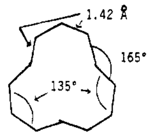
Table I. ESR Coupling Constants, INDO-Calculated p_z Spin Densities, and Resulting Coupling Constants for the Planar [12]Annulene Anion Radical

position	A_H, G (exptl)	ρ_{p_z}(INDO)	A_H(INDO), G ($Q = -24.5$ G)	A_H(INDO), G ($Q = -5.3$ G)
1, 5, 9	1.53	0.288	−7.1	−1.53
2, 4, 6, 8, 10, 12	0.225	−0.120	2.94	0.064
2, 7, 11	1.30	0.285	−7.0	−1.51

[a] The bond distances and angles used for this calculation are shown in structure II. The C-H bond distances are 1.08 Å.



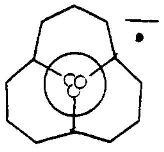
II

G and one set of six equivalent protons with a hyperfine splitting of 0.225 G (Figure 1). This spectrum is invariant from −40 to −120 °C, but the sample decomposes irreversibly at warmer temperatures. The spectrum is consistent with the anion radical having the same structure as does the dianion (groups of six, three, and three protons) if the internal protons have one of the larger coupling constants. The surprising fact is that the total spectral line width is only 9.8 G. This is very small compared to those for the anion radicals of [8]annulene (25.7 G) and [16]annulene (38.5 G).[1,2]

This very small Q value can only mean that the [12]-annulene anion radical is severely distorted from planarity. Distortion from planarity lowers the Q value due to the fact that in addition to the usual σ–π transmission of spin density there is a contribution of the opposite sign to the spin density due to the direct overlap of the hydrogen atoms involved and the p orbitals centered on the carbon atoms in which the unpaired electron is distributed. A similar effect, but of smaller magnitude, was observed in the case of the methano[10]annulene anion radical.[5] This mechanism is thoroughly discussed by Reddoch and coworkers.[6]

Comparison of the EPR coupling constants predicted by an INDO open-shell calculation to the experimental values shows very good agreement if a small Q value is utilized in the McConnell relationship ($A_H = Q\rho$; Table I). However, if the INDO-calculated p_z spin densities are multiplied by −24.5 G (the Q value predicted in the INDO calculation), all of the calculated A_H's are more than 400% too large, and the total spectral width is predicted to be 60 G. The same INDO calculation was carried out on the nonplanar system. The molecule was twisted so that one of the internal protons protruded 0.05 Å above the plane of the ring, one protruded 0.05 Å below the plane of the ring, and the third remained in the plane of the ring. This resulted in a reduction of the predicted spectral line width by 4.4 G. Although the magnitude of this reduction is not nearly large enough, the prediction of a smaller spectral line width with a decrease in the planarity of the ring system supports our conclusion that the [12]annulene anion radical is severely distorted from planarity. The distortion from planarity was intentionally made much smaller in the INDO calculation than that probable in the real anion radical to permit observation of the trend without requiring major structural changes.

To be sure that the effects described above are structural and not an artifact of ion association, we repeated the experiments with 5% HMPA added to the THF solvent. The addition of hexamethylphosphoramide (HMPA) did not result in EPR spectral changes. The anion radical (I) does not exhibit bond alternation but does have a delocalized 13-electron π-bond system.



I

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We are grateful to the Fulbright Foundation for their support of Dr. Concepcion, who is on leave from the Universidad Catolica Madre in the Dominican Republic.

Registry No. [12]Annulene anion radical, 86257-88-7.

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[5] Gerson, F.; Mullen, K.; Wydler, C. *Helv. Chim. Acta*, 1976, *59*, 1371.

[6] Reddoch, A. H.; Dodson, C. L.; Paskovich, D. H. *J. Chem. Phys.* **1970**, *52*, 2318.

[7] The ring proton coupling constants for methano[10]annulene are 2.70 and 0.10 G compared to those of 4.53 and 1.73 G expected for a Q value of 25 G.[5] The loss of spin density (decrease in Q) for this system is comparable to that observed for the [12]annulene anion radical.

Stereoselective Preparation of *trans*-2,3-Dideuterioprop-2-en-1-ol

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cis-2,3-Dideuterioallyl alcohol (*cis*-2,3-dideuterioprop-2-en-1-ol) may be prepared readily through the methyl propiolate–anthracene Diels–Alder adduct, and the same chemistry will provide *cis*-3-deuterioallyl alcohol.[1,2] *trans*-2,3-Dideuterioallyl alcohol and *trans*-3-deuterioallyl alcohol, however, have not been so accessible. Reduction of methyl propiolate with chromous chloride[3] in deuterium oxide affords a plausible precursor to *trans*-2,3-dideuterioallyl alcohol, methyl *trans*-2,3-dideuterioacrylate, with high stereoselectivity but in extremely low yield.[1,4]

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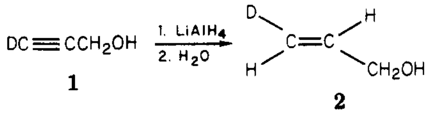
[1] Hill, R. K.; Newkome, G. R. *J. Org. Chem.* **1969**, *34*, 740–741.

[2] Majerski, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 665–671.

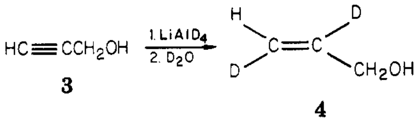
[3] Castro, C. E.; Stephens, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 4358–4363.

[4] Schuerch, C.; Fowells, W.; Yamada, A.; Bovey, F. A.; Hood, F. P.; Anderson, E. W. *J. Am. Chem. Soc.* **1964**, *86*, 4481–4482; Fowells, W.; Schuerch, C.; Bovey, F. A.; Hood, F. P. *Ibid.* **1967**, *89*, 1396–1404.

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]



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**).



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.

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[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

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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-

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[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).