Factors in the Formation of Isomerically and Optically Pure Alkyl Halides. The Preparation of Optically Pure 2-Halogenobutanes Part VI.¹

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Optically active 2-chloro- and 2-bromo-butane are formed, with little or no loss of enantiomeric purity, by the interaction of hydrogen halide (Cl, Br) with (+)-tri-s-butyl phosphite or (+)-s-butyl diphenylphosphinite. The reactions of optically active butan-2-ol with phosphorus trichloride, dichlorophenylphosphine, or chlorodiphenylphosphine similarly yield optically pure 2-chlorobutane, although some loss of rotatory power occurs in the reaction of butan-2-ol with phosphorus tribromide. 2-lodobutane of maximum rotatory power is obtained only if hydrogen iodide is absent, e.g., in the reaction of di-s-butyl hydrogen phosphite with phosphorus tri-iodide. Values obtained for the rotations of the optically pure halides are confirmed by stereospecific conversion into s-butyl ethyl sulphide and are compared with previously reported data.

In the absence of a satisfactory method for the resolution of optically active alkyl halides, the rotatory powers of the pure enantiomers can be determined only by indirect means. An accurate knowledge of such values is however essential for correct interpretations to be made of the mechanisms of reactions in which optically active alkyl halides are involved. The formation of alkyl halides from optically active alcohols, esters, etc. is generally accompanied by some loss in rotatory power, although the highest rotations obtained may be taken as minima for the pure enantiomers. For the 2-halogenobutanes prepared from (+)- or (-)-butan-2-ol, the highest reported values are α_D^{20} 29.7° for the chloride (from thionyl chloride in the presence of dimethylaniline ²), $\alpha_{\rm p}^{20} 40.8^{\circ}$ for the bromide (from phosphorus tribromide ³), and $\alpha_{\rm p}^{20} 54.9^{\circ}$ for the iodide (from phosphorus tri-iodide ⁴).[†] Upper limits for the rotatory powers may be obtained by conversion of a halide of known rotation into another compound whose optical purity can be determined, since any loss of asymmetry in the displacement process will cause the calculated value for optically pure halide to be too high. Using a somewhat uncertain rotatory power for 2-methyl1-phenylbutane, an upper limit of $\alpha_{D}^{\ \ 20}\ 33{\cdot}8^{\circ}$ was thus found for 2-chlorobutane by reaction with benzylsodium.6

Several methods have been devised for obtaining more exact rotations for the optically pure 2-halogenobutanes, e.g., the lithium aluminium hydride reduction of 2-chlorobutanoic acid, which gives 2-chlorobutane without involvement of the asymmetric carbon atom.⁷ Reduction of the partly resolved acid thus led to an estimated value of $\alpha_{\rm p}^{20} 33.4^{\circ}$ for optically pure 2-chlorobutane, although the present work suggests that the figure may be high by ca. 8% (see below).

For 2-bromobutane a variety of procedures has given conflicting results. Treatment of partly resolved s-butylmercuric bromide with bromine at -65° gave 2-bromobutane, $\alpha_{\rm p}^{20}$ 42.8° (calculated for the pure enantiomer),⁸ whilst a study of the dehydrohalogenation of threoand erythro-2-bromo-3-deuteriobutane led to a calculated rotation of α_D^{20} 50.0° for the optically pure halide.³ Conversion of the optically active bromide into s-butyl ethyl sulphide, by what appears to be a stereospecific $(S_{\rm N}2)$ route,⁹ has more recently indicated that the latter figure may be about 10% too high.¹⁰

³ P. S. Skell, R. G. Allen, and G. K. Helmkamp, J. Amer. Chem. Soc., 1960, 82, 410.

⁴ M. C. Berlak and W. Gerrard, J. Chem. Soc., 1949, 2309.

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⁶ R. L. Letsinger, L. G. Maury, and R. L. Burwell, jun., J. Amer. Chem. Soc., 1951, 73, 2373.

⁷ K. Freudenberg and W. Lwowski, Annalen, 1955, 597, 141.
⁸ F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and

J. A. Landgrebe, J. Amer. Chem. Soc., 1960, 82, 2466.
⁹ H. M. R. Hoffmann, J. Chem. Soc., 1964, 1249.

¹⁰ P. Salvadori, L. Lardicci, and M. Stagi, Ricerca sci., 1967, 37. 990.

 $[\]dagger$ All optical rotations in the discussion are given for $l \ 1 \ dm$. and are calculated to correspond to optically pure butan-2-ol, α_D^{20} 11.21° (from $[\alpha]_D^{20}$ 13.87°, d_4^{20} 0.8080).⁵ The use of specific rotations offers no obvious advantage, and indeed introduces a source of uncertainty if the density used in calculation is not given. For comparison with the present results, literature values have been converted from specific to observed rotations, using d_4^{25} 0.867 (Bu^sCl) and d_4^{25} 1.253 (Bu^sBr). Corrections to 20° have also been made (see Experimental) where necessary.

¹ Part V, H. R. Hudson, J. Chem. Soc. (B), 1968, 664.

² J. F. Lane and S. E. Ulrich, J. Amer. Chem. Soc., 1950, 72, 5132.

TABLE 1

Reactions of (+)- or (-)-s-butyl esters with hydrogen halides

Ester $(R = Bu^s)$		Halide			Addn	Further reaction		2-Halogenobutane				
	g.	~	g.	mol.	temp.	Temp.	Time •	g.	mol.	αD ^{20 b}	ap ²⁰ (corr.)	
(RO) ₃ P ^d	7.8	HCl	0.79	0.69	$-2\overline{0}^{\circ}$		0 °	2.0	0.69	$+14.32^{\circ f}$	$+30.83^{\circ}$	
		,,	0.55	0.48	+40	40	168 hr.	$1 \cdot 2$	0.42	+14.170	+30.50	
(RO) ₂ PHO ^A	5.8	HCI	1.0	0.96	25	25	166	1.9	0.69	-29.91 *	-29.91	
		,,	0.79	0.73	25	25	174	1.1	0.40	$-24 \cdot 46^{j}$	-24.46	
		,,	0.46	0.42	25	25	167	0.7	0.25	-17.12	-17.12	
(RO) ₃ P ^k	9.2	HBr	$2 \cdot 3$	0.77	-20		0•	3.8	0.75	-41·88 ¹	-43.73	
(RO) ₃ P	4·1 ∖ ^m	HBr	1.0	0.26	-20		0 e	1.3	0.20	+20.52 n	+41.77	
(RO) ₂ PHO	6∙1∫	,,	1.6	0.41	0	20	12	2.7	0.41	+20.94 °	+42.64	
		,,	$2 \cdot 0$	0.52	0	20	12	$2 \cdot 6$	0.40	$+20.81^{p}$	+42.37	
		,,	$2 \cdot 1$	0.54	0	20	12	$2 \cdot 4$	0.37	+15.089	+30.70	
		,,	$2 \cdot 0$	0.52	0	20	46	$3 \cdot 2$	0.49	+9.69'	+19.72	
ROPPh ₂ ^s	8∙0	HCI	$1 \cdot 2$	1.1	20	20	$2 \cdot 3$	$2 \cdot 1$	0.73	-30.09 *	-31.00	
ROPPh ₂	8.6	HBr	2.7	1.0	20	20	0 °	3.6	0.79	-41·12 "	-42.37	
ROPPh ₂ ⁴	7.8	HI	$3 \cdot 9$	1.0	20	20	0 •	4.8	0.86	-22·95 v	-23.64	

^a Successive reaction periods for the ester specified. ^b After purification by g.l.c. ^c Corrected for optically pure butan-2-ol, $\alpha_D^{20} 11\cdot 21^\circ$. ^d From ROH, $\alpha_D^{20} - 5\cdot 21^\circ$. ^e Volatiles removed at 0.1 mm. immediately after completion of absorption of hydrogen halide. ^f $n_D^{20} 1\cdot 3963$ (Found: Cl, 38·9. Calc. for C₄H₂Cl: Cl, 38·3%). ^g $n_D^{20} 1\cdot 3967$ (Found: Cl, 37·8%). ^k From ROH, $\alpha_D^{20} + 11\cdot 21^\circ$. ⁱ Found: Cl, 38·4%. ^j Found: Cl, 38·6%. ^k From ROH, $\alpha_D^{20} + 10\cdot 73^\circ$. ⁱ $n_D^{20} 1\cdot 4368$. ^m Mixed esters from ROH, $\alpha_D^{20} - 5\cdot 51^\circ$. ⁿ Determined after dilution with racemic Bu*Br. ^o $n_D^{20} 1\cdot 4362$. Identical rotation after 2nd purification by g.l.c. ^p $n_D^{20} 1\cdot 4359$ (Found: Br, 58·1. Calc. for C₄H₉Br: Br, 58\cdot 3%). ^g $n_D^{20} 1\cdot 4360$ (Found: Br, 58·5%). ^r $n_D^{20} 1\cdot 4361$. ^s From ROH, $\alpha_D^{20} + 10\cdot 88^\circ$. ⁱ $n_D^{20} 1\cdot 3968$ (Found: Cl, 38\cdot 5%). ^w $n_D^{20} 1\cdot 4367$. ^w $n_D^{20} 1\cdot 4978$. Purification by g.l.c. caused some racemization to give Bu*I, $\alpha_D^{20} - 20\cdot 78^\circ$.

TABLE 2

Reactions of (+)- or (-)-butan-2-ol with phosphorus halides

						Bus	BusOH		2-Halogenobutane				
Bu®OH		Halide			Addn.	recovered		<u> </u>		α _D ²⁰			
g.	α_D^{20}	1	g.	mol.	temp.	ģ.	mol.	g٠	mol.	1 4	2 ^b	corr.° `	
11.1	$+11.21^{\circ}$	PCl ₃	6.9	0.33	10 ^{° d, e}	0.32	0.03	$\overline{3} \cdot 2$	0.23	-30.69°	$-30.84^{\circ f}$	-30.84	
$7 \cdot 4$	+10.59	PhPCl,	9.0	0.50	0 d,g	Trace		4.4	0.48	-28.76	-29·04 [*]	-30.73	
3.7	-2.93	$Ph_2PC\overline{l}$	11.1	1.00	0 d, i	1.8	0.49	2.5	0.54	+7·88 ^j		+30.10	
$22 \cdot 2$	-5.51	PBr_3	29.3	0.36	$-10^{k,l}$	Trace		18.1	0.44	+19.18	+19.35 m	+39.38	
7.4	+11.21	PBr_3	9.8	0.36	$-20^{k,n}$	0.6	0.08	$3 \cdot 4$	0.25	-38.08	38·11 °	$-38 \cdot 11$	

^a After one purification by g.l.c. ^b After two purifications by g.l.c. ^c Corrected for optically pure butan-2-ol, α_D^{20} 11·21°. ^d Volatile products removed under reduced pressure whilst warming to 20° (60—90 min.) and trapped (-80°). ^e Distillation of residue gave di-s-butyl hydrogen phosphite (7·1 g., 0·24 mol.), b.p. 48°/0·02 mm., n_D^{20} 1·4183, $\alpha_D^{20} + 24\cdot92°$ (Found: P, 15·9. Calc. for C₈H₁₉O₃P: P, 15·95%) [³¹P δ (p.p.m.) -4·7 doublet, J_{PH} 691 c./sec.]. ^f n_D^{20} 1·3966 (Found: Cl. 38·7. Calc. for C₄H₆Cl: Cl. 38·3%). ^e Treatment of residue (8·8 g.) with anhydrous HCl (2·0 g.) (167 hr./25°) gave further 2-chlorobutane (2·2 g., 0·24 mol.), $\alpha_D^{20} - 25\cdot59°$, $\alpha_D^{20} - 27\cdot08°$ corrected. ^h n_D^{20} 1·3967 (Found: Cl. 38·3%). ⁱ Residue (10·1 g.) gave diphenylphosphonic acid, m.p. 191—192° (Found: P, 14·2. Calc. for C₁₂H₁₁O₂P: P, 14·2%), on recrystallization from aqueous ethanol. ^j n_D^{20} 1·3967 (Found: Cl. 38·3%). ^k HBr removed by stream of N₂ during the addition. Ice and water then added immediately, and the organic layer washed and dried (K₂CO₃). ⁱ Bu*Br distilled from dried product up to 92°. Residue afforded di-s-butyl hydrogen phosphite (3·6 g., 0·06 mol.), b.p. 41—43°/0·01 mm., n_D^{20} 1·4186, $a_D^{27\cdot3} - 11\cdot32°$ (Found: P, 15·7%). ^m n_D^{20} 1·4368 (Found: Br, 57·7. Calc. for C₄H₉Br: Br, 58·3%). ⁿ Bu*Br removed from dried product at 20°/0·1 mm. and trapped (-80°). Di-s-butyl hydrogen phosphite (4·8 g., 0·25 mol.), n_D^{20} 1·4182, $\alpha_D^{14\cdot6} + 26\cdot00°$, remained as a residue. ^e n_D^{20} 1·4363.

TABLE 3

Reactions of (+)- or (-)-2-halogenobutanes with sodium ethyl sulphide

Bu ^s X taken			Ets	SNa				Bu	Calc. max. ⁹	
x	g.	α _D ²⁰	 g.	mol.	EtOH	Temp.	Time	g.	α _D ²⁰	α_D^{20}
Cl	1.4	-28.24	$25 \cdot 2$	19.8	90 ml.	60°	6 hr.	0.83	$+23.70^{\circ}$	-30.93°
Br	2.5	+19.28	8.7	5.7	70	60	1	0.53	-11.73	+42.65
\mathbf{Br}	$2 \cdot 0$	-38.35	17.1	13.9	60	60	1	0.96	+23.19	-42.92
I	3∙3	-21.61	9 ·0	6 ∙0	70	60	1	0.80	+9.15	-61.29

^a After purification by g.l.c. All products had n_D^{20} 1.4478. ^b Calculated for optically pure s-butyl ethyl sulphide, α_D^{20} 25.95°

To obtain further data for the 2-halogenobutanes, we have examined the dealkylation of certain phosphorus esters. The stepwise dealkylation of (+)- or (-)tri-s-butyl phosphite by hydrogen chloride or hydrogen bromide followed the pattern previously reported for the 1-methylheptyl ester.¹¹ Removal of one alkyl group per molecule of phosphite occurred with inversion of configuration to give 2-chlorobutane, $\alpha_{\rm D}^{20}$ 30.8°, or 2-bromobutane, α_D^{20} 43.7°, whilst further dealkylation of the di-s-butyl hydrogen phosphite so formed gave 2-halogenobutanes of progressively lower rotatory power (Table 1). The final products showed a considerable loss (ca. 50%) in optical purity. 2-Chlorobutane of maximum rotatory power was also obtained by the addition of phosphorus trichloride (0.33 mol.), dichlorophenylphosphine (0.5 mol.), or chlorodiphenylphosphine (1.0 mol.) to (+)- or (-)-butan-2-ol (Table 2), and by the interaction of (+)-s-butyl diphenylphosphinite and hydrogen chloride. In each case, an $S_N 2$ attack by chloride ion on the protonated intermediate ester is thought to occur [reaction (1): $R = Bu^s$; X = Cl; x = RO or Ph; y = RO or Ph]. It seems unlikely that these different reaction systems would all afford 2-chlorobutane of virtually the same rotatory power if a mixture of mechanisms was in operation, and the value is

$$X^{-} \longrightarrow R \xrightarrow{O = P}_{+} \stackrel{X}{\xrightarrow{}} R \xrightarrow{} RX + O \xrightarrow{P}_{+} \stackrel{H}{\xrightarrow{}} (1)$$

confirmed almost exactly by stereospecific conversion into (+)- or (-)-s-butyl ethyl sulphide as described for the 1-methylheptyl halides (Table 3).⁹ It is also very close to that $(\alpha_p^{20} 30.7^\circ)$ observed for the halide obtained with retention of configuration in the unimolecular vapour-phase decomposition of s-butyl chloroformate.¹² The discrepancy between the present results and the value $(\alpha_p^{20} 33.4^\circ)$ obtained by reduction of 2-chlorobutanoic acid ⁷ is inexplicable unless the rotation currently accepted for optically pure butan-2-ol⁵ is about 8% low; there is, however, no reason for believing this to be so.

Rotations observed for 2-bromobutane obtained by the interaction of hydrogen bromide and tri-s-butyl phosphite or s-butyl diphenylphosphinite differed slightly, probably because of the readier racemization of 2bromobutane by hydrogen bromide in solution. The higher value ($\alpha_{\rm D}^{20}$ 43.7°), obtained from the trialkyl phosphite at -20°, was, however, within 2% of the rotation derived by conversion into s-butyl ethyl sulphide (Table 3), and indicates that the previously estimated rotation, $\alpha_{\rm D}^{20}$ 50.0°,³ is much too high. A similar conclusion has been reached by other workers ¹⁰ who have also converted (+)-2-bromobutane into s-butyl ethyl sulphide. Calculation from their results gives $\alpha_{\rm D}^{20}$ 44.3° or 44.8° for optically pure 2-bromobutane. The addition of phosphorus tribromide to (+)- or (-)-butan-2-ol gave 2-bromobutane with a substantial loss (10-13%) in optical purity, due perhaps to the formation of alkyl halide by reaction sequences other than the dealkylation of tri-s-butyl phosphite in this system. Butan-2-ol did not react with hydrogen bromide under the experimental conditions, but it is probable that some 2-bromobutane was formed by dealkylation of the intermediate bromo-esters.¹³

The dealkylation of s-alkyl diphenylphosphinites [reaction (1): X = Cl, Br, or I; x = y = Ph] promises to afford a procedure for the preparation of good yields of optically active s-alkyl halides, with little or no loss of enantiomeric purity in the case of chlorides or bromides. Thus, (+)-s-butyl diphenylphosphinite afforded 2-chlorobutane, $\alpha_{\rm p}^{20}$ -31.0°, 2-bromobutane, $\alpha_{\rm p}^{20} - 42.4^{\circ}$, and 2-iodobutane, $\alpha_{\rm p}^{20} - 23.6^{\circ}$, on treatment with the appropriate hydrogen halide at 20°. The byproduct, diphenylphosphinous acid, was not isolated as such but yielded diphenylphosphonic acid by disproportionation and/or oxidation. The considerable loss in rotatory power observed for the iodide is attributed to racemization after formation, by contact with hydrogen iodide in solution. 2-Iodobutane of maximum rotatory power $(\alpha_{p}^{20} 60.4^{\circ})$ (confirmed within 1.5% by conversion into the thioether) was obtained by the interaction of di-s-butyl hydrogen phosphite and phosphorus triiodide, *i.e.*, in a system free from hydrogen iodide (cf. refs. 4 and 11).

With present experimental methods it is probably not possible to assign rotatory powers to the optically pure alkyl halides with an accuracy of better than $\pm 1-2\%$, especially since it is necessary to calculate from at least two measured rotations (for alcohol and halide), and possibly from four (alcohol, thioether, halide, and thioether). Errors arising from chemical impurity can be minimized by the use of preparative gasliquid chromatography, and personal errors in measurement eliminated with the aid of photoelectric polarimeters. The rotations reported here for the 2-halogenobutanes, and previously for the 2-halogeno-octanes,¹¹ are thought to be correct within these limits.

EXPERIMENTAL

³¹P chemical shifts are given relative to phosphoric acid. *Polarimetry.*—Optical rotations were measured with a Bellingham and Stanley model A polarimeter ($\pm 0.02^{\circ}$) or a Perkin-Elmer 141 photoelectric polarimeter ($\pm 0.2\%$ of measured rotation) in 0.25, 0.5, or 1 dm. tubes according to sample size. All values are given for l 1 dm. Variations with temperature were determined in water-jacketted cells, and found to be linear over the range 15—25°, as follows (circular degrees per °c for the 2-halogenobutanes of maximum rotatory power): 0.106 (Cl); 0.112 (Br); 0.148 (I). Hence, $\alpha_{\rm p}{}^t = \alpha_{\rm p}{}^{20}[1 + (20 - t)x]$, where x = 0.00342 (Cl), 0.00256 (Br), or 0.00245 (I).

Starting Materials .-- Phosphorus trihalides (Hopkin and

¹² E. S. Lewis, W. C. Herndon, and D. C. Duffey, J. Amer. Chem. Soc., 1961, **83**, 1959.

¹³ W. Gerrard and H. Herbst, J. Chem. Soc., 1955, 277; Research Correspondence, 1955, 8, A1.

¹¹ E. J. Coulson, W. Gerrard, and H. R. Hudson, *J. Chem. Soc.*, **1965**, **2364**; T. M. Cook, E. J. Coulson, W. Gerrard, and H. R. Hudson, *Chem. and Ind.*, 1962, 1506.

Williams) were used as supplied. Dichlorophenylphosphine (Eastman) was redistilled, b.p. $42^{\circ}/0.2$ mm., $n_{\rm D}^{20}$ 1.5982 (Found: Cl, 39.1; P, 17.2. Calc. for C₆H₅Cl₂P: Cl, 39.6; P, 17.3%). Chlorodiphenylphosphine (Aldrich) was redistilled, b.p. 106°/0·1 mm., n_D²⁰ 1·6366 (Found: Cl, 16·1; P, 14.0. Calc. for $C_{12}H_{10}ClP$: Cl, 16.1; P, 14.0%). Butan-2-ol was resolved as described,5 redistilled from barium oxide to constant rotation, and shown to be chemically pure by g.l.c.

Preparation of Tri-s-butyl Phosphite.-Phosphorus trichloride (11.7 g., 1 mol.) was added dropwise with thorough mixing to butan-2-ol (18.9 g., 3 mol.), α_{D}^{20} -5.21°, and dimethylaniline (30.9 g., 3 mol.) in light petroleum (b.p. 30-40°) (250 ml.) at 0°. After filtration from dimethylanilinium chloride (38.9 g., 2.9 mol.), the product was twice distilled, to yield *tri-s-butyl phosphite* (8.62 g., 0.41 mol.), b.p. 101°/10 mm., $n_{\rm p}^{20}$ 1.4286, $\alpha_{\rm p}^{23}$ +1.68° (Found: C, 57.2; H, 11.0; P, 12.5. $C_{12}H_{27}O_3P$ requires C, 57.6; H, 10.9; P, 12.4%) [³¹P δ (p.p.m.) -140 singlet]. Butan-2-ol $(25\cdot3 \text{ g.}), \alpha_{D}^{20} + 10\cdot73^{\circ}, \text{ similarly gave the phosphite (10\cdot3 g., 0\cdot36 \text{ mol.}), \alpha_{D}^{23\cdot5} - 1\cdot81^{\circ}$ (Found: P, $12\cdot6\%$). Lowerboiling fractions from both preparations contained small amounts of di-s-butyl hydrogen phosphite [³¹P δ (p.p.m.) -4.7 doublet, J_{PH} 691 c./sec.]. With pyridine as base and diethyl ether as solvent, it was necessary to wash the product several times to remove pyridine hydrochloride. The distilled ester (Found: P, 14.5%) then contained tri-(39.8%) and di-s-butyl phosphite (60.2%).

Preparation of s-Butyl Diphenylphosphinite.-Chlorodiphenylphosphine (33.1 g., 1 mol.) was added to butan-2-ol (11.1 g., 1 mol.), $\alpha_D^{\ 20}$ +10.88°, and triethylamine (15.2 g., 1 mol.) in light petroleum (b.p. 30-40°) (120 ml.) at 20°. Triethylammonium chloride (20.3 g., 0.98 mol.) was removed by filtration, and the product distilled, to yield s-butyl diphenylphosphinite (26.1 g., 0.67 mol.), b.p. 113-118°/ 0.003 mm., $n_{\rm p}^{20}$ 1.5727, $\alpha_{\rm p}^{20}$ +12.76° (Found: C, 71.6; H, 6.8; P, 12.0. $C_{16}H_{19}$ OP requires C, 74.4; H, 7.4; P, 12.0% [³¹P δ (p.p.m.) - 105 singlet].*

Reactions of Hydrogen Halides with (+)- or (-)-s-Butyl Esters .- The esters were treated with hydrogen halide as specified (Table 1). Volatile products were then removed at 0.1 mm. and trapped (-80°). In certain experiments the reaction residue was treated with successive quantities of hydrogen halide as shown.

Reactions of (+)- or (-)-Butan-2-ol with Phosphorus Halides .- The halide was added dropwise (ca. 30 min.) to (+)- or (-)-butan-2-ol at the specified temperature (Table 2). Alkyl halide was then removed under reduced pressure and trapped at -80° , or distilled from the reaction mixture after aqueous treatment and neutralization (K_2CO_3) as indicated.

Analysis and Purification of Alkyl Halides .--- The products obtained above were washed, dried (K₂CO₃), and analyzed for 2-halogenobutane and butan-2-ol (if present) by g.l.c. on 10% squalane at 40°; the same column demonstrated isomeric purity.14 Only traces of butene were detected. The halides were then purified by preparative g.l.c.: 2-chlorobutane in a 20 ft. \times 3/8 in. stainless steel Autoprep column containing 20% polyethylene glycol 400 on 80-100 mesh Chromosorb W at 25° (N2 flow-rate 100 ml./min.); 2-bromobutane in a 4 ft. \times 5/8 in. glass column containing 10% polyethylene glycol 400 on 85-100 mesh Celite at 40° (N₂ flow-rate 200 ml./min.). Under these conditions no racemization occurred. 2-Iodobutane lost rotatory power to some extent when treated thus, and was therefore distilled.

Interaction of (+)-Di-s-butyl Hydrogen Phosphite and Phosphorus Tri-iodide.-The phosphite (8.1 g., 1 mol.), $\alpha_{\rm D}^{20} + 25 \cdot 10^{\circ}$, from butan-2-ol, $\alpha_{\rm D}^{20} + 10.96^{\circ}$, was cooled to -10° and added to phosphorus tri-iodide (34.2 g., 2 mol.) in carbon disulphide (100 ml.). After 48 hr. at 20°, ice and water were added. The organic layer was washed with water and sodium carbonate solution, dried $(MgSO_4)$, and fractionally distilled, to give 2-iodobutane (0.54 mol.) with traces of carbon disulphide in the lower fractions: (i) 0.53 g., b.p. $21-31^{\circ}/53$ mm., $n_{\rm D}^{20}$ 1·5409; (ii) 0·87 g., b.p. $36-39^{\circ}/45$ mm., $n_{\rm D}^{20}$ 1·5011, $\alpha_{\rm D}^{20}$ -57·93°; (iii) 1·66 g., b.p. $37^{\circ}/40$ mm., $n_{\rm D}^{20}$ 1·5009, $\alpha_{\rm D}^{20}$ -58·57°; (iv) 1·13 g., b.p. $37^{\circ}/40$ mm., $n_{\rm D}^{20}$ 1·5006, $\alpha_{\rm D}^{20}$ -58·96° ($\alpha_{\rm D}^{20}$ -60·31 corrected for optically pure butan-2-ol) (Found: I, 68·7. Calc. for C_4H_9I : I, 69.0%). In a similar experiment, (+)-dis-butyl hydrogen phosphite (4.2 g., 1 mol.), from butan-2-ol, $\alpha_{\rm p}^{20}$ +10.74°, and phosphorus tri-iodide (8.9 g., 1 mol.) in carbon disulphide (32 ml.) gave 2-iodobutane (1.6 g., 0.40 mol.), $\alpha_{\rm D}^{20} - 57.99^{\circ} (\alpha_{\rm D}^{20} - 60.52^{\circ} \text{ corrected})$; mean value $\alpha_{D}^{20} = 60.42^{\circ}$. Preparation of (-)-s-Butyl Ethyl Sulphide.—Butan-2-ol

(4.6 g.), $\alpha_{\rm p}^{20}$ +10.96°, was converted into the methanesulphonate (3.6 g.), $n_{\rm D}^{20}$ 1.4260, as described for the l-methylheptyl ester.⁹ The undistilled s-butyl methanesulphonate was then heated (1 hr./60°) with sodium ethyl sulphide (10.7 g., 5.4 mol.) in ethanol (100 ml.), and the product extracted with light petroleum (b.p. 30-40°) (100 ml.). The washed and dried (MgSO₄) extract was evaporated at 15 mm., to leave an almost colourless liquid (2.6 g.) which contained two components, not separable by fractional distillation. Separation of a quantity (1.8 g.) by g.l.c. in a 4 ft. \times 5/8 in. glass column packed with 10% polyethylene glycol 1500 on 85-100 mesh Celite at 60° $(N_2 \text{ flow-rate } 60 \text{ ml./min.})$ gave s-butyl ethyl sulphide (0.68 g.), $n_{\rm D}^{20}$ 1.4478, $\alpha_{\rm D}^{20}$ -25.37° ($\alpha_{\rm D}^{20}$ -25.95° corrected for optically pure butan-2-ol) (Found: C, 61.7; H, 12.3; S, 27.0. Calc. for C₆H₁₄S: C, 61.0; H, 11.9; S, 27.1%). Repeated chromatography did not change the rotation. The second component was diethyl disulphide (0.18 g.), $n_{\rm p}^{20}$ 1.5065 (identified by infrared and Raman spectroscopy).15

Conversion of (+)- or (-)-2-Halogenobutanes into s-Butyl Ethyl Sulphide.-The 2-halogenobutanes were heated at 60° with sodium ethyl sulphide in ethanol as specified (Table 3); the products were then extracted and purified as described above.

Lack of Reaction between Butan-2-ol and Hydrogen Bromide under Experimental Conditions.-Hydrogen bromide (2.0 g.) was passed (30 min.) into butan-2-ol (11.1 g.) at -20° . After addition of water, and drying (K₂CO₃), the organic layer contained no detectable 2-bromobutane (g.l.c.).

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14 B. A. Chaudri and H. R. Hudson, J. Chromatog., 1967, 27,

^{*} The compound is considered pure on the basis of P analysis, n.m.r., and the constancy of the refractive index throughout the collection of the fraction. Difficulty in obtaining accurate analyses for C and H has been experienced with this and other similar compounds containing Ph-P bonds.

^{240.} ¹⁵ G. B. Bonino and R. Manzoni-Ansidei, Mem. R. Accad. Sci. Ist. Bologna, 1934, 9, 3.