357. *Heterogeneous Catalysis of the Racemisation of* (+)-1-*Phenylethyl Bromide.*

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(+)-1-Phenylethyl bromide in solution in carbon tetrachloride saturated with hydrogen bromide at 73° undergoes racemisation only at a solid surface; the mechanism of racemisation is discussed. Under the conditions employed, the order of effectiveness in catalysis of racemisation is: silver bromide > charcoal > powdered glass ⋙ potassium bromide. The presence of styrene dibromide in the solution accelerates racemisation.

(+)-1-Phenylethyl bromide with bromine in carbon tetrachloride becomes racemised, but some substitution to form hydrogen bromide and (optically inactive) styrene dibromide occurs, and it is uncertain whether bromine-exchange between 1-phenylethyl bromide and elementary bromine takes place; when silver bromide is present racemisation is rapid.

It was observed (Arcus, Campbell, and Kenyon, *J.*, 1949, **1510**) that 1-phenylethyl bromide in solution in carbon tetrachloride racemised rapidly when heated under reflux in the presence of silver bromide and bromine. Hydrogen bromide was evolved during the heating and a small quantity of a compound, shown below to be styrene dibromide, was isolated. Racemisation was much less rapid with bromine alone, and slight with silver bromide alone. The formation of styrene dibromide on heating 1-phenylethyl bromide with bromine was observed by Schramm (*Ber.*, 1885, **18**, 354). In the present investigation, the rates of racemisation of 1-phenylethyl bromide in solution in carbon tetrachloride containing hydrogen bromide or bromine in the presence of various solids, have been measured.

The rate of racemisation of 1-phenylethyl bromide in solution in anhydrous acetone in the presence of dissolved lithium bromide was found to be twice the rate of halogen-exchange as determined by the use of lithium bromide containing radioactive bromine (Hughes, Juliusberger, Scott, Topley, and Weiss, *J.*, 1936, **1173**), whence the racemisation is due to bimolecular halogen-exchange:

$$\mathrm{Br^- + PhMeHC{-}Br \rightsquigarrow Br{-}CHMePh + Br^-}$$

occurring in homogeneous solution. 1-Phenylethyl chloride has been observed to undergo homogeneous unimolecular racemisation in solution in sulphur dioxide (Bergmann, Polanyi, and Szabo, *Z. physikal. Chem.*, 1933, *B*, **20**, 161):

$$\mathrm{CHMePhCl \rightleftharpoons CHMePh^+ + Cl^-}$$

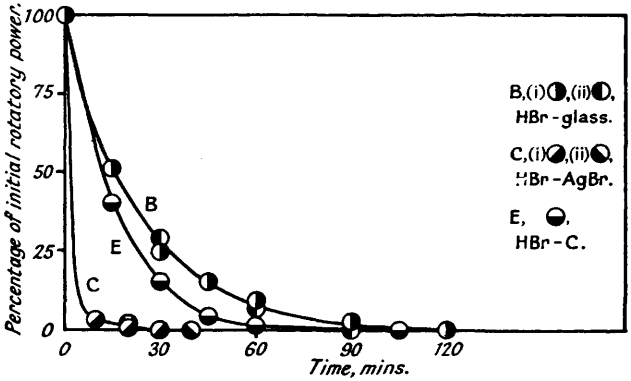
racemisation being due to dissociation to give the planar carbonium ion. Racemisation of 1-phenylethyl chloride occurs by an allied mechanism in the presence of heavy-metal chlorides in solution in organic solvents (Böhme and Bodendorf, *Annalen*, 1935, **516**, 1; Böhme, *Ber.*, 1938, **71**, 2372); a complex is formed which ionises:

$$\mathrm{CHMePhCl + MCl_n \rightleftharpoons CHMePh[MCl_{n+1}] \rightleftharpoons \overset{+}{C}HMePh + [MCl_{n+1}]^-}$$

This mechanism receives support from the facts that an increase in the dielectric constant of the solvent generally increased the rate of racemisation, and that addition of hydrogen chloride or lithium chloride diminished the rate of racemisation by competing with the organic halide for complex-formation with the heavy-metal chloride. Both unimolecular and bimolecular homogeneous racemisations in the presence of constant concentrations of added reagents give rise to a first-order fall in optical rotation, and, as indicated above, other data are necessary to distinguish these two mechanisms.

1-Phenylethyl bromide underwent 10% racemisation in 5 hours when kept at 73° in solution in carbon tetrachloride saturated with hydrogen bromide (Fig. 2, *A*). A saturated solution of hydrogen bromide in carbon tetrachloride had no measurable conductivity, and hence hydrogen bromide does not dissociate in this solvent. It is inferred that the racemisation in *A* did not arise by any mechanism (*e.g.*, bimolecular substitution similar to that with lithium bromide in acetone) which requires appreciable concentrations of ions in homogeneous solution; the rate of racemisation in the presence of hydrogen bromide increased on increasing the surface by the addition of powdered glass (Fig. 1, *B*) and it is concluded that the racemisation in *A* occurred at the glass surface of the flask. A 38-fold increase in surface resulted in a 130-fold increase in the initial velocity of racemisation (Table I). The fractured glass surfaces thus appear more efficient than the fused surface of the flask; a similar effect for the exchange of bromine between hydrogen bromide and ethyl bromide at 180—260° was observed by Peri and Daniels (*J. Amer. Chem. Soc.*, 1950, **72**, 424).

FIG. 1.



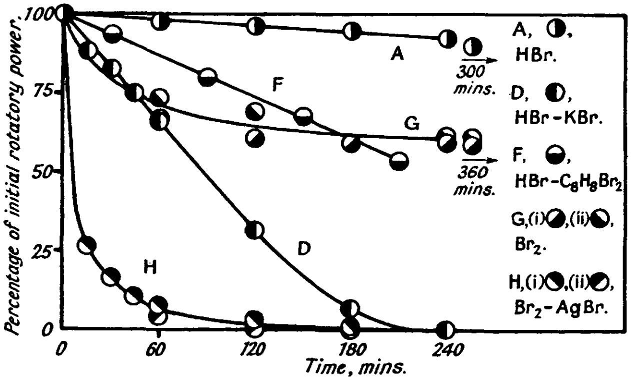
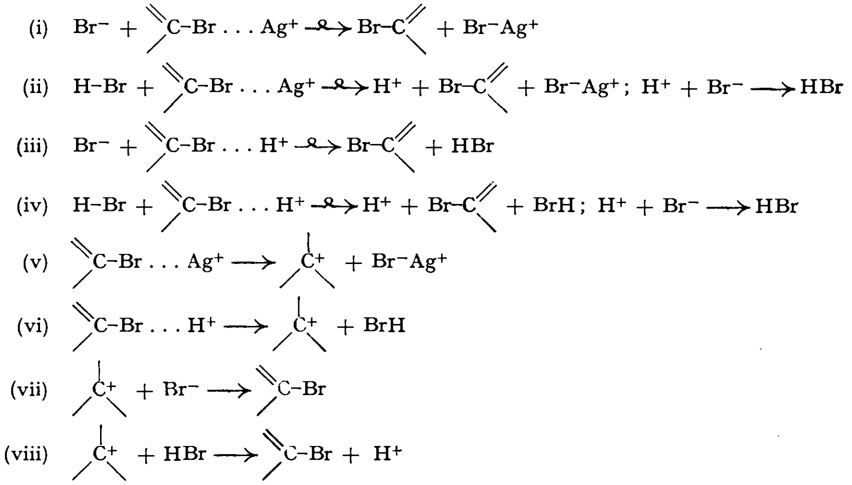


FIG. 2.

Racemisation was most rapid with hydrogen bromide in the presence of silver bromide; the initial rate was 320 times that for *A*, and the solution was optically inactive after 30 minutes (Fig. 1, *C*). Senter (*J.*, 1910, **97**, 346) observed that the silver bromide formed has a marked catalytic effect on the hydrolysis of α-bromopropionic and α-bromo-*n*-butyric acids in aqueous silver nitrate; a similar effect was noticed by Baker (*J.*, 1934, 987) for the alcoholysis of benzyl bromide by ethyl-alcoholic silver nitrate. Kappanna (*Proc. Indian Acad. Sci.*, 1935, **2**, *A*, 512) concluded that in the reaction of sodium α-bromopropionate with aqueous silver nitrate, reaction occurs almost entirely between α-bromopropionate ions and silver ions adsorbed on the surface of the silver bromide. Cowdrey, Hughes, Ingold, and Masterman (*J.*, 1937, 1236, 1243) concluded from the stereochemical and kinetic evidence that the following reactions, *viz.*, (i) hydrolysis and alcoholysis of 2-*n*-octyl bromide in aqueous alcohol containing suspended silver oxide or dissolved silver nitrate or acetate, (ii) hydrolysis of 1-phenylethyl chloride in aqueous acetone with suspended silver oxide, (iii) methoxylation of methyl α-bromopropionate with methyl-alcoholic silver nitrate, and (iv) the hydrolysis of the acid and its sodium salt with a suspension of silver oxide in water or aqueous acetone, proceed wholly or partly by reaction between the halogen-containing organic molecule (or the anion in the cases of the acid and its salt) adsorbed on to the silver halide surface, and that of the silver oxide when present, and the hydroxylic solvent or a hydroxyl or alkoxyl ion. The carbon–halogen bond of the adsorbed halide is stretched and weakened, an adsorbed silver ion detaches the halogen, and the resulting carbonium cation reacts with an adsorbed solvent molecule or appropriate reagent ion. (+)-1-Phenylethyl chloride in benzene solution yielded with silver nitrite a largely racemised 1-phenylethyl nitrite (Eastman and Ross, *J. Amer. Chem. Soc.*, 1946, **68**, 2398) in accord with reaction *via* dissociation of the organic halide on the silver nitrite–silver chloride surface.

It is considered that the silver bromide in the present experiments functioned similarly. The alkyl–bromine bond of an adsorbed 1-phenylethyl bromide molecule is weakened by the interaction of silver ions with the bromine. The adsorbed hydrogen bromide functions as reagent, either by supplying bromide ions (i) or directly (ii). Further, the functions of the silver ions may be in part taken over by adsorbed protons, as in (iii) and (iv) :



The reactions (i)—(iv) lead to racemisation by bimolecular substitution. Some part of the racemisation may proceed by ionisation of the 1-phenylethyl bromide assisted by weakening of the carbon–bromine bond through silver ions (v) or protons (vi), the planar carbonium cation combining to yield the (±)-bromide (vii) and (viii).

Unlike the other catalytic solids investigated, which in the absence of hydrogen bromide effected no racemisation, some specimens of silver bromide had appreciable racemising effect : (*a*) a specimen of silver bromide which had been kept for 3 months caused no racemisation in 2 hours at 73° ; (*b*) a recently-prepared specimen caused 39% racemisation in 2 hours ; (*c*) another recently-prepared specimen caused 22% racemisation in the first hour and thereafter the rotation of the solution remained constant. These results show a similarity to those of Langer (*J. Chem. Physics*, 1943, **11**, 11) who, using sodium bromide containing radioactive bromine, found that there is exchange of bromide ions between silver bromide and aqueous sodium bromide at a rate which decreases with the age of the silver bromide, and finally ceases. Racemisation in the presence of silver bromide alone must proceed by (i) or by (v) followed by (vii), the bromide ion here being that normally present in the silver bromide lattice only.

The much greater rate of racemisation with hydrogen bromide–silver bromide than with silver bromide alone points to attack by adsorbed hydrogen bromide (ii) or bromide ions derived therefrom (i), *i.e.*, to racemisation through inversion mechanisms. Nevertheless, the possibility that some part of the effect of the hydrogen bromide lies in providing adsorbed protons which assist the ionisation of 1-phenylethyl bromide (vi), as well as promoting inversion by mechanisms (iii) and (iv), is not excluded.

The system hydrogen bromide–potassium bromide is much less effective in racemisation than hydrogen bromide–silver bromide, probably owing to the lesser capacity for adsorption of the potassium bromide surface (Fig. 2, *D*).

In the presence of hydrogen bromide–charcoal, the initial rate of racemisation of 1-phenylethyl bromide was slightly less than half that in the presence of hydrogen bromide–silver bromide (Fig. 1, *E*).

Since glass, potassium bromide, and charcoal do not themselves effect racemisation, it is concluded that racemisation when hydrogen bromide is present is due to the operation on the solid surfaces of inversion mechanisms (iii) and (iv) together, possibly, with the ionisation mechanism (vi) followed by (vii) and (viii).

When hydrogen bromide was passed through a solution of 1-phenylethyl bromide in carbon tetrachloride containing styrene dibromide (Fig. 2, *F*), the rate of racemisation was 7 times that for *A*. The mechanism whereby the rate is increased is not known.

The racemisation of any compound by any mechanism in which enantiomeric molecules of the compound suffer reaction at the same rate would be expected to occasion a first-order fall in rotation, provided that conditions are kept constant. In the present work (which was designed to give comparative rates only), racemisation in *B* and *E* was of first-order [for *B* (i), *B* (ii), and *E*, *k* is 0·045, 0·043, and 0·068 min.$^{-1}$, respectively); *A* and *C* were respectively too slow and too fast to permit an estimation of the order; and racemisation in *D* and *F* was zero order (for *D* and *F*, *k* is 0·0026 and 0·00095 mole l.$^{-1}$ min.$^{-1}$, respectively)]. It is possible that during the last two experiments there occurred the formation of an active surface or complex at a rate comparable with the rate of racemisation, yielding an apparently zero-order racemisation.

The course of racemisation in the presence of bromine and bromine–silver bromide is now considered in the light of the above results. Solutions of 1-phenylethyl bromide in carbon tetrachloride containing bromine (1·0 equiv.) after 4 hours at 73° lost 40% of the initial rotatory power (Fig. 2, *G*) and very little bromine remained. Hydrogen bromide was evolved and, in addition to (±)-1-phenylethyl bromide, styrene dibromide was isolated at the end of the experiment. Similar solutions in the presence of silver bromide lost 94% of the initial rotatory power in one hour and became optically inactive after 3 hours (Fig. 2, *H*); hydrogen bromide and styrene dibromide were again formed.

TABLE I.

Expt.	Racemisation of 1-phenylethyl bromide in the presence of :	Racemisation in first 10 mins., %.	Relative extent of racemisation in first 10 mins.
A	HBr	0·3	1
B	HBr + powdered glass	38	130
C	HBr + AgBr	97	320
D	HBr + KBr	5·7	19
E	HBr + charcoal	43	140
F	HBr + styrene dibromide	2·2	7
G	Bromine	10	33
H	Bromine + AgBr	66	220

Thus in the experiments involving bromine, the system hydrogen bromide–styrene dibromide was present, but the racemisation effected by this system, the components of which were present in much smaller concentrations than for *F*, could not have been more than a fraction of the racemisation observed in *G* and *H*. The styrene dibromide isolated from these experiments was optically inactive so that, in proportion as this compound was formed, optically active material was diminished. It has not been found possible to deduce from the data whether or not these two sources of loss of rotatory power account for the whole of the loss occurring in the absence of silver bromide. Assessment is made difficult by the racemisation of 1-phenylethyl bromide which occurs when this compound is separated from styrene dibromide by distillation; 39% racemisation occurred during the distillation of a prepared mixture at 88°/19 mm. Gerrard (*J.*, 1945, 852) found certain specimens of 1-phenylethyl bromide to undergo extensive racemisation on redistillation. It is thus uncertain whether 1-phenylethyl bromide undergoes exchange of bromine ions or atoms with elementary bromine, except that the rate of exchange under the conditions employed cannot be rapid.

In the bromine–silver bromide experiments there was present, in addition to the two sources of loss of rotatory power described above, the system hydrogen bromide–silver bromide which has been shown to be very effective in racemisation; the possible catalytic effect of silver bromide on bromine-exchange between 1-phenylethyl bromide and elementary bromine could not be detected in the presence of these other sources of loss of optical activity. An equation of kinetic order 1·8 empirically satisfies the fall in rotatory power [*k* for *H* (i) is 0·28 mole$^{-0·8}$ l.$^{0·8}$ min.$^{-1}$] but, since the concentrations of bromine and hydrogen bromide alter with time, the value 1·8 has no simple significance.

EXPERIMENTAL.

(±)-1-Phenylethyl alcohol was resolved by Downer and Kenyon's method (*J.*, 1939, 1156). The optically active bromide was prepared by an unpublished method due to Dr. W. Gerrard: phosphorus oxybromide (17·2 g., 0·66 mol., prepared according to Gerrard, Nechvatal, and Wyvill, *Chem. and Ind.*, 1947, **29**, 437) in carbon disulphide (20 ml.) was added dropwise to a solution of (—)-1-phenylethyl alcohol (α_D^{17} —44·35°, *l* 1·0; 11 g.) and pyridine (14·4 g., 2 mols.) in carbon disulphide (40 ml.) at —10°. After 2 hours the reaction mixture was filtered, and the filtrate washed with dilute sulphuric acid, aqueous sodium carbonate, and water, and dried (K_2CO_3). After removal of the carbon disulphide under reduced pressure the residue was distilled and gave (+)-1-phenylethyl bromide (7·0 g., 42%), b. p. 86—87°/11 mm., n_D^{21} 1·5605, α_D^{22} +130·96° (*l* 1·0).

(±)-1-Phenylethyl bromide was prepared from the (±)-alcohol and hydrobromic acid (*d* 1·49) by the method of Norriss, Watt, and Thomas (*J. Amer. Chem. Soc.*, 1916, **38**, 1078); it was twice redistilled and had b. p. 84—84·5°/10 mm., and the variation of n_D with temperature was determined:

t	17°	18°	19°	20°	21°	22°	23°	24°	25°
n_D	1·5634	1·5629	1·5625	1·5619	1·5614	1·5609	1·5604	1·5599	1·5595

Carbon tetrachloride was kept over calcium chloride, distilled from fresh reagent, and the process repeated with phosphoric oxide; it was kept over the latter and distilled immediately before use.

Silver bromide was prepared by adding a slight excess of aqueous potassium bromide (10%) to aqueous silver nitrate (10%); it was washed by thrice boiling with water and filtering, dried at 100°, powdered, and again dried at 100°. Potassium bromide was dried by heating at 150°/20 mm. for 2 hours. Absorbent charcoal (B.D.H.; coarse grains) was dried by heating at 150°/1 mm. for 2 hours. Silica (B.D.H.) was powdered and dried by heating at 150°/2 mm. for 2 hours.

Pyrex glass tubing was washed with concentrated nitric acid and water, dried at 150°, powdered, and sieved mechanically; the portion which passed through a 1/100-inch mesh but not a 1/150-inch mesh was collected, boiled with aqua regia and then 4 times with water, and dried at 130° for 4 hours. The surface area of the glass powder was determined by Kendrick's method (*J. Amer. Chem. Soc.*, 1940, **62**, 2838) and that of Barrett, Birnie, and Cohen (*ibid.*, p. 2841) which depends on the fact that the average of the areas of projection of a unit plane in all random positions is ½ unit, whence the average area of projection of a solid is ¼ of its surface area, since half the planes constituting the surface mask the other half. Small quantities of glass powder were placed on a microscope slide (*a*) by sprinkling, (*b*) by lowering the slide on to a small heap, whereupon, when the slide was withdrawn, a layer of powder adhered. Three slides were prepared by each method and photographed at linear magnification 75, and the areas of the images of the particles on the photographic plate measured with a planimeter. The number of particles per g. (N) was determined by weighing small quantities of powder on a microbalance and counting them on a ruled slide under a low-power microscope: found, (i) $1·039 \times 10^6$, (ii) $1·036 \times 10^6$. Then, where A = average area of a particle image, the surface area per g. of powder $= 4AN/75^2 =$ 710 cm.^{2}/g.

Bromine was kept with phosphoric oxide for 3 days and then distilled from fresh reagent.

Hydrogen bromide was prepared by passing hydrogen saturated with bromine through a heated tube and then through a column packed with copper turnings (to remove any unreacted bromine) (*Org. Synth.*, Coll. Vol. II, p. 338). At the beginning and end of each experiment the rate of passage of hydrogen bromide was determined by passing the gas into water (50 ml.) for 5·0 minutes and titrating the solution with 0·1N-sodium hydroxide. The absence of bromine in the hydrogen bromide was confirmed by testing a similarly prepared solution with potassium iodide and starch.

TABLE II.

Expt.	1-Phenylethyl bromide, g.	CCl_4 to, ml.	Additional reagents.
A	2·00	20	HBr, 2·3 g./hr.
B (i)	1·00	10	„ 2·2 „ ; glass, 1·00 g.
B (ii)	1·00	10	„ 2·1 „ ; glass, 1·00 g.
C (i)	1·00	10	„ 2·3 „ ; AgBr,* 2·00 g.
C (ii)	2·00	20	„ 2·2 „ ; AgBr, 4·00 g.
D	1·50	15	„ 2·1 „ ; KBr, 1·50 g.
E	1·70	17	„ 2·2 „ ; charcoal, 0·57 g.
F	1·00	10	„ 2·5 „ ; styrene dibromide, 0·50 g.
G (i)	3·85	40	Bromine,† 1 equiv.
G (ii)	2·00	20	„ 1 „
H (i)	2·00	20	„ 1 „ ; AgBr, 4·00 g.
H (ii)	3·00	30	„ 1 „ ; AgBr, 6·00 g.

* Freshly prepared. † Added as a standard solution in CCl_4.

Procedure.—The solution of 1-phenylethyl bromide in carbon tetrachloride and the additional reagents were placed in a 50-ml. Pyrex flask fitted (ground-glass joint) with a condenser through which, in those experiments in which hydrogen bromide was used, passed an inlet tube reaching nearly to the bottom of the flask, and to which was fitted an exit tube bearing a calcium chloride tube. The flask was immersed in a thermostat kept at 73·4° ± 0·1° and, in experiments in which a solid was present, the flask was shaken by attaching it to a motor-driven crank. Portions (1—2 ml.) of solution were withdrawn initially and at intervals, and the rotatory power determined; in the experiments with bromine, the withdrawn portion was washed with aqueous sodium sulphite (15%) and dried (Na_2SO_4) for 10 minutes before determination of the rotatory power. The reagents used are given in Table II.

In the experiments *A* and *F*, in which racemisation occurred slowly, correction was made for the concentration of the solution by evaporation of the solvent in the course of the experiment. The flask and the contents were weighed initially, before withdrawing each specimen for the determination of rotation, and after returning the specimen to the flask. Then, where a_0, w_0 are the initial rotation and weight of the solution and a_t, w_t are the rotation after time t and the weight immediately before withdrawing the specimen for determination of this rotation, we have $a_{\text{unracemised.}\,t} = a_0w_0/w_t$, where $a_{\text{unracemised,}\,t}$ is the rotation the solution would have exhibited had evaporation only, without racemisation, occurred. The percentage of initial rotatory power after time $t = 100a_tw_t/a_0w_0$. Further, where w'_t is the weight of solution after replacing the specimen used for rotation, and $a_{t'}$, $w_{t'}$ are the rotation after t' and the weight immediately before the determination of rotation, we have $a_{\text{unracemised,}\,t'} = a_0w_0w'_{t'}/w_tw_{t'}$, and the percentage of initial rotatory power after time $t' = 100a_{t'}\,w_tw_{t'}/a_0w_0w'_t$. In this way corrections were applied for both the concentration of the solution due to evaporation and the small manipulative losses ($w_t - w'_t$, etc.).

In a number of experiments the solution remaining at the end was washed with aqueous sodium carbonate, if hydrogen bromide was present, or with aqueous sodium sulphite, if bromine was present, and with water, and dried (Na_2SO_4). Carbon tetrachloride was removed under reduced pressure, and the residue distilled, yielding 1-phenylethyl bromide having the following characteristics :

Expt.	*A*.	*B* (i).	*C* (ii).	*D*.	*E*.	*G* (i).	*G* (ii).	*H* (ii).
n_D	1·5619	1·5623	1·5628	1·5622	1·5611	1·5654	1·5589	1·5648
t	20°	19°	18°	20°	22°	18°	25°	18°
% of original rotatory power	84	Nil	Nil	Nil	Nil	51	25	Nil

From *G* (i) was obtained a fraction, b. p. 125—132°/10 mm., which solidified; after repeated recrystallisation from ethyl alcohol it yielded styrene dibromide, m. p. 72—73°, optically inactive in ethyl alcohol. The residue from *G* (ii), after distillation of the 1-phenylethyl bromide, was optically inactive in solution in ethyl alcohol and similarly yielded styrene dibromide, m. p. 72·5—73·5° alone and mixed with a specimen of m. p. 73—73·5° prepared according to Glaser (*Annalen*, 1870, **154**, 154). The residue from *H* (ii) also yielded styrene dibromide, m. p. 72°. A larger quantity of the bromination product was prepared, in order to confirm its identity, as follows : bromine (4·9 g., 4·2 equivs.) was added dropwise to (±)-1-phenylethyl bromide (2·7 g.) containing a little iodine : hydrogen bromide was evolved. The mixture was heated for 3 hours on a steam-bath and kept overnight. The solid product was washed with 3N-sodium hydroxide and with water and dried; it (3 g.) was distilled, and the fraction, b. p. 148—151°/22 mm., was thrice recrystallised from light petroleum, giving needles, m. p. 70—72°, undepressed by the materials from *G* (i) and *H* (ii). Oxidation of this bromo-compound (5 g.) with potassium permanganate (10 g.) and sodium carbonate (2·5 g.) in water (240 ml.) gave benzoic acid (1 g.) which, twice recrystallised from water, had m. p. 120—121° alone and mixed with an authentic specimen.

Control Experiments.—A solution of (−)-1-phenylethyl bromide (1·00 g.; a_D^{18} −56·95°, *l* 0·5) in carbon tetrachloride (to 10 ml.) had a_D^{19} −4·05° (*l* 0·5); silver bromide (2·00 g., freshly prepared) was added, and the whole heated with shaking at 73·4°. After 1 hour the solution had a_D^{19} −3·13°, and after 3 further hours a_D^{19} −3·11° (*l* 0·5), 76·8% of the initial value, and on evaporation gave (−)-1-phenylethyl bromide having a_D^{18} −44·18° (*l* 0·5), 77·6% of the original value. A similar experiment employing another specimen of freshly-prepared silver bromide, in which heating was continued for 2 hours, gave 1-phenylethyl bromide having 60·6% of the initial rotatory power. From an experiment similar to the last but employing 3-months aged silver bromide (0·65 g.), (−)-1-phenylethyl bromide (0·8 g.), and carbon tetrachloride (to 8 ml.), the (−)-1-phenylethyl bromide was recovered having 99·9% of the original rotatory power.

Solutions of (+)-1-phenylethyl bromide (2·00 g.) in carbon tetrachloride (to 20 ml.) suffered no racemisation on heating at 73·4° for 2 hours alone and with (*a*) powdered glass (2·00 g.), (*b*) potassium bromide (2·00 g.), or (*c*) styrene dibromide (1·00 g.); on addition of charcoal (0·67 g.) to such a solution the rotatory power fell to 77·0% of the initial rotatory power, but this was due to adsorption since the (+)-1-phenylethyl bromide recovered on evaporation was unchanged in rotatory power. On addition of silica to a similar solution of (−)-1-phenylethyl bromide, the silica swelled and became dark red. The rotation of the solution fell rapidly and became zero after 2 hours. Neither the solution, on evaporation, nor the silica, on heating to 200°/24 mm., yielded any 1-phenylethyl bromide.

Carbon tetrachloride was placed in a 3-necked flask fitted with an inlet tube passing below the surface of the liquid, an exit tube, and a conductivity cell of the dipping type. The resistance of the carbon tetrachloride, measured with a Mullard bridge, was approximately 1·1 × 10^7 ohms at 25°; this value remained unchanged when (*a*) the flask was kept at 73·4°, (*b*) the carbon tetrachloride was saturated at 73·4° with hydrogen bromide by passing the latter at 2·8 g./hour for 30 minutes, (*c*) hydrogen bromide was passed continuously at 73·4°, or (*d*) the carbon tetrachloride was saturated with hydrogen bromide at 25°.

Hydrogen bromide was passed at 4·8 g./hour for 30 minutes into carbon tetrachloride (50 ml.) at 73·4°; 20 ml. of the saturated solution were added to water (50 ml.) and titrated with standard sodium hydroxide. The determination was twice repeated with fresh solvent, and similar determinations were made at 25°. Solubility of hydrogen bromide in carbon tetrachloride : at 25°, 0·87, 0·85, 0·90 g./100 ml. of solution; at 73·4°, 0·106, 0·109, 0·108 g./100 ml. of solution.

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