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}H and ^{13}C NMR) identical with those of trans (B) and cis (A) marmelo oxides, reported in the literature.[2]

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Registry No. (±)-*cis*-**1**, 121009-51-6; (±)-*trans*-**1**, 121009-48-1; (±)-**3**, 120943-91-1; (±)-**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; (±)-*cis*-**9**, 120943-95-5; (±)-*trans*-**9**, 120943-97-7; $CH_2{=}CHCH_2OH$, 107-18-6; $Ph_3P{=}CHC(OEt){=}O$, 1099-45-2; $Ph_3P{=}CHC(Me){=}O$, 1439-36-7; $Ph_3PMe^+Br^-$, 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[1]

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Our previous study[3] of substituent effects on the ^{15}N chemical shifts (δ (^{15}N)) for 4-substituted anilines in dimethyl sulfoxide (Me_2SO) showed distinct substituent solvation-assisted resonance (SSAR) effects. Solvation of certain conjugated π-electron-acceptor (+R) substituents have been found to give significant enhancements in the acidities of anilines, phenols, and other acids,[4,5] and the magnitudes of these enhancements increase with increasing π-electron donation to the conjugated substituent from the deprotonation center of the anionic forms. In the case of anilines in Me_2SO, hydrogen-bond solvation by Me_2SO of the NH's increases the donation of π electrons to the conjugated + R substituent and this electron donation has been found to permit the SSAR enhancement effects on the δ(^{15}N) of the appropriate neutral aniline solutes.[3]

In this work, the SSAR treatment is given two simple but critical tests. First, δ(^{15}N) values for the previously used series of 13 para-substituted anilines have been measured in acetone (Me_2CO), a significantly weaker hydrogen-bond acceptor (HBA) solvent than dimethyl sulfoxide. We anticipated and report here the observed smaller shift dependence on para π-electron-acceptor substituent solvation (SSAR) effects in acetone. Second, we have measured in Me_2SO the δ(^{15}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 N^{15} shifts observed previously[3] for 4-substituted 2-nitroanilines in dimethyl sulfoxide).

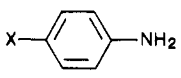
Table I. ^{15}N NMR Spectral Data (δ(^{15}N)) Values (ppm) of 4-Substituted Anilines I in Acetone-d_6 and 5-Substituted 2-Nitroanilines II in Dimethyl Sulfoxide-d_6 and Corresponding Substituent Parameters

substtnt	$-\delta(^{15}N)(I)^a$	$-\delta(^{15}N)(II)^b$	$\sigma_F{}^c$	$\sigma_R{}^c$	$\Delta\sigma_R{}^c$
OCH_3	62.9	32.0	0.25	−0.27	0.00
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
CF_3	52.1	31.5	0.44	0.07	0.00
SCF_3	51.3		0.48	0.10	0.00
H	57.8	34.6	0.00	0.00	0.00
CO_2CH_3	49.1		0.24	0.16	0.08
$CO_2C_2H_5$	49.4	33.2	0.24	0.16	0.08
$COCH_3$	48.3	33.0	0.26	0.17	0.10
CN	47.1		0.60	0.10	0.07
SO_2CH_3	48.0	30.6[d]	0.59	0.12	0.02
NO_2	42.4	29.8	0.65	0.18	0.18

[a] Chemical shift values upfield from $HCONH_2$ as external reference in Me_2CO-d_6 solution. [b] Chemical shift values in Me_2SO-d_6 solution. [c] From ref 4. [d] Cf. ref 7.

Results and Discussion

The ^{15}N chemical shifts, $-\delta$(^{15}N), for 4-substituted anilines I are upfield from $HCONH_2$, an external reference



I

for 1.0 M Me_2CO-d_6 solution and $-\delta$(^{15}N) values obtained are summarized in Table I (together with σ_F and σ_R values).[4] The σ_F and σ_R are field/inductive and resonance effect parameters, respectively, which are applicable to gas-phase proton-transfer equilibria.[4]

For non-substituent solvation assisted resonance (non-SSAR) substituents (OCH_3, CH_3, F, Cl, CF_3, SCF_3, H), the ^{15}N chemical shifts are well correlated by eq 1. Noncolinearity of σ_F and σ_R parameters for this substituent set is shown by $r = 0.071$.

$$\delta(^{15}\mathrm{N})(\mathrm{I},\ \mathrm{Me_2CO}) = (8.9 \pm 0.9)\sigma_F + (25.8 \pm 1.2)\sigma_R - 57.9 \pm 0.3\ \mathrm{ppm}$$

$$n = 7\ (\text{non-SSAR}),\ r = 0.996,\ \mathrm{sd} = 0.4\ \mathrm{ppm} \qquad (1)$$

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

$$\delta(^{15}\mathrm{N})(\mathrm{I},\ \mathrm{Me_2CO}) = (11.0 \pm 1.7)\sigma_F + (32.3 \pm 2.3)\sigma_R - 57.4 \pm 0.7\ \mathrm{ppm}$$

$$n = 13\ (\text{all substituents}),\ r = 0.983,\ \mathrm{sd} = 1.1 \qquad (2)$$

compared to that (0.4) for eq 1.

On the other hand, all 13 δ(^{15}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 π-electron acceptor substituents[4,5] (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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[1] This work was supported in part (UCI) by a grant from the National Science Foundation.

[2] (a) Toyama University. (b) University of California, Irvine.

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$$\delta(^{15}\text{N})(\text{I, Me}_2\text{CO}) = (9.7 \pm 0.6)\sigma_F + (26.7 \pm 1.0)\sigma_R + (25.8 \pm 3.1)\Delta\sigma_R - 57.9 \pm 0.3 \text{ ppm}$$

$$n = 13 \text{ (all substituents)}, r = 0.998, \text{sd} = 0.4 \quad (3)$$

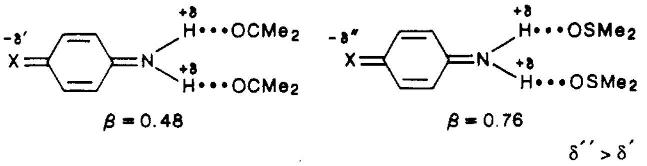
to be noted that eq 1 and 3 are consistent in that the intercept and the coefficients to σ_F and σ_R are the same within the errors of the estimates.

The $\delta(^{15}N)$ values of I in dimethyl sulfoxide were found in the previous study[3] to be well correlated by eq 4, which has the same form as eq 3.

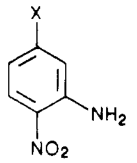
$$\delta(^{15}\text{N})(\text{I, Me}_2\text{SO}) = (11.8 \pm 0.9)\sigma_F + (31.1 \pm 1.5)\sigma_R + (37.4 \pm 4.3)\Delta\sigma_R - 53.0 \pm 0.4 \text{ ppm}$$

$$n = 13, r = 0.998, \text{sd} = 0.7 \text{ ppm} \quad (4)$$

It is important to note that the value (25.8 ± 3.1) of ρ_S (dependence on $\Delta\sigma_R$) for ^{15}N chemical shifts in acetone solution (eq 3) is smaller by a factor of about 1.5 than that (37.4 ± 4.3) for the $\delta(^{15}N)$ shifts in dimethyl sulfoxide solution (eq 4). The smaller response in acetone is due to diminished π-electron-acceptance from the amino group that results from the approximately 1.5 factor weaker hydrogen-bond-acceptor (HBA) ability of acetone (HBA parameter $\beta_1 = 0.48$) than that of dimethyl sulfoxide ($\beta_1 = 0.76$).[6] With decreased HBA ability, the delocalization of π electrons from the hydrogen-bonded NH_2 to the conjugated para π-electron-acceptor substituent is reduced. The reduction of the SSAR effects in acetone solution can be expressed by the following forms:



A further test of the SSAR effect treatment has been carried out for the $\delta(^{15}N)$ of 5-substituted 2-nitroanilines



II

II in which the NH_2 detection center is in the nonconjugated meta position. The correlations of $\delta(^{15}N)$ (in Me_2SO 1.7 M solution) with σ_F, σ_R, and $\Delta\sigma_R$ are as follows.

$$\delta(^{15}\text{N})(\text{II, Me}_2\text{SO}) = (7.4 \pm 0.4)\sigma_F - (1.4 \pm 0.6)\sigma_R - 34.6 \pm 2 \text{ ppm} \quad (5)$$

$$n = 9 \text{ (all substituents)}, r = 0.990, \text{sd} = 0.3 \text{ ppm}$$

$$\delta(^{15}\text{N})(\text{II, Me}_2\text{SO}) = (7.2 \pm 0.4)\sigma_F - (1.9 \pm 0.7)\sigma_R + (2.3 \pm 2.1)\Delta\sigma_R - 34.7 \pm 0.2 \text{ ppm} \quad (6)$$

$$n = 9 \text{ (all substituents)}, r = 0.992, \text{sd} = 0.3 \text{ ppm}$$

In eq 6 the ρ_s coefficient (2.3 ± 2.1) is not truly statistically significant, and eq 5 is the preferred one. The insignificant ρ_s coefficient (in marked contrast to the ρ_s value of 23.5 in eq 7 of our previous study[3] with 4-substituted 2-nitroanilines) can be accounted for by the absence of direct resonance interactions between the NH_2 detection center and the meta substituents.

This work together with our earlier report has provided confirmation that SSAR effects are generally applicable to physical as well as chemical properties and that results similar to the present ones are to be expected, for example, for $\delta(^{17}O)$ shifts of meta- and para-substituted phenols and (particularly) phenoxides.

Registry No. I (X = OCH_3), 104-94-9; I (X = CH_3), 106-49-0; I (X = F), 371-40-4; I (X = Cl), 106-47-8; I (X = CF_3), 455-14-1; I (X = SCF_3), 372-16-7; I (X = H), 62-53-3; I (X = CO_2CH_3), 619-45-4; I (X = $CO_2C_2H_5$), 94-09-7; I (X = $COCH_3$), 99-92-3; I (X = CN), 873-74-5; I (X = SO_2CH_3), 5470-49-5; I (X = NO_2), 100-01-6; II (X = OCH_3), 16133-49-6; II (X = CH_3), 578-46-1; II (X = F), 2369-11-1; II (X = CF_3), 402-14-2; II (X = H), 88-74-4; II (X = $CO_2C_2H_5$), 84228-43-3; II (X = $COCH_3$), 79127-41-6; II (X = SO_2CH_3), 121444-20-0; II (X = NO_2), 619-18-1; A, 23153-09-5; *N*-acetyl-2-nitro-5-(methylthio)aniline, 54029-49-1.

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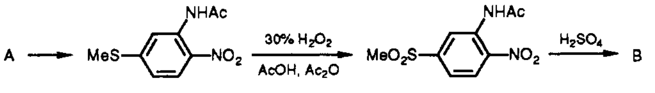
(7) 5-(Methylsulfonyl)-2-nitroaniline (B) (mp 179.0–179.5 °C) was prepared as follows from 5-(methylthio)-2-nitroaniline (A), obtained as reported by Hodgson et al. (Hodgson, H. H.; Handley, F. W. *J. Chem. Soc.* **1928**, 162) from *m*-dichlorobenzene:



B	N	C	H	m/l
Anal. found	12.97	39.19	3.70	216
calcd	12.96	38.89	3.73	216.21

Synthesis of 3-Methoxyestra-1,3,5(10),6-tetraen-17-one

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In connection with our studies of dye-sensitized photooxygenation of styrenic estrogens,[1] we required a method for preparation of the title compound (**5**).

The schemes previously reported for the synthesis of 6-dehydroestrogens either give very low yields[2] or involve complex procedures.[3]

We now report efficient synthesis of **5** from 17β-hydroxyestr-4-en-3-one (**1**) via introduction of the Δ^6 double bond and selective microbial aromatization of ring A in two consecutive steps.

Oxidation of **1** with chromium(VI) oxide in acetic acid[4] followed by treatment of the resulting diketone **2** with chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) in ethanol[5] afforded, after column chromatography and crystallization, **3** in 41% yield from **1**. Attempted aromatization of ring A with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) led to complex mixtures, while treatment of **3** with iodine

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