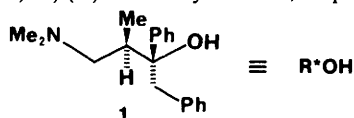




# Chiral<sup>TM</sup>

One of the most avidly explored areas of contemporary synthetic organic chemistry is the use of chiral reagents for the construction of optically active molecules.<sup>1</sup> A very useful reagent — which, to date, has not been readily available — is the amino alcohol **1** [(2*S*,3*R*)-(+)-4-dimethylamino-1,2-diphenyl-3-methyl-

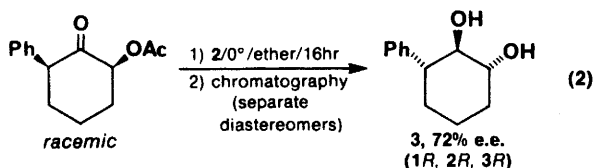


2-butanol].<sup>2</sup> It is now available from Aldrich at very reasonable prices. We call it Chiral<sup>TM</sup>!

When used as a complex (**2**,<sup>3</sup> eq. 1) with lithium aluminum hydride, this reagent effects the enantioselective reduction of  $n$   $R^*OH + LiAlH_4 \xrightarrow[0^\circ/N_2]{Et_2O} "LiAl(OR^*)_nH_{4-n}" + n H_2$  (**1**) **2**  $n=1-3$

prochiral ketones.<sup>4</sup> Complex **2** is prepared *in situ*, and Chiral<sup>TM</sup> can be recovered and reused.<sup>4</sup>

For example, a method for the synthesis of optically active vic-diols employs a freshly prepared, 2:1 complex of Chiral<sup>TM</sup> and  $LiAlH_4$  (eq. 2).<sup>5</sup>

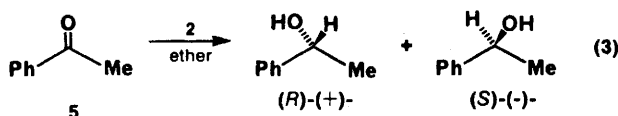


In addition, a wide variety of *R*-propargyl alcohols (**4**) have been synthesized by the reduction of  $\alpha,\beta$ -acetylenic ketones with freshly prepared complex **2**.<sup>6-8</sup> Examples are given in the Table.

TABLE

R <sup>1</sup>	R <sup>2</sup>	% e.e.	ref(s)
Me <sub>2</sub> CHCH <sub>2</sub> -	-Me	82	6,7
C <sub>3</sub> H <sub>11</sub> -	-H	72	7
	-Me	86	6
	-H	82	7,8
	-Me	90	6

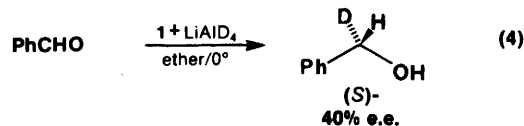
It is interesting that the absolute stereochemistry of the reduction products is often a function of the *age* of the Chiral<sup>TM</sup>- $LiAlH_4$  complex (**2**).<sup>4</sup> As shown in eq. 3,<sup>4b</sup> reduction of acetophenone (**5**) with freshly prepared **2** produces predominantly the *R* alcohol. However, if the complex is allowed to stand overnight,



freshly prepared <b>2</b> (0°):	MAJOR (68% e.e.)	MINOR
"aged" <b>2</b> (r.t.):	MINOR	MAJOR (66% e.e.)

the *S* alcohol is the major product!<sup>4</sup> Although there might appear to be a correlation between the solubilities<sup>9</sup> of the fresh vs. aged complexes and the stereochemical outcome of the reduction, exceptions have been reported.<sup>4b</sup> A generally accepted transition-state model for this phenomenon is yet to be published.

If  $LiAlH_4$  is replaced by lithium aluminum deuteride in eq. 1, the resulting Chiral<sup>TM</sup> complex enables the synthesis of enantiomerically enriched  $\alpha$ -deuterio alcohols (see, for example, eq. 4<sup>4b</sup>).



#### References and Notes:

- See, for example, Szabo, W.A.; Lee, H.T. *Aldrichimica Acta* 1980, 13, 13 and ref. 1 cited therein. Copies of this review are available from Aldrich upon request.
- Although this compound has been referred to in the chemical literature as "Darvon alcohol", the term is not only technically incorrect, its use is strictly unauthorized by Eli Lilly and Company (for whom the trademark Darvon<sup>®</sup> is registered).
- This formula is simply meant to indicate the stoichiometry of the reagents used for the preparation of the Chiral- $LiAlH_4$  complex; see ref. 4.
- (a) Yamaguchi, S.; Mosher, H.S.; Pohland, A. *J. Am. Chem. Soc.* 1972, 94, 9254; (b) Yamaguchi, S.; Mosher, H.S. *J. Org. Chem.* 1973, 38, 1870.
- Kabuto, K.; Ziffer, H. *J. Org. Chem.* 1975, 40, 3467. Kabuto, K.; Shindo, H.; Ziffer, H. *ibid.* 1977, 42, 1742.
- Cohen, N.; Lopresti, R.J.; Neukom, C.; Saucy, G. *J. Org. Chem.* 1980, 45, 582.
- Brinkmeyer, R.S.; Kapoor, V.M. *J. Am. Chem. Soc.* 1977, 99, 8339.
- Johnson, W.S.; Brinkmeyer, R.S.; Kapoor, V.M.; Yarnell, T.M. *ibid.* 1977, 99, 8341.
- Freshly prepared **2** is insoluble in ether; the aged reagent is soluble.

22,740-4	Chiral <sup>TM</sup> [(2 <i>S</i> ,3 <i>R</i> )-(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol]	10g \$7.00; 50g \$28.00
19,987-7	Lithium aluminum hydride	10g \$6.70; 25g \$11.90 100g \$30.90; 1kg \$179.00
21,279-2	Lithium aluminum hydride, 1M solution in diethyl ether	100ml \$11.30; 800ml \$50.25
19,310-0	Lithium aluminum deuteride	1g \$12.00 5g \$49.75

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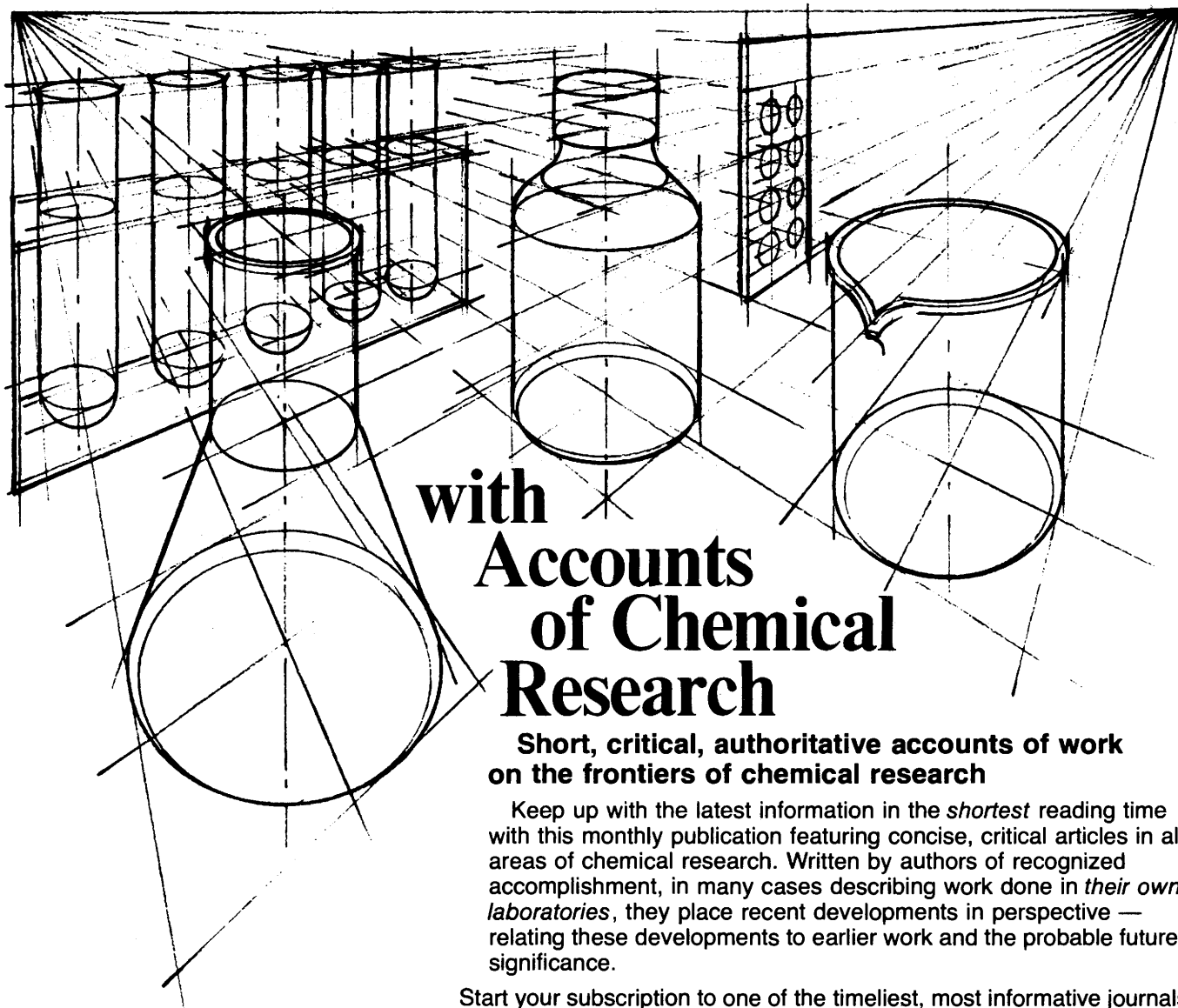


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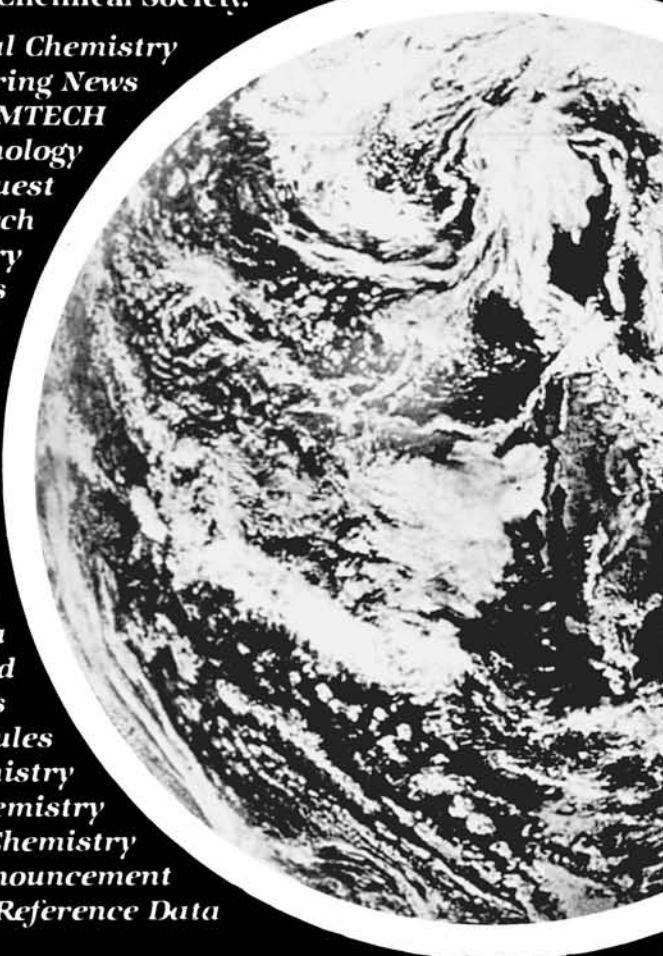
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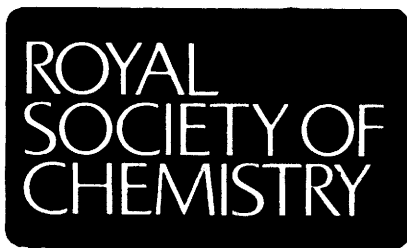
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