Lithium Bronze Route to (+)-6-Epi-α-cyperone (2). Into a three-necked flask equipped with a stirrer, dry ice condenser, and 760 mg (0.11 mol) of lithium wire under argon was distilled 11 mL (0.44 m) of liquid ammonia (from sodium). After the lithium bronze had formed, 30 mL of dry THF was added. To the stirred mixture was added, dropwise at gentle reflux, a solution of 7.5 g (50 mmol) of (+)-carvone and 3.7 g (50 mmol) of *tert*-butyl alcohol in 20 mL of dry THF. After the addition was complete, the dry ice condenser was removed, and the ammonia was allowed to evaporate under a stream of N_2. The mixture was cooled to −78 °C (dry ice–acetone) followed by the addition of 6.72 g (80 mmol) of ethyl vinyl ketone via syringe over 3 min. After the addition was complete, the reaction mixture was allowed to warm to 20 °C at which temperature it was maintained for 1 h. The reaction mixture was quenched with 50 mL of saturated NH_4Cl solution, diluted with water (200 mL), and extracted with ether (3 × 100 mL). The combined extracts were washed with 1 N HCl (50 mL), water (50 mL), and brine (2 × 50 mL), dried ($MgSO_4$), filtered, and concentrated to give 11.2 g of residue. TLC and GC analysis indicated the presence of ketol **1a** and dihydrocarvone. The residue was dehydrated with 8% KOH/EtOH (vide supra) to provide 9.5 g of crude product. Fractional distillation provided dihydrocarvone [1.5 g (20%); bp 49–50 °C (0.17 mmHg) and **2** [5.3 g (49%); bp 80–81 °C (0.01 mmHg)]. The pot residue was chromatographed to give an additional 2.0 g (18%) of the desired enone.

1,4a-Dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (5a). To a solution of LDA (5.0 mmol, generated from 524 mg of diisopropylamine and 2.12 mL of 2.35 M *n*-butyllithium in 5 mL of THF at 0 °C) was added 627 mg of 2-methylcyclohexanone (5.6 mmol) at 0 °C followed by stirring of the solution for 3 h at 20 °C. The reaction mixture was cooled to −78 °C followed by the addition of 672 mg (8.0 mmol) ethyl vinyl ketone over a period of 1 min. The mixture was allowed to warm to 20 °C over 1.5 h and then worked up as described above, providing 1.5 g of oil. Flash chromatography (20% ethyl acetate–hexanes) afforded diketone and two ketols, A and B.

Diketone: 270 mg (27%); ^1H NMR (90 MHz, $CDCl_3$) δ 0.99 (3 H, t, J = 8.2 Hz, CH_2CH_3), 1.00 (3 H, s), 1.20–2.00 (8 H, m), 2.20–2.92 (6 H, m); IR (neat) 1705, 1720 cm^{-1}.

Ketol A: 303 mg (31%); mp 106–108 °C (lit.[9] mp 109–110 °C; trans-fused ketol); ^1H NMR (90 MHz, $CDCl_3$) δ 0.95 (3 H, d, J = 6.8 Hz), 1.25 (3 H, s), 1.40–2.12 (11 H, m), 2.20–2.80 (3 H, m); IR (neat) 3500, 1725 cm^{-1}.

Ketol B: 262 mg (27%); ^1H NMR (90 MHz, $CDCl_3$) δ 0.99 (3 H, d, J = 6.9 Hz), 1.04 (3 H, s), 1.40–2.00 (10 H, m), 2.00–2.60 (3 H, m), 2.92 (1 H, q, J = 5.6 Hz); IR (neat) 3500, 1725 cm^{-1}.

Exposure of ketol A (98 mg, 0.5 mmol) to 1 mL of 8% KOH/EtOH for 10 min at 25 °C followed by a workup (vide supra) and flash chromatography (20% ethyl acetate–hexanes) afforded 81 mg (91% yield) of **5a**: ^1H NMR (90 MHz, $CDCl_3$) δ 1.20 (3 H, s), 1.40–2.28 (12 H, m), 1.76 (3 H, s); IR (neat) 1678 cm^{-1}.

A 260-mg sample of ketol B was converted to **5a** in 94% yield by using the above procedure.

7(*R*)-Isopropenyl-4a(*R*)-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (4a). A solution of LDA (5.0 mmol) in THF (4 mL) was prepared as described at 0 °C. After 10 min, 845 mg (+)-dihydrocarvone (5.5 mmol, from (−)-carvone) in 1 mL of THF was added and allowed to warm to 25 °C. After 2 h, the mixture was cooled to −78 °C, and methyl vinyl ketone was added dropwise via syringe over a period of 1 min. The cooling bath was removed as the temperature was allowed to warm to 25 °C. The workup (vide supra) gave 1.7 g of oil. Flash chromatography (30% ethyl acetate–hexanes) provided the following substances after the initial removal of dihydrocarvone.

Diketone: 133 mg (12%); ^1H NMR (90 MHz, $CDCl_3$) δ 0.96 (3 H, s), 1.12–1.88 (4 H, m), 1.72 (3 H, s, vinylic CH_3), 2.08 (3 H, s, $COCH_3$), 2.20–2.44 (4 H, m), 4.68 (1 H, br s), 4.76 (1 H, br s).

Ketol 3a: 595 mg (53%); ^1H NMR (90 MHz, $CDCl_3$) δ 1.17 (3 H, s), 1.40–2.88 (14 H, m), 1.66 (3 H, s), 4.68 (2 H, br s); IR (neat) 3500, 1710 cm^{-1}.

Ketol 3b: 128 mg (12%); ^1H NMR (90 MHz, $CDCl_3$; partial) δ 1.04 (3 H, s), 1.64 (3 H, s), 4.62 (2 H, br s).

(9) Ayer, W. A.; Browne, L. M.; Fung, S. *Can. J. Chem.* **1976**, *54*, 3276.

Hydroxy ketone **3a** (111 mg) was stirred at 25 °C for 2 h in 0.5 mL of 8% KOH/EtOH. The workup afforded 102 mg of yellow oil which, after flash chromatography (30% ethyl acetate–hexane), provided pure enone **4a**: 72 mg (70% yield); ^1H NMR (90 MHz, $CDCl_3$) δ 1.24 (3 H, s), 1.36–2.80 (11 H, m), 1.72 (3H, s), 4.76 (1 H, br s), 4.88 (1 H, br s), 5.76 (1 H, br s); IR (neat) 1670 cm^{-1}; GC/MS (20 ev), m/e 204 (M^+).

By use of the same procedure, ketol **3b** (128 mg) afforded enone **4b**: 60% yield; ^1H NMR (90 MHz, $CDCl_3$) δ 1.04 (3 H, s) 1.40–3.12 (11 H, m), 1.68 (3 H, s), 4.80 (2 H, br s), 5.80 (1 H, br s); IR (neat) 1680 cm^{-1}; GC/MS (20 eV), m/e 204 (M^+).

4a-Methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (5b). To a solution of LDA (5.0 mmol) in 5 mL of THF was added 627 mg (5.6 mmol) of 2-methylcyclohexanone at 0 °C. The mixture was stirred for 3 h at 20 °C. After the solution was cooled to −78 °C, 700 mg (1.0 mmol) of methyl vinyl ketone was added. The cooling bath was removed, and the reaction mixture was allowed to warm to 20 °C over 1.5 h. The reaction mixture was cooled to −5 °C and quenched with 5 mL of saturated aqueous NH_4Cl, followed by the workup (vide supra). The resultant oil (1.5 g) was flash chromatographed (30% ethyl acetate–hexanes) to afford the following fractions.

Enone 5b: 135 mg (17%); ^1H NMR (90 MHz, $CDCl_3$) δ 1.22 (3 H, s), 1.32–2.56 (12 H, m), 5.72 (1 H, s); IR (neat) 1680 cm^{-1}; GC/MS (20 eV), m/e 164 (M^+).

Ketol 6: 601 mg (contaminated with MVK polymer); ^1H NMR (90 MHz, $CDCl_3$) δ 1.04 (angular methyl). The crude material was exposed to 2 mL of 8% KOH/EtOH at 25 °C for 2 h followed by a workup. The crude residue (470 mg) was subjected to flash chromatography (30% ethyl acetate–hexanes) to provide 119 mg (15%) of enone **5b**. The overall yield was 32%.

Registry No. **1a**, 86785-82-2; **2**, 547-26-2; **3a**, 86785-83-3; **3b**, 86785-84-4; **4a**, 13567-79-8; **4b**, 13918-47-3; **5a**, 878-55-7; **5b**, 826-56-2; **6**, 40573-27-1; (−)-dihydrocarvone, 619-02-3; 2-methylcyclohexanone, 583-60-8; (+)-dihydrocarvone, 5524-05-0; ethyl vinyl ketone, 1629-58-9; methyl vinyl ketone, 78-94-4; (+)-carvone, 2244-16-8; 2-(3-oxopentyl)-2-methylcyclohexanone, 86785-85-5; 1,4aα-dimethyl-8aα-hydroxydecahydronaphthalen-2-one, 86833-39-8; 1,4aα-dimethyl-8aβ-hydroxydecahydronaphthalen-2-one, 86833-40-1; 4(*R*)-isopropenyl-2-methyl-2(3-oxobutyl)cyclohexanone, 66708-16-5.

Examination of (−)-α-Naphthylphenylmethylallylsilane as a Template for Effecting Chirality Transfer from Silicon to Carbon[1]

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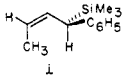
The concept of transferring chirality from asymmetric silicon to carbon, particularly in conjunction with a recyclable chiral silicon pool,[1] holds special interest. We have sought to examine in preliminary fashion the workability of this proposal with (−)-α-naphthylphenylmethylallylsilane (**1**), the most readily available Si-centered[2] optically active allylsilane presently known.[3] Recent reports have

(1) Silanes in Organic Synthesis. 19. For part 18, see: Daniels, R. G.; Paquette, L. A. *Organometallics* **1982**, *1*, 1449.

(2) Asymmetric allylsilanes may owe their optical activity to a chiral silicon atom as in **1** or to a chiral carbon atom as in **i**. To distinguish simply between these intrinsically different forms of optical activity, we propose use of the qualifying adjectives "Si-centered" and "C-centered", respectively.



1

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Table I. Reaction of 1 and 2 Catalyzed by $BF_3 \cdot Et_2O$[a]

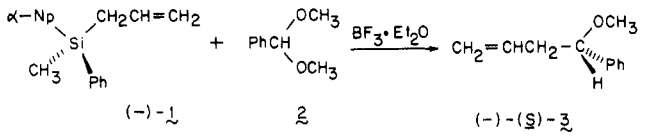
temp, °C	$[\alpha]^{22.5}_D$ ($CHCl_3$), deg	% ee[b]	yield, %
−78	−3.58	5.5	19
	−3.53	5.4	20
−20	−2.63	4.0	29
	−2.54	3.9	25
20	−2.54	3.9	27
	−2.72	4.2	30

[a] The reaction time was 60 min in all cases. [b] The error limits on these measurements are considered to be ±1%.

detailed allyl group transfer from allyltrimethylsilane and its homologues to various aldehydes, ketones, and acetals.[4-7] The use of chiral α-keto esters has led in optical yields as high as 55% to α-hydroxy acids following saponification of the menthyl esters.[8] Still higher stereoselectivity has been realized during the production of homoallylic alcohols from allylsilanes whose optical activity is C-centered.[2,9] We have not uncovered asymmetric reactions of this quality with 1. The following summary of our findings may deter others from pursuing similar lines of investigation based upon this particular substrate.

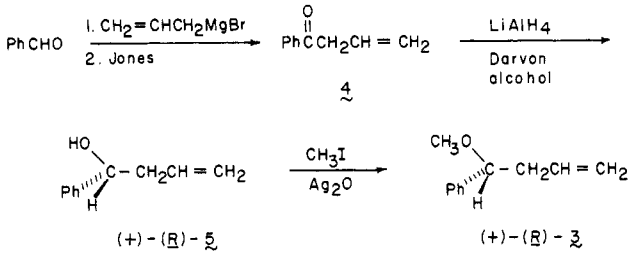
First to be examined was a series of aldehydes of varying steric bulk.[10] It soon became evident, however, that 1 was more susceptible to destruction by certain Lewis acid catalysts ($TiCl_4$, $SnCl_4$) than to capture by the incipient carbocation, at least at those temperatures (0–25 °C)[11] required for observable chemical change. The demise of the aldehydes was observed under other circumstances ($AlCl_3$, $BF_3 \cdot Et_2O$, or Me_3SiOTf; 0–25 °C).[11] Anhydrous zinc chloride proved inert to both reagents. Attempts to achieve analogous condensation reactions with methyl pyruvate and methyl benzoylformate were equally problematical.

Application of the preceding methodology to dimethyl acetals was somewhat more rewarding. Using 2 as the lead



(−)-1 2 (−)-(S)-3

example, we noted that partial condensation could indeed be effected in the presence of trimethylsilyl triflate, although less satisfactorily than with boron trifluoride etherate as the catalyst. The results realized with the latter Lewis acid at three different temperatures are compiled in Table I. The chemical yields proved to be uniformly low, never exceeding 30% of 3 after Kugelrohr distillation.[12] The percent enantiomeric excess was established by ^1H NMR analysis in the presence of tris(*d,d*-dicampholylmethanato)europium(III) [Eu(dcm)$_3$],[13] which led to very satisfactory separation of the methoxyl signal due to each enantiomer. In all cases, isolated ether 3 proved to be levorotatory. For the purpose of absolute configurational assignment, benzaldehyde was sequentially condensed with the allyl Grignard reagent[14] and oxidized with Jones reagent.[15] Reduction of 4 with lithium aluminum



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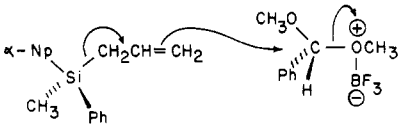
hydride in the presence of Darvon alcohol[16] afforded dextrorotatory 4 whose configuration was considered to be *R* as a result of its close structural relationship to (+)-(*R*)-1-phenyl-1-butanol.[17] Subsequent O-methylation[18] of (+)-5 delivered (+)-(*R*)-3 ($[\alpha]^{22.5}_D$ +35.0°), the enantiomeric composition of which was shown to be 77% *R*/23% *S* (or 54% ee) by lanthanide induced shifting with Eu(dcm)$_3$. In light of this evidence, the maximum rotation of 3 in chloroform solution is approximately 65°, and the highest enantiomeric excess realized in Table I is on the order of 5%.

The stereochemical results achieved with 2 and with *p*-tolualdehyde dimethyl acetal (6; allyl ether produced in 28% yield, $[\alpha]^{22.5}_D$ −3.25°) can be rationalized in terms of a sterically favored transition state (A) wherein one



A

methoxy group departs as the allyl group enters. To the extent that the transition state shifts away from one having S_N2 characteristics to one involving capture of a fully developed oxonium species, asymmetric induction will fall off rapidly. The less chirally profitable S_N1 profile is expected to be favored by the presence of a flanking phenyl substituent as in A and by high levels of peripheral steric strain which should retard direct displacement by the allylsilane. Our observations that hexanal and pivaldehyde dimethyl acetals are allylated by (−)-1 ($TiCl_4$, −78 °C) in 7% and 30% chemical yields without evidence of asymmetric transfer support this view.

A possible source of the complications experienced with 1 is the substitution pattern about the silicon atom. The pendant aryl groups provide steric encumbrances and adverse electronic contributions which substantially di-

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(6) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 71.

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(10) The most exhaustively studied substrates were $PhCH_2CHO$, $Ph(CH_2)_2CHO$, and $(CH_3)_2CHCHO$.

(11) No reaction was observed when these condensations were effected at −78 °C.

(12) The silicon byproduct, which could be distilled in a Kugelrohr apparatus at 250 °C and 0.1 torr, was not characterized.

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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.

Acknowledgment. The partial financial support of the National Science Foundation is gratefully acknowledged. We also thank Eli Lilly Co. for a gift of Darvon alcohol.

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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