(discarded). The aqueous phase was basified (solid KOH, phenolphthalein indicator), 20 mL of brine was added, and the mixture was extracted exhaustively with ether. These combined extracts were dried ($MgSO_4$), concentrated, and distilled in a Kugelrohr apparatus to yield 1.43 g (94%) of *N*-cyclohexylpyrrolidine, identified by comparison (IR) with an authentic sample. GLC analysis indicated >98% purity.

In conclusion, phase-transfer techniques greatly augment the utility of cyanoborohydride for reductive aminations of carbonyls and complement analogous conversions in protic media.

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Registry No. Cyclohexanone, 108-94-1; 4-*tert*-butylcyclohexanone, 98-53-3; pyrrolidine, 123-75-1; morpholine, 110-91-8; *N*-benzylpyrrolidine picrate, 78064-90-1; *N*-benzylmorpholine picrate, 58531-53-6; *N*-(*p*-bromobenzyl)pyrrolidine picrate, 78064-91-2; *N*-(*m*-chlorobenzyl)pyrrolidine picrate, 78064-93-4; *N*-(2,6-dichlorobenzyl)pyrrolidine picrate, 78064-95-6; *N*-(*p*-cyanobenzyl)pyrrolidine picrate, 78064-97-8; *N*-decylpyrrolidine picrate, 78064-98-9; *N*-(α-methylbenzyl)pyrrolidine picrate, 78064-99-0; *N*-(*p*-bromo-α-methylbenzyl)pyrrolidine picrate, 78065-00-6; *N*-cyclohexylpyrrolidine picrate, 33109-41-0; *N*-cyclohexylmorpholine picrate, 33109-39-6; cyclohexylpropylamine picrate, 78065-01-7; cyclohexylisopropylamine picrate, 2499-05-0; *N*,*N*-diethylcyclohexylamine picrate, 78065-02-8; *N*-(4-*tert*-butylcyclohexyl)pyrrolidine picrate, 78065-03-9; 2-pyrrolidinyloctane picrate, 42367-34-0; TBACB, 43064-96-6; $NaBH_3CN$, 25895-60-7; C_6H_5CHO, 100-52-7; *p*-BrC_6H_4CHO, 1122-91-4; *m*-ClC_6H_4CHO, 104-88-1; 2,6-$Cl_2C_6H_3CHO$, 83-38-5; *p*-NCC_6H_4CHO, 105-07-7; $CH_3(CH_2)_8CHO$, 112-31-2; $C_6H_5COCH_3$, 98-86-2; $CH_3(CH_2)_5COCH_3$, 111-13-7; CH_2O, 50-00-0; $(CH_3CH_2)_2NH$, 109-89-7; $(CH_3CH_2)_2NH \cdot HCl$, 660-68-4; $CH_3CH_2CH_2NH_2$, 107-10-8; $(CH_3)_2CHNH_2$, 75-31-0; $CH_3NH_2 \cdot HCl$, 593-51-1; NH_4OAc, 631-61-8; $C_6H_5NH_2$, 62-53-3; $C_6H_5CH_2NHCH_2CH_2CH_3$ Picrate, 78065-04-0; $C_6H_5CH_2NHCH(CH_3)_2$ Picrate, 68723-39-7; $CH_3(CH_2)_8CH_2NHCH(CH_3)_2$ Picrate, 78065-06-2; $C_6H_5CH(CH_3)NHCH_3$ Picrate, 78065-07-3; $C_6H_5CH(CH_3)NH_2$ Picrate, 78065-08-4; $C_6H_5CH(CH_3)NHCH_2CH_2CH_3$ Picrate, 78065-09-5; $CH_3(CH_2)_5CH(CH_3)NHC_6H_5$ Picrate, 78065-10-8; $C_6H_5N(CH_3)_2$ Picrate, 7510-42-1; $C_6H_5CH_2N(CH_2CH_3)_2$ Picrate, 78065-11-9.

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Preparation of Hydroxy Crown Ethers by Reactions of Diphenols with Epichlorohydrin

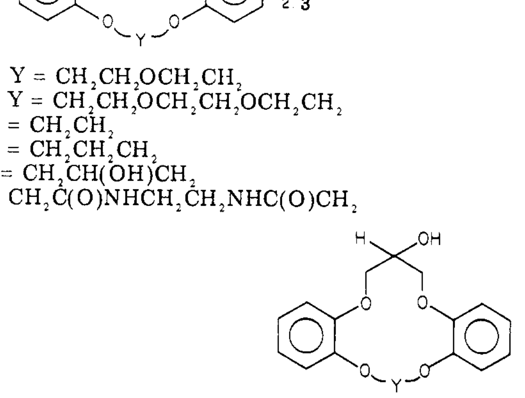
Summary: Reactions of epichlorohydrin with appropriate diphenols in basic aqueous media produce good yields of crown ethers with hydroxyl groups attached to the crown ether ring.

Sir: Synthetic routes to crown ethers which bear pendant functionality have received considerable attention.[1] The functional groups may provide additional liganding atoms for cation complexation,[2,3] serve as sites for further structural elaboration,[3-7] or function as attachment points for binding crown ethers to polymers.[5,6,8] For such purposes, alcohol groups are often the most versatile. Several methods for the preparation of crown ethers with one or more pendant alcohol-containing groups have appeared.[1,2,4,6,8,9] However, many are rather complicated multistep syntheses. We now report the facile ring closure of diphenols **1a–e** to hydroxy crown ethers **2a–e**, using epichlorohydrin (**3**) in basic aqueous media (eq 1).

Table I. Formation of Hydroxy Crown Ethers by Reactions of Diphenols with Epichlorohydrin[a]

diphenol	M of MOH	hydroxy crown ether[b] identity	yield, %	mp, °C
1a	Na	**2a**	60	122-123
1b	K	**2b**	39	73-74
1c	Li	**2c**	50	142-143
1d	Li	**2d**	51	153-154

[a] In a typical procedure, 15 mM of **1**, 30 mM of MOH, and 350 mL of water are stirred under nitrogen at 90-95 °C until solution is achieved. After the solution is cooled to 50 °C, 15 mM of **3** is added over a period of 3 h. Upon completion of the addition, the reaction mixture is stirred at 50 °C for an additional 3-5 h and then cooled to room temperature. The precipitate (for **1b** the oil solidifies when the reaction mixture is cooled to 0 °C) is filtered and dissolved in CH_2Cl_2. The CH_2Cl_2 solution is washed with water and dried over $MgSO_4$, and the solvent is evaporated in vacuo to give the crude **2**. The crude product is placed on top of a short silica gel column and eluted with Et_2O to separate **2** from a small amount of Et_2O-insoluble polymeric material. [b] Satisfactory elemental and spectral analyses were obtained for **2a-d**.



1a,[10-12] Y = $CH_2CH_2OCH_2CH_2$
b,[11,12] Y = $CH_2CH_2OCH_2CH_2OCH_2CH_2$
c,[13] Y = CH_2CH_2
d,[12] Y = $CH_2CH_2CH_2$
e,[9] Y = $CH_2CH(OH)CH_2$
f, Y = $CH_2C(O)NHCH_2CH_2NHC(O)CH_2$

(1)

2a-f

In an isolated report, Ashby et al.[14] noted that reaction of **3** and the amidic diphenol **1f** under basic conditions produced **2f** in very low yield. We were therefore surprised to discover that a slow addition of **3** to an aqueous solution of the disodium salt of **1a** produced a 60% yield of the

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[1] Bradshaw, J. S.; Stott, P. E. *Tetrahedron* **1980**, *36*, 461-510.

[2] Gokel, G. W.; Dishong, D. M.; Diamond, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1053-1054.

[3] Behr, J-P.; Lehn, J-M.; Vierling, P. *J. Chem. Soc., Chem. Commun.* **1976**, 621-623.

[4] Curtis, W. D.; Laidler, D. A.; Stoddart, J. F.; Jones, G. H. *J. Chem. Soc., Chem. Commun.* **1975**, 833-835.

[5] Cinouni, M.; Colonna, S.; Molinari, H.; Montanari, F. *J. Chem. Soc., Chem. Commun.* **1976**, 394-396.

[6] Tomoi, M.; Abe, O.; Ikeda, M.; Kihara, K.; Kakiuchi, H. *Tetrahedron Lett.* **1978**, 3031-3034.

[7] Rastetter, W. H.; Phillion, D. P. *Tetrahedron Lett.* **1979**, 1469-1472.

[8] Montanari, F.; Tundo, P. *Tetrahedron Lett.* **1979**, 5055-5058.

[9] Parsons, D. G. *J. Chem. Soc., Perkin Trans. I* **1978**, 451-455.

[10] Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel, G. W.; Tarnowski, T. L.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 2564-2571.

[11] Oepen, G.; Dix, J. P.; Vögtle, F. *Justus Liebigs Ann. Chem.* **1978**, 1592-1597.

[12] Blasius, E.; Janzen, K. P.; Keller, M.; Lander, H. *Talanta* **1980**, *27*, 107-126.

[13] Pederson, C. *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036.

[14] Ashby, J.; Hull, R.; Cooper, M. J.; Ramage, E. M. *Synth. Commun.* **1974**, *4*, 113-117.

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novel hydroxy crown ether **2a**. Further experiments revealed a similar propensity for ring closure with epibromohydrin. However, with 1,3-dichloro-2-propanol, no **2a** was formed. These observations suggest that the ring closure of **1a** involves an initial nucleophilic attack of a phenoxide oxygen on the epoxide ring of the halohydrin.

Extension of the reaction to the synthesis of hydroxy crown ethers with larger (**2b**) and smaller (**2c**, **2d**) macrocyclic cavities also resulted in 39–51% yields of cyclized products (Table I). In these reactions, the cation was varied to take advantage of the template effect.[15]

Reaction of **3** with diphenol **1e** produced a 55% yield of the previously reported[9] dihydroxy crown ether **2e**. It is interesting to note that the reaction of 1,3-dichloro-2-propanol and diphenol **1e** also forms **2e**, albeit in substantially lower yield[9] than when **3** is employed.

The synthesis of **2a** has also been conducted with 25 times the amounts of reagents and solvents listed in the typical procedure (Table I) with no apparent reduction in yield. Thus the potential of this ring closure method for the synthesis of hydroxy crown ethers on a much larger scale is demonstrated.[16]

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(15) Cook, F. L.; Caruso, T. C.; Byrne, M. P.; Bowers, C. W.; Speck, D. H.; Liotta, C. L. *Tetrahedron Lett.* **1974**, 4029-4032.

(16) Bartsch, R. A. U.S. Patent Application pending.

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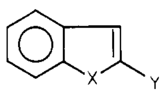
Oxidative Conversions of Sulfene Cycloadducts from Azaheptafulvenes and from Tropone to 1,2-Disubstituted Indoles and 2-Arylbenzofurans, Respectively

Summary: The cycloadducts from azaheptafulvenes and sulfenes as well as from tropone and arylsulfenes rearrange upon oxidation of their corresponding α-sulfonyl anions to give 1,2-disubstituted indoles and 2-arylbenzofurans.

Sir: The cycloadducts from 8-azaheptafulvenes and sulfenes,[1] as well as those from tropone and arylsulfenes,[2] readily undergo metalation (n-BuLi/THF, −78 °C) α to the sulfonyl unit. Subsequent treatment at low temperature with a solution of MoO_5·HMPA[3]–LDA (3 equiv), followed by warming to room temperature, quenching with water, and warming to 45 °C, gives in good yields the corresponding 1,2-disubstituted indoles or the 2-arylbenzofurans, respectively (Table I).

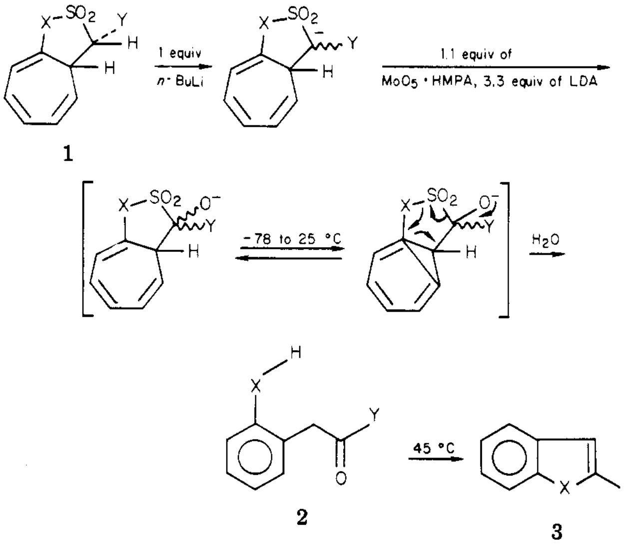
Table I[a,d]



X	Y	% yield[b,c]	mp or bp, °C
CH_3N	H	79	83 (2.5 mm)[e,f] (lit.[9] 133/26 mm)
CH_3N	CH_3	81	55.5-57.5[f] (lit.[10] 55.5-58.0)
$(CH_3)_3CN$	CH_3	52	78.0-79.5
p-$CH_3C_6H_4N$	CH_3	75	113.0-115.0
CH_3N	C_6H_5	72	101.0-103.0[f] (lit.[11] 101.5-102.5)
p-$CH_3C_6H_4N$	CH_3CH_2	78	111.0-113.0
p-$CH_3C_6H_4N$	p-ClC_6H_4	72	oil
p-$CH_3OC_6H_4N$	$(CH_3)_2CH$	78	104.5-105.5
p-BrC_6H_4N	$(CH_3)_2CH$	76	89.5-90.5
p-$CH_3C_6H_4N$	CH_3SO_2	64	oil
O	C_6H_5	75	118.0-119.5[f] (lit.[12] 118.0-119.5)
O	p-$CH_3C_6H_4$	77	126.5-127.5[f] (lit.[13] 127.0-128.0

[a] Reactions carried out in THF. [b] Yields are actual isolated yields. [c] All products were purified by column chromatography. [d] Products were characterized by NMR, IR, and mass spectroscopic data. [e] Picrate derivative of 1-methylindole, mp 149.0-150.0 °C (lit.[14] mp 150 °C). [f] Spectral data matched the NMR and IR data cited in the literature.

Scheme I



This is a one-pot procedure involving the oxidation of the α-sulfonyl anion,[4–6] rearrangement (presumably proceeding through the norcaradiene tautomer)[1,2,7,8] and ring closure to the indole or benzofuran system (Scheme I). The intermediate compound, **2** (X = CH_3N, Y = CH_3), was isolated under nonacidic, low-temperature workup con-

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(1) W. E. Truce and J. P. Shepherd, *J. Am. Chem. Soc.*, **99**, 6453 (1977).

(2) W. E. Truce and C. I. Lin, *J. Am. Chem. Soc.*, **95**, 4426 (1973).

(3) M. Mimoun, I. Seree de Roch, and L. Sajus, *Bull. Soc. Chim. Fr.*, 1481 (1969).

(4) E. Vedejs, D. A. Engler, and J. E. Telschow, *J. Org. Chem.*, **43**, 188 (1978).

(5) R. Daniel Little and Sun Ok Myong, *Tetrahedron Lett.*, 3339 (1980).

(6) Similar conditions were utilized by J. C. Saddler and P. L. Fuchs, Purdue University, in oxidative desulfonylation.

(7) W. von E. Doering and D. B. Denney, *J. Am. Chem. Soc.*, **77**, 4619 (1955).

(8) B. D. Dean and W. E. Truce, *J. Org. Chem.*, **45**, 5429 (1980).

(9) K. T. Potts and J. E. Saxton, *J. Chem. Soc.*, 2641 (1954).

(10) L. Martin and C. W. Oldfield, *Can. J. Res., Sect. B.*, **25**, 1 (1947).

(11) D. J. Gale, J. Lin, and J. F. K. Wilshire, *Aust. J. Chem.*, **29**, 2747 (1976).

(12) K. Nagumi and K. Kurasawa, *Bull. Chem. Soc. Jpn.*, **47**, 505 (1974).

(13) J. N. Chatterjea and S. K. Roy, *Indian J. Chem.*, **34**, 98 (1957).

(14) "CRC Handbook of Tables for Organic Compound Identification", 3rd ed., CRC Press, Cleveland, OH, 1974, p 321.

0022-3263/81/1946-3575$01.25/0 © 1981 American Chemical Society