LXVI.—*Studies on the Walden Inversion. Part XI. Evidence for the Bivalency of Carbon from Some Reactions of α-Chloroethylbenzene. αα′-Diphenyldiethyl Ether.*

By Allan Miles Ward.

The experiments here described were undertaken as a continuation of the method of Part X of this series (J., 1926, 1184) in order to obtain fuller information on the mechanism of the replacement of the halogen in α-chloroethylbenzene; the course of replacement was accordingly followed both by titration and by change of rotation.

The interconversion of the phenylmethylcarbinols was first demonstrated by McKenzie and Clough (J., 1913, **103**, 687); their results may be summarised by the following scheme :

$$\begin{tikzcd}
d\text{-CHPhMe·OH} \arrow[r, "SOCl_2"] \arrow[d, shift left, "PCl_2"] & d\text{-CHPhMeCl} \arrow[d, shift left, "\substack{Ag_2O + \text{water} \\ NaOH + \text{water}}"] \\
l\text{-CHPhMeCl} \arrow[u, shift left, "\substack{Ag_2O + \text{water} \\ NaOH + \text{water}}"] & l\text{-CHPhMe·OH} \arrow[l, "SOCl_2"'] \arrow[u, shift left, "PCl_3"]
\end{tikzcd}$$

Phosphorus trichloride thus behaves like hydrogen chloride towards phenylmethylcarbinol (compare Pickard and Kenyon, J., 1911, **99**, 71), whilst thionyl chloride behaves differently. In each of the above reactions, with the exception of that of thionyl chloride, racemisation is very considerable.

The displacement of the halogen in α-chloroethylbenzene is here studied in aqueous (20% by volume) ethyl-alcoholic solution at 28·7° and at 50·0°, both alone and also in the presence of sodium hydroxide. The products of reaction in each case are α-phenyldiethyl ether and phenylmethylcarbinol, so that the course of the reaction may be represented thus :

$$\text{(I.)}\quad \mathrm{CHPhMeCl} + \mathrm{EtOH} \longrightarrow \mathrm{CHPhMe{\cdot}OEt} + \mathrm{HCl}.$$

$$\text{(II.)}\quad \mathrm{CHPhMeCl} + \mathrm{H_2O} \longrightarrow \mathrm{CHPhMe{\cdot}OH} + \mathrm{HCl}.$$

The most interesting aspect of these reactions is, however, that the displacement of the halogen proceeds at the same speed whether sodium hydroxide is present in or absent from the solution, and in all cases the velocity coefficients for the reactions, calculated on the basis of a unimolecular reaction, are in good agreement, as shown by the following collected data.

r-α-Chloroethylbenzene (approx. *N*/10).
Solvent : Aqueous (20% by volume) ethyl alcohol.

Exper.	Temp.	Conditions.	*k*.
3	28·7°	Alone	0·0560
4	28·7	NaOH (approx. *N*/10)	0·0561
5	28·7	NaOH (approx. *N*/5)	0·0560
6	50·0	Alone	0·589
7	50·0	NaOH (approx. *N*/10)	0·590
8	50·0	NaOH (approx. *N*/5)	0·590

The temperature coefficient for 10° is thus 3·02.

These results are analogous to those obtained by Senter (J., 1915, **107**, 908) for the displacement of the halogen in phenylchloroacetic acid in aqueous solution, and for the sodium salt in aqueous and also in sodium hydroxide solutions, where it was found that the displacement reaction in each case is one and the same, namely, the reaction between water and the phenylchloroacetate ion. Results of a similar nature were obtained by Senter and Tucker (J., 1916, **109**, 690) for phenylbromoacetic acid, and they considered that in addition to the reaction

$$\mathrm{CHPhBr{\cdot}CO_2'} + \mathrm{H_2O}\ \text{(excess)} \longrightarrow \mathrm{CHPh(OH){\cdot}CO_2'} + \mathrm{HBr},$$

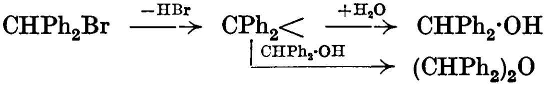
water reacted with the undissociated acid also, but about 120 times more slowly. In the present case equations I and II would represent the reactions from the kinetic point of view, but, just as for the reactions between water and the phenylchloroacetate and phenylbromoacetate ions, they fail to provide an explanation for the non-intervention of sodium hydroxide in these reactions.

The velocities of replacement of the halogen in *d*-α-chloroethylbenzene in aqueous ethyl-alcoholic solution in the presence and the absence of sodium hydroxide were also measured by determining the changes in the rotations of the solutions with time at 28·6°. The total change in the rotations of the solutions was small, so that the experimental error is of sufficient relative magnitude to introduce considerable variation in the velocity coefficients when calculated on the basis of a unimolecular reaction according to the formula $k = 2{\cdot}3/t \, . \log_{10}\{(\theta_0 - \theta_\infty)/(\theta_t - \theta_\infty)\}$. The mean of the coefficients in aqueous ethyl alcohol alone is 0·0608, whilst in the presence of sodium hydroxide the mean obtained is 0·0558. These experiments at least confirm the results derived from the titration experiments, namely, that sodium hydroxide is playing no part in the displacement of the halogen.

The displacement of the halogen in β-chloroethylbenzene is in quite striking contrast with the above. Under similar conditions to those employed for α-chloroethylbenzene, the displacement in aqueous alcohol was negligible, whilst in the presence of sodium hydroxide, velocity coefficients agreeing with a bimolecular reaction were obtained; also the displacement of the halogen takes place very much more slowly from β-chloroethylbenzene than from α-chloroethylbenzene. Sodium hydroxide or its ions are therefore playing some essential part in the elimination of the halogen from β-chloroethylbenzene. In other reactions recorded, α- and β-chloroethylbenzenes behave very differently. Thus alcoholic potassium cyanide, followed by hydrolysis, yields β-phenylpropionic acid from β-chloroethylbenzene (Fittig and Kiesow, *Annalen*, 1870, **156**, 245; Schramm, *Monatsh.*, 1887, **8**, 101; Fischer and Schmitz, *Ber.*, 1906, **39**, 2208), whilst from α-chloroethylbenzene under similar conditions α-phenyldiethyl ether is obtained. This ether was first prepared by Thorpe (*Proc. Roy. Soc.*, 1869, **18**, 123) by the interaction of α-bromoethylbenzene and a saturated solution of ammonia in ethyl alcohol, no α-phenylethylamine being produced; it formed also the main product of the reaction between potassium acetate and α-bromoethylbenzene in ethyl-alcoholic solution. The mechanism of the displacement of the halogen from α-chloroethylbenzene would thus appear to be quite different from that in the case of β-chloroethylbenzene.

It was found also in the present experiments that the replacement of the halogen in α-chloroethylbenzene at 50° gives phenylmethylcarbinol only; at 100°, however, the products consist of styrene, phenylmethylcarbinol and αα′-diphenyldiethyl ether; if the boiling is continued for but 5 minutes, an appreciable amount of the ether is formed. αα′-Diphenyldiethyl ether has previously been prepared, together with phenylmethylcarbinol, by Oddo (*Gazzetta*, 1907, **37**, ii, 360) by the interaction of magnesium methyl iodide and benzaldehyde in the presence of pyridine. Marshall (J., 1914, **105**, 530), in the course of his investigation on the interaction of magnesium methyl iodide and benzaldehyde, obtained a substance which he considered to be αα′-diphenyldiethyl ether, since it did not react with sodium and gave α-chloroethylbenzene on reaction with phosphorus pentachloride. More recently, Wuyts (*Bull. Soc. chim. Belg.*, 1921, **30**, 30), in studying the optical activation of *r*-phenylmethylcarbinol by means of camphorsulphonic acid, found the predominant reaction to be the formation of *l*-αα′-diphenyldiethyl ether with $\alpha_D^{20°} - 1{\cdot}11°$. Descamps (*ibid.*, 1924, **33**, 139) has extended this investigation on the "catalytic dehydration" of phenylmethylcarbinol to αα′-diphenyldiethyl ether. In view of the present results that this ether may be produced readily in the presence of water from α-chloroethylbenzene, and also from phenylmethylcarbinol by boiling with dilute hydrochloric acid, it does not appear justifiable to consider this reaction to be due to a direct dehydration between two molecules of phenylmethylcarbinol.

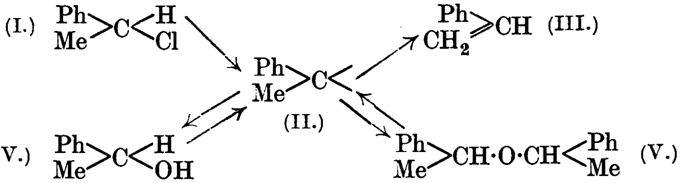
The only similar example of ether formation known to the author is the case of benzhydrol and diphenylbromomethane. Friedel and Balsohn (*Bull. Soc. chim.*, 1880, **33**, 339) found that diphenylbromomethane, on boiling with water, yielded mainly *s*-tetraphenyldimethyl ether together with a small amount of benzhydrol. This ether had previously been prepared by Linnemann (*Annalen*, 1865, **133**, 14) by prolonged heating of benzhydrol at its boiling point (compare also Thörner and Zincke, *Ber.*, 1878, **11**, 1398; Nef, *Annalen*, 1897, **298**, 234). Nef (*loc. cit.*) found that the displacement of the halogen in diphenylbromomethane by means of water at room temperature gave benzhydrol only, but that *s*-tetraphenyldimethyl ether alone resulted when boiling water was used, and to explain this he assumed that the reactions proceed through a stage involving bivalent carbon by the following mechanism :



$$\begin{tikzcd}[column sep=small] CHPh_2Br \arrow[r, "-HBr"] & CPh_2< \arrow[r, "+H_2O"] \arrow[dr, "CHPh_2{\cdot}OH"'] & CHPh_2{\cdot}OH \\ & & (CHPh_2)_2O \end{tikzcd}$$

the addition reactions being exactly analogous to those shown by the *iso*nitriles and the halogenated acetylenes (compare Nef, *Annalen*, 1892, **270**, 267; 1894, **280**, 291; 1895, **287**, 265; 1897, **298**, 202; Lawrie, *Amer. Chem. J.*, 1906, **36**, 489).

In a similar way, the reaction products from α-chloroethylbenzene may be explained by the following scheme :



the first stage of the reaction being the elimination of hydrogen chloride from (I) to yield the highly reactive intermediate phase (II), which then (*a*) undergoes irreversible isomeric change to give styrene (III), (*b*) adds water to give phenylmethylcarbinol (IV), (*c*) adds phenylmethylcarbinol to give αα′-diphenyldiethyl ether (V). The scheme also agrees with the observation that phenylmethylcarbinol, on boiling with *N*/2-hydrochloric acid for 8 hours, yields a mixture of (III), (IV), and (V), and accounts for the similar behaviour of αα′-diphenyldiethyl ether on boiling with *N*/2-hydrochloric acid.

The formation of an intermediate phase involving bivalent carbon is also in accord with the apparent non-intervention of sodium hydroxide as shown in the kinetic results for α-chloroethylbenzene, for if the reaction proceeds by the following stages,

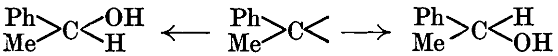
$$\text{(1)}\ \mathrm{CHPhMeCl} \longrightarrow \mathrm{CPhMe}< + \mathrm{HCl}\ \text{(slow)}$$

$$\text{(2)}\ \mathrm{CPhMe}< + \underset{\text{(excess)}}{\mathrm{H_2O}} \longrightarrow \mathrm{CHPhMe{\cdot}OH}\ \text{(rapid)}$$

$$\text{(3)}\ \mathrm{CPhMe}< + \underset{\text{(excess)}}{\mathrm{EtOH}} \longrightarrow \mathrm{CHPhMe{\cdot}OEt}\ \text{(rapid)}$$

then velocity coefficients agreeing with a unimolecular reaction in accordance with stage (1) should be obtained. Further, sodium hydroxide would be expected to play no part in this transformation, for it would be without effect on stage (1), and even should it unite with CPhMe<, such a combination could be only transitory under the conditions of experiment and would lead to the same products as in (2) and (3), and this reaction would be expected to proceed with a velocity comparable with those of (2) and (3). Also by assuming the intermediate phase CPhMe<, the formation of α-phenyldiethyl ether by the reaction between α-chloroethylbenzene and alcoholic ammonia, potassium cyanide or potassium acetate is more readily understood.

The foregoing evidence is thus in accordance with the reaction proceeding through the phase CPhMe<, and it is conceivable that the addition of water to this phase may take place in two ways thus,



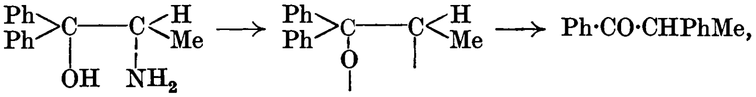
$$\begin{smallmatrix}\mathrm{Ph}\\\mathrm{Me}\end{smallmatrix}\!>\!\mathrm{C}\!<\!\begin{smallmatrix}\mathrm{OH}\\\mathrm{H}\end{smallmatrix} \longleftarrow \begin{smallmatrix}\mathrm{Ph}\\\mathrm{Me}\end{smallmatrix}\!>\!\mathrm{C}\!< \longrightarrow \begin{smallmatrix}\mathrm{Ph}\\\mathrm{Me}\end{smallmatrix}\!>\!\mathrm{C}\!<\!\begin{smallmatrix}\mathrm{H}\\\mathrm{OH}\end{smallmatrix}$$

to give rise to a mixture of *d*- and *l*-phenylmethylcarbinols. In general, this may be stated that CR_1R_2 will react with a substance XY to give a mixture of $CR_1R_2(X)Y$ and $CR_1R_2(Y)X$, the relative amounts of each isomeride produced depending on the experimental conditions. Nef (*Annalen*, 1904, **335**, 241) has employed this methylene theory to account for the racemisation of hydroxy- and halogen acids and esters of the type $CHRX{\cdot}CO_2H$, and also for the autoracemisation of the halogenosuccinic esters (see Walden, " Optische Umkehrerscheinungen," 1919, V Kapitel), by assuming that the racemisation is due to an equilibrium as follows :

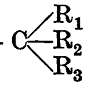
$$\mathrm{CHR(X){\cdot}CO_2H} \rightleftharpoons \mathrm{CR(CO_2H)}< + \mathrm{HX} \rightleftharpoons \mathrm{C(H)RX{\cdot}CO_2H}.$$

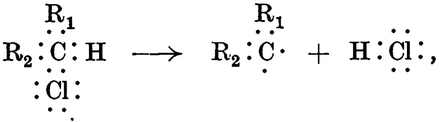
In a further discussion of these views (*J. Amer. Chem. Soc.*, 1908, **30**, 645), Nef concludes that the four valency units of carbon cannot be regarded as identical, but does not enter into a discussion of the problem of the Walden inversion in connexion with his theory, as he regards the reactions dealt with under this subject as being abnormal in character. Walden (*op. cit.*, p. 182) considers that Nef's views on autoracemisation cannot be correct, since the halogenosuccinic esters, both alone and in solution, are non-electrolytes, and that, were any free halogen acid present, then the conductivity would be appreciable; also no reaction for bromine ion is obtained with silver nitrate solution. The autoracemisation observed by Walden was, however, extremely slow, extending over many years, so that the amount of methylene phase necessary in accordance with Nef's theory must be assumed extremely small.

It might be argued that if the reaction proceeded through an unsaturated phase $CR_1R_2<$, then the resulting compound would of necessity be racemic in nature. There is, however, so far as the author is aware, no experimental evidence to support the view that complete racemisation would ensue. The results of McKenzie, Roger, and Wills (J., 1926, 779) on the reaction between nitrous acid and *l*-β-amino-αα-diphenyl-*n*-propyl alcohol, whereby *d*-methyldeoxybenzoin with $[\alpha]_D^{17^\circ} + 158^\circ$ is produced although the reaction is assumed to proceed through a phase in which but three groups are attached to the centre of asymmetry according to the scheme



$$\begin{matrix}\mathrm{Ph}\\ \mathrm{Ph}\end{matrix}\!>\!\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\!-\!\!-\!\underset{\mathrm{NH_2}}{\underset{|}{\mathrm{C}}}\!<\!\begin{matrix}\mathrm{H}\\ \mathrm{Me}\end{matrix} \longrightarrow \begin{matrix}\mathrm{Ph}\\ \mathrm{Ph}\end{matrix}\!>\!\underset{|}{\underset{\mathrm{O}}{\underset{|}{\mathrm{C}}}}\!-\!\!-\!\underset{|}{\mathrm{C}}\!<\!\begin{matrix}\mathrm{H}\\ \mathrm{Me}\end{matrix} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}CHPhMe},$$

furnish evidence somewhat analogous to the present that optically active compounds may be produced through a phase in which less than four groups are attached at least momentarily to the centre of asymmetry. Phillips (J., 1925, **127**, 2567) had previously discussed the possible free existence of the system  $+\mathrm{C}\begin{array}{l}\diagup \mathrm{R_1}\\ \!-\mathrm{R_2}\\ \diagdown \mathrm{R_3}\end{array}$ in an optically active state in connexion with the problem of the Walden inversion. He considers that such inversions are intimately connected with the withdrawal of two electrons from the valency shell of the atom usually designated as asymmetric; this conception is quite in accord with the mechanism now discussed, for on the basis of the Lewis–Langmuir models the reaction would be represented



$$\mathrm{R_2\!:\!\overset{\displaystyle R_1}{\underset{\displaystyle :\!\underset{..}{Cl}\!:}{\ddot{C}}}\!:\!H} \longrightarrow \mathrm{R_2\!:\!\overset{R_1}{\underset{\cdot}{\ddot{C}}}\cdot} + \mathrm{H\!:\!\underset{..}{\ddot{Cl}}\!:},$$

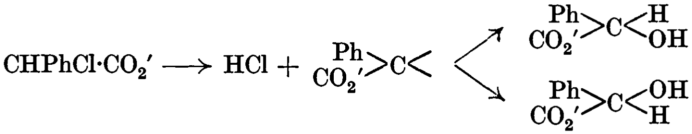
two electrons being withdrawn from the shell of the asymmetric carbon atom as the first stage (slow) of the reaction, to be followed by the addition reactions (rapid).

The kinetic results on the replacement of the halogen in phenylchloroacetic acid and phenylbromoacetic acid (*loc. cit.*) show the mechanisms of the halogen replacements in these cases to be exactly the same as for α-chloroethylbenzene, so that they would be represented thus:

(1) $\mathrm{CHPhX{\cdot}CO_2' \longrightarrow CPh(CO_2') + HX}$.

(2) $\mathrm{CPh(CO_2') + H_2O\ (excess) \longrightarrow CHPh(CO_2'){\cdot}OH}$.

Further, the reaction between water and the *l*-phenylchloroacetate or *l*-phenylbromoacetate ions gives rise to a mixture of *l*- and *d*-mandelic acids, the *l*-acid being in slight excess over the *d*-acid in the case of *l*-phenylchloroacetic acid (McKenzie and Clough, J., 1908, **93**, 811; 1909, **95**, 777), whilst for *l*-phenylbromoacetic acid the reverse holds (McKenzie and Walker, J., 1916, **109**, 1685; Ward, J., 1926, 1190). The mechanisms of the reactions by which the *d*- and *l*-mandelic acids are produced cannot be differentiated (Ward, *loc. cit.*), that is, the mechanisms of the "normal" and "abnormal" reactions are identical from the ordinary kinetic point of view. The production of the mandelic acids by the addition of water in two ways to the intermediate phase, according to the scheme



$$\mathrm{CHPhCl{\cdot}CO_2' \longrightarrow HCl + {}^{Ph}_{CO_2'}{>}C{<}} \begin{array}{l}\nearrow\ \mathrm{{}^{Ph}_{CO_2'}{>}C{<}^{H}_{OH}}\\ \searrow\ \mathrm{{}^{Ph}_{CO_2'}{>}C{<}^{OH}_{H}}\end{array}$$

would agree with the observed identity of the two reactions. The similar production of phenylaminoacetic acids of either sign from a given initial phenylchloroacetic or phenylbromoacetic acid according to the solvent medium used (Senter and Drew, J., 1915, **105**, 638; 1916, **107**, 1091; Senter and Tucker, J., 1918, **113**, 140) would be ascribed to a mechanism of the above type.

EXPERIMENTAL.

r-*Phenylmethylcarbinol* was prepared by the slow addition during 3—4 hours of 72 g. of benzaldehyde, dissolved in ether, to a vigorously stirred, ice-cooled solution of magnesium methyl iodide, prepared from 142 g. of methyl iodide. After the mixture had remained at room temperature for ½ hour, the additive compound was decomposed with water and dilute acid. The *r*-phenylmethylcarbinol was purified and isolated in the usual way; b. p. 101—102°/20 mm., yield 63 g.

d-*Phenylmethylcarbinol* was obtained by the resolution of the *r*-carbinol by Pickard and Kenyon's method (J., 1911, **99**, 45) and had $\alpha_{5780}^{15^\circ} + 22{\cdot}19^\circ$ for $l = 0{\cdot}5$; whence $[\alpha]_{5780}^{15^\circ} + 45{\cdot}0^\circ$, compared with Pickard and Kenyon's values $[\alpha]_{D}^{6^\circ} + 42{\cdot}9^\circ$, $[\alpha]_{D}^{27^\circ} + 42{\cdot}85^\circ$.

r-α-*Chloroethylbenzene* was prepared from *r*-phenylmethylcarbinol by means of thionyl chloride (McKenzie and Clough, J., 1913, **103**, 694); the acidity was almost entirely removed by shaking the product with anhydrous potassium carbonate for a short time and then redistilling it; b. p. 81—82°/17 mm. Results of typical analyses of *r*-α-chloroethylbenzene from different preparations of phenylmethylcarbinol are: Cl, (volumetric), 24·75, 24·98, 24·95, 24·96%; (gravimetric), 25·40, 25·24, 25·18, 25·30%. In the volumetric method, the chlorine was determined by heating a solution of α-chloroethylbenzene in aqueous ethyl alcohol, and titrating the liberated acid with standard alkali until the colour change, with phenolphthalein as indicator, was permanent. For the gravimetric analyses, Stepanow's method was used throughout.

The *r*-α-chloroethylbenzene at first used in these experiments was prepared from phenylmethylcarbinol, obtained by the Grignard reaction from 1 mol. of benzaldehyde and 1 mol. of magnesium methyl iodide. The percentage halogen (gravimetric estimation) in different preparations of this material varied from 23·9 to 24·8 (calc., 25·27%). If the displacement of the halogen was carried out in aqueous (20%) ethyl-alcoholic solution at 28·7°, the final titrations corresponded with Cl = 20·1 to 21·0%, these values being considerably lower than those determined by the gravimetric method. This is not due to an equilibrium of the type $CHPhMeX + H_2O \rightleftharpoons CHPhMe{\cdot}OH + HX$, for under the conditions of experiment phenylmethylcarbinol and hydrogen chloride did not react.

As ordinarily prepared, phenylmethylcarbinol is contaminated with impurities (compare Marshall, J., 1914, **105**, 527; 1915, **107**, 509), which doubtless give chloro-derivatives rendering the α-chloroethylbenzene impure. By preparing the phenylmethylcarbinol as above, with 3 mols. of the Grignard reagent to 2 mols. of benzaldehyde, the values for the percentage halogen in the derived chloro-compound, as shown from the preceding analyses, are in much closer agreement when estimated by the two methods, but in all cases the values found by titration are somewhat lower than those obtained by Stepanow's method. The α-chloroethylbenzene used in the following experiments was prepared by this method.

d-*α-Chloroethylbenzene* was prepared from *d*-phenylmethylcarbinol by McKenzie and Clough's method (*loc. cit.*) and purified as above; b. p. 82—83°/18 mm.; $\alpha_{5780}^{21^\circ}$ + 26·08°, $l = 0{\cdot}5$, $[\alpha]_{5780}^{21^\circ}$ + 49·07° (compare McKenzie and Clough, $[\alpha]_D$ + 50·6°). The percentages of chlorine, determined by the two methods, were (volumetric) 24·77, (gravimetric) 24·86.

β-Chloroethylbenzene prepared from β-phenylethyl alcohol and phosphorus pentachloride (Found: Cl, 25·7. Calc.: Cl, 25·3. Barger, J., 1909, **95**, 2194, found Cl, 25·8%) contained a negligible quantity of hydrogen chloride but an appreciable quantity of phosphorus. Thionyl chloride gave a much purer product: β-Phenylethyl alcohol (25 g.) was slowly added to thionyl chloride (40 g.) at room temperature. Vigorous evolution of hydrogen chloride took place, but the mixture did not become appreciably warm. The reaction mixture was kept for about an hour and then distilled; the product, purified with potassium carbonate, had b. p. 83—84°/14 mm. (yield, 25 g.) (Found: Cl, 25·2%).

α-Phenylethyl p-*Nitrobenzoate.*—Phenylmethylcarbinol (1 g.) was dissolved in pyridine (3 g.), and *p*-nitrobenzoyl chloride (1·8 g.) slowly added with cooling. The mixture was kept for 4 hours, treated with excess of dilute sulphuric acid and filtered, and the precipitate was stirred with sodium carbonate solution. The crude ester (2·25 g.) crystallised from aqueous alcohol in pale yellow needles, m.p. 47—48° (Found: equiv. by hydrolysis, 274. $C_{15}H_{13}O_4N$ requires equiv., 271).

Products of the Reaction of r-*α-Chloroethylbenzene with Aqueous Ethyl Alcohol.*—Ethyl alcohol (280 c.c.) and water (70 c.c.), both at 50°, were added to *r*-α-chloroethylbenzene (7·5 g.). The solution was maintained at this temperature for 12 hours, the water then removed by means of potassium carbonate, and the alcoholic solution fractionated, 5·8 g. of liquid, b. p. 71—94°/15 mm., being obtained. A mixture of this with pyridine (17 g.) and *p*-nitrobenzoyl chloride (10 g.) was kept for 4 hours, excess of dilute sulphuric acid was then added, and the pasty product was filtered off, well pressed, and twice washed with some 25 c.c. of ether; 6·2 g. of solid then remained undissolved. The ethereal solution was shaken with the aqueous filtrate, separated, dried, and distilled; α-phenyldiethyl ether (2·55 g.) was then obtained, b. p. 76°/20 mm. (compare Holmberg, *Ber.*, 1912, **45**, 1002, who gives b. p. 71·5—72°/15 mm.) (Found: OEt, 29·5. Calc.: OEt, 30·0%). The residue (6·5 g.) in the distillation flask slowly crystallised. The combined solid products, after treatment with excess of dilute sodium carbonate solution, gave 6·4 g. of crude α-phenylethyl *p*-nitrobenzoate, m. p. 47° after crystallisation from aqueous alcohol.

Similarly, at 28·7°, *r*-α-chloroethylbenzene (5 g.), reacting with ethyl alcohol (280 c.c.) and water (70 c.c.) for 7 days, gave 3·05 g. of product, b. p. 72—90°/13 mm., which, by the above method of separation, yielded 0·85 g. of α-phenyldiethyl ether, b. p. 75°/19 mm. From *r*-α-chloroethylbenzene (5 g.), reacting with ethyl alcohol (280 c.c.) and aqueous 0·967*N*-sodium hydroxide (70 c.c.) at 28·7° for 8 days, 3·45 g. of product, b. p. 72—90°/14 mm., were obtained, from which was separated α-phenyldiethyl ether (1·4 g.), b. p. 71°/15 mm.

In none of these experiments was any evidence obtained of the formation of αα′-diphenyldiethyl ether.

Reaction between r-*α-Chloroethylbenzene and Water.*—(a) A mixture of 300 c.c. of water and 20 g. of *r*-α-chloroethylbenzene [Cl, 24·65% (volumetric), 25·27% (gravimetric)] was gently boiled under reflux for 2 hours; the products were then extracted with ether and dried. On distillation the following fractions were obtained: (1) b. p. 52—53°/23 mm., 1·7 g.; (2) b. p. 111—113°/27 mm., 3·7 g.; (3) b. p. 112—160°/23 mm., 1·9 g.; (4) b. p. 167—168°/23 mm., 6·3 g.

Fraction (1) distilled at ordinary pressure at 145—146° (styrene has b. p. 146°/759 mm.), leaving a colourless gum, doubtless metastyrene. Fraction (2), on treatment with thionyl chloride and subsequent purification as in the preparation of *r*-α-chloroethylbenzene, gave a product (3·45 g.), b. p. 87—88°/24 mm. [Found: Cl, 23·9% (volumetric), 25·26% (gravimetric)]; 0·15 g. distilled at 88—170°/24 mm., and the residue was negligible. Fraction (3), treated in the same way as (2), gave 1·45 g., b. p. 85—86°/22 mm. [Found: Cl, 23·95% (volumetric), 24·81% (gravimetric)], and 0·15 g., b. p. 86—150°/22 mm. Fractions (2) and (3) therefore consisted of phenylmethylcarbinol, with possibly some αα′-diphenyldiethyl ether; the low value for the halogen determination by the volumetric method is probably due to the accumulation in these fractions of the substances present in the original material containing the less reactive halogen. Fraction (4), b. p. 167—168°/23 mm.

(Oddo, *loc. cit.*, records the b. p. of αα′-diphenyldiethyl ether as 240—245°/20 mm., undoubtedly in error for 140—145°/20 mm.; Marshall, *loc. cit.*, gives b. p. 148—150°/15 mm.; Wuyts, *loc. cit.*, gives b. p. 156·5°/17 mm.), a clear, colourless liquid which was free from halogen and underwent no change on prolonged standing with sodium, was αα′-diphenyldiethyl ether (Found : C, 85·2; H, 8·0; *M*, cryoscopic in naphthalene, 209. Calc.: C, 85·0; H, 8·0%; *M*, 226).

(b) This experiment was a repetition of (a), except that the time of boiling was 5 minutes only. The fractions obtained were: (1) b. p. 73—76°/20 mm., 6·4 g.; (2) b. p. 85—120°/30 mm., 0·8 g.; (3) b. p. 173—175°/30 mm., 6·2 g. Estimations of chlorine in the fractions gave (1) 18·4%, (2) 11·8%, (3) nil, corresponding with (1) and (2) being mixtures of α-chloroethylbenzene, styrene, and phenylmethylcarbinol, and (3) being αα′-diphenyldiethyl ether.

(c) The replacement of the halogen was carried out at 50°, a stirred mixture of *r*-α-chloroethylbenzene (25 g.) and water (400 c.c.) being warmed for 12 hours. The product (19 g.) had b. p. 99—105°/20 mm., and therefore was phenylmethylcarbinol alone; some 0·5 g. of liquid remained in the distilling flask.

Reaction between Phenylmethylcarbinol and Water.—*r*-Phenylmethylcarbinol (10 g.) was heated with water (160 c.c.) at 100° for 8 hours. The bulk (7·5 g.) of the product, b. p. 104—106°/24 mm., was unchanged phenylmethylcarbinol; a second fraction (0·8 g.) had b. p. 106—120°/24 mm.

Reaction between Phenylmethylcarbinol and Hydrochloric Acid.—*r*-Phenylmethylcarbinol (20 g.) was heated with hydrochloric acid (320 c.c.; approx. *N*/2) at 100° for 8 hours. The products were (1) styrene, b. p. 54—58°/24 mm., 1·2 g., (2) phenylmethylcarbinol, b. p. 106—109°/24 mm., 2·5 g., (3) αα′-diphenyldiethyl ether, b. p. 163—165°/21 mm., 9·45 g.

Reaction between αα′-Diphenyldiethyl Ether and Hydrochloric Acid.—The ether (15 g.) was heated under the conditions of the preceding experiment. The products were: (1) styrene, b. p. 47—50°/22 mm., 0·35 g., (2) phenylmethylcarbinol, b. p. 118—126°/31 mm., 2·0 g., (3) αα′-diphenyldiethyl ether, b. p. 175—177°/31 mm., 8·95 g.

Kinetic Experiments.

In the following experiments the solvent medium employed throughout was aqueous (20% by volume) ethyl alcohol. The ethyl alcohol used was commercial absolute alcohol, dried by refluxing and distilling over quick-lime. In preparing the solution the substance under investigation was dissolved in ethyl alcohol, the measured volumes of water, hydrochloric acid, or sodium hydroxide added, and the solution made up to volume with ethyl alcohol, all the reactants being at the temperature of experiment. The amounts of carbinol and chloro-compounds used, and also the concentrations of added hydrogen chloride or sodium hydroxide, are expressed in mols. per litre; all titrations are referred to 20 c.c. of the solution against sodium hydroxide ($N/10$) or alcoholic benzoic acid ($N/10$), the actual experimental figures being converted to this basis. In all titration experiments, phenolphthalein was used as indicator. Unless otherwise stated, the values of k are calculated from the formula $k = 2{\cdot}3/t.\ \log_{10} \{a/(a - x)\}$ for a unimolecular reaction.

(1) *r*-Phenylmethylcarbinol, 0·0983; hydrogen chloride, 0·0935; temp. 28·5°.

Time (hrs.) ...	0·27	1·1	24·7	48	96	216
Titre	18·60	18·67	18·62	18·71	18·78	18·78

(2) *r*-Phenylmethylcarbinol, 0·1211; hydrogen chloride, 0·1870; temp. 28·5°.

Time (hrs.)	2	72	96	120	144
Titre	37·38	37·39	37·43	37·32	37·69

(3) *r*-α-Chloroethylbenzene, 0·0906; temp. 28·7°.

Time (hrs.).	Titre.	*k*.	Time (hrs.).	Titre.	*k*.
0·1	0·185	—	34·1	15·41	0·0569
3·1	2·93	0·0557	55·35	17·09	0·0541
6·1	5·24	0·0557	144	17·81	—
10·1	7·92	0·0570	192	17·97	—
23·1	13·17	0·0568	240	17·98	—

(4) *r*-α-Chloroethylbenzene, 0·0849; sodium hydroxide, 0·0941; temp. 28·7°.

Time (hrs.).	Titre.	*k*.	Time (hrs.).	Titre.	*k*.
0·1	18·69	—	30·1	4·93	0·0566
3·1	16·13	0·0549	54·1	2·62	0·0571
7·1	13·29	0·0552	122·1	1·86	—
10·6	11·18	0·0561	171·1	1·85	—

(5) *r*-α-Chloroethylbenzene, 0·0890; sodium hydroxide, 0·1882; temp. 28·7°.

Time (hrs.).	Titre.	*k*.	Time (hrs.)	Titre.	*k*.
0·1	37·65	—	54·1	20·66	0·0565
3·1	34·84	0·0569	120·1	19·83	—
7·1	31·91	0·0554	144·1	19·83	—
11·1	29·44	0·0551	168·1	19·82	—
30·1	23·09	0·0565			

The mean values of the velocity coefficients obtained at 50·0°, as in (3), (4) and (5), are summarised below.

Exper.	*r*-α-Chloroethylbenzene.	Sodium hydroxide.	*k*.
(6)	0·0903 mol./l.	—	0·589
(7)	0·0833	0·1025 mol./l.	0·590
(8)	0·0924	0·2050	0·590

(9) *d*-α-Chloroethylbenzene, 0·1071; samples were withdrawn at the times shown, and their rotations determined in a 2 dm.-tube for the yellow mercury line; temp. 28·6°.

Time (hrs.).	$\alpha_{5780}^{28\cdot6^\circ}$.	*k*.	Time (hrs.).	$\alpha_{5780}^{28\cdot6^\circ}$.	*k*.
0·19	+ 1·30°	—	27·00	− 0·09°	0·0598
1·17	+ 1·20	0·0603	30·64	− 0·17	0·0611
3·06	+ 1·02	0·0610	48·94	− 0·33	0·0566
5·07	+ 0·85	0·0612	6 days	− 0·39	—
7·02	+ 0·69	0·0631	10 ,,	− 0·43	—
9·06	+ 0·56	0·0624	27 ,,	− 0·43	—
11·93	+ 0·40	0·0619	159 ,,	− 0·44	—

(10) *d*-α-Chloroethylbenzene, 0·0929; sodium hydroxide, 0·1092. The solution was turbid and was filtered before the measurements were made. The initial rotation ($t = 0\cdot18$ hr.) was $\alpha_{5780}^{28\cdot6^\circ} + 0\cdot85^\circ$, and the final value ($t = 120$ hrs.) was $\alpha_{5780}^{28\cdot6^\circ} - 0\cdot36^\circ$, for $l = 2$. The individual values of *k* varied from 0·0539 to 0·0582, giving a mean of 0·0558.

(11) β-Chloromethylbenzene, 0·0996; temp. 28·9°.

Time (days) ...	0	1	5	11	22	55
Titre	0·11	0·09	0·12	0·22	0·25	0·33

(12) β-Chloroethylbenzene, 0·0975; sodium hydroxide, 0·1858; temp. 28·9°.

Time (days).	Titre.	*k*.	Time (days).	Titre.	*k*.
0·0	37·16	—	4	33·38	0·0016
0·5	36·40	0·0022	8	30·30	0·0016
1·07	35·88	0·0018	19	25·90	0·0015
2·01	35·00	0·0016	26	23·98	0·0015
3·02	34·10	0·0016	52	19·94	0·0016

k is equal to $\frac{2\cdot3}{(b-a)t}\log_{10}\frac{a(b-x)}{b(a-x)}$, *t* being measured in days, *a*, *b* and *x* in c.c. of *N*/10-acid.

(13) β-Chloroethylbenzene, 0·0917; sodium hydroxide, 0·0929; temp. 28·9°.

Time (days).	Titre.	*k*.	Time (days).	Titre.	*k*.
0·01	18·48	—	7	14·99	0·0018
0·40	18·35	0·0010	18	11·84	0·0017
1·00	17·79	0·0022	25	10·26	0·0017
2·13	17·34	0·0017	51	6·70	0·0019
3·04	16·95	0·0016			

The formula for a bimolecular reaction where $a = b$, namely, $k = x/ta(a - x)$, was used.

Summary.

(1) The displacement of the halogen in *r*-α-chloroethylbenzene in aqueous ethyl-alcoholic solution alone and also in the presence of sodium hydroxide at 28·7° and at 50·0° yields a mixture of phenyl-

methylcarbinol and α-phenyldiethyl ether; the velocity coefficient obtained in each case is that of a unimolecular reaction, the sodium hydroxide or its ions playing no part in the halogen displacement.

(2) This result is confirmed by a calculation of the velocity coefficients from observations on the change in the rotation of solutions of *d*-α-chloroethylbenzene under comparable conditions.

(3) The displacement of the halogen in β-chloroethylbenzene is in marked contrast to the above; in aqueous ethyl-alcoholic solution the displacement is negligibly slow; in the presence of sodium hydroxide, velocity coefficients of a bimolecular reaction are obtained but the halogen displacement proceeds much more slowly than in the case of α-chloroethylbenzene.

(4) *r*-α-Chloroethylbenzene, on boiling with water, yields mainly αα′-diphenyldiethyl ether, together with styrene and phenylmethylcarbinol. The same products are obtained on boiling phenylmethylcarbinol with *N*/2-hydrochloric acid, and also by submitting αα′-diphenyldiethyl ether to similar treatment.

(5) The experimental evidence under (1), (2), and (4) is in accordance with the reaction proceeding through a phase CPhMe<, in which but two groups are momentarily attached to carbon.

(6) The mechanism under (5) is discussed in connexion with the Walden inversion.

The author wishes to express his thanks to Drs. Senter and Barrow for their valued interest in this research, and also to the Department of Scientific and Industrial Research for a maintenance grant during a part of the time occupied in carrying it out.

Birkbeck College,
University of London, E.C. 4.
[*Received, November* 9*th*, 1926.]