantio- and diastereoselectivity: substitution of the adjacent sp^2 center led to a single trans oxirane with 70−90% ee.

Preparation of enantioenriched vinyl epoxides mediated by sulfur ylides has so far involved an unsaturated aldehyde.[9,11,14,15,40] Our results offer a complementary

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route to enantiopure vinyloxiranes,[34,41−48] which are attractive building blocks for synthesis[49,50] (especially when applied to S_N2 and S_N2' nucleophilic reactions[51]).

Experimental Section

Allyl Iodides. Allyl iodides were prepared by standard routes: methallyl iodide by Finkelstein halogen exchange with NaI, 1-(iodomethyl)cyclohexene according to refs 52 and 53, and 1-iodo-2-phenylpropene according to refs 54 and 55.

Typical Procedure. To a solution of (2*R*,5*R*)-dimethylthiolane[10,11] (0.25 mmol, 250 μL of a 0.2 M solution of dialkylthiolane in *t*-BuOH/H_2O 9/1, 1 equiv) in 250 μL of a mixture of *t*-BuOH/H_2O 9/1 was added allyl iodide (55 μL, 0.5 mmol, 2 equiv), powdered NaOH (20 mg, 0.5 mmol, 2 equiv), and benzaldehyde (26 mg, 0.25 mmol, 1 equiv). The reaction mixture was stirred at room temperature. The reaction was judged complete by thin-layer chromatography (TLC). TLC plates were visualized by UV light and by treatment with a solution of 2,4-DNPH (400 mg in 100 mL of HCl, 1 N) to check the conversion of benzaldehyde, and by a phosphomolybdic acid solution (1 g in 100 mL of *i*-PrOH) to follow the oxirane formation. Water (2 mL) was added. The aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and then concentrated to dryness. The crude product was submitted to rapid column chromatography (silica gel, 94/5/1 petroleum ether/diethyl ether/triethylamine) to give the oxirane as an oil.

3-Ethenyl-2-phenyl-oxirane (10a). Spectra were identical to those in ref 34.

2-Phenyl-3-(2-phenylethenyl)oxirane (10b). Colorless crystals. Mp 75 °C. Trans isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.48 (dd, J = 1.9, 7.7 Hz, 1H), 3.85 (d, J = 1.9 Hz, 1H), 6.04 (dd, J = 7.7, 16.0 Hz, 1H), 6.77 (d, J = 16.0 Hz, 1H), 7.17−7.38 (m, 10H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 60.5, 62.9, 125.4, 126.2, 126.4, 128.0, 128.1, 128.4, 128.6, 134.2, 135.9, 137.0. Cis isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.79 (dd, J = 4.2, 8.7 Hz, 1H), 4.28 (d, J = 4.2 Hz, 1H), 5.72 (dd, J = 8.7 Hz, 15.9 Hz, 1H), 6.81 (d, J = 15.9 Hz, 1H), 7.17−7.38 (m, 10H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 59.3, 59.9, 123.0, 126.2, 126.4, 127.7, 128.2, 128.4, 128.6, 134.3, 135.2, 136.8; IR (KBr) ν 3856, 3652, 3632, 3422, 3058, 3030, 2972, 1492, 1452, 974, 890, 834, 754, 694, 550 cm$^{-1;}$ MS (70 eV, EI) *m*/*z* (%) 222 (9) [M^+], 206 (8), 193 (65), 189 (100), 114 (43), 77 (30), 51 (31).

(2*S*,3*S*)-3-(1-Methylethenyl)-2-phenyloxirane (10c).[56] Trans isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.75 (m, 3H), 3.37 (d, J = 1.9 Hz, 1H), 3.80 (m, 1H), 5.05−5.18 (m, 2H), 6.90−6.70 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.9, 58.2, 64.9, 114.3, 125.5, 128.1, 128.5, 137.4, 140.9. Cis isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.56 (m, 3H), 3.67 (d, J = 4.4 Hz, 1H), 4.19 (d, J = 4.4 Hz, 1H), 4.87−5.00 (m, 2H), 6.90−7.60 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 19.2, 58.5, 61.1, 113.4, 126.6, 127.5, 127.7; IR (NaCl) ν 3032−3066, 2978, 1652, 1496, 1268, 900, 878; MS (70 eV, EI) *m*/*z* (%) 160 (39), 145 (67), 131 (100), 115 (31), 103 (100), 91 (23), 77 (50), 51 (33); HRMS found 160.0877, $C_{11}H_{12}O$ (M^+) 160.0888.

3-(1-Cyclohexenyl)-2-phenyloxirane (10d). Trans isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.2−2.1 (m, 8H), 3.29 (d, J = 1.8 Hz, 1H), 3.86 (d, J = 1.8 Hz, 1H), 5.91 (m, 1H), 7.1−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.2, 22.4, 22.8, 25.2, 57.7, 65.8, 125.4, 126.6, 127.4, 128.4, 133.5, 137.8. Cis isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.2−2.1 (m, 8H), 3.61 (m, 1H), 4.12 (d, J = 4.2 Hz, 1H), 5.70 (m, 1H), 7.1−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.1, 22.2, 24.5, 25.3, 58.3, 61.1, 125.4, 127.3, 127.5, 127.9, 130.5, 135.3.

2-Phenyl-3-(1-phenylethenyl)oxirane (10e). Trans isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.68 (m, 1H), 3.72 (d, J = 2.0 Hz, 1H), 5.46 (br s, 1H), 5.51 (d, J = 1.0 Hz, 1H), 7.30−7.46 (m, 10H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 61.5, 62.5, 112.0, 125.6, 126.0, 128.1, 128.3, 128.5, 128.6, 137.0, 137.8, 143.9; MS (70 eV, EI) *m*/*z* (%) 222 (15), 131 (37), 115 (100), 103 (36), 89 (38), 77 (26).

3-(1-Methylethenyl)-2-(2-naphthyl)oxirane (10f). Colorless needles. Mp 65.5−66.5 °C. Trans isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.76−1.78 (m, 3H), 3.46 (d, J = 1.7 Hz, 1H), 3.96 (d, J = 1.7 Hz, 1H), 5.07−5.08 (m, 1H), 5.20 (s, 1H), 7.23−7.50 (m, 3H), 7.79−7.83 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.9, 58.5, 65.0, 114.4, 122.8, 124.9, 125.7, 126.0, 126.3, 127.7, 128.3, 133.2, 133.3, 134.9, 140.9; MS (70 eV, EI) *m*/*z* (%) 210 (100), 195 (43), 181 (31), 167 (62), 141 (60), 115 (43), 69 (32), 41 (23). Anal. Calcd for $C_{14}H_{14}O$: C, 85.68; H, 6.71; O, 7.61. Found: C, 85.56; H, 6.74; O, 7.70.

2-(4-Chlorophenyl)-3-(1-methylethenyl)oxirane (10g). Trans isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.48 (br s, 1H), 3.67 (d, J = 1.7 Hz, 1H), 3.79 (d, J = 1.7 Hz, 1H), 4.89 (s, 1H), 4.98 (s, 1H), 7.18−7.31 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.8, 57.5, 65.0, 114.7, 126.8, 129.6, 133.9, 135.9, 140.6. Cis isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.72−1.75 (m, 1H), 3.32 (d, J = 4.2 Hz, 1H), 4.15 (d, J = 4.2 Hz, 1H), 5.05−5.08 (m, 1H), 5.18 (br s, 1H), 7.18−7.31 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 19.2, 57.8, 61.1, 113.6, 127.9, 128.0, 133.2, 133.4, 136.8; MS (70 eV, EI) *m*/*z* (%) 194 (26), 179 (61), 165 (79), 159 (100), 144 (38), 139 (41), 130 (86), 115 (40), 89 (86), 69 (28), 63 (30), 50 (25), 41 (18); HRMS found 194.0498, $C_{11}H_{11}ClO$ (M^+) 194.0510.

3-(1-Methylethenyl)2-(2-thienyl)oxirane (10h). Trans isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.73 (m, 3H), 3.57 (d, J = 2.0 Hz, 1H), 4.05 (d, J = 2.0 Hz, 1H), 5.07−5.08 (m, 1H), 5.20 (s, 1H), 6.99 (dd, J = 3.5, 5.0 Hz, 1H), 7.12 (dd, J = 1.0, 3.5 Hz, 1H), 7.26 (dd, J = 1.0, 5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.8, 55.1, 65.5, 114.7, 125.1, 125.8, 127.1, 140.4, 141.3. Cis isomer ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.64 (s, 3H), 3.69 (d, J = 4.0 Hz, 1H), 4.33 (d, J = 4.0 Hz, 1H), 5.04 (s, 1H), 5.15 (s, 1H), 6.95 (dd, J = 3.8, 5.0 Hz, 1H), 7.03−7.06 (m, 1H), 7.21 (dd, J = 1.3, 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 19.2, 55.7, 61.7, 114.1, 125.2, 126.3, 126.8 (detected peaks).

Acknowledgment. We thank the PunchOrga network (Pôle Universitaire Normand de Chimie Organique), the Ministère de la Recherche, CNRS, the Région Basse-Normandie, and the European Union (Fonds FEDER) for their support, and Dr. Catherine Leriverend for her preliminary study.

Supporting Information Available: Enantioselective HPLC chromatograms of the isomers of 3-ethenyl-2-phenyloxirane and 3-(methylethenyl)-2-phenyloxirane. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026085Z

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