^{1}H NMR ($CDCl_3$) δ 1.37 (t, $^{3}J_{HH} = 7$ Hz, CH_3), 4.38 (q, $^{3}J_{HH} = 7$ Hz, OCH_2).

4c ($Z^1 = C_6H_5$, $Z^2 = CHO$). Reaction: 0.3 mL of **c**, 1.45 g of **1** (2 mmol), 0.6 g of sulfur. Results: 0.10 g (22%) of **3c**; mp 105 °C; mass spectrum, *m/e* 238 (M^+; calcd 238); IR (Nujol) 1660, 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.73 (m, C_6H_5), 9.68 (s, CHO).

4d ($Z^1 = C_6H_5$, $Z^2 = COCH_3$). Reaction: 0.3 mL of **d**, 1.45 g of **1** (2 mmol), 1.0 g of sulfur. Results: 0.17 g (31%) of **3d**; mass spectrum, *m/e* 251.9733 (M^+; calcd 251.9737); IR (Nujol) 1660, 1545 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.97 (s, CH_3), 7.90 (m, C_6H_5).

1,3-Dithiole-2-thione (6). To a suspension of complex **1** (1.5 g, 2 mmol) in 15 mL of toluene under a nitrogen atmosphere was added 0.25 mL of alkyne **c** with a syringe. The resulting brown solution was stirred at room temperature for 2 h. A solution of 1 equiv of the Ph_3PCHPh ylide in toluene was then added, and the mixture was stirred at room temperature for 3 h. An excess of sulfur (1 g) was added, and the reaction mixture was refluxed for 5 h. After removal of the solvent the crude product was chromatographed on silica gel column (with hexane–ether as the eluent) to give 0.14 g (19%) of compound **6**: mass spectrum, *m/e* 312.009 (M^+; calcd 312.010); IR (Nujol) 1545, 1075 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.61 and 6.70 (dd, HC=CH, $J_{HH} = 16.0$ Hz), 7.06 (m) and 7.26 (m) (C_6H_5).

1,3-Thiazole-2-thiones 11a and 12a–c. To a solution of complex **7** or **8** in toluene under a nitrogen atmosphere an excess of alkynes **a**, **b**, or **c** was added with a syringe. The solution was stirred at room temperature for 12 h. An excess of sulfur was then added and the mixture was refluxed for 5 h. After removal of the solvent the crude products were chromatographed on silica gel column (with hexane–ether as the eluent). The yellow compounds **11a** and**12a–c** migrate in front of the column.

11a (R = Me, $Z^1 = Z^2 = CO_2Me$). Reaction: 0.4 mL of **a**, 2 g of **7** (2.8 mmol), 0.8 g of sulfur. Results: 0.2 g (32%) of **11a**; mp 78–80 °C; mass spectrum, *m/e* 246.9985 (M^+; calcd 246.9972); IR (Nujol) 1745, 1590, 1120 cm^{-1}; ^{1}H NMR (C_6D_6) δ 3.03 (s), 3.30 (s), 3.43 (s); ^{1}H NMR ($CDCl_3$) δ 3.63 (s), 3.83 (s), 4.00 (s), NMe and two CO_2Me groups.

12a (R = Ph, $Z^1 = Z^2 = CO_2Me$). Reaction: 0.5 mL of **a**, 2 g of **8** (2.6 mmol), 0.8 g of sulfur. Results: 0.2 g (25%) of **12a**; mass spectrum, *m/e* 309.0128 (M^+; calcd 309.0129); IR (Nujol) 1745, 1580, 1120 cm^{-1}; ^{1}H NMR (C_6D_6) δ 3.23 (s, CO_2Me), 3.58 (s, CO_2Me), 7.06 (m, C_6H_5).

12b (R = Ph, $Z^1 = Z^2 = CO_2Et$). Reaction: 0.5 mL of **b**, 2 g of **8** (2.6 mmol), 0.8 g of sulfur. Results: 0.18 g (21%) of **12b**; mass spectrum, *m/e* 337.0439 (M^+; calcd 337.0442); IR (Nujol) 1745, 1580, 1158 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.01 (m, 2 CH_3), 4.12 (q, $^{3}J_{HH} = 7$ Hz, OCH_2), 4.42 (q, $^{3}J_{HH} = 7$ Hz, OCH_2), 7.27–7.53 (m, C_6H_5).

12c (R = Ph, $Z^1 = Ph$, $Z^2 = CHO$). Reaction: 0.4 mL of **c**, 2 g of **8** (2.6 mmol), 0.8 g of sulfur. Results: 0.14 g (18%) of **12c**; mp 142–144 °C; mass spectrum, *m/e* 297.025 (M^+; calcd 297.025).

Registry No. 1, 64424-68-6; **2**, 64424-66-4; **4a**, 7396-41-0; **4b**, 74090-73-6; **4c**, 82679-19-4; **4d**, 82679-20-7; **6**, 82679-21-8; **7**, 82679-17-2; **8**, 82679-18-3; **11a**, 41126-43-6; **12a**, 41126-48-1; **12b**, 41126-49-2; **12c**, 82679-22-9; **a**, 762-42-5; **b**, 762-21-0; **c**, 2579-22-8; **d**, 1817-57-8; $Fe(CO)_5$, 13463-40-6; Ph_3PCHPh, 16721-45-2; PPh_3, 603-35-0; CS_2, 75-15-0.

The 3-(Fluoromethyl)phenyl Group. A Useful Moiety for the Study of Solvolysis Reactions with Large Negative ρ Values

Paul G. Gassman* and Thomas L. Guggenheim

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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The use of $\rho\sigma$ linear free-energy[1] relationships has proven to be extremely advantageous for a wide variety of mechanistic studies in organic chemistry. Of particular value to the investigation of the chemistry of carbocations has been the $\rho\sigma^+$ relationships devised by Brown and Okamoto[2] and our use of this relationship in the study of delocalized carbocations through the "tool of increasing electron demand".[3,4] When this concept is applied to systems in which strong electron-withdrawing substituents are attached directly to the incipient positive center,[5] the size of ρ can dramatically increase and, as a result, the rate differences between the commonly used aryl substituents often become very large.[5a,b,f] Since careful examination of systems having a large ρ generally requires a variety of extrapolations, it is important to have available substituents with intermediate σ^+ values in order to minimize the error involved in such extrapolations. As part of our detailed investigation of α-cyanocarbocations, we had need of an aryl substituent that would fall between hydrogen ($\sigma_{meta}^+ = 0$) and 3-chloro ($\sigma_{meta}^+ = 0.399$). Although 3-phenyl, 3-methylthio, 4-chloro, 4-bromo, 4-iodo, and 4-acetoxy fall within the desired range, they did not fulfill our desire for a group that (a) could not interact in a conjugative manner either through π conjugation or through interaction with nonbonding electrons and (b) were stable to our synthetic and solvolytic conditions. A substituent that appeared to be attractive was the 3-fluoromethyl moiety. If the influence of fluorines on a 3-methyl group were approximately additive, a σ^+ value for a 3-fluoromethyl group would be predicted to be about 0.13.[6] We report in this note the synthesis and kinetic determination of the σ^+ value of the 3-(fluoromethyl)phenyl moiety.

Reduction of commercially available 3-bromobenzaldehyde (**1**) with lithium aluminum hydride gave the known[7] 3-bromobenzyl alcohol (**2**) in 84% yield. When **2** was allowed to react with methanesulfonyl chloride in methylene chloride containing triethylamine at 0 °C, **3** was produced in 75% yield. Treatment of **3** with potassium fluoride and 18-crown-6 in acetonitrile gave 84% of **4**. Attempts to generate a Grignard from **4** resulted in the formation of 1,1′-(1,2-ethanediyl)bis-3-bromobenzene (**5**) as the major product. Fortunately, **4** was readily transmetalated with *n*-butyllithium in tetrahydrofuran at −78

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(6) The σ_{meta}^+ for methyl is −0.066 and for trifluoromethyl is 0.520. This gave an average change in σ_{meta}^+ of 0.195/fluorine.

(7) Fang, F. T.; Kochi, J. K.; Hammond, G. S. *J. Am. Chem. Soc.* **1958**, *80*, 563.

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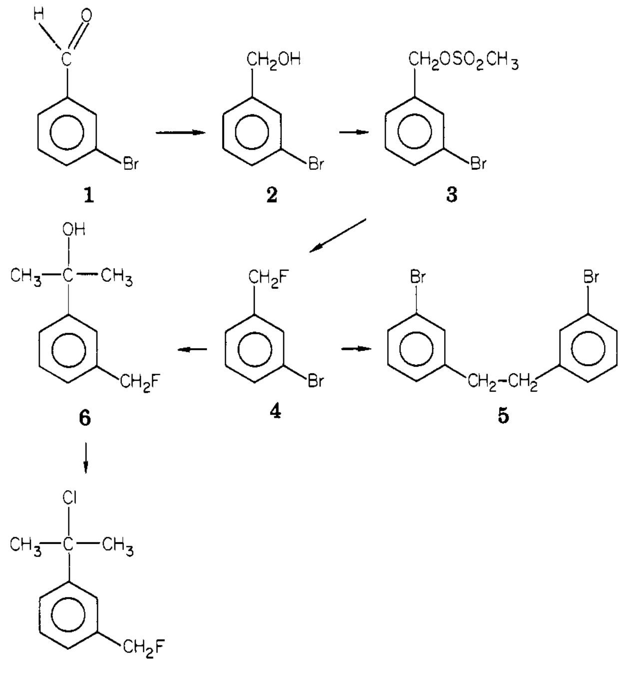

°C. On addition of acetone to this transmetalation product, **6** was obtained in 39% yield. When a solution of **6** in methylene chloride at 0 °C was exposed to gaseous hydrogen chloride, **7** was obtained in 88% yield.

Solvolysis of **7**, according to the classical method,[2] in 90% aqueous acetone (v/v) gave the results shown in Table I. The rate data obtained from the hydrolysis of **7** was then fit to the plot established by Brown and Okamoto for the psuedo-first-order solvolysis of a series of 2-phenyl-2-propyl chlorides. In this manner, it was established that $\sigma_{\text{meta}}{}^{+}$ for the fluoromethyl group is 0.104.

Table I. Rates of Solvolysis of 2-[3-(Fluoromethyl)phenyl]-2-propyl Chloride in 90% Aqueous Acetone (v/v)

temp, °C (±0.05 °C)	rate,[a] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
35.00	$(1.17 \pm 0.01) \times 10^{-4}$	18.1 ± 0.2	−17.8 ± 0.6
50.00	$(5.03 \pm 0.08) \times 10^{-4}$		
65.00	$(1.77 \pm 0.03) \times 10^{-3}$		
25.00[b]	4.18×10^{-5}		

[a] Rates were determined conductometrically. [b] Rate extrapolated from higher temperature.

Experimental Section[8]

3-Bromobenzyl Alcohol (2). A solution of 15.0 g of 3-bromobenzaldehyde (**1**; Aldrich Chemical) in 75 mL of diethyl ether was added dropwise over a 20-min period to a stirred slurry of 3.08 g of lithium aluminum hydride in 225 mL of diethyl ether at 0 °C. The reaction was then heated to reflux for 2 h. After cooling, the reaction mixture was worked up by the sequential dropwise addition of 3 mL of water, 3 mL of 10% sodium hydroxide solution, and 9 mL of water. The precipitated salts were removed by filtration and washed thoroughly with ether. The combined ethereal solutions were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed to give a clear colorless residue. Vacuum distillation of the residue gave 12.78 g (84%) of **2**: bp 95–100 °C (1.75 mm) [lit.[7] bp 90.5–92.0 °C (0.65 mm)].

3-Bromobenzyl Methanesulfonate (3). The sample of **2** (12.76 g) prepared above was converted into the corresponding methanesulfonate according to the general procedure of Crossland and Servis.[9] Low-temperature recrystallization of the crude product from ether/60–70 °C petroleum ether gave 13.50 g (75%) of **3** as white flakes: mp 39.5–41.5 °C. Two additional recrystallizations gave an analytical sample: mp 40.0–41.5 °C; ^{1}H NMR (CDCl$_3$) δ 2.96 (3 H, s), 5.13 (2 H, s), 7.2–7.6 (4 H, m); ^{13}C NMR (CDCl$_3$) δ 135.46 (s), 131.98 (d), 131.12 (d), 130.15 (d), 126.82 (d), 122.39 (s), 69.86 (t), 37.81 (q); exact mass calcd for C$_8$H$_9$BrO$_3$S 263.9456, found 263.9456.

Anal. Calcd for C$_8$H$_9$BrO$_3$S: C, 36.24; H, 3.42. Found: C, 36.37; H, 3.46.

3-Bromobenzyl Floride (4). According to the general procedure of Liotta,[10] a solution of 5.8 g of potassium fluoride, 1.3 g of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), and 30 mL of dry acetonitrile was stirred for 10 min and then 13.49 g of **3** was added. The reaction mixture was heated to 80 °C for 1 h, at which time a white paste had formed. The reaction mixture was maintained at this temperature for 48 h and cooled, and 100 mL of ether was added. The organic layer was separated and washed sequentially with 50 mL of 3 N hydrochloric acid, two 50-mL portions of saturated sodium bicarbonate solution, and 50 mL of brine. The ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure. The residual oil was fractionally distilled to give 7.86 g (82%) of **4**: bp 55–57 °C (1.50 mm); ^{1}H NMR (CDCl$_3$) δ 5.29 (2 H, d, $J_{\text{HF}} = 46.8$ Hz), 7.15–7.60 (4 H, br m); ^{13}C NMR (CDCl$_3$) δ 138.28 (d, $J_{\text{CCF}} = 17.5$ Hz), 131.50 (d of d, $J_{\text{CCCCF}} = 2.1$ Hz), 130.00 (d of d, $J_{\text{CCCF}} = 6.6$ Hz), 129.98 (d), 125.48 (d of d, $J_{\text{CCCF}} = 6.0$ Hz), 122.42 (s), 83.25 (d of t, $J_{\text{CF}} = 168.2$ Hz); exact mass calcd for C$_7$H$_6$BrF 187.9636, found 187.9638.

Anal. Calcd for C$_7$H$_6$BrF; C, 44.48; H, 3.20. Found: C, 44.54; H, 3.26.

Reaction of 4 with Magnesium. Generation of 1,1′-(1,2-Ethanediyl)bis-3-bromobenzene (5). An efficiently stirred Morton reactor was charged with 0.35 g of magnesium turnings and 25 mL of dry ether. A small amount of 1,2-dibromoethane was added to activate the magnesium and 2.5 g of **4** in 15 mL of dry ether was added dropwise. When the addition was complete, the reaction mixture was refluxed for 3 h. Addition of 10 mL of acetone to the reaction mixture gave no apparent reaction. The solution was then diluted with 100 mL of ether and poured into 100 mL of 3 N hydrochloric acid. The solutions were mixed, and the organic phase was then separated. The ethereal solution was washed with 50 mL of saturated sodium bicarbonate solution and 50 mL of brine. The organic phase was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure to afford an oily residue. Fractional distillation gave 0.25 g of a mixture of compounds [bp 75–80 °C (0.1 mm)] and 1.10 g (50%) of **5**, which crystallized on standing: bp 140–145 °C (0.1 mm); mp 55–60 °C. Recrystallization from 95% ethanol gave white needles: mp 66.5–67.5 °C; ^{1}H NMR (CDCl$_3$) δ 2.86 (4 H, s), 7.05–7.32 (8 H, m); ^{13}C NMR (CDCl$_3$) δ 143.32 (s), 131.35 (d), 129.81 (d), 129.11 (d), 126.97 (d), 122.33 (s), 37.08 (t); exact mass calcd for C$_{14}$H$_{12}$Br$_2$ 337.9305, found 337.9307.

Anal. Calcd for C$_{14}$H$_{12}$Br$_2$: C, 49.45; H, 3.56. Found: C, 49.53; H, 3.70.

2-[3-(Fluoromethyl)phenyl]-2-propanol (6). To a well-stirred solution of 1.27 g of **4** in 20 mL of dry tetrahydrofuran at −78 °C was added 3 mL of 2.3 M *n*-butyllithium in hexane. After 10 min at −78 °C, a white precipitate formed. The reaction mixture was stirred for 1 h at −78 °C and then 4 mL of acetone was added slowly, which resulted in the disappearance of the precipitate. The reaction mixture was allowed to warm to room temperature and then diluted with 100 mL of ether. The reaction mixture was poured into 50 mL of cold 3 N hydrochloric acid with stirring. The organic layer was separated and washed with 50 mL of saturated sodium bicarbonate and 50 mL of brine. The organic phase was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure to

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(8) Melting points and boiling points are uncorrected. Elemental analyses were obtained from the Scandinavian Microanalytical Laboratories, Herlev, Denmark.

(9) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

(10) Liotta, C. L.; Harris, H. P. *J. Am. Chem. Soc.* **1974**, *96*, 2250.

give an oily residue, which was purified by preparative high-performance chromatography (Waters Preparative Liquid Chromatographic System 500A), using 15% ethyl acetate–85% petroleum ether (60–70 °C) and a silica gel column. This gave 0.55 g (47%) of **6**, which was distilled to give 0.45 g (39%) of analytically pure material: bp 78–79 °C (0.35 mm); ^{1}H NMR ($CDCl_3$) δ 1.52 (6 H, s), 2.20 (1 H, br s), 5.31 (2 H, d, J_{HF} = 48.0 Hz), 7.10–7.60 (4 H, br m); ^{13}C NMR ($CDCl_3$) δ 149.53 (s), 135.90 (d, J_{CCF} = 16.9 Hz), 128.33 (d), 125.68 (d of d, J_{CCCF} = 5.7 Hz), 124.74 (d of d, J_{CCCCF} = 3.11 Hz), 123.48 (d of d, J_{CCCF} = 5.9 Hz), 84.61 (d of t, J_{CF} = 166.0 Hz), 72.26 (s), 31.55 (q); exact mass calcd for $C_{10}H_{13}FO$ 168.0950, found 168.0951.[11]

2-[3-(Fluoromethyl)phenyl]-2-propyl Chloride (7). A solution of 0.32 g of **6** in 2 mL of dry methylene chloride was cooled to 0 °C and dry hydrogen chloride gas was bubbled into the solution for 1.75 h. The solvent was removed under reduced pressure to give 0.31 g (88%) of **7**, which contained no alcohol or substituted propene on analysis by ^{1}H NMR. All attempts at additional purification resulted in decomposition (loss of hydrogen chloride). Thus, the material was used without additional purification: ^{1}H NMR ($CDCl_3$) δ 1.99 (6 H, s), 5.38 (2 H, d, J_{HF} = 47.7 Hz), 7.29–7.60 (4 H, m); exact mass calcd for $C_{10}H_{12}ClF$ 186.0610, found 186.0605.[11]

Kinetic Procedure. The kinetic procedure was essentially that of Brown and Okamoto except that the rates were measured conductometrically. Excellent psuedo-first-order kinetics were observed for at least 5 half-lives.

Acknowledgment. We are indebted to the National Science Foundation for Grants CHE78-10231 and CHE81-14772, which supported this investigation.

Registry No. 1, 3132-99-8; 2, 15852-73-0; 3, 82732-02-3; 4, 456-43-9; 5, 82732-03-4; 6, 82732-04-5; 7, 82732-05-6; *m*-lithiobenzyl fluoride, 82732-06-7; acetone, 67-64-1.

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[11] Due to the tendency of this compound to slowly decompose, an elemental analysis was omitted.

Communications

High Asymmetric Induction in the 1,3-Dipolar Cycloaddition of (*R*)-(+)-*p*-Tolyl Vinyl Sulfoxide with Acyclic Nitrones

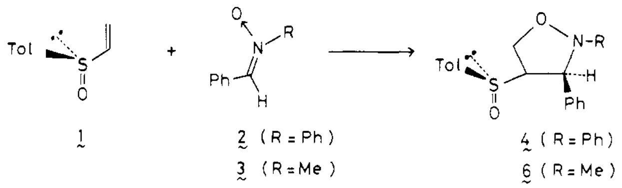
Summary: High chiral induction was observed in the 1,3-dipolar cycloaddition of (*R*)-(+)-*p*-tolyl vinyl sulfoxide with two typical acyclic nitrones.

Sir: In contrast to the well-documented asymmetric Diels–Alder reactions,[1] asymmetric 1,3-dipolar cycloadditions have been little explored. Recently, Uskokovic[2] and Belzecki[3] observed asymmetric inductions in the cycloaddition of chiral nitrones.[4] To our best knowledge, however, there have been no reports concerning asymmetric 1,3-dipolar cycloaddition using chiral dipolarophiles.

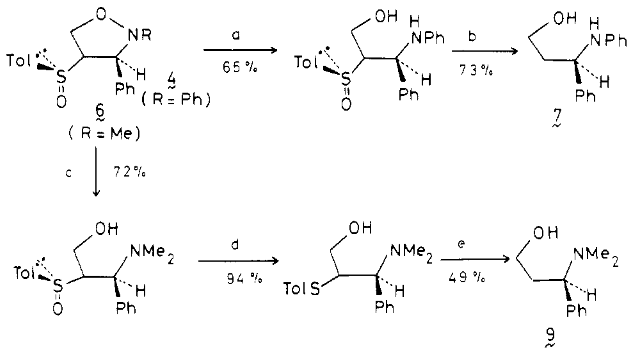
We here report that a chiral vinyl sulfoxide,[5] (*R*)-(+)-*p*-tolyl vinyl sulfoxide, exhibits high chiral induction in the 1,3-dipolar cycloaddition with typical nitrones.

A benzene solution of (*R*)-(+)-*p*-tolyl vinyl sulfoxide **1**[6] and 3 molar equiv excess of *C,N*-diphenylnitrone (**2**) was heated under reflux for 20 h, and the reaction product was separated by silica gel column chromatography to afford 3-phenyl-4-(*p*-tolylsulfinyl)isoxazolidines[7] **4a** and **4b**[8] in 54% and 3% yields, respectively (Scheme I). Both **4a** and **4b** afforded the same sulfide **5**[9] after $LiAlH_4$ reduction,

Scheme I



Scheme II



^{a} Raney Ni-H_2. ^{b} Raney Ni-EtOH, 60 °C. ^{c} (i) MeI; (ii) Zn-AcOH, room temperature. ^{d} $TiCl_3$-AcOH-AcONa, room temperature. ^{e} Raney Ni-EtOH, room temperature.

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[2] P. M. Wovkulich and M. R. Uskokovic, *J. Am. Chem. Soc.*, **103**, 3956 (1981).

[3] C. Belzecki and I. Panfil, *J. Org. Chem.*, **44**, 1212 (1979).

[4] A. Vasella, *Helv. Chim. Acta*, **60**, 1273 (1977).

[5] Chiral vinyl sulfoxides have been extensively employed as Michael acceptors: (a) G. H. Posner, J. P. Mallamo, K. Miura, and M. Hulce, *Pure Appl. Chem.*, **53**, 2307 (1981), and references cited therein; (b) G.-I. Tsuchihashi, S. Mitamura, S. Inoue, and K. Ogura, *Tetrahedron Lett.*, 323 (1973).

[6] (a) (*R*)-(+)-*p*-Tolyl vinyl sulfoxide 1 [bp 110 °C (1.0 torr); $[\alpha]^{26}_D$ +421°(*c* 0.15, EtOH)] was prepared according to the method of D. J. Abbott, S. Colonna, and C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 1*, 492 (1976); (b) All numbered compounds had satisfactory mass and/or combustion analyses and IR and ^{1}H NMR spectral properties. All distillations were carried out by use of Kugelrohr apparatus, and the bath temperatures are described.

[7] Other isoxazolidines were not observed even by the careful examination of every chromatographic fraction. The 4-substituted isoxazolidine structure for **4** was assigned by ^{1}H NMR spectra and the subsequent transformations.

[8] Both **4a** and **4b** decomposed on the attempted microdistillation. **4a**: viscous oil; mass spectrum, *m/z* 363 (M^+); TLC (silica gel) R_f 0.52 (benzene–AcOEt 6:1); $[\alpha]^{24}_D$ +246°(*c* 0.63, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.39 (3 H, s), 3.81 (1 H, 7-line m, J = 7, 5, 3 Hz), 4.11 (1 H, dd, J = 10, 5 Hz), 4.18 (1 H, dd, J = 10, 7 Hz), 5.37 (1 H, d, J = 3 Hz), 6.96–7.60 (14 H). **4b**: viscous oil; mass spectrum, *m/z* 363 (M^+); TLC R_f 0.45 (benzene–AcOEt, 6:1); $[\alpha]^{24}_D$ −11.7° (*c* 0.69, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.41 (3 H, s), 3.74 (1 H, sextet, J = 7, 4, 4 Hz), 4.33 (1 H, dd, J = 10, 7 Hz), 4.44 (1 H, d, J = 4 Hz), 4.66 (1 H, dd, J = 10, 4 Hz), 6.80–7.62 (14 H).

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