Product Studies of Vinylsilane Condensations.—Tetracyclone (0.001 mol) and vinylsilane (0.0011 mol) were dissolved in 10 ml of solvent and heated in a sealed, evacuated tube. Volatile materials were removed by evaporation, the residue was dissolved in chloroform-*d*, and its nmr spectrum was recorded. Product distributions were obtained by the relative areas of the methyl and/or ethoxy signals and the total aromatic signal. Attempts to isolate pure products were not attempted unless there was a relatively high percentage of one component.

1,2,3,4-Tetraphenylbenzene.—Isolated from the reaction of trimethylvinylsilane with tetracyclone in toluene, this compound melted at 191.4° (lit.[24] mp 191°).

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(24) K. Mackenzie *J. Chem. Soc.*, 437 (1960).

Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.79. Found: C, 94.04; H, 5.84.

2,3,4,5-Tetraphenylphenyltriethoxysilane.—Isolated from the reaction of triethoxyvinylsilane with tetracyclone in toluene, this yellow oil was purified by column chromatography.

Anal. Calcd for $C_{36}H_{36}SiO_3$: C, 79.37; H, 6.66; Si, 5.15. Found: C, 79.15; H, 6.74; Si, 5.36.

2,3,4,5-Tetraphenylphenyltrimethylsilane.—Isolated from the reaction of trimethylvinylsilane with tetracyclone in nitrobenzene, this compound melted at 193° (lit.[12] mp 200°).

Anal. Calcd for $C_{33}H_{30}Si$: C, 87.17; H, 6.65; Si, 6.17. Found: C, 86.90; H, 6.33; Si, 6.76.

Registry No.—17, 18866-47-2; 19, 18856-11-6; 20, 2170-08-3; 1,2,3,4-tetraphenylbenzene, 1487-12-3.

Asymmetric Reduction. II. Preparation of Optically Active Benzyl-α-d Alcohol[1]

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Optically active benzyl-α-*d* alcohol has been prepared by asymmetric reduction of benzaldehyde-1-*d* (or benzaldehyde) with six different reagents, namely, isobornyloxyaluminum dichloride, α-*d*-isobornyloxyaluminum dichloride, bornyloxyaluminum dichloride, isobornyloxymagnesium bromide, α-*d*-isobornyloxymagnesium bromide, and bornyloxymagnesium bromide. The extent of asymmetric induction is, respectively, 10.4, 17.8, 32.7, 52.2, 64.1, and 64.5%. The absolute configurations of benzyl-α-*d* alcohol from reduction with isoborneol complexes are in agreement with the preferred six-membered cyclic transition state where the bulky C-1 atom of the camphor nucleus and the phenyl group are oppositely placed, but the results of reduction with borneol complexes are anomalous. The extent of asymmetric reduction is greatly influenced by the reactivity of the reducing agent; the slower the rate, the greater the asymmetric induction.

In previous publications,[1,3,4] we have reported asymmetric reduction of a number of aliphatic and aromatic ketones with isobornyloxyaluminum dichloride[5] (1), a reagent easily prepared from commercially available (+)-camphor, lithium aluminum hydride, and anhydrous aluminum chloride.[6] The high asymmetric induction encountered in the reduction of aromatic ketones (the highest being 84% in the preparation of phenylisopropylcarbinol[4]) prompted us to examine its applicability in the preparation of optically active α-deuterated primary alcohols, e.g., PhCHDOH, of known configuration, which are of importance for mechanistic and biochemical studies. Several reductions of this type involving hydride or deuteride transfer from optically active reagents to aliphatic or aromatic aldehydes are already known.[7–9] The general principle of these reactions is exemplified in the reduction of benzaldehyde-

1-*d* with isobornyloxyaluminum dichloride (1) as shown below.
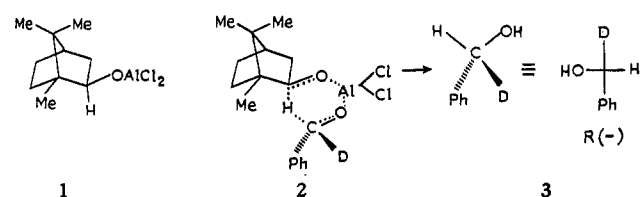
On the basis of the usually accepted six-membered cyclic transition state for these reactions,[10] the preferred transition state is the one (2) where the bulkier C_1–Me side of the camphor nucleus and phenyl group are oppositely placed in the quasi-six-membered ring.[11] The preponderant enantiomer of the deuteriobenzyl alcohol that results from the reaction will therefore have the *R* configuration (3), which is levorotatory.[12] Six such asymmetric reductions, including the one described above, have now been carried out with reagents derived from (−)-isoborneol and (−)-borneol, all leading to optically active benzyl-α-*d* alcohol. The results are summarized in Table I, along with some earlier data from the literature.

(1) Paper I: D. Nasipuri and G. Sarkar, *J. Indian Chem. Soc.*, **44**, 425 (1967).

(2) To whom all inquiries should be made.

(3) D. Nasipuri and G. Sarkar, *ibid.*, **44**, 165 (1967).

(4) D. Nasipuri, G. Sarkar, and C. K. Ghosh, *Tetrahedron Lett.*, 5189 (1967).

(5) E. L. Eliel and D. Nasipuri, *J. Org. Chem.*, **30**, 3809 (1965).

(6) See also D. Mea-Jacheet and A. Horeau, *Bull. Soc. Chim. Fr.*, 3040 (1966).

(7) (a) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **75**, 5014 (1953); (b) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **78**, 5597 (1956); (c) A. Streitwieser, Jr., and J. R. Wolfe, Jr., *ibid.*, **79**, 903 (1957).

(8) A. Streitwieser, Jr., and M. R. Granger, *J. Org. Chem.*, **32**, 1528 (1967).

(9) (a) V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *J. Amer. Chem. Soc.*, **88**, 3595 (1966); (b) V. E. Althouse, E. Kaufmann, P. Loeffler, K. Ueda, and H. S. Mosher, *ibid.*, **83**, 3138 (1961).

(10) M. S. Kharasch and O. Reinmuth in "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Inc., Englewood, Cliffs, N. J., 1954, p 160; H. S. Mosher and E. La Combe, *J. Amer. Chem. Soc.*, **72**, 3994 (1950); W. E. Doering and R. W. Young, *ibid.*, **72**, 631 (1950).

(11) A. Streitwieser, Jr., J. R. Wolfe, and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959).

(12) D. Arigoni and E. L. Eliel in "Topics in Stereochemistry," Vol. 4, E. L. Eliel and N. L. Allinger, Ed., John Wiley & Sons, New York, N. Y., 1969.

TABLE I

ASYMMETRIC SYNTHESIS OF PhCHDOH BY ALKOXYMETAL HALIDES

Compd no.	Reagent	Aldehyde	$[\alpha]_D$ (exptl)[a]	Optical purity[b]	Configuration
1	(−)-Isobornyloxy-aluminum dichloride	PhCDO	−0.165	10.4	R
2	(−)-α-d-Isobornyloxy-aluminum dichloride	PhCHO	+0.281	17.8	S
3	(−)-Bornyloxy-aluminum dichloride	PhCDO	+0.517	32.7	S
4	(−)-Isobornyloxy-magnesium bromide	PhCDO	−0.824	52.2[c]	R
			−0.715	45.3[d]	R
			−0.98	62.5[e]	R
5	(−)-α-d-Isobornyloxy-magnesium bromide	PhCHO	+1.007	64.1	S
6	(−)-Bornyloxy-magnesium bromide	PhCDO	−1.019	64.5	R
7	(+)-2-Methyl-1-butyl-magnesium chloride	PhCDO	+0.29	18.0[f]	S

[a] All optical rotations were measured at 25°, neat, corrected for one deuterium atom per molecule, and converted into specific rotation values assuming the density [A. McLean and R. Adams, *J. Amer. Chem. Soc.*, **58**, 804 (1936)] of benzyl-α-d alcohol as 1.052. [b] Optical purity was calculated as $[\alpha]_D$ (exptl)/$[\alpha]_D$ (max) × 100; $[\alpha]_D$ (max) was assumed to be 1.58° according to Mosher, *et al.*;[9a] cf. also A. Horeau and A. Nouaille, *Tetrahedron Lett.*, 3953 (1966). [c] Present work. [d] Reference 11. [e] H. Gerlach, *Helv. Chim. Acta*, **49**, 2481 (1966). [f] Reference 9a.

Mixtures obtained from reduction of (+)-camphor with lithium aluminum hydride and lithium aluminum deuteride were used in place of (−)-isoborneol and (−)-isoborneol-1-d, respectively, for the preparation of the reagents (compounds 1, 2, 4, and 5). These were contaminated with approximately 10% (+)-borneol, which would not affect the results appreciably because of its much lower reactivity. Pure (−)-borneol obtained by hydrolysis of (−)-bornyl acetate[13] was used for the preparation of the corresponding borneol complexes (compounds 3 and 6). The reductions of aldehydes with alkoxyaluminum dichlorides were carried out first by forming lithium tetraalkoxyaluminum derivatives in ether, then adding the aldehydes all at once, and finally introducing a solution of anhydrous aluminum chloride dropwise into the mixture. Reductions with alkoxymagnesium bromides were effected exactly as described by Streitwieser, *et al.*[7c]

Benzaldehyde-1-d with approximately 0.98 deuterium atom per molecule was prepared in quantity by the adaptation of a method recently published by Bennett, *et al.*,[14] starting from α-morpholinobenzyl cyanide.[15] This appears to be simpler than the other methods available for its preparation.[16] Benzyl-α-d alcohol obtained in the asymmetric reduction was isolated in nearly 90% yield. After careful purification, the deuterium content of each sample was determined by nmr.

The data in Table I present certain interesting features. Our original expectation that such reductions would lead to products of high optical purity in view of the large difference in steric bulk between phenyl and hydrogen (or deuterium) was not fulfilled. Obviously, as pointed out by Mosher, *et al.*,[17] the difference in

steric bulk is just one of the many factors influencing asymmetric induction. One other important factor is rate—in general the slower the rate, the higher is the stereoselectivity. This has been amply demonstrated in the present experiments. Thus deuteride transfer is a slower process than hydride transfer,[18] and asymmetric inductions with deuterated reagents (compounds 2 and 5) are correspondingly higher than those with similar but undeuterated reagents (compounds 1 and 4), although the difference is not so large as that reported[9b] for the reduction of trimethylacetaldehyde. Bornyl-oxyaluminum dichloride is a weaker reducing agent[5] and it brings about higher asymmetric induction than the corresponding isoborneol complexes, though these two systems cannot really be compared with each other since they present different steric situations. The results are also consistent with the fact that alkoxyaluminum dichlorides are much more reactive than alkoxymagnesium bromides.[5]

Finally, the absolute configurations of benzyl-α-d alcohol obtained from reduction with (−)-isoborneol complexes are all as expected from the preferred transition state 2. If the same assumption, that the C_1-Me side of the camphor nucleus is more crowded than the C_3-methylene, is valid in the transition states concerning (−)-borneol complexes, the reduction by the latter reagents would lead to the same benzyl-α-d alcohol as by the corresponding (−)-isoborneol complexes. In actual fact, however, bornyloxyaluminum dichloride (compound 3) and bornyloxymagnesium bromide (compound 6), both from (−)-borneol, furnish benzyl-α-d alcohol of opposite configuration. The result from the latter reagent is consistent with the above hypothesis, but that from bornyloxyaluminum dichloride is clearly unexpected. A similar anomalous result was obtained when phenylglyoxylic acid was reduced with (−)-bornyloxyaluminum dichloride,[19] (R)(−)-mandelic acid being obtained in 57% optical purity. It is just possible that in the (−)-borneol case, the over-hanging *gem*-dimethyl group introduces an additional

(13) Supplied by Aldrich Chemical Co., Inc.

(14) D. J. Bennett, G. W. Kirby, and V. A. Mess, *Chem. Commun.*, 218 (1967).

(15) G. F. Morris and C. R. Hauser, *J. Org. Chem.*, **26**, 4741 (1961); L. H. Goodson and H. Christopher, *J. Amer. Chem. Soc.*, **72**, 358 (1950).

(16) D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966), and references cited therein; also R. A. Olofson and D. M. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 5057 (1967); A. I. Meyers and A. Nabeya, *Chem. Commun.*, 1163 (1967). For preparation of other C₁-deuterated aldehydes, see A. I. Meyers, *et al.*, *J. Amer. Chem. Soc.*, **91**, 763, 764 (1969).

(17) E. P. Burrows, F. J. Welch, and H. S. Mosher, *ibid.*, **82**, 880 (1960).

(18) G. E. Dunn and J. Warkentin, *Can. J. Chem.*, **34**, 75 (1956).

(19) D. Nasipuri and C. K. Ghosh, *J. Indian Chem. Soc.*, **44**, 556 (1967).

unfavorable interaction with the large group, Ph, in the transition state **4** so that the C_3-methylene side is now more crowded and the other transition state **5** is
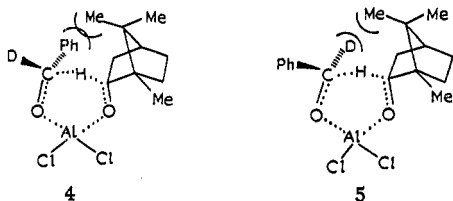
favored. However, it is not at all obvious why this interaction will not be operative in the transition state involving bornyloxymagnesium bromide as well. We are currently carrying out additional asymmetric reductions with borneol complexes, which may throw further light on this point.

Experimental Section

Benzaldehyde-1-d.—A large quantity of benzaldehyde-1-d was prepared according to the following procedure.

2-Morpholino-2-phenylacetonitrile-2-d.—Dried and powdered α-morpholinobenzyl cyanide (50 g) was dissolved in dry and redistilled dimethylformamide (100 ml) and deuterium oxide (80 ml, >99% purity). The solution was heated on the steam bath in a sealed tube for 5 hr. The solvent was then completely removed in a rotary evaporator at 100° (0.5 mm). The resultant solid was dissolved in a fresh mixture of dimethylformamide (60 ml) and deuterium oxide (50 ml) and heated in a sealed tube for a further period of 8 hr. The solvent was removed again as before. The residue was a crystalline solid: 50 g (100%), mp 68–70°. The nmr spectrum was identical with that of 2-morpholino-2-phenylacetonitrile, except that the benzylic proton peak was completely absent.

Benzaldehyde-1-d.—The above deuterated compound (50 g) was refluxed with 10 N hydrochloric acid (50 ml) and water (250 ml) under nitrogen for 5 hr. The mixture was cooled and the organic matter extracted with ether (three 100-ml portions). The ethereal layer was washed with sodium bicarbonate solution, then water, and dried (MgSO₄), and the solvent distilled through a fractionating column. The residue was distilled giving 22 g (82%) of benzaldehyde-1-d, bp 178–180° (760 mm). The product on nmr analysis was found to contain 0.985 atom of deuterium per molecule. A more precise analysis was carried out by admixing the sample with 0.5% of anisole and then comparing the aldehyde and the methoxy proton peaks, which were of comparable intensity. The measurement gave a value of 0.984 atom of deuterium per molecule. The result was reproducible and was independent of the period of heating with hydrochloric acid.

Reduction of Benzaldehyde-1-d with (−)-Isobornyloxyaluminum Dichloride (1).—(+)-Camphor (15.2 g, 0.1 mol) (Aldrich Chemical Co.) was reduced with a 1 M solution of lithium aluminum hydride (25 ml) in ether by refluxing for a period of 4 hr. Any excess of the hydride was destroyed by addition of 1 or 2 drops of t-butyl alcohol. The solution was cooled to room temperature and 7.5 g (0.07 mol) of benzaldehyde-1-d in 10 ml of ether was added all at once. There was no visible sign of reaction. The mixture was kept cooled at 0° by placing the flask in an ice water bath, and a solution of 12.5 g of anhydrous aluminum chloride in 100 ml of ether slowly dropped in within a 20–30-min period, with stirring. The stirring was continued for a 30-min period more, allowing the temperature to rise to 20° gradually. The mixture was cooled and decomposed with cold 10% aqueous sulfuric acid. The ethereal layer was separated, the aqueous part once extracted with ether, and the combined ether extract washed with a little water. The solvent was removed through a fractionating column and the residue was mixed with water (300–400 ml) in a 1-l. flask. A slow stream of steam was passed through the mixture and the distillate collected in a flask. After a few minutes, most of the benzyl alcohol went into water solution, leaving the camphoraceous matter as a solid cake, which was filtered through glass wool. The filtrate was set aside while the solid residue and the steam distillate were mixed with 300 ml of water and again steam distilled. This time

the camphoraceous residue, completely extracted of benzyl alcohol, formed a white foamy mass which was easily separated. The procedure was repeated once more, the combined filtrates were placed in a 2-l. flask and a vigorous stream of steam was passed into the solution until the smell of camphor was imperceptible. The solution was cooled, saturated with potassium carbonate, and thoroughly extracted with ether. The ethereal extract was dried (MgSO₄) and the solvent evaporated through a fractionating column. The residue was distilled under reduced pressure giving 7.3 g (93%) of benzyl-1-d alcohol, bp 118° (50 mm). Gas chromatographic analysis showed it to be a mixture of 95% benzyl alcohol and traces of camphor, borneol, and isoborneol. This was purified by preparative gas chromatography on a Carbowax column (20M, 30%) supported on Chromosorb. The alcohol (3.3 g), α^{25}D −0.170° (l 1, neat), was heated with 5.86 g of phthalic anhydride in 23 ml of dry pyridine for 4 hr at 100°. The reaction mixture was poured into dilute hydrochloric acid. The acid phthalate was crystallized three times from benzene–petroleum ether (bp 60–80°) and the final sample obtained as a crystalline solid: 5.5 g (72%), mp 105–108°. This was decomposed with dilute alkali in the usual way to afford 2.05 g (90%) of pure benzyl-α-d alcohol: α^{25}D −0.170° (l 1, neat); n^{25}D 1.5290. The deuterium content of the alcohol as determined by nmr was 0.98 atom per molecule and the calculated $[\alpha]^{25}$D was −0.164°, corresponding to an asymmetric induction of 10.4%.

Reduction of Benzaldehyde with (−)-α-d-Isobornyloxyaluminum Dichloride.—Lithium aluminum deuteride[20] (2 g) was dissolved in 100 ml of ether. (+)-Camphor (30 g) in 100 ml of ether was slowly added to it and the solution heated under reflux for 6 hr. An aliquot of the solution was decomposed, and on glpc analysis was found to consist of 20% camphor, 70% isoborneol, and 10% borneol (ratio of isoborneol to borneol 87.5: 12.5). To the original solution, freshly distilled benzaldehyde (10.6 g) was added followed by a slow addition of 18 g of anhydrous aluminum chloride in 150 ml of ether. The mixture was kept stirring at room temperature for 40 min and the product worked up as in the previous experiment. Benzyl-α-d alcohol was obtained as a transparent liquid (9.5 g, 90%) and was further purified by glpc. The purified product had α^{25}D +0.260° (l 1, neat), n^{25}D 1.5287, and contained 0.88 atom deuterium per molecule. The calculated $[\alpha]^{25}$D +0.280 corresponded to an asymmetric induction of 17.8%.

Reduction of Benzaldehyde-1-d with (−)-Bornyloxyaluminum Dichloride.—(−)-Borneol, $[\alpha]^{25}$D −37.9°, was obtained from (−)-bornyl acetate by alkaline hydrolysis. To a 1.04 M solution of lithium aluminum hydride (25 ml) was added 21 g of (−)-borneol in 60 ml of ether. The turbid solution was gently refluxed for 1 hr when it became clear. It was cooled to room temperature, 6.5 g of benzaldehyde-1-d added all at once, and the reduction was carried out by slow addition of 13 g of anhydrous aluminum chloride in 150 ml of ether. The solution turned milky white and was stirred for 1 hr at room temperature, following which the product was worked up in the usual way to give benzyl-α-d alcohol (5.4 g, 83%). This was purified by glpc as well as through conversion into acid phthalate, and had α^{25}D +0.535° (l 1, neat), n^{25}D 1.5290. The deuterium content was 98.4% of the theoretical. The calculated $[\alpha]^{25}$D +0.517° corresponded to an asymmetric induction of 32.7%.

Reduction of Benzaldehyde-1-d with (−)-Isobornyloxymagnesium Bromide.—The reduction was carried out exactly as described by Streitwieser, *et al.*[7c] Separation and purification, however, were done as in the previous experiments. Benzaldehyde-1-d (6.0 g) was reduced by a bromomagnesio complex prepared from 24 g of (−)-isoborneol to give crude deuterated benzyl alcohol (4.4 g, 73%) which, after conversion into acid phthalate and regeneration, gave a clear liquid: 2.5 g (42%); α^{25}D −0.850 (l 1, neat); n^{25}D 1.5288. This was further purified by glpc but the rotation remained unchanged. The deuterium content was 98% of the theoretical; $[\alpha]^{25}$D −0.824° corresponded to an asymmetric induction of 52.2%.

Reduction of Benzaldehyde with (−)-α-d-Isobornyloxymagnesium Bromide.—The reagent was prepared by the reaction of (−)-α-d-isoborneol (11.0 g) and n-propylmagnesium bromide according to Streitwieser, *et al.*[8] Benzaldehyde (3.0 g) was added to the mixture, which was stirred at room temperature for 3 hr and then refluxed for 30 min. The product was worked up in the

(20) Lithium aluminum deuteride (over 99% purity) was supplied by Fluka AG.

usual way to give the crude alcohol (2.15 g, 75%). This was purified by glpc to benzyl-α-d alcohol: α^{25}D +0.900° (l 1, neat); n^{25}D 1.5285. The deuterium content was found to be 85% of the theoretical, and $[\alpha]^{25}$D and asymmetric induction were +1.007° and 64.1%, respectively.

Reduction of Benzaldehyde-1-d with (−)-Bornyloxymagnesium Bromide.—The reagent was prepared in the same way as described before by using 8.7 g of (−)-borneol, 6.2 g of n-propyl bromide, and 1.3 g of magnesium. To the homogeneous solution of the reagent in ether–benzene, 2.5 g of benzaldehyde-1-d was added. The solution was stirred at room temperature for 1 hr, then at 60° for 1 hr, and finally decomposed with 10% aqueous sulfuric acid. The product was worked up in the usual way to give benzyl-α-d alcohol (2.0 g, 80%). The alcohol obtained after purification through glpc and acid phthalate had α^{25}D −1.008°, n^{25}D 1.5293, and a deuterium content of 94% of the theoretical. The $[\alpha]^{25}$D and asymmetric induction were −1.019° and 64.5%, respectively.

Heterogeneous Reactions with Zinc. II.[1] A General Synthesis of Ketones from 1,2-Trisubstituted Glycol Monoesters and the Mechanism of the Serini Reaction

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Secondary monoesters of open-chain, trisubstituted 1,2-glycols have been converted into ketones on heating with zinc dust. The reaction was found valid for benzoate and p-nitrobenzoate esters, as well as for acetates, better synthetic results being obtained with the former. In the presence of aromatic substituents at the secondary carbon atom, 1,2-aryl shifts, affording aldehydes, can also take place. Reactions of trisubstituted 1,2-glycol monoesters catalyzed by anhydrous zinc acetate led to results similar to those obtained using metallic zinc. These findings, in addition to other observations disproving the previously accepted assumptions concerning the mechanism of the Serini reaction in steroid systems, support the role of the zinc catalyst as a complexing Lewis acid. The values of the isotope effects k_H/k_D observed during the rearrangements suggest the participation of the migrating hydrogen in the ionization at the tertiary carbon atom. Diastereomeric systems have been used for the investigation of steric effects.

The zinc-promoted rearrangement of 17-hydroxy-20-acetoxy-sterol derivatives into C-20 ketones (eq 1) is

(1)
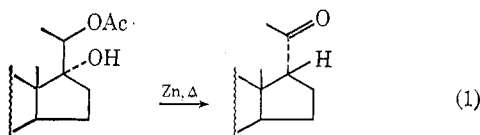
know as the Serini reaction,[2] and occurs with complete inversion at the C-17 center, even when less stable derivatives of "unnatural" configuration are formed. By labeling[3,4] it was found that the oxygen atom of the ester group attached to C-20 is not removed during the reaction, and that the conversion takes place by migration of the C-20 hydrogen to the C-17 center. After being considered of limited applicability even in the steroid field,[4] the Serini reaction was recently found to be of synthetic value in cyclic *cis* systems[5] where the application of other methods failed to lead to the desired results.

The objective of the present work was to extend the study of zinc-promoted rearrangements to open-chain, trisubstituted glycol monoacetates and to investigate the behavior of esters other than acetates, in order to define the scope of the reaction. The aim was also to gain more understanding of the reaction mechanism and of the influence of steric and electronic properties of the reactants on the reaction results.

Starting Materials and Synthetic Results.—The trisubstituted 1,2-glycols were prepared by appropriate methods, *e.g.*, hydroxylation of trisubstituted double bonds or adaptation of the Elphimoff-Felkin procedure[6] for the preparation of α-hydroxy ketones. The diastereomers 9–12 were prepared *via* reduction of 3-phenyl-3-hydroxy-2-butanone by lithium aluminum hydride followed by esterification. The *threo* isomer was predominant (66%), in agreement with Cram's rule for addition to α-hydroxy ketones (cyclic model).[7] The degree of stereospecificity was established by the nonequivalence of shifts in the nmr spectrum, the diastereomers being separated, after esterification, by column chromatography. The chemical shift of the secondary methyl group appears in the nmr spectrum at a higher file in the *threo* esters 11 and 12 than in the *erythro* esters 9 and 10, indicating more shielding by the

(1) For part I, see E. Ghera, *Chem. Commun.*, 1639 (1968).

(2) For reviews, see (a) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 628; (b) N. L. Wendler in "Molecular Rearrangements," Vol. II, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1039.

(3) F. Goto and L. F. Fieser, *J. Amer. Chem. Soc.*, **83**, 251 (1961).

(4) N. L. Wendler, *Proc. Chem. Soc.*, 422 (1960).

(5) E. Ghera, M. Gibson, and F. Sondheimer, *J. Amer. Chem. Soc.*, **84**, 2953 (1962); E. Ghera and F. Sondheimer, *Tetrahedron Lett.*, 3887 (1964); E. Ghera, *J. Org. Chem.*, **33**, 1042 (1968).

(6) I. Elphimoff-Felkin, *Bull. Soc. Chim. Fr.*, 784 (1955).

(7) D. J. Cram and K. R. Kopecky, *J. Amer. Chem. Soc.*, **81**, 2478 (1959).