

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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Registry No. Dibenzo-18-crown-6, 14187-32-7.

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

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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,

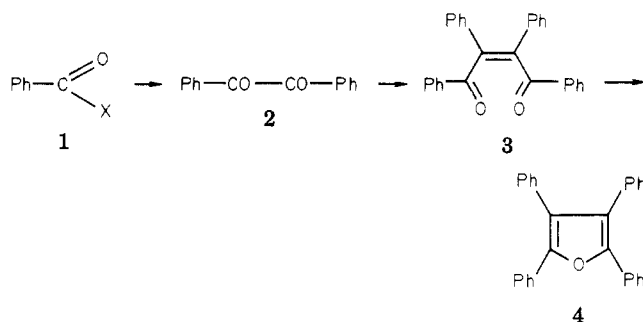
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Table I. Product Balance of the Reaction of C_6H_5COX with $LiAlH_4 + TiCl_3$

X	% 4	% 3	% 2	% unreacted starting material
OCH ₃	30	2	43	20
ONa	10	8	21	45
OH	8	1	10	75
Cl	80	5	10	0
OCH ₂ CH ₃	30	8	40	15
OC ₆ H ₅	10	3	55	20

can reverse this process. Also they are known to produce dibenzoylstilbene from benzil.¹¹ Third, the titanium reagent will abstract many oxygen- and halogen-containing groups from organic molecules, suggesting that benzil could be formed from C_6H_5COX (X = OCH₃, OH, ONa, Cl, etc.).

Indeed the expected sequence of reactions 1 → 2 → 3 → 4 was observed, although with different X groups in 1



the products 2-4 are produced in different relative amounts (see Table I). The reason why benzoyl chloride produces the highest yield of 4 is not yet clear. However, it could be coupled to differences in the Ti species involved in the sequence 2 → 3 → 4. Obviously, the properties of the coupling site can be influenced when different leaving groups (e.g., Cl or OCH₃) become ligands to the low-valent Ti species.

Experimental Section

Instrumentation. The ¹H NMR spectra were recorded on a JEOL PS 100 spectrometer, the IR on a Perkin-Elmer 580 IR-spectrophotometer between 3000 and 600 cm⁻¹, the mass-spectra with a JEOL 01SG2 mass spectrometer, and the UV spectra on a Beckman Model DBG7. Melting points are uncorrected.

Reagents. TiCl₃ (Alpha Ventron) and LiAlH₄ (Merck) were stored under a nitrogen atmosphere in a glovebox. THF (Aldrich) was dried over Na and LiAlH₄ and was distilled under Ar prior to use. Benzoyl chloride, methyl benzoate, ethyl benzoate, phenyl benzoate, and benzoic acid (Aldrich) were used without further purification. All reactions were carried out under argon in Schlenk-type glassware.

Procedure for Reductive Coupling. Lithium aluminum hydride (0.38 g, 0.01 mol) was added in small portions to an ice-cooled slurry of TiCl₃ (3.12 g, 0.02 mol) in 80 mL of dry THF

under an Ar atmosphere. Immediate H₂ evolution was observed. The resulting black suspension was refluxed for 1 h.

Next, 0.005 mol of carbonyl compound was added in small portions, after which the mixture was refluxed for 24 h. The reaction was stopped by adding 20 mL of 2 N hydrochloric acid and the mixture was extracted with 40 mL of CHCl₃ and 40 mL of diethyl ether. The combined organic layers were dried over anhydrous MgSO₄. After removal of the solvent, the reaction mixture was separated by column chromatography on alumina. The eluant was petroleum ether-ethyl acetate (10:1). Three reaction products—benzil¹³ (mp 95 °C), dibenzoylstilbene¹² (mp 213-214 °C), and tetraphenylfuran⁷ (mp 172-174 °C)—were obtained. Melting points and UV, IR, NMR, and mass spectra correspond to those reported.

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Registry No. 1 (X = OCH₃), 93-58-3; 1 (X = ONa), 532-32-1; 1 (X = OH), 65-85-0; 1 (X = Cl), 98-88-4; 1 (X = OCH₂CH₃), 93-89-0; 1 (X = OC₆H₅), 93-99-2; 2, 134-81-6; 3, 6313-26-4; 4, 1056-77-5; TiCl₃, 7705-07-9.

(12) N. M. Bikales and E. I. Becker, *J. Org. Chem.*, **21**, 1405 (1956).
(13) H. T. Clarke and E. E. Oreger, "Organic Syntheses", Collect. Vol. I, Wiley, New York, 1941, p 87.

Synthetic Methods and Reactions. 101. Reduction of Sulfonic Acids and Sulfonyl Derivatives to Disulfides with Iodide in the Presence of Boron Halides¹

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Many sulfonic acid derivatives can be reduced to compounds of lower oxidation state by using traditional reducing agents (metal/acid,² HI,³ SO₃²⁻,²⁻⁴ etc.). Two reports dealing with improved methods to reduce sulfonic acids and their derivatives have appeared in the recent literature. We reported⁵ that iodotrimethylsilane or its in situ equivalents can be used to reduce sulfonyl halides and sulfonic acid derivatives to the corresponding symmetrical disulfides under mild, neutral conditions. Oae et al.⁶ reported the reduction of sulfonic acids to thiols and thiol derivatives on treatment with trifluoroacetic anhydride/sodium iodide.

All of the reported reductions presumably proceed via initial complexation of a sulfonyl oxygen with a Lewis acid which facilitates stepwise reduction of the sulfur. Our previous work with iodotrimethylsilane and our continued

(1) A. A. Gorman, G. Lovering, and M. A. J. Rodgers, *J. Am. Chem. Soc.*, **101**, 3050 (1979).

(2) D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus, and I. D. Menzies, *J. Chem. Soc., Perkin Trans. 1*, 2055 (1975).

(3) K. D. Gundermann and M. Steinfatt, *Angew. Chemie.*, **87**, 546 (1975).

(4) M. Libert and C. Caultet, *Bull. Soc. Chim. Fr.*, 805 (1974).

(5) Limpricht and Schwarner, *Chem. Ber.* **4**, 335 (1871).

(6) R. E. Lutz, C. R. Bauer, R. G. Lutz, and J. S. Gillespie, *J. Org. Chem.*, **20**, 218 (1955).

(7) D. R. Berger and R. K. Summerbell, *J. Org. Chem.*, **24**, 1881 (1959).

(8) D. H. R. Barton, J. A. Blair, P. D. Magnus, and R. K. Norris, *J. Chem. Soc., Perkin Trans. 1*, 1037 (1973).

(9) S. K. Kar and A. Kar, *J. Org. Chem.*, **42**, 390 (1977).

(10) M. J. Haddadin, B. J. Agha, and R. F. Tabri, *J. Org. Chem.*, **44**, 494 (1979).

(11) R. Dams, unpublished results.

(1) For part 100 see: Olah, G. A.; Chao, Y. L.; Arvanaghi, M. *Synthesis*, submitted.

(2) Adams, R.; Marvel, C. S. "Organic Syntheses"; Wiley: New York, 1956; Collect. Vol. 1, pp 504-506.

(3) Sheppard, W. A. "Organic Syntheses"; Wiley: New York, 1970; Collect. Vol. 5, pp 843-845.

(4) Kulka, M. *J. Am. Chem. Soc.* **1950**, **72**, 1215-1218.

(5) Olah, G. A.; Narang, S. C.; Field, L. S.; Salem, G. F. *J. Org. Chem.* **1980**, **45**, 4792-4793.

(6) Numata, T.; Awano, H.; Oae, S. *Tetrahedron Lett.* **1980**, **21**, 1235-1238.