2.85, 2.88 Hz, 1 H, β-enol ether CH), 4.15 (d, J = 3.24 Hz, 1 H, oxetane junction CH), 3.92 (br d, J = 7.33 Hz, 1 H, allylic oxy CH), 3.47 (m, 1 H, allylic CH), 2.20 (br, 1 H, OH), 0.98, 0.96 (s, 3 H), 0.91 (s, 3 H) ppm; $^{13}$C NMR (62.81 MHz, $CDCl_3$) 161.71, 161.0, 107.78, 101.71, 101.04, 100.2, 100.0, 76.24, 75.91, 45.76, 45.76, 35.02, 34.04, 26.00, 25.90, 22.92 ppm; IR (film) ν 1600 (w), 1479 (m), 1364 (m), 972 (s) cm$^{-1}$. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 69.82; H, 9.95.

**[1(*R*,*S*),5(*R*,*S*)]-3-Methyl-6(*R*,*S*)-(1,1-dimethylethyl)-2,7-dioxabicyclo[3.2.0]hept-3-ene (Table I, entry 2)**: $^1$H NMR (500 MHz, $CDCl_3$) δ 6.13 (d, J = 4.5 Hz, 1 H, acetal CH), 4.87 (m, 1 H, β-enol ether CH), 4.16 (d, J = 3.31 Hz, 1 H, oxetane junction CH), 3.43 (m, 1 H, allylic CH), 0.92 (s, 9 H, tBu) ppm; MS, m/e (percent) 43 (10.87), 45 (23.3), 59 (46.9), 74 (41.5), 82 (100.0), 149 (29.5), 168 (2.1); HRMS (DIP, CI) calcd for $C_{10}H_{16}O_2$ (M + 1) 169.1229, found 169.1222.

**[1(*R*,*S*),5(*R*,*S*)]-3-(Trimethylstannyl)-6(*R*,*S*)-(1,1-dimethylethyl)-2,7-dioxabicylo[3.2.0]hept-3-ene (Table I, entry 3)**: $^1$H NMR (250 MHz, $CDCl_3$) δ 6.19 (d, J = 4.32 Hz, 1 H, acetal CH), 5.37 (d, J = 2.84 Hz, 1 H, β-enol ether CH), 4.11 (d, J = 3.28 Hz, 1 H, oxetane junction CH), 3.41 (m, 1 H), allylic CH), 0.92 (s, 9 H, tBu), 0.26 (t, $J_{Sn-H}$ = 27.86 Hz, 9 H, $SnMe_3$); $^{13}$C NMR (62.81 MHz, $CDCl_3$) δ 166.8, 116.0, 108.6, 99.7, 46.3, 34.2, 24.1, -9.7 ppm; IR (film) 1600 (w), 1363 (w), 1057 (m), 968 (s), 775 (s), 534 (m) cm$^{-1}$.

**[1(*R*,*S*),5(*R*,*S*)]-3-(2,2-Dimethyl-1(*R*,*S*/*S*,*R*)-hydroxypropyl)-6(*R*,*S*)-*n*-octyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (Table I, entry 5)**: 1:1 mixture of diastereomers; $^1$H NMR (250 MHz, $CDCl_3$) δ 6.24 (overlapping d, J = 4.09 Hz, 1 H, acetal CH), 5.16, 5.13 (d, J = 2.6, 2.9 Hz, 1 H, β-enol ether (CH) 4.49 (m, 1 H, oxetane junction (CH), 3.94 (br m, 1 H, allylic oxy CH), 3.46 (m, 1 H, allylic CH), 1.78 (br s, 1 H, OH), 1.24 (br m, 14 H, aliphatic methylenes), 0.85 (virtual t, J = 6.9 Hz, 3 H, terminal $CH_3$); $^{13}$C NMR (62.81 MHz, $CDCl_3$) δ 161.6, 160.85, 108.1, 101.4, 100.7, 92.6, 92.4, 76.2, 75.8, 49.4, 49.3, 37.0, 35.0, 31.7, 29.4, 29.3, 29.1, 26.6, 26.0, 25.9, 24.3, 22.5, 13.9 ppm; IR (film) ν 3400 (m), 1605 (m), 1465 (m), 1015 (s) cm$^{-1}$; MS, m/e (percent) 71 (6.3), 97 (100.0), 154 (4.0); HRMS (DIP, CI) calcd for $C_{18}H_{32}O_3$ (M + 1) 297.24309, found 297.2433.

**[1(*R*,*S*),5(*R*,*S*)]-3-(Tributylstannyl)-6(*R*,*S*)-ethyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (Table I, entry 6)**: $^1$H NMR (250 MHz, $CDCl_3$) δ 6.26 (d, J = 4.25 Hz, 1 H, acetal CH), 5.36 (d, J = 2.84 Hz, 1 H, β-enol ether CH), 4.35 (m, 1 H, oxetane junction CH), 3.35 (m, 1 H, allylic CH), (1.7, m, 2 H, Et $CH_2$), 1.56 (m, 6 H, Sn $CH_2$), 1.32 (m, 6 H, Sn $CH_2$), 1.04 (m, 6 H, Sn $CH_2$), 0.95 (t, J = 5.84 Hz, 3 H, Et $CH_3$), 0.87 (t, J = 7.1 Hz, 9 H, Sn $(CH_2)_3CH_3$) ppm; $^{13}$C NMR (62.81 MHz, $CDCl_3$) δ 166.6, 147.0, 121.2, 116.0, 109.0, 108.65, 93.1, 49.4, 30.1, 29.2, 29.0, 28.9, 28.7, 27.5, 27.3, 27.1, 26.6, 13.5, 12.6, 12.46, 10.04, 9.75, 8.77, 8.42, 7.03 ppm; IR (film) ν 1464 (w), 955 (m), 737 (w) cm$^{-1}$; MS, m/e (percent) 241 (27.2), 243 (46.2), 245 (62.8), 297 (41.2), 298 (27.6), 299 (65.7), 300 (35.9), 301 (100.0), 305 (17.4). Anal. Calcd for $C_{19}H_{36}O_2Sn$: C, 54.95; H, 8.74. Found: C, 55.03; H, 8.75.

**[1(*R*,*S*),5(*R*,*S*)]-3-(2,2-Dimethyl-1(*R*,*S*/*S*,*R*)-hydroxypropyl)-6(*R*,*S*)-ethyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (Table I, entry 7)**: mp (hexanes 37 °C; $^1$H NMR (250 MHz, $CDCl_3$) δ 6.23 (overlapping d, J = 4.45 Hz, acetal CH), 5.16, 5.13 (d, J = 2.71, 2.87 Hz, 1 H, β-enol ether CH), 4.43 (m, 1 H, oxetane junction CH), 3.93 (br d, J = 4.20 Hz, 1 H, allylic oxy CH), 3.41 (m, 1 H, allylic CH), 2.14 (br, 1 H, OH), 1.75 (m, 2 H, Et $CH_2$), 0.99, 0.97 (overlapping s, 9 H, tBu, 0.92 (t, J = 7.41 Hz, 3 H Et $CH_3$) ppm; $^{13}$C NMR (62.81 MHz, $CDCl_3$) δ 161.6, 160.7, 108.06, 101.47, 100.7, 93.6, 93.4, 76.21, 75.86, 48.96, 48.88, 35.06, 35.02, 29.82, 25.97, 25.85, 8.31 ppm; IR (film) ν 3450 (m), 1638 (m), 1469 (m), 1357 (m), 1076 (m), 1016 (m), 960.9 (m), 893.1 (w) cm$^{-1}$. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.66; H, 9.42.

**Coupling Procedure. [1(*R*,*S*),5(*R*,*S*)]-3-(1-Oxo-2-phenylethyl)-6(*R*,*S*)-phenyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (Table II, entry 3).** The vinyl stannane (74.9 mg, 0.16 mmol) was dissolved in dry benzene (500 mL) and *trans*-benzylchlorobis(triphenylphosphine)palladium(II) (7 mg, 9.0 mmol) was added, followed by phenylacetyl chloride (28 mL, 1.3 equiv). The solution was stirred at room temperature for 4 h and purified directly by silica gel chromatography (6:1 hexanes/ethyl acetate, 1% triethylamine as eluant) to afford 29.3 mg (62%) of the enone as a colorless crystalline solid: mp 93-94 °C (hexanes/$CH_2Cl_2$); $^1$H NMR (250 MHz, $CDCl_3$) δ 7.42-7.28 (m, 10 H, Ar), 6.63 (d, 1 H, J = 4.22 Hz), 6.35 (d, 1 H, J = 3.30 Hz), 5.63 (d, 1 H, J = 3.23 Hz), 4.04 (s, 2 H, $CH_2CO$), 3.82 (m, 1 H, allylic CH) ppm; $^{13}$C NMR ($CDCl_3$) δ 190.7, 157.2, 140.6, 133.5, 129.7, 128.9, 128.7, 128.6, 1272, 125.3, 112.0, 109.0, 91.7, 53.6, 46.1 ppm; IR (thin film) ν 1690 (s), 1610 (m), 1495 (m), 1455 (m), 1040 (s), 960 (s), 700 (s) cm$^{-1}$; HRMS (CI, DIP) calcd for $C_{19}H_{14}O_2$ 275.1073, found 275.1067.

**[1(*R*,*S*),5(*R*,*S*)]-Butyl 3-(1-oxoethyl)-2,7-dioxabicyclo-[3.2.0]hept-3-ene-6(*R*,*S*)-carboxylate (Table II, entry 1)**: mp (ether) 42 °C; $^1$H NMR (250 MHz, $CDCl_3$) δ 6.52 (d, J = 4.04 Hz, 1 H), 6.23 (d, J = 2.90 Hz, 1 H), 4.94 (d, J = 3.14 Hz, 1 H, oxetane junction CH), 4.21 (t, J = 6.67 Hz, 2 H, $OCH_2CH_2$), 3.93 (m, 1 H, allylic CH), 2.36 (s, 3 H, $COCH_3$), 1.65 (tt, J = 7.97 Hz, 2H $OCH_2CH_2$), 1.38 (m, 2 H, $O(CH_2)_2CH_2$), 0.92 (t, J = 7.40 Hz, 3 H, $CH_2CH_3$) ppm; $^{13}$C NMR (62.81 MHz, $CDCl_3$) δ 190.36, 169.99, 157.76, 110.58, 109.53, 85.30, 65.65, 50.24, 30.50, 26.67, 18.91, 13.42 ppm; IR (film) ν 1748 (s), 1694 (s), 1615 (m), 1182 (m), 949 (m) cm$^{-1}$; MS, m/e (percent) 95 (80.5), 110 (100.0), 111 (13.9), 139 (7.3), 240 (0.2); HRMS (DIP, EI) calcd for $C_{12}H_{16}O_5$ 240.0998, found 240.1005.

**[1(*R*,*S*),5(*R*,*S*)]-3-Phenyl-6(*R*,*S*)-phenyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (Table II, entry 2)**: colorless amorphous solid; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.69/7.34 (m, 10 H, Ar), 6.67 (d, J = 4.35 Hz, 1 H, acetal CH), 5.81 (d, J = 3.09 Hz, 1 H, β-enol ether CH), 5.62 (d, J = 3.05 Hz, oxetane junction CH), 3.84 (m, 1 H, allylic CH) ppm; IR (film) ν 1634 (w), 1451 (m), 1012 (m), 945 (s), 745 (s) cm$^{-1}$.

**[1(*R*,*S*),5(*R*,*S*)]-3-((*R*,*S*/*S*,*R*)-Hydroxyphenylmethyl)-6(*R*,*S*)-(1,1-dimethylethyl)-2,7-dioxabicyclo[3.2.0]hept-3-ene (Table II, entry 4)**: 1:1 mixture of diastereomers; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.47-7.30 (m, 5 H, Ar), 6.20 (overlapping d, J = 4.67 Hz, acetal CH), 5.41, 5.37 (overlapping d, J = 2.90, 2.86 Hz, 1 H, β-enol ether (CH), 5.12, 5.00 (m, 1 H, allylic oxy CH), 4.21 (overlapping d, J = 4.09, 3.68 Hz, 1 H, oxetane junction CH), 3.48 (m, 1 H, allylic CH), 2.57, 2.43 (br s, 1 H, OH), 0.92 (br s, 9 H, tBu) ppm; $^{13}$C NMR (62.81 MHz, $CDCl_3$) δ 186.47, 186.34, 177.86, 177.72, 162.04, 161.89, 140.10, 128.51, 128.29, 128.24, 126.89, 125.76, 125.08, 108.37, 101.67, 100.96, 99.96, 99.91, 70.40, 70.26, 45.95, 45.91, 35.83, 34.06, 23.91, 14.04, 10.20 ppm; IR (film) ν 3400 (m), 1144 (w), 1197 (m), 971 (s), 699 (m) cm$^{-1}$; HRMS (DIP, CI) calcd for $C_{16}H_{20}O_3$ (M + 1) 261.14913, found 261.1495.

**[1(*R*,*S*),5(*R*,*S*)]-3-(Ethoxyoxomethyl)-6(*R*,*S*)-phenyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (Table II, entry 5)**: $^1$H NMR (250 MHz, $CDCl_3$) δ 7.42-7.33 (m, 5 H, Ar), 6.63 (d, J = 4.33 Hz, 1 H, β-enone CH), 6.37 (d, J = 3.23 Hz, 1 H, acetal CH, 4.34 (q, J = 7.12 Hz, 2 H, $OCH_2CH_3$), 3.82 (m, 1 H, allylic CH), 1.33 (t, J = 7.12 Hz, 3 H, $OCH_2CH_3$) ppm; $^{13}$C NMR (62.81 MHz, $CDCl_3$) δ 160.04, 151.40, 140.67, 128.91, 125.40, 112.86, 109.12, 91.87, 61.52, 53.56, 14.08 ppm; IR (film) ν 1732 (s), 1634 (m), 1313 (m), 1115 (s), 703 (m) cm$^{-1}$; MS, m/e (percent) 68 (10.2), 95 (39.6), 96 (27.6), 112 (100.0), 141 (11.1); HRMS (DIP, CI) calcd for $C_{14}H_{14}O_4$ (M + 1) 247.09705. found 247.0963.

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## Stereoselective Syntheses of *S*-Phenyl Tetrahydrofuran-2-thiocarboxylate and Tetrahydropyran-2-thiocarboxylate Derivatives Using (Phenylthio)nitromethane

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We have recently described[1] the use of (phenylthio)-nitromethane[2,3] as a convenient reagent for the homolo-

(1) Banks, B. J.; Barrett, A. G. M.; Russell, M. A. *J. Chem. Soc., Chem. Commun.* **1984**, 670. Barrett, A. G. M.; Graboski, G. G.; Russell, M. A. *J. Org. Chem.* **1986**, *51*, 1012.

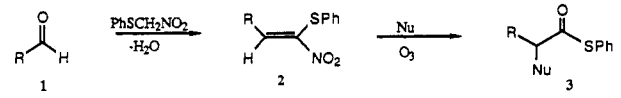
0022-3263/89/1954-4723$01.50/0 

**Table I**

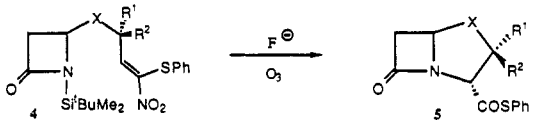
| starting aldehyde | method | yield of nitroalkene, % | thioester | yield, % | isomer ratio[a] |
|---|---|---|---|---|---|
| **6a** | A | 63 | | 0 | |
| **6b** | A[b] | 48 | **10a** | 68 | |
| | B[c] | 58 | | | |
| **6c** | A | 52 | **11a** | 75 | |
| **6d** | B | 54 | **12** | 11 | |
| **6e** | A | 57 | **10b** | 67 | 1:1 |
| **6f** | A | 50 | **10c** | 56 | 1.4:1 |
| **6g** | A | 51 | **10d** | 71 | trans only |
| **6h** | A | 48 | **11b** | 77 | 9.1:1 cis/trans |
| **6i** | A | 54 | **11c** | 67 | trans only |

[a] Determined from the $^1$H NMR spectrum of crude product. [b] See method A in Experimental Section. [c] See method B in Experimental Section.

gation of aldehydes to produce $\alpha$-substituted *S*-phenyl thioesters. In this process an aldehyde 1 was condensed

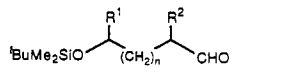


with (phenylthio)nitromethane to give the (*Z*)-nitroalkene **2**. Subsequent addition of a nucleophile followed by direct ozonolysis, according the McMurray procedure,[4] gave the $\alpha$-substituted thioester **3**. This chemistry has been successfully applied to the synthesis of several bicyclic $\beta$-lactams **5**[5] using as a key step the intramolecular addition



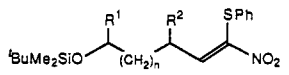
of a nitrogen (amide) nucleophile to a nitroalkene **4**. Herein, we report our observations that the intramolecular nucleophilic addition of an alkoxide to a nitroalkene may be used to prepare oxacycles in good yields.

The nitroalkene intermediates **7a–i** were prepared by the condensation reaction of the *tert*-butyldimethylsilyl-protected hydroxy aldehydes **6a–i**[6] with (phenylthio)-



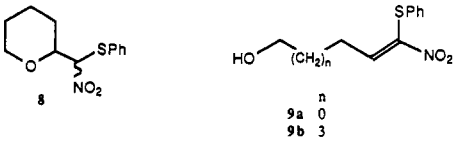
6 a-i

| Compound | $R^1$ | $R^2$ | n |
|---|---|---|---|
| a | H | H | 0 |
| b | H | H | 1 |
| c | H | H | 2 |
| d | H | H | 3 |
| e | Me | H | 1 |
| f | Ph | H | 1 |
| g | H | Ph | 1 |
| h | Ph | H | 2 |
| i | H | Ph | 2 |



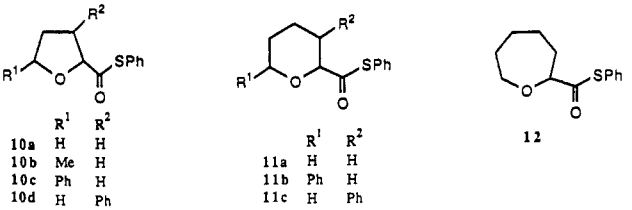
7 a-i

nitromethane. Thus the aldehydes were reacted with (phenylthio)nitromethane and potassium *tert*-butoxide in THF and *tert*-butyl alcohol followed by dehydration using methanesulfonyl chloride and ethyldiisopropylamine in dichloromethane (method A). Alternatively, the nitroalkenes were prepared directly from the aldehyde and (phenylthio)nitromethane using piperidinium acetate catalysis[7] (method B). Both methods gave the derived nitroalkenes in comparable yields although purification proved to be more straightforward with method A. Attempts to cyclize the nitroalkene **7c** using tetrabutylammonium fluoride in THF[5] resulted in extensive decomposition. However, treatment of **7c** with HF/pyridine resulted in smooth desilylation and cyclization to produce the nitroalkane **8**[8] (90%). Subsequent reaction of **8** with



potassium *tert*-butoxide and ozone gave the corresponding thioester **11a** (75%). This cyclization and oxidation process was successfully applied to the preparation of several tetrahydrofuran and tetrahydropyran systems (Table I). In contrast, nitroalkenes **7a** and **7d** failed to cyclize, and only the free alcohols **9a** and **9b** were isolated. Under more forcing conditions ($^t$BuOK, THF; $O_3$, $CH_2Cl_2$) alcohol **9b** was converted into the oxepane thioester **12** albeit in low yield (11%). Attempted cyclization of **9a** under these conditions resulted in extensive decomposition.

The 2,3-disubstituted tetrahydrofuran **10d** and tetrahydropyran **11c** were formed exclusively as the trans diastereoisomers.[9] Additionally, the 2,6-disubstituted tetrahydropyran **11b** was formed predominantly as the cis



| | $R^1$ | $R^2$ |
|---|---|---|
| 10a | H | H |
| 10b | Me | H |
| 10c | Ph | H |
| 10d | H | Ph |

| | $R^1$ | $R^2$ |
|---|---|---|
| 11a | H | H |
| 11b | Ph | H |
| 11c | H | Ph |

12

isomer (9.1:1). Clearly in this case cyclization took place with the phenyl substituent and nitroalkene residue pseudoequatorial in the transition state. In contrast, formation of the 2,5-disubstituted tetrahydrofuran derivatives **10b** and **10c** proceeded with little diastereoselectivity.

These results clearly demonstrate that (phenylthio)nitromethane is a useful reagent for the synthesis of tetrahydrofuran and tetrahydropyran derivatives from $\gamma$- and $\delta$-hydroxy aldehydes.

## Experimental Section

Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr disks or films on a Sargent Welch SP3-100, Perkin-Elmer 283, or Nicolet 7199 FT instrument. $^1$H NMR spectra were recorded on a Varian EM390A, JEOL FX270, Varian XL-400, or Varian VXR-300 spectrometer with tetramethylsilane as internal standard.

Mass spectra were recorded on a VG70700F or VG70-250SE mass spectrometer or were determined at the Midwest Center for Mass Spectrometry. Microanalyses were determined by G.D.

(2) Bordwell, F. G.; Bartmess, J. E. *J. Org. Chem.* **1978**, *43*, 3101.
(3) Miyashita, M.; Kumazawa, T.; Yoshikoshi, A. *J. Chem. Soc., Chem. Commun.* **1978**, 362.
(4) McMurry, J. E.; Melton, J.; Padgett, H. *J. Org. Chem.* **1974**, *39*, 259.
(5) Barrett, A. G. M.; Graboski, G. G.; Sabat, M.; Taylor, S. J. *J. Org. Chem.* **1987**, *52*, 4693.
(6) Aldehydes **6a–d** were prepared by monoprotection of the appropriate diol followed by pyridinium dichromate oxidation. Aldehydes **6e**, **6f**, and **6h** were prepared by ozonolysis of the *tert*-butyldimethylsilyl-protected hydroxy alkene. Aldehydes **6g** and **6i** were derived from phenylacetic acid by alkylation, (LDA (2 equiv), HMPA, THF), reduction ($BH_3$·$Me_2S$, THF), and oxidation (PDC, $CH_2Cl_2$).
(7) Ashwell, M.; Jackson, R. F. W. *J. Chem. Soc., Chem. Commun.* **1988**, 282.
(8) The cyclic nitroalkane 8 was isolated as a 5.2:1 mixture of diastereoisomers.
(9) The assigned stereochemistry of tetrahydropyran **11c** was consistent with the observed axial–axial coupling ($J$ = 9.6 Hz) of protons C2-H and C3-H. Tetrahydrofuran **10d** was converted to the known methyl ester ($Hg(OAc)_2$/MeOH); see: Nozaki, H.; Takaya, H.; Noyori, R. *Tetrahedron* **1966**, *22*, 3401.

Searle and Company, Skokie, IL 60077. Samples for microanalyses that were oils were purified by flash chromatography, rotary evaporated, and subsequently further evaporated at ca. 0.1 mmHg.

Hexane, diethyl ether, and ethyl acetate were purified by distillation. THF was dried by distillation under nitrogen from sodium benzophenone ketyl. DMF, $CH_2Cl_2$, and $Et_3N$ were freshly distilled from $CaH_2$. All reactions were carried out under dry nitrogen. Silica gel for chromatography refers to the Merck product Kieselgel 60 (Art. 9385). Thin-layer chromatography was performed on Merck Kieselgel 60 F254 (Art. 5715).

**Preparation of Nitroalkenes. Method A.** $^t$BuOK in $^t$BuOH (1.0 M; 0.15 mL, 10 mol %) was added to a solution of (phenylthio)nitromethane (0.51 g) in $^t$BuOH and THF (1:1, 20 mL) at 0 °C. After 15 min the aldehyde (3 mmol) in THF (2 mL) was added. The solution was allowed to warm to room temperature and to stir for 4–8 h (TLC). The solution was diluted with pH 7.0 phosphate buffer (75 mL) and extracted with $Et_2O$ (3 × 30 mL). The combined $Et_2O$ extracts were washed with water (2 × 25 mL), dried, and evaporated in vacuo. Chromatography ($SiO_2$; hexanes:$Et_2O$ 10:1) gave the pure nitro alcohols which were used directly in the next step. To a solution of the nitro alcohol (1.1 mmol) in $CH_2Cl_2$ (20 mL) at −78 °C was added $MeSO_2Cl$ (0.13 mL) and $EtN^iPr_2$ (0.57 mL) simultaneously. The solution was stirred at −78 °C for 10 min and at −30 °C for an additional 10 min. The solution was washed with $H_2O$ (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and $H_2O$ (10 mL), dried, and evaporated in vacuo in the presence of silica. Chromatography ($SiO_2$; 10:1 hexanes:$Et_2O$) gave the pure nitroalkene which was used directly in the next step.

**Method B.** Piperidinium acetate (22 mg) was added to a solution of aldehyde (3 mmol) and (phenylthio)nitromethane (558 mg) in $CH_2Cl_2$ (20 mL) at room temperature. The resulting mixture was stirred for 1 h, and then it was washed with $H_2O$ (10 mL), dried, and evaporated in vacuo in the presence of silica. Chromatography ($SiO_2$; hexanes:$Et_2O$ 10:1; twice) gave the pure nitroalkene which was used directly in the next step.

**1-[(*tert*-Butyldimethylsilyl)oxy]-4-nitro-4-(phenylthio)-(*Z*)-3-butene (7a)**: an oil; $R_f$ 0.70 (hexanes:$Et_2O$ 3:1); IR (film) 2950, 1540, 1335, 1105 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.82 (t, 1 H, $J$ = 7.6 Hz), 7.30 (m, 5 H), 3.83 (t, 2 H, $J$ = 5.6 Hz), 2.81 (q, 2 H, $J$ = 7.2 Hz), 0.9 (s, 9 H), 0.07 (s, 6 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 148.3, 146.0, 132.4, 129.4, 129.0, 127.6, 61.0, 34.3, 25.9, 18.3, −5.4; mass spectrum (EI), $m/e$ 320, 252, 160, 105, 73.

**1-[(*tert*-Butyldimethylsilyl)oxy]-5-nitro-5-(phenylthio)-(*Z*)-4-pentene (7b)**: an oil; $R_f$ 0.70 (hexanes:$Et_2O$ 3:1); IR (film) 2960, 2870, 1620, 1535, 1325, 840 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83 (t, 1 H, $J$ = 7.6 Hz), 7.3 (m, 5 H), 3.68 (t, 2 H, $J$ = 6 Hz), 2.69 (q, 2 H, $J$ = 7.2 Hz), 1.76 (m, 2 H), 0.89 (s, 9 H), 0.05 (s, 6 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 148.8, 147.1, 132.6, 129.4, 129.1, 127.6, 62.2, 31.3, 27.7, 25.9, 18.3, −5.4; mass spectrum (EI), $m/e$, 266, 192, 159, 149, 75.

**1-[(*tert*-Butyldimethylsilyl)oxy]-6-nitro-6-(phenylthio)-(*Z*)-5-hexene (7c)**: an oil; $R_f$ 0.87 (hexanes:$Et_2O$ 2:1); IR (film) 2940, 1618, 1535, 1328, 1105, 840 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.77 (t, 1 H, $J$ = 8 Hz), 7.3 (m, 5 H), 3.63 (t, 2 H, $J$ = 8 Hz), 2.92 (q, 2 H, $J$ = 8 Hz), 1.61 (m 4 H), 0.89 (s, 9 H), 0.04 (s, 6 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 148.5, 147.5, 132.0, 129.4, 129.0, 127.6, 62.4, 32.4, 30.4, 25.9, 24.7, 18.5, −5.4; mass spectrum (EI), $m/e$ 158, 141, 110, 94, 85.

**1-[(*tert*-Butyldimethylsilyl)oxy]-7-nitro-7-(phenylthio)-(*Z*)-6-heptene (7d)**: an oil; $R_f$ 0.77 (hexanes:$Et_2O$ 3:1); IR (film) 2960, 1630, 1545, 1345, 845 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.71 (t, 1 H, $J$ = 8 Hz), 7.24 (m, 5 H), 3.55 (t, 2 H, $J$ = 6.4 Hz), 2.55 (q, 2 H, $J$ = 7.6 Hz), 1.51 (m, 4 H), 1.37 (m, 2 H), 0.85 (s, 9 H), 0.00 (s, 6 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 148.5, 147.2, 132.5, 129.4, 128.9, 127.5, 62.7, 32.3, 30.6, 27.9, 25.9, 25.6, 18.3, −5.33; mass spectrum (EI), $m/e$, 324, 294, 226, 185, 93.

**2-[(*tert*-Butyldimethylsilyl)oxy]-6-nitro-6-(phenylthio)-(*Z*)-5-hexene (7e)**: an oil; $R_f$ 0.77 (hexanes:$Et_2O$ 3:1); IR (film) 2940, 2870, 1545, 1330, 840 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 (t, 1 H, $J$ = 6 Hz), 7.3 (m, 5 H), 3.90 (m, 1 H), 2.67 (m, 2 H), 1.65 (m, 2 H), 1.16 (d, 3 H, $J$ = 7 Hz), 0.89 (s, 9 H), 0.06 (s, 3 H), 0.04 (s, 3 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 148.9, 147.0, 132.5, 129.4, 129.0, 127.6, 67.8, 37.6, 27.0, 25.8, 23.5, 18.1, −4.3, −4.8; mass spectrum (EI), $m/e$, 250, 218, 109, 85.

**1-[(*tert*-Butyldimethylsilyl)oxy]-1-phenyl-5-nitro-5-(phenylthio)-(*Z*)-5-pentene (7f)**: an oil; $R_f$ 0.52 (hexanes:$Et_2O$ 3:1); IR (film) 2970, 2880, 1620, 1435, 1330, 840 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.88 (t, 1 H, $J$ = 7.8 Hz), 7.4 (m, 10 H), 4.92 (m, 1 H), 2.76 (m, 2 H), 2.05 (m, 2 H), 1.04 (s, 9 H), 0.19 (s, 3 H), 0.01 (s, 3 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 148.6, 147.1, 144.1, 132.5, 129.4, 129.1, 128.2, 128.1, 127.5, 127.3, 125.7, 74.0, 38.7, 26.6, 25.8, 18.1, −4.7; mass spectrum (EI), $m/e$ 351, 218, 147, 109, 75.

**1-[(*tert*-Butyldimethylsilyl)oxy]-3-phenyl-5-(phenylthio)-5-nitro-(*Z*)-4-pentene (7g)**: an oil; $R_f$ 0.72 (hexanes:$Et_2O$ 4:1); IR (film) 3000, 2800, 1480, 1100, 750 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.87 (d, 1 H, $J$ = 8 Hz), 7.18–7.40 (m, 10 H), 4.37 (m, 1 H), 3.58 (m, 2 H), 2.08 (m, 2 H), 0.89 (s, 9 H), 0.01 (s, 6 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 150.2, 146.4, 140.4, 132.2, 129.4, 129.2, 129.1, 127.8, 127.6, 60.2, 43.9, 38.6, 25.8, 18.2, −5.4, −5.5; mass spectrum (FAB), $m/e$ 430 ($M^+$ + H), 404, 383, 298, 279, 250.

**1-[(*tert*-Butyldimethylsilyl)oxy]-1-phenyl-6-nitro-6-(phenylthio)-(*Z*)-5-hexene (7h)**: an oil; $R_f$ 0.70 (hexanes:$Et_2O$ 3:1); IR (film) 2960, 2860, 1620, 1435, 1225, 840, 690 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.87 (d, 1 H, $J$ = 8 Hz), 7.4 (m, 10 H), 4.83 (m, 1 H), 2.73 (m, 2 H), 1.8 (m, 4 H), 1.04, (s, 9 H), 0.18 (s, 3 H), 0.00 (s, 3 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 148.3, 147.3, 144.9, 132.3, 129.4, 128.9, 128.1, 127.6, 127.0, 125.7, 74.4, 40.3, 30.6, 25.8, 24.1, 18.2, −4.6, −5.0; mass spectrum (EI), $m/e$ 386, 265, 207, 187, 155, 117, 91, 75.

**1-[(*tert*-Butyldimethylsilyl)oxy]-4-phenyl-6-(phenylthio)-6-nitro-(*Z*)-5-hexene (7i)**: an oil; $R_f$ 0.72 (hexanes:$Et_2O$ (4:1) IR (film) 3000, 2800, 1490, 1100, 760 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 (d, 1 H, $J$ = 8 Hz), 7.18–7.54 (m, 10 H), 4.11 (m, 1 H), 3.60 (m, 2 H), 1.94 (m, 2 H), 1.48 (m, 2 H), 0.89 (s, 9 H), 0.01 (s, 6 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 150.3, 142.6, 140.3, 132.2, 130.1, 130.0, 129.5, 129.4, 129.1, 128.9, 127.6, 62.3, 46.9, 31.7, 30.4, 25.9, 18.2, −5.4; mass spectrum (FAB), $m/e$ 444 ($M^+$ + H), 397, 356, 265, 222.

**Deprotection and Cyclization of the Nitroalkenes.** To a solution of the nitroalkene (1 mmol) in $CH_2Cl_2$ (25 mL) at −78 °C was added HF/pyridine complex (70% HF; 1 mL). After 30 min, pyridine (2 mL) was added and the reaction mixture was warmed to 0 °C. The solution was washed with $H_2O$ (10 mL) and aqueous copper(II) sulfate (2 × 15 mL), dried, and evaporated in vacuo. The crude product was dissolved in THF (4 mL) and cooled to −78 °C, and $^t$BuOK in $^t$BuOH (1.0 M; 1.1 mL) was added. After 15 min, the solution was diluted with $CH_2Cl_2$ (20 mL), and ozone introduced[10] until the yellow/orange color faded to a colorless end point. The solution was purged of excess ozone with a stream of $N_2$, and the solution was washed with aqueous HCl (2 M, 10 mL) and $H_2O$ (10 mL), dried, and evaporated in vacuo. Chromatography ($SiO_2$, hexanes:$Et_2O$) gave the pure thioester.

**2-[(Phenylthio)carbonyl]tetrahydrofuran (10a)**: an oil; $R_f$ 0.38 (hexanes:$Et_2O$ 3:1); IR (film) 2960, 1705, 1445, 1070 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 (s, 5 H), 4.58 (dd, 1 H, $J$ = 5.2, 8.8 Hz), 4.15 (q, 1 H, $J$ = 6 Hz), 4.01 (q, 1 H, $J$ = 8 Hz), 2.25 (m, 1 H), 2.14 (m, 1 H), 1.99 (m, 2 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 202.3, 134.5, 129.1, 129.0, 127.6, 83.6, 70.0, 31.1, 25.2; mass spectrum (EI), $m/e$ 208 ($M^{\cdot+}$), 180, 110, 71. Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.13; H, 6.03.

**2-[(Phenylthio)carbonyl]tetrahydropyran (11a)**: mp 48–49 °C (hexanes); $R_f$ 0.54 (hexanes:$Et_2O$ 3:1); IR (KBr) 2950, 2860, 1705, 1445, 1050 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (s, 5 H), 4.19 (m, 1 H), 4.07 (dd, 1 H, $J$ = 2.8, 10.4 Hz), 3.58 (td, 1 H, $J$ = 2.4, 11.2 Hz), 2.0 (m, 1 H), 1.92 (m, 1 H), 1.62 (m, 4 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 199.6, 134.9, 129.3, 129.1, 127.3, 82.7, 68.6, 29.2, 25.5, 22.8; mass spectrum (EI), $m/e$ 222 ($M^{\cdot+}$), 194, 110, 85. Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35. Found: C, 64.68; H, 6.17.

**2-[(Phenylthio)carbonyl]oxapan (12)**: an oil; $R_f$ 0.69 (hexanes:$Et_2O$ 3:1); IR (film) 3070, 2930, 2870, 1700, 1440, 1130 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (s, 5 H), 4.26 (m, 1 H), 4.00 (m, 1 H), 3.84 (m, 1 H), 2.19 (m, 1 H), 1.86 (m, 3 H), 1.71 (m, 2 H) 1.58 (m, 2 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 201.8, 134.7, 129.14, 129.08, 128.1, 84.5, 69.1, 32.5, 31.0, 27.1, 25.8; mass spectrum (EI), $m/e$ 236 ($M^{\cdot+}$) 221, 208, 99, 81, 55. Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: 65.86; H, 7.12.

(10) Ozone was produced by using a Welsbach T-23 Laboratory Ozonator and bubbled directly into the reaction flask via pipette.

**2-[(Phenylthio)carbonyl]-5-methyltetrahydrofuran (10b, less polar isomer)**: an oil; $R_f$ 0.53 (hexane:$Et_2O$ 3:1); IR (film) 2900, 1705, 1450, 975, 650 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 (s, 5 H) 4.65 (dd, 1 H, $J$ = 5.6, 8.4 Hz), 4.42 (m, 1 H), 2.38 (m, 1 H), 2.13 (m, 2 H), 1.56 (m, 1 H), 1.33 (d, 3 H, $J$ = 6 Hz); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 202.7, 134.7, 129.2, 129.1, 127.7, 83.6, 77.7, 32.8, 31.0, 20.9; mass spectrum (EI), $m/e$ 222 ($M^{\cdot+}$), 194, 137, 110, 85, 67, 43. Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35. Found: 64.55; H, 6.09.

**2-[(Phenylthio)carbonyl]-5-methyltetrahydrofuran (10b, more polar isomer)**: an oil; $R_f$ 0.45 (hexane:$Et_2O$ 3:1); IR (film) 2980, 1705, 1445, 750 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 (s, 5 H), 4.55 (dd, 1 H, $J$ = 3.6, 8.8 Hz), 4.24 (m, 1 H), 2.30 (m, 1 H), 2.22 (m, 1 H), 2.04 (m, 1 H), 1.65 (m, 1 H), 1.48 (d, 3 H, $J$ = 6 Hz); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 202.8, 134.6, 129.2, 129.1, 128.0, 83.7, 78.5, 32.2, 31.8, 20.7; mass spectrum (EI), $m/e$ 222 ($M^{\cdot+}$), 194, 110, 85. Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35. Found: C, 64.64; H, 6.50.

**2-[(Phenylthio)carbonyl]-5-phenyltetrahydrofuran (10c, less polar isomer)**: mp 52–53 °C (hexanes); $R_f$ 0.40 (hexane:$Et_2O$ 3:1); IR (KBr) 2885, 1700, 1445, 750 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 (s, 5 H), 7.38 (m, 5 H), 5.34 (dd, 1 H, $J$ = 6, 7.6 Hz), 4.87 (dd, 1 H, $J$ = 6, 7.6 Hz), 2.44 (m, 2 H), 2.25, (m, 1 H), 1.93 (m, 1 H); $^{13}C$ NMR (101 MHz, $CDCl_3$) 202.3, 141.6, 134.6, 129.2, 129.1, 128.4, 127.6, 127.5, 125.5, 84.1, 82.7, 34.1, 30.8; mass spectrum (EI), $m/e$ 284 ($M^{\cdot+}$), 256, 147, 129, 91. Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.50; H, 5.61.

**2-[(Phenylthio)carbonyl]-5-phenyltetrahydrofuran (10c, more polar isomer)**: an oil; $R_f$ 0.30 (hexane:$Et_2O$ 3:1); IR (film) 3070, 2950, 1703, 1445, 750 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 (m, 2 H), 7.4 (m, 8 H), 5.05 (dd, 1 H, $J$ = 5.2, 10 Hz), 4.73 (dd, 1 H, $J$ = 4, 9.6 Hz), 2.47 (m, 1 H), 2.34 (m, 2 H), 1.97 (m, 1 H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 201.6, 140.5, 134.7, 129.3, 129.1, 128.4, 127.8, 127.5, 126.3, 83.6, 83.5, 33.4, 31.7; mass spectrum (EI), $m/e$ 284 ($M^{\cdot+}$), 147, 129, 109, 91. Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.53; H, 5.71.

**(2*R*(*S*),3*S*(*R*))-2-[(Phenylthio)carbonyl]-6-phenyltetrahydropyran (11b)**: mp 89–90 °C (hexanes); $R_f$ 0.60 (hexane:$Et_2O$ 3:1); IR (KBr) 2800, 1700, 1445, 750 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.4 (m, 10 H), 4.55 (dd, 1 H, $J$ = 2, 11.2 Hz), 4.30 (dd, 1 H, $J$ = 2.4, 11.6 Hz), 2.07 (m, 2 H), 1.95 (m, 1 H), 1.8 (m, 1 H), 1.6 (m, 2 H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 200.0, 142.3, 134.9, 129.2, 129.1, 128.4, 127.4, 125.4, 82.9, 80.1, 33.7, 28.9, 23.4; mass spectrum (EI), $m/e$ 298 ($M^{\cdot+}$), 270, 161, 117, 91, 77. Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08. Found: C, 72.10; H, 5.96.

**(2*R*(*S*),3*S*(*R*))-2-[(Phenylthio)carbonyl]-3-phenyltetrahydrofuran (10d)**: mp 33 °C (hexanes); $R_f$ 0.45 (hexanes:$Et_2O$ 4:1); IR (Nujol) 1715, 1470, 1060, 920, 910 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 (s, 5 H), 7.22–7.35 (m, 5 H), 4.63 (d, 1 H, $J$ = 5.6 Hz), 4.28 (m, 2 H), 3.64 (dt, 1 H, $J$ = 5.6, 7.6 Hz), 2.49 (m, 1 H), 2.16 (m, 1 H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 201.3, 141.2, 134.6, 129.29, 129.26, 129.16, 128.8, 127.5, 127.3, 127.0, 89.7, 69.9, 50.0, 34.5; mass spectrum (EI), $m/e$ 284 ($M^{\cdot+}$), 147, 91. Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.66; H, 5.62.

**(2*R*(*S*),3*S*(*R*))-2-[(Phenylthio)carbonyl]-3-phenyltetrahydropyran (11c)**: mp 92 °C (hexanes); $R_f$ 0.49 (hexane:$Et_2O$ 4:1); IR (Nujol) 3100, 2550, 1710, 1470, 1380, 1090 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.2–7.4 (m, 10 H), 4.40 (m, 1 H), 4.30 (d, 1 H, $J$ = 9.6 Hz), 3.64 (m, 1 H), 3.0 (dt, 1 H, $J$ = 4, 10.4 Hz), 2.1 (m, 1 H), 1.92 (m, 2 H), 1.77 (m, 1 H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 195.9, 140.5, 134.6, 129.2, 129.0, 128.5, 127.9, 127.1, 127.0, 87.3, 68.2, 46.2, 31.3, 25.3; mass spectrum (FAB), $m/e$ 299 ($M^+$ + H), 270, 256, 228, 214, 199. Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08. Found: C, 72.35; H, 6.17.

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# *Additions and Corrections*

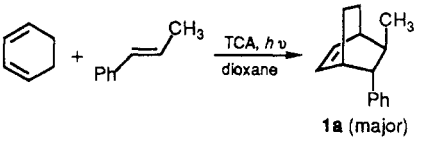
Vol. 54, 1989

**Robert E. Gawley,* Georgina C. Hart, and Libero J. Bartolotti***. Chiral Dipole-Stabilized Anions: Experiment and Theory in Nonbenzylic Systems. 100% Stereoselective Deprotonation and Two-Electron vs Single-Electron Transfer in the Chemistry of Lithium and Copper Piperidinooxazolines.

Page 180, column 2, lines 52 and 53. The $^{13}C$ NMR data for compound **3** are incorrect and should be as follows. $^{13}C$ NMR: 160.91, 69.97, 69.84, 46.25, 33.05, 25.00, 23.96, 18.58, 17.53.

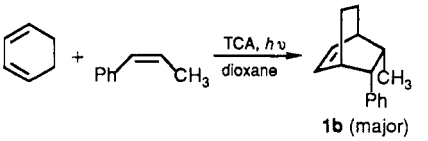
**Nihat Akbulut, David Hartsough, Ji-In Kim, and Gary B. Schuster***. The Triplex Diels–Alder Reaction of 1,3-Dienes with Enol, Alkene, and Acetylenic Dienophiles: Scope and Utility.

Page 2551, column 1. The product structures in eq 1 and 2 are identified properly in the text, but drawn incorrectly. These structures should be replaced with those below.




(1)

**1a** (major)




(2)

**1b** (major)

Page 2554, column 2, lines 11 and 16. In the description of the spectral data for the bicyclic aldehydes, the descriptors exo and endo should be switched. In the description of the identification of the exo and endo trans stereoisomers (6th line from bottom of column 2), the first line of the second paragraph should read: The *exo*-phenyl stereochemistry....