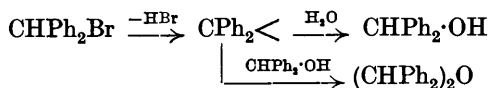


CCCVI.—*Investigations on the Bivalency of Carbon.*
Part I. The Displacement of Chlorine from
Diphenylchloromethane. s-Tetraphenyldimethyl
Ether.

By ALLAN MILES WARD.

THE formation of *s*-tetraphenyldimethyl ether on boiling diphenylbromomethane with water was explained by Nef (*Annalen*, 1897, 298, 234) on the assumption that the reaction proceeded through a phase involving bivalent carbon :



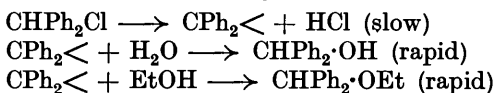
If this be so, the same considerations as those advanced for α -chloroethylbenzene (Ward, this vol., p. 445) should apply to the velocity coefficients for the displacement of the halogen atom from diphenylchloromethane. Thus the rates of displacement of the chlorine should be uninfluenced by the presence or the absence of sodium hydroxide. This is now shown to be the case for aqueous (10% by vol.) ethyl-alcoholic solutions at 25°. When sodium hydroxide is present in a concentration equivalent to the diphenylchloromethane, the velocity coefficient is that of a unimolecular reaction and of the same value as when sodium hydroxide is absent. When the concentration of the sodium hydroxide is doubled, the reaction remains unimolecular, but the velocity is somewhat decreased. A similar observation is recorded by Senter and Tucker (*J.*, 1916, 109, 697) for the reaction between water and the phenylbromoacetate ion.

In ethyl-alcoholic solution without added water, the presence of sodium ethoxide produced no change in the velocity of the displacement of the halogen (it was unnecessary for the alcohol to be completely anhydrous in these experiments, and lime-dried material was therefore used throughout); the presence of sodium hydroxide caused a considerable increase in the rate at 25.0°, but the reaction remained unimolecular. Observations at 35.0° in the presence and in the absence of sodium hydroxide showed similar differences, but the temperature coefficients calculated from the two sets of results were in agreement. With increasing concentration of water, the velocity of the reaction increased, being about 30 times as great when 20% of water was present as in the absolute-alcoholic solution. In the previous communication on α -chloroethylbenzene (*loc. cit.*), all velocity measurements were made in 20% aqueous-alcoholic solutions, and comparison with the velocity coefficients

of the present reaction under similar conditions shows that the halogen is displaced some 166 times more rapidly from CHPh_2Cl than from CHPhMeCl .

In the kinetic experiments, the products from diphenylchloromethane were benzhydrol and diphenylmethyl ethyl ether. These conclusions are based on (1) a Zeisel determination on the products, and (2) the reaction between the products and hydrogen chloride, whereby diphenylchloromethane is re-formed from both benzhydrol and diphenylmethyl ethyl ether. In some of the experiments described, the estimation of chlorine by (2) gave low results for diphenylchloromethane, and repeated treatment with hydrogen chloride did not alter these values. In these experiments, the products were distilled at atmospheric pressure, but when all distillations were carried out under reduced pressure, the chlorine thus estimated agreed more closely with the calculated value for diphenylchloromethane. There can thus be no doubt that the low values obtained in some experiments were due to the presence of other substances formed during the distillation of the benzhydrol-diphenylmethyl ethyl ether mixture. Indeed, it was found by Goldthwaite (*Amer. Chem. J.*, 1903, **30**, 461) that *pp'*-dibromodiphenylmethyl ethyl ether on being heated at 300° decomposed entirely to *pp'*-dibromodiphenylmethane and *pp'*-dibromobenzophenone, together with a lower-boiling fraction, probably ethyl alcohol, and a gas, possibly ethylene. Bacon (*ibid.*, 1905, **33**, 92) obtained benzophenone, tetraphenylethane, and acetaldehyde on submitting diphenylmethyl ethyl ether to similar treatment. Nef (*loc. cit.*, p. 236) had previously observed that benzhydrol at 300° decomposes completely to diphenylmethane, benzophenone, and tetraphenylethane. The analytical results would point, however, to the decomposition of the ether being very much less at atmospheric pressure than that of the benzhydrol. The Zeisel determinations are of interest in showing that some 8% of benzhydrol is formed when lime-dried alcohol is used, this no doubt being due to the water present in this solvent. In aqueous (10% by vol.) ethyl-alcoholic solution, the proportion of benzhydrol formed is higher in the absence of sodium hydroxide than in its presence, being 18% and 14%, respectively, and this provides further evidence that hydroxyl ions are not directly active in the substitution.

The reaction mechanism derived from the kinetic results and from the products of reaction may thus be stated

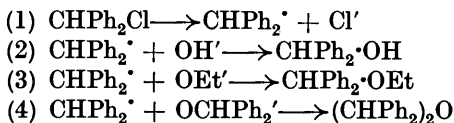


exactly as for α -chloroethylbenzene, and no experimental results are obtained contrary to Nef's hypothesis that the reaction proceeds through the phase $CPh_2<$.

It is shown also that *s*-tetraphenyldimethyl ether may be formed with ease from benzhydrol by boiling it under reflux with hydrochloric acid, just as, under similar conditions, $\alpha\alpha'$ -diphenyldiethyl ether and styrene are formed from phenylmethylcarbinol (Ward, *loc. cit.*). If the former reaction proceeds through the phase $CPh_2<$ as postulated, no unsaturated hydrocarbon of the styrene type could be formed, and the ether was, in fact, the only product isolated. The effects of varying the times of heating at 100° and of altering the concentration of hydrochloric acid were observed in relation to the proportion of ether formed. With increasing concentration of hydrochloric acid, the proportion of ether formed passed through a maximum, and the amount of diphenylchloromethane increased from zero at first, until, with concentrated acid, it became the main product of reaction. Conversely, when *s*-tetraphenyldimethyl ether was boiled with concentrated hydrochloric acid, diphenylchloromethane was the main product, whereas with *N/2*-acid no change occurred. Moreover, it was found in these experiments that when the products were distilled and then treated with hydrogen chloride, values for the chlorine content were obtained which were too low for diphenylchloromethane. This was doubtless due to the decomposition of the original products of reaction on distillation, as in the case of the benzhydrol-diphenylmethyl ethyl ether mixtures (p. 2286). Thus Nef (*loc. cit.*, p. 236) found that *s*-tetraphenyldimethyl ether on being heated at 300° decomposed to benzophenone, diphenylmethane, and tetraphenylethane. In the present experiments, the products of distillation were not systematically examined except in the case of one experiment with *s*-tetraphenyldimethyl ether, in which diphenylmethane was isolated. The presence of this as a product of secondary decomposition would account for the anomalous chlorine results. When the products of the reaction between concentrated hydrochloric acid and benzhydrol or *s*-tetraphenyldimethyl ether were examined by methods avoiding distillation or heating at higher temperatures, no evidence was obtained for the formation of any substances other than diphenylchloromethane, benzhydrol, and *s*-tetraphenyldimethyl ether.

Although the results find a complete explanation on the basis of Nef's hypothesis, other interpretations may possibly be formulated. Thus assuming that diphenylchloromethane reacts in virtue of its ions as in (1)—(4), the kinetic results would then necessitate

that (1) should be a time reaction and (2) and (3) extremely rapid.



Although an increase in the hydroxyl-ion concentration from about 10^{-8} (in 10% aqueous ethyl-alcoholic solution) to 0.176 (in the presence of sodium hydroxide) would thus greatly increase the velocity of (2), it would not affect the measured velocity, which *ex hypothesi* depends solely on (1). Also, from the equilibrium $\text{EtOH} + \text{OH}' \rightleftharpoons \text{OEt}' + \text{H}_2\text{O}$, an increase is seen to take place in the ethoxyl-ion concentration parallel with that in the hydroxyl-ion concentration, but the increased velocity of (3) would not influence the measurable velocity. Slowness of (1) and rapidity of (2) and (3) would be almost inevitably connected, since each represents the very slight tendency for the formation of CHPh_2^* ions. The same considerations hold concerning phenylmethylcarbinol (*loc. cit.*). Should the reaction in this case proceed through the phase CHPhMe^* , it must be assumed that this is capable of losing a hydrogen ion in order to account for the production of styrene. The halogen displacement from the triarylmethyl chlorides may be assumed to take place as in (1), but the hexaryldimethyl ethers have not been prepared by this method (compare Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 200). In this connexion an examination of systems of the type $\text{CR}_1\text{R}_2\text{R}_3\text{Cl}$ should provide valuable data.

EXPERIMENTAL.

Diphenylchloromethane was prepared from benzhydrol by means of hydrogen chloride in benzene solution (Böeseken, *Rec. trav. chim.*, 1903, **22**, 313; Montagne, *ibid.*, 1906, **25**, 405) and was obtained as a colourless liquid, b. p. $158.5\text{--}159.5^\circ/12$ mm., which solidified to a colourless solid, m. p. 20.5° (Engler and Berthge, *Ber.*, 1874, **7**, 1128, give m. p. 14° , and Böeseken gives m. p. $12\text{--}14^\circ$). It was kept in small sealed glass tubes, for turbidity developed rapidly in contact with the atmosphere. The chlorine was determined (i) by heating a weighed sample in aqueous ethyl alcohol and titrating the liberated acid with standard alkali until the colour change of the indicator (phenolphthalein) was permanent (Found : Cl, 17.64. Calc. : Cl, 17.53%), and (ii) by Stepanow's method (Found : Cl, 17.47%). In all subsequent analyses, the chlorine was estimated as under (i).

Diphenylchloromethane was also prepared by suspending *s*-tetraphenyldimethyl ether (90 g.) in benzene (180 c.c.) and passing in a rapid stream of hydrogen chloride for 1 hour at room temperature. The ether dissolved completely and an aqueous layer formed; this was separated and the benzene solution dried by means of calcium chloride. The hydrogen chloride was removed in a current of carbon dioxide, and the product, b. p. 165.5°/15 mm., collected; yield, 88 g. (Found: Cl, 17.57%). Some tar remained in the distilling flask.

Products of the Reaction of Diphenylchloromethane and Ethyl Alcohol.—(a) Ethyl alcohol (250 c.c.), dried by refluxing and distilling over quick-lime, was added to diphenylchloromethane (5 g.). The solution was maintained at 25° for 5 days, free hydrogen chloride was then removed by means of potassium carbonate, and the alcoholic solution fractionated, 4.9 g. of liquid, b. p. 146—147°/9 mm., being obtained (Nef, *loc. cit.*, p. 234, gives b. p. 153°/15 mm. for diphenylmethyl ethyl ether) (Found: OEt, 19.6. Calc. for diphenylmethyl ethyl ether: OEt, 21.2%). The product redistilled at 281°/766 mm. (Kostanecki and Lampe, *Ber.*, 1906, 39, 4019, give b. p. 288°) (Found: OEt, 19.2%).

(b) Repetition of this experiment with 15 g. of diphenylchloromethane and 500 c.c. of alcohol for 10 days gave 14.2 g., b. p. 115—119°/4 mm. (Found: OEt, 19.5, 19.4%).

(c) Hydrogen chloride was passed through the liquid obtained in (a) at room temperature. Considerable heat was developed, and after some time separation into two layers took place. Calcium chloride was added, and after standing, the products, which remained heterogeneous, were distilled. On heating, appreciable charring and marked evolution of gas took place, the material then distilling smoothly, b. p. 156—158°/11 mm. (Found: Cl, 16.1. Calc. for diphenylchloromethane: Cl, 17.53%).

(d) 5 G. of the product from (b) were dissolved in benzene (15 c.c.) and hydrogen chloride was passed in rapidly for 2 hours. Two layers were again formed and remained after drying by means of calcium chloride. The hydrogen chloride was removed in a stream of carbon dioxide, the benzene distilled under diminished pressure, and a colourless liquid obtained (4.2 g.), b. p. 120—121°/3 mm. (Found: Cl, 17.25%). Considerable dark brown gum remained in the distilling flask.

Products of the Reaction of Diphenylchloromethane with Aqueous Ethyl Alcohol.—(e) A solution of diphenylchloromethane (5 g.) in ethyl alcohol (225 c.c.) and water (25 c.c.) was kept at 25° for 12 hours, the water then removed by means of potassium carbonate, and the products distilled, giving 4.5 g. of liquid, b. p. 113—120°/3

mm., which redistilled at 281—288°/766 mm. (Found : OEt, 17·8%), some charred material remaining in the distilling flask. The liquid was dissolved in petroleum ether and treated with hydrogen chloride as under (c) above, a fraction of b. p. 162—163°/16 mm. (Found : Cl, 16·58%) being obtained.

(f) Ethyl alcohol (1125 c.c.), water (125 c.c.), and diphenylchloromethane (25 g.) were treated as in (b) and gave 21·5 g., b. p. 125—130°/3 mm. (Found : OEt, 17·3, 17·4%). Treatment of a sample (5 g.) as under (d) above, gave 4·4 g. of colourless liquid, b. p. 115°/1 mm. (Found : Cl, 17·22%). Some gum remained in the distilling flask.

Products of the Reaction of Diphenylchloromethane with Aqueous Ethyl-alcoholic Sodium Hydroxide.—(g) Diphenylchloromethane (5 g.) was dissolved in ethyl alcohol (225 c.c.) and aqueous 1·76*N*-sodium hydroxide (25 c.c.). The solution was kept at 25° for 12 hours, dried, and the liquid distilled, b. p. 116—124°/3 mm.; yield, 4·3 g. The products redistilled at 279—285°/766 mm. (Found : OEt, 18·2%). After treatment with hydrogen chloride in benzene solution, the liquid distilled at 156—158°/11 mm. (Found : Cl, 16·6%). This product was again treated with hydrogen chloride, but the chlorine content remained unchanged.

(h) The water in Expt. (f) was replaced by the same volume of aqueous 2*N*-sodium hydroxide and the same procedure followed; yield, 21·5 g.; b. p. 114—121°/3 mm. (Found : OEt, 18·2, 18·1%). A small amount of gum remained in the distilling flask. Treatment of a sample (5 g.) as under (d) above, gave 4·3 g. of a colourless liquid, b. p. 121—124°/4 mm. (Found : Cl, 17·29%). A small amount of brown oil remained in the distilling flask.

Reaction between Benzhydrol and Hydrochloric Acid.—In each experiment benzhydrol (5 g.) and hydrochloric acid of the normality stated were heated in a pressure flask immersed in a bath of boiling water for the times shown in the following table. The products solidified on being poured into cold water, and the *s*-tetraphenyldimethyl ether and benzhydrol were then readily separated by dissolving the mixture in hot alcohol, the main bulk of the ether crystallising in a pure condition on cooling. Addition of a little water to the alcoholic mother-liquor precipitated a mixture of the ether and benzhydrol, which was separated into its components by a repetition of this process, whilst by the addition of the aqueous alcoholic solution to excess of water, the benzhydrol was obtained in a pure condition. The purity of the benzhydrol (m. p. 68°) and of the *s*-tetraphenyldimethyl ether (m. p. 110°) was checked in these and in all subsequent experiments by determining the m. p.'s both alone and when mixed with authentic specimens. In the

HCl, <i>N</i> .	Time (hrs.).	Yields, g.		HCl, <i>N</i> .	Time (hrs.).	Yields, g.	
		Ether.	Benz- hydrol.			Ether.	Benz- hydrol.
0.5	1	—	5.0	1	6	2.1	2.3
0.5	4	1.2	3.5	2	1	1.55	3.0
0.5	8	1.75	2.85	2	6	3.5	0.75
0.5	20	2.55	2.4	3.5	1	3.6	0.95
1	1	0.8	4.05	3.5	6	3.9	—

final experiment, no precipitate but only a turbidity was formed on adding the aqueous alcoholic solution to excess of water. In several of the preceding experiments, mainly those in which the higher concentrations of acid were used or in which the times of heating were longer, the total yield of ether and carbinol was lower than the theoretical, and in these cases the filtrate after separation of the benzhydrol was turbid, doubtless due to the partial formation of diphenylchloromethane, as shown in the following experiments.

(i) Benzhydrol (5 g.) and 5*N*-hydrochloric acid (75 c.c.) were heated in a pressure flask at 100° for 1 hour. The products on being poured into cold water solidified to a pasty mass. On the addition of petroleum ether (b. p. 40—60°), a white solid was at once obtained, which on crystallisation from alcohol gave *s*-tetraphenyldimethyl ether (2.2 g.). Dilution of the alcoholic filtrate with water produced a turbidity only. The petroleum-ether solution was dried, and the solvent evaporated completely at room temperature, a pasty mass (2 g.; Cl, 7.7%) thus being obtained.

(j) Benzhydrol (10 g.) was boiled under reflux with concentrated hydrochloric acid (100 c.c.) for 2 hours. The oil, which did not solidify on cooling, was extracted with ether, dried and distilled; b. p. 160—161°/15 mm.; yield, 7.85 g.; Cl, 15.4%. A black gum remained in the distilling flask. In a second experiment, with only 1 hour's boiling, the following results were obtained: b. p. 159—161°/14 mm.; yield 7.6 g.; Cl, 15.2%; whilst in a third experiment, the reaction being carried out in a pressure flask immersed in a bath of boiling water for 1 hour, 7.4 g. of product (Cl, 14.9%) were obtained. This was dissolved in benzene, saturated with hydrogen chloride, and on distillation gave a liquid, b. p. 156—158°/12 mm. (Cl, 14.7%).

(k) Benzhydrol (50 g.) was boiled under reflux with concentrated hydrochloric acid (500 c.c.) for 2 hours. The cooled products were extracted with ether, dried, and the ether distilled under diminished pressure at room temperature. The oil (50 g.; Cl, 15.3%) so obtained was dissolved in some 250 c.c. of petroleum ether (b. p. 40—60°), but no solid separated on standing. The petroleum ether was completely removed by distillation at room temperature, excess of water added, and the mixture maintained at 25° for 3 weeks with

occasional shaking. The displacement of the halogen at the end of this period was still incomplete, and the mixture was therefore gently warmed until no further acidity developed. On cooling, the products solidified to a hard mass, which was filtered, washed with water, and dried (yield 45.5 g.). Crystallisation from petroleum ether gave a crop of 41.6 g., yielding benzhydrol (20.9 g.) and *s*-tetraphenyldimethyl ether (20.3 g.). From the petroleum-ether liquors on evaporation at room temperature a solid (3.35 g.) was obtained; on recrystallisation from petroleum ether, this gave a product (2.5 g.) which was separated into benzhydrol (0.8 g.) and *s*-tetraphenyldimethyl ether (1.6 g.). The residual liquors on evaporation at room temperature gave a small amount of solid, from which 0.1 g. of the ether was separated, and a yellow oil (ca. 0.5 c.c.) which completely decomposed on attempted distillation.

Reaction between s-Tetraphenyldimethyl Ether and Hydrochloric Acid.—(l) *s*-Tetraphenyldimethyl ether (10 g.) and *N*/2-hydrochloric acid (150 c.c.) were boiled under reflux for 8 hours. Solid was present all the time and 9.9 g. of ether were recovered.

(m) *s*-Tetraphenyldimethyl ether (50 g.) and concentrated hydrochloric acid (500 c.c.) were boiled under reflux for 1 hour. The products were cooled, extracted by ether, dried, and the solvent was removed on the water-bath. During the heating, the liquid darkened considerably (Found: Cl, 6.54%). The products on inoculation with *s*-tetraphenyldimethyl ether solidified to a stiff paste, which was filtered and washed with petroleum ether (b. p. 40—60°), *s*-tetraphenyldimethyl ether (10.5 g.) being thus obtained pure. The filtrate was distilled under diminished pressure, b. p. 145—170°/12 mm.; yield 25 g. (Found: Cl, 10.5%). A considerable amount of dark brown gum remained in the distilling flask, but the only product which was separated from this was *s*-tetraphenyldimethyl ether (1.7 g.). The above distillate (25 g.) was boiled with water for $\frac{1}{2}$ hour (reflux), but remained liquid on cooling. Addition of petroleum ether yielded a solid (6.7 g.) which gave benzhydrol (5.9 g.) and *s*-tetraphenyldimethyl ether (0.4 g.). The petroleum-ether solution was dried and distilled; b. p. 146—160°/14 mm.; yield, 10 g. A considerable amount of oil, which solidified to a hard mass, remained in the distilling flask, and this on crystallisation from alcohol gave *s*-tetraphenyldimethyl ether (3 g.). Phenylhydrazine (7 g.) and alcohol (20 c.c.) were added to the distillate (10 g.) and the solution was refluxed for 9 hours, but even on cooling it remained homogeneous, thus showing benzophenone to be absent. Excess of dilute hydrochloric acid was added and the products were distilled in steam; a pleasant-smelling oil was obtained, which was extracted with ligroin, dried, and distilled,

giving fractions (1) b. p. 129—135°/11 mm., 2 c.c.; (2) b. p. 135—155°/11 mm., 4 c.c.; a small amount of liquid remained. An authentic specimen of diphenylmethane distilled at 129—130°/11 mm., and remained liquid for a considerable time after distillation, but on seeding solidified to a hard mass of long, colourless needles. Fraction (1) was similarly treated, and its behaviour was identical.

(n) *s*-Tetraphenyldimethyl ether (50 g.) and concentrated hydrochloric acid (500 c.c.) were boiled under reflux for 4 hours. The cooled products were extracted by ether, dried, and the solvent was removed under diminished pressure at room temperature during 7 hours; yield 47.5 g. (Found: Cl, 12.4%). The addition of petroleum ether caused a colourless solid (6.2 g.) to separate on standing, giving *s*-tetraphenyldimethyl ether (5.7 g.) and benzhydrol (0.25 g.). The petroleum ether was removed under diminished pressure at room temperature, and the colour of the products darkened, although to a very much less degree than in the preceding experiment; yield, 40.5 g. (Found: Cl, 14.2%). The replacement of the halogen was carried out exactly as in the corresponding benzhydrol experiment, a colourless, crystalline solid (37 g.) being obtained. On crystallisation from light petroleum, this gave a crop (31 g.) which yielded *s*-tetraphenyldimethyl ether (11 g.) and benzhydrol (19.5 g.). On evaporation of the liquors at room temperature a pasty solid was formed, which was washed with petroleum ether; 3.5 g. remained, yielding 3.3 g. of *s*-ether. The liquors on evaporation gave 2.3 g. of oil, which, since it still contained diphenylchloromethane, was boiled with water; on cooling, it solidified to a pasty solid, from which were separated *s*-ether (0.7 g.) and benzhydrol (0.8 g.), whilst the distillate from the small quantity of residual oil was insufficient for further examination.

Kinetic Experiments.

In the following experiments, a weighed amount of diphenylchloromethane was dissolved in ethyl alcohol (prepared by refluxing and distilling commercial absolute alcohol over quick-lime); the required amounts of water (by volume) and of sodium hydroxide or sodium ethoxide solutions were added, at the temperature of experiment, and the volume in each case was made up to 100 c.c. with ethyl alcohol. The method of experiment was that described previously (*loc. cit.*, p. 455) and the results are expressed as before, except that titrations refer to 10 c.c. of solution against alcoholic sodium hydroxide (*N*/20) or alcoholic benzoic acid (*N*/20). In each case *k* is calculated from the formula $k = 2.3/t \cdot \log_{10} a/(a - x)$ for a unimolecular reaction, *t* throughout being expressed in minutes, and *a* being based on the first titre. Typical experiments showing

the extent of the variations amongst the individual values of k are given (1 and 2), and the complete results are then summarised.

(1) Diphenylchloromethane, 0.0906 mol./l.; water, 10% (by vol.); temp. 25.0°.

t .	Titre.	k .	t .	Titre.	k .
4	1.47	—	64	15.23	0.0294
14	5.87	0.0307	84	16.60	0.0301
24	8.87	0.0294	144	17.94	—
44	13.01	0.0296	1350	18.09	—

(2) Diphenylchloromethane, 0.0818 mol./l.; sodium hydroxide, 0.0880 mol./l.; water, 10% (by vol.); temp. 25.0°.

t .	Titre.	k .	t .	Titre.	k .
3	15.98	—	63	3.46	0.0301
13	12.32	0.0280	83	2.46	0.0291
23	9.40	0.0289	279	1.06	—
43	5.62	0.0294	1260	1.00	—

(3) Temp. 25.0°.

CHPh ₂ Cl (mol./l.).	Water (% by vol.).	NaOH (mol./l.).	NaOEt (mol./l.).	k .
0.0696	—	—	—	0.00341
0.0781	—	—	—	0.00349
0.0974	—	—	0.1297	0.00345
0.1167	—	—	0.2407	0.00354
0.1059	—	—	0.2315	0.00343
0.0733	—	0.0914	—	0.00395
0.0764	1	—	—	0.00468
0.0956	2	—	—	0.00638
0.1054	5	—	—	0.0115
0.0906	10	—	—	0.0298
0.0776	10	—	—	0.0294
0.0818	10	0.0880	—	0.0291
0.0811	10	0.0880	—	0.0293
0.0878	10	0.1760	—	0.0272
0.0845	10	0.1760	—	0.0277
0.0795	20	—	—	0.103

(4) Temp. 35.0°.

CHPh ₂ Cl (mol./l.).	Water (% by vol.).	NaOH (mol./l.).	k .	Temp. coeff. (10°).
0.0828	—	—	0.0101	2.98
0.0867	—	—	0.0101	
0.1942	—	—	0.0104	
0.0980	—	0.0982	0.0117	2.95
0.0818	—	0.1848	0.0116	

Summary.

(1) The displacement of the halogen from diphenylchloromethane at 25° in ethyl-alcoholic solution (lime-dried) and in aqueous ethyl-alcoholic solutions, both alone and in the presence of sodium hydroxide, yields a mixture of diphenylmethyl ethyl ether (main product) and benzhydrol.

(2) The velocity coefficients obtained for this displacement in ethyl-alcoholic solution alone, and also in the presence of sodium hydroxide and of sodium ethoxide, at 25° and at 35°, are those of a unimolecular reaction, the sodium hydroxide, sodium ethoxide, or their ions playing no direct part in the halogen displacement. Similar results are obtained in aqueous-alcoholic solutions.

(3) Benzhydrol gives *s*-tetraphenyldimethyl ether in good yield on being boiled with dilute hydrochloric acid. With increasing concentration of acid, the yield of *s*-tetraphenyldimethyl ether passes through a maximum, and the yield of diphenylchloromethane rises, becoming the main product of the reaction when concentrated acid is used.

(4) *s*-Tetraphenyldimethyl ether is unchanged on boiling with *N*/2-hydrochloric acid, but with concentrated acid it is largely converted to diphenylchloromethane. Diphenylchloromethane may be prepared readily in a pure condition and in good yield by the action of hydrogen chloride on *s*-tetraphenyldimethyl ether suspended in benzene.

(5) The experimental evidence under (1), (2), (3), and (4) is in accordance with the hypothesis of Nef that the reactions proceed through a phase $CPh_2<$, in which but two groups are momentarily attached to carbon. An alternative mechanism involving the $CHPh_2^+$ ion is also discussed.

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