Table I. Best Sphere Fit Radii for Migrating Hydrogen in Suprafacial [1,5]-Sigmatropic Rearrangements[a]

reaction	radius of migrating hydrogen, Å	Mulliken charge on migrating hydrogen, electrons
	1.385	0.22
	1.374	0.23
	1.283	0.31

[a] 3-21G//3-21G. See ref 8 for discussion of numerical methods. [b] Data for 1,3-pentadiene and cyclopentadiene from ref 6b.

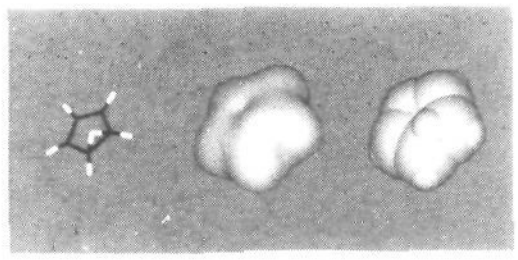


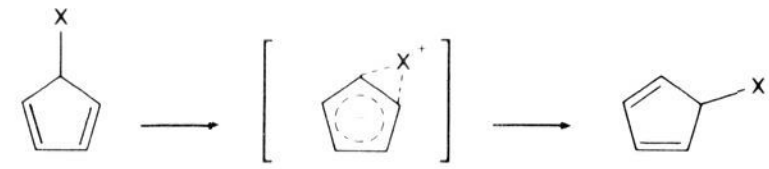
Figure 1. Skeletal representation (left), total electron density surface (middle), and sphere fit to electron density surface (right) for transition state for [1,5]-sigmatropic migration in cyclopentadiene (3-21G//3-21G).

electron density surface and the sphere fit representation for the transition state for [1,5] migration in cyclopentadiene is shown in Figure 1.

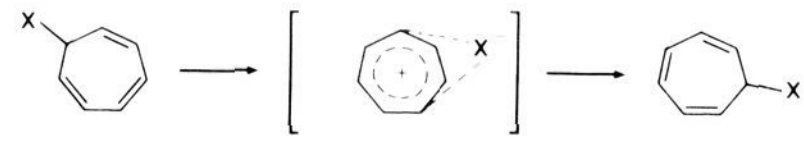
The data indicate that as the underlying skeleton becomes better able to support negative charge, the size of the migrating group decreases, i.e., the hydrogen becomes increasingly more protonic. The migrating hydrogen in cyclopentadiene is somewhat smaller than a neutral hydrogen atom (1.332 Å), suggestive of a partial positive charge. Nevertheless, it is still larger than a methylene hydrogen (the methylene hydrogen radius in cyclopentadiene is 1.185 Å), suggesting that the migrating hydrogen in the transition structure is more negatively charged than that in cyclopentadiene itself. The radius of the migrating hydrogen in 1,3-pentadiene, while somewhat larger than that for hydrogen atom, is much smaller than that found in the free hydride anion (1.574 Å). This suggests that it is slightly negatively charged. The hydrogen in the transition state for sigmatropic rearangement in 3-cyano-1,3-pentadiene is slightly smaller than the corresponding atom in 1,3-pentadiene but is still larger than free hydrogen atom. In both of the acyclic systems, the migrating hydrogens are characterized by radii similar to those in typical "hydridic" molecules, e.g., 1.351 Å in borane and 1.363 Å in silane. Given the relative insensitivity of atomic sizes of hydrogen bonded to carbon,[8] the span of 0.1 Å noted for the systems here is significant and indicative of a marked change in the charge on the migrating species.

Mulliken charges[12] for the migrating hydrogens in 1,3-pentadiene, 3-cyano-1,3-pentadiene, and cyclopentadiene are also provided in Table I. While the migrating atoms in all three systems are indicated to be positive (consistent with the known tendency of Mulliken analysis to allocate insufficient electron population to hydrogen[12b]) the ordering of hydrogen charges, 1,3-pentadiene $\simeq$ 3-cyano-1,3-pentadiene < cyclopentadiene (the latter the most positive), is consistent with the assignments based on atomic sizes.

The migratory aptitude of a group should be related to its inherent ability to stabilize charge. For example, groups that are able to accommodate positive charge, e.g., trimethylsilyl (Me_3Si), should migrate more readily in cyclopentadiene than in 1,3-pentadiene, while those able to bear negative charge, e.g., methyl, should show the opposite behavior. the available experimental data are in accord. The known migratory abilities for substituents on cyclopentadiene (Me_3Si >> H > Me[13,14]) are consistent with a limiting representation of the transition state as incorporating an aromatic cyclopentadienyl anion; i.e.,



In contrast, hydrogen migration in cycloheptatriene is more rapid than migration of a trimethylsilyl group.[15] As illustrated below,



the transition state here may be viewed in terms of migration of an "anion" across a positively charged skeleton (in the limit, the aromatic tropylium cation).

In summary, we have found that [1,5]-sigmatropic hydrogen rearrangements, while concerted, exhibit subtle differences in their transition structures, depending on the substrate. [1,5]shifts on cyclopentadiene are characterized by a relatively "cationic" migrating group, while rearrangements on 1,3-pentadiene reflect the (relatively) anionic composition of the group that migrates. Rational substitution onto the substrate skeleton should permit fine control both of migratory aptitude and stereochemistry.[16]

Registry No. 1,3-Pentadiene, 504-60-9; 3-cyano-1,3-pentadiene, 98875-36-6; cyclopentadiene, 542-92-7; cycloheptatriene, 544-25-2.

(12) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343. For detailed discussion see: (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. "Ab Intio Molecular Orbital Theory"; Wiley: New York, 1986; p 25 ff.

(13) (a) Ashe, A. J., III *J. Am. Chem. Soc.* **1970**, *92*, 1233. (b) McLean, S.; Reed, G. W. B. *Can. J. Chem.* **1970**, *48*, 3110.

(14) Roth, W. R.; König, J. *Justus Liebigs Ann. Chem.* **1966**, *699*, 24. (b) Hedaya, E.; McNeil, D. W.; Schissel, P.; McAdoo, D. J. *J. Am. Chem. Chem. Soc.* **1968**, *90*, 5284. (c) McLean, S.; Webster, C. J.; Rutherford, R. J. D. *Can. J. Chem.* **1969**, *47*, 1555.

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(16) Kahn, S. D.; Hehre, W. J.; Okamura, W. H., research in progress.

X-ray Crystal Structure and Hydrocarbon Solution Dynamics of Tetrameric 1-(Dimethylamino)-3-lithiopropane

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So far precise determination of the structures of Lewis base adducts[1,2] of alkyllithium tetramers has been impossible. Solutions of alkyllithiums containing Lewis base do not normally yield crystals[3] and loosely bound Lewis base is given off again upon

(1) Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664.

(2) Regarding the tetrahedral nature of alkyllithium tetramers in diethyl ether: Brown, T. L. *Pure Appl. Chem.* **1970**, *23*, 447. McKeever, L. D. "Ions and Ion pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972; Vol. 1, p 263 and references given in these papers.

(3) Formation of precipitates: Screttas, C. G.; Eastham, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 3276.

0002-7863/85/1507-8292$01.50/0

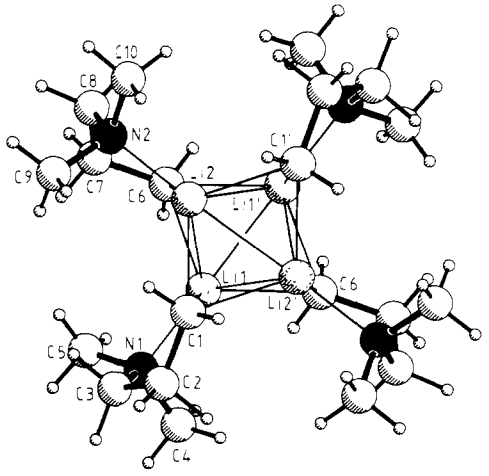
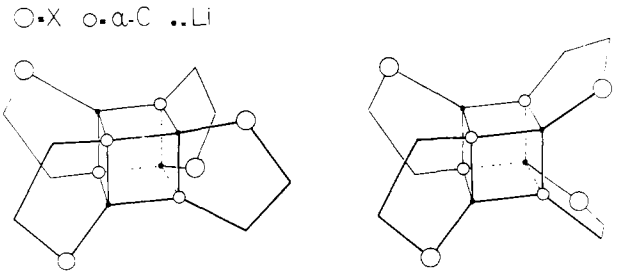


Figure 1. Structure of the tetramer as viewed down the crystallographic twofold axis. Some important distances (Å) are the following: Li(1)–Li(2) 2.476 (5); Li(1)–Li(2′) 2.476 (5); Li(1)–Li(1′) 2.544 (5); Li(2)–Li(2′) 2.551 (5); Li(1)–C(1) 2.273 (4); Li(1)–C(6) 2.283 (4); Li(1)–C(6′) 2.252; Li(1)–N(1) 2.071 (4); Li(2)–C(1) 2.255 (4); Li(2)–C(1′) 2.278 (4); Li(2)–C(6) 2.279 (4); Li(2)–N(2) 2.065 (4); C(1)–plane through Li(1), Li(2), and Li(2′) 1.74 (1); C(6)–plane through Li(2), Li(1), Li(1′) 1.76 (1); symmetry code, a prime = $^1/_2-x, y, ^1/_2-z$.

concentration of these solutions.[4,5] We have circumvented these difficulties by studying *intramolecular* Lewis base alkyllithium adducts.[6] The ease of crystallization of these compounds from hydrocarbon solutions has now enabled us to investigate the structure of crystalline 1-(dimethylamino)-3-lithiopropane (I)[7] by X-ray crystallography. ^{7}Li, ^{13}C, and ^{1}H NMR studies have provided information on the dynamics of I in hydrocarbon solvents. We regard our results as exemplary for systems $(RLi)_4$–$(NR'_3)_{4-n}$ (n = 0–3) and we believe that they shed light on the question concerning the origins of the activation of alkyllithium *tetramers* by coordination of Lewis base.[8]

Crystals of I grown from solution in pentane are composed of the tetrameric units II shown in detail in Figure 1 and located at C_2 symmetry sites in the unit cell.[9] The four lithium atoms and the four α-carbon atoms constitute a distorted cube. Each nitrogen is coordinated as a fourth ligand (X) to one of the lithium atoms. The arrangement of the $CH_2CH_2NMe_2$ chains in II differs from the arrangement found previously for the CH_2CH_2OMe chains in the crystalline state of tetrameric 3-lithio-1-methoxybutane (III).[6]



II, α-C = CH_2, X = NMe_2

III, α-C = $CHCH_3$, X = OMe
IV, α-C = CH_2, X = NMe_2

The C_4Li_4 core of II is very similar to that of crystalline ethyllithium.[10] Average core distances (Å) II (ethyllithium): C–Li, 2.272 (2.271); Li–Li, 2.525 (2.553); C–C, 3.69 (3.67). In ethyllithium the role of X is played by an α-carbon of a neighboring tetrameric unit (C_4Li_3Li–CC_3Li_4 = 2.501 Å). Substituting it by a tertiary amine nitrogen placed much closer (Li–N = 2.062 Å) and pointing to lithium with its lone electron pair as in II *does not* change the dimensions of the Li_4C_4 core to any significant degree. This finding runs counter to the popular notion that the higher reactivity of (tetrameric) σ-organolithiums in the presence of Lewis base is due to "activation" (by lengthening and increased polarity) of C–Li bonds induced by coordination of a donor ligand to lithium.[11] It suggests that the lowerings of the free energies of alkyllithiums by Lewis base association[12] are due solely to the coordinative bonds formed and that the rate enhancements[8] are the results of still greater lowerings of the free energies of organolithium transition states if they contain Lewis base.[11,13]

At −38 °C I (ca. 0.08 M) in toluene (cyclopentane) shows ^{7}Li NMR signals at 2.14 and 2.05 ppm (2.31 and 2.19 ppm).[14] The intensity ratio [63:37 (56:44)] is both temperature- and concentration-independent the latter indicating that the two types of lithium atoms belong to species with the same degree of aggregation. I is tetrameric in benzene[7] and we assume that this is also the case in toluene and cyclopentane. At 21 °C the Li nuclei have a coalesced chemical shift at 2.08 (2.20) ppm. At −38 °C in toluene ^{13}C NMR signals for the major species appear at 65.42 (NCH_2), 45.06 (NCH_3), 26.84 [$C(CH_2)_2$] and 8.8 (CLi) ppm and for the minor species at 65.02, 44.08 + 46.07 (intensity ratio 1:1), 26.84 and 8.8 ppm. At 21 °C coalesced ^{13}C chemical shifts are observed at 65.55, 45.13, 26.82, and 8.8 ppm. The two NCH_3 signals of the minor species at −38 °C are assigned to the diastereotopic methyl groups in a tetramer IV which coexists with II in solution. In the ^{1}H NMR spectrum of I in pentane-d_{12} at −40 °C, signals are observed for the NCH_3 protons of IV (2.255 and 2.246 ppm) and of II (2.273 ppm) while the diastereotopic CH_2Li protons of IV are discerned at −0.81 and −1.06 ppm besides the homotopic CH_2Li protons of II (−0.99 ppm). The intensity ratios for the two sets of CH_3 and CH_2 protons, respectively, are equal to the ratio of signals in the low-temperature ^{7}Li NMR spectrum. At 30 °C the CH_2Li signals are merged to a triplet (J = 7.0 Hz) and the CH_3 signals to a singlet.[15] Line-shape analysis at different temperatures of the two ^{7}Li signals of 0.08

(4) E.g.: Hay, J. N.; McCabe, J. F.; Robbe, J. C. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1. Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 5321.

(5) Novel method for investigating the solution structures of organolithium compounds: Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1984**, *106*, 4627.

(6) Klumpp, G. W.; Geurink, P. J. A.; Spek, A. L.; Duisenberg, A. J. M. *J. Chem. Soc. Chem. Commun.* **1983**, 814. Spek, A. L.; Duisenberg, A. J. M.; Klumpp, G. W.; Geurink, P. J. A. *Acta Crystallogr., Sect. C* **1984**, *C40*, 372.

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(9) Crystals of I were block-shaped, transparent, and colorless, $C_{20}H_{48}N_4Li_4$, M_r = 372.39, monoclinic, space group $P2/n$, a = 9.753 (1) Å, b = 7.102 (3) Å, c = 19.093 (1) Å, β = 97.41 (1)°, U = 1311.5 (6) Å, Z = 2, D_c = 0.943 g cm^{-3}, Zr-filtered Mo Kα radiation, λ = 0.71073 Å. The specimen, in vacuo, was mounted in a Lindemann glass capillary; 2420 reflections (θ < 25°; $\omega/2\theta$ scan) were measured on an Enraf-Nonius, CAD4F diffractometer. The structure was solved by direct methods (MULTAN80) and refined by full-matrix least squares (SHELX76) to a final R = 0.0575 for 1648 unique reflections with $I > 2.5\sigma(I)$ and $w^{-1} = \sigma^2(F)$. The structure is slightly disordered at C(2) and C(7): full details will be published elsewhere.

(10) Dietrich, H. J. *Organomet. Chem.* **1981**, *205*, 291.

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(12) Kminek, I.; Kaspar, M.; Trekoval, J. *Coll. Czech. Chem. Commun.* **1981**, *46*, 1132. Quirk, R. P.; Kester, D. E. *J. Organomet. Chem.* **1977**, *127*, 111. Geurink, P. J. A. Thesis, Vrije Universiteit, 1982; Geurink, P. J. A.; Klumpp, G. W. *J. Am. Chem. Soc.*, in press.

(13) Cf.: Darensbourg, M. Y.; Kimura, B. Y.; Hartwell, G. E.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 1236.

(14) Relative to external 1 M dry LiBr in THF (δ(50% LiBr in H_2O) −1.04 and δ(2-lithiobutane) 0.77). Not corrected for volume magnetic susceptibility.

(15) ^{1}H NMR [toluene-d_8 (cyclopentane), 21 °C, δ] 2.11 (2.20) [CH_3N], 2.1–2.3 [NCH_2CH_2], −0.78 (−0.95) [CH_2Li].

M I in toluene (cyclopentane) yielded the rate constants k and the activation parameters ($\Delta H^{\ddagger}$ = 17 (16) ± 2 kcal/mol, $\Delta S^{\ddagger}$ = 13 (10) ± 3 cal/(mol deg) for the isomerization II → IV.

Isomerization could occur by intramolecular nitrogen lithium exchange and/or intramolecular carbon lithium exchange.[16] Degenerate rearrangement of IV (IV ⇌ II ⇌ IV') interchanges the diastereotopic protons of this species. The temperature-dependent line shape of the CH_2Li protons of I in pentane-d_{12} could be simulated on this basis. Apparently, exchange of the methylene protons by inversion at C-α[17] is much slower and need not be taken into account.

Supplementary Material Available: Tables of X-ray crystallographic data for I (6 pages). Ordering information is given on any current masthead page.

(16) Cf.: Fraenkel, G.; Henrichs, M.; Hewitt, M.; Su, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 255.

(17) Fraenkel, G.; Beckenbaugh, W. E., Yang, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 6878.

Highly Stereoselective Reduction of α-Substituted β-Keto Amides by Means of Hydrosilane/F^- and Hydrosilane/H^+ Reagent. A Practical Approach to Aldols of Both Threo and Erythro Configurations

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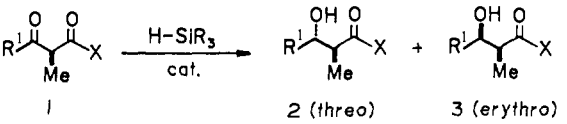
Although the aldol reaction has been well established as a reliable method for the construction of acyclic systems having adjacent chiral centers,[1] difficulties[2] frequently encountered in this process have stimulated search for more practical alternative approaches to the aldols. Stereoselective reduction of α-substituted β-keto acid derivatives has been recognized to be the solution.[3,4] However, it still seems to be problematic in synthetic viewpoints. For example, erythro-selective reduction of high selectivity[4] requires the use of commercially nonavailable pyrophoric zinc borohydride,[5] and threo selective reduction[6] of the same substrates remains unsolved yet. We report that hydrosilane-based reduction[7] of α-substituted β-keto amides proceeds under high stereocontrol. Our disclosure offers a practical approach to aldols of both threo and erythro configurations.[8,9]

The β-keto amide **1a** (1 mmol) was treated with dimethylphenylsilane (1.2 mmol) in 1,3-dimethyl-3,4,5,6-tetrahydro-2-(1*H*)-pyrimidinone (DMPU) (2 mL) in the presence of tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF)[10] (10 mol %) at 0 °C for 12 h. After acid treatment (1 M HCl–MeOH, room temperature, 0.25 h)[11] followed by usual workup, an analysis of the crude mixture[12] by 400-MHz ^{1}H NMR showed exclusive formation of the threo isomers **2a** (>99% selectivity). Isolation



I 2 (threo) 3 (erythro)

X = NR^2_2, OR^2

of the pure material (98% yield) was carried out by preparative TLC (silica gel, AcOEt–hexane 1:1). Other examples are shown in Table I. High threo selectivities (>98%) were also recognized for **1b–d** (R^1 = aryl) in sharp contrast to the conventional hydride reduction.[6] The threo selectivity is explained in terms of the Felkin-type model.[13] An ester derivative, methyl 2-benzoylpropionate (**1g**), failed to be reduced due possibly to the abstraction of an active methine proton by the fluoride ion catalyst.[14] In the reduction of **1e** and **1f** (R^1 = alkyl), the erythro isomers were formed predominantly.[15]

Highly erythro-selective reduction of **1** was also achieved by means of hydrosilane/H^+ reagent[16] (Table II). When **1a** (1 mmol) was allowed to react with dimethylphenylsilane (1.2 mmol) in trifluoroacetic acid (2 mL) at 0 °C for 6 h, the erythro alcohol **3a** was afforded exclusively in 98% isolated yield. The erythro selectivity is ascribed to the proton-bridged Cram's cyclic model.[17] The amide derivatives having alkyl, alkenyl, and aryl groups for R^1 underwent the erythro-selective reduction (selectivity >98%). The ester derivatives **1g** also gave erythro isomer **3g** predominantly, but no selectivity was observed in the case of **1l** (R^1 = Me) which probably failed to be reduced through a rigid cyclic transition state.

Noteworthy is that no epimerization at the chiral center takes place during the reaction under these acidic conditions: an optically active substrate **1k**[18] was succesfully transformed to methyl *erythro*-2-methyl-3-phenyl-3-hydroxypropanoate[19] by $PhMe_2SiH/H^+$ reduction followed by methanolysis (0.1 M MeONa in MeOH, 0 °C, 15 min, 93%) without loss of the enantiomeric purity.[21]

The stereocontrolled reduction of α-methyl-β-keto amide opens a way to each diastereomer of α-aryl-β-methyl-γ-aminopropyl alcohols of pharmacological interest.[22] For example, $PhMe_2SiH/F^-$ or H^+ reduction of **1m** followed by $LiAlH_4$ reduction gave *threo* or *erythro*-γ-amino alcohol **4**,[23] respectively.

(1) (a) Heathcock, C. H. "Asymmetric Synthesis"; by Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 111–212. (b) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Topics Stereochem.* **1984**, *13*, 1–116.

(2) Careful experiments at low temperatures are required for high selectivities. Strongly basic conditions of lithium enolate reactions or oxidative workup involved in boron enolate reactions are not applicable to the substrates which are sensitive to these conditions.

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(4) (a) Nakata, T.; Oishi, T. *Tetrahedron Lett.* **1980**, *21*, 1641. (b) Nakata, T.; Kuwabara, T.; Tani, Y.; Oishi, T. *Ibid.* **1982**, *23*, 1015. (c) Ito, Y.; Yamaguchi, M. *Ibid.* **1983**, *24*, 5385. (d) Dipardo, R. M.; Bock, M. G. *Ibid.* **1983**, *24*, 4805. (e) Evans, D. A.; Ennis, M. D.; Le, T. *J. Am. Chem. Soc.* **1984**, *106*, 1154.

(5) Gensler, W. J.; Johnson, F.; Sloan, A. D. B. *J. Am. Chem. Soc.* **1960**, *82*, 6074.

(6) Although it is reported that KBH_4[3] or Me_4NBH_4[4a] reduction of methyl 2-benzoylpropionate gave the threo alcohol predominantly, the selectivity is moderate (threo:erythro = ca. 7:3). **Note Added in Proof**: Quite recently, Yamaguchi et al. found threo-selective reduction of β-keto amides with $KBEt_3H$. Ito, Y.; Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* **1985**, *26*, 4643.

(7) (a) Fujita, M.; Hiyama, T. *J. Am. Chem. Soc.* **1984**, *106*, 4629. (b) Hiyama, T.; Kobayashi, K.; Fujita, M. *Tetrahedron Lett.* **1984**, *25*, 4959.

(8) Although racemic **1** was employed unless noted, one enantiomer is shown for the sake of simplicity.

(9) The relative stereochemical nomenclature: Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598, ref. 32.

(10) For the fluoride ion source, TASF was used throughout this work instead of tetrabutylammonium fluoride (TBAF) employed in the previous work.[7] Preparation of TASF: *U.S. Patent* 3 940 402; *Chem. Abstr.* **1976**, *85*, 6388*j*.

(11) In a parallel experiment without acid treatment, the *O*-silyl derivative was isolated in >90% yield.

(12) Rapidly filtered through silica gel short-path column to remove the solvent.

(13) (a) Chêrest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. (b) Anh, N. T.; Eisenstein, O. *Nouv. J. Chem.* **1977**, *1*, 61.

(14) Fluoride ion has a weak basicity in aprotic polar solvents: Parker, A. J. *Adv. Org. Chem.* **1965**, *5*, 1. Yakobson, G. G.; Akhmetova, N. E. *Synthesis* **1983**, 169.

(15) Enantioface selectivity in the hydrosilylation of prochiral ketones catalyzed by fluoride ion is discussed; Fry, J. L.; McAdam, M. A. *Tetrahedron Lett.* **1984**, *25*, 5859.

(16) Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633.

(17) Cram, D. J.; Wilson, D. R. *J. Am. Chem. Soc.* **1963**, *85*, 1245.

(18) Prepared according to the method reported by Evans et al.: $[\alpha]^{20}_D$ +153° (*c* 0.5, CH_2Cl_2) (lit.[4e] $[\alpha]_D$ +154.5° (*c* 0.5, CH_2Cl_2)).

(19) $[\alpha]^{25}_D$ −24.7° (*c* 1, $CHCl_3$); lit.[20] $[\alpha]^{25}_D$ −23.1° (*c* 3.2, $CHCl_3$).

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