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The Reductive Coupling Reactions of Some Chloromethylbenzene Derivatives with Iron(II) and Copper(I) Complexes[*1]

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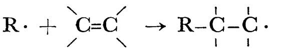
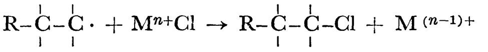
The reductive coupling reactions of some chloromethylbenzene derivatives with ferrous and cuprous chloride in ethanol or in acetonitrile and the effect of some additives on this reaction have been investigated. Benzotrichloride has been reduced selectively to tolan tetrachloride with ferrous chloride, while with cuprous chloride-ethylenediamine (a stronger reductant than ferrous chloride) mixtures of tolan and tolan dichloride or tolan tetrachloride are obtained depending on the condition. Similarly benzal chloride, diphenylmethyl chloride and diphenyldichloromethane are also reduced to give coupling products. In case of ferrous chloride the addition of ethylenediamine or pyrophosphoric acid raises the yield considerably and in case of cuprous chloride selection of the ratio, organic halide: copper (I): ethylenediamine, makes it possible to control the product distribution. The reaction mechanism and the effect of the additives are discussed.

Progress in the study of the iron- or copper ion catalyzed organic reactions[1-12] has revealed some catalytic features of these ions. As an example, the iron- or copper ion catalyzed addition of organic chloride to olefins[1,2] can be understood through the redox-transfer chain mechanism, metal ion being a chlorine-atom transfer agent.

$$\mathrm{RCl} + \mathrm{M}^{(n-1)+} \rightarrow \mathrm{R}\cdot + \mathrm{M}^{n+}\mathrm{Cl} \qquad (1)$$



$$\mathrm{R}\cdot + \mathrm{\gt C{=}C\lt} \rightarrow \mathrm{R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot} \qquad (2)$$



$$\mathrm{R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot} + \mathrm{M}^{n+}\mathrm{Cl} \rightarrow \mathrm{R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Cl} + \mathrm{M}^{(n-1)+} \qquad (3)$$

Reaction (3) is a relatively well studied "ligand transfer oxidation" process.[13-16] On the other hand step (1), which is just the reverse reaction of step (3), may be named tentatively "ligand transfer reduction" and about this much is left to be learned.

From this point of view we investigated previously the reductive coupling reaction of benzyl chloride by copper(I) complexes.[17] In this paper, application of this reductive coupling reaction with ferrous or cuprous chloride to some polyhalomethylbenzene derivatives and the effect of some additives will be studied.

Results and Discussion

Reductive Coupling by Ferrous Chloride. Simple ferrous ion is only a weak reductant compared with iron metal[18-20] and little is known

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[*1] Oxidation-Reduction Reactions by Transition Metal Complexes. V.

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about the interaction of ferrous ion with organic halides except for the case of ferrous porphyrin.[21] Actually, benzyl chloride does resist ferrous ion. It is well known, however, that the replacement of hydrogen atom attached to methyl carbon by phenyl group or chlorine atom considerably activates the molecule, and several polychloromethylbenzene derivatives were reduced by ferrous chloride. The reactions were carried out mostly in ethanol solvent and in a few cases in acetonitrile, under a nitrogen atmosphere and in the range from 70°C to reflux temperature. The results with benzotrichloride, benzal chloride, diphenyldichloromethane and diphenylmethyl chloride are tabulated in Tables 1—5.

Ethanol is a good solvent for both reactants but the ethanolysis of organic halides is unavoidable and always competes with the reduction reaction. In the case of acetonitrile homogeneity can be reached only at reflux temperature.

Table 1. REDUCTIVE COUPLING OF BENZOTRICHLORIDE BY FERROUS CHLORIDE TETRAHYDRATE IN ETHANOL

$C_6H_5CCl_3$: 2.00×10^{-2} mol
Solvent C_2H_5OH: 50—60 m*l*
Reaction temperature: 72.0 ± 3.0°C

Additive	$C_6H_5CCl_3$: $FeCl_2 \cdot 4H_2O$: additive (mole ratio)	Reaction time hr	$C_6H_5 \cdot CCl_2 \cdot CCl_2 \cdot C_6H_5$[a] %
—	1 : 1	6	49
	1 : 3	6	67
en[b]	1 : 1 : 1	4	54
	1 : 1 : 2	4	74
	1 : 1 : 3	4	87
$H_4P_2O_7$	1 : 1 : 0.5	4	70
	1 : 1 : 1	4	81

a) In every run ethyl benzoate was recognized as a solvolysis product.
b) "en" is ethylenediamine and in this case the reaction system is heterogeneous.

Table 2. REDUCTIVE COUPLING OF BENZOTRICHLORIDE BY FERROUS SALTS

$C_6H_5CCl_3$: 2.00×10^{-2} mol
Ferrous salt: 2.00×10^{-2} mol
Solvent: 50 m*l*

Ferrous salt	Solvent	Temp. °C	Reaction time hr	$C_6H_5 \cdot CCl_2 \cdot CCl_2 \cdot C_6H_5$ %
$FeCl_2 \cdot 4H_2O$	CH_3CN	82	6	71[a]
$FeSO_4 \cdot 6H_2O$[b]	C_2H_5OH	71	2.5	8.1[c]
$FeCl_2 \cdot 4H_2O$	C_2H_5OH	r.t.	70	9.8[c]

a) 17% of benzoic acid was obtained other than coupling product.
b) Heterogeneous system.
c) Ethyl benzoate and unreacted benzotrichloride were recognized.

Table 3. REDUCTIVE COUPLING OF DIPHENYLDICHLOROMETHANE BY FERROUS CHLORIDE TETRAHYDRATE IN ETHANOL

$FeCl_2 \cdot 4H_2O$: 4.00×10^{-2} mol
$(C_6H_5)_2CCl_2$: 2.00×10^{-2} mol
C_2H_5OH: 50—70 m*l*, 71.0 ± 1.0°C, 3 hr

Additive	Fe(II) : additive (mole ratio)	$(C_6H_5)_2C{=}C(C_6H_5)_2$[a] %
—	—	39
en[b]	1 : 2	67
$H_4P_2O_7$	1 : 0.5	36

a) Benzophenone was also obtained as solvolysis product.
b) heterogeneous.

Table 4. REDUCTIVE COUPLING OF BENZAL CHLORIDE BY FERROUS COMPLEXES

$C_6H_5CHCl_2$: 2.00×10^{-2} mol
solvent: 50—60 m*l*, 3 hr

Additive	$C_6H_5CHCl_2$: $FeCl_2 \cdot 4H_2O$: additive (mole ratio)	Solvent	Temp. °C	$C_6H_5 \cdot CHCl \cdot CHCl \cdot C_6H_5$ %
—	1 : 1.5	C_2H_5OH	70	0[a]
$H_4P_2O_7$[b]	1 : 2 : 1	C_2H_5OH	70	0[a]
en[b]	1 : 2 : 2	C_2H_5OH	70	4
en[b]	1 : 1 : 3	C_2H_5OH	78[c]	8
—	1 : 1	CH_3CN	82[c]	trace[d]
en[b]	1 : 1 : 3	CH_3CN	82[c]	3[e]

a) Hydrolyzed benzaldehyde and unreacted benzal chloride were recognized.
b) heterogeneous
c) under reflux
d) all converted to benzaldehyde
e) Organic substance other than coupling product was original benzal chloride.

Table 5. REDUCTIVE COUPLING OF DIPHENYLMETHYL CHLORIDE BY FERROUS AND CUPROUS CHLORIDE

$(C_6H_5)_2CHCl$: 2.00×10^{-2} mol
metal salt: 2.00×10^{-2} mol, CH_3CN; 50 m*l*
under reflux, 3 hr

Metal salt	$(C_6H_5)_2CHCl$: Metal salt : en (mole ratio)	Product (%)	
		$(C_6H_5)_2CH$-$CH(C_6H_5)_2$	$(C_6H_5)_2CH$-$NHCOCH_3$
$FeCl_2 \cdot 4H_2O$[a]	1 : 1	51	50
$FeCl_2 \cdot 4H_2O$	1 : 1 : 2	57[b]	
CuCl	1 : 1	0	
CuCl	1 : 1 : 2	100	

a) 1.00×10^{-2} mol of $(C_6H_5)_2CHCl$ was used.
b) 39% of hydrolyzed benzhydrol was obtained.

Reduction Products. From Tables 1 and 2 it can be seen that for benzotrichloride the yield of coupling product increases with increase of ferrous ion concentration, and the additive such as ethylenedi-

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[21] C. E. Castro, *J. Amer. Chem. Soc.*, **86**, 2310 (1964).

amine (en) or pyrophosphoric acid increases the yield considerably. The product is always tolan tetrachloride showing that ferrous ion is a weak reductant and additives have no marked effect on reducing power of ferrous ion.

$$2C_6H_5CCl_3 + 2Fe^{II}Cl_2 \rightarrow C_6H_5CCl_2\cdot CCl_2C_6H_5 + 2Fe^{III}Cl_3 \qquad (4)$$

Low yield in the case of ferrous sulfate seems to be due to the insolubility of the salt.

Table 3 contains the result of diphenyldichloromethane. It is noted that the product is tetraphenylethylene, being all chlorine atom split off. It seems that tetraphenylethylene is formed by step-wise reduction, that is, tetraphenyldichloroethane which is formed intermediately is further reduced because of steric and electronic instability.

$$2(C_6H_5)_2CCl_2 \xrightarrow{2Fe^{II}} (C_6H_5)_2CClCCl(C_6H_5)_2 \xrightarrow{2Fe^{II}} (C_6H_5)_2C{=}C(C_6H_5)_2 \qquad (5)$$

However, the possibility of the formation of diphenylcarbene cannot be ruled out since this carbene is known to be fairly stable.[22] It was reported recently that dichlorocarbene was produced from tetrachloromethane and ferrous chloride.[1e]

As seen from Table 4 benzal chloride can not be reduced by ferrous chloride only. However, when ethylenediamine is added as an additive, reduction takes place and stilbene dichloride is obtained though the yield is poor. Some discussions on this effect will be made later.

Diphenylmethyl chloride is also reduced to produce tetraphenylethane (Table 5). It is of interest to note that in case of the use of ferrous chloride *tetrahydrate* in acetonitrile *N*-benzhydrylacetamide is also produced. Evidently this amide results from interaction of diphenylmethyl chloride or its hydrolysis product, benzhydrol with acetonitrile by the aid of ferrous or ferric chloride as a Lewis acid (this is a variation of well known Ritter reaction[23]).

These reactions give only coupling products as the reduction products. No hydrogenated materials are detected in contrast to the case of chromous ion.[24]

Effect of Additives. As pointed out before, when ethanol is used as solvent the solvolysis reaction of organic halides inevitably competes the reduction reaction (Tables 1—4). In addition ferric chloride is known to be a good catalyst for hydrolysis of organic halides. In fact preliminary experiment showed that a) at 70.5°C benzotrichloride is solvolyzed in ethanol and after 4 hr about 20% of the halide is converted to ethyl benzoate b) addition of 1/10 equiv. ferric chloride increases the solvolysis rate twice. If this solvolysis is suppressed by some means, increase of the yield of coupling product will be expected. As mentioned before, additives such as ethylenediamine and pyrophosphoric acid increase the yield of coupling products considerably. It seems reasonable that the primary effect of these additives lies in the suppression of the solvolysis of the organic substrates. Additives which can coordinate to ferric (or ferrous) ion will occupy the catalytic sites and suppress the solvolysis. The reaction of benzal chloride in acetonitrile (Table 4) supports this idea. Here in the presence of ferrous chloride *tetrahydrate* benzal chloride is completely converted to benzaldehyde (hydrolysis product of benzal chloride). But when ethylenediamine is added the starting material is recovered except for 3% of coupling product. This means that ethylenediamine expels water from the metal ion sphere and suppresses hydrolysis.

It may also be necessary to consider some other factors on the effect of ethylenediamine. As seen in Table 4 addition of ethylenediamine gives rise to form stilbene dichloride from benzal chloride which can not be reduced by ferrous ion only. This suggests the coordination of ethylenediamine to ferrous ion enhances the reducing power of the ion just as in the case of cuprous chloride (see below). Instability of Fe(III) complexes of amines is generally explained as Fe(III) state having half-filled d^5 system and, therefore, no CFSE in high spin state. Recently, however, ethylenediamine complex of ferric chloride—$Fe(en)_3Cl_3$—was reported to be synthesized and have spin-paired d^5 system.[25] Thus, it is not improbable to conceive that ethylenediamine has some coordination effect.

Some comments should be made on the possibility of the interaction of the organic halides with ethylenediamine as the reaction of amines with organic halides are fairly well known. Actually products which were thought to be formed from organic halides and ethylenediamine were detected. But they are only trace amount and supplementary experiments on the ethanolysis rate of benzotrichloride showed ethylenediamine has practically no effect on the rate. Moreover electronic spectra of benzotrichloride in ethanol does not change on addition of ethylenediamine in contrast to carbon tetrachloride which forms charge-transfer complexes with some amines.[26,27] These facts indicate that there is no need to consider the specific interaction.

Reductive Coupling by Cuprous Chloride.

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[26] D. P. Stevenson and G. M. Coppinger, *ibid.*, **84**, 149 (1962).

[27] W. J. Lautenberger, E. N. Jones and J. G. Miller, *ibid.*, **90**, 1110 (1968).

Cuprous chloride as well as ferrous chloride is only a weak reductant. Still it may be surprising that even diphenylmethyl chloride can not be reduced in acetonitrile. In dimethyl sulfoxide solvent, on the other hand, benzal chloride and benzotrichloride were reported to give coupled products by cuprous chloride.[28)] Therefore this unusual inertness of cuprous chloride is attributable to a specific interaction with acetonitrile. In fact redox potential of Cu^I-Cu^{II} couple shows clearly stability of low valent state.[29,30)]

As reported by us previously,[17)] however, addition of ethylenediamine enhances the reducing power of cuprous ion strikingly and bibenzyl has been obtained from benzyl chloride. Here some application of this reaction is made and the results are in Tables 5—7. From diphenylmethyl chloride 100% yield is obtained, whereas the yield does not exceed 80% in case of benzal chloride and benzotrichloride. Probably side reactions leading to resinous products have occurred partly by relatively activated Cu(I) - ethylenediamine system.

TALEE 6. REDUCTIVE COUPLING OF BENZOTRICHLORIDE BY CUPROUS CHLORIDE-ETHYLENEDIAMINE IN ACETONITRILE

$C_6H_5CCl_3$: 2.00×10^{-2} mol

CH_3CN 50 m*l*, 82°C, 1 hr, heterogeneous

$C_6H_5CCl_3$: CuCl : en (mole ratio)	Product (%)		
	$C_6H_5CCl_2$-$CCl_2C_6H_5$	$C_6H_5\cdot CCl$= $CCl\cdot C_6H_5$[b)]	$C_6H_5C\equiv CC_6H_5$
1 : 1 : 1	79	—	—
1 : 3 : 3[a)]	—	47	8
1 : 3 : 6	—	54	5

a) 5.00×10^{-2} mol of benzotrichloride and 100 m*l* of acetonitrile were used.
b) mixture of *cis*- and *trans*-isomer.

TABLE 7. REDUCTIVE COUPLING OF BENZAL CHLORIDE BY CUPROUS CHLORIDE-ETHYLENEDIAMINE IN ACETONITRILE

$C_6H_5CHCl_2$: 2.00×10^{-2} mol

CH_3CN 50 m*l*, 82°C, 1 hr, heterogeneous

$C_6H_5CHCl_2$: CuCl : en (mole ratio)	Product (%)	
	C_6H_5CHCl-$CHClC_6H_5$	*trans*-C_6H_5CH=CHC_6H_5
1 : 1 : 1	10[a)]	—
1 : 2 : 2[b)]	—	50
1 : 2 : 4	—	65

a) Unreacted benzal chloride was recognized.
b) 5.00×10^{-2} mol of benzal chloride and 100 m*l* of acetonitrile were used.

It is of interest to note that selection of the ratio, organic halide: cuprous chloride: ethylenediamine, can control the product distribution (Tables 6 and 7). This also suggests that the reaction proceeds stepwise, that is, from benzotrichloride tolan tetrachloride is produced first and this tetrachloride is again reduced to dichloride in the presence of excess active reductant.

$$2C_6H_5CCl_3 \xrightarrow{2Cu(I)\text{-en}} C_6H_5CCl_2\text{–}CCl_2C_6H_5 \xrightarrow{2Cu(I)\text{-en}} C_6H_5CCl{=}CClC_6H_5 \qquad (6)$$

As shown in a previous report,[17)] copper complexes which have been taken out after the reaction are $Cu^{II}(en)_nCl_2$ ($n=1$ or 2), and this shows that, in this case too, cuprous complexes of the type $Cu^I(en)_nCl$ are the intrinsic reagent. Such reactivity may reflect the effect of ligands on redox potential[31)] (see Ref. 17).

An Approach to Reaction Mechanisms. From the mechanism of ligand transfer oxidation by ferric or cupric chloride, the most plausible mechanism of the reduction seems to be the reverse process of the oxidation as follows (in the following equations iron ion is used as metal ion for convenience).[1e,17,32)]

$$RCl + Fe^{II}Cl_2 \rightleftharpoons RCl\cdot Fe^{II}Cl_2 \qquad (7)$$

$$RCl\cdot Fe^{II}Cl_2 \rightarrow R\cdot ClFe^{III}Cl_2 \qquad (8)$$

A kinetic study of the reduction of benzotrichloride by ferrous chloride *tetrahydrate* in ethanol has shown that plots of the initial rate of disappearance of Fe(II) *vs.* both initial concentration of organic halide and ferrous ion have first order dependence (Fig. 1), and the rate law is written as follows.

$$R = k[RCl][Fe(II)] \qquad (9)$$

This is compatible with the mechanistic scheme if we take step (8)—electron transfer or in other word chlorine transfer step—as rate determining step.

Another information to support this scheme is available from electronic spectra of cuprous chloride. On addition of benzotrichloride to the system of cuprous chloride - acetonitrile new absorption mixima appear at 310 and 463 mμ (75°C, under nitrogen). The absorption at the same wavelength is also observed in the case of benzal chloride. The fact that these absorption maxima

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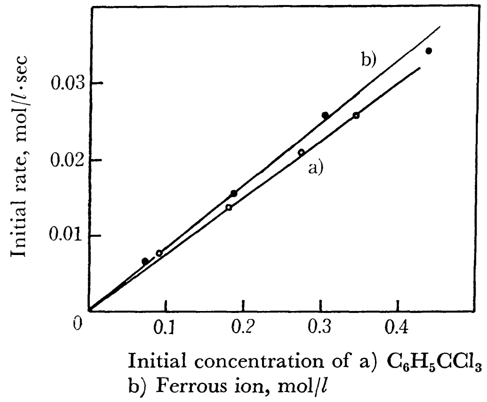

Fig. 1. Rate of reduction of benzotrichloride by ferrous chloride tetrahydrate.
a) $[Fe(II)]_0 = 0.30 \pm 0.01$ mol/l, 71±1°C
b) $[C_6H_5CCl_3]_0 = 0.35 \pm 0.01$ mol/l, 71±1°C

are the same with both organic halides suggests that the absorption is caused from the interaction between cuprous chloride and acetonitrile with the help of organic halide but it is also possible that the interaction between cuprous chloride and halogen atom of organic chloride is causative of the band. At any rate formation of intermediate complex between organic halide and cuprous chloride is indicative and in case of cuprous ion, unlike ferrous ion, electron transfer in the complex may be sustained.

The latter part of the reaction path is more complicated.[32,33] The formation of cupling products suggests radical feature of the reaction, whereas absence of hydrogen atom abstration products makes it uncertain. It should be noted also that solvent effect on product yield was hardly appreciable in the previous study.[17] From these facts the existence of radical in its free state seems unacceptable. Even if such a radical species is formed intermediately, it may be trapped by ferrous ion immediately (see Ref. 17).

Experimental

Materials. Reagent grade ferrous chloride tetrahydrate, ferrous sulphate hexahydrate and ferric chloride hexahydrate were used without further purification. As the hydration number of ferrous chloride was not accurately 4, Fe(II) equivalent was determined by ceric titration method. Reagent grade anhydrous cuprous chloride was further purified by the usual method.

Reagent grade benzotrichloride and diphenyldichloromethane and first grade benzal chloride, checked by NMR and gas chromatography, were used without further purification. Diphenylmethyl chloride was prepared from benzhydrol by the modification of Grice's method[34] for the preparation of *p*-methoxybenzyl chloride. Ethylenediamine (reagent grade) was distilled and used. Pyrophosphoric acid was used without further purification.

Absolute ethanol was purified by the conventional method and acetonitrile was purified according to O'Donnell's method.[35]

Typical Reaction Procedure. Ferrous or cuprous chloride (2.00×10^{-2} mol for example) was dissolved in 40 m*l* of absolute ethanol or acetonitrile in a four-necked, 50 m*l*, round-bottomed flask equipped with a 30 cm Dimroth condenser, a nitrogen inlet, a thermometer, a dropping funnel and a magnetic stirrer. The solution was then swept with oxygen-free nitrogen and heated to the required temperature. To this a solution of organic halide (2.00×10^{-2} mol) and, if necessary, ethylenediamine or pyrophosphoric acid in 10 m*l* solvent was added through the dropping funnel. The reaction was continued for required time under nitrogen stream.

Product Analyses. *A. Reduction of Benzotrichloride by Ferrous Chloride Tetrahydrate.* When the reaction was carried out in homogeneous system in ethanol solvent, the reaction mixture was cooled and 200 m*l* of water was added. The precipitated organic substance was filtered off and the filtrate was extracted with benzene, dried on sodium sulfate, concentrated to about 5 m*l* volume and the precipitated organic substance was also filtered and combined with the former. The filtrate was analyzed by g.l.c. to check the unreacted benzotrichloride and the solvolysis product, ethyl benzoate. The organic product was dried *in vacuo*, weighed for crude product yield and analyzed by IR, NMR, mp and also elementary analysis after recrystallization. The product was tolan tetrachloride, $C_6H_5 \cdot CCl_2CCl_2 \cdot C_6H_5$, mp 162.5—163.0°C (Found: C, 52.65; H, 3.13; Cl, 44.59%. Calcd: C, 52.54; H, 3.15; Cl, 44.31%). When the reaction mixture was heterogeneous insoluble iron complexes were filtered, washed four times with 50 m*l* hot benzene and the combined benzene solution was washed with water, dried on sodium sulfate, concentrated to about 5 m*l* volume and analyzed. When acetonitrile was used as solvent the reaction mixture was treated as in section D and the extracted benzene layer was again extracted by aqueous sodium bicarbonate for benzoic acid.

B. Reduction of Diphenyldichloromethane by Ferrous Chloride Tetrahydrate in Ethanol. Reaction mixture was treated as above. The product was 1,1,2,2-tetraphenylethylene, $(C_6H_5)_2C{=}C(C_6H_5)_2$, mp 223.5—224.0°C (Found: C, 93.80; H, 5.82%. Calcd: C, 93.94; H, 6.06%).

C. Reduction of Benzal Chloride by Ferrous Chloride Tetrahydrate. Reaction mixture was treated as in section A. The product was stilbene dichloride, $C_6H_5 \cdot CHCl\text{-}CHCl \cdot C_6H_5$, mp 189.0—191.0°C (lit, for *meso* 191—193°C, racemic 93—94°C) (Found: C, 66.55; H, 4.61%. Calcd: C, 66.95; H, 4.82; Cl, 28.23%).

D. Reduction of Benzotrichloride and Benzal Chloride by Cupurous Chloride in Acetonitrile. As ethylenediamine was used as additive all runs were heterogeneous and the reaction was carried out under reflux temperature.

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[35] J. F. O'Donnell, J. T. Ayres and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

After the reaction was ended the solvent was removed by distillation from the reaction mixture taking an hour, then the remainder was filtered and washed with hot benzene. The benzene filtrate was dried, concentrated and analyzed. The product was, if necessary, pretreated with column chromatography (300 mesh alumina) to remove resinous materials. When the products were mixtures of tolan and tolan dichloride (it was proved by IR, NMR and g.l.c.) the percentage of both substances were calculated from elementary analysis value or by g.l.c. peak area with *p*-nitrotoluene as a marker. The mp of the mixture was 60.5—62.5°C (lit, tolan; 62.5°C; tolandichloride *cis*, 142°C; *trans*, 63°C). *trans*-Stilbene was also produced form benzal chloride, C_6H_5–CH=CH–C_6H_5, mp 124.0—125.5°C (Found: C, 92.90; H, 6.46%. Calcd: C, 93.29; H, 6.71%).

E. Reduction of Diphenylmethyl Chloride by Ferrous Chloride Tetrahydrate of Cuprous Chloride. All runs were treated similarly. When the products were mixtures of tetraphenylethane and *N*-benzhydrylacetamide, they were easily separated from the difference of the solubility to benzene (this amide is hardly soluble to benzene). Hydrolysis product, benzhydrol was also separated because of the easy solubility. 1,1,2,2-Tetraphenylethane, $(C_6H_5)_2\cdot CH\cdot CH\cdot (C_6H_5)_2$, mp 210.5—211.0°C (Found: C, 93.22; H, 6.53%. Calcd: C, 93.37; H, 6.63%). *N*-Benzhydrylacetamide, $(C_6H_5)_2CH\cdot NH\cdot CO\cdot CH_3$, mp 148.0—149.0°C, (Found: C, 79.62; H, 6.67; N, 6.12%. Calcd: C, 79.97; H, 6.71; N, 6.22; O, 7.10.%)

Other Experimental Procedures. For the rate of the solvolysis of benzotrichloride the modification of Vorhard's method was used and for the kinetics of the reduction of benzotrichloride by ferrous chloride tetrahydrate, the decrease in concentration of Fe(II) ion was followed by titration with cerium(IV) solution, ferroin as indicator.$^{36)}$

The visible and ultraviolet spectra were measured using Shimadzu MPS-50L multipurpose spectrophotometer and for g.l.c. a 2-m silicone DC550 column was employed.

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36) M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N.Y. (1957), p. 147.