

141-75-3; Li(*t*-BuO)₃AlH, 17476-04-9; CuBr, 7787-70-4; NaCNBH₃, 25895-60-7; (Ph₃P)₂CuBH₄, 34010-85-0; (Ph₃MeP)₃CuBH₄, 63371-86-8; NaCuH₂, 90838-89-4; LiCuH₂, 53201-99-3; NaBH₄, 16940-66-2; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 3-ethylpyridine, 536-78-7; 3-chloropyridine, 626-60-8; methyl 3-pyridinecarboxylate, 93-60-7.

Absolute Configuration of Optically Active Propargyl Alcohols: A Circular Dichroism Approach

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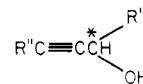
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Optically active α -acetylenic alcohols are useful intermediates in the synthesis of natural products as alkaloids, pheromones, prostaglandines, steroids, and vitamins.¹ However, in spite of their importance in organic synthesis, only the empirical method of Mori and Akao² for determining their absolute configuration has been proposed so far. Recently, the comparison of the experimental values of the circular dichroism (CD), allied to electrically allowed transitions, with those of the CD calculations by means of the De Voe model³ has permitted nonempirical configurational determinations of simple organic molecules where a chromophore is perturbed by alkyl groups only.⁴ Unfortunately, in the case of simple α -acetylenic alcohols, the absence of an electrically allowed transition in the spectral range accessible to the commercial CD instruments ($\lambda > 185$ nm) prevents an immediate application of the above method, on the basis of the De Voe calculations. This difficulty can be overcome by means of the use of the benzoates of propargyl alcohols, which, having an intense transition band at 230 nm ($\epsilon \approx 14000$)⁵ well separated from other absorptions, can provide the systems suitable for the De Voe calculations.

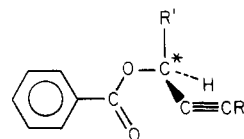
A quantitative evaluation of the benzoate CD absorptions will be carried out, taking into account the chiral perturbation on the above transition due to the acetylenic and the alkyl groups.

A series of α -acetylenic carbinols, having general formula I, has been obtained by enantioselective reduction of the corresponding ketones with optically active organo-aluminum compounds.⁶ Their enantiomeric purity has been determined by analysis of the ¹⁹F NMR spectra of



Ia, R' = Me; R'' = *n*-Bu
 Ib, R' = Et; R'' = *n*-Bu
 Ic, R' = *i*-Pr; R'' = *n*-Bu
 Id, R' = *t*-Bu; R'' = *n*-Bu
 Ie, R' = *t*-Bu; R'' = H
 If, R' = *t*-Bu; R'' = Br

the corresponding MPTA esters. The alcohols have been then converted into the corresponding benzoates: they all show around 230 nm a positive Cotton effect having $\Delta\epsilon$ from +1 to +3 (Table I). The conformational analysis, taking into account only the steric hindrance of the groups surrounding the chiral carbon atom shows that the same preferred conformer should be dominant in solution for all the compounds examined. In fact, three limit conformers can exist for the alcohols Ia-f, as reported in Chart I, assuming a *S* absolute configuration. Inspection of molecular models suggests that the conformer II, in which the largest groups (i.e., the benzoate and R') are in an "antiperiplanar" position, should be the most populated one, since the steric interactions between the benzoate and R', particularly when R' is the bulky *t*-Bu group, make conformers III and IV less stable.⁷ Therefore the conformation II, depicted below to show the overall molecular structure, was chosen to carry out the CD calculations.



De Voe calculations of the CD of electrically allowed transitions in simple organic molecules have been described in detail elsewhere:⁴ in this model each allowed electronic transition is represented in terms of experimental data such as polarization direction of absorption bands and ultraviolet spectra of suitable model compounds. In the present case (i) the triple-bond chromophore is described by only the allowed $^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$ transition, polarized along the C≡C axis. Only a few data are known on the far uv spectra of internal and terminal acetylenes (models of compounds Ia-d and Ie, respectively); however, it is generally accepted⁸ that the above transition is allied to the band having the maximum around 170 nm, with $\epsilon \approx 10000$. As far as the 1-bromo-1-alkynylcarbinol, If, is concerned, this allowed transition has been placed at about 185 nm.⁹ (ii) The benzoate chromophore is represented by only its allowed 230-nm transition ($\epsilon \approx 14000$), polarized along the long axis and then approximately parallel to the alcoholic C*-O bond.⁵ (iii) The methyl and *tert* butyl groups are described by a set of three mutually perpendicular oscillators: each of them is attributed with a fixed fraction of the UV spectrum of methane and 2-methylpropane, respectively, as previously reported in detail.⁴ Unfortunately, since only for these groups a satisfactory description has been provided so far, De Voe calculations have been actually carried out only for the compounds having these substituents. The results of the calculations executed for II with the above-mentioned parametrization are reported in Table I. The present calculations can reproduce the sign and a large part of the intensity of the experimental CD values, indicating that

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(8) See for instance: Dale, J. In "The Chemistry of Acetylenes"; Viehe, H. G., Ed.; Marcell Dekker: New York, 1969, p 3.

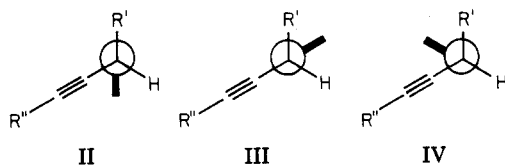
(9) Moreau, C.; Serre, J. *Theroet. Chim. Acta* 1964, 2, 40.

Table I. Circular Dichroism of Benzoates of Propargyl Alcohols

	I		$[\alpha]^{25}_D$	abs config	ee, %	$\Delta\epsilon$	
	R'	R''				exptl ^a	calcd
Ia	Me	<i>n</i> -Bu	-14.51 (c 3.1, ether)	S	36.2	+1.8	+0.9
Ib	Et	<i>n</i> -Bu	-9.94 (c 3.7, hexane)	S	64.1	+1.3	
Ic	<i>i</i> -Pr	<i>n</i> -Bu	-6.43 (c 6.3, hexane)	S	78.1	+2.3	
Id	<i>t</i> -Bu	<i>n</i> -Bu	-13.72	S	84.8	+1.9	+1.3
Ie	<i>t</i> -Bu	H	-2.38	S	13.4	+2.2	+1.1
If	<i>t</i> -Bu	Br	not determined	S	13.4	+3.7	+1.8

^a Reported to 100% ee.

Chart I



positive benzoate Cotton effects are correlated to the absolute *S* configuration of II, the nature of the alkyl group R' on the asymmetric carbon atom affecting only the intensity values. It is noteworthy that the present assignment of the *S* absolute configuration to the alcohols Ia-f is in agreement with the GLC method proposed by Mori and Akao.² The most important aspect of this CD investigation is that the relationship between the absolute configuration and the sign of the benzoate Cotton effect is largely independent of the nature of the substituent on the triple-bond moiety. In fact this will be certainly valid for all the groups which will not change the polarization direction of the allowed transition of the acetylenic group. Therefore substituents like alkyl, acetylenic, and cyano groups and halogen atoms, when present in II, will give rise to a positive Cotton effect for the 230-nm benzoate transition.

In conclusion, a nonempirical rule emerges that correlates the positive sign of the above Cotton effect to the absolute *S* configuration of the alcoholic chiral center. This result is coming from a detailed calculation of the benzoate Cotton effect at 230 nm, by means of the De Voe polarizability model for optical activity. It is then to be noted that the approach used in the present work (formation of chromophoric derivatives of "transparent" molecules for measuring the CD and comparison of the experimental value with the result of calculations) can constitute a general method for assigning absolute configurations. In fact, the use of the De Voe model, which accounts for even alkyl perturbers, provides the opportunity to treat also very simple compounds where the chromophoric group is perturbed by alkyl groups only in contrast to the Harada and Nakanishi rules,⁵ and it is therefore of larger applicability.

Experimental Section

All solvents were reagent-grade materials, purified by standard methods, and redistilled before use. Optical rotations were measured on a Perkin-Elmer 142 automatic polarimeter in a 1-dm tube; unless otherwise specified, rotations refer to those of the pure liquid. GLC analyses (Perkin-Elmer 3920 B) on the methoxy(trifluoromethyl)phenylacetates were performed with 2-m Carbowax 20M columns, at 170 °C, nitrogen flow rate 15 mL min⁻¹; ¹⁹F NMR (94.1 MHz) spectra were obtained with a Varian XL-100 spectrometer on CDCl₃ solutions with Me₄Si as an internal standard. Absorption and CD spectra were obtained by means of JASCO Uvidec-710 spectrophotometer and a JASCO J-500 C spectropolarimeter equipped with a DP-500 N data processor, respectively, using heptane solutions in standard 0.01-cm cylindrical quartz cells.

The optically active carbinols were obtained from the corresponding acetylenic ketones by reducing them with [(1*S*,2*R*)-

6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methyl]aluminum dichloride^{6a} (Ia-d) and tris[(*S*)-2-methylbutyl]aluminum (Ie)^{6b} according to published procedures.⁶ Compound If was obtained from Ie by treatment with bromine in alkaline solution at 0 °C. Both MPTA esters and the benzoates of Ia-f were prepared according to the following representative procedure. (2-Methyl-4-nonyl-3-ol (0.200 g, 1.30 mmol) and distilled (+)-MPTA or benzoyl chloride (1.55 mmol) were mixed with CCl₄ (1.1 mL) and dry pyridine (1.1 mL) and allowed to stand for 12 h at room temperature; then the mixture was diluted with water and extracted with ether (20 mL), washed with dilute HCl, saturated Na₂CO₃, and water, and dried (Na₂SO₄). Removal of the solvent under vacuum furnished the crude esters. While the MPTA ester was used without any purification, the benzoate was purified by flash-chromatography (hexane/acetone, 90:10).

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Registry No. (*S*)-Ia, 90792-10-2; (*S*)-Ia benzoate, 90792-04-4; Ia MPTA ester, 90792-14-6; (*S*)-Ib, 90792-11-3; (*S*)-Ib benzoate, 90792-06-5; Ib MPTA ester, 90792-15-7; (*S*)-Ic, 87682-11-9; (*S*)-Ic benzoate, 90792-06-6; Ic MPTA ester, 90792-16-8; (*S*)-Id, 90792-12-4; (*S*)-Id benzoate, 90792-07-7; Id MPTA ester, 90792-17-9; (*S*)-Ie, 90865-49-9; (*S*)-Ie benzoate, 90792-08-8; Ie MPTA ester, 90792-18-0; (*S*)-If, 90792-13-5; (*S*)-If benzoate, 90792-09-9; If MPTA ester, 90792-19-1.

Stereochemistry and Mechanisms in Eliminations from Some 1,2-Dihalo-1,2-diphenylethanes Promoted by Potassium *tert*-Butoxide in *tert*-Butyl Alcohol

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In our recent study of hydrogen halide eliminations from 1,2-dihaloacenaphthenes¹ and 2,3-dihalo-2,3-dihydrobenzofurans² promoted by *t*-BuOK in *t*-BuOH, we found that fluorine is a better leaving group than chlorine in the syn reactions of compounds where chlorine is the β halogen. This result was interpreted as involving a stepwise elimination through an irreversibly formed carbanion: an (E1cB)₁ mechanism.

Since both these investigations have involved cyclic substrates, it seemed of interest to determine whether similar results would be obtained with β-aryl-activated acyclic dihalides. We here report on a kinetic and product study of eliminations from *meso*-1,2-dichloro-1,2-diphenylethane (1), *erythro*-1-chloro-2-fluoro-1,2-diphenyl-

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