minish the reactivity of this substrate. Consequently, it remains a challenging goal to design a less congested and deactivated optically active Si-centered allylsilane in order to achieve efficient Si → C chirality transfer.

Experimental Section

(−)-α-Naphthylphenylmethylallylsilane (1).[3] To a flame-dried flask were added under nitrogen 1200 mL of pentane and *n*-butyllithium (189 mL of 1.5 M in hexane, 0.284 mol). Tetraallyltin (39.9 g, 0.142 mol) was added rapidly, and a white precipitate of allyllithium appeared during 20 min of stirring. The solvent was removed through a filter stick under nitrogen pressure, and the precipitate was rinsed with dry pentane (2 × 300 mL) and dissolved in dry ether (850 mL). A solution of (−)-α-naphthylphenylmethylchlorosilane[3] (29.9 g, 0.103 mol) in 150 mL of ether was added rapidly. The reaction mixture was stirred at room temperature for 10 min and poured into pentane (1200 mL). Crushed ice was added, and the organic phase was washed three times with water and dried prior to concentration under reduced pressure. Distillation of the resulting oil afforded **1** (25.08 g, 84.5%) as a clear, viscous oil: bp 155–170 °C (0.3 torr); $[\alpha]^{22.5}_D$ −13.22 (*c* 6.05, pentane); ^{1}H NMR ($CDCl_3$) δ 7.85–7.02 (m, 12 H), 5.95–5.27 (m, 1 H), 5.0–4.62 (m, 2 H), 2.23 (d, *J* = 8 Hz, 2 H), 0.70 (s, 3 H).

Condensation of 1 with Benzaldehyde Dimethyl Acetal. Prototypical Procedure. To a cold (−78 °C), stirred, nitrogen-blanketed solution of **2** (304 mg, 2.0 mmol) in dry dichloromethane (3 ml) was added via syringe 284 mg (2 mmol) of boron trifluoride etherate. A solution of (−)-**1** (576 mg, 2.0 mmol) in the same solvent (2 mL) was introduced dropwise, and stirring was maintained for 1 h at −78 °C. Following the addition of water, the product was extracted into ether, and the combined organic phases were dried and concentrated. The resulting oil was transferred to a Kugelrohr apparatus where distillation afforded 61.4 mg (19%) of (−)-(*S*)-**3** as a colorless oil: $[\alpha]^{22.5}_D$ −3.58° (*c* 6.14, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.22 (m, 5 H), 5.98–5.45 (m, 1 H), 5.14–4.8 (m, 2 H), 4.08 (t, *J* = 6 Hz, 1 H), 3.12 (s, 3 H), 2.7–2.18 (m, 2 H); MS, *m/e* calcd (M^+ - CH_3) 131.0863, obsd 131.0874.

The best conditions for the Eu(dcm)$_3$ measurements were determined to be when lanthanide reagent and **3** were present in equimolar quantities.

Independent Synthesis of (+)-(*R*)-1-Methoxy-1-phenyl-3-butene (3). The Grignard reagent solution prepared from 5.8 g (0.24 mol) of magnesium turnings and allyl bromide (12.1 g, 0.1 mol) in anhydrous ether at 0 °C under nitrogen was decanted into a clean, dry flask under a stream of nitrogen. Benzaldehyde (7.42 g, 0.07 mol) was added dropwise to the cold (0 °C), magnetically stirred solution. The reaction mixture was stirred at room temperature for 1 h and hydrolyzed with saturated ammonium chloride solution. The aqueous phase was extracted with ether, and the combined organic layers were dried and evaporated. Distillation afforded 9.86 g (95%) of 1-phenyl-3-buten-1-ol [bp 125–129 °C (23 torr)] which was utilized directly in the next step.

A cold (5–10 °C) acetone solution (100 mL) of the homoallylic alcohol (6.90 g, 4.67 mmol) was titrated with Jones reagent to an orange-green end point and allowed to stand at room temperature for 15 min. The chromium salts were removed by filtration, and the filtrate was evaporated. The orange residue was taken up in ether, washed with saturated sodium bicarbonate solution, dried, and concentrated. Distillation afforded 5.1 g (75%) of **4** as a pale yellow oil [bp 120–125 °C (21 torr)] which was not further purified.

Into a flame-dried, nitrogen-blanketed flask was placed 590 mg (10.6 mmol) of lithium aluminum hydride and 40 mL of anhydrous ether. The stirred suspension was cooled to 0 °C and a solution of Darvon alcohol [10.19 g, 36 mmol; $[\alpha]^{23.5}_D$ +8.28° (*c* 9.99, C_2H_5OH)] in ether (20 mL) was added as rapidly as possible. Within 10 min, an ethereal solution (5 mL) of **4** (1.46 g, 10 mmol) was added, and the reaction mixture was allowed to warm to room temperature where it was stirred overnight. The excess hydride was destroyed by the careful addition of water and dilute hydrochloric acid. The product was taken up in ether, dried, and concentrated to furnish an oil which upon distillation furnished (+)-(*R*)-**5**: bp 125–126 °C (18 torr); $[\alpha]^{23.5}_D$ +15.04° (*c* 5.85, C_6H_6); 900 mg (60%).

A solution of (+)-(*R*)-**5** (310 mg, 2.1 mmol) in methyl iodide (1.07 g, 7.5 mmol) was slowly treated with dry silver(I) oxide (875 mg, 3.75 mmol). This mixture was heated on a steam bath for 24 h. Portions of methyl iodide were added periodically to maintain a moist suspension. After cooling, the product was taken up in ether, filtered, and concentrated. Distillation of the residue in a Kugelrohr apparatus afforded (+)-(*R*)-**3** as a colorless liquid: bp 35–40 °C (0.1 torr); $[\alpha]^{22.5}_D$ +35.02 (*c* 2.17, $CDCl_3$). The ^{1}H NMR spectrum was identical with that recorded above for the levorotatory enantiomer.

(−)-1-Methoxy-1-*p*-tolyl-3-butene. Condensation of *p*-tolualdehyde dimethyl acetal (332 mg, 2.0 mmol) with (−)-**1** (576 mg, 2.0 mmol) in the presence of boron trifluoride etherate as before afforded 98.6 mg (28%) of the title compound as a clear light oil after Kugelrohr distillation: $[\alpha]^{22.5}_D$ −3.25 (*c* 9.86, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.12 (s, 4 H), 6.07–5.40 (m, 1 H), 5.27–4.75 (m, 2 H), 4.08 (t, *J* = 6 Hz, 1 H), 3.18 (s, 3 H), 2.6–2.17 (m, 2 H), 2.33 (s, 3 H); MS, *m/e* (M^+ - C_3H_6) 135.0810, obsd 135.0817.

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Registry No. (−)-**1**, 38106-30-8; **2**, 1125-88-8; (−)-(*S*)-**3**, 86766-44-1; (+)-(*R*)-**3**, 86766-46-3; **4**, 6249-80-5; (+)-(*R*)-**5**, 85551-57-1; **6**, 3395-83-3; (−)-1-methoxy-1-*p*-tolyl-3-butene, 86766-45-2; 1-phenyl-3-buten-1-ol, 936-58-3.

Convenient Synthesis of Medium-Ring *cis*-1,2-Dichlorocycloalkanes

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For studies of complex base-promoted eliminations from 1,2-dihalocycloalkanes,[1,2] medium-ring *cis*-1,2-dichlorocycloalkanes (C_7, C_8, C_{12}) were required. A literature search revealed that although these compounds were known,[3-5] the reported synthetic routes were multistep procedures that either involved expensive reagents or provided low yields of impure products that required extensive chromatographic purification. We therefore undertook the development of a more viable preparative method for these compounds.

In 1972, Isaacs and Kirkpatrick[6] reported the synthesis of *cis*-1,2-dichlorocyclopentane and *cis*-1,2-dichlorocyclohexane in high yields by refluxing the corresponding cycloalkane epoxides with triphenylphosphine in carbon tetrachloride for 1–2 h. With the very brief experimental description, we successfully repeated their synthesis of *cis*-1,2-dichlorocyclopentane. However, our attempt to extend this method directly to the preparation of *cis*-1,2-

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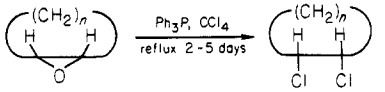
dichlorocycloheptane was unsuccessful. Monitoring the reaction by GLC analysis of the reaction mixture for unconsumed cycloheptene oxide revealed that the reaction was very slow and required several days of refluxing for completion.

By making adjustments for the slower than anticipated reaction and for release for the desired products from occlusion within the triphenylphosphine oxide mass, *cis*-1,2-dichlorocycloalkanes **2a–c** were prepared in 70–80% yields (eq 1). Contamination of the *cis*-1,2-dichloro-



(1)

1a, $n = 5$
b, $n = 6$
c, $n = 10$

2a–c

cycloalkane products by the corresponding *trans*-dichlorides was undetectable by GLC (<1%). In an attempt to shorten the reaction time, epoxide **1b** and triphenylphosphine in carbon tetrachloride were heated at 150 °C in a sealed tube for 24 h. GLC analysis revealed the presence of unconsumed epoxide (27%), *cis*-1,2-dichlorocyclooctane (47%), and *trans*-1,2-dichlorocyclooctane (30%). Thus the use of higher temperature is found to destroy the stereospecificity.

Experimental Section

Materials. Carbon tetrachloride, triphenylphosphine, and petroleum ether (30–60 °C) were reagent grade and were used as received. Epoxide **1a** was obtained from Aldrich Chemical Co. Epoxides **1b** and **1c** were prepared from cycloheptene (Aldrich) and *cis*-cyclododecene,[7] respectively, by reaction with *m*-chloroperbenzoic acid, using the general method of Servis et al.[8]

Preparation of Medium-Ring *cis*-1,2-Dichlorocycloalkanes. The epoxides **1a–c** (0.10 mol) and triphenylphosphine (0.15 mol) in 100 mL of carbon tetrachloride were refluxed under nitrogen. Periodically, an aliquot of the reaction mixture was removed and petroleum ether (30–60 °C) was added. The supernant liquid was analyzed by GLC for unconsumed epoxide. Upon completion of the reaction, the mixture was allowed to cool and was poured into 250–500 mL of petroleum ether (30–60 °C). The supernant liquid was decanted and the residual brown solid was ground (in portions) in a mortar and pestle with portions of the petroleum ether decantate until only light tan triphenylphosphine oxide crystals and a yellow petroleum ether solution remained. The solid was removed by filtration and the filtrate was evaporated on a rotary evaporator. The residual liquid was distilled under reduced pressure to yield (compound, reaction time, yield, boiling point): **2a**,[3] 3 days, 80%, 70 °C (1.1 torr); **2b**,[4] 2 days, 74%, 80–81 °C (0.8 torr); **2c**,[5] 5 days, 70%, 145–147 °C (2.5 torr). IR and ^{1}H NMR spectra were consistent with the proposed structures. Compound **2c** was further characterized by reaction with $NaNH_2$–NaO-*t*-Bu in THF followed by stereospecific dehalogenation[9,10] of the resulting vinyl chloride to yield *cis*-cyclododecene.

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Registry No. **1a**, 76519-87-4; **1b**, 4925-71-7; **1c**, 1502-29-0; **2a**, 32718-96-0; **2b**, 16250-67-2; **2c**, 86782-61-8; Ph_3P, 603-35-0; CCl_4, 56-23-5.

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Novel Trialkoxymethyl Disulfides via Nucleophilic Addition to Thionocarbonates: Tris(2-fluoro-2,2-dinitroethoxy)methyl Trichloromethyl Disulfide and Related Products

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As possible starting materials for the synthesis of trialkoxychloromethanes (chloroorthoformates), we were interested in the preparation of trialkoxymethyl disulfides, more specifically, tris(2-fluoro- and/or 2-nitroethoxy)methyl disulfides. However, no examples of trialkoxymethyl disulfides were reported in the literature, presumably because the required trialkoxymethyl thiols[1] are not available. Although it would appear that such thiols could be prepared by the nucleophilic addition of an alkoxide ion to a thionocarbonate (eq 1), in practice the equilibrium

$$RO^- + (RO)_2C{=}S \rightleftarrows (RO)_3C{-}S^- \qquad (1)$$

is unfavorable, and the thiol cannot be isolated. Nevertheless it seemed reasonable to expect that a certain finite concentration of the trialkoxymethanethiolate ion would exist in solution and possibly could be trapped as the disulfide by reaction with a sulfenyl chloride. This expectation has now been realized experimentally. Under basic conditions, 2-fluoro-2,2-dinitroethanol reacted with bis(2-fluoro-2,2-dinitroethyl)thionocarbonate[2] (**1**) in the presence of trichloromethanesulfenyl chloride to give tris(2-fluoro-2,2-dinitroethoxy)methyl trichloromethyl disulfide **2** (eq 2). The thionocarbonate **1** does not have

$$FC(NO_2)_2CH_2OH + \underset{\mathbf{1}}{[FC(NO_2)_2CH_2O]_2C{=}S} + Cl_3CSCl \xrightarrow[CH_2Cl_2/H_2O]{OH^-/PTC} \underset{\mathbf{2}\ (65\text{–}80\%)}{[FC(NO_2)_2CH_2O]_3CSSCCl_3} + \underset{\mathbf{3}\ (6\text{–}11\%)}{([FC(NO_2)_2CH_2O]_3CS)_2} \qquad (2)$$

PTC = phase transfer catalyst

to be present initially but can be formed in situ by the reaction of fluorodinitroethanol with thiophosgene although the yield of **2** is somewhat lessened. The symmetrical disulfide **3** was also isolated as a minor product (6–11%).

At first, it was assumed that **2** was formed in a straightforward manner by nucleophilic attack of the tris(fluorodinitroethoxy)methanethiolate ion on trichloromethanesulfenyl chloride; however, the isolation and identification of the constituents of a partially complete reaction indicated the presence of a considerable concentration of 2-fluoro-2,2-dinitroethyl trichloromethanesulfenate (**4**). When the reaction was followed by TLC, there was an initial increase in the concentration of the ester **4** which then gradually disappeared during the course of the reaction. The ester **4** was independently synthesized by the base-catalyzed reaction of fluorodinitroethanol with trichloromethanesulfenyl chloride[3] (eq 3). Substitution of

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(3) Compound **4**, in contrast to typical sulfenates, is quite stable. A sample remained unchanged after storage in a desiccator at ambient temperature for 3 years.

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