The method of Schulze[8] for the determination of side chain chlorine was used. In certain cases the time of refluxing the halide with the alcoholic solution of silver nitrate was increased to two hours. Experiments with *p*- and *o*-chlorodiphenylcarbinol showed that the halogen in the ring was not removed by the solution of silver nitrate.

The ethyl alcohol used in the determination of velocity constants was purified in the usual way and dried over lime. The density of the samples used varied from d_4^{25}, 0.78501 to 0.78511. The *iso*propyl alcohol (from petroleum) was purified by the method of Lebo.[9] It boiled at 82.3–82.4°. The samples used varied in density from d_4^{25}, 0.7824 to 0.7821.

Summary

1. The velocity constants of the reaction between ethyl alcohol and the following derivatives of diphenylchloromethane have been determined: *o*-chloro, *p*-chloro, *p,p'*-dichloro, *p*-bromo, *p*-methyl, *p*-phenyl. Similar constants for the reactions between ethyl alcohol and benzyl phenylchloromethane, *iso*propyl alcohol and diphenylchloromethane, and *iso*propyl alcohol and *p,p'*-dichlorodiphenylchloromethane have been determined.

2. The effect of substituents in diphenylchloromethane on the reactivity of the side chain halogen is marked. Halogen atoms depress reactivity, the greatest effect resulting from substitution in the ortho position. The methyl and phenyl radicals increase reactivity, the greatest effect resulting from substitution in the para position.

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THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. V. THIRD CONTRIBUTION ON THE CARBON–CHLORINE BOND: THE RATES OF THE REACTIONS OF CERTAIN DERIVATIVES OF DIPHENYLCHLOROMETHANE WITH ETHYL ALCOHOL

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In this paper are reported the results of the determination of the rates at which nine derivatives of diphenylchloromethane react with ethyl alcohol. The compounds which had not been previously prepared were selected in such a way that the results could be used along with those obtained by Banta[2] in determining the effect of the position of a substituent on the reactivity of the carbon–chlorine bond.

In some of the compounds the chlorine atom was exceedingly labile.

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[8] Schulze, *Ber.*, **17**, 1675 (1884).

[9] Lebo, THIS JOURNAL, **43**, 1005 (1921).

[1] From the thesis of John Twiss Blake presented in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, 1924.

[2] Norris and Banta, THIS JOURNAL, **50**, 1804 (1928).

The determination of the very high reaction velocities was made possible only as a result of the use of the rapid method of measuring the concentration of the reacting substances by means of the conductivity of the solution. Even with this aid it was necessary to make observations toward the end of the reaction, and as a result the first order constant could not be calculated by using the usual formula. When the method of treating the results in the way described by Morton[3] was used satisfactory constants were obtained from the changes in concentration up to the point where over 80% of the substances had reacted.

Of the substituents studied the CH_3O and C_6H_5O groups in the para position were found to have the greatest effect in increasing the reactivity of the carbon–chlorine bond. The velocity constant of the reaction between ethyl alcohol and *p*-phenoxydiphenylchloromethane was 31.6 times that of diphenylchloromethane. The *p*-methoxy derivative contained such an active carbon–chlorine bond that the true velocity constant of the reaction between it and ethyl alcohol has not yet been determined. An examination of the reaction of the chloride in *iso*propyl alcohol at 0° indicates that the carbon–chlorine bond in *p*-methoxydiphenylchloromethane is over 1000 times as reactive as is the same bond in diphenylchloromethane. Both the *p*-phenoxy and the *p*-methoxy compounds contain chlorine atoms that are more reactive toward ethyl alcohol than the chlorine atom in benzoyl chloride. The constant of the reaction with *p*-phenoxydiphenylchloromethane is about 20 times that of the constant in the case of benzoyl chloride, both being determined at 25°. In these cases an oxygen atom singly linked to the ring in the para position has a greater effect on the carbon–chlorine bond than the same atom doubly linked to the carbon with which the chlorine is combined. These substitution products of an alkyl chloride are more reactive than benzoyl chloride.

When *p*-methoxydiphenylchloromethane in the form of drops is placed under cold water it is converted into the carbinol in less than one minute. Under the same conditions benzoyl chloride reacts very slowly. Both the *p*-methoxy and the *p*-phenoxy derivatives are colored. It is possible that molecular rearrangements have taken place and that the compounds do not have the structure assigned to them or are in equilibrium with quinoid forms.[4] It has been shown, however, that when the methoxy compound reacts with alcohol the chlorine atom is replaced and hydrochloric acid is formed in the normal way. The colored chloride gives the colorless carbinol when it reacts with water.

When the hydrogen of the benzene ring of diphenylchloromethane is replaced by either methyl or phenyl, the lability of the carbon–chlorine

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[3] Norris and Morton, THIS JOURNAL, **50,** 1795 (1928).

[4] Bistrzycki and Herbst, *Ber.*, **36,** 2335 (1903).

bond is increased. It was inferred from these facts that α-naphthylphenylchloromethane would react with alcohol more rapidly than does diphenylchloromethane. The constant of the former reaction was found to be about 7 times that of the latter.

The values of the velocity constants determined are given in Table I. The measurements were made in solutions less than 0.1 *N*. A fuller condensation of the effect of structure in the reactivity of the carbon–chlorine bond in the derivatives of diphenylchloromethane is given in the paper by Norris and Banta,[5] in which all the results are brought together.

TABLE I

FIRST ORDER VELOCITY CONSTANT OF THE REACTIONS BETWEEN ETHYL ALCOHOL AND CERTAIN DERIVATIVES OF DIPHENYLCHLOROMETHANE

Temperature, 25.0°. Time in minutes

Derivative of diphenylchloromethane	*K*	Average *K*
m-Chloro	0.0000583, 0.0000606, 0.0000590	0.0000593
p-Bromo	.000859, 0.000867, 0.000898, 0.000918	.000883
m-Methyl	.00545, 0.00563, 0.00563, 0.00544	.00554
o-Methyl	.00743, 0.00754, 0.00775, 0.00785	.00764
p-Ethyl	.0545, 0.0550, 0.0570, 0.0569	.0558
o-Methoxy	.251, 0.252, 0.239, 0.246	.247
p-Phenoxy	.846, 0.833, 0.842, 0.851	.843
p,p'-Dimethyl	1.09, 1.06, 1.16	1.10
α-Naphthylphenylchloromethane	0.0183, 0.0196, 0.0200	0.0193

Preparation and Properties of Compounds Used

A brief account of the methods by which the compounds used in the determination of velocity constants were prepared is given below. Details are indicated only in the case of compounds not heretofore described. Especial care was taken to have each compound free from structural isomers.

The derivatives of diphenylchloromethane were prepared from the corresponding carbinols by treatment of the latter, dissolved in petroleum ether and benzene, with hydrogen chloride. Anhydrous calcium chloride was placed in the solution to react with the water formed. After the solution was poured off from the solid, fresh calcium chloride was added and the treatment with hydrogen chloride repeated. The solution was filtered and evaporated at room temperature under diminished pressure. When the chloride was an oil the solution was evaporated to constant weight and the residue was then analyzed. Care had been taken to use solvents that left no residue on evaporation. The petroleum ether used was freed from unsaturated compounds by treatment with bromine, washing with alkali and subsequent distillation. The portion boiling between 35 and 60° was used. The compounds prepared in this way were obtained in a high degree of purity.

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[5] Norris and Banta, THIS JOURNAL, **50**, 1804 (1928).

o-**Methyldiphenylchloromethane.**—*o*-Methyldiphenylcarbinol (m. p. 93°), prepared by the Grignard reaction from *o*-bromotoluene (b. p. 58–59° at 13 mm.) and benzaldehyde, was converted into the chloride in the way described above. The latter crystallizes in colorless plates (m. p. 40–40.5°) and is quite soluble in the usual solvents; Cl formed, 16.30 and 16.37%; calcd., 16.37%.

p-**Methoxydiphenylchloromethane.**—Fifteen grams of *p*-methoxybenzophenone (m. p. 62°) prepared from anisole and benzoyl chloride was reduced to the corresponding alcohol by refluxing with 10 g. of sodium hydroxide, 10 g. of zinc dust and 100 cc. of alcohol for two and one-half hours. The solution was filtered and poured into ice water. The solid after crystallization from dilute alcohol melted at 59–60°; yield, 10 g. The melting point of the compound prepared in other ways[6,7] is given as 58 and 60°.

The carbinol was converted by means of hydrogen chloride into *p*-methoxydiphenylchloromethane. During its formation a reddish color developed which could not be removed by treatment of the solution with bone black. The chloride was obtained as a red oil which reacted rapidly with water. In less than one minute a sample of it was converted into the colorless carbinol. Analyses of the oil gave 15.23 and 15.18% chlorine; calcd., 15.24%.

p,p'-**Dimethyldiphenylchloromethane.**—*p,p'*-Dimethylbenzophenone (m. p. 92°) prepared from carbonyl chloride and toluene[8] was reduced in alcoholic solution with zinc and sodium hydroxide to the carbinol (m. p. 71°). The latter was converted by hydrogen chloride into *p,p'*-dimethylchloromethane, which crystallizes from petroleum ether in white prisms (m. p. 45–46°); Cl found, 15.35 and 15.39%; calcd., 15.37%.

p-**Phenoxydiphenylchloromethane.**—Ten grams of *p*-phenoxybenzophenone (m. p. 71°) prepared from diphenyloxide and benzoyl chloride[9] was heated for two hours on a water-bath with 100 cc. of alcohol, 10 g. of sodium hydroxide and 10 g. of zinc dust. The filtered solution was poured into ice water. The colorless oil was extracted with ether and the solution dried. On long standing *p*-phenoxydiphenylcarbinol, which has not been described, crystallized in white rosets which melted at 75°.

The carbinol was converted by the usual procedure into the chloride, which crystallizes in needles possessing a pale orange color; m. p. 49–50°; Cl found, 12.00 and 11.96; calcd., 12.02%.

p-**Ethylbenzophenone.**—*p*-Ethylbenzophenone was prepared from ethylbenzene and benzoyl chloride.[10,11] After four fractionations the ketone boiled at 328–330°. Smith gives 330–332° as the boiling point and Vorländer gives 328°. A sample of the ketone gave on oxidation *p*-ethylbenzoic acid (m. p. 192°).

p-**Ethyldiphenylcarbinol** has not been described. It was prepared from the ketone by the method outlined above and was obtained as an oil which was converted into white needles (m. p. 33°) when a solution of the oil in petroleum ether evaporated slowly.

p-**Ethyldiphenylchloromethane** which was prepared from the carbinol is a colorless liquid which boils at 122° (1–2 mm.) and shows a slight purple fluorescence. It did not solidify at −15°; Cl found, 14.92 and 14.97%; calcd., 15.37%.

o-**Methoxydiphenylchloromethane.**—*o*-Methoxybenzaldehyde (b. p. 241–242°) was prepared by a method similar to that of Clarke[12] from salicylic aldehyde and methyl sulfate. The aldehyde was converted into *o*-methoxydiphenylcarbinol (m. p. 139°)

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[6] Busch and Leefhelm, *J. prakt. Chem.*, **77**, 20 (1908).

[7] Cohen, *Rec. trav. chim.*, **38**, 122 (1919).

[8] Ador and Crafts, *Ber.*, **10**, 2174 (1877).

[9] Kipper, *Ber.*, **38**, 2492 (1905).

[10] Smith, *Ber.*, **24**, 4029 (1891).

[11] Vorländer, *Ber.*, **44**, 2462 (1911).

[12] H. T. Clarke, private communication.

through the use of the Grignard reaction.[13] The carbinol yielded *o*-methoxydiphenylchloromethane when treated with hydrogen chloride. The compound is a pale pink oil; Cl found, 15.14 and 15.10%; calcd., 15.24%.

α-Naphthylphenylchloromethane.—α-Naphthylphenyl ketone (m. p. 74°)[14] was reduced in the usual way to the carbinol (m. p. 85°). The latter yielded the chloride, which crystallized from ligroin in needles (m. p. 64–64.5°); Cl found, 13.97 and 14.01%; calcd., 14.08%.

***p*-Bromodiphenylchloromethane.**—It was found impossible to prepare in a pure condition *p*-bromodiphenylcarbinol by reducing the corresponding ketone. Apparently some of the halogen is removed during the reaction. The carbinol was prepared with a good yield from *p*-bromobenzaldehyde by the Grignard reaction. The compound as crystallized from dilute alcohol melted at 63°. It was converted into *p*-bromodiphenylchloromethane, which proved to be a colorless oil; Cl found, 12.53 and 12.57%; calcd., 12.59%.

***m*-Methyldiphenylchloromethane.**—*m*-Bromotoluene[15] (b. p. 183–184°) was used with benzaldehyde to prepare *m*-methyldiphenylcarbinol (m. p. 52°). The melting point agrees with that obtained with the product formed by reducing *m*-methylbenzophenone with sodium amalgam[16], and not with that of a substance described as this compound by E. and O. Fischer.[17] *m*-Methyldiphenylchloromethane prepared from the carbinol is a colorless oil; Cl found, 16.20 and 16.22; calcd., 16.37%.

***m*-Chlorodiphenylchloromethane.**—*m*-Chlorobenzoyl chloride was prepared by the method of Hope and Riley.[18] The crude product was distilled at 10 mm. pressure and the fraction boiling below 100° was fractionated four times at atmospheric pressure. The chloride boiled at 224–227°. Hantzsch[19] gives the boiling point as 225°. The compound was used in making *m*-chlorobenzophenone (m. p. 81°), which was reduced to the carbinol (m. p. 39–40°) in the usual way. Koopal[20] gives 40° as the melting point.

m-Chlorodiphenylchloromethane is a colorless oil that did not solidify at $-10°$; Cl found, 14.80 and 14.87%; calcd., 14.96%.

The ethyl alcohol used had the specific gravity 0.78506^{25}_{4}, which agrees with the value given by the Bureau of Standards.

Summary

1. The properties and methods for the preparation of the following new derivatives of diphenylchloromethane are described: *o*-CH_3, *m*-CH_3, *o*-CH_3O, *p*-CH_3O, *p,p*-$(CH_3)_2$, *p*-C_6H_5O, *p*-C_2H_5, *m*-Cl and *p*-Br. α-Naphthylphenylchloromethane is also described.

2. The first order velocity constants of the reactions between ethyl alcohol and the chlorides listed above have been determined.

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[13] Stoermer and Friderici, *Ber.*, **41**, 332 (1908).

[14] Elbs, *J. prakt. Chem.*, [2] **35**, 502 (1887).

[15] Bigelow, THIS JOURNAL, **44**, 2012 (1922).

[16] Montagne and Charante, *Rec. trav. chim.*, **31**, 348 (1912).

[17] E. and O. Fischer, *Ann.*, **194**, 265 (1878).

[18] Hope and Riley, *J. Chem. Soc.*, **121**, 2515 (1922).

[19] Hantzsch, *Ber.*, **24**, 57 (1891).

[20] Koopal, *Rec. trav. chim.*, **34**, 115 (1915).