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.

$E^{\circ\prime}$ 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 $E^{\circ\prime}$ 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 $E^{\circ\prime}$ 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 $E^{\circ\prime}$ to IP_v changes caused by lengthening alkyl groups is substantially less. For *n*-alkyl-2-tetrazenes, a plot of $E^{\circ\prime}$ vs. IP_v is also linear but has a slope of 0.20_6.[4] Taft and co-workers[14] 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 sp²-hybridized β carbon could well make benzyl electronically cation destabilizing in solution.

Experimentally, dibenzyldimethyl-2-tetrazene **5** has a 3.5 kcal/mol higher $E^{\circ\prime}$ than the linear correlation from straight-chain alkyl groups predicts (Table I), while the $E^{\circ\prime}$ derivation for the tetrabenzyl compound **6** is 6.0 kcal/mol. Although hydrazine $E^{\circ\prime}$ 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 $E^{\circ\prime}$ values for 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^0 changes for electron transfer.

Conclusion

Despite the lowering of IP_v observed when benzyl is substituted for methyl on hydrazines and 2-tetrazenes, ΔG^0 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-methylhydrazine[18] 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]

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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
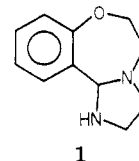
1

tricyclic ring system in a low oxidation state. More highly unsaturated imidazobenzoxazepines[1] and highly subsituted tetrahydroimidazo[5,1-*d*][1,4]benzoxazepines[2] 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 $C_{22}H_{29}N_4O_3BrNi$ by elemental analysis. Though this formula corresponds to the composition of two SalAEA ligands, one

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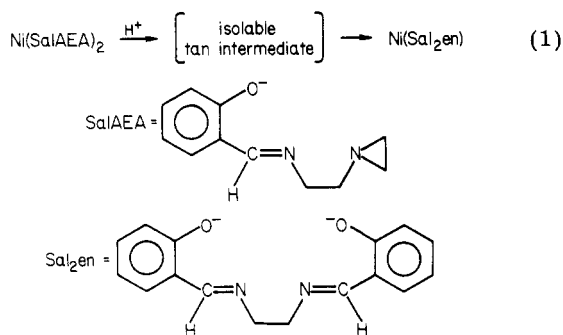
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$$\text{Ni(SalAEA)}_2 \xrightarrow{H^+} \begin{bmatrix} \text{isolable} \\ \text{tan intermediate} \end{bmatrix} \longrightarrow \text{Ni(Sal}_2\text{en)} \qquad (1)$$

SalAEA =

Sal₂en =

nickel ion, one HBr, and one water, a peak at 3120 cm⁻¹ in the N–H stretching region provides evidence that at least one of the SalAEA ligands has undergone a structural change. Since the structure of the coordinated ligand(s) in the intermediate cannot be learned by NMR spectroscopy due to the paramagnetism of the metal ion, we attempted to isolate the organic ligand by removing the metal ion from the complex. Demetalation was accomplished by reaction of the intermediate complex with KCN or reaction with the chelating agent EDTA in aqueous solution. The organic products from these aqueous reactions were extracted into methylene chloride.

After treatment of the complex with EDTA, two compounds were extracted and separated on a silica gel column. One compound was SalAEAH, the parent phenol of the ligand in the starting complex. The other was characterized by ¹H NMR, ¹³C NMR, infrared, and mass spectroscopy and analysis and shown to be the title compound, **1** (see Experimental Section). When KCN was used for the demetalation reaction, SalAEAH and **1** were isolated when extraction was done within 15 min of the addition of cyanide to the aqueous solution. After 1 h of reaction with aqueous cyanide, an additional compound was isolated. This product was shown to be **2** by ¹H NMR,

2
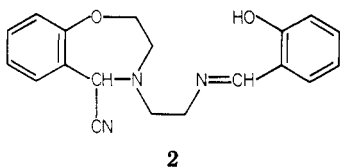
infrared, and mass spectroscopy. In addition to the physical data supporting the assignment of structure **1**, the characterization of **2** as a logical derivative of **1** upon reaction with excess cyanide in the basic medium which also contains a salicylaldimine Schiff base lends circumstantial support to the structure assignment of **1**.

The formation of **1** in this complex system was unexpected. The crystal structure of the tan intermediate will establish whether **1** is a ligand or is formed from some other isomeric ligand. There is evidence that the metal ion does participate in the formation of **1** (or its precursor) since a control reaction run without a metal ion present results in a different product. This ability of metal ions to alter the reactivity of aziridine-containing compounds could provide a useful synthetic entry to new heterocyclic systems.

Further details of the reactions of the metal complexes and ligands are published elsewhere.[4]

Experimental Section

Tan Intermediate. To 4.00 g (9.11 mmol) of Ni(SalAEA)₂ in 100 mL of MeCN was added 1.60 g (9.49 mmol) of 48% aqueous

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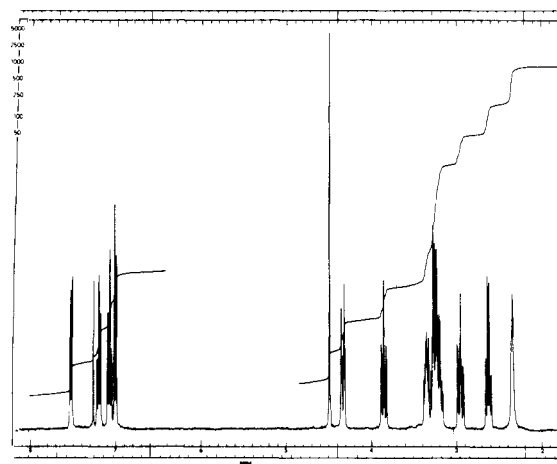
Figure 1. 360-MHz ¹H NMR spectrum of 1,2,3,5,6,11b-hexahydroimidazo[1,2-*d*][1,4]benzoxazepine in CDCl₃.

HBr. The original green solution immediately turned blue-green and after 1.5 h of reflux was red-brown. Upon concentration to about 10 mL a tan powder precipitated, which was isolated by filtration and dried in vacuo for 2 h at 30 °C, yield 3.60 g (73.5%). Recrystallization from a saturated solution of *n*-BuOH at 70 °C, which was filtered by gravity and allowed to stand about 3 days, gave small dark brown prisms. The tan intermediate is very soluble in H₂O, CH₂Cl₂, and MeOH but insoluble in EtOAc and Et₂O: IR (Nujol) 3460 (m, br), 3120 (s), 1655 (s), 1630 (s), 1605 (s), 1530 (m), 1400 (m), 1360 (m), 1208 (s), 1191 (m), 1148 (s), 1130 (m), 1105 (s), 1061 (s), 1028 (m), 999 (s), 913 (m), 900 (s), 862 (m), 793 (s), 759 (s), 743 (m), 732 (m), 645 (w), 600 (w), 551 (w), 499 (w), 484 (w), 467 (w), cm⁻¹; electronic spectrum (MeOH), λ 830 nm (34.2) 785 (32.5), 537 (39.9), 370 (9540). Anal. Calcd for NiC₂₂H₂₉N₄O₃Br: C, 49.29; H, 5.45; N, 10.45; Br, 14.90. Found: C, 49.28; H, 5.91; N, 10.35; Br, 14.26.

Upon treatment with 0.5 M AgNO₃, the tan intermediate gave a precipitate of AgBr. It also gave a positive phenol test in 1:1 EtOH–H₂O when treated with 1% aqeuous FeCl₃; magnetic moment 2.96 (Gouy method, solid), 3.05 μ_B (NMR method in MeOH).

Demetalation of Tan Intermediate with EDTA. A 5-g sample (9.30 mmol) of tan intermediate, 10.0 g (26.6 mmol) of trisodium ethylenediaminetetraacetic acid, and enough KOH to dissolve the latter were placed in 300 mL of water. After being stirred at room temperature for 1 h, the solution was extracted with three 250 mL portions of CH₂Cl₂. The blue nickel–EDTA complex remained in the aqueous layer. The yellow CH₂Cl₂ solution was dried (MgSO₄) and evaporated to a yellow oil which was added to a 1 × 12 in. silica gel column prepared with heptane. Elution with Et₂O produced a narrow yellow band which contained a single compound (TLC). ¹H NMR shows this compound to be SalAEAH. After the Et₂O elution, the column was washed with EtOAc and then eluted with absolute EtOH to give **1**, which crystallized after evaporation. Recrystallization from Et₂O gave nearly white prisms: mp 69–71 °C; IR (Nujol) 3245 (s), 3055 (m), 1610 (m), 1585 (m), 1490 (m), 1325 (s), 1295 (s), 1285 (m), 1220 (s), 1163 (m), 1135 (m), 1045 (s), 1031 (s), 953 (s), 904 (s), 864 (s), 814 (s), 784 (s), 763 (s), 719 (m), 684 (w), 634 (w), 585 (m), 542 (w), 514 (m) cm⁻¹; ¹H NMR (CDCl₃), see (Figure 1, δ 2.35 (s, 1 H), 2.63 (q, 1 H, J = 8.1 Hz), 2.96 (m, 1 H), 3.12–3.40 (m, 4 H), 3.86 (m, 1 H), 4.34 (dt, J_1 = 13.0, J_2 = 3 Hz, 1 H), 4.60 (s, 1 H), 7.00 (dd, 1 H, J_1 = 9, J_2 = 1.5 Hz), 7.08 (td, 1 H, J_1 = 9, J_2 = 1.5 Hz), 7.20 (td, 1 H, J_1 = 9 Hz, J_2 = 1.5 Hz), 7.52 (dd, 1 H, J_1 = 9, J_2 = 1.5 Hz); mass spectrum, *m/e* 190 (M⁺), 189 (base), 161, 147, 119, 97, 91; ¹³C NMR (CDCl₃) δ 44.08, 56.03, 56.09, 72.26, 78.89, 121.10, 123.74, 126.11, 128.79, 133.66, 158.71. Anal. Calcd for C₁₁H₁₄N₂O: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.34; H, 7.47, N, 14.76.

Demetalation of Tan Intermediate with KCN. CHCl₃ (50 mL) containing 0.500 g (9.930 mmol) of tan intermediate was mixed and stirred rapidly with 50 mL of H₂O containing 0.302 g (4.64 mmol) of KCN. After 1 h the yellow CHCl₃ layer was separated and evaporated to a yellow oil. Two components in-

dicated by TLC were separated by chromatography on a 1 × 12 in. silica gel column. Elution with dry Et₂O gave a narrow yellow band. Evaporation of the ether eluate gave a yellow oil which was shown by TLC to be a single compound, **2**, but could not be crystallized: IR (CHCl₃, 0.0269-mm pathlength) 2425 (w), 1645 (s), 1600 (m), 1505 (s), 1475 (m), 1295 (s), 1170 (m), 680 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 2.7–4.5 (m, 8 H), 4.95 (s, 1 H), 6.8–7.8 (m, 8 H), 8.30 (s, 1 H), 12.98 (br s, 1 H), exchanges with D₂O); mass spectrum, *m/e* 321 (M⁺), 294, 263, 225, 187, 167, 149 (base).

The second product was eluted with absolute EtOH after the column was washed with EtOAc. The light yellow eluate was evaporated to an oil which crystallized on standing. After recrystallization from Et₂O, the ¹H NMR was identical with that of **1** described previously. **Caution:** The aqueous CN⁻ layer from the extraction is reacted with excess KMnO₄ to destroy the cyanide ion. **Extreme care must be exercized in all procedures involving KCN.**

Spectral Interpretation. Several spectral features of **1** and **2** are in support of our structure assignments. Both **1** and the tan intermediate complex have IR bands assignable as N–H stretching at 3245 and 3120 cm⁻¹, respectively. The energy difference between the bands indicates that the secondary amine in the complex is coordinated,⁵ providing some evidence that **1** could be a ligand in the tan intermediate.

The structure of **1** is supported by the 360-MHz ¹H NMR spectrum shown in Figure 1. Integration shows the ratio of methylene to aromatic protons to be 2:1. The four methylene protons in the imidazolidine ring are very nearly equivalent and are observed as a complex multiplet centered at δ 3.3. Similar patterns have been observed for other imidazolidines.⁶,⁷ The four aliphatic protons of the benzoxazepine ring are magnetically nonequivalent and display complex miltiplets at δ 2.6, 3.0, 3.9, and 4.3. The slightly broad singlet at δ 2.35 exchanges with D₂O and is assigned to the secondary amine proton. The sharp singlet at δ 4.6 is assigned to the CH between two nitrogens.

Structure **1** is also supported by the ¹³C NMR spectrum which shows 11 carbon atoms, six of which are aromatic and two of which at δ 133.66 and 158.71, have decreased intensity, indicating the absence of hydrogens on them. Three of the remaining five carbons have chemical shifts compatible with assignments as CH₂N⁸ and two of these at δ 56.03 and 56.09 are very similar and are assigned to the imidazolidine ring. The carbon at δ 72.26 is assigned to the CH₂O carbon.⁸ The resonance at δ 78.89 is assigned to the geminal diamine carbon. None of the spectral data is consistent with the presence of an aziridine ring or a Schiff base linkage.

The ¹H NMR of **2** shows eight aromatic protons, eight aliphatic protons in a complex pattern at δ 2.7–4.5 assigned to the CH₂ groups of the seven-membered ring and the NCH₂CH₂N linkage, and two singlets at δ 8.30 and 4.95 assigned to the Schiff base ηH and the CH bearing the nitrile group, respectively. The broad singlet at δ 12.98 exchanges with D₂O and is assigned to the phenol proton. The mass spectrum shows the parent ion peak at *m/e* 321 and a peak at 294 resulting from loss of HCN.

Registry No. 1, 77123-89-8; **2**, 77123-90-1; Ni(SalAEA)₂, 38966-31-3.

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Characterization and Properties of Dibenzo-18-crown-6 Covalently Bonded to Silica Gel

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Since Pedersen's classic paper,¹ interest in the preparation and chemistry of crown ethers has been intense and varied. Crown ethers have recently been useful in organic synthesis,² in the solubilization of metal salts in nonpolar solvents,³ as chiral complexing agents with amino esters,⁴ and as model ionophores.⁵ In addition to possible applications as organic reagents, a silica gel immobilized crown ether sample could have an important impact on metal ion chromatography and, as a chelating group, on the concentration and subsequent analysis of metal ions from dilute aqueous solutions.⁶ Therefore, the development of a simple method for covalently bonding a crown ether to silica gel is of immediate significance. In this regard, *polymer*-supported crown ethers⁷ have been shown to effectively coordinate transition-metal anions.⁸

The reaction of Dow-Corning XZ-8-5058 silane in dry toluene with silica gel G (EM Reagents) gave immobilized benzyl chloride **1**. The sample contained 0.34 mmol of
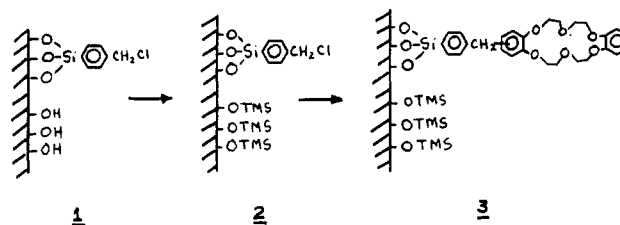
benzyl chloride/g of silica gel as indicated by percent carbon analysis (2.87%). After the unreacted hydroxyl groups in **1** were capped with trimethylsilyl chloride in benzene, the solid **2** (6.19% carbon, 0.92 mmol of Me₄Si/g of silica gel) was treated in carbon disulfide with dibenzo-18-crown-6 and aluminum chloride. The immobilized dibenzo-18-crown-6 (**3**) contained 7.11% carbon after thorough drying (0.038 mmol of crown ether/g of silica gel).

A Fourier transform infrared spectrum of **3** (KBr pellet) showed, after computer subtraction of the silica gel spectrum, the following major absorptions (cm⁻¹): 1251 (Ar–O–R stretching and SiMe₃), 1120 (R–O–R′ stretching), 865

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