

indicated 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 exercised 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 multiplets 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.

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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

Thomas G. Waddell*

Department of Chemistry, University of Tennessee at Chattanooga, Chattanooga, Tennessee 37402

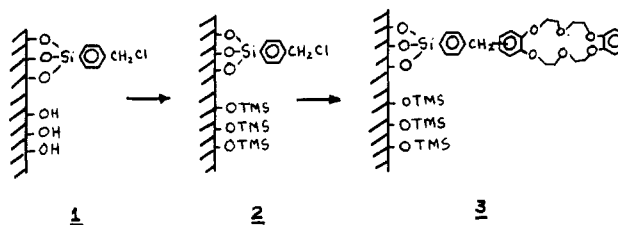
Donald E. Leyden

Department of Chemistry, University of Denver, Denver, Colorado 80208

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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 Me₃Si/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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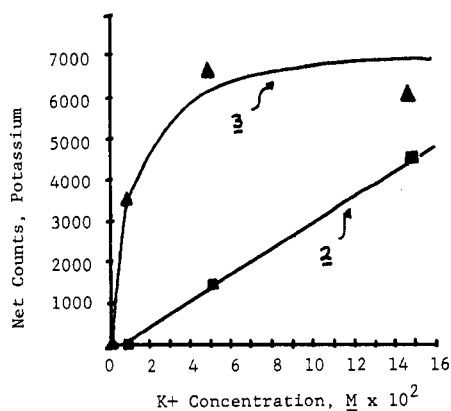


Figure 1. Potassium ion uptake as a function of KCl concentration for samples 2 and 3. Eighty-milligram samples of 2 and 3 were stirred individually covered by 3.0 mL of KCl solutions of the indicated concentrations. Prior to X-ray fluorescence analysis, each sample was washed three times with distilled water and vacuum-oven dried at 78 °C.

(1,4-disubstituted Ar), 846 (SiMe₃), 756 (SiMe₃), 742 (1,2-disubstituted Ar). It is particularly noteworthy that the 1120-cm⁻¹ absorption is found in an authentic dibenzo-18-crown-6 infrared spectrum but not in an authentic benzyl chloride spectrum.

From the percent carbon data determined for samples 1 and 2, it is calculated that the trimethylsilyl/benzyl chloride ratio is approximately 3:1 as indicated by the above values and in structure 2. The 0.92% increase in carbon in converting 2 to 3 corresponds to an 11% substitution of chlorine by crown ether. This result has been independently verified by X-ray fluorescence spectrometry where a 14% loss in net counts for chlorine was noted in the conversion of 1 to 3.

The behavior of sample 3 toward dilute aqueous potassium chloride solutions provides confirmation of immobilized crown ether. The figure shows the dependence of potassium ion uptake by 2 and 3 (measured by X-ray fluorescence) as a function of potassium ion concentration in the supernatant solution. As expected, crown ether 3 (80-mg samples) takes up more potassium than 2 at all concentrations of potassium chloride examined. Whereas 3 complexes K⁺ at the crown ether site, sample 2 most probably takes up the element by simple ion exchange on the silica surface. By absorbing 5 × 10⁻³ mmol of K⁺ on 80 mg of silica gel, it was determined that in these experiments 2.3 × 10⁶ counts are detected per millimole of K⁺. From percent carbon data, an 80-mg sample of 3 contains 3.1 × 10⁻³ mmol of dibenzo-18-crown-6. Therefore, at saturation (3.1 × 10⁻³ mmol of K⁺), 7130 counts are expected. Indeed, Figure 1 indicates that sample 3 takes up nearly 1 equiv of potassium at concentrations above 0.05 M. The imprecision of the points on the curve for 3 reflects the counting error in routine X-ray fluorescence measurements.

The easily prepared, immobilized crown ether 3, or similar samples containing a higher crown ether/benzyl chloride ratio, should provide a method of concentrating certain metal ions from dilute solutions and may serve in organic synthesis by immobilizing ionic organic reagents. Since crown ethers can be selective toward the metal ions which they complex,¹ ion-specific metal-ion chromatography is possible.

Experimental Section

All carbon analyses were performed by Galbraith Laboratories. The FT IR spectra were obtained after 320 scans by using a Nicolet MX-1 spectrophotometer. X-ray fluorescence measure-

ments (counting time 100 s) were taken with a United Scientific 440 instrument coupled to a Tracor-Northern 880 spectrum analyzer.

Immobilized Benzyl Chloride (2). To 100 mL of 5% (v/v) Dow-Corning XZ-8-5058 silane in dry toluene was added 25 g of silica gel G (EM Reagents). After 1 h at room temperature, the reaction slurry was filtered and the solid washed thoroughly with benzene. After being cured at 85 °C for 2 h and vacuum dried, the sample 1 showed 2.87% carbon.

To 5.04 g of 1 in a 100-mL, round-bottomed flask was added 20 mL of reagent-grade benzene followed by 5 mL of trimethylsilyl chloride. The slurry was covered with a calcium chloride drying tube and stirred at room temperature for 24 h. After filtration and methanol washing, the product 2 contained 6.19% carbon.

Immobilized Crown Ether (3). A 0.12-g sample of dibenzo-18-crown-6 in 15 mL of carbon disulfide was stirred at room temperature in a stoppered flask. To this suspension was added 1.01 g of 2 followed by 0.062 g of anhydrous aluminum chloride. After 1 h, the mixture was filtered and washed with large quantities of carbon tetrachloride followed by methanol. The immobilized dibenzo-18-crown-6 contained 7.11% carbon after thorough drying.

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Titanium-Induced Reductive Coupling Reactions. A Facile Route to Tetraphenylfuran

Rudy Dams, Marek Malinowski,[†] Ingrid Westdorp, and Herman J. Geise*

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

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The electron-rich tetraphenylfuran is widely used as a test compound in (photo) oxidation experiments.¹⁻⁴

The compound was first synthesized by Limpricht and Schwarnert⁵ in 1871 by the action of concentrated sulfuric acid on an aqueous solution of benzoin. This procedure was later reported⁶ to give erratic results and was consequently modified and improved by replacing the sulfuric acid by *p*-toluenesulfonic acid and refluxing the mixture in dry toluene with azeotropic removal of water.⁷⁻⁹ However, the yields remained low (ca. 25%) and at least five other compounds are formed as well. One of these byproducts, benzil, occurs in as much as 45% yield.

Recently, tri- and tetraarylfurans have been prepared from 2-ene-1,4-diones, using trialkyl phosphites as a coupling reagent.¹⁰ The advantage of this procedure is its generality, but for the specific synthesis of tetraphenylfuran the disadvantage is that the required 1,2-dibenzoylstilbene is not easily available and that the yield of tetraphenylfuran is still only 42%.

We report here a one-flask preparation which gives tetraphenylfuran in 80% yield starting from benzoyl chloride. The rationalization of the process is the following. First, oxidation experiments²⁻⁴ have shown that tetraphenylfuran can be oxidized to *cis*-dibenzoylstilbene. Second, low-valent titanium species, prepared by the action of, e.g., LiAlH₄ on TiCl₃, having strong reducing properties,

[†] On leave from Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka, 44, Warszawa, Poland.