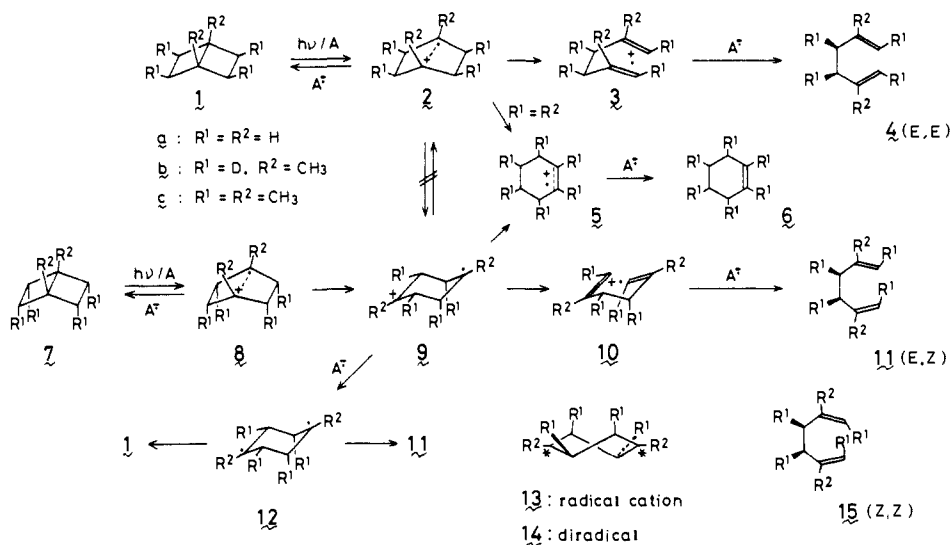**Scheme I**

stereospecific production of **4c** from **1c** thus indicates the generation of boat **2c** which underwent [2$_s$ + 1$_s$] cleavage while retaining its configuration. Resultant **3c** could be reduced to **4c** without loss of its stereochemical integrity via back ET from an acceptor radical anion. Closely related 2-methyl-2-butene radical cation has been shown to prefer a planar geometry and to be configurationally relatively stable.[11] The cleavage of **1b** with relatively high stereospecificity reinforces the above mechanism.

The formation of **11c** but not of **15c** from **7c** suggests that radical cation **8c**, in contrast to **2b** and **2c**, underwent ring flipping to give **9c**[14] prior to the cleavage reaction. The conformational instability of **8c** may be attributable to repulsive interactions among the four endo-methyl groups.[15] The observed correlation between the product composition and the $E_{1/2}^{red}$ of acceptor in the reaction of **7c** suggests the involvement of back ET in the product-determining stage. The oxidation potential ($E_{1/2}^{ox}$) of tert-butyl radical has been reported to be 0.09 V vs SCE.[17] If the $E_{1/2}^{ox}$ value of **12c** is assumed not to be greatly different from that value, free energy changes for the back ET from the radical anions of the acceptors here employed to **9c** [$\Delta G = E_{1/2}^{red}$(acceptor) − $E_{1/2}^{ox}$(**12c**)] should be in the range of −1.4–0.1 eV. In this range of ΔG, it is reasonable to assume that the higher the exothermicity of the back ET (−ΔG), the faster the process tends to be.[18] Thus, the isomerization of **7c** to **1c** and **11c** via the back ET to **9c** would predominate when the $E_{1/2}^{red}$ of acceptor was <−0.8 V vs SCE. As the exothermicity decreased, the back ET to **9c** would become slower and eventually overshadowed by the transformation of **9c** into **5c** and **10c**. The above scheme is supported by the reported formation of **1c** and **11c** upon thermolysis of **7c**[9] and the known tendency of **9a** to isomerize to **5a**.[1a,e] The invariably observed production of **11c** demonstrates that it derived from both the intermediates **9c** and **12c**.

The different stereospecificities of the ET-induced cleavage reactions of **1c** and **7c** clearly indicate that a concerted, one-step mechanism did not operate and that **2c** and **9c** did not interconvert to an appreciable extent within their lifetimes under the present conditions. Although the possibility that the acceptors might somehow influence the stereochemical course of the reactions of the radical cations is not rigorously ruled out, the stereochemical outcome of the observed rearrangements would most probably be due to their inherent properties. The boat structure of **2** would

be held in its form by virtue of a single-electron 1,4-bond. The stereospecific reaction pathway from **1** to **3** via **2** seems in good accord with the energy profile calculated by Pabon and Bauld for [2 + 1] olefin cyclodimerization.[19]

(19) Pabon, R.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 1145.

Highly Stereocontrolled Syntheses of Isomeric Pairs of Di- and Trisubstituted Olefins through [2,3] Sigmatropic Rearrangement of Allyldimethylammonium Methylides

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[2,3] and [3,3] sigmatropic rearrangements are often used for the stereoselective preparation of di- and trisubstituted olefins.[1] Herein we report an interesting [2,3] sigmatropic N-ylide rearrangement that provides Z- or E-homoallylic dimethylamines with ≥95% stereoselectivity as exemplified in Scheme I.

Quaternization of allylic amine **1a** with MeI (24 h, 25 °C) furnished trimethylammonium iodide **2a** quantitatively. Treatment of **2a** (1 mmol) with excess NaNH$_2$ (20 mmol) in NH$_3$ (100 mL) resulted in the formation of the ammonium ylide intermediate followed by spontaneous [2,3] sigmatropic rearrangement (30 min, −33 °C) to give homoallylic dimethylamine **3a** in 72% yield. Capillary GC analysis showed **3a** to be 100% one isomer. The examination of **3a**[2] by ^{1}H NMR after derivatization to the corresponding trimethylammonium salt [NMR (CD$_3$OD) δ 5.71 (=CH, dq, J = 6.6, 10.6 Hz), 5.35 (=CH, dt, J = 7.0, 10.6 Hz)] and the observation of 20% NOE between the C-5 methyl protons

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(14) Chair **9** and **12** cannot be distinguished from twist-boat forms **13** and **14**, respectively, in the present reactions. The parent species has been shown to possess a chair structure.[1e]

(15) According to molecular mechanics calculations (MM2),[16] **7c** is less stable by 8 kcal/mol than **1c** and a dihedral angle between the two rings in **7c** is significantly widened (by ca. 10°) compared to that in **1c**.

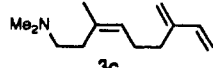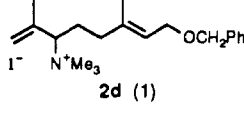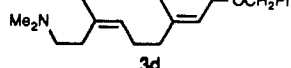(16) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.
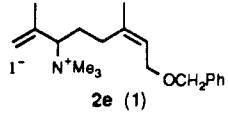
(17) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

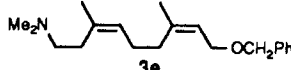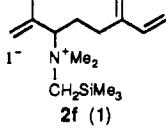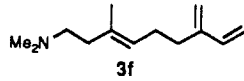(18) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(1) Review: Faulkner, D. J. *Synthesis* **1971**, 175. [2,3]: (a) Büchi, G.; Wuest, H. *Helv. Chim. Acta* **1967**, *50*, 2440. Sharpless, K. B.; Lauer, F. J. *Am. Chem. Soc.* **1972**, *94*, 7154. Grieco, P. A.; Boxler, D.; Hiroi, K. *J. Org. Chem.* **1973**, *38*, 2572. Brownbridge, P. B.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 212. Still, W. C.; Mitra, A. *J. Am. Chem. Soc.* **1978**, *100*, 1927. (b) Inoue, S.; Iwase, N.; Miyamoto, O.; Sato, K. *Chem. Lett.* **1986**, 2035. [3,3] review: Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.

(2) **3a** and **3b** formed azeotropic mixtures with the extracting solvent (ether, pentane).

Table I. Applicability of the Present Method for the Stereoselective Preparation of Trisubstituted Olefins

ammonium salt (mmol)	base or reagent and solvent (mmol/mL)	conditns, °C/h	product[a,b]	yield, % (Z:E)
2c (1)	LiN(SiMe₃)₂/NH₃ (40/100)	−70/1.0	3c	76 (95:5)
2d (1)	LiN(SiMe₃)₂/NH₃ (40/100)	−70/2.0	3d	70 (95:5)
2e (1)	LiN(SiMe₃)₂/NH₃ (40/100)	−70/2.0	3e	76 (95:5)
2f (1)	nBu₄NF/HMPA (2/50)	25/1.0	3f	61 (0:100)
2f (1)	CsF/HMPA (2/50)	25/1.0	3f	55 (0:100)

[a] An examination by ¹H NMR (CDCl₃) [3c, δ 1.71 (CH₃, s); 3d, δ 1.69 (CH₃, s), 1.65 (CH₃, s); 3e, δ 1.76 (CH₃, s), 1.68 (CH₃, s)] suggested that each isomer should be the Z isomer. Each minor isomer 3g and 3h in 3d and 3e was separated carefully by column chromatography on silica gel, and the examination by ¹H NMR (CDCl₃) [3g, δ 1.62 (2 CH₃, s); 3h, δ 1.76 (CH₃, s), 1.60 (CH₃, s)] showed them to be the E isomers. [b] Capillary GC analysis showed 3f to be 100% one isomer, and this was identical with the minor isomer in 3c [3f, ¹H NMR (CDCl₃) δ 1.62 (CH₃, s)].

Scheme I

Scheme II
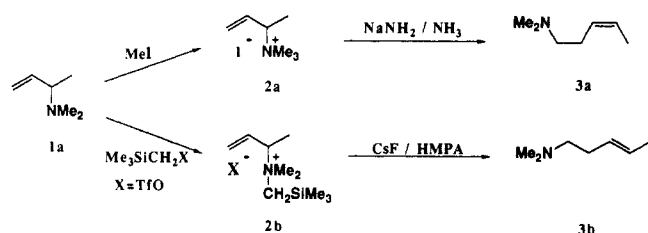
and the C-2 methylene protons strongly suggested that this isomer should be the Z isomer.

On the other hand, quaternization of **1a** with (trimethylsilyl)methyl triflate (24 h, 25 °C) afforded salt **2b** quantitatively. Desilylation of **2b** (1 mmol) with CsF (2 mmol) in HMPA (50 mL) resulted in the formation of a methylide intermediate followed by rearrangement (60 min, 25 °C) to afford amine **3b** in 68% yield. Capillary GC analysis showed **3b**[2] to be 100% one isomer and different from **3a**. The examination of the derived trimethylammonium salt by ¹H NMR [NMR (CD₃OD) δ 5.74 (=CH, dq, J = 6.7, 17.3 Hz), 5.31 (=CH, dt, J = 7.0, 17.3 Hz)] supported it as the E isomer.
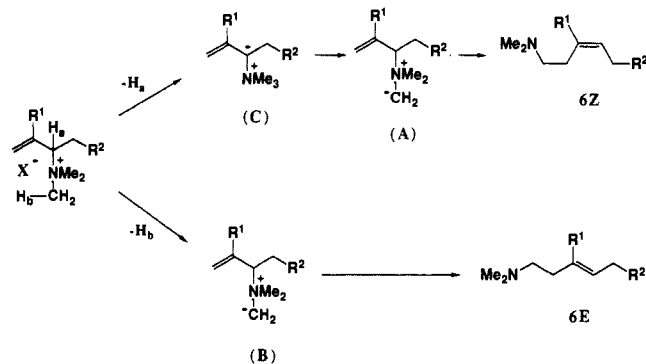
More remarkable is the successful applicability of the present method for the stereoselective preparation of trisubstituted olefins with high stereoselectivity (Table I).

In order to find out why the rearrangement under basic conditions afforded Z olefins predominantly, the following experiments were undertaken.
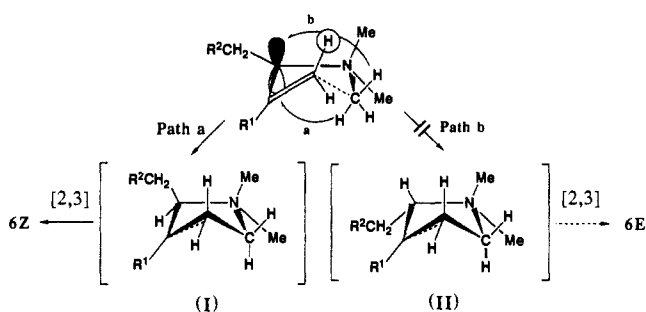
Treatment of 1-deuterio ammonium salt **4** (96 ± 4% D)[3] with NaNH₂ afforded again (Z)-amine **3a** with complete stereoselectivity. Assay of **3a** by NMR spectroscopy showed no detectable deuterium in the olefinic region. Another deuterium-containing ammonium salt, **5** (96 ± 4% D),[3] was treated with NaNH₂ to give a mixture of Z and E olefinic amines.[4] The deuterium content

Scheme III

of (Z)-amine **3c** was analyzed as above and found to be nearly 0, and that of (E)-amine **3f** was 96 ± 4% D.

These experimental facts obviously suggest that the formation of Z olefins **6Z** involves a two-step mechanism for the ylide generation and that the rearrangements of both ylide A and ylide B are stereospecific (Scheme II). Although both ylides are identical in their molecular formula, one should differ from the

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(3) The deuterium contents were calculated from ¹H NMR integration.
(4) The Z and E olefins (3c and 3f) were obtained in a ratio of 57:43 (by GC) in 72% combined yield and were separated carefully by column chromatography on silica gel. A similar rearrangement of unlabeled ammonium salt 2c with NaNH₂ afforded again the Z and E olefins (3c and 3f) in a ratio of 57:43 (by GC) in 75% combined yield (cf. the first run of Table I). Thus the isotope effect was not observed in the rearrangement.
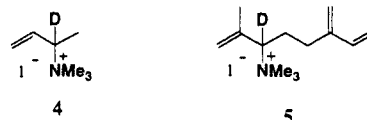
other in geometry, which consequently determines the stereo-chemistry of the olefin produced.

As to the formation of *E* olefins via ylide **B**, the direct removal of a proton from an *N*-methyl group or removal of the tri-methylsilyl group from **2b** or **2f** affords ylide **B**, which may undergo [2,3] sigmatropic rearrangement leading to *E* olefins via the usual concerted transition state of a doubly suprafacial mode.[5,1b]

On the other hand, the [2,3] sigmatropic rearrangement of ylide **A** may take place via transition state **I** or **II** to give the *Z* or *E* olefin, respectively (Scheme III). It should be noted that the conformational preference of **I** over **II** (R^1 = H and CH_3) does not originate from the vicinal repulsion between R^2CH_2 and R^1 on the vinyl carbon, which was claimed as an important factor for the *Z*-selective Wittig rearrangement (R^1 = CH_3 only) by Still et al.[1a] The present [2,3] sigmatropic rearrangement as well as other examples[6,7] takes place very rapidly at low temperature, so the rearrangements seem to have a very early (i.e., reactant-like) transition state, and then methylide intermediate **A** undergoes spontaneous rearrangement as it is formed, before conformational equilibrium to afford the *Z* olefin. A definitive explanation for this exceptional preference of **I** over **II** cannot be offered at the present time, but one possible explanation may be that only one direction (path a) may be available for the [1,3] shift of a proton in ylide **C** because the *cis*-hydrogen of the vinyl group interferes with proton migration in the other direction (path b).

It will require much more experimentation to determine the precise reaction mechanism, including whether it involves inter- or intramolecular proton transfer.[8]

Since the product amines can be converted into the corresponding aldehydes via the Polonovsky reaction,[9] we think the present method will find application in the field of the synthesis of terpenoids and biologically active substances.

(5) Yamamoto, Y.; Oda, J.; Inouye, Y. *J. Org. Chem.* **1976**, *41*, 303.
(6) Baldwin, J. E.; Patrik, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 3556.
(7) Evans, D. A.; Andrews, G. C. *J. Am. Chem. Soc.* **1972**, *94*, 3672.
(8) For example; Cerè, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *Tetrahedron Lett.* **1983**, 839. Vedejs, E.; Hagen, J. P.; Roach, B. L.; Spear, K. L. *J. Org. Chem.* **1978**, *43*, 1185. Padwa, A.; Gasdaska, J. R. *Tetrahedron* **1988**, *44*, 4147.
(9) Cave, A.; Kan-Fan, C.; Potier, P.; Le Men, J. *Tetrahedron* **1967**, *23*, 4681.

Geometry Dependence of the Effect of a β-Substituent on the Rate of H–D Exchange: Evidence for a Stereoelectronic Component of the Polar Effect

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It is well-known that the ease of formation of an α-sulfonyl carbanion, $>\bar{C}-SO_2^-$, depends on the orientation of the bond being cleaved to yield the carbanion,[1] the readiest deprotonations, for example, being observed when the C–H bond is as shown in **1**, i.e., aligned with the internal bisector of the O–S–O angle, or, equivalently, antiperiplanar to the S–$C_{\alpha'}$ bond. The stereoelec-

1
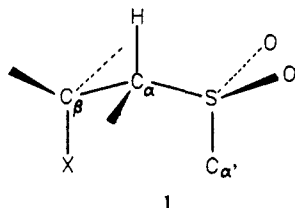
(1) For a recent review of α-sulfonyl carbanions, see: Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277–297.

Table I. Rate Constants for H–D Exchange of α-Hydrogens in Six-Membered Cyclic Sulfones[a]

compound[b]	reaction	$k_{exch}{}^c$ (M^{-1} s^{-1})
2	C3-H_{eq} → C3-D_{eq} C3-H_{ax} → C3-D_{ax} C10-H_{ax} → C10-D_{ax}	3.2×10^{-2} 1.6×10^{-4} $<3 \times 10^{-8d}$
3	(C3-H_2 + C5-H_2) → (C3-D_2 + C5-D_2)	2.15×10^{-2} $(4.30 \times 10^{-2})^c$
4	C2-H_{eq} → C2-D_{eq} C2-H_{ax} → C2-D_{ax}	4.5×10^{-4} *e*
5	(C2-H_2 + C6-H_2) → (C2-D_2, C6-D_2)	$\sim 10^{-6}$ $(\sim 2 \times 10^{-6})^c$
6	C2-H_{eq} → C2-D_{eq} C2-H_{ax} → C2-D_{ax}	1.2×10^{-6f} est. $\sim 10^{-8f}$
7	C3-H_{eq} → C3-D_{eq} C5-H_{eq} → C5-D_{eq} (C3-H_{ax} + C5-H_{ax}) → (C3-D_{ax} + C5-D_{ax})	1.6×10^{-2} 2.3×10^{-2} $\sim 2 \times 10^{-4}$
8	C2-H_2 → C2-D_2	4.8×10^{-3} $(9.6 \times 10^{-3})^c$

[a] With NaOD (0.017–0.05 M) in D_2O at 20 °C; determined by ^1H NMR (and ^{13}C NMR) spectroscopy. [b] Compounds **2**,[3] **3**, **4**,[4] **5**, and **6**[5] were either commercial materials or obtained as in the sources cited; **7** and **8** were obtained by simple syntheses from known precursors and were characterized by IR, ^1H and ^{13}C NMR spectra, and exact mass determinations. [c] The values shown in parentheses are second-order rate constants for H–D exchange on a per-hydrogen basis and were obtained by multiplying the experimental value (k_{exch}) by the statistical factor of two. This factor has its origin in the circumstance that at any particular instant half of the exchanging hydrogens (i.e., those that are axial at that time) are not in a conformation favorable for exchange. The values in parentheses are used in calculating the relative rates discussed in the text. [d] ^1H NMR showed <5% reaction after 6 months in 0.13 M NaOD at 20 °C. [e] Not determined, but NMR spectra show the axial exchange in **4** to be at least 25 times slower than the equatorial. [f] Reaction run in 0.20 M NaOD in D_2O–DMSO (80–20). The relative rates of the equatorial and axial hydrogens were determined in NaOD in D_2O–CD_3OD which showed a 90-fold greater rate for the equatorial exchange. Heating of the same mixture for a further 24 h at 80 °C gave total exchange of the C-2 hydrogens and no sign of any exchange at C-9.

tronic control exerted by the sulfonyl group enables us to find out if any related geometry-dependent factors operate at adjacent carbon centers. In this study we have looked at the effect of the geometry of an alkoxyl group β to the sulfonyl function, as in **1** (X = OR).[2] We have found that the orientation of the alkoxyl group with respect to the C–H bond significantly affects the ease of α-sulfonyl carbanion formation and suggest that this observation may provide insight into the nature of the polar effect in chemistry.

In NaOD in D_2O at 20 °C the equatorial hydrogen on C-3 of **2** exchanges readily, with a first-order dependence on [OH⁻].

(2) Experiments on the detritiation of $PhSO_2CHTCH_2X$ (Stirling, C. J. M.; Thomas, P. J. *J. Chem. Soc., Perkin Trans 2* **1977**, 1909–1913) show the rate to depend strongly on X, with an increase of about 5×10^4 on changing X from CH_3 to OPh; this effect was large enough that we were encouraged in our idea that a geometry-dependent effect might be both present and detectable.