255. *Reaction Kinetics and the Walden Inversion. Part IV. Action of Silver Salts in Hydroxylic Solvents on β-n-Octyl Bromide and α-Phenylethyl Chloride.*

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Our investigation of the Walden inversion having thus far been confined to homogeneous mechanisms of substitution, we here set out to cover similar ground with respect to the important group of heterogeneous mechanisms which involve the use of silver salts. This paper deals with the hydroxylation and ethoxylation of halides containing hydrogen and alkyl groups only, or hydrogen, alkyl and aryl groups, at the seat of substitution, the examples being β-*n*-octyl bromide and α-phenylethyl chloride.

In the controlling kinetic investigation it is proved that the reaction with silver oxide is catalysed by silver bromide, and that, at equivalent concentrations and similar conditions of catalysis by silver halide, silver nitrate and silver acetate act at the same rate. In all cases the reagent is adsorbed silver ions: with soluble salts the only surface catalyst is the silver halide, but with silver oxide the reaction goes both on the silver halide and on the silver oxide: the primary function of silver oxide is to maintain a supply of silver ions, but it also provides an active surface.

The optical investigation deals with the hydroxylation and ethoxylation of β-*n*-octyl bromide by means of silver oxide, nitrate and acetate, and the hydroxylation of α-phenylethyl chloride by means of silver oxide. All the products of substitution have a predominantly inverted configuration, but all are more or less considerably racemised, especially that from the aralphyl halide. The amount of racemisation is increased when the hydroxylic solvent is diluted with a non-hydroxylic solvent. Quantitative particulars are given.

In the following experiments we endeavour to establish the space-orientation of the hydroxylation or alkoxylation of alkyl halides by means of silver salts in aqueous or alcoholic media. We have used two alkyl halides, one of which, β-*n*-octyl bromide, is typically aliphatic, whilst the other, α-phenylethyl chloride, may be taken to represent the series of aralphyl halides. The problem of halogeno-acids and their derivatives is considered separately in Part V. As silver salts, we have used silver oxide in suspension, and the nitrate and acetate in solution.

The work divides itself as usual into the study of the kinetics of substitution and the examination of the optical effect, and we shall consider first the evidence of mechanism given by the kinetic observations.

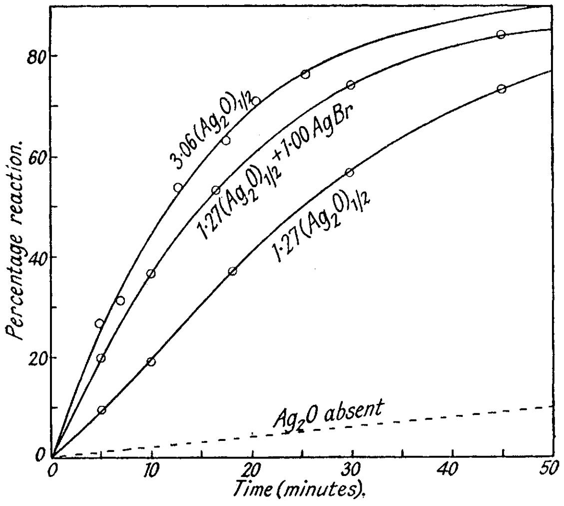
A number of experiments have been made on the hydrolysis of β-*n*-octyl bromide with a suspension of silver oxide in "63%" aqueous ethyl alcohol at the boiling point. At this temperature the displacement of bromine from the alkyl bromide in the absence of an added reagent becomes substantially complete only after several days; whereas in the presence of a moderate excess of silver oxide the reaction is completed in a few hours. Hence we can assume that the reaction which takes place in the presence of silver oxide depends in an essential way on this reagent, although homogeneous interaction with the solvent must also occur to a small extent.

The product of the reaction with silver oxide is not simply β-*n*-octyl alcohol, but a mixture of this and ethyl β-*n*-octyl ether; in fact, the two substances which would be formed by interaction of the bromide with the solvent alone, in the absence of any silver oxide. Unless we assume that the silver ethoxide can exist in the presence of a large amount of water, it is necessary to conclude that the ethoxyl, and likewise the hydroxyl, groups in the reaction products come directly from alcohol and water molecules of the solvent, not from silver compounds. Thus the suggestion arises that the essential function of the silver oxide is to supply silver ions.

Further evidence of mechanism arises from our observation that the reaction is autocatalytic with respect to silver bromide, and can be considerably accelerated by the prior addition of this substance. The reaction obviously occurs on the surface of the silver bromide; and since we cannot suppose that so rapid a process involves the interaction of two solids, the adsorbed reagents must be the soluble alkyl halide and some dissolved ion derived from the silver oxide—evidently the silver ion.

Although heterogeneous catalysis by silver bromide in the hydrolysis of alkyl halides has not previously been observed for the reaction with silver oxide, it is well known for the reaction with soluble silver salts, such as silver nitrate. Reactions with soluble silver salts were at first thought to be homogeneous and bimolecular (Chiminello, *Gazzetta*, 1895, **25**, [ii], 410; v. Biron, *J. Russ. Phys. Chem. Soc.*, 1900, **30**, 667), but more comprehensive investigations revealed relations which were not consistent with any simple form of kinetics (Burke and Donnan, J., 1904, **85**, 555; *Z. physikal. Chem.*, 1909, **69**, 148; Donnan and Potts, J., 1910, 1882; Pierce and Weigle, *Amer. Chem. J.*, 1912, **48**, 243). The heterogeneous catalysis by silver bromide was discovered by Senter for methyl iodide (J., 1910, **97**, 346), and was confirmed by Baker for benzyl bromide (J., 1934, 987). Further confirmation has arisen in the study of halogeno-acids. In all these cases in which soluble silver salts are employed, the reagent must be silver ions; and hence it would appear that heterogeneous catalysis by silver halides is diagnostic of the reaction of silver ions with alkyl halides.

There is one respect in which the behaviour of silver oxide is more complicated than that of soluble silver salts, as our results with β-*n*-octyl bromide show. Although the reaction of this substance with silver oxide in aqueous alcohol is demonstrably autocatalytic with respect to silver bromide, it commences, in the absence of any initially added silver bromide, with a finite velocity, which is much too great to represent merely the homogeneous interaction with the solvent. Moreover, the reaction–time curve shows no marked point of inflexion, and usually appears to be concave to the time-axis right from the origin. The rate throughout a run increases, furthermore, with the amount of silver oxide employed, although we may presume that the volume-concentration of silver ions in solution, and therefore their surface-density in any given surface, being determined by a solubility, would be independent of the quantity of suspended silver oxide. These points are illustrated by the reaction–time curves of the figure. The facts are all explained if we suppose that silver oxide, as well as silver halides, can provide an active surface: in hydrolysis by silver oxide, unlike hydrolysis with fully dissolved silver salts, a suitable surface is available from the commencement of reaction, and the greater this surface the greater the speed of reaction. A curious result of this catalysis is that the decrease of speed due to the destruction of silver oxide in the course of a run is often more or less off-set by the increase due to the formation of silver bromide: with suitably chosen initial quantities and concentrations the two effects can be made to balance sufficiently well to enable the reaction to be expressed by means of a first-order rate equation; the constant of which, however, has no definite chemical meaning. Many such accidental compensations occur in the literature of hydrolysis with silver salts.



Our kinetic observations on the hydrolytic action of silver oxide thus lead us to the view that this reagent has two functions: first, it maintains a supply of silver ions in the solution: and secondly, it provides a surface on which the attack of these ions on the alkyl halide can proceed. The precipitated silver halide furnishes a second surface also suitable for this purpose.

Since the concentration of dissolved silver ions which can be maintained by suspended silver oxide is inevitably small, our interpretation requires that, in the initial presence of suitable amounts of silver bromide, hydrolysis with moderately concentrated solutions of soluble silver salts, such as silver nitrate, should proceed very much more rapidly than hydrolysis with suspensions of silver oxide. We have verified this by qualitative observations on a number of alkyl halides, and a more quantitative illustration is provided by observations on the hydrolysis of β-*n*-octyl bromide, initially in *M*/35-concentration in "63%" aqueous ethyl alcohol at 35°. When 1·25 mols. of dissolved silver nitrate were used as the hydrolysing agent (concentration *M*/28), without the initial addition of silver bromide, the time of half-change was 85 minutes; whilst with 1·00 mol. silver bromide in addition, it was 67 minutes; on the other hand, with 1·25 mols. of suspended silver oxide as hydrolysing agent the time of half-change was about 650 minutes. It should be mentioned that the solubility of silver oxide in the hydrolysis solutions is distinctly greater than in the pure solvent; thus a particular solution, filtered at about 35° after the completion of hydrolysis, was found to be *N*/780 with respect to silver ions.

In further support of the theory that the reagent is the adsorbed silver ion, we have made a comparison between silver nitrate and silver acetate with respect to the rates at which they effect the hydrolysis of β-*n*-octyl bromide at similar concentrations. It seemed the more desirable to do this inasmuch as the peculiar kinetics obtaining in hydrolyses with silver nitrate have been repeatedly interpreted by assuming attack by undissociated silver nitrate molecules—a convenient theory since nobody claims to know the concentration of these molecules. A pair of experiments were carried out in which β-*n*-octyl bromide in *M*/100-solution in "63%" aqueous ethyl alcohol at 85° was hydrolysed on the one hand by means of 1·15 mols. of dissolved silver nitrate, and, on the other, by a similar amount of dissolved silver acetate. The two rate curves were coincident up to 40% of reaction, after which the experiment with the nitrate proceeded slightly faster than the other, probably on account of a difference in the condition or specific area of the silver halide surface in the two cases.

Heterogeneous catalysis by silver bromide in the hydrolysis of alkyl halides by means of soluble silver salts is confirmed by our experiments with β-*n*-octyl bromide. In all runs in which silver nitrate was employed without an initial addition of silver bromide, the reaction commenced with a period of acceleration, followed by an inflexion point and a deceleration. The initial addition of silver bromide removed the induction period, and accelerated the reaction, especially in the early stages.

Our general conclusion is that the hydrolysis of alkyl halides, either by means of sparingly soluble silver compounds such as the oxide, or of soluble silver salts such as the nitrate, consists essentially in the heterogeneous attack by silver ions on the alkyl halide at the surface of the silver halide, and also at the surface of silver oxide, if any is present. The available evidence does not, however, exclude the possibility that in the presence of considerable concentrations of silver ion some part of the attack may be homogeneous. It may be noted that the rôle ascribed to the silver halides is in general conformity with the large amount of available evidence concerning the tendency of those aliphatic halides which are not easily hydrolysed to combine with silver salts; and with the ability of soluble (ionised) silver salts to combine with silver halides: the adsorption equilibrium of silver ions on silver bromide has been studied by Fajans and Frankenburger (*Z. physikal. Chem.*, 1923, **105**, 255).

We now turn to the optical side of the research, and recall, first, that when β-*n*-octyl bromide, β-*n*-octyl alcohol and ethyl β-*n*-octyl ether have rotations of the same sign they have corresponding configurations (Part I); and also that a like statement is true for α-phenylethyl chloride, α-phenylethyl alcohol, and α-phenylethyl ethyl ether (Part II); so that in the case of either of these halides we can deduce the spatial orientation of hydroxylation or ethoxylation from the observed effect on the sign of rotation.

As far as we are aware, the previous literature contains only two records of the hydrolysis of optically active alkyl halides by means of silver salts; and one relates to β-*n*-octyl bromide, the other to α-phenylethyl chloride. Pickard and Kenyon state that, using moist silver oxide, they converted β-*n*-octyl bromide having $[\alpha]_D^{20^\circ} \pm 27{\cdot}5^\circ$ into optically pure β-*n*-octyl alcohol with $[\alpha]_D^{20^\circ} \pm 9{\cdot}9^\circ$ (*Ber.*, 1912, **45**, 1592); there must, however, be some inaccuracy here, because the rotation of the optically pure bromide is at least $[\alpha]_D^{20^\circ} \pm 32{\cdot}5^\circ$, and is probably close to $[\alpha]_D^{20^\circ} \pm 33{\cdot}8^\circ$, so the material used could not have given optically pure alcohol. We can suggest a possible cause of this discrepancy inasmuch as the authors' description is not specific with regard to the solvent used, and does not include any record of an analysis of the alcohol: if the solvent were aqueous ethyl alcohol, the isolated β-*n*-octyl alcohol would contain ethyl β-*n*-octyl ether, which is not easily removed by distillation, and has a considerably higher specific rotation than the β-*n*-octyl alcohol. McKenzie and Clough shook α-phenylethyl chloride with silver oxide and water at room temperature, and obtained a much racemised alcohol with an inverted sign of rotation (J., 1913, **103**, 687). These authors did not, however, show to what extent the reaction under these conditions is independent of the hydrolysis which readily takes place in the presence of water alone: a demonstration on this point is necessary, because we know that the addition of, *e.g.*, potassium hydroxide to a mixture of α-phenylethyl chloride and water makes no difference to the hydrolysis, either kinetically or stereochemically (Part II). However, we have found that the hydrolysis under McKenzie and Clough's conditions takes place very much more rapidly than if the silver oxide is omitted, so the optical results which they obtained must relate essentially to the reaction involving silver oxide.

In our further experiments we have employed solvents which completely dissolve the alkyl halides. β-*n*-Octyl bromide has been hydrolysed and alcoholysed in 60—63% aqueous ethyl alcohol under the following conditions: (1) With excess of silver oxide at the b. p. of the suspension. The products were β-*n*-octyl alcohol and ethyl β-*n*-octyl ether, formed in comparable amounts, and a little octylene. (2) With a small excess of silver nitrate in an initial concentration of approximately *M*/20 at 35°. The products were the alcohol and ether as before, together with small amounts of β-*n*-octyl nitrate and octylene. Qualitative examination of the stability of the nitrate towards hydrolysis indicated the improbability that any appreciable amount of alcohol or ether could have been formed by way of the nitrate; and this point is of importance in the interpretation of the optical results of substitution, since, if any appreciable amount of alcohol or ether were formed through a directly produced nitrate, we should have to consider the steric orientation of the decompositions of this substance. (3) With a small excess of silver acetate in an initial concentration of about *M*/80 at 80°. The products were β-*n*-octyl alcohol, ethyl β-*n*-octyl ether, and very small amounts of the octyl acetate and octylene. In this case it is unnecessary to consider whether or not any of the alcohol or ether arises by hydrolysis or alcoholysis of first-formed β-*n*-octyl acetate, because we know that the hydrolysis of a carboxylic ester does not involve an exchange of any bond of the alcoholic residue, and, therefore, that the configuration of any β-*n*-octyl alcohol or ether produced by way of the acetate would indicate the steric orientation of the nucleophilic substitution, just as well as alcohol and ether which are formed directly. (4, 5) α-Phenylethyl chloride has been hydrolysed in 60% and in 80% aqueous acetone by means of excess of silver oxide at the b. p.'s of the respective suspensions. The sole product in these experiments was α-phenylethyl alcohol.

Results and Conclusions.

The results are given in Table I, in which we have included the data obtained by McKenzie and Clough. The headings of the first six cols. of the table are self-explanatory. Col. 7 records the rotatory powers of the alkyl halides used, and col. 8 those of the alcohols, alkyl ethyl ethers or alkyl esters produced. Col. 9 shows the rotations of these substances, calculated to correspond to the best values we are able to assign to the rotatory powers of the optically pure halides: for β-*n*-octyl bromide we take the value $[\alpha]_D^{20°}$ 33·8°, or $\alpha_D^{20°}$ (l = 10 cm.*) 36·9°; and for α-phenylethyl chloride, the value $\alpha_D^{20°}$ 53·8°. In col. 10 these rotatory powers of the products of substitution are, where possible, expressed as percentages of the rotations of optically pure products: we assume the following values of $\alpha_D^{20°}$, *viz.*, β-*n*-octyl alcohol 8·1°, ethyl β-*n*-octyl ether 13·4°, α-phenylethyl alcohol 44·0°. In the last col. we give for comparison the similarly calculated percentage optical purity of the products formed by homogeneous unimolecular hydrolysis or alcoholysis (S_N1; cf. Part I and II) under conditions approximately corresponding as to solvent and temperature with those of the silver salt experiments.

The figures given in the penultimate column for the percentage retention of optical purity permit the following statements. In all cases the products of substitution show an inverted sign of rotation, and this, as we have seen, means an inverted configuration; all products, however, are more or less considerably racemised; the aralphyl halide undergoes substitution with particularly extensive racemisation; and in the hydrolysis of this halide racemisation increases markedly on diluting the reagent water with the inert solvent acetone.

Comparison of the last two columns indicates a close qualitative parallelism between the optical results obtained in the reactions with silver salts and those recorded in Parts I and II for substitution by the homogeneous unimolecular mechanism. Thus all the statements of the preceding paragraph would apply equally well to the data of the last column, even though the individual figures differ rather considerably from those of the penultimate column. The main general difference is that in the heterogeneous reactions

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* All subsequent values of α_D refer to l = 10 cm. unless otherwise specified.

TABLE I.

Optical Effects of Reactions between Alkyl Halides and Silver Salts.

							Alcohol, etc., $\alpha_D^{20°}$.			
Alkyl halide.	Re-agent.	Equivs. Ag.	Solvent.	Approx. temp.	En-trant group.	Halide $\alpha_D^{20°}$.	Obs.	Corr. stand. halide.	Opt. purity, %.	Do. for S_N1, %.
$C_8H_{17}Br$	Ag_2O	3·32	60% aq.-EtOH	80°	OH	−26·8°	+ 4·40°	+ 6·05°	−74·5	−66
,,	,,	3·32		80	OEt	−26·8	+ 9·22	+12·7	−94·0	−74
,,	$AgNO_3$	1·21	63% aq.-EtOH	35	OH	−34·5	+ 5·68	+ 6·07	−74·8	—
,,	,,	1·21		35	OEt	−34·5	+11·70	+12·5	−93·0	—
,,	,,	1·21		35	ONO_2	−34·5	+11·36	+12·1	—	—
,,	AgOAc	1·00		35—80	OH	−11·6	+ 1·78	+ 5·65	−70·0	—
,,	,,	1·00		35—80	OEt	−11·6	+ 4·00	+12·7	−94·0	—
CHPhMeCl	Ag_2O	1·20	H_2O	20	OH	−32·0	+ 7·4	+12·4	−29·0*	−17
,,	,,	1·54		20	,,	+53·7	−13·2	−13·2		
,,	,,	1·20	60% aq.-Me_2CO	70	,,	−47·2	+ 4·16	− 4·7	−10·7	− 5
,,	,,	1·20	80% aq.-Me_2CO	70	,,	−34·0	+ 0·80	− 1·3	− 3·0	− 2

* Experiments by McKenzie and Clough, *loc. cit.*

with silver salts the retention of optical purity is greater than in the homogeneous unimolecular reactions. These comparisons are discussed in Part VI.

EXPERIMENTAL.

Rate of Reaction between β-n-*Octyl Bromide and Silver Oxide in* 63% *Aqueous Alcohol.*—(i) The " 63% " aqueous alcohol was prepared by mixing 13 vols. of purified anhydrous ethyl alcohol and 8 vols. of water. Three parallel experiments were performed each with a 0·14*M*-solution of the bromide in the solvent at its b. p. In the first experiment (*a*) 1·27 equivs. of silver oxide were added, in the second (*b*) 3·06 equivs., and in the third (*c*) 1·27 equivs. of silver oxide plus 1·00 equiv. of silver bromide. Samples (10 c.c.) were removed at various times from the boiling suspensions (by using a temporary increase of pressure over the surface of the liquid in order to fill the pipette), and run into an excess of concentrated chloride-free alcoholic potassium hydroxide (30 c.c.). This solution was filtered, and the precipitate was washed with anhydrous alcohol; the combined filtrate and washings were then hydrolysed completely by boiling for 2 hours under reflux. The liberated chloride ion was then estimated by the addition of silver nitrate, and back-titration with ammonium thiocyanate, ferric sulphate being used as indicator. The results are in Table II.

(ii) Two parallel experiments were carried out each with a 0·0285*M*-solution of the bromide in the same solvent at 35°. In one (*d*) 1·25 equivs. of silver oxide were added, and in the other (*e*) 5·00 equivs. The suspensions were stirred continuously, and samples were analysed as described above with results which are given in Table II.

In sets of parallel experiments silver oxide from the same batch was used. It was prepared with a small excess of silver nitrate, since the alternative of a small excess of alkali hydroxide involved some risk that adsorbed hydroxide ion would modify the solubility of the precipitate with respect to silver ion.

Reaction of l-β-n-*Octyl Bromide with Silver Oxide in* 60% *Aqueous Alcohol at the Boiling Point.*—The bromide (15 g.) was treated with silver oxide (30 g.) in the boiling solvent, which was prepared by mixing 6 vols. of purified anhydrous ethyl alcohol with 4 vols. of water. After 2 days the silver salts were filtered off, and washed first with ethyl alcohol and then with light petroleum. The organic materials were extracted with light petroleum, and, after the removal of most of the solvent, treated with sufficient bromine to convert the octene into dibromo-octane. The octyl alcohol and ethyl octyl ether were then isolated together by distillation. The former was converted into its acid phthalic ester by treatment with phthalic anhydride at 110—115°, and the neutral and acid products were separated with the aid of ether and sodium carbonate. The neutral product, ethyl β-*n*-octyl ether, had b. p. 68°/18 mm. (1·5 g.) (Found : C, 76·0; H, 13·9. Calc. : C, 75·9; H, 14·0%). The hydrogen phthalate (4·65 g.) had $[\alpha]_D^{20°}$ + 26·04° in dry ethyl-alcoholic solution, and this allows us to calculate the rotation given in Table I for the alcohol.

TABLE II.

Reaction of β-n-*Octyl Bromide with Silver Oxide in* 63% *Alcohol.*

At the boiling point.

(a) $1{\cdot}27(Ag_2O)_{1/2}$.		(b) $3{\cdot}16(Ag_2O)_{1/2}$.		(c) $1{\cdot}27(Ag_2O)_{1/2} + 1{\cdot}00AgBr$.	
Time (min.).	Reaction (%).	Time (min.).	Reaction (%).	Time (min.).	Reaction (%).
5·0	9·7	4·8	26·6	5·0	19·9
10·0	19·2	7·0	31·1	10·0	36·8
18·1	37·3	12·7	53·7	18·0	53·4
29·8	56·8	17·6	63·3	30·0	74·4
45·0	73·3	20·6	71·3	45·0	84·2
209·0	96·7	26·0	76·4	70·0	95·4

At 35°.

(d) $1{\cdot}25(Ag_2O)_{1/2}$.		(e) $5{\cdot}00(Ag_2O)_{1/2}$.	
Time (min.).	Reaction (%).	Time (min.).	Reaction (%).
226·0	28·0	55·0	17·3
451·0	45·4	156·0	38·8
2711·0	93·4	225·0	55·0
4296·0	94·5	463·0	82·7
		1218·0	95·4

Rate of Reaction of β-n-*Octyl Bromide with Soluble Silver Salts in* 63% *Aqueous Alcohol.*—Two parallel experiments (*f* and *g*) were carried out at 35° with solutions initially 0·0285*M* with respect to β-*n*-octyl bromide and 0·0357*M* with respect to silver nitrate. In one of these experiments (*g*) silver bromide was suspended in the solution in quantity equivalent to 1 mol. per mol. of octyl bromide.

Two further experiments were performed at 35° with solutions originally 0·0100*M* with respect to β-*n*-octyl bromide and 0·0116*M* with respect to silver. The reagent was in the one case (*h*) silver nitrate and in the other (*i*) silver acetate.

TABLE III.

Reaction of β-n-*Octyl Bromide with Silver Nitrate and Acetate in* 63% *Aqueous Alcohol at* 35°.

(f) $1{\cdot}25AgNO_3$.		(g) $1{\cdot}25AgNO_3 + 1{\cdot}00AgBr$.		(h) $1{\cdot}16AgNO_3$.		(i) 1·16AgOAc.	
Time (min.).	Reaction (%).	Time (min.).	Reaction (%).	Time (min.).	Reaction (%).	Time (min.).	Reaction (%).
5·5	2·7	4·2	4·7	24·0	1·3	19·5	3·9
14·5	11·8	9·0	10·9	60·0	9·1	60·0	11·0
32·0	24·7	16·0	18·7	127·5	20·1	114·0	16·9
45·5	31·3	27·0	27·5	188·5	27·1	172·0	25·3
67·7	42·8	47·0	40·5	244·5	34·9	211·0	29·6
105·5	57·4	67·0	49·6	321·5	41·7	305·0	38·4
145·0	69·3	87·0	56·9	473·5	54·3	424·0	45·6
182·7	74·7	107·0	62·9	620·0	61·1	612·0	53·6
217·5	77·8	146·5	72·9	1265·0	80·8	1216·0	67·5
256·2	83·2	212·0	82·9	1511·0	83·2	1542·0	71·7
		274·5	88·6	2076·0	88·3	2070·0	74·9
				2727·0	92·7	2846·0	83·5

Reaction of l-β-n-*Octyl Bromide with Silver Nitrate in* 63% *Aqueous Alcohol.*—The bromide (8·2 g.) and a solution of silver nitrate (8·7 g.) in the aqueous-alcoholic solvent (100 c.c.) were together added to 1 l. of the solvent at 35°. After 2 hours a further quantity of bromide (8·2 g.) was added, and at the same time a further amount of silver nitrate (8·7 g.), previously dissolved in 100 c.c. of the solvent. After a further 18 hours had been allowed for completion of the reaction, the mixture was worked up for the organic products as described for the similar experiment with silver oxide as reagent. Octylene (1·3 g.) was removed by distillation, octyl alcohol was isolated as its hydrogen phthalate (8 g.), and ethyl octyl ether and octyl nitrate were obtained together and subsequently separated as well as possible by distillation; the ether was finally purified (1·5 g.) by distillation after being heated under reflux with metallic sodium. The hydrogen phthalate had $[\alpha]_D^{18^\circ} + 33{\cdot}47^\circ$ in ethyl alcohol; the other rotations are given in Table I.

Reaction of l-β-n-*Octyl Bromide with Silver Acetate in* 63% *Aqueous Alcohol.*—Owing to the limited solubility of silver acetate in the solvent, the reagents were added in eight equal portions, the additions being timed to keep pace with the reaction. The reaction was started at 35°, but it was found to be very slow, and was completed at the b. p. Each addition to the medium (1 l.) consisted in 1·82 g. of silver acetate, which, after dissolution, was followed by 2·05 g. of β-*n*-octyl bromide. The products, worked up as usual, gave β-*n*-octyl hydrogen phthalate (6 g.) having $[\alpha]_D^{20°}$ + 10·58° in ethyl alcohol, ethyl β-*n*-octyl ether (b. p. 65°/16 mm., yield 1·6 g. after purification by heating with sodium), and small amounts of octylene (0·7 g., b. p. 85°/17 mm.) and α-*n*-octyl acetate (not purified).

Reaction of l-α-*Phenylethyl Chloride with Aqueous Acetone* [with A. D. Scott].—(i) The solvent (1200 c.c.) was a mixture of 6 vols. of purified acetone and 4 vols. of water. A solution of the chloride (6·5 g.) in this solvent was digested with silver oxide (6·5 g.) at 70° for 6 hours. The product was isolated by extraction with ether, shown to be free from halogen and from styrene, and distilled, b. p. 98°/19 mm. (3·0 g.) (Found : C, 77·9; H, 8·3. Calc. for α-phenylethyl alcohol : C, 78·7; H, 8·2%).

(ii) The solvent (300 c.c.) was a mixture of 8 vols. of purified acetone and 2 vols. of water. A solution of the chloride (6·5 g.) in this solvent was digested with silver oxide (6·5 g.) at 70° for 44 hours. The alcohol, b. p. 99°/20 mm. (3·0 g.), was isolated as before.

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