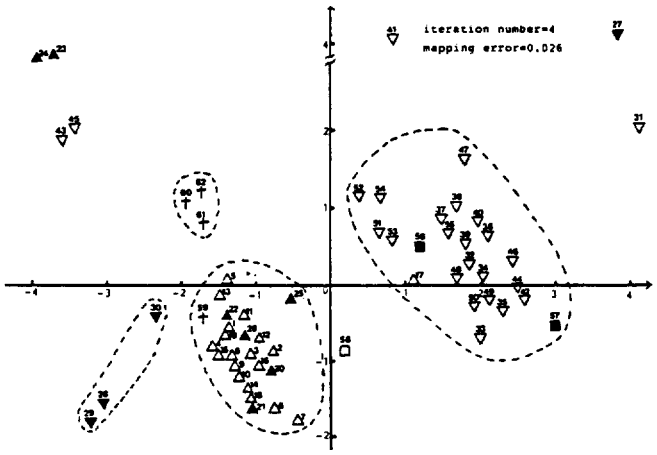

Figure 5. Nonlinear mapping from eigenvector projections using 7 elements.

sults are in accord with those obtained by SLDA as well as NLM.

Acknowledgement. The present studies are supported by Basic Science Research Institute Program, Ministry of Education, 1989.

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A Synthetic Study on *Trans*-2,5-Disubstituted Tetrahydrofurans via Phenylselenoetherification

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2,5-Disubstituted tetrahydrofurans **11-13** were prepared by phenylselenoetherification of 1-alkyl-4-phenyl-(3E)-butenols **8-10** under kinetic conditions. Their stereochemical outcome and reactivity were controlled by solvent, reaction temperature and the alkyl substituent. While the cyclization was stereorandom in dichloromethane, its stereoinduction was moderate to good in propionitrile and good to excellent in diethyl ether. The reaction went to completion in dichloromethane and propionitrile, but it did not in diethyl ether. The results can be rationalized by the degree of reversibility in the formation of episelenonium cation and 1,3-diaxial interactions in the transition state of the formation of tetrahydrofuranonium cation.

Introduction

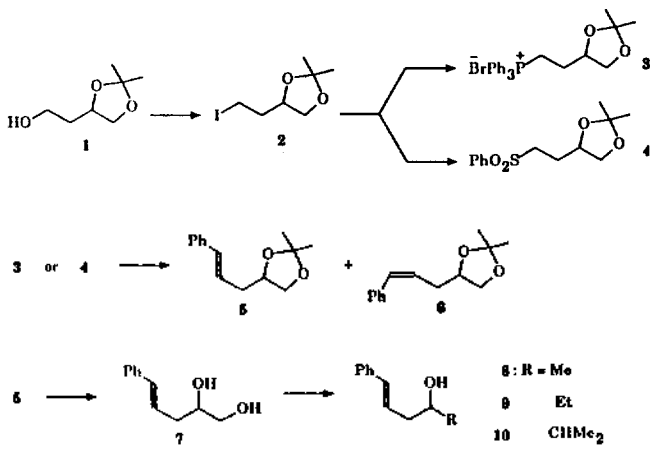
Since 2,5-disubstituted tetrahydrofurans are crucial structural units in many natural products such as polyether antibiotics,[1] furanoterpenes[2] and polyene mycotoxins,[3] there has been increasing interest in the synthesis of the ring sys-

tem.[4] One of the most effective routes to the tetrahydrofurans is electrophile-promoted cyclizations of 4-alkenols.[5] Several electrophiles can be used in the cyclizations, of which phenylselenonium cation is considered as one of the most versatile electrophiles due to the diverse functionalization of phenylselenyl group.[6] If the cyclization of 3-alkenols with phenylselenonium cations is attained *via* 5-Endo mode, it will be complementary to the above 5-Exo favored process[7] due to the feasible generation of 2,5-dihydrofurans, of which the double bond can serve as two endocyclic prochiral centers. Since the 5-Endo cyclization is disfavored due to geometric constraint, it was inferred that electronically favored factor(s) should be introduced to 4-position of 3-alkenols for the desired cyclization. Accordingly, 4-pehenyl-3-buten-1-ol derivatives were chosen as the promising substrates for our study. On the other hand, the introduced phenyl ring can not only be converted into one-carbon functionality by ruthernium tetroxide[8] but also facilitate the reductive cleavage of the benzylic oxygens of the tetrahydrofurans to provide a way to acyclic 1,2,3-arrays of stereogenic centers. Furthermore, the phenyl group may induce the cyclization in a stereocontrolled manner due to its bulkiness.

In this paper we describe our study on phenylselenoetherification of model substrates **8-10** to investigate the effect of the substituent's size, solvent and reaction temperature on stereoselectivity and reactivity in the formation of 2,5-disubstituted tetrahydrofurans.

Results and Discussion

Substrates **8-10** were prepared from 1,2-isopropylidenebutane-1,2,4-triol **1** (Scheme 1). Impure alcohol **1**[9] was treated with *p*-toluenesulfonyl chloride (*p*-TsCl) in triethylamine and dichloromethane in the presence of 4-dimethylaminopyridine (DMAP), and then with sodium iodide in refluxing acetone to give acetonide iodide **2** in 79% yield. Iodide **2** was reacted with triphenylphosphine in acetonitrile in the presence of potassium carbonate, which was essential to the conversion, to afford phosphonium iodide **3** in 95% yield. Wittig olefination of phosphonium iodide **3** and benzaldehyde was carried out with *n*-butyllithium in tetrahydrofuran (THF) and hexamethylphosphoramide(HMPA) at -78°C to -50°C to provide a 1:6 mixture of *trans*-olefinic acetonide **5** and the corresponding *cis*-isomer **6** in 76% yield. On the other hand, the reaction in the absence of HMPA at 0°C furnished a 4.2:1 mixture of **5** and **6** in 78% yield. Since the *cis*-isomers corresponding to **8-10** were resistant to phenylselenoetherification, it was necessary to find out a more efficient route to secure the *trans*-isomer **5**. Iodide **2** was heated with sodium benzenesulfinate in ethanol to produce the expected sulfone **4** in 80% yield along with 5% of the isomeric benzenesulfinate ester. Sequential treatment[10] of sulfone **4** with *n*-butyllithium in THF, benzaldehyde and acetic anhydride in triethylamine in the presence of DMAP gave β-acetoxysulfone, which was reductively eliminated with 5% sodium-amalgam in methanol and ethyl acetate to afford a 5:1 mixture **5** and **6** in 74% overall yield. Since the obtained stereoselectivity was not satisfactory, the isomeric mixture of **5** and **6** was heated in benzene with a catalytic amount of thiophenol and azobisisobutyronitile (AIBN)[11] to provide a 20:1 mixture **5**



Scheme 1.

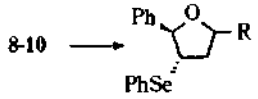
and **6** in 96% yield. After chromatographic removal of **6**, **5** was deprotected in hot aqueous acetic acid to furnish diol **7** in 95% yield. Diol **7** was oxidatively cleaved with sodium metaperiodate in aqueous methanol, and the resulting aldehyde was treated with methylmagnesium bromide, ethylmagnesium bromide and isopropylmagnesium bromide to produce alcohols **8**(92%), **9**(89%) and **10**(87%), respectively.

Substrates **8-10** were cyclized with phenylselenyl chloride in the presence of potassium carbonate in dichloromethane, propionitrile and diethyl ether to produce tetrahydrofurans **11-13**. Their relative stereochemistry and isomeric ratios were determined by NOE experiments and HPLC analyses, repectively. The results are summarized in Table 1, which reveals the great dependence of the stereoselectivity on solvent, reaction temperature and the substituent's size. The cyclization in the absence of potassium carbonate resulted in variable isomeric ratios depending on reaction time and scale, probably due to thermodynamic conditions.[12] Since the presence of potassium carbonate makes the last step of the cyclization irreversible, it seems to be essential to the consistent results.

With a given substrate and reaction temperature, the cyclization was the fastest in dichloromethane and the slowest in diethyl ether. In accordance with the relative reaction rate, the stereoselectivity was poor in dichloromethane, moderate to good in propionitrile and good to excellent in diethyl ether. The observations can be reasoned by the degree of reversibility in the formation of episelenonium cation (or charge-transfer complex),[5b] which is though to be closely related with solvent's polarity, and the relative energy in the chairlike transition state of the formation of 2,5-disubstituted tetrahydrofuranonium cation. The detailed mechanistic pathway is depicted in Figure 1.

Since episelenonium cations **14** and **15** are not much stabilized in dichloromethane due to its relatively low polarity, they will be highly energetic. The internal hydroxyl group is expected to attack them indiscriminately to produce tetrahydrofuranonium cations **16** and **17**, of which the stereochemical outcomes are presumably governed by the intrinsic conformational preference of the starting olefin. Therefore, the cyclization in dichloromethane is anticipated to proceed relatively fast and stereorandomly. On the other hand, episelenonium cations **14** and **15** in propionitrile and

Table 1. Cyclization of **8-10** with PhSeCl in the presence of K_2CO_3



11a: R = α-Me **12b**: R = β-Et
11b: β-Me **13a**: α-$CHMe_2$
12a: α-Et **13b**: β-$CHMe_2$

Entry	Substrate	Solvent	Reaction temp. (°C)	Ratio	% Yield	% Recovered substrate
1	**8**	CH_2Cl_2	0	**11a:11b** = 1:1.4	68	—
2	**8**	EtCN	0	**11a:11b** = 2.4:1	82	—
3	**8**	Et_2O	0	**11a:11b** = 5.9:1	73	11
4	**8**	CH_2Cl_2	-78	**11a:11b** = 1:1.3	82	—
5	**8**	EtCN	-78	**11a:11b** = 4.0:1	91	—
6	**8**	Et_2O	-78	**11a:11b** = 7.1:1	68	26
7	**9**	CH_2Cl_2	0	**12a:12b** = 1:1.3	72	—
8	**9**	EtCN	0	**12a:12b** = 1.4:1	90	—
9	**9**	Et_2O	0	**12a:12b** = 5.5:1	80	10
10	**9**	CH_2Cl_2	-78	**12a:12b** = 1.1:1	84	—
11	**9**	EtCN	-78	**12a:12b** = 5.8:1	93	—
12	**9**	Et_2O	-78	**12a:12b** = 11.9:1	70	24
13	**10**	CH_2Cl_2	0	**13a:13b** = 1:1.3	76	—
14	**10**	EtCN	0	**13a:13b** = 1.2:1	88	—
15	**10**	Et_2O	0	**13a:13b** = 5.8:1	85	8
16	**10**	CH_2Cl_2	-78	**13a:13b** = 1.9:1	84	—
17	**10**	EtCN	-78	**13a:13b** = 16.9:1	82	10
18	**10**	Et_2O	-78	**13a:13b** = 21.3:1	70	8

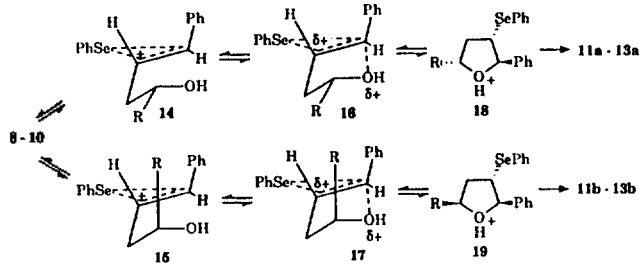


Figure 1. The detailed mechanistic pathway for phenylselenoetherification of 3-alkenols

diethyl ether will be tightly solvated by their relatively high nucleophilicity. It is likely that the stabilized cations are discriminately cyclized into tetrahydrofuranonium ions **18** and **19** due to the energy difference between the transition states **16** and **17**. Since **14** has less 1,3-diaxial interactions than **15**, the former will be preferably transformed into tetrahydrofuranonium ion to the latter. During this process, **15** can be reversibly converted into **14** to enhance the *trans*-stereoselectivity.

The cyclization in propionitrile and in diethyl ether also showed some differences in stereoselectivity and reactivity. In other words, diethyl ether gave higher stereoinduction but lower chemical conversion. The observations might be rationalized by assuming that episelenonium cations are not stabilized so efficiently in diethyl ether as in propionitrile, and the insufficiently stabilized cations in diethyl ether interact with the internal oxygen atom.[13] Since the interaction certainly prevents the cations from the desired cyclization due to geometric constraint, it may induce their reversible formation more effectively to result in higher stereoselectivity as well as lower chemical conversion.

Finally, the stereoselectivity was greatly influenced at -78 °C by the sizes of the substituents at 1-position of 3-alkenols **8-10**. This fact is also explained by considering 1,3-diaxial interactions in the aforementioned chair-like transition states **16** and **17**. The energy difference between **16** and **17** will be the least with methyl substituent but the greatest with isopropyl substituent. This explanation is consistent with the data as shown in Table 1.

In any event, our study provided a clue to attain *trans*-2,5-disubstituted tetrahydrofurans with high stereoinduction. Now we are investigating how to drive the cyclization in diethyl ether to completeness without losing the high *trans*-stereoselectivity.

Experimental

The NMR spectra and NOE experiments were recorded on a Bruker AM-300 spectrometer. Deuteriochloroform was used as the solvent and tetramethylsilane as the internal standard. The high resolution mass spectra were recorded on a Jeol JMS-DX 303 mass spectrometer, and the low resolution mass spectra on a Shimadzu GCMS-QP 1000. HPLC analyses were done on a Waters Associates model equipped with Waters 510 pump, U6K injector, 440 absorbance detector and 740 data module. Melting points were determined on a Thomas Hoover Melting Point Apparatus and were uncorrected. The normal work-up included extraction, drying over magnesium sulfate and evaporation of solvents *in vacuo*. Purifications by column chromatography were performed using Merk silica gel 60 (70~230 mesh or 230~400 mesh).

1,2-O-Isopropylidene-4-iodo-1,2-butanediol 2. To impure 1,2-O-isopropylidene-1,2,4-butanetril 1(5.84g, 40.0 mmole) in 20 m*l* of triethylamine and 60 m*l* of dichloromethane were p-TsCl (9.20g, 48.3 mmole) and 50 mg of DMAP added, and the reaction mixture was stirred in an ice bath for 5 hours. After evaporation of the volatile materials *in vacuo*, normal work-up with diethyl ether and column chromatography(hexane: diethyl ether = 5:1) gave the expected tosylate(11.28g, 94%), which seemed to be contaminated with the isomeric tosylate from 2,4-isopropylidene-1,2,4-triol. The impure tosylate(6.0g, 20.0 mmole) and sodium iodide(16.0g, 106.7 mmole) in 100 m*l* of acetone were heated at reflux for 3 hours. After removal of acetone *in vacuo*, normal work-up with diethyl ether and column chromatography(hexane: diethyl ether = 4:1) produced the pure iodide 2(4.31g, 84%). ^{1}H NMR δ 1.35(s, 3H), 1.41(s, 3H), 1.97-2.17(m, 2H), 3.17-3.32(m, 2H), 3.57(dd, 1H, J = 7.9 and 6.3 Hz), 4.08(dd, 1H, J = 7.9 and 6.1 Hz) and 4.13-4.22 ppm (m, 1H); ^{13}C NMR δ 25.5, 26.9, 37.8, 68.6, 75.6 and 109.1 ppm.

3,4-O-Isopropylidene-3,4-dihydroxybut-1-yltriphenylphosphonium iodide 3. Iodide 2(5.12g, 20.0 mmole), triphenylphosphine(15.8g, 60.2 mmole) and potassium carbonate(0.83g, 6.0 mmole) in 100 m*l* of acetonitrile were heated at reflux for 4 hours. After removal of acetonitrile *in vacuo*, column chromatography (methanol: dichloromethane = 1:10) of the residue furnished phosphonium salt 3(9.85g, 95%) as a white solid(decomposed at 213-220 °C). ^{1}H NMR δ 1.30(s, 3H), 1.32(s, 3H), 1.70-1.87(m, 1H), 2.03-2.19(m, 1H), 3.38-3.53(m, 1H), 3.62(dd, 1H, J = 8.5 and 5.8 Hz), 4.15(dd, 1H, J = 8.5 and 6.3 Hz), 4.10-4.26(m, 1H), 4.52-4.62(m, 1H), 7.69-7.78(m, 6H) and 7.78-7.90 ppm(m, 9H); ^{13}C NMR δ 25.0, 26.8, 27.3(d, J = 16 Hz), 68.8, 74.5(d, J = 60 Hz), 109.1, 117.28(d, J = 44 Hz), 130.5(d, J = 50 Hz), 133.6(d, J = 40 Hz) and 135.1 ppm(d, J = 11 Hz).

Wittig Olefination of Phosphonium Iodide 3 and Benzaldehyde in THF and HMPA. n-Butyllithium(1.6 M in hexane; 8.0 m*l*, 12.8 mmole) was slowly added to phosphonium iodide 3(5.18g, 10.0 mmole) in 40 m*l* of THF and 10 m*l* of HMPA in an ice bath, and the resulting solution was stirred for 20 minutes. Benzaldehyde(1.28g, 12.1 mmole) was added to the generated yield at -78 °C, and the reaction temperature was maintained between -78 °C and -50 °C for 40 minutes. After quenching the reaction with water, normal work-up with diethyl ether followed by column chromatography (hexane:diethyl ether = 6:1) provided a 1:6 mixture of *trans*-olefin 5 and *cis*-olefin 6(1.66g, 76%), of which the ratio was determined by ^{1}H NMR spectrum.

Wittig Olefination of Phosphonium Iodide 3 and Benzaldehyde in THF. n-Butyllithium(1.6 M in hexane, 8.0 m*l*, 12.8 mmole) was slowly added to phosphonium iodide 3(5.18g, 10.0 mmole) suspended in 50 m*l* of THF in an ice bath to give a homogeneous dark reddish solution. To the generated yield was benzaldehyde (1.28g, 12.1 mmole) added and the reaction mixture was stirred in an ice bath for 30 minutes. After quenching the reaction with water, normal work-up with diethyl ether followed by column chromatography (hexane:diethyl ether = 6:1) afforded a 4.2:1 mixture of 5 and 6(1.71g, 78%), of which the ratio was determined by ^{1}H NMR spectrum.

1-Phenylsulfonyl-3,4-O-isopropylidine-3,4-butanediol 4. Iodide 2(2.56g, 10.0 mmole) and sodium benzenesulfinate(1.93g, 30.0 mmole) were heated at reflux in 30 m*l* of ethanol for 5 hours. After removal of ethanol *in vacuo*, column chromatography (hexane:diethyl ether = 2:3) of the residue gave sulfone 4(2.18g, 81%) and the isomeric benzenesulfinate ester(0.12g, 4%). 4: ^{1}H NMR δ 1.29(s, 3H), 1.33(s, 3H), 1.83-2.08(m, 2H), 3.11-3.35(m, 2H), 3.55(dd, 1H, J = 8.1 and 6.1 Hz), 4.04(dd, 1H, J = 8.1 and 6.1 Hz), 4.10-4.18(m, 1H), 7.55-7.70(m, 3H) and 7.90-7.94 ppm(m, 2H); ^{13}C NMR δ 25.3, 26.8, 26.9, 52.8, 68.7, 73.7, 109.4, 128.0, 129.3, 133.8 and 138.9 ppm. The isomeric benzenesulfinate ester: ^{1}H NMR δ 1.33(d, 3H, J = 2.9 Hz), 1.36(s, 3H), 1.80-2.05(m, 2H), 3.50-3.56(m, 1H), 3.65-3.85 (m, 1H), 3.99-4.08(m, 1H), 4.10-4.21(m, 2H) and 7.45-7.80 ppm(m, 5H); ^{13}C NMR δ 25.6, 26.8, 33.9, 61.2, 61.7, 69.2, 72.8, 72.9, 108.8, 125.1, 125.2, 129.0, 132.1, 132.2 and 144.5 ppm.

1,2-O-Isopropyliden-5-phenyl-4-pentene-1,2-diols 5 and 6 from Sulfone 4 and Benzaldehyde. Sulfone 4(2.7g, 10.0 mmole) in 30 m*l* of THF was treated with n-butyllithium(2.6 M in hexane, 4.6 m*l*, 12.0 mmole) at -30 °C to -20 °C for 15 minutes. The resulting anion was reacted with benzaldehyde(1.28g, 12.0 mmole) at -78 °C to room temperature for 2 hours. After normal work-up with diethyl ether and column chromatography (hexane:diethyl ether = 2:3) to remove the remained benzaldehyde, somewhat impure products were subjected to acetic anhydride (2.1g, 20.6 mmole) in 30 m*l* of triethylamine in the presence of 50 mg of DMAP at room temperature for 10 hours. After removal of the volatile materials *in vacuo*, the curde β-acetoxysulfone was reductively eliminated with sodium-amalgam (5%, 18g) in 20 m*l* of methanol and 10 m*l* of ethyl acetate at -40 °C to -30 °C for 5 hours. Normal work-up with diethyl ether followed by column chromatography (hexane: diethyl ether = 1:6) furnished a 5:1 mixture of 5 and 6(1.62g, 74%), of which the ratio was determined by ^{1}H NMR.

1,2-O-Isopropylidene-5-phenyl-(4E)-pentene-1,2-diol 5. An isomeric mixture of 5 and 6(2.18g, 10.0 mmole) in 30 m*l* of benzene was heated with 70 mg of thiophenol and 50 mg of AIBN at 55 °C for 3 hours. After removal of th volatile materials *in vacuo*, column chromatography(hexane:diethyl ether = 1:6) of the residual oil provided *trans*-olefin 5(2.01g, 92%) and *cis*-olefin 6(0.10g, 5%). 6: ^{1}H NMR δ 1.36(s, 3H), 1.41(s, 3H), 2.51-2.74(m, 2H), 3.56 (dd, 1H, J = 8.0 and 7.2 Hz), 4.04(dd, 1H, J = 8.0 and 6.0 Hz), 4.20(p, 1H, J = 6.2 Hz), 5.69(td, 1H, J = 7.2 and 11.7 Hz), 6.57(broad d, 1H, J = 11.7 Hz) and 7.16-7.37 ppm (m, 5H): ^{13}C NMR δ 25.6, 26.8, 32.6, 69.0, 75.5, 109.0, 126.8(2 carbons), 128.2, 128.7, 131.4 and 137.1 ppm. 5: ^{1}H NMR δ1.36(s, 3H), 1.44(s, 3H), 2.37-2.60(m, 2H), 3.59-3.65(m, 1H), 4.01-4.06(m, 1H), 4.21(p, 1H, J = 6.2 Hz), 6.18(td, 1H, J = 7.1 and 15.8 Hz), 6.46(broad d, 1H, J = 15.8 Hz) and 7.16-7.36 ppm(m, 5H); ^{13}C NMR δ 25.6, 26.8, 37.2, 68.8, 75.3, 108.9, 125.1, 126.0, 127.2, 128.4, 132.6 and 137.2 ppm; MS *m/e*(relative intensity) 218(M^+, 1), 203(9), 143(16), 101(81), 53(100).

5-Phenyl-(4E)-pentent-1,2-diol 7. *Trans*-olefin 5(2.18g, 10.0 mmole) in 20 m*l* of acetic acid and 5 m*l* of water was heated at 55 °C for 5 hours. After evaporation of the volatile materials *in vacuo*, column chromatography(hexane:

ethyl acetate = 1:5) afforded diol **7**(1.69g, 95%) as a white solid(mp. 53~55 °C). ^{1}H NMR δ 2.33-2.39(m, 2H), 3.49(dd, 1H, J = 11.3 and 7.4 Hz), 3.67(broad d, 1H, J = 11.3 Hz), 3.77-3.88(m, 1H), 6.18(td, 1H, J = 7.0 and 15.8 Hz), 6.45(d, 1H, J = 15.8 Hz) and 7.17-7.35 ppm(m, 5H); ^{13}C NMR δ40.0, 66.2, 71.7, 125.5, 126.0, 127.3, 128.5, 133.0 and 137.1 ppm; MS *m/e* (relative intensity) 178(M^+, 6), 160(8), 147(4), 117(100) and 91(34).

5-Phenyl-(4E)- penten-2-ol 8,6-Phenyl-(5E)-hexen-3-ol 9 and 2-Methyl-6- phenyl-(5E)-hexane-3-ol 10. Diol **7**(890 mg, 5.0 mmole) in 10 m*l* of methanol and 2 m*l* of water was stirred with sodium metaperiodate (3.2 g, 15.0 mmole) at room temperature for 2 hours. The white precipitate was filtered through celite and washed with diethyl ether. Afte the filtrate was condensed *in vacuo*, the residue was subjected to normal work-up with diethyl ether. The resulting aldehyde in 10 m*l* of THF was treated with methymagnesium bromide (3.0 M in diethyl ether, 2.2 m*l*, 6.6 mmole), ethylmagnesium bromide (2.0 M in THF, 3.8 m*l*, 7.6 mmole) or isopropylmagnesium bromide (2.0 M in THF, 3.8 m*l*, 7.6 mmole) in an ice bath for an hour. After quenching the reaction with water, normal work-up with diethyl ether followed by column chromatography (hexane:diethyl ether = 1, 2 or 4:1) produced alcohol **8**(745 mg, 92%), **9**(783 mg, 89%) or **10**(827 mg, 87%). **8**: ^{1}H NMR δ 1.24(d, 3H, J = 6.2 Hz), 2.27-2.45(m, 2H), 3.86-3.97(m, 1H), 6.22(td, 1H, J = 7.5 and 15.9 Hz), 6.47(d, 1H, J = 15.9 Hz) and 7.18-7.38 ppm(m, 5H); ^{13}C NMR δ 22.8, 42.9, 67.3, 126.1, 126.2, 127.2, 128.5, 133.1, and 137.2 ppm; high resolution mass spectrum, *m/e* calcd for $C_{11}H_{14}O$ 162.1045, found 162.1030. **9**: ^{1}H NMR δ0.99(t, 3H, J = 7.4 Hz), 1.48-1.72(m, 2H), 2.25-2.51(m, 2H), 3.62-3.71(m, 1H), 6.24(td, 1H, J = 7.6 and 15.9 Hz), 6.49(d, 1H, J = 15.9 Hz) and 7.19-7.39 ppm(m, 5H); ^{13}CNMR δ 9.94, 29.7, 40.6, 72.5, 126.1, 126.4, 127.2, 128.5, 130.2 and 133.1 ppm; high resolution mass spectrum, *m/e* calcd for $C_{12}H_{16}O$ 176.1201, found 176.1184. **10**: ^{1}H NMR δ 0.97(dd, 6H, J = 6.7 and 2.3 Hz), 1.68-1.80 (m, 1H), 2.23-2.35 (m, 1H), 2.42-2.51(m, 1H), 3.45-3.52(m, 1H), 6.25(ddd, 1H, J = 15.8, 7.9 and 6.6 Hz), 6.49(d, 1H, J = 15.8 Hz) and 7.18-7.39 ppm(m, 5H); ^{13}C NMR δ 17.5, 18.8, 33.2, 38.0, 75.9, 126.1, 126.9, 127.2, 128.5, 132.9 and 137.3 ppm; high resolution mass spectrum, *m/e* calcd for $C_{13}H_{18}O$ 190.1357, found 190.1329.

Phenylselenoetherification of 3-Hydroxyalkenes 8, 9 and 10. To 3-hydroxyalkene **8**, **9** or **10**(0.3 mmole) in 3 m*l* of solvent(dichloromethane, propionitrile or diethyl ether) was patassium carbonate(62 mg, 0.45 mmole) added. After adjusting the reaction temperature in an ice bath or a dry ice bath, phenylselenyl chloride (69 mg, 0.36 mmole) was added as solid, and then the reaction mixture was stirred in an ice bath or a dry ice bath for 2 hours. The reactin was quenched with 1 m*l* of triethylamine and 1 N aqueous NaOH solution. Normal work-up with diethyl ether followed by column chromatography (hexane: diethyl ether = 20:1) yielded tetrahydrofuran **11**, **12**, or **13**. The results are described in Table 1. **11a**: ^{1}H NMR δ 1.32(d, 3H, J = 6.1 Hz), 1.75-1.87(m 1H), 2.53-2.63(m, 1H), 3.51-3.61(m, 1H), 4.31-4.43(m, 1H), 4.89(d, 1H, J = 8.3 Hz) and 7.17-7.43 ppm(m, 10H); ^{13}C NMR δ 21.5, 42.9, 48.1, 75.4, 85.5, 126.2, 127.7(2 carbons), 128.3, 128.5, 129.0 134.9 and 141.2 ppm; high resolution mass spectrum, *m/e* calcd for $C_{17}H_{18}OSe$ 318.0523, found 318.0544. **11b**: ^{1}HNMR δ 1.39(d, 1H, J = 6.1 Hz), 2.03-2.25(m, 2H), 3.55-3.62(m, 1H), 4.23-4.37 (m, 1H), 4.84(d, 1H, J = 6.3 Hz) and 7.17-7.46 ppm(m, 10H); ^{13}C NMR δ 20.6, 41.6, 75.0, 86.8, 126.1, 127.6, 127.7, 128.3, 128.5, 129.0, 134.5 and 141.2 ppm; high resolution mass spectrum, *m/e* calcd for $C_{17}H_{18}OSe$ 318.0523, found 318.0541. **12a**: ^{1}H NMR δ0.93(t, 3H, J = 7.4 Hz), 1.48-1.88 (m, 3H), 2.50-2.60(m, 1H), 3.48-3.58(m, 1H), 4.10-4.20(m, 1H), 4.83(d, 1H, J = 8.5 Hz) and 7.14-7.42 ppm (m, 10H); ^{13}C NMR δ 10.0, 28.9, 40.7, 47.9, 80.7, 85.4, 126.3, 127.7(2 carbons), 128.3, 128.4, 128.9, 134.8 and 141.2 ppm; high resolution mass spectrum, *m/e* $C_{18}H_{20}OSe$ 332.0679, found 332.0682. **12b**: ^{1}H NMR δ 1.00(t, 3H, J = 7.5 Hz), 1.57-1.88(m, 2H), 2.06-2.24(m, 2H), 3.51-3.58(m, 1H), 4.02-4.13(m, 1H), 4.83 (d, 1H, J = 6.5 Hz) and 7.17-7.47 ppm(m, 10H); ^{13}CNMR δ10.2, 28.2, 39.4, 47.7, 80.3, 86.5, 126.1, 127.6, 127.7, 128.3, 128.4, 129.0, 134.4 and 141.2 ppm; high resolution mass spectrum, *m/e* calcd for $C_{18}H_{20}OSe$ 332.0679, found 332. 0658. **13a**: ^{1}H NMR δ0.86(d, 3H, J = 6.7 Hz), 0.97(d, 3H, J = 6.7 Hz), 1.71-1.84 (m, 1H),1.83-1.95(m, 1H), 2.42-2.52(m, 1H), 3.46-3.56(m, 1H), 3.85-3.91(m, 1H), 4.80(d, 1H, J = 8.7 Hz) and 7.13-7.43 ppm(m, 10H); ^{13}C NMR δ 18.1, 19.1, 33.3, 38.8, 48.1, 84.7, 85.5, 126.3, 127.7, 128.3, 128.9, 134.8 and 141.3 ppm; high resolution mass spectrum, *m/e* calcd for $C_{19}H_{22}OSe$ 346.0836, found 346.0842. **13b**: ^{1}H NMR δ 0.94(d, 3H, J = 6.8 Hz), 1.05(d, 3H J = 6.7 Hz), 1.81-1.91(m, 1H), 2.05-2.25(m, 2H), 3.47-3.55(m, 1H), 3.80-3.89(m, 1H), 4.82(d, 1H, J = 6.5 Hz) and 7.17-7.45 ppm(m, 10H); ^{13}C NMR δ 18.5, 19.2, 32.8, 37.4, 47.9, 84.2, 86.1, 126.1, 127.5, 127.7, 128.2, 128.9, 129.0, 134.3 and 141.2 ppm; high resolution mass spectrum, *m/e* calcd for $C_{19}H_{22}OSe$ 346.0836, found 346.0826.

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Dopping Effect of Fluorine Atom on the Superconductivity of $YBa_2Cu_3O_{7-x}F_y$

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The normal and fluorinated high-Tc superconducting materials, $YBa_2Cu_3O_{7-x}F_y$ with $0.25 \le x \le 0.55$ and $0.00 \le y \le 0.30$, were synthesized to investigate the dopping effect of fluorine atom on the superconductivity of Y123 and studied by X-ray diffraction analysis and electron probe microanalysis, resistivity and thermopower measurements, and polarized micro-Raman spectroscopy. The reproducible micro-Raman spectra were recorded and analyzed. The coherent assignments could be suggested for the spectra of normal and fluorinated samples. The fluorine atoms introduced were found to be substituted for oxygen in pyramidal Cu-O units rather than in Cu-O chains. The unit cell parameters were decreased upon the substitution of oxygen by fluorine atom. From the decreasing cell parameters and Tc, the increasing thermopower, and the possible assignments of the vibrational modes, it could be suggested that the dopping of fluorine atom localizes the superconducting electrons in Y123.

Introduction

The thermopower measurement has been considered to be a fine method to study the electronic properties of superconductor based on its sensitivity to the electron energy-band structure and the electron-excitation interactions. Since the experimental results as well as their interpretations differ from one to another[1-9], this is true only if the obtained experimental results are comprehensive and interpreted exactly. It is well known that the oxygen content in a superconducting $YBa_2Cu_3O_{7-x}$ is an important parameter to determine its superconductivity. In this point of view, it is important to study the thermopower of the new oxide superconductors as a function of the oxygen content for a exact superconducting properties.

The thermopower of $YBa_2Cu_3O_{7-x}$ superconductive ceramic samples was measured as a function of oxygen concentration based on the different baking temperatures of the samples[10]. Choi *et al.*[10] found that both the magnitude and the temperature dependence of the thermopower strongly depend on the oxygen deficiency in the $YBa_2Cu_3O_{7-x}$.

It was also found and suggested that the magnitude of the thermopower as a function of oxygen deficiency varied consistently with the change of the superconducting electron density and the magnon-drag effect should be considered seriously for the superconducting $YBa_2Cu_3O_{7-x}$.

On the other hand, it is helpful in order to understand superconductivity of $YBa_2Cu_3O_{7-x}$ to investigate whether the fluorine atoms are substituted for oxygen atoms in the chain Cu-O or the pyramidal Cu-O of the superconductor $YBa_2Cu_3O_{7-x}$ by Raman spectroscopy. It has been reported by several workers[11-16] that the Cu-O vibrations in the superconducting Y123 system are consisted of Cu-O bending, chain Cu-O stretching and pyramidal Cu-O stretching based on Raman spectroscopy studies. The Raman lines at 335,506 and 601 cm^{-1} have been assigned to Cu-O bending, pyramidal Cu-O strectching and chain Cu-O stretching vibrations, respectively. The symmetric and asymmetric pyramidal Cu-O stretching vibrational modes have also been observed at 502 and 589 cm^{-1} respectively in Y123 superconductors[13,15].

The aim of this work is to investigate the dopping effect of the fluorine atom on the superconductivity of the fluorinated Y123 system from X-ray and electron probe microanalyses, resistivity and thermopower measurements, and Raman spectroscopy.

Experimental

$YBa_2Cu_3O_{6.75}$ was prepared from the following mixture: 0.5000 Y_2O_3, 2.000 $BaCO_3$ and 3.000 CuO. $Y123O_{7-x}F_y$