isopropylidene-6-*O*-(triphenylmethyl)-α-D-allofuranose (**2**, 1.2 g, 2.2 mmol) was dissolved in EtOH-free $CHCl_3$ (10 mL) to which was added activated RuO_2 (20 mg, KIO_4 (1 g), K_2CO_3 (5.0 mg), $PhCH_2Et_3NCl$ (100 mg), and H_2O (10 mL). The solution was stirred for 48 h at which time TLC (9:1 $PhCH_3$–Et_2O) showed complete conversion of **2** to **5**. The unreacted KIO_4 and RuO_4 were consumed with 2-propanol (2 mL), and the mixture was filtered through Celite. The organic layer was separated and dried ($MgSO_4$) and solvent removed to give 1.0 g (83%) of **5** as an oil which was crystallized with $PhCH_3$–hexane to give **5** as white crystals: mp 185 °C; $[\alpha]^{24}_D$ +30.0° (*c* 1.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.313 and 1.548 (s, 3 H each, CH_3), 3.736 (dd, 1 H, H-3, $J_{3,4}$ = 8.96), 4.020 (q, 2 H, CH_2Ph), 4.449 (t, 1 H, H-2, $J_{2,3}$ = 4.33), 4.537 (d, 1 H, H-4), 4.574 (AB quartet, 2 H, H-6a, H-6b) 5.696 (d, 1 H, H-1, $J_{1,2}$ = 3.48), and 7.15–7.5 (bm, 20 H, Ar); IR 1750 cm^{-1} (C=O). Anal. Calcd for $C_{35}H_{34}O_6$: C, 76.34; H, 6.22. Found: C, 76.24; H, 6.25.

3-*O*-Benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-galactofuranose (15). 1,2:5,6-Di-*O*-isopropylidene-α-D-galactofuranose (**16**, 12.0 g, 46 mmol), prepared by the method of Lemieux and Stick,[22] was dissolved in dry THF (20 mL) and added dropwise under N_2 to a stirred THF solution containing NaH (70 mmol). After the last addition of alcohol, the solution was refluxed for 2 h at 70 °C. The solution was allowed to cool, and benzyl chloride (5.7 mL, 50 mmol) in THF (10 mL) was added and the solution refluxed (70 °C) overnight. The THF was removed, and petroleum ether (200 mL) was added, and the solution was washed with H_2O (2 × 50 mL). The organic layer was dried ($MgSO_4$) and reduced to give 10.1 g (28 mmol, 63%) of **15** as an oil: ^1H NMR ($CDCl_3$) δ 1.544, 1.420, 1.370, and 1.353 (s, 3 H each, CH_3), 3.722 (t, 1 H, H-4, $J_{4,5}$ = 7.26), 3.809 (dd, 1 H, H-3, $J_{3,4}$ = 1.09), 3.907 (m, 1 H, H-5), 4.262 (m, 2 H, H-6a, H-6b), 4.598 (AB quartet, 2 H, CH_2Ph), 4.637 (d, 1 H, H-2, $J_{2,3}$ = 1.27), 5.858 (d, 1 H, H-1, $J_{1,2}$ = 4.01), and 7.341 (m, 5 H, Ar).

3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-galactofuranose (14). 3-*O*-Benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-galactofuranose (**15**, 4.0 g, 11 mmol) was dissolved in aqueous HOAc (10 mL) and the solution stirred for 6 h at which time TLC (Et_2O) showed complete conversion of **15** to **14**. The solution was neutralized with saturated aqueous K_2CO_3 and extracted with CH_2Cl_2 (2 × 100 mL), and the organic layers were combined, dried ($MgSO_4$), and reduced to give **14** (3.2 g, 10 mmol, 91%) as a wax. Crystallization with MeOH–EtOAc gave **14** as white crystals: mp 95–100 °C; $[\alpha]^{21.5}_D$ −22.6° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.337 and 1.521 (*s*, 3 H each, CH_3), 2.570 and 3.061 (bs, 1 H each, OH), 3.622 (m, 2 H, H-6a, H-6b), 3.796 (m, 1 H, H-5, $J_{5,6a}$ = 4.41, $J_{5,6b}$ = 5.06), 4.001 (d, 1 H, H-3, $J_{3,4}$ = 3.23), 4.122 (dd, 1 H, H-4, $J_{4,5}$ = 6.79), 4.600 (AB quartet, 2 H, CH_2Ph), 4.676 (d, 1 H, H-2), 5.908 (d, 1 H, H-1, $J_{1,2}$ = 4.13), and 7.338 (m, 5 H, CH_2Ph). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.94; H, 7.10. Found: C, 61.85; H, 7.17.

3-*O*-Benzyl-1,2-*O*-isopropylidene-6-*O*-(triphenylmethyl)-α-D-galactofuranose (3). 3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-galactofuranose (**14**, 3.0 g, 9.7 mmol) was dissolved in dry pyridine (50 mL) and the solution stirred with chlorotriphenylmethane (2.8 g, 10 mmol). TLC (9:1 $PhCH_3$–Et_2O) at 50 h showed complete conversion of **14** to **3**. The reaction mixture was poured onto ice–H_2O (500 mL) and the product collected by vacuum filtration. The gum was dissolved in CH_2Cl_2 (50 mL) and washed with 10% HOAc (2 × 35 mL), 10% $NaHCO_3$ (2 × 35 mL), and H_2O until neutral to litmus. Workup gave 4.9 g (8.8 mmol, 91%) of **3**. Recrystallization with $PhCH_3$–hexane gave an analytical sample of **3** as white crystals: mp 118–120 °C; $[\alpha]^{21.5}_D$ −6.9° (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.321 and 1.506 (s, 3 H each, CH_3), 2.651 (d, 1 H, 5-OH), 3.254 (d, 2 H, H-6a, H-6b), 3.869 (m, 1 H, H-5, $J_{5,6}$ = 5.28, $J_{5\text{-OH}}$ = 4.54), 4.008 (d, 1 H, H-3, $J_{3,4}$ = 2.8), 4.253 (dd, 1 H, H-4, $J_{4,5}$ = 3.14), 4.444 (AB quartet, 2 H, CH_2Ph), 4.648 (d, 1 H, H-2), 5.894 (d, 1 H, H-1, $J_{1,2}$ = 4.12), 7.254 (m, 15 H, OTr), and 7.449 (m, 5 H, CH_2Ph). Anal. Calcd for $C_{35}H_{36}O_6$: C, 76.08; H, 6.52. Found: C, 76.02; H, 6.59.

3-*O*-Benzyl-1,2-*O*-isopropylidene-6-*O*-(triphenylmethyl)-β-L-*arabino*-hexofuranos-5-ulose (6). 3-*O*-Benzyl-1,2-*O*-isopropylidene-6-*O*-(triphenylmethyl)-α-D-galactofuranose (**3**, 3.6 g, 6.6 mmol) was dissolved in EtOH-free $CHCl_3$ (75 mL). To this solution were added activated RuO_2 (60 mg), $NaIO_4$ (3 g), K_2CO_3 (300 mg), $PhCH_2Et_3NCl$ (15.0 mg), and H_2O (50 mL). The solution was stirred for 24 h at which time TLC (9:1 $PhCH_3$–Et_2O) showed complete conversion of **3** to **6**. 2-Propanol (25 mL) was added to consume unreacted $NaIO_4$ and RuO_4 and the solution was passed through a bed of Celite. The organic layer was separated, dried ($MgSO_4$), and removed to give 3.4 g (94%) of oily **6** which crystallized on standing. Recrystallization with $PhCH_3$–hexane gave an analytical sample: mp 128–130 °C; $[\alpha]^{24}_D$ −1.9° (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.128 and 1.192 (s, 3 H each, CH_3), 4.230 (AB quartet, CH_2Ph), 4.315 (bs, 1 H, H-4), 4.508 (bs, 1 H, H-3), 4.550 (d, 1 H, H-2), 4.560 (bs, 2 H, CH_2OTr), 5.875 (d, 1 H, H-1, $J_{1,2}$ = 3.83), and 7.15–7.55 (bm, 20 H, Ar); IR 1720 cm^{-1} (C=O). Anal. Calcd for $C_{35}H_{34}O_6$: C, 76.34; H, 6.22. Found: C, 76.44; H, 6.27.

1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one (Camphor, 10). Isoborneol (**9**, 30.8 g, 0.2 mol) was dissolved in EtOH-free $CHCl_3$ (250 mL) and the solution mechanically stirred with activated RuO_2 (500 mg), $NaIO_4$ (43 g), K_2CO_3 (1.0 g), $PhCH_2Et_3NCl$ (450 mg), and H_2O (250 mL). After 40 h TLC (1:1 Et_2O–hexane) showed complete conversion of **9** to **10**. The oxidation was stopped by the addition of 2-propanol (25 mL) and usual workup gave 27.1 g (88%) of **10** as a white crystalline mass: mp 177–180 °C (lit.[23] mp 179–180 °C); IR 1720 cm^{-1} (C=O).

Cholestan-3-one (12). (+)-Dihydrocholesterol (**11**, 7.8 g, 20 mmol) was dissolved in EtOH-free $CHCl_3$ (50 mL) and the solution stirred with activated RuO_2 (50 mg), K_2CO_3 (500 mg), $PhCH_2Et_3NCl$ (50 mg), and H_2O (50 mL). Potassium periodate (4.5 g, 20 mmol) was then added in small portions to prevent heating of the reaction mixture (ca. 30 min). Complete conversion of **11** to **12** required 4 h, TLC (1:1 Et_2O–hexane). 2-Propanol (15 mL) was added to quench the reaction and usual workup gave 5.9 g (15 mmol, 76%) of **12** as a white crystalline solid. Recrystallization with MeOH gave **12**: mp 126–128 °C (authenic material mp 128–130 °C, Aldrich Chemical Co., Milwaukee, WI); IR 1710 cm^{-1} (C=O).

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Registry No. **1**, 37073-70-4; **2**, 106734-68-3; **3**, 106734-69-4; **4**, 17278-21-6; **5**, 106761-49-3; **6**, 106734-70-7; **7**, 582-52-5; **8**, 10578-85-5; **9**, 124-76-5; **10**, 76-22-2; **11**, 80-97-7; **12**, 566-88-1; **13**, 57099-04-4; **14**, 65434-49-3; **15**, 65451-98-1; **16**, 10368-86-2; $PhCH_2Et_3NCl$, 56-37-1; Ph_3CCl, 76-83-5; benzyl chloride, 100-44-7; ruthenium tetraoxide, 20427-56-9.

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Analytical Resolution of Secondary Methyl Ethers by Chiral Complexation Gas Chromatography

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One of the challenges in developing enantioselective synthetic methods is the rapid and accurate determination of the efficacy that the process provides.[3] We recently

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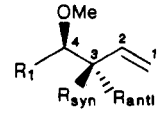
Table I. Analytical Resolution of Homoallyl Methyl Ethers



				Ni-R-Cam[a]			Ni-4-Pin[a]		
no.	R_1	R_{syn}	R_{anti}	temp[b]	t_R[c]	α[d]	temp[b]	t_R[c]	α[d]
1	Ph	H	H	65	15.6	1.02	90	5.6	1.43
2	4-Tol	H	H	75	21.0	1.02	90	8.2	1.38
3	4-Anis	H	H	80	46.0	1.02*			
4	4-BrPh	H	H				90	5.1	1.42
5	C_6H_{11}	H	H	75	6.5	1.05	75	10.0	1.14
6	n-C_9H_{19}	H	H	90	19.8	1.02*	90	56.4	1.06*
7	n-C_5H_{11}	H	H				80	9.4	1.08*
8	Ph	H	CH_3	90	4.7	1.06	90	4.9	1.13
9	C_6H_{11}	H	CH_3	90	5.1	1.09	90	5.8	1.09
10	n-C_9H_{19}	H	CH_3	95	21.0	1.04	90	35.8	1.04
11	n-C_5H_{11}	H	CH_3	75	4.3	1.05	90	5.9	1.00
12	1-nonenyl	H	CH_3	95	20.6	1.04	90	40.6	1.09*
13	$PhCH_2$	H	CH_3	90	8.5	1.03	90	10.0	1.03
14	PhC_2H_4	H	CH_3	90	17.5	1.03			
15	Ph	CH_3	H	90	3.6	1.00	90	4.4	1.05
16	C_6H_{11}	CH_3	H	90	4.6	1.00	90	5.7	1.00
17	n-C_9H_{19}	CH_3	H	95	20.0	1.00	90	37.0	1.04
18	1-nonenyl	CH_3	H	95	18.0	1.00			

[a] For a description of the columns, see ref 9. [b] The head pressure was 30 psi in all cases except for the analyses of 1–3 on the Ni-R-Cam column where it was 15 psi. The runs were isothermal at the indicated temperature (°C). [c] t_R refers to the retention time (min) of the first enantiomer to elute. Unretained solvent elutes at ca. 0.6 min. [d] α is a measure of separation defined as $[t_R(\text{compd } 2) - t_R(\text{unretained solvent})]/[t_R(\text{compd } 1) - t_R(\text{unretained solvent})]$. Except where indicated by an asterisk, peak shapes are sharp and give good relative integration.

have been interested in the stereoselectivity of reactions of tartrate ester modified allylic boronates with aldehydes.[4] In studies with chiral aldehydes, product diastereoselectivities were easily measured by capillary gas chromatography.[4,5] For the reactions with achiral aldehydes, we originally determined the enantioselectivity by NMR analysis of Mosher ester derivatives.[6a] This method, however, proved to be inconvenient for careful optimization studies owing to the dependence on the availability of high-field ^1H and ^{19}F NMR time. Moreover, this procedure suffers from analytical imprecision due to possible kinetic fractionation during the esterification step[7] and the questionable enantiomeric purity of the commercial reagents.[6b] Wishing to employ an analytical procedure not requiring NMR[8] or the analysis of diastereomeric derivatives, we investigated the use and herein report the results of direct enantiomer resolution using the chiral Ni-R-Cam and Ni-4-Pin derived capillary GC columns developed by Schurig.[9]

We initially attempted to separate the product homoallylic alcohols corresponding to ethers **1–18** directly on the Ni-R-Cam column according to literature precedent.[9b] Although resolution was observed in some cases, the retention times were generally long and the broad peak shapes gave poor electronic integration. In an attempt to increase volatility and decrease overly strong complexation with the metal, we examined the previously unreported method of separating methyl ethers.[15] Although this method requires a derivatization, methylations are clean and rapid and are unlikely to give accidental stereoisomeric enrichment[7,10] as can be the case in the preparation of diastereomeric derivatives.

Reported in Table I are the resolution data for the products deriving from the reactions of tartrate ester modified allyl-, (*E*)-crotyl-, and (*Z*)-crotylboronates with achiral aldehydes.[4] As hoped, the methyl ethers did prove to be superior substrates as compared to the corresponding alcohols in giving short retention times, sharp peaks, and for most compounds resolution by at least one column. In general, the Ni-4-Pin column was markedly superior for aromatic substrates (entries 1–4, 8, 15), while the Ni-R-Cam column with its higher temperature limit proved more useful for the less volatile, higher molecular weight compounds. Every 3-unsubstituted or 3-*anti*-methyl homoallyl alcohol tested (compounds **1–14**) was separable by both columns. None of the syn diastereomers (**15–18**) resolved on the Ni-R-Cam column, although in two cases (**15, 17**)

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(5) (a) Roush, W. R.; Adam, M. A.; Harris, D. J. *J. Org. Chem.* **1985**, *50*, 2000. (b) Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 3422.

(6) (a) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543. (b) We have observed that several recent commercial batches (Aldrich) of (*S*)-(−)-[α-methoxy-α-(trifluoromethyl)phenyl]acetic acid are only 94% ee (by comparison, the (*R*)-(+) acid is >98% ee). This has caused incorrect % ee data to be reported in ref 4a. Corrected values will be reported in due course: Hoong, L. K., unpublished work.

(7) For an example of kinetic resolution during the preparation of a Mosher ester derivative, see: Dutcher, J. S.; Macmillan, J. G.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41*, 2663.

(8) For leading references to other NMR methods for optical purity determinations, see: (a) Yamaguchi, S. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 1, p 125. (b) Weisman, G. R. *Ibid.*, p 153. (c) Fraser, R. R. *Ibid.*, p 173. See also: (d) Feringa, B. L.; Smaardijk, A.; Wynberg, H. *J. Am. Chem. Soc.* **1985**, *107*, 4798. (e) Johnson, C. R.; Elliott, R. C.; Penning, T. D. *Ibid.* **1984**, *106*, 5019. (f) Anderson, R. C.; Shapiro, M. J. *J. Org. Chem.* **1984**, *49*, 1304.

(9) Ni-R-cam = nickel(II) bis[(1*R*)-3-(heptafluorobutyryl)camphorate]; Ni-4-pin = nickel(II) bis[(1*R*,2*S*)-(3-heptafluorobutyryl)pinan-4-onate). The temperature limits for these columns are 110 and 100 °C, respectively. See ref 3b, 3d, and: (a) Schurig, V.; Weber, R. *J. Chromatogr.* **1984**, *289*, 321. (b) Schurig, V.; Wistuba, D. *Tetrahedron Lett.* **1984**, *25*, 5633.

(10) For a case of enantiomer enrichment during chromatography see: Tsai, W.-L.; Hermann, K.; Hug, E.; Rohde, B.; Dreiding, A. S. *Helv. Chim. Acta* **1985**, *65*, 2238.

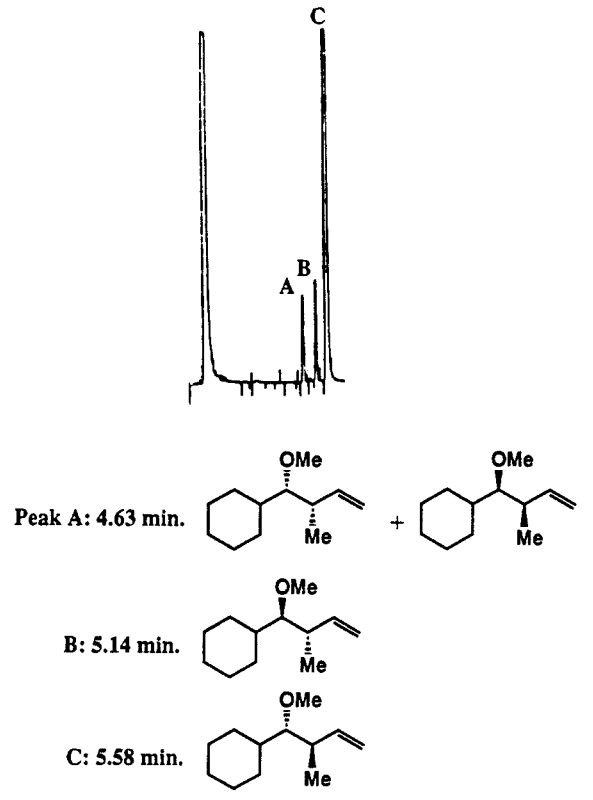


Figure 1. Chromatogram of **9** and **16** on a Ni-R-Cam column (90 °C, 30 psi).

resolutions were successful on the Ni-4-Pin column. We note that the upper limit to the usefulness of this method, dependent on substrate volatility and the temperature limit of the columns,[9] appears to be around the C_{14} alcohols. Interestingly, though, the heavier 3-methyl products (**10**, **17**) elute faster on the Ni-4-Pin column than the corresponding unsubstituted substrate (**6**). This is perhaps due to less hindrance about the ethereal oxygen and subsequent greater complexation in the latter case.

Figure 1 shows a representative chromatogram obtained for the products arising from the addition of the (*R*,*R*)-diisopropyl tartrate modified (*E*)-crotylboronate to cyclohexanecarboxaldehyde. The syn product **16** (5%), as an unresolved mixture of enantiomers, is seen to elute first, followed by the (3*S*,4*R*) and the (3*R*,4*S*) enantiomers of the anti diastereomer **9** (95% of mixture; 88% ee).[4c]

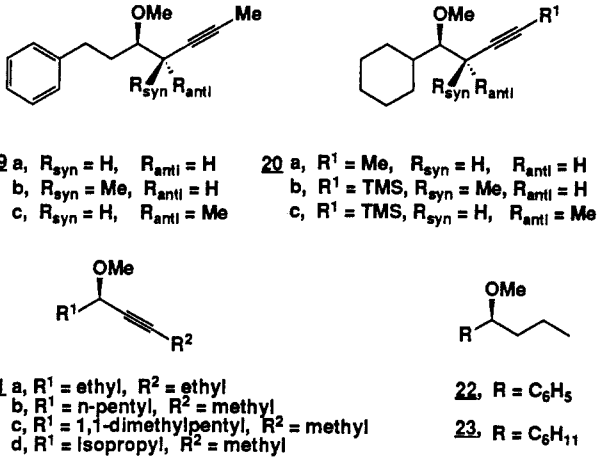
With both tartrate enantiomers in the allylic boronate aldehyde addition reactions, either enantiomer of the homoallylic alcohols corresponding to the ethers listed in Table I were generated selectively. Since the absolute configuration of the majority of these compounds has been assigned,[4a,c] it was interesting to note that for crotyl addition products **8**–**18** the enantiomer with the absolute configuration as shown in Table I always eluted first on the Ni-R-Cam column and second on the Ni-4-Pin column. The corresponding enantiomer of the allyl addition products (**1**–**7**) again eluted second in all cases on the Ni-4-Pin column and with the exception of the *n*-alkyl examples (**6**, **7**) first on the Ni-R-Cam column. Thus, for similar substrates, determining the order of elution on these columns could provide a rapid method for assigning absolute configuration.

The enantioselective synthesis of homopropargyl,[11] propargyl,[12] and saturated secondary alcohols[13] is of considerable current interest. Extensions of the method described above could potentially be beneficial in determining enantioselectivities in those cases. Therefore, we examined the methyl ethers of several representative racemic alcohols; results are listed in Table II. The homopropargyl methyl ethers (**19**, **20**) gave results similar to analogous homoallyl methyl ethers in Table I. Most notable is that the anti isomer (**20c**) resolved while the corresponding syn isomer (**20b**) did not. The propargyl methyl ethers gave in all cases good separation.

Table II. Analytical Resolution of Homopropargyl, Propargyl, and Saturated Secondary Methyl Ethers[a]

no.	column	temp	t_R	α
19a	Ni-R-Cam	95	36.8	1.05
19b	Ni-R-Cam	95	14.5	1.02
19c	Ni-R-Cam	95	15.1	1.02
20a	Ni-R-Cam	95	12.5	1.12
20b	Ni-R-Cam	95	18.7	1.00
20c	Ni-R-Cam	95	19.8	1.02
21a	Ni-R-Cam	75	1.8	1.31
21b	Ni-R-Cam	90	3.3	1.17
21c	Ni-R-Cam	50	2.5	1.08
21d	Ni-R-Cam	95	51.5	1.05*
22	Ni-4-Pin	90	6.1	1.68
23	Ni-4-Pin	75	10.6	1.08

[a] See corresponding references in Table I.



In conclusion, we have demonstrated that the analytical resolution of the methyl ether derivatives of chiral homoallylic, homopropargylic, propargylic, and saturated secondary alcohols is in most cases rapidly accomplished using the commercially available Ni-R-Cam and Ni-4-Pin capillary GC columns. This method for determining enantiomeric excesses and perhaps assigning absolute configuration should be of benefit to those involved in developing methodology for the enantioselective synthesis of chiral secondary alcohols.[14]

Experimental Section

Methylations.[15] Typically 10 mg of the alcohol was treated with excess sodium hydride in DMF followed by addition of excess

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(13) Masamune, S.; Kim, B. M.; Peterson, J. S.; Sato, T.; Veenstra, S. J.; Imai, T. *J. Am. Chem. Soc.* **1985**, 107, 4549.

(14) We have also recently observed that methyl ethers of several chiral tertiary alcohols can be resolved on these columns.

(15) Other methods of derivatization (Ac, Me_3Si) gave unsatisfactory results.

methyl iodide. After 30 min water was added, the mixture was extracted with hexane, and the combined organic extracts were dried and concentrated. Material sufficiently pure for GC analysis was obtained by preparative TLC (0.5-mm Analtech silica gel plate, 5:1–10:1 hexane:ether). A liberal cut was taken to preclude enantiomeric fractionation.[10] Formation of the methyl ethers was confirmed by 300-MHz ^{1}H NMR analysis.

GC Analyses. The columns, nickel(II) bis[(1*R*)-3-(heptafluorobutyryl)camphorate] and nickel(II) bis[(1*R*,2*S*)-(heptafluorobutyryl)pinan-4-onate], both 10% in OV-1, 25 m × 0.25 mm, have been obtained from Chiral Complexation Capillary Columns (CC & CC), D7402 Kirchentellinsfurt, West Germany. The chromatograms were obtained with the use of a Hewlett-Packard HP5890 gas chromatograph configured for dual capillary columns with dual flame-ionizing detectors. A HP3392A recording integrator recorded the traces. The carrier gas was helium, and split ratios were set at 100:1.

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Registry No. (±)-**1**, 106756-91-6; (±)-**1** alcohol, 80735-94-0; (±)-**2**, 106650-72-0; (±)-**2** alcohol, 106756-92-7; (±)-**3**, 106650-73-1; (±)-**3** alcohol, 106650-97-9; (±)-**4**, 106680-47-1; (±)-**4** alcohol, 106650-98-0; (±)-**5**, 106650-74-2; (±)-**5** alcohol, 106756-93-8; (±)-**6**, 106650-75-3; (±)-**6** alcohol, 74851-31-3; (±)-**7**, 106650-76-4; (±)-**7** alcohol, 106756-94-9; (±)-**8**, 106680-33-5; (±)-**8** alcohol, 63553-62-8; (±)-**9**, 106650-77-5; (±)-**9** alcohol, 106650-99-1; (±)-**10**, 106650-78-6; (±)-**10** alcohol, 106680-36-8; (±)-**11**, 106650-79-7; (±)-**11** alcohol, 106651-00-7; (±)-**12**, 106650-80-0; (±)-**12** alcohol, 106651-01-8; (±)-**13**, 106650-81-1; (±)-**13** alcohol, 106651-02-9; (±)-**14**, 106650-82-2; (±)-**14** alcohol, 106756-95-0; (±)-**15**, 106650-83-3; (±)-**15** alcohol, 63553-63-9; (±)-**16**, 106650-84-4; (±)-**16** alcohol, 106651-03-0; (±)-**17**, 106650-85-5; (±)-**17** alcohol, 106651-04-1; (±)-**18**, 106680-34-6; (±)-**18** alcohol, 106651-05-2; (±)-**19a**, 106650-86-6; (±)-**19a** alcohol, 106680-48-2; (±)-**19b**, 106650-87-7; (±)-**19b** alcohol, 106651-06-3; (±)-**19c**, 106680-35-7; (±)-**19c** alcohol, 106680-37-9; (±)-**20a**, 106650-88-8; (±)-**20a** alcohol, 106651-07-4; (±)-**20b**, 106650-89-9; (±)-**20b** alcohol, 106651-08-5; (±)-**20c**, 106650-90-2; (±)-**20c** alcohol, 106651-09-6; (±)-**21a**, 106650-91-3; (±)-**21a** alcohol, 106756-96-1; (±)-**21b**, 106650-92-4; (±)-**21b** alcohol, 106756-97-2; (±)-**21c**, 106650-93-5; (±)-**21c** alcohol, 106651-10-9; (±)-**21d**, 106650-94-6; (±)-**21d** alcohol, 106756-98-3; (±)-**22**, 106650-95-7; (±)-**22** alcohol, 21632-18-8; (±)-**23**, 106650-96-8; (±)-**23** alcohol, 106756-99-4; Ni-R-cam, 68457-34-1; Ni-4-pin, 87306-50-1.

Complexation Effects in the Photochlorination of 2,3-Dimethylbutane in the Presence of Fluorinated Benzenes

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The presence of benzene and other "complexing" solvents has long been known to increase the selectivity of attack of elemental chlorine on substrates such as 2,3-dimethylbutane.[1] This phenomenon was originally ascribed to the intervention of a second, more selective, hydrogen-abstracting agent which was proposed to be a benzene–chlorine atom π complex. The Cl_2/benzene/2,3-dimethylbutane system recently received renewed attention[2,3] especially with regard to the number of hydrogen abstractors needed to explain observed concentration effects on selectivity and to the nature of the complexed abstracting agent(s). We argued[3] that the selectivity data in this system could be explained adequately in terms of a two abstractor model (Scheme I), in which the second abstractor C_6H_6Cl was assigned to a chlorine atom–benzene π complex, in conformity with Russell's original proposal.[1a] In Scheme I, 3°-R$^\bullet$ and 1°-R$^\bullet$ are $(CH_3)_2\dot{C}(CH_3)_2$ and $(CH_3)_2CHCH(CH_3)CH_2^\bullet$, and 3°-RCl and 1°-RCl are the corresponding alkyl chlorides.

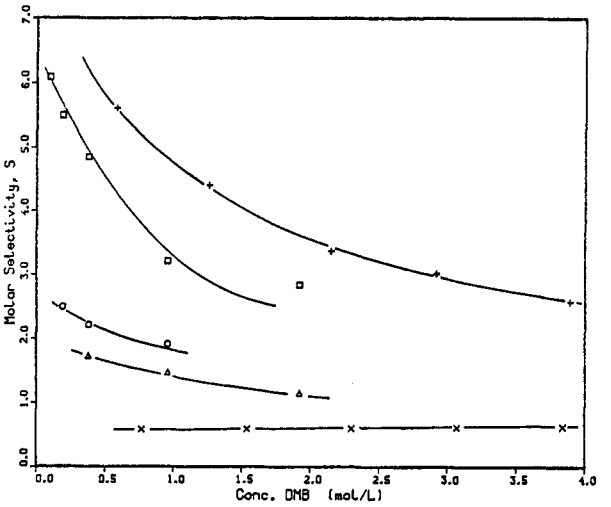

Figure 1. Variation in the molar selectivity S with dimethylbutane concentration at constant concentrations of benzene derivatives: (+) benzene; (□) fluorobenzene; (○) difluorobenzene; (△) trifluorobenzene; (×) hexafluorobenzene. All benzene concentrations were 4.0 M except for hexafluorobenzene (3.0 M).

Scheme I

$$Cl^\bullet + DMB \xrightarrow{k_1} 3°\text{-}R^\bullet \rightarrow 3°\text{-}RCl$$

$$Cl^\bullet + DMB \xrightarrow{k_2} 1°\text{-}R^\bullet \rightarrow 1°\text{-}RCl$$

$$Cl^\bullet + ArH \xrightarrow{k_3} (ArHCl)^\bullet$$

$$(ArHCl)^\bullet \xrightarrow{k_4} Cl^\bullet + ArH$$

$$(ArHCl)^\bullet + DMB \xrightarrow{k_5} 3°\text{-}R^\bullet \rightarrow 3°\text{-}RCl$$

$$(ArHCl)^\bullet + DMB \xrightarrow{k_6} 1°\text{-}R^\bullet \rightarrow 1°\text{-}RCl$$

We now report the extension of our studies to the chlorination of 2,3-dimethylbutane in the presence of a series of fluorinated benzenes. The trends in selectivity as a function of reactant concentrations can be explained in terms of Scheme I, and we have been able to trace the effect of increasing fluorination of the benzene derivative upon the tertiary-to-primary (3°/1°) selectivity of the complexed chlorine atom.

Results and Discussion

The selectivity for attack on 2,3-dimethylbutane was determined by monitoring the ratio of the two monochlorination products; i.e., the distribution of monochlorides was assumed to reflect the distribution of tertiary

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