at 3000 cm^{-1} and the carbonyl (CO_2H) at 1670 cm^{-1}. The NMR spectrum (Me_2SO-d_6) shows the vinyl and aromatic proton multiplet δ 6.7–7.5 and the bridgehead proton multiplets centered at δ 6.30 and δ 5.22.

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.14; H, 4.84.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the San Diego State University Foundation for support of this research.

Registry No. **1a**, 60573-55-9; **2a**, 60618-78-2; **3**, 91798-50-4; **4**, 91798-51-5; **5**, 91782-23-9; **6**, 38378-63-1.

Diastereoselective Synthesis of an (Arene)chromium Tricarbonyl Complex

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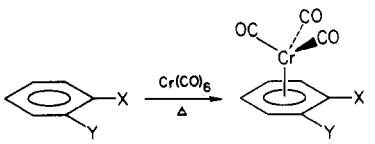
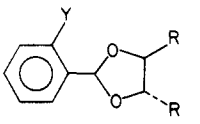
The distinctive chemical and physical properties of (arene)chromium tricarbonyl(CT) complexes[1,2] have been investigated from several points of view since 1959 when their direct preparation from the parent arene was first described[3] (eq 1). The stereochemical properties of these



(1)

1

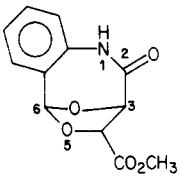
compounds have attracted particular attention. A complexed benzene with unlike *ortho* substituents 1 ($X \neq Y$) is chiral and several such derivatives have been obtained in optically active form by classical optical resolution procedures.[4,5] Furthermore, the generation of a new chiral center within X or Y is typically found to occur with very high diastereoselectivity.[6] These facts combine to suggest the potential utility of compounds of type 1 as chiral synthons and, therefore, the desirability of developing alternative, more general methods for their production in optically active form. Solladie-Cavallo and co-workers[7] have resolved racemates of type 1 (X = CHO) via reaction with (*S*)-(−)-5-(α-phenylethyl)semioxamazide and chromatographic separation of the diastereomeric semioxazones 1 (X = $PhCHCH_3NHCOCONHN{=}CH$). The same investigators also tried the strategy of asymmetric induction in the complexation process, but with disappointing results. Acetals of type **2a** derived from (*S*,*S*)-(+)-butane-2,3-diol underwent complexation with, at most, 20% asymmetric induction. In this report we describe the facile and inexpensive preparation of an optically active derivative of



2a, R = CH_3
2b, R = CO_2CH_3, Y = NO_2
2c, R = CO_2CH_3, Y = NH_2

o-aminobenzaldehyde and its conversion to a CT complex with nearly complete asymmetric induction. Unfortunately, this complex was resistant to hydrolysis except under strenuous conditions and its conversion to optically active (*o*-aminobenzaldehyde)CT was not achieved.

Dimethyl 2-nitrobenzylidine-L-tartarate (**2b**) was prepared from 2-nitrobenzaldehyde and (+)-dimethyl L-tartarate in 55% yield. Catalytic hydrogenation of the acetal followed by heat-induced lactamization produced the benzoxazocine **4** (87% yield) as a colorless solid, mp 167.5 °C. The complexation reaction was conducted by heating **3** with chromium hexacarbonyl in refluxing dioxane under



3 (benzoxazocine numbering)

argon in a Strohmeier apparatus[8] for 72 h. Chromatographic removal of unreacted starting material and NMR examination[9] of the total complexation product disclosed that two diastereomers were present in a ratio of about 50:1. One recrystallization gave the major isomer as a yellow needles, mp >300 °C, in 42% yield. The structure and stereochemistry of the complex were determined by single-crystal X-ray analysis which led to the ORTEP[10] plot shown in Figure 1; this structure and the derived perspective drawing **4** reveal that complexation has taken place on that face of the aromatic ring which is syn to the 3,6-epoxy bridge.

The X-ray crystal structure of **4** also provides a reasonable explanation for the high degree of diastereoselectivity of the complexation reaction. Firstly, no short nonbonded distances involving the $Cr(CO)_3$ grouping are found. Secondly, inspection of the stereoplot (Figure 1) leads to the inference that the alternative complexation product would be subject to significant steric compression. This qualitative assessment was substantiated by calculation. By considering the aromatic ring to determine a mirror plane and by projecting the atomic centers of the CT group across the plane, one arrives at a model of the alternative complexation product.[11] A survey of interatomic distances within the model now reveals that the C-4 hydrogen is compressed by the oxygen of the nearest CO group. This interatomic distance is calculated as 1.84 Å whereas the sum of the pertinent van der Waals radii is 2.6 Å. It is worth pointing out that the carbonyl oxygens of the CT group are located approximately 3.5 Å above the plane of the aromatic ring and that steric guidance of the

(1) Jaouen, G. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2, pp 65–120.
(2) Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379.
(3) Nicholls, B.; Whiting, M. C. *Proc. Chem. Soc.* **1958**, 152.
(4) Mandelbaum, A.; Neuwirth, Z.; Cais, M. *Inorg. Chem.* **1963**, *2*, 902.
(5) Meyer, A. *Liebigs Ann. Chem.* **1973**, 379.
(6) For example, see: Meyer, A.; Debard, R. *J. Organomet. Chem.* **1972**, *36*, C38.
(7) Solladie-Cavallo, A.; Solladie, G.; Tsamo, E. *J. Org. Chem.* **1979**, *44*, 4189.
(8) Strohmeier, W. *Chem. Ber.* **1961**, *94*, 2490.
(9) Signals due to the C-6 proton of the major and minor complexation products from **4** were seen at δ 6.05 and 6.13, respectively.
(10) Johnson, C. K. ORTEP Report ORNL-3794, **1965**, Oak Ridge National Laboratory, TN.
(11) The orientation of the chromium tricarbonyl group with respect to the aromatic ring in determined by the electronic character of the carbon atoms of that ring and therefore should not be altered by the mirror inversion. The energy value of this conformation is, however, unknown.

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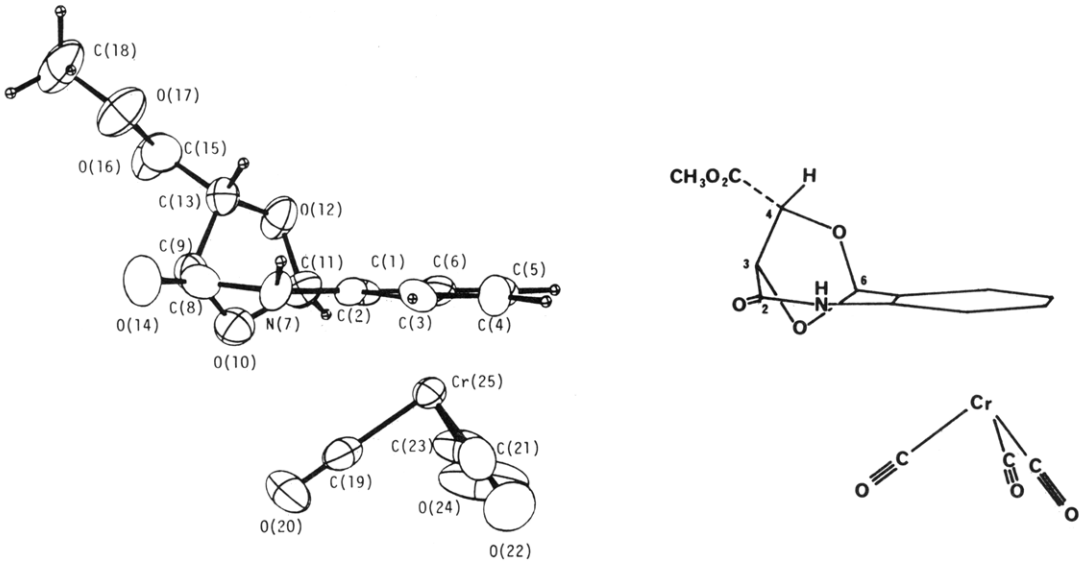

Figure 1. ORTEP plot of **4**. The numbering system is arbitrary and corresponds to that used in the supplementary material.

complexation process by the C-4 hydrogen relies on its likewise significant elevation (2.24 Å) above the ring. This factor should be significant in designing other potential substrates for diastereoselective complexation.

Experimental Section

Melting points were taken on a Kofler micro hot stage and are uncorrected. IR spectra were recorded with a Beckman Acculab 1 spectrometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. High-resolution ^1H NMR spectra were obtained at 250 MHz with a Brucker W.M. 250 spectrometer; chemical shifts are reported in ppm downfield from Me_4Si. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA.

Methyl (3*R*,4*R*,6*S*)-1,3,4,6-Tetrahydro-2-oxo-3,6-epoxy-2*H*-5,1-benzoxazocine-4-carboxylate (3). A solution of dimethyl L-tartarate (32.0 g, 0.180 mol), *o*-nitrobenzaldehyde (27.2 g, 0.180 mol), and sulfuric acid (3 mL) in benzene (750 mL) was heated under reflux with a Dean–Stark water separator for 60 h by which time slightly over the calculated volume of water had collected. After removal of solvent, the residue, in 500 mL of ether, was shaken for 16 h with saturated aqueous sodium bisulfite. The organic layer, after drying ($MgSO_4$) and removal of solvent, provided 35.3 g (68% yield) of acetal **3b** suitable for use in the reduction step to follow. A sample of **2b** was further purified by Kugelrohr distillation (170 °C and 0.1 torr): IR ($CHCl_3$) 3040, 2970, 1775, 1535, 1350 cm^{-1}; ^1H NMR δ 3.71 (s, 3 H), 3.86 (s, 3 H), 4.88 (d, 1 H, J = 3.7 Hz), 4.90 (d, 1 H, J = 3.7 Hz), 6.77 (s, 1 H), 7.53 (td, 1 H, J = 7.4, 1.5 Hz), 7.65 (td, 1 H, J = 7.4, 1.5 Hz), 7.95 (dd, 1 H, J = 8.1, 1.5 Hz), 7.99 (dd, 1 H, J = 8.1, 1.8 Hz).

A sample of the nitro acetal **2b** (16.3 g, 0.053 mol) and 10% palladium on carbon (0.3 g) in absolute ethanol (250 mL) was subjected to hydrogenation in a Parr shaker at approximately 2 atm pressure for 2 h. Removal of catalyst and solvent left amine **2c** (14.6 g, 98% yield): ^1H NMR δ 3.82 (s, 3 H), 4.26 (s, 2 H), 4.83 (d, 1 H, J = 4.4 Hz), 4.87 (d, 1 H, J = 4.4 Hz), 6.04 (s, 1 H), 6.65–6.74 (m, 2 H), 7.16 (td, 1 H, J = 8.1, 1.5 Hz), 7.27 (dd, 1 H, J = 7.7, 1.5 Hz). This product underwent slow conversion to lactam **4** in solution at room temperature. Preparative ring closure is achieved as described below.

The amino acetal **2c** (5.63 g, 0.020 mol) was heated under reflux in 200 mL of benzene for 5 h. Concentration at reduced pressure left a tan solid (4.89 g) which was recrystallized from hot chloroform/hexane, yielding lactam **3** (3.48 g, 88% yield) as a white solid: mp 167–8 °C; $[\alpha]_D$ −141.4° (c 2.0, $CHCl_3$); IR 3370, 3030, 2590, 1750, 1670; ^1H NMR δ 3.85 (s, 3 H), 5.11 (d, 1 H, J = 1.5 Hz), 5.21 (d, 1 H, J = 1.5 Hz), 6.38 (s, 1 H), 6.95 (d, 1 H, J = 8.1 Hz), 7.05 (td, 1 H, J = 7.4, 0.7 Hz), 7.22 (dd, 1 H, J = 7.4, 1.5 Hz), 7.31 (td, 1 H, J = 7.7, 1.8 Hz), 8.95 (s, 1).

Anal. Calcd for $C_{12}H_{11}NO_5$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.96; H, 4.52; N, 5.61.

(Methyl (3*R*,4*R*,6*S*)-1,3,4,6-Tetrahydro-2-oxo-3,6-epoxy-2*H*-5,1-benzoxazocine-4-carboxylate)chromium Tricarbonyl (4). The lactam **3** (2.92 g, 0.012 mol) and chromium hexacarbonyl (5.15 g, 0.23 mol) in dioxane (150 mL, freshly distilled from Na benzophenone) were heated at reflux under argon in a Strohmeier apparatus for 72 h. The reaction solution, after cooling to room temperature, was concentrated at reduced pressure. Addition of ether to the residue caused crystallization of unreacted chromium hexacarbonyl which was removed by filtration through a Celite pad. Removal of solvent left a yellow residue (4.08 g) which was chromatographed on a column of silica gel (120 g). Elution with ethyl acetate–hexane (1:1) led to a yellow solid which was recrystallized from methyl *tert*-butyl ether–hexane, yielding 1.95 g (42% yield) of **4**: mp >300 °C; $[\alpha]_D$ −203.5° (c 2.0, $CHCl_3$); ^1H NMR δ 3.85 (s, 3 H), 4.89–5.02 (m, 3 H), 5.19 (s, 1 H), 5.53–5.58 (m, 2 H), 6.05 (s, 1 H), 8.17 (s, 1 H).

Anal. Calcd for $C_{15}H_{11}NO_8Cr$: C, 46.75; H, 2.88; N, 3.63. Found: C, 46.83; H, 2.94; N, 3.61.

Crystals suitable for X-ray analysis were obtained by slow infusion of hexane into a solution of **4** in methyl *tert*-butyl ether.

Attempted Hydrolysis of 4. A solution of complexed lactam **4** (0.125 g) in a mixture of dioxane (10 mL), water (7 mL), and concentrated HCl (1 mL) was heated at reflux under nitrogen for 0.5 h. The cooled reaction mixture was then concentrated at reduced pressure, dissolved in ether, and washed twice with saturated sodium chloride solution. The dried organic layer, after removal of solvent, left a residue (0.065 g) which proved to be largely starting material by thin-layer and spectral analysis.

Longer periods of heating led to an intractable mixture of complexed and decomplexed products from which pure components could not be obtained by crystallization or chromatography.

Single-Crystal X-ray Analysis. The crystals of $C_{15}H_{11}NO_8Cr$ (385.25) were found to be monoclinic and belonged to the space group $P2_1$ with cell dimensions of a = 6.997 (1) Å, b = 7.897 (2) Å, c = 14.357 (3) Å, and β = 90.60 (2)°.

The crystal density was determined by flotation in aqueous potassium iodide to be 1.59 g/cm^3. Based on 2 molecules per unit cell, the calculated density was 1.61 g/cm^3. A 1 Å data set (maximum sin θ/λ = 0.5) of 895 reflections ($I > 3.0\sigma$) was collected on a Syntex P1 diffractometer using copper radiation (λ = 1.5418 Å). A trial structure was produced with the aid of the MULTAN[13] program. Hydrogen positions were calculated wherever possible. The methyl hydrogens and nitrogen hydrogen were located by difference Fourier techniques. The hydrogen parameters were

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(13) Germain, G.; Main, P.; Wolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

added to the structure factor calculations but were not refined. The structure refined to a value of $R = 0.043$. A final difference Fourier plot revealed no missing or extra electron density.

Registry No. 2b, 92056-07-0; **2c**, 92056-08-1; **3**, 92056-09-2; **4**, 92056-10-5; $Cr(CO)_6$, 13007-92-6; (+)-dimethyl L-tartarate, 608-68-4; *o*-nitrobenzaldehyde, 552-89-6.

Supplementary Material Available: Tables of (a) atomic position parameters, (b) atomic thermal parameters, and (c) bond distances and angles of **4** (5 pages). Ordering information is given on any current masthead page.

Lithium Aluminum Hydride Reduction of Allylic Substrates. Notable Leaving Group Effects on the Product Regiochemistry

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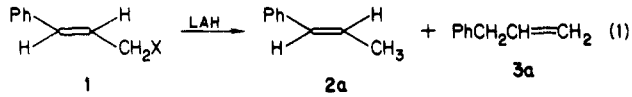
Lithium aluminum hydride (LAH) reduction of allylic halides and their homologues generally proceeds readily to give the S_N2 and/or S_N2' products, the composition being influenced by variable factors.[1] We considered that leaving group effects would be a large, single factor in determining the product regiochemistry[2,3] and, therefore, performed LAH reduction of allylic substrates having a variety of leaving groups.

Treatment of 3-substituted 1-phenyl-1-propenes **1a–c**, having *E* configurations, with LAH gave (*E*)-1-phenyl-1-propene (**2a**; attack by hydride ion at the α-position), while the substrates having poor leaving groups **1d–h** led to the formation of 1-phenyl-2-propene (**3a**; attack at γ-position) together with **2a** (eq 1 and Table I). Triphenylphosphonium salt **1i** afforded exclusively the S_N2' product **3a**. As might be expected, treatment of **1i** with lithium aluminum deuteride yielded 1-phenyl-2-propene-1-*d*. It was also noted that two salts **1f** and **1h** seem to have a similar steric hindrance for hydride-ion attack at the α-position and, nevertheless, these two salts show a significant difference in the reactivity and the regiochemistry; i.e., the reduction of ammonium salt **1f** was considerably slower than that of phosphonium salt **1h**,[4,5] and, moreover, **2a** was predominantly obtained from **1f** and in direct contrast, **3a** was the major product in the case of **1h**.



(1)

1 **2a** **3a**

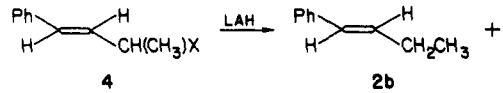
a, X = Br
b, X = Cl
c, X = 4-$CH_3C_6H_4SO_3$
d, X = $^+SMe_2Br^-$
e, X = $^+NEt_3Br^-$
f, X = $^+NBu_3Br^-$
g, X = $P(O)(OEt)_2$
h, X = $^+PBu_3Br^-$
i, X = $^+PPh_3Br^-$

Table I. LAH Reduction of Allylic Substrates[a]

substrate	reaction time, h	products[b] % yield	products[b] 2/3 ratio	products[b] *E*/*Z* ratio in **3b**
1a	0.5	100	100:0	
1b	0.5	78	100:0	
1c	1	50	100:0	
1d	0.5	90	90:10	
1e	0.5	62	76:24	
1f	6	2[c]	76:24	
1g	0.5	46	2:98	
1h	0.5	90	7:93	
1i	0.5	95	0:100	
4a	1	100	96:4	9:1
4b	1	68	67:38	9:1
4c	1	13[d]	69:31	9:1
4d	5	0[c]		
4e	5	74	0:100	2:3
5a	1	66	100:0	
5b	1	59	100:0	
5c	1	10[d]	74:26	
5d	1	10[c]	39:61	
5e	1	87	74:26	
5f	1	89	0:100	

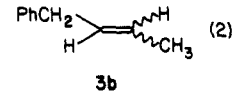
[a] Reaction with 5 molar equiv of LAH in ether at 20 °C. [b] The isolated yield. Product composition was determined by GLC. [c] The starting material was recovered in a considerable amount. The formation of byproducts was not detected. [d] The corresponding alcohol was isolated in around 70%.

For LAH reduction of 3-substituted 1-phenyl-1-butenes **4a–e** (eq 2) and 3-substituted 1,1-diphenyl-1-propenes **5a–f** (eq 3), similar leaving group effects on the product composition were observed (Table I). Of particular interest is the fact that the triphenylphosphonium salt **5f**, the γ-position of which is extremely crowded, gave exclusively the γ-hydrogenolysis product **3c**. To know the scope of



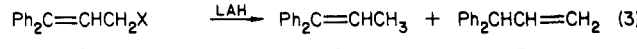
4 **2b**

a, X = Br
b, X = Cl
c, X = 4-$CH_3C_6H_4SO_3$
d, X = $^+NEt_3Br^-$
e, X = $^+PPh_3Br^-$



(2)

3b



(3)

5 **2c** **3c**

a, X = Br
b, X = Cl
c, X = 4-$CH_3C_6H_4SO_3$
d, X = $^+NEt_3Br^-$
e, X = $P(O)(OEt)_2$
f, X = $^+PPh_3Br^-$

(1) (a) Pizey, S. S. "Synthetic Reagents"; Wiley: New York, Vol. 1, 1974. (b) Magid, R. M. *Tetrahedron* **1980**, *36*, 1907.

(2) (a) Treatment of (9-anthrylmethyl)trimethylammonium chloride with LAH gave predominantly 9-methylene-9,10-dihydroanthracene, whereas 9-methylanthracene was the sole product from 9-chloromethylanthracene.[3a] (b) α,γ,γ-Trisubstituted and α,γ-disubstituted allylphosphonates gave exclusively the S_N2' products, the configurations of the alkenes being *E*.[3b] (c) One example has been reported for LAH reduction of α,γ,γ-trisubstituted allyltriphenylphosphonium bromide, in which attack by hydride ion occurs exclusively at the γ-position.[3c] (d) LAH reduction of octyl halides and tosylates in ether revealed that the order of reactivity follows the sequence OTs > I > Br > Cl.[3d] In the case of allylic substrates **1a–c**, however, our preliminary work suggests that the order follows the sequence Br > Cl ≃ OTs.

(3) (a) Takagi, M.; Hirabe, T.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1311. (b) Kondo, K.; Negishi, A.; Tsunemoto, O. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 407. (c) Axelrod, E. H.; Milne, G. M.; van Tamelen, E. E. *J. Am. Chem. Soc.* **1970**, *92*, 2139. (d) Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 2550.

(4) Leaving group ability in 1,2-eliminations has been, however, found to follow the sequences $S^+MePh > N^+Me_2Ph > P^+Ph_3$.[5]

(5) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1975**, 940.

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