Supplementary Material Available: Proton NMR spectra for **19b** and **25**; carbon NMR spectra for **19b** and **21**; full details on X-ray crystallographic analyses for compounds **9a**, **24**, and **25** including tables of coordinates, anisotropic temperature factors, distances, and angles (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal and can be ordered from the ACS; see any current masthead page for ordering information.

Diastereoselection in the Lewis Acid Catalyzed Cycloaddition Reaction of α-Alkoxy Imines[1]

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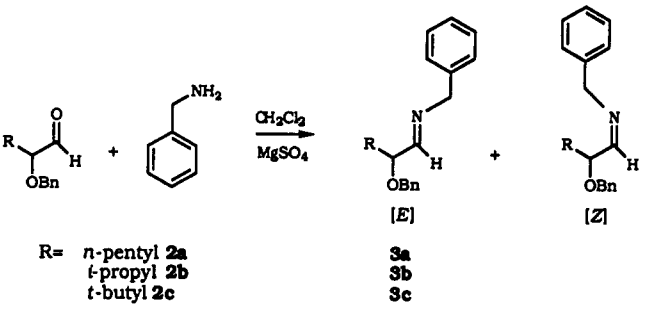
The Lewis acid catalyzed cycloaddition reactions of α-benzyloxy imines ($RCH(OCH_2C_6H_5)CH{=}NCH_2C_6H_5$) were investigated using 1,3-dimethoxy-1-[(trimethylsilyl)oxy]-1,3-butadiene. The observed diastereoselectivity was dependent on both the Lewis acid and substrate structure. Strong Lewis acids such as diethylaluminum chloride (DEAC) exhibited moderate to good success in promoting the cycloaddition reaction. When DEAC was used as the Lewis acid, the diastereoselectivity was also dependent on the stoichiometry of the Lewis acid to the substrate. In general, the diastereoselectivity increased with increasing steric bulk of the R group.

Introduction

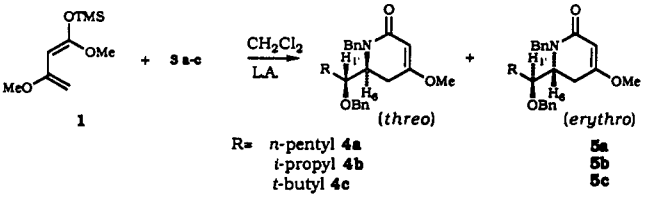
The use of heteroatom dienophiles in the Diels–Alder reaction has received much attention in recent years.[2] We have been interested in the cycloaddition reactions of α-heterosubstituted dienophiles such as α-alkoxy aldehydes,[3] α-amino aldehydes,[4] and α-alkoxy ketones.[5] The use of imines as dienophiles has also been of interest, and results using an α,β-dialkoxy imine have been reported.[6]

Cycloaddition reactions of imine and iminium species are of use in the construction of complex natural products and thus this reaction has received considerable attention.[2] Grieco has described cycloaddition reactions of iminium ion species generated under Mannich-type conditions.[7] Danishefsky has reported the Lewis acid catalyzed cycloaddition of simple alkyl imines in the synthesis of the natural product ipaldibine.[8] Ojima has observed reactions of imines with silyl ketene acetals catalyzed by titanium tetrachloride ($TiCl_4$).[9] Ojima provided evidence suggesting that the reaction proceeds by an addition–cyclization pathway rather than a cycloaddition pathway. Kunz has reported the Lewis acid mediated cycloaddition reaction of imines derived from pivaloylated sugars.[10] Kunz rationalized a "chelation-controlled" mechanism based upon the observed diastereoselectivities. The role of the group on the imine nitrogen has been the focus of recent work involving imine cycloadditions.[11] The endo/exo approach of the dienophile was influenced by the group on the imine nitrogen. The selectivity of these reactions was also dependent on whether kinetic or thermodynamic control was employed.

Scheme I



Scheme II



In our own laboratories, we have investigated the cycloaddition reactions of simple aldimines with an activated diene 1,3-dimethoxy-1-[(trimethylsilyl)oxy]-1,3-butadiene (Brassard's diene,[12] **1**).[13] The reaction proceeds efficiently when a strong Lewis acid such as diethylaluminum chloride (DEAC) or $TiCl_4$ is used. Boron trifluoride and magnesium dibromide ($MgBr_2$) were also efficient catalysts. Preliminary results also indicated that the choice of Lewis acid was important in the stereochemical outcome of cycloadditions involving α,β-dialkoxy imines.

Stereochemical results of cycloadditions using a variety of α-alkoxy imines and diene **1** are reported within. The nature of the Lewis acid in promoting the cycloaddition

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Table I. Cycloaddition Results of α-Alkoxy Imines with Diene 1

imine	Lewis acid	threo:erythro	yield,[a] %
3a	$SnCl_4$	83:17	15[c]
3b	$SnCl_4$	91:9	20[c]
3c	$SnCl_4$	>99:1[d]	10[c]
3a	Et_2AlCl[e]	50:50	60[f]
3a	Et_2AlCl[g]	90:10	55[f]
3b	Et_2AlCl[e]	40:60	64[f]
3b	Et_2AlCl[g]	60:40	58[f]
3c	Et_2AlCl[e]	91:9	68[f]
3c	Et_2AlCl[g]	>99:1[d]	75[f]

[a] Isolated yield of lactam(s). [b] 1.1 equiv of Lewis acid. [c] Large portion of starting aldehyde recovered. [d] Only one diastereomer observed by capillary GC. [e] 0.9 equiv of Lewis acid. [f] Small amount (<10%) of starting aldehyde recovered. [g] 2.0–2.1 equiv of Lewis acid.

was also investigated, and those results are reported.

Results and Discussion

Preparation and Configuration of α-Alkoxy Imines. The α-alkoxy imines (**3a–c**) were prepared from the corresponding α-alkoxy aldehydes (**2a–c**, Scheme I) and benzylamine.[14] The addition of a heterogeneous drying agent provided complete conversion to the imine which was typically not isolated prior to the cycloaddition reaction. Samples of each imine were obtained, however, for spectroscopic characterization. The stability of the imines was not extensively investigated, but solutions were stable for several days when kept under anhydrous conditions.

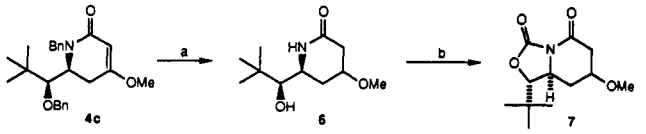
The imines **3a–c** may exist as either *E* or *Z* geometrical isomer. There has been some discussion concerning imine geometry,[15] and it has been assumed that the *E* isomer predominates based upon steric arguments.[16] The ^{13}C NMR spectra for imines **3a–c** was consistent with that expected for an *E* isomer.[17]

Cycloaddition Reactions. Scheme II depicts the cycloaddition reaction of imines **3a–c** with **1** to provide two possible diastereomeric cycloaddition products. A variety of conditions were employed, and the results are summarized in Table I. The reactions were performed in anhydrous methylene chloride as solvent.

Tin tetrachloride promoted cycloaddition but only to a small extent. To date, attempts to improve the extent of cycloaddition have not been successful. The cycloadducts were obtained in sufficient quantities to obtain a preliminary determination of diastereoselectivity. There was a preference in all cases for the threo diastereomer ("chelation" product). There was also an increase in the threo selectivity as the steric bulk of the side chain was increased. This trend would be expected from a "chelation-controlled" cycloaddition. Tin tetrachloride has been known to provide chelation with α- and β-alkoxy carbonyl compounds.[18]

The lanthanide shift reagent $Eu(hfc)_3$, which is an excellent catalyst for aldehydes,[3,4] did not promote cycloaddition when used in 5 mol %. NMR spectroscopic investigation seemed to indicate very little or no complexation of the shift reagent to the imine.[19] The reason for this may be based upon steric interference as the Lewis basicity of the imine should be sufficient for complexation. The use of stoichiometric quantities of $Eu(hfc)_3$ is not synthetically practical.

Scheme III[a]



[a] (a) Na/NH_3; (b) carbonyldiimidazole/THF.

The strong Lewis acid DEAC was known to promote cycloadditions from previous work in our laboratories.[3a,4a,5,6] The cycloaddition reaction of imines was promoted readily with DEAC. The extent of the reaction was near virtual completion (>90% based upon TLC and recovered starting materials). The moderate yields may be reflective of the difficulty in the extractive workup of aluminum-containing reaction mixtures.

A noticeable change in the diastereoselectivity was observed when the steric nature of the substrate was changed from **3a** to **3b** and **3c**. There was also a change in diastereoselectivity depending upon the stoichiometry of the Lewis acid to the substrate.[20] Increasing the stoichiometry from less than 1 equiv to 2 equiv resulted in an increase in threo selectivity. This change in selectivity was evident in all three examples (**3a–c**).

With **3b**, the reaction with either 1 or 2 equiv of catalyst provided relatively poor observed diastereoselectivity. In a strict "chelation" mechanism, the selectivity would be expected to be intermediate of those observed for **3a** and **3c**. The unusual selectivity change observed when the substrate structure was altered indicated that the mechanism may be more complicated than either a "chelation" or a "nonchelation" rationale can explain. This was also supported by the results when 2 equiv of DEAC was used rather than 1 equiv. More detailed data is required to understand the nature of the aluminum complex with the α-alkoxy imine and thus the possible mechanism of the cycloaddition.[21]

Determination of Relative Stereochemistry. Previous experience in the spectroscopic characteristics of lactone and lactam products of cycloadditions involving diene **1** has allowed for preliminary assignment of relative stereochemistry for the lactams. Typically, the coupling constant for the proton of the 6-position (H_6, see Scheme II) and the 1′-position of the side chain ($H_{1'}$) has had a larger value in the threo isomer compared to that measured in the erythro isomer.[3a,b] In each lactam mixture, the first

(14) The benzyl protecting group was chosen for nitrogen as it proved to be one of the more versatile protecting groups for Lewis acid conditions for cycloaddition.

(15) Fraser, R. R.; Banville, J.; Akiyama, F.; Chuaqui-Offermanns, N. *Can. J. Chem.* **1981**, *59*, 705.

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(18) For $SnCl_4$ chelates with α-alkoxy carbonyls, see: Reetz, M. T.; Harms, K.; Reif, W. *Tetrahedron Lett.* **1988**, *29*, 5881. For alkoxy aldehydes, see: Keck, G. E.; Andrus, M. B.; Castellino, S. *J. Am. Chem. Soc.* **1989**, *111*, 8136 and references therein.

(19) NMR studies were performed as lanthanide-induced shift studies. There were no observable shifts in either the proton or carbon NMR spectrum for the substrate imine **3a**.

(20) The effect of Lewis acid stoichiometry on the selectivity of C–C bond forming reactions has also been noted by the Heathcock group. See Heathcock, C. H. *Aldrichimica Acta* **1990**, *23*, 99.

(21) For discussions concerning the nature of organoaluminum compounds, see: Yamamoto, H. *Tetrahedron* **1988**, *44*, 5001. Sobota, P.; Mustafa, M. O.; Utico, J.; Lis, T. *J. Organomet. Chem.* **1989**, *368*, 257. van Koten, G.; van Vliet, M. R. P.; Rotteveel, M. A.; Schrap, M.; Vrieze, K.; Kojic-Prodic, B.; Speck, A. L.; Duisenberg, A. T. M. *Organometallics* **1986**, *5*, 1389. van Koten, G.; Vrieze, K.; Jastrzebski, J. T. B. H. *J. Organomet. Chem.* **1983**, *250*, 49. Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1976**, *15*, 2110. van Vliet, M. R. P.; Buysingh, P.; van Koten, G.; Vrieze, K. *Organometallics* **1985**, *4*, 1701. Benn, R.; Rufinska, A.; Janssen, E.; Lehmkuhl, H. *Organometallics* **1986**, *5*, 825. Benn, R.; Rufinska, A.; Janssen, E.; Lehmkuhl, H.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779. Robinson, G. H.; Sangokoya, S. A. *Organometallics* **1988**, *7*, 1453.

eluting isomer (via capillary GC) was found to be the isomer with the larger $J_{6-1'}$ constant (this was also the major isomer that was obtained when tin tetrachloride, a catalyst known to chelate, was used).

The circumstantial evidence was not sufficient to positively identify each isomer. To provide additional evidence, lactam **4c** was synthetically modified to bicyclic compound **7** which is more readily characterized with respect to relative stereochemistry (Scheme III).

Spectroscopic experiments (decoupling and nuclear Overhauser effect (NOE) spectroscopy) provided additional evidence for the relative stereochemistry. Coupling constants were established from decoupling experiments on **7** (described in the Experimental Section). The vicinal coupling constants were compared to constants that were calculated from MM2 calculations for each of the possible isomers.[22] The comparison of the observed constants ($J_{6-1'}$ = 9.40 Hz) with the calculated constants (9.11–9.35 Hz threo, 6.96–7.03 Hz erythro) indicated that the relative configuration of **7** was threo. Consistent with this assignment no NOE enhancement was observed between H_6 and $H_{1'}$ while there was an NOE enhancement between H_6 and the *tert*-butyl methyl protons.

The spectroscopic evidence, coupled with the previous knowledge of related compounds, indicated that the isomers **4a–c** were of threo relative stereochemistry. This stereochemistry is consistent with a chelation model although it should be noted that there is no directed evidence for a chelation mechanism.

Summary

The most efficient catalyst for the cycloaddition reactions was the strong Lewis acid DEAC. The selectivity of the reaction was dependent on both the substrate structure and the stoichiometry of the DEAC catalyst. Additional experimentation and knowledge concerning the nature of the DEAC–substrate complex must be obtained to clarify the mechanistic pathway.

Both a small substrate (**3a**) and a large substrate (**3c**) give a high degree of "chelation-control" product. This is in contrast to the corresponding aldehyde related to **3a** and **3b**[3a] which give the opposite stereochemistry when DEAC is used as a catalyst. Unfortunately, the *tert*-butyl substrate fails to give product in the aldehyde case. The cause for the change in stereoselectivity between aldehydes and imines remains to be explored.

Experimental Section

General Methods. NMR spectra were recorded at 199.50 or 300.15 MHz for proton, 49.92 or 75.10 MHz for carbon, using chloroform as reference unless otherwise noted. Benzylamine, diethylaluminum chloride (neat), zinc chloride (anhydrous), tin tetrachloride, titanium tetrachloride, magnesium dibromide etherate, palladium on carbon, cyclohexene, $Eu(hfc)_3$, ammonium formate, and carbonyldiimidazole were obtained from Aldrich Chemical Co. Dichloromethane was obtained from Fisher Scientific Products and was distilled over calcium hydride and stored over molecular sieves (4A). Tetrahydrofuran was obtained from Fisher and was distilled over potassium. Thin-layer chromatography (TLC) was performed using Merck aluminum-backed plates (silica gel 60, F-254) and were visualized by sulfuric acid char unless otherwise noted. Silica gel (230 mesh) was obtained from Fluka. High-performance liquid chromatography (HPLC) was performed with a Macro silica column using an RI detector. Capillary gas chromatography (GC) was performed using a methylphenyl silicone (OV-3) 50-m column and flame-ionization detection. All glassware was flame-dried under argon prior to use in anhydrous reactions.

(22) PCMODEL available from SERENA Software, Bloomington, IN.

General Procedure for the Preparation of α-Alkoxy Imines (3a–c). To a 1.0 M solution of aldehyde **2a–c** (typical scale 1 mmol, 1.0 equiv) in dichloromethane was added $MgSO_4$ (0.5 g per mmol aldehyde). Benzylamine was added slowly (1.0 equiv), and the suspension was stirred at room temperature for 1–4 h. The suspension was filtered through a pad of $MgSO_4$ into a predried flask equipped with stirbar and septum. If necessary, the imine solution was concentrated under an argon stream to a concentration of 1–2 M. If desired, the crude imine was isolated by complete removal of solvent. Yields were quantitative, and the purity was >90% as estimated by proton and carbon NMR.

General Procedure for the Cycloaddition Reaction with DEAC Catalysis. A solution of imines **3a–c** as described above (typical scale 0.5–1.0 mmol) was cooled under argon to −78 °C. Diethylaluminum chloride (0.9 or 2.1 equiv) was added slowly via syringe. After a 5-min equilibration, diene **1** (1.2–1.5 equiv) was added slowly (5–10 min). After 4 h, the red solution was warmed to −23 °C and stirred for 4–6 h. The solution was warmed to rt for 12 h. The reaction was quenched at 0 °C by careful addition of an equal volume of methanol. The solution was warmed to room temperature and diluted with diethyl ether (2× volume). An equal volume of water was added and the layers were separated. The aqueous layer was extracted with diethyl ether (2×), and the combined ether layers were dried ($MgSO_4$), filtered, and concentrated to yield the crude lactam as an oil. The crude lactam was purified via flash chromatography (ethyl acetate/hexanes, 1:1). The mixture of diastereomers was analyzed by capillary GC. Each diastereomer was isolated via preparative HPLC.

Lactam 4a: mass calculated for $C_{26}H_{34}NO_3$ (M + 1) 408.25387, mass found (Cl, M + 1), 408.2520; MS (Cl) 408.216 91; ^1H NMR ($CDCl_3$) δ 3.62 (dt, J = 6.83, 7.81 Hz, 1-H, H_1), 3.40 (dd, J = 7.32, 7.81 Hz, 1-H, H6); ^{13}C NMR ($CDCl_3$) δ 167.5, 138.1, 138.4, 128.6, 128.3, 127.8, 127.8, 127.7, 127.3, 93.4, 79.2, 72.9, 67.4, 55.5, 55.7, 48.3, 31.9, 28.6, 25.2, 22.7, 14.1; IR (NaCl, cm^{-1}) 3050, 2950, 1650, 1610, 1450, 1380, 1230. Capillary GC indicated a purity of 100% (250 °C for 2 min, 10 °C/min to 275 °C for 20 min, retention time was 16.9 min).

Lactam 5a: exact mass same as **4a**; ^1H NMR ($CDCl_3$) δ 3.60 (m, 1-H, $H_{1'}$), 3.40 (ddd, J = 1.95, 7.32, 5.70 Hz, 1-H, H_6); ^{13}C NMR ($CDCl_3$) δ 167.5, 138.4, 128.8, 128.6, 128.3, 127.8, 127.7, 127.3, 93.4, 79.2, 72.9, 67.4, 55.7, 55.2, 48.3, 31.9, 28.6, 25.2, 22.7, 14.1. Capillary GC indicated a purity of 100% (conditions as described for **4a**, retention time was 17.5 min).

Lactam 4b: mass calculated for $C_{24}H_{30}NO_3$ (M + 1) 380.2226, mass found (Cl, M + 1) 380.2201; MS (Cl) 380.216 91; ^1H NMR ($CDCl_3$) δ 3.52 (dd, J = 1.90, 6.83 Hz, 1-H, $H_{1'}$), 3.40 (ddd, J = 1.0, 4.9, 6.83 Hz, 1-H, H_6); ^{13}C NMR ($CDCl_3$) δ 166.7, 138.8, 138.4, 128.6, 128.2, 127.8, 127.3, 92.9, 84.6, 75.4, 55.3, 54.2, 47.7, 28.3, 20.3, 17.7; IR (NaCl, cm^{-1}) 3050, 2975, 1630, 1610, 1450, 1380, 1220. Capillary GC indicated a purity of 99% (conditions as described for **4a**, retention time was 12.2 min).

Lactam 5b: exact mass same as **4b**; ^1H NMR ($CDCl_3$) δ 3.44 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 166.0, 138.4, 138.3, 128.2, 128.0, 127.8, 127.5, 127.0, 94.0, 83.4, 75.2, 55.6, 54.6, 49.5, 30.3, 20.6, 15.0. Capillary GC indicated a purity of 100% (conditions as described for **4a**, retention time was 12.8 min).

Lactam 4c: mass calculated for $C_{25}H_{32}NO_3$ (M + 1) 394.2382, mass found (Cl, M + 1) 394.2406; MS (Cl) 394.216 91; ^1H NMR ($CDCl_3$) δ 3.49 (dd, J = 6.8, 8.3 Hz, 1-H, H_6), 3.15 (d, J = 8.3 Hz, 1-H, $H_{1'}$); ^{13}C NMR ($CDCl_3$) δ 166.5, 138.8, 138.1, 128.4, 128.2, 127.6, 127.5, 126.9, 94.4, 86.3, 75.3, 55.7, 52.5, 49.1, 35.9, 33.5, 26.2; IR (NaCl, cm^{-1}) 3050, 2950, 1640, 1620, 1425, 1380, 1210. Capillary GC indicated a purity of 100% (conditions as described for **4a**, retention time was 13.2 min).

Lactam 5c: exact mass same as **4c**; ^1H NMR ($CDCl_3$) δ 3.56 (dd, J = 1.45, 8.3 Hz, 1-H, H_6), 3.33 (s, 1-H, $H_{1'}$); ^{13}C NMR ($CDCl_3$) δ 166.2, 138.8, 138.1, 128.2, 128.0, 127.6, 127.4, 127.0, 93.1, 86.0, 75.0, 56.2, 53.4, 49.1, 36.0, 33.5, 26.2. Capillary GC indicated a purity of 100% (conditions as described for **4a**, retention ime was 13.6 min).

Cycloaddition Reactions with Tin Tetrachloride Catalyst. The solution of imine (typical scale was 0.5 mmol) was cooled under argon to −78 °C, and $SnCl_4$ (1.1 equiv) was added. The red solution was equilibrated for 5 min, and **1** (1.2–1.5 equiv) was added slowly. A gel typically formed, the flask was warmed to −23 °C (homogeneous), and the solution was stirred for 4–8 h.

The solution was warmed to room temperature over 12-16 h. Quench and workup were identical to that described above for DEAC.

Deprotection of Lactam 4c: Formation of 6. Lactam 4c (0.100 g, 0.30 mmol) was dissolved in 20 mL of liquid ammonia. Sodium metal (0.069 g, 3.0 mmol, 10 equiv) was added, and a deep blue color was obtained. The solution was allowed to reflux for 1 h with the persistence of blue color. The reaction was quenched with ammonium chloride (0.200 g, 13 equiv) and allowed to warm to room temperature in a hood. The residue was triturated with acetonitrile (5 mL), and the decanted solution was concentrated to a residue. The residue was triturated with methanol (5 mL) and was filtered through cotton. The filtrate was concentrated to yield an oil. The oil was purified by column chromatography (silica gel, $CHCl_3$/MeOH, 9/1) to yield 0.030 g of semisolid (57% yield). Purity was >90% as established by TLC: ^{1}H NMR ($CDCl_3$) δ 6.20 (bs, 1-H), 3.79 (m, 2-H), 3.35 (s, 3-H), 3.12 (bs, 1-H), 2.54 (t, 1-H), 2.46 (d, J = 4.1 Hz, 1-H), 2.06 (dt, J = 1.0, 13.5 Hz, 1-H), 1.74 (ddd, J = 2.4, 11.1, 13.5 Hz, 1-H), 0.996 (s, 9-H).

Preparation of 7. Deprotected compound 6 (0.030 g, 0.14 mmol) was dissolved in anhydrous THF (1 mL). 1,1'-Carbonyldiimidazole (0.024 g, 0.14 mmol) was added, and the solution was warmed to 35-40 °C for 24 h. The solution was concentrated in vacuo, and the crude oil was purified by column chromatography (silica gel 230 m, $CHCl_3$/MeOH, 9/1). The desired fractions were combined and concentrated to yield 15 mg of oil (50% yield). Purity was >90% as determined by TLC: exact mass calculated for $C_{12}H_{20}NO_4$ (M + 1), 242.13923, exact mass found (Cl, M + 1), 242.1400; MS (Cl) 242.210 128; ^{1}H NMR ($CDCl_3$) δ 4.25 (ddd, J = 3.00, 9.40, 11.1 Hz, 1-H), 3.90 (d, J = 9.40 Hz, 1-H), 3.85 (m, J = 3.00, 3.30, 5.10 Hz, 1-H), 3.36 (s, 3-H), 2.75 (dd, J = 3.00, 5.10 Hz, 2-H), 2.30 (ddd, J = 3.00, 3.30, 13.8 Hz, 1-H), 1.75 (ddd, J = 3.30, 11.1, 13.8 Hz, 1-H), 1.03 (s, 9-H); ^{13}C NMR ($CDCl_3$) δ 166.6, 150.9, 87.3, 72.5, 56.3, 51.7, 38.6, 33.8, 33.3, 25.1.

Nuclear Overhauser Effect (NOE) Spectroscopy. Homonuclear decoupling was first performed (QE 300 NMR spectrometer) to identify irradiation frequencies. The irradiation power was 2900, and the offset was determined from chloroform at 7.26 ppm. Irradiation and pulse length were 20 s followed by a 0.5-s delay. The spectrum was obtained after 24 pulses. The NOE experiment was performed with irradiation power of 3200 under identical pulse conditions. The reference spectrum was obtained with a 10 000-Hz offset.

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Registry No. 1, 74272-66-5; **2a**, 96759-99-8; **2b**, 96925-01-8; **2c**, 128495-75-0; **3a**, 137869-45-5; **3b**, 137869-46-6; **3c**, 137869-47-7; **4a**, 137869-48-8; **4b**, 137869-49-9; **4c**, 137869-50-2; **5a**, 137895-23-9; **5b**, 137869-51-3; **5c**, 137869-52-4; **6**, 137869-53-5; **7**, 137895-24-0; $SnCl_4$, 7646-78-8; $PhCH_2NH_2$, 100-46-9; diethylaluminum chloride, 96-10-6.

Supplementary Material Available: Spectral data for compounds **3a-c**, **4a-c**, **5a-c**, and 7 (16 pages). Ordering information is given on any current masthead page.

Tunable Regioselectivity Associated with the Reaction of 2,3-Dihalo-1-(phenylsulfonyl)-1-propenes with Ambident Nucleophilic Reagents

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2,3-Dihalo-1-(phenylsulfonyl)-1-propenes, obtained by the addition of bromine or iodine onto (phenylsulfonyl)propadiene, were found to exhibit interesting reactivity as both mono- and dielectrophiles, with the mode of reactivity depending upon the nature of the nucleophile as well as the reaction conditions. Thus, amines or thiophenols smoothly effected substitution at the allylic site, while sodium methoxide reacted at the vinylic position through an addition-elimination process. In the realm of ambident nucleophiles, β-dicarbonyl compounds in a medium of NaH/*tert*-butoxide/THF gave 2-alkyl-3-acyl-4-[(phenylsulfonyl)methyl]furans, produced by initial allylic S_N2 displacement followed by 5-*exo-trig* cyclization. Conversely, such β-dicarbonyls in a methoxide/methanol system yielded 2-alkyl-4-[(phenylsulfonyl)methyl]furans, where reaction proceeds by initial addition-elimination on the vinyl sulfone moiety. In contrast, silyl enol ethers in the presence of silver tetrafluoroborate resulted in products derived from S_N2 displacement at the allylic site. Thioamides could be used to form 2-substituted thiazoles by initial allylic displacement by the sulfur atom followed by an addition-elimination reaction. Thus, a variety of compounds were prepared from 2,3-dihalo-1-(phenylsulfonyl)-1-propenes by the proper choice of reagents and reaction conditions.

Allenes play an important role in many aspects of organic chemistry.[1-3] Their ability to enter into reactions as either a nucleophile or an electrophile provides the synthetic chemist with a variety of methods for preparing more complex compounds.[4] The addition of electrophilic reagents to allenes is a well-studied process,[5] as is the synthesis of alkene-substituted heterocycles via intramolecular nucleometallations of allenes using mercury(II) or silver(I) salts.[6-9] For simple alkyl-substituted allenes,

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