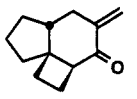
(d, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 221.65 (s), 62.82 (d), 59.40 (s), 51.46 (d), 43.00 (t), 41.39 (t), 41.27 (t), 38.62 (d), 35.80 (t), 35.36 (t), 27.06 (t), 15.45 (q); MS m/e (rel intensity) 178 (M^+, 47), 109 (77), 96 (100); HRMS calcd for $C_{12}H_{18}O$ 178.1357, found 178.1375.

(1*S,4*S**,8*R**)-5,5-Dimethyltricyclo[6.3.0.0^{1,4}]undecan-5-one (15).** Cyclopropanation of 6-methylenetricyclo[6.3.0.0^{1,4}]-undecan-5-one (**20**)[15] (1.62 g, 9.20 mmol) using Me_3SOI and NaH–DMSO was carried out according to the procedure of Corey[16] to give cyclopropyl ketone **21** (1.18 g, 68%) after flash chromatography (elution with ether–petroleum ether, 5:95): IR (neat) 3050, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.81 (dd, J = 8.5, 7.0 Hz, 1 H), 2.6–1.1 (m, 15 H), 0.9–0.5 (m, 2 H).



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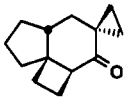


21

A mixture of **21** (188 mg, 0.99 mmol) and platinum(IV) oxide (150 mg, 0.66 mmol) in acetic acid (7 mL) was stirred at rt for 3 h under 1 atm of H_2. The mixture was filtered through a pad of Celite, and the filtrate was concentrated to give the crude product containing **15** and overreduced alcohols. To a stirred solution of pyridine (1.39 mL, 17.3 mmol) in CH_2Cl_2 (10 mL) was added chromium(VI) oxide (866 mg, 8.66 mmol) at rt. The mixture was stirred for 20 min, and then a solution of the above product in CH_2Cl_2 (5 mL) was added in one portion at rt. The mixture was stirred for additional 1 h, and the solution was decanted from the residue, which was washed with ether. The combined organic solutions were washed twice with 10% NaOH, 10% HCl, aqueous $NaHCO_3$, and brine, successively, and dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (elution with ether–petroleum ether, 5:95) of the crude product gave **15** (152 mg, 80% from **21**).

15: IR (neat) 1700, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.77 (dd, J = 9.3, 4.9 Hz, 1 H), 2.32–2.14 (m, 2 H), 2.07–1.91 (m, 2 H), 1.89–1.65 (m, 5 H), 1.58–1.43 (m, 4 H), 1.21 (s, 3 H), 1.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 220.58 (s), 51.68 (s), 47.80 (d), 44.80 (t), 43.42 (s), 40.04 (d), 39.20 (t), 35.30 (t), 31.55 (t), 27.41 (q), 25.40 (q), 24.01 (t), 21.82 (t); MS m/e (rel intensity) 192 (M^+, 12), 108 (100); HRMS calcd for $C_{13}H_{20}O$ 192.1514, found 192.1511.

3,3-Dimethylbicyclo[6.3.0]undeca-1(8),4-dien-4-yl Acetate (16) and (1*R,5*S**,8*S**)-3,3-Dimethyltricyclo[6.3.0.0^{1,5}]undecan-4-one (17).** Reaction of **15** (45 mg, 0.23 mmol) with BF_3·OEt_2 (5.8 μL, 0.046 mmol) in Ac_2O (1 mL) at 0 °C for 19 h as described above gave **16** (20 mg, 45%), **17** (16 mg, 45%), and **15** (8 mg). Reaction of **15** (50 mg, 0.26 mmol) with $AlCl_3$ (69 mg, 0.52 mmol) in CH_2Cl_2 (2.5 mL) was done according to the procedure described previously[2] to give **17** (43 mg, 86%).

16: IR (neat) 3000, 1750, 1660, 1355, 1210, 1060, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.22 (t, J = 9.5 Hz, 1 H), 2.55–2.47 (m, 4 H), 2.44–2.37 (m, 2 H), 2.29–2.19 (m, 4 H), 2.12 (s, 3 H), 1.79–1.69 (m, 2 H), 1.08 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.91 (s), 154.79 (s), 134.79 (s), 131.50 (s), 116.67 (d), 42.45 (t), 41.75 (s), 39.52 (t), 39.15 (t), 31.07 (t), 28.09 (q, 2 C), 22.16 (t), 21.92 (t), 21.12 (q); MS m/e (rel intensity) 234 (M^+, 6), 98 (100); HRMS calcd for $C_{15}H_{22}O_2$ 234.1619, found 234.1642.

17: IR (neat) 1730, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (t, J = 6.4 Hz, 1 H), 2.22–2.12 (m, 1 H), 1.98–1.78 (m, 6 H), 1.76–1.52 (m, 4 H), 1.48–1.40 (m, 1 H), 1.34–1.25 (m, 1 H), 1.10 (s, 3 H), 1.05 (s, 3 H): ^{13}C NMR ($CDCl_3$) δ 225.80 (s), 60.18 (d), 55.49 (s), 53.25 (d), 50.95 (t), 47.50 (s), 43.12 (t), 33.36 (t), 33.30 (t), 29.56 (t), 26.96 (t), 26.54 (q), 24.63 (q); MS m/e (rel intensity) 192 (M^+, 47), 135 (100), 80 (53); HRMS calcd for $C_{13}H_{20}O$ 192.1514, found 192.1532.

Acknowledgment. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining NMR and mass spectra on JEOL JNM-GTX-400 and Bruker AM-600, and JEOL JMS-DX303 spectrometers, respectively.

Registry No. **1**, 136780-97-7; **4**, 92590-09-5; **7a**, 137946-48-6; **7b**, 137946-49-7; **8a**, 137946-50-0; **8b**, 137946-51-1; **9**, 102794-91-2; **10**, 137946-52-2; **11**, 137946-53-3; **12**, 137946-54-4; **13**, 137946-55-5; **14**, 137946-56-6; **14** enol acetate, 137946-61-3; **15**, 137946-57-7; **16**, 137946-58-8; **17**, 91854-72-7; **18**, 138124-75-1; **19**, 138124-76-2; **20**, 138124-77-3; **21**, 137946-59-9; $Zn(OAc)_2$, 557-34-6; Bf_3·OEt_2, 109-63-7; $(EtCO)_2O$, 123-62-6; BBr_3, 10294-33-4; $AlCl_3$, 7446-70-0; $SnCl_4$, 7646-78-8; CF_3SO_3H, 1493-13-6.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of **7a,b**, **8a,b**, and **10–17** and 2D ^1H–^1H COSY spectrum of **8a** (25 pages). Ordering information is given on any current masthead page.

(15) Ue, M.; Tsukahara, H.; Kobiro, K.; Kakiuchi, K.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.* **1987**, *28*, 3979.
(16) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1313.

Higher Order Zinc Cuprate Reagents. Very High 1,3-Chirality Transfer Reaction of γ-(Mesyloxy)-α,β-unsaturated Carbonyl Derivatives

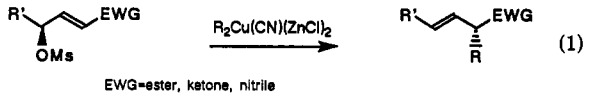
Yoshinori Yamamoto,*[†] Yukiyasu Chounan,[†] Miwa Tanaka,[†] and Toshiro Ibuka[‡]

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan, and Pharmaceutical Sciences, Kyoto University, Kyoto 606, Japan

Received July 31, 1991

We previously reported that chiral γ-(mesyloxy)-α,β-unsaturated esters undergo, 1,3-chirality transfer to form chiral α-alkyl-β,γ-unsaturated esters with high optical purity using organocopper–BF_3 reagents.[1] The use of BF_3 was essential in this highly efficient chirality transfer reaction. However, in some cases, this strong Lewis acid caused undesired side reactions and prevented the use of acid-labile functional groups. Development of milder reagents with wide applicability is highly desirable.

We wish to report that higher order zinc cuprates $R_2Cu(CN)(ZnCl)_2$, prepared from CuCN and 2 equiv of RZnCl, react with γ-(mesyloxy)-α,β-unsaturated esters, ketones, and nitriles in an anti-S_N2' manner without the assistance of BF_3·OEt_2 to give the corresponding 1,3-chirality transfer product with very high de in essentially quantitative yield (eq 1). The method for the preparation



EWG=ester, ketone, nitrile (1)

of higher order zinc cuprates is shown in eq 2. A THF

$$RLi + ZnCl_2 \xrightarrow[-78 \rightarrow 0\ °C]{THF} RZnCl + LiCl \qquad (2)$$

$$2(RZnCl + LiCl) + CuCN \xrightarrow[-78 \rightarrow 0\ °C]{THF} R_2Cu(CN)(ZnCl)_2 + 2LiCl$$

solution of alkylzinc chloride and LiCl, prepared from RLi and $ZnCl_2$, was added to a THF slurry of 0.5 equiv of CuCN. Needless to say, "higher order" does not mean that the copper species possesses the structure $R_2Cu(CN)(ZnCl)_2$, but indicates that the stoichiometry of R, Cu, CN, and ZnCl is 2:1:1:2.[2] Previously, "lower order" zinc cuprates have been prepared by the reaction of CuCN·2LiX

[†] Tohoku University.
[‡] Kyoto University.

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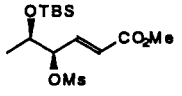
Table I. Reaction of Higher Order Zinc Cuprates with γ-(Mesyloxy)-α,β-unsaturated Carbonyl Derivatives

entry	substrate	reagent RCuLn	product	% yield (de)
1	1	$Me_2Cu(CN)(ZnCl)_2$	2 (R = Me)	99 (>99:1)
2	1	n-$Bu_2Cu(CN)(ZnCl)_2$	2 (R = n-Bu)	98 (>99:1)
3	1	$MeCu(CN)ZnCl{\cdot}BF_3$	2 (R = Me)[a]	47 (>99:1)
4	1	MeCu(CN)ZnCl		[b]
5	3	$Me_2Cu(CN)(ZnCl)_2$	4 (R = Me)	97 (97:3)
6	3	n-$Bu_2Cu(CN)(ZnCl)_2$	4 (R = n-Bu)	98 (>99:1)
7	3	$Me_2CuZnCl$	4 (R = Me)	95 (>99:1)
8	5	$Me_2Cu(CN)(ZnCl)_2$	6	98 (98:2)
9	5	$MeCu(CN)MgBr{\cdot}BF_3$	6	96 (98:2)
10	5	$Me_2Cu(CN)(MgBr)_2{\cdot}BF_3$	6	90 (98:2)
11	5	$Me_2Cu(CN)Li_2{\cdot}BF_3$	6	92 (>99:1)
12	7	$MeCu(CN)(ZnCl)_2$	8	99 (>99:1)
13	7	$Me_2CuZnCl$	8	98 (>99:1)
14	7	$Me_2Cu(CN)Li_2{\cdot}BF_3$	8	98 (>99:1)
15	7	$Me_2CuLi{\cdot}BF_3$	8	91 (>99:1)
16	7	$MeCu(CN)MgBr{\cdot}BF_3$	8	60 (95:5)
17	9	$Me_2Cu(CN)(ZnCl)_2$	10	98 (>99:1)
18	9	$Me_2CuZnCl$	10	98 (>99:1)
19	9	$Me_2Cu(CN)Li_2{\cdot}BF_3$	10	98 (>99:1)
20	9	$Me_2CuLi{\cdot}BF_3$	10	89 (>99:1)
21	9	$MeCu(CN)MgBr{\cdot}BF_3$	10[c]	57 (>98:2)

[a] The starting material was recovered in 13% yield. [b] The starting material was recovered quantitatively. [c] The SN_2 substitution product 11 was obtained as a byproduct (the stereochemistry was not determined).

with RZnI which in turn was prepared from RI and activated Zn[3] or by the reaction of zinc chloride with R_2CuLi.[4]



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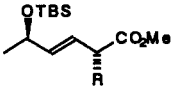

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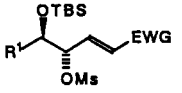
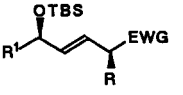
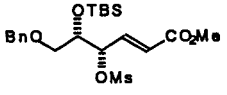


3; R[1]=Me, EWG=CO_2Me
7; R[1]=Me, EWG=COPh
9; R[1]=Me, EWG=CN



4; R[1]=Me, EWG=CO_2Me
8; R[1]=R=Me, EWG=COPh
10; R[1]=R=Me, EWG=CN



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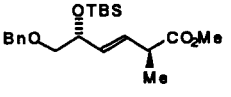

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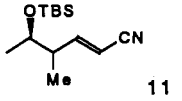

11

The results are summarized in Table I. Upon treatment with 1 higher order zinc cuprates gave 2 in essentially quantitative yield with nearly 100% de (entries 1 and 2), whereas the lower order zinc cyanocuprate did not react with 1 (entry 4). The lower order reagent was prepared from MeZnCl and CuCN. Even with the aid of $BF_3{\cdot}OEt_2$, the lower order reagent gave 2 in only 47% yield (entry 3). The conversion of 3 and 4 proceeded very well with the higher order zinc cuprates (entries 5 and 6). Interestingly, the zinc homocuprate also produced very high chemical yields and diastereoselectivity (entries 7, 13, 18).[5] In conclusion, it is now clear that the newly developed higher order zinc cuprates are very useful in the 1,3-chirality transfer reaction; not only unsaturated esters but also enones and unsaturated nitriles can be used as starting materials and high diastereoselectivity can be realized.

Experimental Section

Preparation of $Me_2Cu(CN)(ZnCl)_2$ and Its Reaction with 1. To a 20-mL flask cooled at −78 °C under Ar were placed a magnetic stirring bar, 1.5 mL of dry THF, and 1.8 mL of a 1.0 M ether solution of MeLi(LiI) (1.8 mmol). An ether solution of $ZnCl_2$ (1.0 M × 1.8 mL) was added, and the mixture was warmed to 0 °C with stirring. In an another 30-mL flask cooled at −78 °C under Ar were placed 81 mg (0.9 mmol) of CuCN and 4 mL of THF. To this flask was added the solution from the 20-mL flask through a double-ended needle. The mixture was allowed to warm to 0 °C, and the stirring was continued for 10 min.

To this higher order zinc cuprate, cooled at −78 °C, was added a THF solution (1.5 mL) of 1 (107 mg, 0.3 mmol).[1] Stirring was continued at −78 °C for 30 min, and the mixture was allowed to warm to 0 °C. After 1 h, the reaction was quenched with aqueous pH 8 ammonium chloride solution. The mixture was stirred for 30 min at rt. Extraction with ether, washing with 2 N HCl, 0.5 M aqueous $NaHCO_3$, water, and brine, drying with anhyd $MgSO_4$, and removal of the solvents gave an oil. Purification by silica gel column chromatography using n-hexane–AcOEt (10:1) as an eluant gave 83 mg (99%) of 2 (R = Me) as a colorless oil. MeLi (LiI) indicates that the MeLi is prepared from MeI and Li and that it contains LiI as a soluble salt.

Preparation of $Bu_2Cu(CN)(ZnCl)_2$ and Its Reaction with 1. Instead of MeLi in the above procedure, a hexane solution of n-BuLi (1.58 M × 1.15 mL, 1.8 mmol) was used. To a pale yellow solution of the butylzinc cuprate was added a THF solution of 1 (107 mg in 2 mL of THF, 0.3 mmol) at −78 °C, and the resulting mixture was stirred for 3 h. An aqueous pH 8 ammonium chloride solution was added, and the mixture was stirred for 30 min at rt. The same workup as above gave 94 mg (98%) of 2 (R = Bu).

Reactions of Other Michael Acceptors. Essentially the same procedure as that above was used for 3, 5, 7, and 9. For the preparation of other copper reagents, see ref 1.

Preparation of 7. A similar procedure described previously[1] was used. Instead of (carbomethoxymethylene)triphenylphosphorane, $(EtO)_2P(O)CH_2COPh$ was used.

(*E*,4*S,5*R**)-4-[(Methanesulfonyl)oxy]-5-[(*tert*-butyldimethylsilyl)oxy]-2-hexenophenone**: pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.10 (s, 6 H), 0.90 (s, 9 H), 1.22 (d, J = 6.1, Hz, 3 H), 3.10 (s, 3 H), 4.12 (dq, J = 6.1 and 3.7 Hz, 1 H), 5.20 (ddd, J = 5.5, 3.7, and 1.7 Hz, 1 H), 6.96 (dd, J = 15.3 and 5.5 Hz, 1 H), 7.24 (dd, J = 15.3 and 1.7 Hz, 1 H), 7.46–7.64 (m, 3 H), 7.94–8.01 (m, 2 H); IR (CCl_4) 2960, 2935, 2860, 1735, 1680, 1630, 1600, 1450, 1370, 1255, 1180, 970, 935, 840, and 635 cm^{-1}; exact MS (EI) calcd for $(M - CH_3)^{\cdot+}$ $C_{18}H_{27}O_5SiS$ m/z 383.1348, found m/z 383.1349.

(*E*,2*S,5*R**)-2-Methyl-5-[(*tert*-butyldimethylsilyl)oxy]-3-hexenophenone (8)**: pale yellow oil; ^1H NMR ($CDCl_3$) δ −0.01 (s, 3 H), 0.00 (s, 3 H), 0.85 (s, 9 H), 1.15 (d, J = 6.2 Hz, 3 H), 1.31 (d, J = 6.7 Hz, 3 H), 4.06–4.18 (m, 1 H), 4.18–4.30 (m, 1 H), 5.58 (ddd, J = 15.4, 5.5, and 0.7 Hz, 1 H), 5.73 (ddd, J = 15.4, 7.6, and 0.9 Hz, 7.40–7.58 (m, 1 H), 7.92–8.01 (m, 2 H); IR (CCl_4) 2970, 2940, 2865, 1745, 1695, 1600, 1450, 1370, 1255, 1090, 972, 835, and 705 cm^{-1}; exact MS (EI) calcd for $(M - CH_3)^{\cdot+}$

(1) (a) Ibuka, T.; Tanaka, M.; Nishii, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4864. (b) Ibuka, T.; Akimoto, N.; Tanaka, M.; Nishii, S.; Yamamoto, Y. *J. Org. Chem.* **1989**, *54*, 4055. (c) Ibuka, T.; Tanaka, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 967. (d) Ibuka, T.; Habashita, H.; Funakoshi, S.; Fujii, N.; Oguchi, Y.; Uyehara, T.; Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 801.

(2) For discussions on "higher order" cyano cuprates, see: Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031. Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *Ibid.* **1990**, *112*, 4032.

(3) Chen, H. G.; Gage, J. L.; Barrett, S. D.; Knochel, P. *Tetrahedron Lett.* **1990**, *31*, 1829. Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390.

(4) Nakamura, E.; Sekiya, K.; Arai, M.; Aoki, S. *J. Am. Chem Soc.* **1989**, *111*, 3091.

(5) The zinc homocuprate was prepared by treating Me_2CuLi in THF with 1 equiv of $ZnCl_2$ in ether at 0 °C. The dimethylhomocuprate was prepared by adding 2 equiv of MeLi (LiBr) in ether to $CuBr{\cdot}Me_2S$ in THF at −78 °C.

$C_{18}H_{27}O_2Si$ m/z 303.1780, found m/z 303.1758.

Preparation of (*E*,4*S,5*R**)-4-[(Methanesulfonyl)oxy]-5-[(*tert*-butyldimethylsilyl)oxy]-2-hexenenitrile (9).** As a phosphonate reagent, $(EtO)_2P(O)CH_2CN$ was used: colorless oil; ^1H NMR ($CDCl_3$) δ 0.10 (s, 3 H), 0.10 (s, 3 H), 0.90 (s, 9 H), 1.18 (d, J = 6.5 Hz, 3 H), 3.09 (s, 3 H), 4.05 (dq, J = 6.5 and 3.7 Hz, 1 H), 5.01 (ddd, J = 5.6, 3.7, and 1.7 Hz, 1 H), 5.73 (dd, J = 16.1 and 1.7 Hz, 1 H), 6.71 (dd, J = 16.1 and 5.6 Hz, 1 H); IR ($CHCl_3$) 3030, 2965, 2940, 2870, 2245, 1475, 1465, 1365, 1355, 1260, 1185, 1120, 980, 945, 850, cm^{-1}; exact MS (EI) calcd for $(M - CH_3)^{+}$ $C_{12}H_{22}NO_4SiS$ m/z 304.1039, found m/z 304.1034.

(*E*,2*S,5*R*)-2-Methyl-5-[(*tert*-butyldimethylsilyl)oxy]-3-hexenenitrile (10):** colorless oil; ^1H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.90 (s, 9 H), 1.21 (d, J = 6.5 Hz, 3 H), 1.40 (d, J = 7.2 Hz, 3 H), 3.24–3.37 (m, 1 H), 4.27–4.38 (m, 1 H), 5.55 (ddd, J = 15.0, 6.0, and 1.6 Hz, 1 H), 5.84 (ddd, J = 15.0, 4.8, and 1.5 Hz, 1 H); IR (CCl_4) 2960, 2930, 2850, 2230, 1725, 1470, 1460, 1368, 1358, 1250, 1148, 1090, 1050, 968, and 835 cm^{-1}; exact MS (EI) calcd for M^+ $C_{13}H_{25}NOSi$ m/z 239.1705, found m/z 239.1707.

Registry No. 1, 129389-01-1; 2 (R = Me), 138126-75-7; 2 (R = *n*-Bu), 138126-76-8; 3, 129389-00-0; 4 (R = Me), 138126-77-9; 4 (R = *n*-Bu), 138126-78-0; 5, 138009-29-7; 6, 138009-30-0; 7, 138009-31-1; 8, 138009-32-2; 9, 138009-33-3; 10, 138009-34-4; 11, 138009-35-5; 12, 81028-12-8; 13, 138009-36-6; $ZnCl_2$, 7646-85-7; CuCN, 544-92-3; MeLi, 917-54-4; *n*-BuLi, 109-72-8; MeI, 74-88-4; Zn, 7440-66-6; Me_2CuLi, 15681-48-8.

Supplementary Material Available: Synthetic methods and spectral data for 1–11 (13 pages). Ordering information is given on any current masthead page.

Stereoselective Dimerizations of Arene-*cis*-diol Acetonides Derived from the Oxidation of Halobenzenes by *Pseudomonas putida*: Absolute Configuration of the Adducts by X-ray Crystallography

Tomas Hudlicky,*,† Eric E. Boros, Horacio F. Olivo, and Joseph S. Merola‡

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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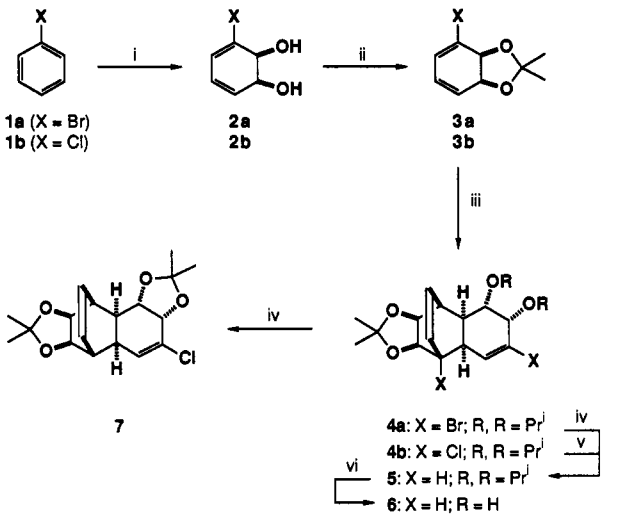
The microbial oxidation of aromatic compounds to the corresponding arene-*cis*-diol metabolites by mutant strains of *Pseudomonas putida* (e.g. 1 → 2) has been the subject of considerable biochemical research since its introduction in 1970 by Gibson et al.[1] The high degree of stereospecificity, substrate variability, and procedural ease inherent with these microbial oxidations have made the diols especially attractive in recent years as starting materials in enantiocontrolled total synthesis.[2] This has subsequently led to their commercial availability as chiral synthons.[3] In response to this wave of interest, Boyd and co-workers have recently developed a general method for determining absolute configuration and optical purity of *cis*-diol metabolites.[4]

Synthetic applications involving *cis*-diol metabolites often require protection of the hydroxyl groups in the form of an acetonide. We wish to report that halogenated arene-*cis*-diol acetonides (3) dimerize in a completely stereoselective fashion to highly stable crystalline dimers (4) (Scheme I).[5] In addition, the absolute configuration of the bromo dimer (4a) was established by X-ray crystallography which confirmed independently the absolute configuration of the *P. putida* 39-D metabolite 2a of bromobenzene. The absolute configuration of the chloro dimer (4b) was established by chemical correlation which involved reduction of both 4a and 4b to the nonhalogenated adduct 5, followed by partial deprotection to the diol 6.

Scheme I[a]



[a] (i) *P. putida* 39-D; (ii) DMP, pTsOH (cat.), acetone; (iii) neat, 0 °C → rt; (iv) Bu_3SnH, AIBN, tol., Δ; (v) Na^0, EtOH, Δ; (vi) HOAc, H_2O, rt.

Table I. Reaction Conditions and Yields for the Dimerizations of 3 to 4

acetonide	X	reaction conditions	% yield of 4[a]
3a	Br	neat, 0 °C, 15 d	32 (61)
3b	Cl	neat, 0 °C, 23 d	49 (51)
3a	Br	neat, rt 8 d	80
3b	Cl	neat, rt, 8 d	71
3a	Br	$CDCl_3$, 60 °C, 8 d (sealed tube)	70[b]
3a	Br	$CDCl_3$, 100 °C, 2 d (sealed tube)	–[c]
3b	Cl	$CDCl_3$, 100 °C, 6 d (sealed tube)	>95[b]

[a] Isolated yield of 4, percent recovery of unreacted 3 from chromatography is given in parentheses. [b] Determined from the ^1H NMR spectra. [c] Starting material underwent significant aromatization.

Reaction conditions and yields for the dimerizations of 3 to 4 are provided in Table I. The acetonide 3a of bro-

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‡ To whom correspondence concerning the X-ray crystallographic studies should be addressed.

(1) Gibson, D. T.; Hensley, M.; Yoshioka, H.; Mabry, T. J. *Biochemistry* **1970**, *9*, 1626.

(2) (a) Hudlicky, T.; Luna, H.; Price, J. D.; Rulin, F. *Tetrahedron Lett.* **1989**, *30*, 4053. (b) Hudlicky, T.; Seoane, G.; Pettus, T. *J. Org. Chem.* **1989**, *54*, 4239. (c) Hudlicky, T.; Luna, H.; Price, J. D.; Rulin, F. *J. Org. Chem.* **1990**, *55*, 4683. (d) Hudlicky, T.; Price, J. D. *Synlett* **1990**, 159. (e) Hudlicky, T.; Rulin, F.; Tsunoda, T.; Price J. D. *J. Am. Chem. Soc.* **1990**, *112*, 9439. (f) Ley, S. V. *Pure Appl. Chem.* **1990**, *62*, 2031. (g) Ley, S. V.; Redgrave, A. J. *Synlett* **1990**, *7*, 393. (h) Carless, H. A. J.; Billinge, J. R.; Oak, O. Z. *Tetrahedron Lett.* **1989**, *30*, 3113. (i) Carless, H. A. J.; Oak, O. Z. *J. Chem. Soc., Chem. Commun.* **1991**, 61.

(3) A variety of arene-*cis*-diols are available in multigram quantities from Genencor International, Inc., Rochester, NY, and ICI Fine Chemicals, P.O. Box 42 Hexagon House, Blackley, Manchester, M9 3DA, England.

(4) Boyd, D. R.; Dorrity, M. R. J.; Hand, M. V.; Malone, J. F.; Sharma, N. D.; Dalton, H.; Gray, D. J.; Sheldrake, G. N. *J. Am. Chem. Soc.* **1991**, *113*, 666.

(5) A similar dimerization involving the acetonide of trifluorotoluenediol has been described (e.g. 3 → 4; X = CF_3). Our crystal structure of 4a concurs with the stereochemistry assigned to the trifluoro dimer which was deduced using a variety of NMR methods, see: Pittol, C. A.; Pryce, R. J.; Roberts, S. M.; Ryback, G.; Sik, V.; Williams, J. O. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1160.

0022-3263/92/1957-1026$03.00/0