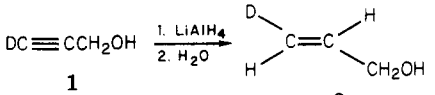
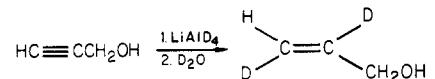
Attempted synthesis of *trans*-3-deuterioallyl alcohol **2** through reduction of the deuteriopropargyl alcohol **1** with $LiAlH_4$ in ether, followed by an aqueous workup, gave a mixture of allyl alcohols: according to analysis by ESR spectroscopy of the derived radical, the alcohol was 68% **2**, 14% of its *cis*-3-deuterio isomer, and 18% unlabeled material. Reduction of propargyl alcohol with $LiAlH_4$, followed by a D_2O quench, gave a mixture containing *cis*-3-, *trans*-3-, and 2-deuterioallyl alcohols in 58:9:8 proportions, along with unlabeled and dilabeled product.[5] Contrary to reports in the literature, it was noted[5] that the reduction of sterically nonhindered propargylic alcohols does not proceed stereospecifically.[6,7]



1 **2**

We experienced similar frustrations with this route using tetrahydrofuran as solvent: reduction of propargyl alcohol (**3**) with $LiAlH_4$ followed by a D_2O quench gave a mixture of *cis*-3-, *trans*-3-, and 2-deuterioallyl alcohols. We did not achieve substantially improved selectivity through addition of aluminum chloride or 18-crown-6 to reaction mixtures, but we did find that when the reduction was carried out initially at 5–10 °C, and then at 25 °C for 14 h, only a trace of *trans*-3-deuterioallyl alcohol was produced. Under these conditions, then, the reduction serves as a very convenient and effective route to *trans*-2,3-dideuterioallyl alcohol when $LiAlD_4$ and a D_2O quench are employed (**3** → **4**).



3 **4**

According to the ^1H NMR spectrum of the product **4**, it has 99% deuterium incorporation at C(2) and greater than 96% deuterium at C(3), with trans stereochemistry exclusively. The same chemistry with 3-deuteriopropargyl alcohol should provide *trans*-3-deuterioallyl alcohol with high stereoselectivity (**1** → **2**).

Experimental Section

***trans*-2,3-Dideuterioprop-2-en-1-ol.** A solution of $LiAlD_4$ (1.50 g, 35.7 mmol; Aldrich, 98% deuterium) in dry THF (100 mL) was stirred under a nitrogen atomosphere and cooled to 5–10 °C. Propargyl alcohol (2.20 g, 39.3 mmol) was added dropwise to the solution in 10 min; the solution was then allowed to warm to room temperature and was stirred for 14 h. The mixture was cooled to 0 °C and deuterium oxide (2 mL; Aldrich 99.8% deuterium) was added dropwise over a 10-min period. The solution was stirred another 15 min before 15% aqueous sodium hydroxide (1.5 mL) and then water (4.5 mL) were added. The solution was dried ($MgSO_4$), filtered, and concentrated with use of a 1-m vacuum-jacketed distillation column packed with glass helices. A sample of the product allyl alcohol was purified by preparative VPC on a 4-m × 6.2-mm 30% Carbowax 20M on Chromosorb Q column at 142 °C; ^1H NMR at 100 MHz ($CDCl_3$) δ 1.52[8] (1 H, m), 4.18 (2 H, d, J = 5 Hz), 5.13 (1 H, m). Expanded sweepwidth examination and integration of the chemical shift regions appropriate to C(2)-H and C(3)-cis-H (δ 5.97 and 5.31) showed relative absorption intensities of less than 1% and 4%, respectively.

Acknowledgment. This preparation was developed in the course of labeling studies supported by the National Science Foundation.

Registry No. $LiAlD_4$, 14128-54-2; *trans*-2,3-dideuterioprop-2-en-1-ol, 86437-20-9; propargyl alcohol, 107-19-7; deuterium oxide, 7789-20-0.

(5) Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483–4489.

(6) Reductions of substituted propargyl alcohols are often of great synthetic utility, and in favorable cases proceed with reasonable stereoselectivity: see, inter alia, Corey, E. J.; Kalzenellenbogen, J. A.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 4245–4257. Borden, W. T. *Ibid.* **1970**, *92*, 4898–4901. Stork, G.; Jung, M. E.; Colvin, E.; Noel, Y. *Ibid.* **1974**, *96*, 3684–3686. Grant, B.; Djerassi, C. *J. Org. Chem.* **1974**, *39*, 968–970. Fujimoto, Y.; Morisaki, M.; Ikekawa, N. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2302–2307. Damm, L. G.; Hartshorn, M. P.; Vaughan, J. *Aust. J. Chem.* **1976**, *29*, 1017–1021. Johnson, W. S.; Escher, S.; Metcalf, B. W. *J. Am. Chem. Soc.* **1976**, *98*, 1039–1041. Parry, R. J.; Kunitani, M. G. *Ibid.* **1976**, *98*, 4024–4026. Chan, K.-K.; Cohen, N.; DeNoble, J. P.; Specian, A. C., Jr.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 3497–3505. Oritani, T.; Overton, K. H. *J. Chem. Soc., Chem. Commun.* **1978**, 454–455. Parry, R. J.; Kunitani, M. G. *Methods Enzymol.* **1979**, *62*, 353–370. Patrick, T. B.; Melm, G. F. *J. Org. Chem.* **1979**, *44*, 645–646. Magid, R. M.; Fruchey, O. S. *J. Am. Chem. Soc.* **1979**, *101*, 2107–2112.

(7) Grant, B. D. Ph.D. Dissertation, Stanford University, Stanford, CA, 1974. Reduction of 1-heptyn-3-ol with $LiAlH_4$ in THF, followed by D_2O, gives mostly *cis*-1-deuterio-1-hepten-3-ol, yet some lack of complete stereoselectivity is evident from the ^1H NMR absorption at δ 5.3 from C(1)-cis-H (Figure 7, p 60).

(8) The chemical shift of the hydroxyl proton is very concentration dependent.

Useful Routes to 9-Anthryl Ethers and Sulfides

William H. Pirkle* and John M. Finn

Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Received February 16, 1982

Our chiral HPLC stationary phase studies required a series of 9-anthryl ethers and sulfides. Such compounds have been prepared by alkylation of the anions of anthrone[1] and 9-anthryl thiol.[2] Barnett and Needham[3] investigated the *p*-toluenesulfonic acid catalyzed formation and dehydration of anthrone hemiketals, found such reactions to occur incompletely, and went on to develop transetherification of 9-methoxyanthracene as a two-step synthesis of 9-alkoxyanthracenes. The one-step dehydration procedure becomes feasible for the preparation of primary 9-alkoxyanthracenes when a large excess (ca. 10-fold) of alcohol is used with sulfuric acid catalysis and the water byproduct is removed.[4] Such reactions are easily conducted on a large scale and avoid the necessity of using dimethyl sulfate (toxic) to first prepare 9-methoxyanthracene.[5] However, if the alcohol were precious, nonvolatile, or immiscible with water (workup considera-

(1) Barnett, E. de B.; Cook, J. W.; Matthews, M. A. *J. Chem. Soc.* **1923**, *123*, 1994.

(2) Conway, W.; Tarbell, D. *J. Am. Chem. Soc.* **1956**, *78*, 2228.

(3) Barnett, W. E.; Needham, L. L. *J. Org. Chem.* **1971**, *36*, 4134.

(4) Water was removed either as the benzene azeotrope (Dean–Stark trap) in the case of alcohols with a boiling point >100 °C (method A) or by addition of the corresponding ortho ester (method B). In this reaction, sulfuric acid is considerably more effective as a catalyst than is *p*-toluenesulfonic acid.

(5) This compound is readily prepared by the procedure of: Willner, I.; Halpern, M. *Synthesis* **1979**, 177. One should be wary that residual dimethyl sulfate may be present in the crude product.

(6) Melting points of 97–98,[1] 97,[5] and 94–95 °C[7] have been reported for **1b**, and a melting point of 73 °C[8] has been reported for **1c**. We note that our melting points are lower, even though samples **1b** and **1c** were purified by recrystallization followed by sublimation and were analytically pure.

(7) Krollpfeiffer, F. *Justus Liebigs Ann. Chem.* **1923**, *430*, 161.

(8) Meyer, K. H.; Schlösser, H. *Justus Liebigs Ann. Chem.* **1920**, *420*, 126.

(9) These compounds are more fully described in the Ph.D. thesis of J.M.F., University of Illinois, 1982. Anal. (for **2b**) Calcd for $C_{20}H_{14}S$: C, 83.88; H, 4.93; S, 11.19. Found: C, 83.84; H, 4.88; S, 11.26. Anal. (for **2c**) Calcd for $C_{21}H_{16}S$: C, 83.96; H, 5.36; S, 10.67. Found: C, 83.80; H, 5.32; S, 10.37. For **2c**, calcd for $C_{17}H_{16}S$ mol wt, 252.0979, found mol wt 252.0976 (HREIMS).

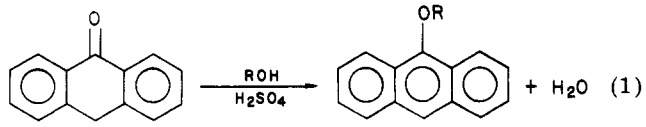
0022-3263/83/1948-2779$01.50/0

Table I. Synthesis of 9-Anthryl Ethers and Sulfides

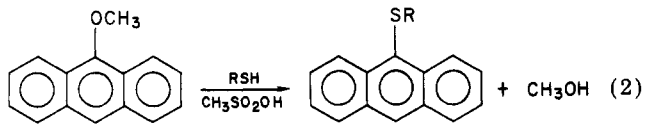
1	R	method[a]	% yield	mp, °C	2	R	% yield	mp, °C
a	CH_2CH_2Br	A	74	119–120	a	n-C_4H_9	85	
b	CH_3	B	90	88–89[6]	b	phenyl	74	99–100[9]
c	C_2H_5	B	74	66–67[6]	c	p-tolyl	63	108–109[9]
d	CH_2CH_2OH	A	70	110–113	d	i-C_3H_7	23	ref 9

[a] In method A, water is removed as the benzene azeotrope; in method B, the appropriate ortho ester is added to the reaction.

tions), the two-step procedure may be preferred. Alkyl or aryl thiols may similarly be used to afford 9-anthryl alkyl or aryl sulfides. These reactions are rather slow, however, and the anthryl sulfides can be obtained more readily by a variation of Barnett and Needham's trans-etherification reaction.[3] Alkyl or aryl thiols undergo methanesulfonic acid catalyzed methanol–thiol exchange with 9-methoxyanthracene to afford 9-anthryl alkyl or aryl sulfides. Methanol removal is unnecessary for completion of these exchanges. Equations 1 and 2 illustrate the preceding reactions.



1



1b 2

Table I provides representative examples of each type of reaction. The indicated yields pertain to purified products. These examples are offered not necessarily as the best procedure for making any given compound but rather to illustrate simple, convenient procedures amenable to large-scale operation.

Experimental Section

All compounds described in this paper were adequately characterized in terms of spectral measurement, melting points (when reported) and elemental composition. Representative synthetic procedures are described. Varian EM-390 and Nicolet 7000 FT IR spectrometers were used to obtain NMR and infrared spectra. A Büchi apparatus was used to determine melting points (uncorrected). Mass spectra were obtained on a Varian MAT CH-5 or MAT 311A spectrometer. Microanalyses were performed by J. Nemeth and Associates, University of Illinois.

9-(2-Bromoethoxy)anthracene (1a). Method A. A stirred solution of anthrone (1.94 g, 10 mmol), 2-bromoethanol (12.5 g, 100 mmol), and sulfuric acid (0.5 mL) in 40 mL of benzene was heated to reflux; water being azeotropically removed by a Dean–Stark trap. After 48 h, when NMR analysis showed the absence of anthrone (δ 4.31 (s, 2 H)), the reaction was cooled to room temperature, poured into 100 mL of saturated $NaHCO_3$ solution, and extracted with ether (3 × 50 mL). The organic extracts were washed with brine (2 × 100 mL) and dried over $MgSO_4$, and the solvent was removed in vacuo, affording a brown syrup. Recrystallization from ethanol afforded yellow 9-(2-bromoethoxy)anthracene: 2.24 g (74%); mp 119–120 °C; NMR ($CDCl_3$) δ 3.75 (t, 2 H), 4.92 (t, 2 H), 7.20–7.48 (m, 4 H), 7.70–7.92 (m, 2 H), 8.12–8.38 (m, 2 H); IR (KBr) 3300–2917, 1628, 1433, 1415, 1248 (s), 1277, 1222, 1168, 1098 (vs) 997 cm^{-1}; MS (70 eV), m/e (relative intensity) 302 (9, M^+), 300 (9, M^+), 193 (49), 178 (15), 178 (100), 176 (17), 165 (10), 89 (15), 76 (17). Anal. Calcd for $C_{16}H_{13}BrO$: C, 63.81; H, 4.32; Br, 26.55. Found: C, 64.69; H, 4.26; Br, 26.35.

9-Methoxyanthracene (1b). Method B. A stirred solution of anthrone (1.94 g, 10 mmol), trimethyl orthoformate (1.06 g) and concentrated sulfuric acid (10 drops) in methanol (30 mL) and benzene (30 mL) was heated to reflux for 4 days. At this time, NMR analysis of the reaction mixture showed the absence of anthrone (δ 4.31 (s, 2 H)). The reaction was cooled to room temperature, poured onto 100 mL of a saturated $NaHCO_3$ solution, and extracted with ether (3 × 50 mL). The organic extracts were washed with brine, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo, leaving a brown solid. Recrystallization from ethanol afforded 9-methoxyanthracene: 1.85 g (89%); NMR ($CDCl_3$) δ 4.08 (s, 3 H), 7.22–7.42 (m, 4 H), 7.75–7.95 (m, 2 H), 8.07–8.30 (m, 3 H); IR (KBr) 2930 (w), 1348 (s), 1092, 972, 880, 842, 738 cm^{-1}.

***n*-Butyl 9-Anthryl Sulfide (2a).** A solution of 9-methoxyanthracene (1 g, 4.8 mmol), n-butyl mercaptan (2.5 mL), and 5 drops of methanesulfonic acid in benzene (20 mL) was heated to reflux for 15 h. After being allowed to cool to room temperature, the reaction mixture was poured into 5% NaOH and extracted with ether (50 mL). The organic extracts were washed with 5% NaOH and brine and dried over $MgSO_4$. Removal of the solvent and chromatography on silica (CH_2Cl_2/hexane elutent) afforded ***n*-butyl 9-anthryl sulfide**: 1.09 g (85%); yellow oil; NMR ($CDCl_3$) δ 0.79 (t, 3 H), 1.10–1.63 (m, 4 H), 2.78 (t, 2 H), 7.20–7.62 (m, 4 H), 7.73–8.03 (m, 2 H), 8.34 (s, 1 H), 8.72–8.98 (m, 2 H); IR (neat) 3010, 2900, 2850, 1440, 1310, 1270, 1015, 887, 845, 780, 735 cm^{-1}; MS (10 eV) m/e (relative intensity) 266 (100, M^+), 210 (59), 209 (38), 178 (10), 71 (10); calcd for $C_{18}H_{18}S$ mol wt 266.1129, found mol wt 266.1135 (HREIMS).

Acknowledgment. This work has been partially supported by a grant from the National Science Foundation.

Registry No. **1a**, 86129-58-0; **1b**, 2395-96-2; **1c**, 6487-28-1; **1d**, 86129-59-1; **2a**, 74851-72-2; **2b**, 74851-75-5; **2c**, 86129-60-4; **2d**, 86129-61-5; H_2SO_4, 7664-93-9; CH_3SO_2OH, 75-75-2; $HOCH_2CH_2OH$, 107-21-1; $HC(OEt)_3$, 122-51-0; PhSH, 108-98-5; 4-MeC_6H_4SH, 106-45-6; Me_2CHSH, 75-33-2; anthrone, 90-44-8; 2-bromoethanol, 540-51-2; trimethyl orthoformate, 149-73-5; n-butyl mercaptan, 109-79-5.

O-Trimethylsilyl Hydroxamoyl Chlorides as Nitrile Oxide Precursors

Robert F. Cunico* and Louis Bedell

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received December 22, 1982

Lately, a number of synthetic methodologies based on the manipulation of Δ^2-isoxazolines have appeared that point to a greatly expanded utility for this class of compounds.[1] Probably the most general synthetic approach to these species entails the cycloaddition of olefins to nitrile oxides generated by a variety of methods.[2] Of these, several have been employed extensively: the dehydro-

(1) (a) Curran, D. P. *J. Am. Chem. Soc.* **1982**, *104*, 4024 and references cited therein. (b) Grund, H.; Jäger, V. *Liebigs Ann. Chem.* **1980**, 80 and previous papers in the series. (c) Cunico, R. F. *J. Organomet. Chem.* **1981**, *212*, C51.

(2) Review: Grundmann, Ch.; Grünanger, P. "The Nitrile Oxides"; Springer-Verlag: New York, 1971.

0022-3263/83/1948-2780$01.50/0