

Experimental Section

General Procedure for the Preparation of Sulfones. A mixture of 17 g (0.09 mol) of sodium *p*-toluenesulfinate,⁵ 0.06 mol of alkyl halide or epoxide, and 1.5 g of the phase-transfer catalyst (tetra-*n*-butylammonium bromide or iodide) in a solvent system consisting of 20 mL of water, 15 mL of benzene, and 15 mL of acetone was placed in a flask equipped with a mechanical stirrer and a reflux condenser. Upon heating to 80–85 °C a two-phase liquid mixture was obtained. The course of reaction was generally monitored by following the disappearance of organic halide by GC or TLC. After the indicated period, the reaction mixture was poured into a separatory funnel containing 50 mL of water and 50 mL of ether. The layers were separated, the aqueous layer was extracted again with ether, and the combined extracts were dried (MgSO₄) and concentrated. The resulting viscous oil usually crystallized on standing or upon the addition of a small amount of hexane with cooling. The crude product was collected and recrystallized from ethanol.

Cyclopropyl *p*-Tolyl Sulfone. A mixture of 1.63 g of 3-chloropropyl *p*-tolyl sulfone, 15 g of NaOH, 1.5 g of tetra-*n*-butylammonium iodide, 15 mL of water, 8 mL of benzene, and 8 mL of acetone was placed in a flask equipped with a mechanical stirrer and a reflux condenser. A two-phase mixture was obtained upon heating at 80 °C. After 18 h the reaction mixture was poured into a mixture of water and ether. The organic layer was separated, washed with dilute hydrochloric acid, and dried (MgSO₄). Removal of the solvent gave 1.3 g of an oil. Distillation under vacuum gave 0.82 g (61%) of cyclopropyl *p*-tolyl sulfone, which readily crystallized: bp 175–178 °C (0.05 torr), mp 65–66 °C (lit.⁶ mp 65–66 °C); IR (CCl₄) 1300, 1150 cm⁻¹; NMR (220 MHz, CCl₄) δ 1.04 (m, 2), 1.36 (m, 2), 2.46 (m, 1), 2.45 (s, 3), 7.45 (m, 4).

trans-2-[(*p*-Methylphenyl)sulfonyl]cyclohexanol (4). The reaction of 5.9 g of cyclohexene oxide by the general procedure required 20 h. Recrystallization from 1:1 acetone–water gave 12.3 g (89%) of 4: mp 120–121 °C (lit.¹⁴ mp 123 °C); IR 3500, 1260, 1160 cm⁻¹; NMR (90 MHz) δ 1.2–2.0 (m, 8), 2.45 (s, 3), 2.95 (m, 1), 3.90 (m, 1), 4.4 (br s, 1), 7.45 (m, 4).

Registry No. 1a, 544-10-5; 1b, 629-04-9; 1c, 75-03-6; 1d, 1974-05-6; 1e, 75-30-9; 1f, 100-44-7; 1g, 563-47-3; 1h, 870-63-3; 1i, 78-95-5; 1j, 535-11-5; 1k, 75-11-6; 1l, 109-70-6; 2b, 95314-81-1; 2c, 7569-34-8; 2e, 51751-71-4; 2f, 5395-20-0; 2g, 16192-04-4; 2h, 15543-64-3; 2i, 5366-49-4; 2j, 95314-82-2; 2k, 37891-96-6; 2l, 19432-95-2; 3a, 95314-83-3; 3b, 95314-84-4; 3c, 95314-85-5; 4, 95314-86-6; 2-(chloromethyl)-2-methyloxirane, 598-09-4; 2-(bromomethyl)oxirane, 3132-64-7; cyclopropyl *p*-tolyl sulfone, 91061-30-2; sodium *p*-toluenesulfinate, 824-79-3; cyclohexene oxide, 286-20-4.

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Hindered Amines.¹ Hindered Monoazacrown Ethers

John T. Lai

BFGoodrich Company, R&D Center, 9921 Brecksville Road, Brecksville, Ohio 44141

Received April 10, 1984

There has been wide interest in the chemistry of hindered amines² and azacrown ethers.³ The hindered azacrown ethers 1 contain both of these structural features and might offer many other unique applications. For example, the potassium salts of 1 could provide nonassoci-

(1) Part 8 of a series. For part 7, see: Lai, J. T. *Synthesis* 1984, 124.
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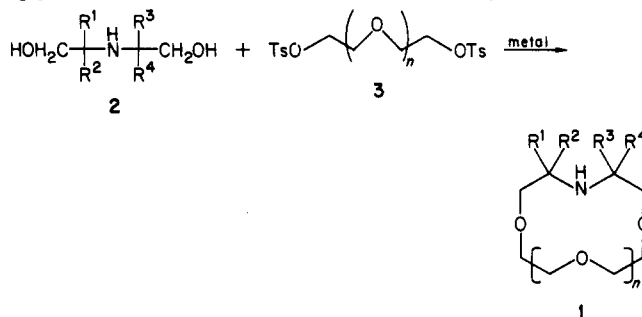
Table I

	template metal (M)	yield, ^b %	bp, °C/mmHg
a	Na	60	88–91/0.04
b	K	41	101–2/0.05
c	Na	55	92–6/0.05
d	Na	49	132–5/0.07
e	Li	7	68–9/0.20 (mp 39–42 °C)

^a All compounds have acceptable microanalyses: C, ±0.29; H, ±0.20; N, ±0.18. ^b Yield of pure product.

ated, nonnucleophilic bases in elimination reactions.⁴ The stable nitroxyl radicals of 1 may be the ideal probe for studying dynamic processes in micellar and related membrane-like systems.⁵ In this note we would like to report a simple synthesis of the hindered azacrown ethers 1.

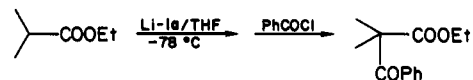
Bis(1,1-dialkyl-2-hydroxyethyl)amine 2 can be prepared in large quantities from very inexpensive raw materials according to our recent report.⁶ When the metal salts of 2 were alkylated with the ditosylates of oligomeric ethylene glycols 3,⁷ 1 were obtained in reasonable yields.



- a, R¹, R², R³, R⁴ = Me; n = 2
 b, R¹, R², R³, R⁴ = Me; n = 3
 c, R¹, R², R³ = Me; R⁴ = Et; n = 2
 d, R¹, R² = Me, R³, R⁴ = -(CH₂)₅; n = 2
 e, R¹, R², R³, R⁴ = Me; n = 1

The nitroxyl radical of 1a or 1b (4 × 10⁻⁴ M in methanol) shows a typical triplet with α_n = 15.5 G in its ESR spectra. The splitting constant does not change⁵ when the same methanol solution is saturated with either NaSCN or KSCN.

The lithium amide from 1a (Li-1a) can deprotonate⁸ ethyl isobutyrate in THF at -78 °C; reaction with benzoyl chloride then gives ethyl α-benzoylisobutyrate in >80% yield.



Experimental Section

¹H NMR spectra were recorded on a Bruker WH-200 spectrometer. CDCl₃ was used as solvent with Me₄Si added as internal standard. Mass spectra were obtained on a Varian MAT 311A spectrometer. Microanalyses were performed by Huffman Lab, in Wheatridge, CO.

General Procedure for Preparing 1. Metal (0.03 mol) was added in small portions to a solution of 2 (0.01 mol) in 85 mL of *tert*-butyl alcohol, and the mixture was slowly warmed to 60

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°C under argon. When hydrogen evolution ceased, 3 (0.01 mol) in 50 mL of dioxane was added dropwise in 2 h. The reaction was continued for 8 h, cooled, and filtered. An oil, concentrated in 1, was eluted with toluene from a flash alumina (neutral) column and then further purified by distillation.

¹H NMR (δ) of 1. **1a**: 1.16 (s, 12 H), 2.5 (br s, 1 H), 3.22 (s, 4 H), 3.5-3.7 (m, 12 H). **1b**: 1.16 (s, 12 H), 2.2 (br s, 1 H), 3.21 (s, 4 H), 3.5-3.8 (m, 16 H). **1c**: 0.85 (t, 3 H), 1.11 (s, 3 H), 1.14 (s, 3 H), 1.18 (s, 3 H), 1.2-1.5 (AB m, 2 H), 2.3 (br s, 1 H), 3.23 (s, 2 H), 3.27 (AB q, 2 H), 3.3-3.9 (m, 12 H). **1d**: 1.0-2.1 (m, 10 H), 1.17 (s, 6 H), 2.2 (br s, 1 H), 3.27 (s, 2 H), 3.42 (s, 2 H), 3.5-3.7 (m, 12 H). **1e**: 1.15 (s, 12 H), 2.8 (br s, 1 H), 3.25 (s, 4 H), 3.4-3.8 (m, 8 H).

Nitroxyl Radicals of 1.⁹ To a solution of 1 (3 mmol) in 5 mL of methanol were added 0.35 mL of acetonitrile, 0.18 g of sodium bicarbonate, and 0.03 g of sodium tungstate. While stirring, 1 mL of 30% hydrogen peroxide was added in 5 min. The reaction was stirred under argon for 2 days. Saturated sodium chloride solution (20 mL) was added and the pH was adjusted to ~4 with 1 N HCl (~3 mL was needed). This aqueous solution was extracted with 3 \times 50 mL of ether. The combined etherate solution was dried over magnesium sulfate and concentrated under vacuum. The wine-colored oil was pure in field-desorption mass spectrum.

Registry No. **1a**, 93565-31-2; **1a** nitroxyl radical, 93565-35-6; **1a-Li**, 93565-37-8; **1b**, 93565-32-3; **1b** nitroxyl radical, 93565-36-7; **1c**, 93604-19-4; **1d**, 93565-33-4; **1e**, 93565-34-5; **2a**, 44982-72-1; **2c**, 90017-23-5; **2d**, 90017-24-6; **3a**, 19249-03-7; **3b**, 37860-51-8; **3e**, 7460-82-4; Na, 7440-23-5; K, 7440-09-7; Li, 7439-93-2; (CH₃)₂CHC(O)OEt, 97-62-1; PhC(O)C(CH₃)₂C(O)OEt, 25491-42-3; PhC(O)Cl, 98-88-4.

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Supported Cyanides: The Interaction of Potassium Cyanide with High Surface Area Inorganic Support Materials and the Development of Highly Reactive Cyanide Reagents

James H. Clark* and Catherine V. A. Duke

Department of Chemistry, University of York,
York YO1 5DD, England

Received September 18, 1984

Supported reagents formed by the adsorption of reagent molecules or ions onto the surface of inorganic solid supports have been successfully applied to a wide variety of organic reactions and have been shown to have many advantages over the pure reagents including increased selectivity, reactivity, and stereospecificity as well as manipulative convenience.^{1,2} The subject was reviewed by McKillop in 1979¹ and a large number of articles have appeared in the literature since then. While supported reagents have been applied to many of the most important organic reaction types, little progress has been made with studies on the supported reagents themselves although significant improvements in reagent reactivity can be gained from such studies.^{3,4} We have used infrared spectroscopy and X-ray diffraction to study one particular group of these materials, supported cyanides, which are known to be useful⁵⁻⁷ but sometimes troublesome⁷ sources

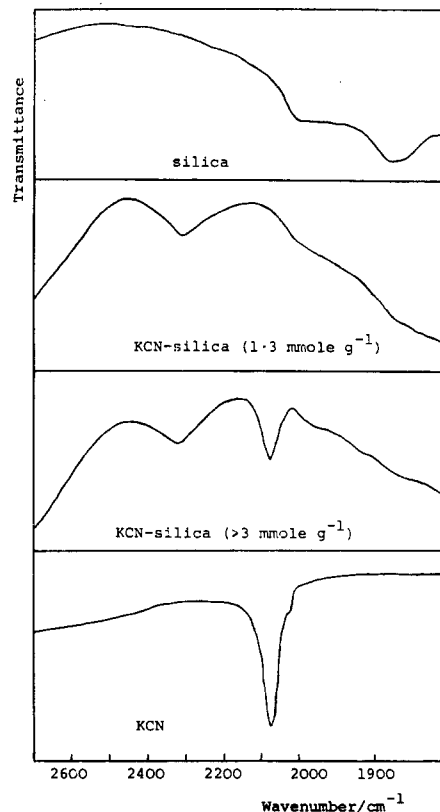


Figure 1. Infrared spectra of KCN-silica and its parents.

of the cyanide ion in nucleophilic displacement reactions. Our analytical studies have enabled us to produce reagents that are significantly more reactive and more selective than previous materials.

Results and Discussion

There are many high surface area inorganic materials that can be used as supports for preparing supported reagents. The two most popular support materials are silica gel and alumina and we have chosen these materials for our investigations. Many different commercial forms of these materials are available and this can lead to considerable confusion among workers attempting to reproduce literature recipes. We have consistently used three support materials, a Merck silica gel (surface area 400 m² g⁻¹, average pore diameter 100 Å), a BDH neutral alumina (surface area ca. 100 m² g⁻¹, average pore diameter 40 Å), and a partially fluorinated BDH alumina. The last of these materials was used so as to investigate the effects of enhanced surface acidity⁸ on the reactivity of the resulting KCN-"F-alumina" reagent. Potassium cyanide was used throughout the study.

Potassium cyanide can be easily adsorbed onto supports by slow evaporation of a well-agitated mixture of the support and aqueous KCN. The resulting solid reagents are free flowing powders only if the KCN loading is below 5 molecules/nm² (this corresponds to at least one surface hydroxyl/KCN). Analysis of such free flowing powders enables us to distinguish between chemisorbed and physisorbed cyanide and to optimize dispersion of KCN on the surface of the support.

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