

Hz, $\Delta\nu_{AB}$ = 12.70 Hz), 1.03 (s, 3 H), 0.90 (s, 3 H), 0.11 (s, 9 H).

9,9-Dimethylspiro[4.5]deca-1,6-dien-3-one (1a). To a solution of 1.67 g (6.68 mmol) of aldehyde **5a** in 20 mL of acetone at 0 °C was added 2.5 mL (6.68 mmol) of Jones reagent (2.67 M) dropwise via syringe. After being stirred at 0 °C for 2 h the reaction mixture was allowed to warm to room temperature over a 1-h period. The reaction was neutralized with aqueous sodium bicarbonate and extracted several times with ether. The combined ether extracts were washed with dilute aqueous HCl and brine, dried (Na₂SO₄), and concentrated under reduced pressure. Filtration of an ether solution of the crude product through a pad of silica gel provided 1.73 g (97%) of the carboxylic acid.

To a solution of 50 mg (0.188 mmol) of the carboxylic acid in 1 mL of dry benzene was added 73 μ L (0.84 mmol) of oxalyl chloride dropwise via syringe. After the reaction mixture was stirred for 3 h at room temperature the benzene and excess oxalyl chloride were removed in vacuo and 3.0 mL of dry methylene chloride was added. After the solution was cooled to -30 °C, 62 μ L (0.56 mmol) of titanium tetrachloride was added. The reaction mixture was stirred 2 h at -30 °C and was allowed to warm to room temperature and stir for 15 h, at which time the solution was poured into saturated aqueous sodium bicarbonate. The organic material was extracted with ether and the combined extracts were dried (MgSO₄) and concentrated. Purification was effected by chromatography on a column of silica gel. Elution with hexanes, followed by 1:8 ether-hexanes, afforded 27 mg (82%) of the desired spiro[4.5]decadienone **1a**, homogeneous by TLC and spectroscopic methods, as an oil (crystalline at subambient temperature): *R_f* 0.46 (1:1 ether-hexanes); IR (CCl₄) 1723 (C=O); ¹H NMR (400 MHz) (CDCl₃) δ 7.29 (d, 1 H, *J* = 5.50 Hz), 6.02 (d, 1 H, *J* = 5.50 Hz), 5.68 (ddd, 1 H, *J* = 9.68, 5.22, 2.90 Hz), 5.27 (br d, 1 H, *J* = 9.68 Hz), 2.34 (AB q, 2 H, *J_{AB}* = 18.77 Hz, $\Delta\nu_{AB}$ = 63.98 Hz), 1.78-1.86 (m, 2 H), 1.51 (AB q, 2 H, *J_{AB}* = 13.73 Hz, $\Delta\nu_{AB}$ = 85.87 Hz), 0.97 (s, 3 H), 0.92 (s, 3 H); ¹³C NMR (CDCl₃) δ 208.67, 171.77, 131.00, 128.80, 126.40, 48.77, 46.46, 45.58, 37.78, 30.64, 28.89, 26.75. Distillation [bath temperature 80 °C (1.4 mmHg)] gave an analytical sample of **1a**.

Anal. Calcd for C₁₂H₁₆O: C, 81.77; H, 9.15. Found: C, 81.85; H, 9.23.

6,9,9-Trimethylspiro[4.5]deca-1,6-dien-3-one (1b). To a solution of 7.51 g (28.4 mmol) of aldehyde **5b** in 90 mL of acetone at 0 °C was added 10.65 mL (28.4 mmol) of 2.67 M Jones reagent in dropwise fashion. After being stirred for 2.5 h at 0 °C and 6 h at room temperature, the reaction mixture was neutralized with saturated aqueous bicarbonate and extracted repeatedly with ether. The combined ether extracts were dried (MgSO₄) and concentrated in vacuo to give 7.77 g (98%) of the corresponding carboxylic acid.

To a solution of 11.05 g (39.5 mmol) of this acid in 230 mL of dry benzene was added 12.5 mL (143 mmol) of oxalyl chloride. After the reaction mixture was stirred at room temperature for 3.5 h, the benzene and excess oxalyl chloride were removed in vacuo and 350 mL of dry methylene chloride was added. The solution was cooled to -30 °C and 12.95 mL (118 mmol) of titanium tetrachloride was added dropwise. After the solution had been stirred for 2 h at -30 °C and 14 h at room temperature, the reaction was poured into saturated aqueous sodium bicarbonate. The organic material was extracted with ether, and the combined extracts were dried (MgSO₄) and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel. Elution with hexanes followed by 1:8 ether-hexanes afforded 6.30 g (84%) of the spiro[4.5]decadienone **1b**, homogeneous by TLC and spectroscopic criteria, as an oil (crystalline at subambient temperature): *R_f* 0.66 (1:1 ether-hexanes); IR (film) 1720 cm⁻¹ (C=O); ¹H NMR (400 MHz) (CDCl₃) δ 7.29 (d, 1 H, *J* = 5.37 Hz), 6.14 (d, 1 H, *J* = 5.37 Hz), 5.50 (br s, 1 H), 2.39 (s, 3 H), 1.86 (AB q, 2 H, *J_{AB}* = 16.65 Hz, $\Delta\nu_{AB}$ = 39.96 Hz), 1.53 (AB q, 2 H, *J_{AB}* = 13.67 Hz, $\Delta\nu_{AB}$ = 116.19 Hz), 1.49 (s, 2 H), 0.98 (s, 3 H), 0.94 (s, 3 H).

Anal. Calcd for C₁₃H₁₈O: C, 82.06; H, 9.53. Found: C, 81.88; H, 9.63.

Acknowledgment. Grateful acknowledgment is extended to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to Re-

search Corporation, to the National Institutes of Health (Biomedical Research Support Grant 5 S07 RR07160), and to the American Cancer Society (Grant IN-107F, awarded to C.W.M.) for their generous support of this research. High-field NMR spectra were obtained through the National Science Foundation Regional NMR Center at the University of South Carolina (Grant CHE 78-18723).

Registry No. **1a**, 76999-33-2; **1b**, 76999-34-3; **2a**, 4683-45-8; **2b**, 76999-35-4; **3a**, 76999-36-5; **3b**, 76999-37-6; **4a**, 76999-38-7; **4b**, 77011-22-4; **5a**, 76999-39-8; **5a** carboxylic acid, 76999-40-1; **5b**, 76999-41-2; **5b** carboxylic acid, 76999-42-3; *trans*-1-(trimethylsilyl)-2-(tributylstanny)ethylene, 58207-97-9; ethyl vinyl ether, 109-92-2.

Effect of Benzyl Groups on Electron Loss from Tetraalkylhydrazines and 2-Tetrazenes

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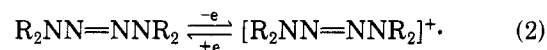
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The thermodynamics of the tetraalkylhydrazine one electron oxidation equilibrium (eq 1) has been studied for



a variety of alkyl groups by determining the formal potentials for electron transfer (*E*^{o'}), using cyclic voltammetry (CV).¹ Equation 1 provides an opportunity to study the effect of R group substitution on a reaction where these effects are unusually large. Changes in the thermodynamics for eq 1 with R group substitution have proven to be dominated by steric effects, although electronic and solvation effects are clearly also present. The alkyl groups on adjacent nitrogens are eclipsed in the radical cation, which has an olefin-like equilibrium geometry with a substantially shorter NN distance,² greatly increasing the vicinal R group interaction over that in the neutral form. The majority of this increase in vicinal steric interaction is removed in the tetraalkyl-2-tetrazene electron-transfer equilibrium (eq 2).³ Comparison of *E*^{o'} values for these



equilibria with vertical, vapor-phase ionization potentials (IP_v) measured by photoelectron (PE) spectroscopy has allowed estimation of the importance of steric, electronic, and solvation changes with alkyl group substitution on these equilibria.⁴ Our discussion of these factors has previously been limited to the effects of saturated alkyl substituents. We turn our attention here to considering

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Table I. PE and CV Data for Benzylated Hydrazines and 2-Tetrazenes

compd	IP _v , eV ^a	E ^{o'} , V ^b	E ^{o'} - E ^{o'} (corr), ^c kcal/mol
Me ₂ NNMe ₂ (1)	8.27, 8.82	0.28	0
Bz ₂ NNMe ₂ (2)	8.15, 8.67, 9.23	0.43	3.9
Bz ₂ NNBz ₂ (3)	8.01, 8.70, 9.22	0.60	8.3
Me ₂ NN ₂ NMe ₂ (4)	7.71, 9.32, 9.80 ^d	0.417 ^d	0
BzMeNN ₂ NMeBz (5)	7.43, 9.25	0.51	3.5
Bz ₂ NN ₂ NBz ₂ (6)	ca. 7.3, 9.25	0.59	6.0

^a Positions of Gaussian peaks which superimpose to fit the low-energy ionization region of the PE spectrum.

^b Versus SCE, in acetonitrile containing 0.1 M sodium perchlorate as supporting electrolyte.³ ^c From ref 4a: hydrazines, E^{o'}(corr) = -0.96₁ + 0.15(IP_v); tetrazenes, E^{o'}(corr) = -1.17₀ + 0.20₆(IP_v). Entry is 23.06 (E^{o'} - E^{o'}(corr)) to convert from electron volts to kilocalories/mole. ^d Data from ref 4a.

the effect of benzyl group substitution on these electron transfers.

Results

Table I lists data derived from the PE spectra for methyl- and benzyl-substituted hydrazines and 2-tetrazenes. The PE spectra for the benzylated compounds are rather complex in the low-energy ionization region, because of several overlapping one pair and benzyl π system ionizations. We were able to fit the benzylated hydrazines (2, 3) spectra with three Gaussian peaks, and the dimethyldibenzyltetrazene (5) spectrum with two peaks. We do not claim to be able to accurately measure IP_v for the higher ionization potential lone pair combination orbital or the π ionizations from our data but believe that the reported first vertical IP for these compounds is accurate to 0.1 eV. Tetrabenzyl-2-tetrazene (6) was so unvolatile that our PE data were poor, and the first ionization peak observed was very weak compared to the π -region peak; here we do not even know IP₁ very accurately.

The electrochemical E^{o'} values also given in Table I have been reported previously.³

Discussion

Electronic Effect of the Benzyl Substituent from IP_v Measurements. We previously pointed out that the E^{o'} values for 1-3, benzyltrimethylhydrazine, and symmetrical dibenzyltrimethylhydrazine give a linear correlation with $\sigma^* - E^o'$, increasing as benzyl groups are substituted for methyl. This shows that benzyl for methyl substitution increases the radical cation-neutral compound energy gap, so that benzyl is effectively electron withdrawing relative to methyl.

Taft⁵ quantitatively expressed the idea that the electron-releasing effect of alkyl substituents increases with homologation and α branching by his σ^* constants, which have been fairly widely employed by organic chemists.⁶

The effects are usually not large, and indeed, Taft correlations have been shown for some cases to fit as well with σ^* is assigned as zero for all saturated alkyl groups.⁷ Charton⁸ has restudied ester and amide hydrolysis data extensively, concluding that σ^* values, as they were determined, do not reflect differences in "electrical effects" but involve steric factors, and that alkyl groups do not differ significantly in their electrical effects.^{8a} Nevertheless, vapor-phase work has shown that there is a significant effect of alkyl group size on ion stability, although this effect should not be thought of as "inductive"—*tert*-butyl stabilizes anions as well as cations relative to methyl in the vapor phase.⁹ Ionization potentials have been used extensively to measure the electron-delocalizing ability of alkyl groups toward adjacent positive charge in the absence of solvation effects and steric effects as a result of geometry change during a reaction. Danby and co-workers¹⁰ derived substituent constants closely resembling σ^* by using lone pair vertical ionization potentials IP_v measured by PE spectroscopy for various RX compounds, where X is a heteroatom or heteroatom-containing group, and showed that eq 3 is followed for a wide variety of X.¹¹ A similar

$$\text{IP}_v(\text{RX}) = \text{IP}_v(\text{MeX}) + \chi\mu_R \quad (3)$$

treatment of photoionization data has been employed by Levitt.¹² Comparison of μ^* with σ^* shows that σ^* gives a remarkably good correlation of the effect of α branching in alkyl groups on ionization potential, although the effect of homologation on the positive-charge-stabilizing ability of alkyl groups is somewhat underestimated.⁴

The benzyl group is a particularly significant alkyl group to consider in comparing σ^* and μ^* . Benzyl is substantially electron withdrawing relative to methyl in solution ($\sigma^* = +0.215^1$), but as a larger and more polarizable group, benzyl lowers vertical ionization potentials relative to methyl. Benzyl was not considered in the work of Danby and co-workers,¹⁰ but from the benzyl halide IP_v measurements of Schmidt and Schweig,¹³ $\mu^*(\text{benzyl})$ values of -0.14 (X = Cl) and -0.13 (X = Br and I) are obtained. The interaction of a benzyl group with an attached lone pair bearing substituent is clearly going to depend on orientation. The high-lying aryl π -system orbitals will mix with the CH₂X: orbitals, and one might well not see a constant $\mu^*(\text{benzyl})$ value when X is varied. As previously discussed,⁴ variations in effective μ^* are even seen for saturated alkyl groups with β branching such as isobutyl and neopentyl, when these groups are placed in sterically crowded situations, as in tetraalkylhydrazines.

It is clear that $\mu^*(\text{benzyl})$ is not as negative for hydrazine as it is for halides, because if $\mu^*(\text{benzyl})$ were -0.13, IP_v would be 8.04 and 7.82 for 2 and 3, respectively, but higher IP_v values are observed. The observed $\mu^*(\text{benzyl})$ values are -0.07 (2) and -0.08 (3). In contrast to the case of benzyl halides, the nitrogen lone-pair energy is higher than that of the highest aryl π orbital. We suggest that aryl π -X: interaction is principally responsible for the rather large difference in $\mu^*(\text{benzyl})$ as calculated from the IP_v of halides and hydrazines. Despite the variability of $\mu^*(\text{benzyl})$, depending on what X is, it is clear that $\mu^*(\text{benzyl})$

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(11) To facilitate comparison with σ^* , we discuss $\mu^* = \mu_R/1.95$. This simply redefines the slope, so that $\mu^*(\text{Et}) = \sigma^*(\text{Et}) = -0.10$, allowing direct comparisons to be made.⁴

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is negative, in contrast to the positive value of σ^* (benzyl). Benzyl groups clearly stabilize hydrazine and tetrazene radical cations relative to methyl groups in the vapor phase.

E° Values for Benzylated Hydrazines and Tetrazenes. The IP_v measurements show that benzyl is cation stabilizing relative to methyl in the vapor phase, while the E° measurements show that benzyl is cation destabilizing relative to methyl in solution. The question of why their effects are opposite in different phases remains to be considered.

It is well-known that the ease of electron loss in solution depends upon the energy of the HOMO, a measure of which is IP_v . For polycondensed aromatic hydrocarbons, a plot of E° vs. IP_v is linear and has a slope of 0.89.⁴ Lengthening alkyl groups is another way of changing IP_v , but the sensitivity of E° to IP_v changes caused by lengthening alkyl groups is substantially less. For *n*-alkyl-2-tetrazenes, a plot of E° vs. IP_v is also linear but has a slope of 0.20.⁴ Taft and co-workers¹⁴ have pointed out that the polarizability effect of alkyl group enlargement is effectively lost in solution, while inductive effects are attenuated much less. The large and polarizable benzyl group is cation stabilizing in the vapor phase, but the polarizability effect is effectively lost upon going to solution, and the inductive effect from the presence of the sp^2 -hybridized β carbon could well make benzyl electronically cation destabilizing in solution.

Experimentally, dibenzyl-dimethyl-2-tetrazene **5** has a 3.5 kcal/mol higher E° than the linear correlation from straight-chain alkyl groups predicts (Table I), while the E° derivation for the tetrabenzyl compound **6** is 6.0 kcal/mol. Although hydrazine E° values are more subject to steric effects, the deviations of **2** and **3** from the hydrazine correlation line are only a little larger, at 3.9 and 8.3 kcal/mol, respectively. We note that, in the most recent correlation of Z/E ratios for alkylated olefins,¹⁵ benzyl was found to be effectively no larger than ethyl in determining the Z/E ratio and that the E° values for hydrazines reveal that hydrazine radical cations resemble olefins in steric demands.⁴ Both inductive effects and solvation effects (larger alkyl groups excluding the more polar acetonitrile solvent from the region near the strongly positive nitrogens, thus destabilizing a radical cation relative to cases with smaller alkyl groups) will contribute to the more difficult oxidation for benzyl than for methyl substituted compounds. There is evidence in the saturated alkyl-2-tetrazene data for such a solvation effect. β -branched alkyl 2-tetrazenes (isobutyl, neopentyl) show rather small (0.3 to 0.6 kcal/mol) positive deviations from the *n*-alkyl correlation line.⁴ The positive deviations exhibited by the benzyl-substituted compounds discussed here are substantially larger, but we unfortunately have no way at present to estimate the relative importance of inductive and solvation contributions to the observed ΔG° changes for electron transfer.

Conclusion

Despite the lowering of IP_v observed when benzyl is substituted for methyl on hydrazines and 2-tetrazenes, ΔG° for electron loss in solution is raised 1.5–2.1 kcal/mol for each benzyl for methyl replacement. The opposite direction of the effect of replacing benzyl by methyl in solution and vapor phases is caused by the great attenuation

of polarizability effects upon going to solution.¹⁴

Experimental Section

Preparations of **2**,¹⁶ **3**,¹⁶ and **6**¹⁷ have been previously described.

1,4-Dibenzyl-1,4-dimethyl-2-tetrazene (5). A solution of 5.44 g (0.04 M) of 1-benzyl-1-methylhydrazine¹⁸ in 200 mL of ether containing 15 mL of diethylamine was stirred at 0 °C and titrated with a solution of iodine in ether.¹⁹ After filtration, solvent removal gave 2.3 g (33%) of **5**, mp 27–28 °C after crystallization from ethanol. The empirical formula was established by high-resolution mass spectroscopy: ¹H NMR (CDCl₃) δ 2.85 (s, 3 H), 4.43 (s, 2 H), 7.34 (s, 5 H); no NH or C=O observed by IR.

The PE and CV measurements have been previously described.^{1,4a}

Acknowledgment. We thank the National Science Foundation for partial financial support of this work, both through a research grant and the Major Instrument Program.

Registry No. **1**, 6415-12-9; **2**, 65114-31-0; **3**, 5416-62-6; **4**, 6130-87-6; **5**, 65114-29-6; **6**, 23456-88-4; 1-benzyl-1-methylhydrazine, 3931-52-0.

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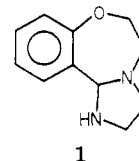
Isolation and Characterization of 1,2,3,5,6,11b-Hexahydroimidazo[1,2-d][1,4]benzoxazepine from an Aziridine Ligand Reaction

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Received October 27, 1980

We report the isolation and characterization of 1,2,3,5,6,11b-hexahydroimidazo[1,2-d][1,4]benzoxazepine, **1**, which to our knowledge, is the first example of this



1

tricyclic ring system in a low oxidation state. More highly unsaturated imidazobenzoxazepines¹ and highly substituted tetrahydroimidazo[5,1-d][1,4]benzoxazepines² have been described, although the position of the heteroatoms is different than that in the compound reported here. The compound was isolated by demetalation of an isolated tan intermediate complex from the transformation of bis-[N-[2-(1-aziridinyl)ethyl]salicyladimino]nickel(II), Ni(SalAEA)₂, to disalicylideneethylenediiminonickel(II), Ni(Sal₂en)³ (see eq 1).

The tan intermediate has the empirical formula C₂₂H₂₉N₄O₃BrNi by elemental analysis. Though this formula corresponds to the composition of two SalAEA ligands, one

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