

butadiene will rotate inward, resulting in increased overlap, but the other 2p AO will rotate outward, resulting in a reduction of the overlap. Overall, this should result in a less favorable process than in the case of the observed anti outward disrotatory motion, but better than in the anti inward disrotatory process. It is believed that this electronic factor is the dominant factor which controls the direction of rotation of the two termini of a bisallene in a concerted (4 + 2) cycloaddition process.

### Experimental Section

**Reaction of a Mixture of erythro- and threo-8,8-Dimethyl-2,3,5,6-nonatetraene (11e and 11t) with *N*-Phenylmaleimide.** A solution of 22.8 mg of a 59.9:40.1 mixture of 11e and 11t (0.154 total mmol with 0.092 mmol of 11e) and 16.0 mg (0.092 mmol) of *N*-phenylmaleimide in 1.5 mL of CDCl<sub>3</sub> in a capped NMR tube was maintained at 25 °C for 22 h. The NMR spectrum was recorded showing the presence of essentially pure 11t (less than 1% of 11e remained unreacted) and essentially only the one (4 + 2) cycloadduct 12 present (less than 2% of 13 was present in the reaction mixture). The pure 11t was isolated by chromatography on a short silica gel column eluting with 95:5 Skelly B-ether, along with essentially pure 12: NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.21 (s, 9 H, *t*-Bu), 1.82 (dd,  $J$  = 7.17, 1.35 Hz with unresolved coupling to H<sub>3</sub> and H<sub>4</sub>, 3 H, CH<sub>3</sub>), 3.67 (dd,  $J$  = 8.83, 1.32 Hz with unresolved coupling to H<sub>4</sub>, 1 H, H<sub>6</sub>), 3.79 (ddq,  $J$

= 8.83, 1.57, 1.35 Hz with unresolved coupling to H<sub>3</sub>, 1 H, H<sub>1</sub>), 5.77 (ddd,  $J$  = 1.31, 1.30, 0.98 Hz, 1 H, H<sub>5</sub>), 5.94 (qddd,  $J$  = 7.17, 1.57, 1.47, 1.12 Hz, 1 H, H<sub>2</sub>), 6.45 (ddd,  $J$  = 10.74, 1.30, 1.12 Hz with unresolved coupling to the CH<sub>3</sub> and H<sub>6</sub>, 1 H, H<sub>4</sub>), 7.0-7.7 (m, 5 H, aromatic H); MS (on mixture)  $m/e$  321.

**Cycloaddition of 11t with *N*-Phenylmaleimide.** The pure 11t isolated from the above experiment was dissolved in 1.5 mL of CDCl<sub>3</sub>. A slight excess of NPMI was added, and the solution was allowed to stand at 25 °C for 5 days. Analysis by NMR showed the presence of unreacted 11t and NPM, and the presence of a single cycloadduct, 13, which was isolated by chromatography on a small silica gel column eluting with 95:5 Skellysolve B-ether: NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.16 (s, 9 H, *t*-Bu), 1.94 (dd,  $J$  = 7.17, 0.7 Hz with unresolved coupling to H<sub>3</sub>, 1 H, CH<sub>3</sub>), 3.73 (dd,  $J$  = 8.99, 1.59 Hz with unresolved coupling to H<sub>4</sub>, 1 H, H<sub>6</sub>), 4.19 (ddq,  $J$  = 8.99, 1.22, 0.7 Hz with unresolved coupling to H<sub>3</sub>, 1 H, H<sub>1</sub>), 5.87 (ddd,  $J$  = 1.59, 1.12, 1.12 Hz, 1 H, H<sub>5</sub>), 5.92 (qd,  $J$  = 7.17, 1.22 Hz with unresolved coupling to H<sub>3</sub>, 1 H, H<sub>2</sub>), 6.13 (dd,  $J$  = 10.57, 1.12 Hz with unresolved coupling to CH<sub>3</sub>, H<sub>1</sub> and H<sub>2</sub>, 1 H, H<sub>3</sub>), 6.54 (dd,  $J$  = 10.57, 1.12 Hz with unresolved coupling to CH<sub>3</sub>, H<sub>2</sub> and H<sub>6</sub>, 1 H, H<sub>4</sub>), 7.0-7.7 (m, 5 H, aromatic H).

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## Notes

### Synthesis of (±)-Marmelo Oxides by a Radical Cyclization Reaction

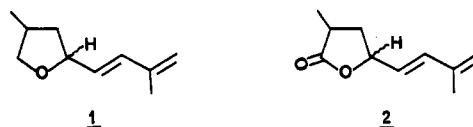
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Marmelo oxides A and B (1), irregular monoterpenes, are characteristic flavor components of the quincefruit (*Cydonia oblonga*) isolated by Tsuneya et al. together with marmelolactones A and B (2).<sup>1</sup> The relative (A as cis and B as trans) as well as absolute stereochemistry was established by Nishida et al. by converting marmelolactones (2) to oxides 1.<sup>2</sup> Currently the radical cyclization reaction is widely accepted as a powerful tool in organic synthesis.<sup>3</sup> In continuation of our interest in the application of radical cyclizations to various furanoid compounds,<sup>4</sup> we now describe a route to marmelo oxides A and B (1), based on a radical cyclization reaction.

The synthetic sequence is depicted in Scheme I; radical cyclization of the bromo alcohol 3 generates the tetra-



hydrofuran 5, which on oxidation followed by Wittig olefination results in the target 1. Thus, dispersion of *N*-bromosuccinimide in allyl alcohol furnished the requisite bromo alcohol 3 in 55% yield. The key radical cyclization of the bromo alcohol 3 was carried out by using in situ generated<sup>5</sup> catalytic tri-*n*-butyltin hydride (from *n*-Bu<sub>3</sub>SnCl and NaCNBH<sub>3</sub> in *t*-BuOH)<sup>4</sup> in the presence of a catalytic amount of AIBN, and the cyclized alcohol 5 was obtained in 43% yield as a 1:3 mixture (by NMR) of cis and trans isomers. The radical cyclization was found to be efficient with the corresponding acetate 4 (68% yield). The oxidation of the alcohol 5 was tried with a variety of reagents, but we were unable to isolate the aldehyde 7, probably due to the instability of 7. We finally resorted to Ireland's procedure<sup>6</sup> of trapping the aldehyde 7 with Wittig ylides. Swern oxidation (ClCOCOCl, DMSO, NEt<sub>3</sub>) followed by the addition of (carbethoxymethylene)triphenylphosphorane (or acetonilidenephosphorane) furnished the olefins 8 and 9, with excellent *E* selectivity (NMR), albeit in low yields. Application of Taber's modification<sup>7</sup> (P<sub>2</sub>O<sub>5</sub>, DMSO, NEt<sub>3</sub>) followed by the addition of Wittig ylides, however, generated the olefins 8 and 9 in respectable yields (65% and 50%). It is worth mentioning, in the synthesis of Nishida et al. via marme-

(1) Tsuneya, T.; Ishihara, M.; Shiota, H.; Shiga, M. *Agric. Biol. Chem.* 1983, 47, 2495.

(2) Nishida, Y.; Ohru, H.; Meguro, H. *Agric. Biol. Chem.* 1983, 47, 2969. To our knowledge, this is the only synthesis reported in the literature so far.

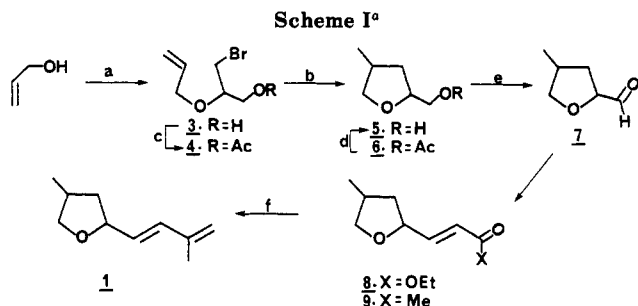
(3) Ramaiah, M. *Tetrahedron* 1987, 43, 3541. Curran, D. P. *Synthesis* 1988, 417, 489.

(4) Srikrishna, A.; Pullaiah, K. C. *Tetrahedron Lett.* 1987, 5203. Srikrishna, A.; Sunderbabu, G. *Tetrahedron Lett.* 1987, 28, 6393. Srikrishna, A. *Indian J. Chem.* 1987, 26B, 1113. Srikrishna, A.; Sunderbabu, G. *Chem. Lett.* 1988, 371. Srikrishna, A.; Krishnan, K. *Tetrahedron Lett.* 1988, 29, 4995.

(5) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* 1986, 108, 303.

(6) Ireland, R. E.; Norbeck, D. W. *J. Org. Chem.* 1985, 50, 2198.

(7) Taber, D. F.; Amedio, J. C., Jr.; Jung, K.-Y. *J. Org. Chem.* 1987, 52, 5621.



<sup>a</sup> (a) NBS,  $\text{CH}_2\text{Cl}_2$ , 0 °C–room temperature, 15 h, 55%; (b)  $n\text{-Bu}_3\text{SnCl}$  (0.15 equiv),  $\text{NaCNBH}_3$  (1.5 equiv),  $t\text{-BuOH}$ , AIBN, 80 °C, 6 h; (c) Py,  $\text{Ac}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$ , room temperature, 18 h, 80%; (d)  $\text{MeOH}$ ,  $\text{K}_2\text{CO}_3$ , room temperature, 3 h, 76%; (e) (i)  $\text{DMSO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{CH}_2\text{Cl}_2$ , 0 °C; (ii)  $\text{NET}_3$ ,  $\text{Ph}_3\text{P}=\text{CHC}(\text{X})=\text{O}$ , room temperature, 2 h; (f)  $\text{Ph}_3\text{P}^+\text{CH}_3\text{Br}^-$ ,  $t\text{-AmO}^-$ ,  $t\text{-AmOH}$ ,  $\text{C}_6\text{H}_6$ , room temperature, 50%.

lactones, that they obtained a 5:4 mixture of *E,Z* isomers in the Wittig olefination of the corresponding aldehyde with methallylidenetriphenylphosphorane.<sup>2</sup> Finally the enone **9** was transformed to the marmelo oxides **1** via Wittig olefination. The major and minor isomers exhibited spectral data identical<sup>2</sup> with those of the *trans* and *cis* isomers (i.e., marmelo oxides B and A), respectively. In conclusion, we have described here a regio- and geometroscopic route to racemic marmelo oxides based on a radical cyclization reaction.

### Experimental Section

IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer.  $^1\text{H}$  NMR (270, 90, 60 MHz) and  $^{13}\text{C}$  NMR (22.5 MHz) spectra were recorded on Bruker WH 270, JEOL FX 90Q, and Varian T 60 spectrometers. Chemical shifts and splittings are reported in standard fashion ( $\delta$ ) with reference to internal tetramethylsilane; "st" indicates additional fine structure. High-resolution mass measurements were carried out on a JEOL JMS-DX 303 GC MS instrument. Acme 100–200-mesh silica gel was used for column chromatography. Methylene chloride was distilled over phosphorus pentoxide.

**3-Bromo-2-(allyloxy)propanol (3).** To a magnetically stirred solution of allyl alcohol (6 mL) in 10 mL of methylene chloride was added NBS (3.56 g, 20 mmol), and the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was diluted with methylene chloride (100 mL), washed with 10% aqueous sodium hydroxide solution (3  $\times$  25 mL) followed by brine, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification over a silica gel column using 1:6 ethyl acetate–hexane as eluent furnished the bromoalcohol **3** (2.15 g, 55%) as an oil: IR (neat)  $3400\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  2.7 (1 H, br s), 3.45 (2 H, d,  $J = 5\text{ Hz}$ ), 3.6–4.1 (3 H, m), 4.17 (2 H, d with st,  $J = 5\text{ Hz}$ ), 5.1–5.45 (2 H, m), 5.95 (1 H, tdd,  $J = 18, 11, 5\text{ Hz}$ );  $^{13}\text{C}$  NMR (22.5 MHz,  $\text{CDCl}_3$ )  $\delta$  134.1 (d), 117.4 (t), 78.3 (d), 70.8 (t), 62.1 (t), 30.9 (t).

**3-Bromo-2-(allyloxy)propanol Acetate (4).** To a magnetically stirred solution of bromo alcohol **3** (1.2 g, 7.6 mmol) in 5 mL of methylene chloride were added pyridine (1.26 mL, 15 mmol) and acetic anhydride (0.716 mL, 7.6 mmol). The reaction mixture was stirred for 14 h at room temperature, diluted with methylene chloride (50 mL), washed with 1 N HCl followed by brine, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by filtration through a silica gel column using 1:20 ethyl acetate–hexane furnished the bromoacetate **4** (1.45 g, 80%): IR (neat)  $1740\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  2.1 (3 H, s), 3.45 (2 H, d,  $J = 7\text{ Hz}$ ), 3.8 (1 H, m), 4.14 (2 H, d with st,  $J = 5.5\text{ Hz}$ ), 4.25 (2 H, d,  $J = 5\text{ Hz}$ ), 5.1–5.5 (2 H, m), 5.95 (1 H, m);  $^{13}\text{C}$  NMR (22.5 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8 (s), 134.1 (d), 117.0 (t), 75.4 (d), 70.7 (t), 63.4 (t), 31.1 (t), 20.2 (q); HRMS  $\text{C}_6\text{H}_{13}\text{O}_3\text{Br}$  requires 238.0181, found 238.0186.

**Radical Cyclization of Bromo Alcohol 3.** To a magnetically stirred solution of bromo alcohol **3** (196 mg, 1 mmol) in *tert*-butyl alcohol (7.5 mL) were added sodium cyanoborohydride (93 mg,

1.5 mmol), tri-*n*-butyltin chloride (0.04 mL, 0.15 mmol), and a catalytic amount of AIBN, and the reaction mixture was refluxed for 6 h. Solvent was evaporated under reduced pressure, and the crude material was charged on a silica gel column and chromatographed by using 1:4 ethyl acetate–hexane as eluent to furnish the cyclized alcohol **5** (50 mg, 43%): IR (neat)  $3400, 1050\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (90 MHz,  $\text{C}_6\text{D}_6$ , 3:1 mixture of *trans* and *cis* diastereomers)  $\delta$  0.83 and 0.84 (3 H, d,  $J = 6\text{ Hz}$ ), 1.0–2.2 (3 H, m), 3.0–4.15 (6 H, m).

**Radical Cyclization of Bromo Acetate 4.** To a magnetically stirred solution of bromo acetate **4** (476 mg, 2 mmol) in *tert*-butyl alcohol (15 mL) were added tri-*n*-butyltin chloride (0.08 mL, 0.3 mmol), sodium cyanoborohydride (186 mg, 3 mmol), and a catalytic amount of AIBN, and the reaction mixture was refluxed for 6 h. The solvent was evaporated under reduced pressure, and the remaining material was diluted with ether (60 mL), washed with 1% aqueous ammonia followed by brine, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification over a silica gel column using 1:20 ethyl acetate–hexane furnished the cyclized acetate **6** (220 mg, 70%): IR (neat)  $1740\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ , 3:1 mixture of *trans* and *cis* isomers)  $\delta$  1.05 and 1.06 (3 H, d,  $J = 7\text{ Hz}$ ), 1.65 (1 H, m), 1.75 (1 H, m), 2.1 (3 H, s), 2.3 (1 H, m), 3.35 and 3.6 (1 H, m), 3.9–4.3 (5 H, m);  $^{13}\text{C}$  NMR (22.5 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9 (s), 75.4 and 76.6 (d), 74.5 and 74.1 (t), 65.9 (t), 35.5 and 36.1 (t), 32.5 and 33.4 (d), 20.0 (q), 16.9 and 16.5 (q); HRMS ( $M - \text{AcOH}$ )  $\text{C}_6\text{H}_{10}\text{O}$  requires 98.0731, found 98.0697.

**Hydrolysis of Acetate 6.** A solution of bromo acetate **6** (220 mg, 1.39 mmol) and potassium carbonate (400 mg, 2.9 mmol) in methanol (5 mL) was magnetically stirred at room temperature for 5 h. Evaporation of the solvent under reduced pressure followed by filtration through a short silica gel column using 1:4 ethyl acetate–hexane furnished the alcohol **5** (123 mg, 76%), which was used in the next oxidation reaction without storage as it is not very stable.

**Ethyl  $\beta$ -(4-Methyltetrahydro-2-furyl)-(E)-acrylate (8).** To an ice-cold magnetically stirred solution of alcohol **5** (116 mg, 1 mmol) in dry methylene chloride (5 mL) were sequentially added dimethyl sulfoxide (0.14 mL, 2 mmol) and phosphorus pentoxide (282 mg, 2 mmol). The reaction mixture was allowed to warm up to room temperature over a period of 30 min. The reaction mixture was recooled in an ice bath, and triethylamine (0.48 mL, 3.5 mmol) was added dropwise followed by (carboxymethylene)triphenylphosphorane (1.04 g, 3 mmol). The reaction mixture was stirred at room temperature for 3 h, quenched with 1 N HCl, and extracted with methylene chloride. The organic extract was washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by filtration through a silica gel column using 1:10 ethyl acetate–hexane furnished the acrylate **8** (120 mg, 65%): IR (neat)  $1720, 1660\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  1.0 (3 H, d,  $J = 7\text{ Hz}$ ), 1.21 (3 H, t,  $J = 7\text{ Hz}$ ), 1.6–1.84 (2 H, m), 2.2 (1 H, m), 3.3 (1 H, t,  $J = 7\text{ Hz}$ ), 3.97 (1 H, t,  $J = 7\text{ Hz}$ ), 4.12 (2 H, q,  $J = 7\text{ Hz}$ ), 4.53 (1 H, q,  $J = 7\text{ Hz}$ ), 5.92 (1 H, dd,  $J = 16, 1.5\text{ Hz}$ ), 6.83 (1 H, dd,  $J = 16, 5\text{ Hz}$ ).

**(E)-4-(4-Methyltetrahydro-2-furyl)but-3-en-2-one (9).** To an ice-cold magnetically stirred solution of bromo alcohol **5** (116 mg, 1 mmol) in methylene chloride (5 mL) were sequentially added dimethyl sulfoxide (0.14 mL, 2 mmol) and phosphorus pentoxide (282 mg, 2 mmol), and the reaction mixture was allowed to warm to room temperature over a period of 30 min. The reaction mixture was recooled in an ice bath, and triethylamine (0.48 mL, 3.5 mmol) was added dropwise followed by acetonilidenetriphenylphosphorane (954 mg, 3 mmol). The reaction mixture was stirred at room temperature for 3 h, quenched with 1 N HCl, and extracted with methylene chloride. The organic extract was washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by filtration through a silica gel column using 1:9 ethyl acetate–hexane furnished the enone **9** (77 mg, 50%): IR (neat)  $1680, 1630\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ , 3:1 mixture of *trans* and *cis* diastereomers)  $\delta$  1.0 (3 H, d,  $J = 7\text{ Hz}$ ), 1.6–1.8 (2 H, m), 2.2 (3 H, s), 2.1–2.58 (1 H, m), 3.32 and 3.35 (1 H, t,  $J = 7\text{ Hz}$ ), 3.99 and 3.92 (1 H, t,  $J = 7\text{ Hz}$ ), 4.56 and 4.46 (1 H, q,  $J = 7\text{ Hz}$ ), 6.13 (1 H, d,  $J = 16\text{ Hz}$ ), 6.7 (1 H, dd,  $J = 16, 5\text{ Hz}$ );  $^{13}\text{C}$  NMR (22.5 MHz,  $\text{CDCl}_3$ )  $\delta$  198.0 (s), 147.3 and 147.0 (d), 128.6 (d), 76.9 and 78.2 (d), 75.0 (t), 39.3 and 40.5 (t), 32.7 and 34.4 (d), 26.9 and 24.7 (q), 16.9 (q); HRMS  $\text{C}_9\text{H}_{14}\text{O}_2$

requires 154.0995, found 154.0998.

**Marmelo Oxides 1.** To a magnetically stirred suspension of methyltriphenylphosphonium bromide (155 mg, 0.5 mmol) in dry benzene (3 mL) was added a 1 M solution of potassium *tert*-amylate in *tert*-amyl alcohol (0.5 mL, 0.5 mmol), and the resulting yellow solution was stirred at room temperature for 20 min. To this solution was added a benzene (1 mL) solution of the enone 9 (31 mg, 0.2 mmol), and the resulting orange brown solution was stirred at room temperature for 2 h, quenched with 1 N HCl, and extracted with hexane. The organic extract was washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by filtration through a short silica gel column using hexane as eluent furnished the marmelo oxide 1 (16 mg, 50%). The major and minor isomers exhibited spectral data ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) identical with those of *trans* (B) and *cis* (A) marmelo oxides, reported in the literature.<sup>2</sup>

**Acknowledgment.** One of the authors (K.K.) wishes to thank CSIR, New Delhi for the research fellowship.

**Registry No.** ( $\pm$ )-*cis*-1, 121009-51-6; ( $\pm$ )-*trans*-1, 121009-48-1; ( $\pm$ )-3, 120943-91-1; ( $\pm$ )-4, 120943-92-2; DL-*threo*-5, 121009-49-2; DL-*erythro*-5, 121009-50-5; DL-*threo*-6, 120943-93-3; DL-*erythro*-6, 120943-96-6; 8, 120943-94-4; ( $\pm$ )-*cis*-9, 120943-95-5; ( $\pm$ )-*trans*-9, 120943-97-7;  $\text{CH}_2=\text{CHCH}_2\text{OH}$ , 107-18-6;  $\text{Ph}_3\text{P}=\text{CHC}(\text{OEt})=\text{O}$ , 1099-45-2;  $\text{Ph}_3\text{P}=\text{CHC}(\text{Me})=\text{O}$ , 1439-36-7;  $\text{Ph}_3\text{PMe}^+\text{Br}^-$ , 1779-49-3.

## Resonance and Solvent Effects on Absorption Spectra. 7. Substituent Solvation Effects on Nitrogen-15 Chemical Shifts of Para-Substituted Anilines and Meta-Substituted 2-Nitroanilines<sup>1</sup>

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Our previous study<sup>3</sup> of substituent effects on the  $^{15}\text{N}$  chemical shifts ( $\delta$  ( $^{15}\text{N}$ )) for 4-substituted anilines in dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ) showed distinct substituent solvation-assisted resonance (SSAR) effects. Solvation of certain conjugated  $\pi$ -electron-acceptor (+R) substituents have been found to give significant enhancements in the acidities of anilines, phenols, and other acids,<sup>4,5</sup> and the magnitudes of these enhancements increase with increasing  $\pi$ -electron donation to the conjugated substituent from the deprotonation center of the anionic forms. In the case of anilines in  $\text{Me}_2\text{SO}$ , hydrogen-bond solvation by  $\text{Me}_2\text{SO}$  of the  $\text{NH}$ 's increases the donation of  $\pi$  electrons to the conjugated + R substituent and this electron donation has been found to permit the SSAR enhancement effects on the  $\delta$  ( $^{15}\text{N}$ ) of the appropriate neutral aniline solutes.<sup>3</sup>

In this work, the SSAR treatment is given two simple but critical tests. First,  $\delta$  ( $^{15}\text{N}$ ) values for the previously used series of 13 para-substituted anilines have been measured in acetone ( $\text{Me}_2\text{CO}$ ), a significantly weaker hydrogen-bond acceptor (HBA) solvent than dimethyl sulfoxide. We anticipated and report here the observed

**Table I.**  $^{15}\text{N}$  NMR Spectral Data ( $\delta$  ( $^{15}\text{N}$ )) Values (ppm) of 4-Substituted Anilines I in Acetone- $d_6$  and 5-Substituted 2-Nitroanilines II in Dimethyl Sulfoxide- $d_6$  and Corresponding Substituent Parameters

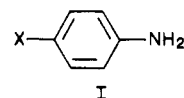
substitnt	$-\delta$ ( $^{15}\text{N}$ ) (I) <sup>a</sup>	$-\delta$ ( $^{15}\text{N}$ ) (II) <sup>b</sup>	$\sigma_F$ <sup>c</sup>	$\sigma_R$ <sup>c</sup>	$\Delta\sigma_R$ <sup>c</sup>
$\text{OCH}_3$	62.9	32.0	0.25	-0.27	0.00
$\text{CH}_3$	59.9	34.6	0.00	-0.08	0.00
F	60.7	31.4	0.44	-0.25	0.00
Cl	57.5		0.45	-0.17	0.00
$\text{CF}_3$	52.1	31.5	0.44	0.07	0.00
$\text{SCF}_3$	51.3		0.48	0.10	0.00
H	57.8	34.6	0.00	0.00	0.00
$\text{CO}_2\text{CH}_3$	49.1		0.24	0.16	0.08
$\text{CO}_2\text{C}_2\text{H}_5$	49.4	33.2	0.24	0.16	0.08
$\text{COCH}_3$	48.3	33.0	0.26	0.17	0.10
CN	47.1		0.60	0.10	0.07
$\text{SO}_2\text{CH}_3$	48.0	30.6 <sup>d</sup>	0.59	0.12	0.02
$\text{NO}_2$	42.4	29.8	0.65	0.18	0.18

<sup>a</sup> Chemical shift values upfield from  $\text{HCONH}_2$  as external reference in  $\text{Me}_2\text{CO}-d_6$  solution. <sup>b</sup> Chemical shift values in  $\text{Me}_2\text{SO}-d_6$  solution. <sup>c</sup> From ref 4. <sup>d</sup> Cf. ref 7.

smaller shift dependence on para  $\pi$ -electron-acceptor substituent solvation (SSAR) effects in acetone. Second, we have measured in  $\text{Me}_2\text{SO}$  the  $\delta$  ( $^{15}\text{N}$ ) shifts for nine typical 5-substituted 2-nitroanilines. We anticipated and report here the observations that there are no significant SSAR effects for the meta-substituted compounds (in contrast to the relatively large SSAR  $\text{N}^{15}$  shifts observed previously<sup>3</sup> for 4-substituted 2-nitroanilines in dimethyl sulfoxide).

## Results and Discussion

The  $^{15}\text{N}$  chemical shifts,  $-\delta$  ( $^{15}\text{N}$ ), for 4-substituted anilines I are upfield from  $\text{HCONH}_2$ , an external reference



for 1.0 M  $\text{Me}_2\text{CO}-d_6$  solution and  $-\delta$  ( $^{15}\text{N}$ ) values obtained are summarized in Table I (together with  $\sigma_F$  and  $\sigma_R$  values).<sup>4</sup> The  $\sigma_F$  and  $\sigma_R$  are field/inductive and resonance effect parameters, respectively, which are applicable to gas-phase proton-transfer equilibria.<sup>4</sup>

For non-substituent solvation assisted resonance (non-SSAR) substituents ( $\text{OCH}_3$ ,  $\text{CH}_3$ , F, Cl,  $\text{CF}_3$ ,  $\text{SCF}_3$ , H), the  $^{15}\text{N}$  chemical shifts are well correlated by eq 1. Noncolinearity of  $\sigma_F$  and  $\sigma_R$  parameters for this substituent set is shown by  $r = 0.071$ .

$$\begin{aligned} \delta(^{15}\text{N})(\text{I}, \text{Me}_2\text{CO}) = & (8.9 \pm 0.9)\sigma_F + (25.8 \pm 1.2)\sigma_R - 57.9 \pm 0.3 \text{ ppm} \\ n = 7 \text{ (non-SSAR)}, r = 0.996, \text{sd} = 0.4 \text{ ppm} \quad (1) \end{aligned}$$

When the data for all 13 substituents are examined in such a correlation,  $\delta$  ( $^{15}\text{N}$ ) values are relatively poorly fitted as shown in eq 2. The sd of 1.1 ppm is unacceptably high

$$\begin{aligned} \delta(^{15}\text{N})(\text{I}, \text{Me}_2\text{CO}) = & (11.0 \pm 1.7)\sigma_F + (32.3 \pm 2.3)\sigma_R - 57.4 \pm 0.7 \text{ ppm} \\ n = 13 \text{ (all substituents)}, r = 0.983, \text{sd} = 1.1 \quad (2) \end{aligned}$$

compared to that (0.4) for eq 1.

On the other hand, all 13  $\delta$  ( $^{15}\text{N}$ ) values are as well correlated as in eq 1 by utilizing eq 3, which incorporates the SSAR effect parameter ( $\Delta\sigma_R$ ) for appropriate  $\pi$ -electron acceptor substituents<sup>4,5</sup> (the  $\Delta\sigma_R$  values are given in Table I). Noncolinearity of the three different kinds of substituent parameters (in eq 3 is shown by  $r(\sigma_F \text{ vs } \sigma_R) = 0.218$ ;  $r(\sigma_F \text{ vs } \Delta\sigma_R) = 0.318$ ;  $r(\sigma_R \text{ vs } \Delta\sigma_R) = 0.655$ . It is also

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