TABLE V

Compd	Bp (mm) or mp, °C	Formula	Registry no.	Calcd, % C	Calcd, % H	Found, % C	Found, % H
2-OCH_3	74 (0.05)	$C_{13}H_{16}O$	27124-70-5	82.93	8.57	83.08	8.60
3-OCH_3	83 (0.05)	$C_{13}H_{16}O$	27124-71-6	82.93	8.57	82.82	8.62
2,5-OCH_3	93 (0.07)	$C_{14}H_{18}O_2$	27124-72-7	77.03	8.31	76.76	8.34
2,6-OCH_3	68–69.5	$C_{14}H_{18}O_2$	27124-73-8	77.03	8.31	76.81	8.34
2,3,4-OCH_3	110 (0.05)	$C_{15}H_{20}O_3$	27124-74-9	72.55	8.12	72.54	8.09
2,4-OCH_3	108 (0.1)	$C_{14}H_{18}O_2$	27124-75-0	77.03	8.31	77.17	8.29

methoxyphenyl)cyclohexanemercaptoacetic acid, 27124-87-4; *cis*-2-(3′,4′-dimethoxyphenyl)cyclohexanemercaptoacetic acid, 27124-88-5; *cis*-2-(2′,5′-dimethoxyphenyl)cyclohexanemercaptoacetic acid, 27124-89-6; *cis*-2-(2′,3′-dimethoxyphenyl)cyclohexanemercaptoacetic acid, 27124-90-9; 1-(2′,5′-dimethoxyphenyl)cyclohexene, 1848-14-2; 1-(2′,6′-dimethoxyphenyl)cyclohexene, 27124-92-1; 1-(2′,4′-dimethoxyphenyl)cyclohexene, 27098-25-5; 1-(3′,4′-dimethoxyphenyl)cyclohexene, 27124-93-2; *trans*-2-(2′,4′-dimethoxyphenyl)cyclohexanemercaptoacetic acid,[13] 27124-94-3; *trans*-2-(3′,4′-dimethoxyphenyl)cyclohexanemercaptoacetic acid,[13] 27124-95-4; *trans*-2-(2′-methoxyphenyl)cyclohexanemercaptoacetic acid,[13] 27124-96-5.

Acknowledgments.—This investigation was supported by Public Health Service Research Grant No. CA-10270 from the National Institutes of Health.

Stereochemistry of Displacement Reactions at the Neopentyl Carbon. Further Observations on the Triphenylphosphine–Polyhalomethane–Alcohol Reaction[1]

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Received October 20, 1969

R$Me_3CCHDOH$ was prepared by asymmetric reduction of pivaldehyde-*1*-d_1 with isobornyloxymagnesium bromide. Displacement of the tosyl group in (*R*)-$Me_3CCHDOTs$ by acetate ion occurs with 85 ± 17% inversion. Reaction of (*R*)-$Me_3CCHDOH$ with Ph_3P and CCl_4 affords (+)-$Me_3CCHDCl$, assigned the *S* configuration, of greater optical purity than that resulting from chloride displacement on the tosylate. The analogous reaction using CBr_4 affords bromide which seems to be significantly racemized. The characteristics of the title reaction are summarized to point out major differences between it and an SN2 process.

The sluggishness of neopentyl esters or halides to nucleophilic displacement reactions, both SN1 and SN2, is a well-recognized property of that carbon skeletal system. Yet there are several reactions in which "nucleophilic" substitution does occur fairly readily; these reactions have the common property of employing phosphorus-containing reagents and seem to comprise a mechanistically homogenous set.

$$(PhO)_3P + Me_3CCH_2OH + MeI \longrightarrow Me_3CCH_2I^{2,3} \quad (+6\%\ EtCMe_2I)$$

$$(PhO)_3P + Me_3CCH_2OH + PhCH_3X \longrightarrow Me_3CCH_2X \qquad X = I, Br^4$$

$$Ph_3PX_2 + Me_3CCH_2OH \longrightarrow Me_3CCH_2X + Ph_3PO + HX \qquad X = Br, Cl^5$$

Furthermore, there seems to be no case in which the stereochemistry of substitution in the parent neopentyl system has been studied. We report herein the stereochemical course of the neopentyl alcohol–chloride conversion using triphenylphosphine–carbon tetrachloride and the analogous reaction with CBr_4, a study performed with the hope of gaining further insight into the mechanistic process involved. We also determined the stereochemical course of a typical SN2 reaction of neopentyl tosylate to serve as a reference point for the title reaction.

Results

When the reaction of triphenylphosphine, carbon tetrachloride, and neopentyl alcohol at ambient temperature was monitored by nmr, only the characteristic resonances of reactants and neopentyl chloride were observed. Examination by glpc showed no evidence of formation of isomeric C-5 chlorides. These results are similar to those of Downie, *et al.*[6] We prepared chiral neopentyl-*1*-d_1 alcohol by asymmetric reduction (Scheme I). This afforded low yields of alcohol whose acid phthalate showed a specific rotation, after correc-

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[1] This investigation was made possible by grants from the National Science Foundation and Petroleum Research Fund. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support.

[2] N. Kornblum and P. C. Iffland, *J. Amer. Chem. Soc.*, **77**, 6653 (1955).

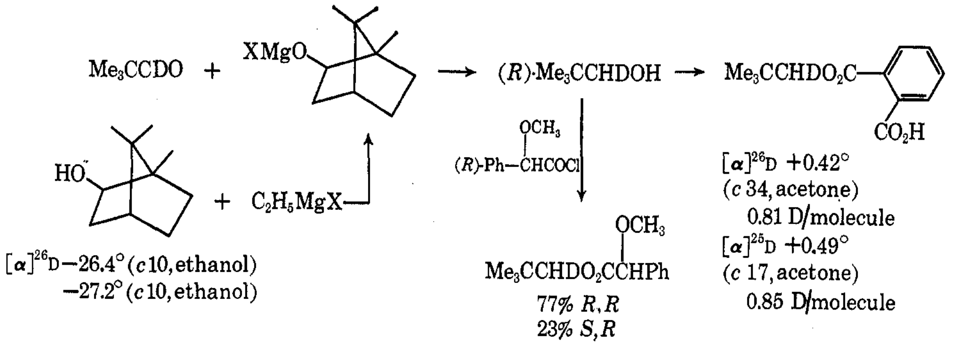
[3] S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).

[4] G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *J. Amer. Chem. Soc.*, **86**, 1994 (1964). Although the authors obtained only unrearranged iodide and bromide they obtained approximately equal amounts of neopentyl and *tert*-amyl chloride.

[5] G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *ibid.*, **86**, 964 (1964).

[6] I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind.* (*London*), 900 (1966).

SCHEME I[a]

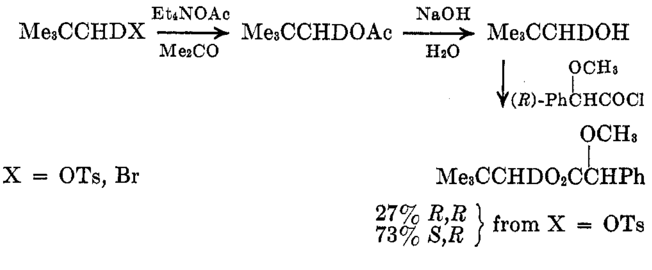


[a] The alcohol was a 10:90 mixture of borneol–isoborneol.

tion to one deuterium per molecule, indicative of about 50% optical purity,[7] and whose dextrorotation showed we had formed the *R* alcohol. (That formed from fermentation[8] is the *S* alcohol[7]). Comparison of the nmr spectrum of the neopentyl ester formed from (*R*)-*O*-methylmandelic acid with that published[9] for the ester from the *S* alcohol confirmed that we had formed predominately the *R* alcohol. Analysis[9] of this spectrum showed the composition of deuterated ester was 77% (*R*)-neopentyl-*1*-d_1 (*R*)-*O*-methylmandelate and 23% (*S*,*R*) ester (with a possible error estimated at ±4%).

The stereochemistry of a typical SN2 reaction was simply determined by acetate displacement on tosylate (Scheme II). The results are clear and unambiguous.

SCHEME II



$$\mathrm{Me_3CCHDX} \xrightarrow[\mathrm{Me_2CO}]{\mathrm{Et_4NOAc}} \mathrm{Me_3CCHDOAc} \xrightarrow[\mathrm{H_2O}]{\mathrm{NaOH}} \mathrm{Me_3CCHDOH} \xrightarrow{(R)\text{-}\mathrm{PhCH(OCH_3)COCl}} \mathrm{Me_3CCHDO_2CCH(OCH_3)Ph}$$

X = OTs, Br

27% *R*,*R*, 73% *S*,*R* from X = OTs

That *S* alcohol is formed from *R* tosylate means the acetate displacement–hydrolyses sequence occurs with overall inversion (85%, estimated error of 17%).[10] Discounting the unlikely possibility that acetate hydrolysis proceeds with C–O bond cleavage, this shows that a typical SN2 reaction in the neopentyl system occurs with the inversion so characteristic of this reaction class.

Our original hope was to convert neopentyl chloride *via* another typical SN2 reaction (whose stereochemistry presumably would be that of the tosylate–acetate conversion) to neopentyl alcohol or some derivative of it. All such reactions were unsuccessful in our hands (10% or less conversion; see Experimental Section) and in fact led to significant amounts of products lacking the neopentyl skeletal system (as judged from their nmr spectrum), none of which were identified. Consequently, (*R*)-$\mathrm{Me_3CCHDOTs}$ was allowed to react with LiCl in DMSO, and the small optical rotation of the resulting $\mathrm{Me_3CCHDCl}$ served as a reference for a typical SN2 (inversion) reaction. From Table I one sees that the optical rotation of the chloride prepared from the alcohol *via* $\mathrm{Ph_3P–CCl_4}$ is 50% higher in magnitude and of the same sign as that obtained from the tosylate, thus showing that the former reaction, at least in the neopentyl system, proceeds with greater stereospecificity (inversion) than chloride displacement on the tosylate.

Neopentyl bromide does undergo displacement with acetate, although the reaction is attended by formation of significant amounts of material lacking the neopentyl skeleton (as judged from their nmr spectrum). The bromide prepared from the reaction (*R*)-$\mathrm{Me_3CCHDOH–Ph_3P–CBr_4}$ was converted first to the acetate, then to the (*R*)-*O*-methylmandelate ester *via* the alcohol. Examination of the ester by nmr showed the alcohol portion was racemic within experimental error. Because of the possibility that racemization may have occurred in the acetate displacement step the bromide preparation was repeated, and the optical rotation of the product was obtained. A sample of bromide from the LiBr–(*R*)-$\mathrm{Me_3CCHDOTs}$ displacement was prepared to serve as a reference point (see Table I). It is clear that the bromide prepared *via* the latter is largely, if not wholly, racemic. Since specific rotations of bromides generally are larger than those of the corresponding chlorides, it seems that bromide prepared directly from the alcohol is also extensively racemized.

Discussion

We have shown that the reaction under discussion yields chlorides with predominant, if not exclusive, inversion in acyclic primary and secondary alcohols,[11] a primary thiol,[11] in 7-norbornanol and *exo*-2-bicyclo[3.2.0]heptanol,[12] and also proceeds with significant, if not predominant, inversion in such systems as *anti*-7-norbornenol and *exo*-2-norbornanol.[11] Our present results show a greater extent of inversion in neopentyl alcohol than the classical chloride displacement on tosylates.

Relatively little seems known about analogous conversions of alcohol to bromide. Downie and Lee have claimed[13] the reaction of 2-octanol with $\mathrm{Ph_3P–CBr_4}$ proceeds with complete inversion. This is contrary to our observations[14] that *threo*-PhCHDCHDOH reacts with $\mathrm{CBr_3Cl}$ to afford inverted chloride but equal amounts of

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[7] W. Sanderson and H. S. Mosher, *J. Amer. Chem. Soc.*, **88**, 4185 (1966).

[8] V. E. Althouse, K. Ueda, and H. S. Mosher, *ibid.*, **82**, 5938 (1960).

[9] K. Mislow and M. Raban, *Tetrahedron Lett.*, 3961 (1966).

[10] If individual peak areas are measured with an absolute accuracy of 4%, the absolute error in the extent of inversion is 2 × 4%/(%*R*,*R* − %*S*,*R*) ≅ 17%.

[11] R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968).

[12] R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, **35**, 1627 (1970).

[13] D. Brett, I. M. Downie, J. B. Lee, and M. F. S. Matough, *Chem. Ind.* (*London*), 1017 (1969).

[14] R. G. Weiss, Ph.D. Thesis, University of Connecticut, 1969.

TABLE I

SPECIFIC ROTATIONS OF Me_3CCHDX

X	Origin[a]	$[\alpha]^{25}D$
Cl	(R)-$Me_3CCHDOTs + LiCl$ (DMSO, 90°, 48 hr)	$+0.085 \pm 0.005$[b]
Cl	(R)-$Me_3CCHDOH + Ph_3P + CCl_4$ (rt,[c] 48 hr).	$+0.13 \pm 0.01$[b]
Br	(R)-$Me_3CCHDOTs + LiBr$ (DMSO, 90°, 19 hr)	$+0.016 \pm 0.008$
Br	(R)-$Me_3CCHDOH + Ph_3P + CBr_4$ (CH_2Cl_2, rt, 19 hr)	$+0.057 \pm 0.008$

[a] All preparations utilized (R)-$Me_3CCHDOH$ containing 0.85 D/molecule, whose acid phthalate showed $[\alpha]^{25}D$ +0.49°. [b] Specific rotations calculated from measured weight percentage of neopentyl chloride in CCl_4 using reported densities for solute and solvent and assuming ideal solution. [c] rt = room temperature.

erythro and threo bromide, which is tantamount to racemization. In this case we were able to demonstrate that erythro–threo isomerization occurred under reaction conditions. The reaction $ROH + Ph_3PBr_2 \rightarrow RBr + Ph_3PO + HBr$, which we feel is mechanistically analogous to the title reaction, was shown[15] to proceed with 50% net inversion using 2-butanol. The recent report of Arain and Hargreaves[16] shows the reaction of 3-methyl-2-butanol proceeds with overall inversion. However, the lower specific rotation of the bromide relative to starting alcohol suggests appreciable racemization.[17] It seems that neopentyl alcohol affords bromide with overall inversion accompanied by extensive racemization, but no quantitative statement is possible. It seems significant that the bromide obtained directly from the alcohol is at least partly optically active, whereas that from the tosylate–bromide sequence is effectively racemic.

Any mechanism for the alcohol–polyhalomethane reactions must accommodate the following observations. (1) The alkyl portion of the alkyl halide seems to have little or no cation character at any stage of the reaction coordinate, except for those systems where a highly stabilized cation (*e.g.*, *anti*-7-norbornenyl) may result. That such is the case follows from the lack of skeletal rearrangement in the neopentyl system, exclusive inversion[12] in 7-norbornanol (solvolyses occur with retention[18]), significant inversion in *exo*-2-norbornanol,[11] and significant retention of the cyclopropyl skeleton in reactions of cyclopropanol.[14] Even the observation[11] of some *syn*-chloride from *anti*-7-norbornenol shows that an inversion path can compete with an energetically extraordinary favorable retention (carbonium ion) path. (2) The stereochemical path is typical of SN2 reactions. (3) However, a number of properties are distinctly different from those expected for SN2 reactions. (a) In both the 7-norbornyl and the 2-phenylethyl system it has not been possible for an external nucleophile to compete with chloride.[14] In the latter system we have shown (see Experimental Section) that, in competition for 2-phenylethyl tosylate, cyanide is a far better nucleophile than chloride. Yet the reaction of 2-phenylethanol with triphenylphosphine and carbon tetrachloride in DMSO in the presence of a large excess of cyanide affords *only* 2-phenylethyl chloride. (b) The *absolute* reactviity of the neopentyl system seems qualitatively far too high to be adequately accounted for by a typical SN2 reaction.[19,19a] (c) Decomposition of 7-norbornyloxychlorophosphorane occurs with first-order kinetics.[12]

Because of the reasons enumerated above we have postulated a four-centered, fairly concerted decomposition of a pentacovalent haloalkoxyphosphorane.[12,20]

Experimental Section

Nmr spectra were recorded using an A-60 spectrometer system equipped with an NMR Specialties HD-60A spin decoupler or a Jeolco C-60H with a JNM SD-HC decoupler. Deuterium analyses were performed by Mr. Josef Nemeth, Urbana, Ill. We are indebted to Dr. Robert Fitch of the University of Connecticut for use of his Du Pont Model 310 curve resolver, and to Mr. John Surridge of Esso Research and Engineering Co., Corporate Research Laboratories, for some of the reported polarimetric data obtained with a Perkin-Elmer 141 polarimeter. All observed rotations are for a 1-dm cell length.

(R)-2,2-Dimethylpropanol-d_1.—A solution of 81 g (0.53 mol) of a 9:1 mixture of isoborneol–borneol, $[\alpha]^{25}D$ −27.2° [from $LiAlH_4$ reduction of (+)-camphor], in 100 ml of THF was added to a solution at 0° of ethylmagnesium bromide (from 0.5 mol of ethyl bromide and 0.5 g-atom of magnesium in 350 ml of THF). Pivaldehyde-d_1[7,21] (30.4 g, 0.35 mol) was added and the mixture was stirred at reflux for 7 hr. The cooled mixture was decomposed with water (75 ml) and filtered, and the solid was washed well with ether. The filtrates were dried ($MgSO_4$) and distilled through a short column virtually to dryness. Because of the volatility of neopentyl alcohol, adequate separation of solvent and other lower boiling components (*e.g.*, unreacted aldehyde) was satisfactorily achieved only by distillation through a Nester-Faust Auto Annular spinning-band column. In this way there was collected 12 g (39%) of crystalline alcohol, mp 53.0–54.2° (lit.[22] mp 52–53°). The acid phthalate, mp 71.0–71.5° (lit.[22] mp 68.5–69.5°), had 5.30 atom % excess deuterium, or 0.85 atom per molecule, and showed $\alpha^{25}D$ $+0.083 \pm 0.002$, or $[\alpha]^{25}D$ +0.57 (*c* 17, acetone, corresponding to 1 deuterium per molecule) [lit.[7] $[\alpha]^{31}D$ −1.15 (*c* 20, acetone), calculated for 100% deuterated (S)-$Me_3CCHDOH$], or 50% optical purity (sample 1). An earlier preparation afforded material of $[\alpha]^{26}D$ +0.52° (calculated for 100% deuterium), or 45% optical purity (sample 2).

(R)-*O*-Methylmandelic acid was prepared as described[23] starting from (R)-mandelic acid[24] of $[\alpha]^{26}D$ 151.6° (*c* 3.3, water) and showed mp 62–67°, $[\alpha]^{25.5}D$ +149.55° [lit. mp 65–66°,[23] $[\alpha]^{17}D$ +150.1° (ethanol)[25]].

(R)-2,2-Dimethylpropyl-d_1 (R)-*O*-Methylmandelate.[26]—The ester was prepared from 0.178 g (2.00 mmol) of alcohol (sample 2) and acid chloride which was prepared from 0.5 g (3 mmol) of acid; the reaction mixture was distilled (0.05 mm) to give 0.3 g of ester. *Anal.* Calcd for $C_{14}H_{19}DO_3$: C, 70.90; H, 8.81. Found: C, 71.07; H, 8.84. Examination of its nmr spectrum

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(15) G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Lett.*, 2509 (1964).

(16) R. A. Arain and M. K. Hargreaves, *J. Chem. Soc. C*, 67 (1970).

(17) It is puzzling that the authors of ref 13 seem to be the only ones who have demonstrated total, or nearly so, inversion using either Ph_3P–CBr_4 or Ph_3PBr_2.

(18) P. G. Gassman and J. M. Hornback, *J. Amer. Chem. Soc.*, **89**, 2487 (1967); F. B. Miles, *ibid.*, **90**, 1265 (1968).

(19) However, the *relative* reactivity of the neopnentyl system, which may be of far greater mechanistic importance, is not yet known, although initial studies indicate *n*-amyl alcohol is at last 20 times more reactive than neopentyl toward Ph_3P and CBr_4.

(19a) NOTE ADDED IN PROOF.—For the reaction with Ph_3P–CCl_4 competition experiments show *n*-amyl alcohol is *only* 14 ± 2 times more reactive than neopentyl alcohol. This ratio in a typical SN2 reaction would be expected to be *ca.* 10^5!

(20) This possibility was suggested initially by Kornblum.[2]

(21) A. Richard, *Ann. Chim. Phys.*, **21**, 323 (1910).

(22) M. Samec, *Justus Liebigs Ann. Chem.*, **351**, 256 (1907).

(23) W. A. Bonner, *J. Amer. Chem. Soc.*, **73**, 3126 (1951).

(24) Norse Chemical Co., Santa Barbara, Calif.

(25) A. McKenzie and H. Wren, *J. Chem. Soc.*, **97**, 484 (1910).

(26) J. A. Dale and H. S. Mosher, *J. Amer. Chem. Soc.*, **90**, 3732 (1968).

failed to show the presence of any material other than the desired ester. Careful examination of the deuterium-decoupled methylene resonances followed by curve resolution showed the composition of deuterated ester was 77% *R,R* and 23% *S,R*.

Acetate Displacement on (*R*)-2,2-Dimethylpropyl-d_1 Tosylate.—The tosylate (from alcohol sample 2) was prepared in the usual way, mp 44–45°. A solution of 3.25 g (13.4 mmol) of tosylate and 3.0 g (16 mmol) of tetraethylammonium acetate in 25 ml of acetone was heated at 100° for 10 days. The reaction mixture was distilled directly to give a fraction of bp >34° (100 mm) which was stirred with 100 ml of 0.75 *N* NaOH at 70° for 44 hr, after which the solution was extracted continuously with 1:1 pentane–ether for 2 days. Solvent was distilled from the dried ($MgSO_4$) extracts through a 12-in. tantalum wire spiral column, and residue was converted to the (*R*)-*O*-methylmandelate ester. Short-path distillation (0.07 mm) afforded 0.125 g of ester, bp 54–56°, which was eluted through 1 g of Florisil with ether. The solvent was evaporated and the nmr spectrum of the ester (CCl_4) showed no observable impurities. Curve resolution of the deuterium-decoupled methylene resonances showed the composition of deuterated ester was 27% *R,R* and 73% *S,R*.

Reaction of (*R*)-$Me_3CCHDOTs$ with LiCl.—A solution of 1.992 g (8.23 mmol) of tosylate (from sample I) and 0.384 g (9.04 mmol) of dried LiCl in 4 ml of DMSO was maintained at 90° for 48 hr. The mixture was diluted with 3 ml of water and distilled (35 mm) to afford 0.55 g (78%) of neopentyl chloride. Examination by nmr showed the resonances of the latter at 57 (s) and 189 (m) Hz, with a small, sharp resonance at 120 Hz (*not* DMSO), whereas the glpc trace (6 ft × 0.25 in. FFAP, 50°) showed the chloride accounted for 96.4% of the total area, with all impurities of quite short retention time, and with no evidence for the presence of other C_5 chlorides or neopentyl alcohol. A solution containing 0.356 g of chloride (assumed 96% pure) in 0.939 g of CCl_4 (weight ratio 0.379:1) showed $\alpha^{25}D$ +0.034 ± 0.002°. Assuming densities of solute and solvent of 0.88 and 1.60, respectively, the concentration is 0.40 g/ml.

Reaction of (*R*)-$Me_3CCHDOH$ with Ph_3P in CCl_4.—A solution of 1.02 g (11.5 mmol) of (*R*)-$Me_3CCHDOH$ (sample 1) and 3.66 g (14.0 mmol) of Ph_3P in 4 ml of CCl_4 remained at ambient temperature for 48 hr. The chilled (0°) solution was diluted with 2 ml of pentane and filtered with the solid being washed with 1:1 pentane–CCl_4. Volatile liquids were collected by a bulb-to-bulb distillation (40 mm), and pentane, chloroform, and most of the carbon tetrachloride were removed by careful distillation through an annular spinning-band column. In our hands it was not possible to satisfactorily separate neopentyl chloride from carbon tetrachloride without significant loss. Using response curves prepared for various solutions of the two chlorides, glpc examination showed in the redistilled pot residue a weight ratio of neopentyl chloride: carbon tetrachloride of 0.3000:1.0, with no other components present (especially neopentyl alcohol). This solution showed $\alpha^{25}D$ +0.046 ± 0.002 (*c* 35.0 calcd).

Reaction of (*R*)-$Me_3CCHDOTs$ with LiBr.—A solution of 1.552 g (6.38 mmol) of tosylate (from alcohol sample 1) and 0.548 g (6.30 mmol) of dried LiBr in 3 ml of DMSO was heated at 90° for 19 hr. The solution was diluted with water and distilled in a sealed system (1 mm) at ambient temperature to afford 0.507 g of bromide (52%). Redistillation through a short-path apparatus afforded 0.253 g of bromide, 98% pure by glpc examination (6 ft × 0.25 in. SE-30, 70°): $\alpha^{25}D$ +0.004 ± 0.002 (*c* 25.3, $CDCl_3$); nmr ($CDCl_3$) 61 (s) and 190 Hz (m).

Reaction of (*R*)-$Me_3CCHDOH$ with Ph_3P and CBr_4.—A solution of 3.23 g (12.3 mmol) of Ph_3P in 5 ml of CH_2Cl_2 was added dropwise to a cooled solution of 0.944 g (10.6 mmol) of alcohol (sample 1) and 4.62 g (14.0 mmol) of freshly recrystallized CBr_4 in 10 ml of CH_2Cl_2. After 19 hr at ambient temperature the mixture was concentrated to *ca.* half its volume by careful fractionation, the residue was chilled and filtered, and the filtrate was distilled bulb to bulb (1 mm) in a sealed system. The distillate so collected was carefully distilled through a short column affording 0.70 g of neopentyl bromide (42%). Redistillation afforded material whose purity according to glpc examination was 95%, the impurities being roughly equally distributed among CH_2Cl_2 and two other unidentified components of shorter retention time than neopentyl bromide; there was no evidence for the presence of neopentyl alcohol. The sample showed $\alpha^{25}D$ +0.014 ± 0.002 (*c* 24.6, $CDCl_3$).

Reaction of (*R*)-$Me_3CCHDOH$, Ph_3P, and CBr_4.—A solution of alcohol (1.74 g, 20 mmol), Ph_3P (5.24 g, 20 mmol), and CBr_4 (9.96 g, 30 mmol) in 15 ml of CH_2Cl_2 was stirred at ambient temperature for 4 hr. Material was distilled up to bp 57° (80 mm) and then was redistilled through a 6-in. tantalum wire spiral column to afford 1.17 g (38%) of neopentyl bromide. The nmr spectrum showed the presence of some alcohol, but did not have signals expected for rearranged products. Alcohol was removed by elution through 1 g of florisil with 10 ml of acetone. A solution of the bromide in 10 ml of acetone containing 6.8 g of Et_4NOAc was heated at 105° for 6 days; the cooled mixture was filtered and then distilled to afford 0.55 g of distillate, bp >65. (Experiments on undeuterated neopentyl bromide showed, from nmr examination, several acetates lacking the neopentyl skeleton are formed in this displacement.) The distillate was again eluted through Florisil (ether) and then converted to the (*R*)-*O*-methylmandelate as described above. Curve resolution of the deuterium decoupled methylene proton signals showed the *R,R* and *S,R* esters present in equal amounts.

Unsuccessful Attempts to Effect Displacement on Neopentyl Chloride.—Yields of 10% or less (usually the latter) of substitution product were obtained from neopentyl chloride under the following conditions: Et_4NOAc in acetone (120–130°, 9 days) and DMSO (105°, 5 days); KO_2CH in acetone–methanol (120–130°, 4 days); KOAc in DMSO (105°, 4 days); Ac_2O–Ag_2O, (90–95°, 1 day plus 120–130°, 1 day); Et_4NOH in acetone (120–130°, 7.5 days); NaOMe in DMSO (105°, 6 days).

Competition of External Cyanide.—A solution of 1.5 g (12 mmol) of 2-phenylethanol in 8 ml of CCl_4 was added to a solution of 4.32 g (16.5 mmol) of Ph_3P and 1.5 g (30 mmol) of NaCN in 10 ml of DMSO. After being heated at 60–65° for 5.5 hr 150 ml of saturated salt solution was added and the resulting mixture was extracted with three 40-ml portions of pentane. The pentane extract was washed well with water and dried ($MgSO_4$), and the solvent was distilled. The residue was chromatographed on 15 g of Florisil, eluted first with 250 ml of pentane and then with 100 ml of methanol. Concentration of the eluents and examination by vpc (10 ft × 0.25 in. 10% DC550 on 80–100 Chromosorb W at 130°) under conditions permitting facile separation of the alcohol, 2-phenylethyl chloride, and 3-phenylpropionitrile showed the pentane fraction contained only chloride, whereas the methanol eluate contained only unreacted alcohol.

To demonstrate that cyanide competes more effectively than chloride toward a common reagent, a solution of 2-phenylethyl tosylate (4.75 g, 17 mmol), sodium chloride (2.0 g, 34 mmol), and sodium cyanide (1.92 g, 34 mmol) in 25 ml of DMSO was allowed to react for 2 hr at ambient temperature. A saturated salt solution (100 ml) was added and the mixture was extracted with two 50-ml portions of ether. The dried extracts were concentrated, and vpc analysis of the residue showed the ratio of nitrile: chloride was >19:1.

Registry No.—(*R*)-$Me_3CCHDOTs$, 27024-75-5; lithium chloride, 7447-41-8; (*R*)-$Me_3CCHDOH$, 14207-74-0; triphenylphosphine, 603-35-0; lithium bromide, 7550-35-8; CCl_4, 56-23-5; CBr_4, 558-13-4.

Acknowledgment.—Eugene I. Snyder is particularly indebted to East Tennessee State University for its hospitality and the use of its facilities during 1969–1970.