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The Reductive Coupling Reactions of Benzyl Chloride by Copper(I) Complexes*[1]

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The reactions between benzyl chloride and cuprous chloride were studied. It was found that good yields of bibenzyl were obtained by the addition of ethylenediamine, diethylenetriamine, triethylenetetramine, acetylacetone and EDTA. Nothing of bibenzyl was observed in the cases of ethanolamine, pyridine, dipyridyl, phenanthroline and triphenylphosphine. These facts, together with the spectral studies of copper complexes can reasonably be explained by the formation of reactive species of the type $Cu^{I}(en)_{n}Cl$. The course of the reaction was discussed on the basis of the substituent and medium effects. Radical but not free type mechanisms which include the transient organocopper species were considered. Some additional comments were also made.

It may safely be pointed out that in many of the copper-catalyzed organic reactions the redox ligand transfer processes key roles. In other words, the reaction of organic substrate XY and cuprous complex $Cu^{I}Z$, for example, can be delineated in the following way. $(M=Cu)$.

$$XY + M^{(n-1)+}Z \rightarrow X\cdot + M^{n+}YZ \tag{1}$$

$$X\cdot + M^{(n-1)+}Z \rightarrow XM^{(n-1)+}Z \tag{2}$$

$$X\cdot + X\cdot \rightarrow XX \tag{3}$$

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

$$\mathrm{X\cdot} + \mathrm{M}^{n+}\mathrm{YZ} \rightarrow \mathrm{XZ} + \mathrm{M}^{(n-1)+}\mathrm{Y} \quad \text{or } \mathrm{XY} + \mathrm{M}^{(n-1)+}\mathrm{Z} \tag{4}$$

$$\mathrm{X\cdot} + \mathrm{SH} \rightarrow \mathrm{XH} + \mathrm{S\cdot} \tag{5}$$

$$\mathrm{S\cdot} + \mathrm{M}^{n+}\mathrm{YZ} \rightarrow \mathrm{SZ} + \mathrm{M}^{(n-1)+}\mathrm{Y} \quad \text{or } \mathrm{SY} + \mathrm{M}^{(n-1)+}\mathrm{Z} \tag{4'}$$

$$\mathrm{X\cdot} + \mathrm{C{=}C} \rightarrow \mathrm{X{-}C{-}C\cdot} \tag{6}$$

$$\mathrm{X{-}C{-}C\cdot} + \mathrm{M}^{n+}\mathrm{YZ} \rightarrow \mathrm{X{-}C{-}C{-}Z} + \mathrm{M}^{(n-1)+}\mathrm{Y} \quad \text{or } \mathrm{X{-}C{-}C{-}Y} + \mathrm{M}^{(n-1)+}\mathrm{Z} \tag{4''}$$

The well-known copper-catalyzed peroxide reactions are typical of these processes.[1,2] Similar argument may possibly be made to the Sandmeyer-Meerwein reactions,[3] to the copper-catalyzed halogen transfer reactions[4-13] and, to some extent, to the copper-catalyzed halogen exchange reactions of aryl halides.[14-16]

The reaction (4) is commonly called "ligand transfer oxidation." This process, though not sufficiently, is relatively well studied and some discussion was already made by us in the previous studies of this series.[17] Little is known, however, about the reaction (1) which we tentatively named "ligand transfer reduction." Much is to be learned about the nature of the interaction of low valent copper complexes with organic structures in somewhat simplified reaction environments.

In this paper, the reactions of cuprous complexes and organic halides will be discussed.

Experimental

Materials. Cuprous perchlorate $CuClO_4\cdot CH_3CN$ was prepared according to the method of Kubota and Johnston.[18] Cuprous chloride, bromide, iodide and cyanide were commercial reagent grade and purified as usual manner. Authentic samples of dichloro-bis-ethylene-diamine copper(II) and dichloro-monoethylenediamine copper(II) were prepared by the method of Olszewski and Martin.[19]

Benzyl chloride and benzyl bromide were reagent grade and distilled twice. Benzyl iodide was prepared according to the method of Coleman and Hanser.[20] *p*-Methoxybenzyl chloride was synthesized from *p*-methoxybenzyl alcohol.[21] *p*-Methylbenzyl chloride, *p*-chlorobenzyl chloride and *p*-nitrobenzyl chloride were commercially first grade. All of these benzyl chlorides were checked by NMR spectra.

Reagent grade ethanolamine, ethylenediamine, diethylenetriamine, triethylenetetramine, pyridine, bipyridyl, phenanthroline, EDTA, triphenylphosphine and acetylacetone were used. Some of these were recrystallized or distilled if necessary. Sodium acetylacetonate was prepared from acetylacetone and sodium metal.

Acetonitrile was purified by the method of O'Donnell *et al.*[22] Dimethyl sulfoxide and Dimethylformamide were purified according to the method of Gutmann *et al.*[23] and Thomas *et al.*[24]

Typical Reaction Procedure. Benzyl chloride (0.633 g, 0.500×10^{-2} mol) and cuprous chloride (0.990 g, 1.00×10^{-2} mol) were dissolved in 40 m*l* of acetonitrile in a four-necked, 100 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 with stirring to the refluxing temperature. At that time, a solution of ethylenediamine (0.601 g, 1.00×10^{-2} mol) in 10 m*l* of acetonitrile was added through the dropping funnel. The reaction was continued for an hour under nitrogen stream.

Product Analyses. Two types of the standard methods were employed for the product analysis. In the first method the reaction mixture was treated with water, extracted with heptane, dried on sodium sulfate, concentrated to *ca.* 5 m*l* volume and analyzed by g.l.c. In the second, the solvent was removed by distillation from the reaction mixture. In this procedure the temperature of oil bath was maintained at 90°C. The remaining solid was treated with benzene and filtered. The filtrate was again concentrated to *ca.* 5 m*l* and analyzed by g.l.c. employing a 2 m silicone DC 550 column at 80 and 160°C. Bromobenzene and *p*-nitrotoluene were used as markers. The qualitative analyses by NMR and IR spectra were also made in some cases. The analytical values of the products but toluene did not markedly differ from one another

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TABLE 1. THE CHEMICAL SHIFTS OF BENZYLIC METHYLENE PROTONS IN BENZENE

Benzyl halide	τ, ppm	$Y\text{-}C_6H_4CH_2CH_2C_6H_4\text{-}Z$		τ ppm
$C_6H_5CH_2Cl$	5.85	Y = CH_3O	Z = CH_3O	—
$C_6H_5CH_2Br$	6.00	CH_3O	CH_3	—
$C_6H_5CH_2I$	6.12	CH_3	CH_3	7.20
$CH_3O\text{-}C_6H_4CH_2Cl$	5.76	CH_3	H	7.20
$CH_3\text{-}C_6H_4CH_2Cl$	5.90	H	H	7.20
$Cl\text{-}C_6H_4CH_2Cl$	6.13	H	Cl	7.30
$NO_2\text{-}C_6H_4CH_2Cl$	6.19	Cl	Cl	7.55
		CH_3	NO_2	7.40
$C_6H_5CH_2C_6H_5$	6.27	NO_2	NO_2	7.65

TABLE 2. EFFECTS OF ETHYLENEDIAMINE CONCENTRATION

$C_6H_5CH_2Cl$: 0.500×10^{-2} mol 81.6°C
CH_3CN: 50 m*l*, 60.0 min

$CuClO_4\cdot4CH_3CN$ $\times10^{-2}$ mol	en $\times10^{-2}$ mol	$C_6H_5CH_2CH_2C_6H_5$ $\times10^{-3}$ mol	$C_6H_5CH_3$ $\times10^{-3}$ mol
1.00	0.000	0.000	0.000
0.500	0.500	0.088	0.020
0.500	1.00	1.61	0.000
1.00	0.500	0.170	0.024
1.00	1.00	0.565	0.019
1.00	2.00	2.02	0.000
1.00	4.00	1.56	0.021
1.00	4.00	1.52	0.014
1.50	1.50	0.713	0.000
1.50	3.00	2.03	0.000

in these two methods. Hence, almost all analyses were conducted according to the latter. The violet crystals remaining in the filter were dried *in vacuo* for several days and checked by elemental analyses, powdered X-ray diffraction patterns, electronic, vibrational and paramagnetic resonance spectra.

In the cases of competitive reactions of *p*-substituted benzyl chlorides, quantitative analyses were undertaken by nuclear magnetic resonance spectra. The chemical shifts used to identify the materials were tabulated in Table 1. Diphenylmethane was used as marker.

Results and Discussion

The Effect of Ethylenediamine. The results of reactions in acetonitrile are summarized in Tables 2, 3, 4 and 5. It should be noted that complexing of the cuprous ion with ligands such as ethylenediamine greatly enhance its ability to reduce benzyl chloride to toluene and bibenzyl. It was also found that even the less reactive iodobenzene is successfully reduced by these cuprous complexes. These results are somewhat interesting since only the reactive substrates such as organic peroxides and polyhalohydrocarbons have shown to be sensitive to the normal cuprous ion at moderately low temperature.[1-13]

The yield of bibenzyl increases monotonously with cuprous ion concentration. In contrast, a small but definite retarding effect is observed when a large excess of ethylenediamine exists in the system. This may possibly be due to the

TABLE 3. EFFECTS OF LIGANDS

$C_6H_5CH_2Cl$: 0.500×10^{-2} mol
$CuClO_4\cdot4CH_3CN$: 1.00×10^{-2} mol, 81.6°C
CH_3CN: 50 m*l*, 60.0 min

Ligand (amine) $\times10^{-2}$ mol		$C_6H_5CH_2CH_2C_6H_5$ $\times10^{-3}$ mol	$C_6H_5CH_3$ $\times10^{-3}$ mol
ethanolamine			
	1.00	0.000	0.065
	2.00	0.000	0.016
en	1.00	0.565	0.019
dien	1.00	1.58	0.016
trien	1.00	1.47	0.015
	0.500	1.27	0.020
py	2.00	0.000	0.009
phen	1.00	0.000	0.060
dipy	1.00	0.000	0.065
EDTA	1.00	0.000	0.012
	1.00[a)]	0.401	0.064
Hacac	1.00	0.066	0.040
Naacac	1.00	0.061	0.026
TPP	2.00	0.000	0.000

a) CH_3CN 25 m*l* H_2O 25 m*l*

TABLE 4. THE REACTIONS OF BENZYL HALIDES
$C_6H_5CH_2X$: 2.50×10^{-2} mol CH_3CN: 50 ml
$ClC_6H_4CH_2Cl$: 2.50×10^{-2} mol, 81.6°C
en: 1.00×10^{-2} mol, 60.0 min
CuCl: 0.500×10^{-2} mol ($\times10^{-3}$ mol)

X	Substituted bibenzyl			Relative reactivity[a)]
	H-H	H-Cl	Cl-Cl	
Cl	0.380	0.722	0.708	1.00
Br	1.88	0.351	0.249	7.66
I				b)

a) Calcd from substituted bibenzyls.
b) Considerably reactive and side-reactions with ethylenediamine can not be neglected.

TABLE 5. THE REACTIONS WITH CUPROUS HALIDES
$C_6H_5CH_2Cl$: 0.500×10^{-2} mol, 81.6°C
en: 1.00×10^{-2} mol, 60.0 min
CuX: 1.00×10^{-2} mol
CH_3CN: 50 ml ($\times10^{-2}$ mol.)

Cuprous salt	$C_6H_5CH_2CH_2C_6H_5$	$C_6H_5CH_3$
$CuClO_4$	0.565	0.019
CuCl	1.32	0.032
CuBr	1.30	0.023
CuI	1.38	0.037
CuCN[a)]	trace	0.000

a) heterogeneous

inaccessibility of benzyl chloride to the coordinative site of copper ion by the intervention of ethylenediamine which occupy the coordination sphere preferentially. This view of the reaction is supported by the results of supplementary experiments C and D in Table 6. To some extent, the retarding effect is also ascribed to the side-reaction of benzyl chloride with ethylenediamine. The NMR studies of the reaction products, however, have shown that the effect is not interpreted by the latter mechanism only.

Furthermore, the experiments C and D in Table 6 support the idea that the intrinsic reagent in the system is cuprous complexes of the type $Cu^I(en)_nCl$. Though the details of the complexes are not yet clear, the species is found to be sensitive to the molecular oxygen and oxidized easily to the stable copper(II) state. This is cofirmed by the reaction E in Table 6. The yield of bibenzyl is considerably decreased by the preliminary contact with oxygen. The marked difference between the reactions B and E may be understood if we assume that the rates of the reactions between the complexes and benzyl chloride are faster than that of air oxidation.

As is seen in Table 3, in addition to ethylenediamine, several other ligands such as diethylenetriamine, triethylenetetramine, EDTA and acetylacetone are effectively used to promote the reaction. Monoethanolamine, however, and pyridine, dipyridyl, *o*-phenanthroline and triphenylphosphine are ineffective. These facts remind us of the change in the oxidation-reduction potential of copper(II)-copper(I) couple by complexing. The data of the potentials from references are listed in Table 7. There seems to be a certain relationship between the ligand effect and the potentials.[25-30] Thus, we conclude with some hesitation that the accelerating effects of the ligands exist in the formation of the reactive copper(I) complexes.

Studies of Copper(I) and Copper(II) Complexes. From the discussion given above the general feature of the reaction is profiled as follows.

$$Cu^ICl + n(en) \rightarrow Cu^I(en)_nCl \qquad (7)$$

$$2C_6H_5CH_2Cl + 2Cu^I(en)_nCl \rightarrow (C_6H_5CH_2)_2 + 2Cu^{II}(en)_nCl_2 \qquad (8)$$

As is shown in Fig. 1, a remarkable spectral change is observed when ethylenediamine is added to the solution of cuprous chloride in acetonitrile, assuring the formation of cuprous complexes. Further

TABLE 6. SUPPLEMENTARY REACTIONS
CuCl: 0.500×10^{-2} mol, 81.6°C CH_3CN: 50 ml, 60.0 min
($\times10^{-2}$ mol)

				CuCl : en : halide	$C_6H_5CH_2CH_2C_6H_5$
A	CuCl, $C_6H_5CH_2Cl$ followed by en		(N_2)	1 : 2 : 1	0.125
B			(air)	1 : 2 : 1	0.105
C	CuCl, en	followed by $C_6H_5CH_2Cl$	(N_2)	1 : 2 : 1	0.138
D			(N_2)	1 : 3 : 1	0.0751
E	CuCl, en, air	followed by $C_6H_5CH_2Cl$	(air)	1 : 2 : 1	0.0783

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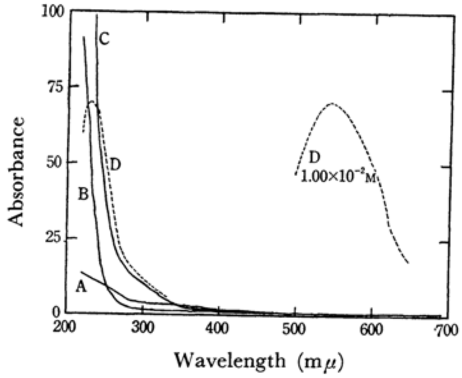

Fig. 1. Electronic spectra of copper complexes in nitrogen atmosphere.

A	en	1.00×10^{-4} M
B	CuCl	1.00×10^{-4} M
C	CuCl	1.00×10^{-4} M, en 2.00×10^{-4} M 10 min after mixing
D	CuCl	1.00×10^{-4} M en 2.00×10^{-4} M benzyl chloride 1.00×10^{-4} M 60 min after mixing

change is also observed if an amount of benzyl chloride is introduced to this solution. This last spectrum, together with the studies about isolated cupric complexes from typical runs, strongly suggests the production of cupric complexes of the type $Cu^{II}(en)_nCl_2$. These are illustrated in Table 8. It has been shown that the complexes produced are $Cu^{II}(en)Cl_2$ and $Cu^{II}(en)_2Cl_2$ in the reactions of ratios halide: Cu^I : en = 1 : 2 : 2 and 1 : 2 : 4, respectively.

The Mechanisms of the Reaction. As in the case of ligand transfer oxidation, the reverse process is explainable by the following scheme.

$$C_6H_5CH_2Cl + Cu^ICl \rightarrow C_6H_5CH_2Cl\cdot Cu^ICl \tag{9}$$

$$\begin{aligned} &C_6H_5CH_2Cl\cdot Cu^ICl \rightarrow \\ &\quad [C_6H_5CH_2\overset{\circ}{\underset{\circ}{}}Cl\circ Cu^{II}Cl \longleftrightarrow \\ &\quad\quad (J) \\ &\quad C_6H_5CH_2{-}\overset{\circ}{\underset{\circ}{\overset{\circ}{}}}Cl^{+}Cu^{II}Cl \longleftrightarrow \\ &\quad\quad (K) \\ &\quad C_6H_5CH_2{}^{+}\circ Cl^{-}\overset{\circ}{\underset{\circ}{}}Cu^{II}Cl] \rightarrow \\ &\quad\quad (L) \\ &C_6H_5CH_2{}^{\circ}\cdot ClCu^{II}Cl \end{aligned} \tag{10}$$ [31]

Table 7. The oxidation potentials of copper(I)-copper(II) couple

Copper complex	E°	E° (pH=7.0)
en (dien, trien)		0.37
Acetylacetone		
EDTA		
Ethanolamine		
Perchlorate	−0.15	0.17
Chloride	−0.54	
Pyridine	Ref. 27	
Diquinolyl (dipy, phen)		−0.77
Triphenylphosphine	Ref. 30	

Table 8. Physical properties of copper complexes

	Electronic spectra[a)]		Far infrared spectra[b)] cm⁻¹			
	max (ε)	mμ				
A-1[d)]	680 (30)	232 (3000)	623	525	473	
Cu(en)Cl₂	680 (32)	231 (3200)	623	525	473	
A-2[e)]	550 (63)	231 (6450)	643	523	474	450
Cu(en)₂Cl₂	550 (65)	232 (6500)	643	523	474	450

a) 1.00×10^{-2} M for visible spectra solvent: H_2O
4.00×10^{-5} M for ultraviolet spectra temp: 20—22°C
b) The spectra of KBr pellet

	ESR spectra[c)]		Elementary analysis				
	g	g	Cu	Cl	C	H	N
A-1	2.049	2.339	32.58	36.82	12.54	4.34	14.08
Cu(en)Cl₂	2.049	2.339	32.66	36.45	12.34	4.14	14.40
A-2	2.040	2.236	24.87	28.02	18.69	6.42	21.85
Cu(en)₂Cl₂	2.040	2.236	24.96	27.80	18.80	6.31	22.01

c) The spectra in powder state
d) CuCl : en : benzyl chloride = 2 : 2 : 1
e) CuCl : en : benzyl chloride = 2 : 4 : 1

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[31] Some comments may be need for the Eq. (10). The equation somewhat differs from a generally accepted Russell's mechanism for the hydrogen abstraction reaction by organic radical of Eq. (19).[32]

[32] G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4578 (1955).

TABLE 9. THE COMPETITIVE REACTIONS

$YC_6H_4CH_2Cl$: 0.500×10^{-2} mol; en: 1.00×10^{-2} mol; CH_3CN: 50 m*l*;
$ClC_6H_4CH_2Cl$: 0.500×10^{-2} mol; CuCl: 0.500×10^{-2} mol, 81.6°C, 60.0 min

Y		Recovered $YC_6H_4CH_2Cl$		Substituted bibenzyl			Relative reactivity	
		Y or	a) Y=Cl b) $Y=CH_3$	Y-Y Y-Y	Y-Cl $Y-CH_3$	Cl-Cl CH_3-CH_3	R_1	R_2
CH_3O	(b)	0.611	1.84	0.327	0.848		not determined	
CH_3	(a)	1.43	1.29	0.402	0.802	0.782	0.992	0.967
H	(a)	1.38	1.27	0.370	0.694	0.674	1.000	1.000
Cl							1.03	1.43
NO_2	(b)	1.07	2.81	0.677	0.752	0.201	1.74	2.05

R_1: relative conversion ($\times10^{-3}$ mol)
R_2: calcd from produced bibenzyls

TABLE 10. THE EFFECT OF SOLVENT

$C_6H_5CH_2Cl$: 0.500×10^{-2} mol, 81.6°C; en: 1.00×10^{-2} mol, 60.0 min; $CuClO_4\cdot4CH_3CN$: 1.00×10^{-2} mol

Solvent	m*l*	$C_6H_5CH_2CH_2C_6H_5$ $\times10^{-3}$ mol	$C_6H_5CH_3$ $\times10^{-3}$ mol
CH_3CN	50	0.565	0.019
CH_3CN-DMSO	(25—25)	0.000	0.000
-DMF	(25—25)	0.255	0.006
-HOAc	(25—25)	0.000	0.015
-HOAc	(45— 5)	0.125	0.020
$-H_2O$	(25—25)	0.033	0.015
$-H_2O$	(45— 5)	0.455	0.010
$-(CH_3)_2CHOH$	(25—25)	0.323	0.017
$-(CH_3)_2CHOH$	(45— 5)	0.627	0.009
DMSO	50	0.000	0.000
DMF	50	0.000	0.000

TABLE 11. THE EFFECTS OF ADDITIVE

CuCl: 0.00×10^{-2} mol, 81.6°C; $ClC_6H_4CH_2Cl$: 0.500×10^{-2} mol, 60.0 min; en: 1.00×10^{-2} mol
($\times10^{-3}$ mol)

Solvent	Additive	$ClC_6H_4CH_2CH_2C_6H_4Cl$	$ClC_6H_4CH_3$
CH_3CN 50 m*l*		1.53	0.020
CH_3CN 25 m*l*	$(CH_3)_2CHOH$ 25 m*l*	0.852	0.005
CH_3CN 50 m*l*	HOC_6H_4OH 0.500×10^{-2} mol.	1.35	0.014

This scheme certainly reflects the close similarity to the chlorine atom abstraction reactions by organic radicals. The contribution of step (9) is fairly plausible since our recent work have revealed that a stable cuprous complex $Cu^ICl(C_6H_5CH_2I)(TPP)_2$ is quantitatively obtained in the reaction of cuprous chloride, benzyl iodide and triphenylphosphine in acetonitrile.[33]

Concerning the reaction step (10), the substituent effect on benzyl chloride was examined. The results are in Table 9. Though the effect observed is very feasible, its electrophilic character may probably refer to the contribution of the structure (K).[31] The extraordinary large effect of nitro group, reminiscent of its effect in Ullmann coupling reaction,[34] can be ascribed to the considerable resonance term. *p*-Methoxybenzyl chloride is so unstable that certain side reactions must be present in its competitive reaction, and hence the datum is that for only reference.

Although the radical feature of the reaction is backed up by the formation of coupling product and the data in Table 3, there remains some uncertainty. To assure this, several additional experiments were achieved. Tables 10 and 11 illustrate the effects of solvents and hydrogen donors. No appreciable change, however, is observed in the yield of toluene despite rather large

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33) K. Wada and H. Hashimoto, to be published.

34) P. E. Fanta, *Chem. Revs.*, **64**, 613 (1964).

changes in environment. Therefore, the existence of benzyl radical in its free state is hardly accepted. Hence, it appears plausible to presume the mechanisms depicted below.

$$2C_6H_5CH_2\cdot ClCu^{II}Cl \rightarrow (C_6H_5CH_2)_2 + 2Cu^{II}Cl_2 \tag{11}$$

$$C_6H_5CH_2\cdot ClCu^{II}Cl + C_6H_5CH_2Cl + Cu^{I}Cl \rightarrow (C_6H_5CH_2)_2 + 2Cu^{II}Cl_2 \tag{12}$$

$$C_6H_5CH_2\cdot ClCu^{II}Cl + Cu^{I}Cl \rightarrow C_6H_5CH_2\cdot Cu^{I}Cl + Cu^{II}Cl_2 \tag{13}$$

$$C_6H_5CH_2\cdot Cu^{I}Cl + C_6H_5CH_2Cl \rightarrow (C_6H_5CH_2)_2 + Cu^{II}Cl_2 \tag{14}$$

$$2C_6H_5CH_2\cdot Cu^{I}Cl \rightarrow (C_6H_5CH_2)_2 + 2Cu^{I}Cl \tag{15}$$

At the present stage, however, we are not able to decide which of these processes prevails.

Finally, some comments must be made about the reactions of chromous species. Recent works by several groups of laboratories have shown that the relatively longlived organochromium species are effectively formed in the reactions of alkyl halides and chromous ion.[35–39] The hydrolysis and dimerization reactions of these species were also studied and various mechanisms have been discussed for these reactions. For example, Kochi and his coworkers have suggested the following scheme.[29,30,35–38]

$$C_6H_5CH_2Br + Cr^{II}{}_{aq} \rightarrow C_6H_5CH_2\cdot + Cr^{III}Br_{aq} \tag{16}$$

$$C_6H_5CH_2\cdot + Cr^{II}{}_{aq} \rightarrow C_6H_5CH_2\cdot Cr^{II}{}_{aq} \tag{17}$$

$$C_6H_5CH_2Cr^{II}{}_{aq} + C_6H_5CH_2Br \rightarrow (C_6H_5CH_2)_2 + Cr^{III}Br_{aq} \tag{18}$$

In contrast to our results mentioned above, free benzyl radical is included in their scheme.

Further works must be necessary for the discussion of this discrepancy.

$$R\cdot + S\text{–}T \rightarrow [R\cdot S{:}T \longleftrightarrow R^{-}{:}S\cdot{}^{+}T \longleftrightarrow R{:}S\cdot T] \rightarrow R\text{–}S + \cdot T \tag{19}$$

The mechanism (19), however we think, is erroneous or not sufficient for its unreasonably estimated resonance terms.

Here, we are rather inclined to suggest a more reasonable reformation. The Eq. (20) is a schematical description of transition state in our idea.

$$\underset{(O)}{R\cdot S{:}T} \longleftrightarrow \underset{(P)}{R^{-}{:}S^{+}\cdot} \longleftrightarrow \underset{(Q)}{R^{+}S^{-}\vdots T} \tag{20}$$

The structure (O) represents the system in which one electron stays in the half-occupied orbital of group R and two electron in the S–T bonding orbital. The structure (P) is a picture of a charge transfer from S–T bonding orbital to originally half-occupied orbital of group R. A charge transfer from half-occupied orbital to S–T antibonding orbital is drawn out by the structure (Q). It may be considered that the position of group S and the charge distribution in the transition state and hence the degree of the contribution of (O), (P) and (Q) are changed variously from reaction to reaction.

In most of the organic reactions, the contribution of the structure (P) prevails. In the reactions of copper complexes, however, the larger contribution may be expected from the structure (Q).

In the case of ligand transfer oxidation of phenyl radical,[17] the groups R, S and T, correspond to phenyl group, chlorine atom and cupric ion, respectively. In this system the structure (P) needs the unstable $(3d)^8$ configuration of copper moiety. In the ligand transfer reduction of benzyl chloride, cuprous ion, chlorine atom and benzyl group are expressed by R, S and T respectively. In this case, the structure (P) demands the configuration of $(3d)^{10}$ $(4s)$ character. This configuration is also rather difficult to be achieved at the condition employed. Thus, it may be concluded that the substituent effects in both of the reactions are well explained by the contribution of relatively favourable structure (Q).

It may safely be pointed out also that the nucleophilic character of attacking radical which is overlooked by Russell's mechanism can successfully be introduced by this consideration.

The comments mentioned above is not at all a qualitative one. Thus, a more elaborated refinement must be made for the discussion of the detail aspects of the group transfer reactions.

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