Kinetics of Exchange Reactions of 2-Halogeno-3-Bromonitrobenzenes with Tetrabutylammonium Dihalogenocuprates(I)

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The copper(I)-catalyzed halogen exchange reactions of 2,3-dibromonitrobenzene with tetrabutylammonium dichloro-, diiodo- and bromochlorocuprates(I), together with the exchange reactions of 3-bromo-2-iodonitrobenzene with tetrabutylammonium dichloro- and dibromocuprates(I), have been kinetically studied in chlorobenzene. The reactions exhibit second order kinetics, first order in both aryl halide and halogen. As judged from the results of our kinetic investigations and of the ^{1}H NMR spectra of tetrabutylammonium dihalocuprates(I), obtained in chlorobenzene, the CuX_2^- anion seems to be the relevant nucleophile in the present reaction. The large negative entropy of activation, -119 J $K^{-1}mol^1$, found for the reaction of 2,3-dibromonitrobenzene with tetrabutylammonium dichlorocuprate(I), indicates a highly ordered transition state.

Copper(I)-catalyzed halogen exchange reactions of halonitrobenzenes with chloride ion in aqueous hydrochloric acid-acetic acid medium have previously been kinetically studied.[1-2] A large accelerating effect of a nitro group *ortho* to the reaction center was observed, together with steric and polar effects of a substituent in the other *ortho* position. In the investigation of the exchange reaction of 2-bromo-3-X-nitrobenzene, an increase of the rate of reaction correlated well to increasing van der Waals volume of a halogen in the 3-position. Owing to these results and to the strongly negative $\Delta S^{\ddagger}$ values, from -211 to -155 J $K^{-1}mol^{-1}$, a tetrahedral intermediate was proposed in which the *ortho* nitro group and the

bromine undergoing replacement interact with the dichlorocuprate(I) ion.[1-2]

The results of the investigations of copper(I)-promoted reactions have been the source of much discussion and speculation concerning the reaction mechanism. Cohen, et al.[3] have suggested an oxidative addition–reductive elimination reaction *via* an organocopper(III) intermediate in the exchange reactions of aryl halides with salts of copper(I) in organic solvents, while Bacon, et al.[4] have proposed a copper-assisted nucleophilic displacement *via* a four-center intermediate and van Koten, et al.[5], single electron-transfer steps.

The present work was undertaken with the intention of further elucidating the mechanism of copper(I)-catalyzed substitution of the halogen in the 2-position in 2-halogeno-3-bromonitrobenzenes. Recent work[6,8b] has made $CuCl_2^-$ available as $(C_4H_9)_4N^+$ $CuCl_2^-$ in a crystalline state, together with $(C_4H_9)_4N^+$ $CuBr_2^-$, $(C_4H_9)_4N^+$ CuBrCl$^-$ and $(C_4H_9)_4N^+$ CuI_2^-. The exchange reactions of these salts with 2-halogeno-3-bromonitrobenzenes under homogenous conditions have now been studied in chlorobenzene, which is a suitable solvent for these salts. The crystal structures of the tetrabutylammonium dihalogenocuprates(I) have been determined from single crystal X-ray diffractometer data.[7-8b] The $CuCl_2^-$, the $CuBr_2^-$ and the CuBrCl$^-$ ions are linear monomers, whereas the diiodocuprate(I) ion is seen to be a trigonal planar dimer ($Cu_2I_4^{2-}$). The "state" of the tetrabutylammonium dihalocuprates(I) in an organic

solvent, however, is uncertain. Chlorobenzene is thought to solvate the tetrabutylammonium cation but not the anion, leading to a greater interionic distance and thereby reducing the cation−anion interaction and making the anion more reactive.[9]

RESULTS AND CALCULATIONS

The exchange reactions between 3-bromo-2-halonitrobenzenes and tetrabutylammonium dihalocuprates(I) were kinetically studied in chlorobenzene at 80−100 °C and at varied concentrations. The reaction rates were determined
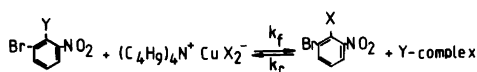
(1) Y = Br or I and X = Cl

(2) Y = I   and X = Br

(3) Y = Br   and X = I

by means of GLC. In a reference run without copper(I), 2,3-dibromonitrobenzene and tetrabutylammonium chloride in chlorobenzene were heated at 90 °C for 20 h, but no reaction took place.

The reaction of 2,3-dibromonitrobenzene and tetrabutylammonium dichlorocuprate(I) was followed to >99 %. It became evident from the kinetic investigations, that both of the Cl of the dichlorocuprate(I) participated in the substitution reaction, which was seen to be of first order
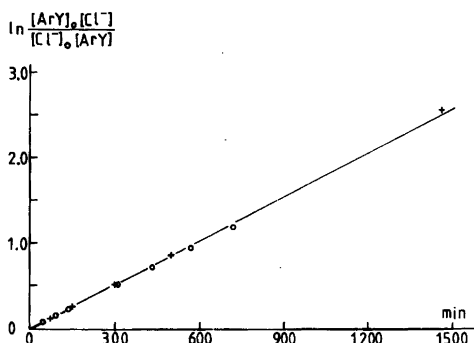

Fig. 1. Two representative runs (○ and ×) in the exchange reaction of 2,3-dibromonitrobenzene (0.0546 M) and tetrabutylammonium dichlorocuprate(I) (0.0819 M, Cl=0.1638 M) at 90 °C.

in both aryl halide and chloride ion (Fig. 1). A separate run was made with 3-bromo-2-chloronitrobenzene and tetrabutylammonium dibromocuprate(I). No reaction was observed during the current reaction time, thus confirming that the reaction of 2,3-dibromonitrobenzene with dichlorocuprate(I) ion was not complicated to any marked extent by reversibility. The rate expression (1) is applicable.

$$-\frac{d[ArY]}{dt} = k_f [ArY][Cl^-] \quad Y = Br \text{ or } I \quad (1)$$

Because we are unable to assign individual rate constants for the first and the second chloride of the tetrabutylammonium dichlorocuprate(I) in the reaction with the aromatic compound, k_f stands for the average value of the rate constant.

The rate constants are calculated from the integrated form

$$\frac{1}{[Cl^-]_o - [ArY]_o} \ln \frac{[ArY]_o[Cl^-]}{[Cl^-]_o[ArY]} = k_f \cdot t$$

The reaction of 2,3-dibromonitrobenzene with tetrabutylammonium bromochlorocuprate(I) was also investigated (Table 1).

The reaction of 3-bromo-2-iodonitrobenzene with tetrabutylammonium dichlorocuprate(I) and the reverse reaction, 3-bromo-2-chloronitrobenzene and tetrabutylammonium diiodocuprate(I), were investigated at 90 °C. The latter reaction did not occur during the reaction time in question. The substitution reaction of 3-bromo-2-iodonitrobenzene and $CuCl_2^-$, which was followed to >95 %, exhibits second order kinetics, first order in both aryl halide and Cl; see Table 1.

The reaction of 3-bromo-2-iodonitrobenzene with the tetrabutylammonium dibromocuprate(I), however, was a reversible second order reaction with both of the Br participating in the reaction.

$$-\frac{d[ArI]}{dt} = k_f[ArI][Br^-] - k_r [ArBr][I^-] \quad (2)$$

$$A \quad B \quad \quad C \quad D$$

The stoichiometric value of K_{eq} was 1.819. k_f and k_r were calculated from the integrated form[10]

Table 1. Rate parameters for exchange reactions of 2-halo-3-bromonitrobenzenes and tetrabutyl ammonium dihalogenocuprates(I) (Q^+ CuX_2^-) in chlorobenzene.

Aromatic compound/M	Q^+ CuX_2^-	X/M	Temp./°C	K_{eq}	$k_f/10^{-4}$ $s^{-1}M^{-1f}$	$k_r/10^{-4}s^{-1}M^{-1f}$
2,3-Dibromonitrobenzene						
0.0541	$Q^+CuCl_2^-$	0.2164	90.02	>50	2.422 ± 0.031^a	
0.0546	$Q^+CuCl_2^-$	0.1638	90.02		2.568 ± 0.050^a	
0.0551	$Q^+CuCl_2^-$	0.1102	90.02		2.659 ± 0.025^a	
0.0556	$Q^+CuCl_2^-$	0.0556	90.02		3.280 ± 0.129^a	
0.0546	$Q^+CuCl_2^-$	0.1638	98.0		4.386 ± 0.050^a	
0.0546	$Q^+CuCl_2^-$	0.1638	79.8		1.267 ± 0.016^a	
0.0541	$Q^+CuBrCl^-$	0.1082^c	90.02		2.038 ± 0.016^a	
3-Bromo-2-chloronitrobenzene						
0.0546	$Q^+CuBr_2^-$	0.1638	90.02	<0.02	no reaction	
0.0541	$Q^+CuBrCl^-$	0.1082^d	90.02	<0.02	no reaction	
0.0276	$(Q^+CuI_2^-)_2$	0.1104	90.02	<0.02	no reaction	
3-Bromo-2-iodonitrobenzene						
0.0546	$Q^+CuCl_2^-$	0.1638	90.02	>50	3.196 ± 0.029^a	
0.0546	$Q^+CuBr_2^-$	0.1638	90.02	1.819	18.49^e	10.16^e
2,3-Dibromonitrobenzene						
0.0546	$(Q^+CuI_2^-)_2$	0.1638	90.02	0.547	4.43^b	8.10^b
0.0541	$(Q^+CuI_2^-)_2$	0.2164	90.02	0.520	3.79^b	7.29^b
0.0276	$(Q^+CuI_2^-)_2$	0.1287	90.02	0.546	4.08^b	7.46^b
0.0276	$(Q^+CuI_2^-)_2$	0.1106	90.02	0.507	3.84^b	7.33^b
0.0138	$(Q^+CuI_2^-)_2$	0.0553	90.02	0.516	3.67^b	7.11^b

[a] The errors are 2 S.E. from the least-squares method calculations. 2–4 different runs in every calculation. [b] Simulated values. [c] As Cl. [d] As Br. [e] The limits in (k_f-k_r) are $\pm0.31\cdot10^{-4}$. (2 S.E.). [f] k_f and k_r are average values. See Text.

$$\ln \frac{(A_o-A_e)(A-A_e+Q)}{(A-A_e)(A_o-A_e+Q)} = (k_f-k_r)\ Q\cdot t$$

$$\text{where } Q=\frac{1}{K_{eq}-1}\ \times$$

$$[K_{eq}^2\ (B_o-A_o)^2+4\ A_oB_o\cdot K_{eq}]^{\frac{1}{2}}$$

The rate constants, k_f and k_r, were also obtained using a simulation procedure for the differential equation.[11] The A_o, B_o, C_o and D_o values were fed in as starting values in a numerical integration, together with assumed k_f and k_r values, and with $\Delta t=0.1$ min. The rate constants from the simulation procedure were in excellent agreement with the constants calculated from the integrated form of the rate expression, see above. The triangles in Fig. 2 are the experimental
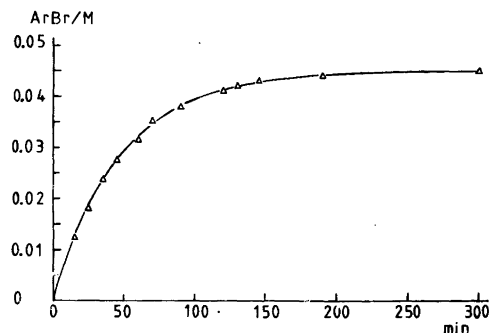

Fig. 2. The formation of 2,3-dibromonitrobenzene in the exchange reaction of 3-bromo-2-iodonitrobenzene with tetrabutylammonium dibromocuprate(I). The triangles are the experimental results and the curve is calculated in the simulation procedure. ArI=0.0546 M and Br=0.1638 M.
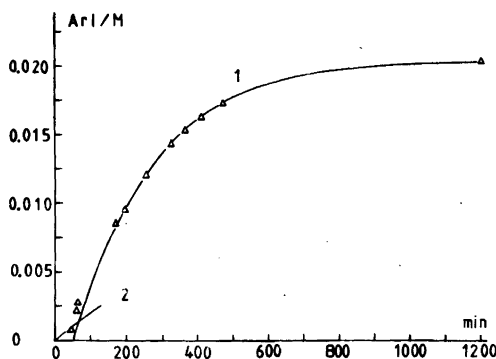
Fig. 3. The formation of 3-bromo-2-iodonitro-benzene in the reaction of 2,3-dibromonitro-benzene (0.0276 M) with the dimeric tetrabutyl-ammonium diiodocuprate(I) (0.0322 M). The simulated curve 1 has $t(0)=52$ min and $I=0.1287$ M, curve 2 has $I=0.0322$ M.

results and the curve has been calculated by the simulation procedure.

The reverse reaction between 2,3-dibromoni-trobenzene and the dimeric tetrabutylammonium diiodocuprate(I) was also studied at different concentrations at 90 °C. A number of complications, in addition to the low solubility of the tetrabutylammonium diiodocuprate(I) dimer in chlorobenzene, appeared in this reaction. The simulation described above revealed a slow initial step before the reversible step of second order (Fig. 3). In the initial step, obviously not all of the iodine of the tetrabutylammonium diiodocup-rate(I) dimer is available to participate in the reaction, but after an induction period, all of the four I took part in the reaction. The rate constants from the simulation procedure for this reaction are shown in Table 1. The stoichiometric K_{eq} for different concentrations varied from 0.507 to 0.547, but it is in good agreement with $1/K_{eq}$ for the reverse reaction between 3-bromo-

Table 2. Activation enthalpy and entropy for the substitution reaction of 2,3-dibromonitrobenzene and tetrabutylammonium dichlorocuprate(I).

$\Delta H^{+}/kJ\ mol^{-1}$	$\Delta S^{+}/J\ K^{-1}\ mol^{-1}$
71.2±1.2[a]	−119.0±3.3[a]

[a] The error is 3 S.E. from the least-squares method calculation. The temperature interval is 79.8−98.0 °C.

2-iodonitrobenzene and dibromocuprate(I), at identical concentrations (compare 0.547 to 0.550).

Activation parameters (Table 2) were calculated for the reaction of 2,3-dibromonitro-benzene with tetrabutylammonium dichloro-cuprate(I) using the Eyring equation.[12a,2]

^{1}H NMR spectra were recorded to provide information about the "state" of the tetrabutyl-ammonium salts in chlorobenzene.

The chemical shifts for the tetrabutylammo-nium protons are seen to be unaffected by a change of the anion. The anions CuI_2^-, $CuBr_2^-$, $CuCl_2^-$ and $CuBrCl^-$, in fact, gave the same values, in chlorobenzene; α H 3.0, β H 1.45, γ H 1.30 and δ H 0.91 (δ-values at 35 °C). In acetone the corresponding values are 3.45, 1.80, 1.45 and 0.98 and in chloroform 3.28, 1.69, 1.49 and 1.03. The H 6 proton of 2,3-dibromonitrobenzene had the shift 7.28 in chlorobenzene, 8.15 in acetone and 7.85 in chloroform. See Experimental.

Temperature variation from +100 to −40 °C caused an upfield shift in chlorobenzene for α H and β H (0.1−0.2 ppm), the shifts for the γ and δ protons were almost unaltered and the resonance signals for the aromatic protons are also shifted upfield. In acetone (+57 to −80 °C) the shift of the α H is unaltered, while the signals for β, γ and δ H are shifted upfield <0.1 ppm. The shifts of the aromatic protons are displaced downfield. See Fig. 4.

Only one set of solvent molecules is observed in chlorobenzene, as well as in acetone, even at very low temperatures, −40 and −80 °C, respectively.

As a reference ^{1}H NMR spectra were obtained for tetrabutylammonium chloride, bromide and iodide in chlorobenzene at 35 °C. The α protons of the cations gave the δ-values: 3.46, 3.37 and 3.26, respectively.

DICUSSION

The bulky tetrabutylammonium cation hinders a close approach of the dihalocuprate(I) anion and lowers the stability of the contact ion pair. Quaternary ammonium salts, in fact, are considered to be good models of loose ion pairs in organic solvents of low polarity.[13b,14] This is also supported by the ^{1}H NMR spectra of the tetra-butylammonium salts in chlorobenzene, identical
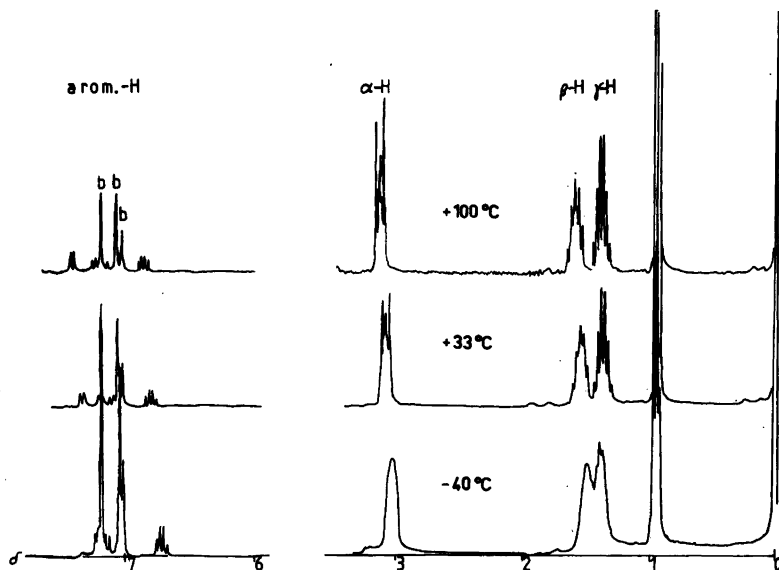
Fig. 4. ¹H NMR spectrum of the reaction mixture of 2,3-dibromonitrobenzene and tetrabutylammonium diiodocuprate(I) at +100, +33 and −40 °C in C_6D_5Cl. δ-Values from TMS in ppm. *b* are solvent peaks.

chemical shifts are obtained for the protons of the cation, independent of the anion species (CuI_2^-, $CuBr_2^-$, $CuCl_2^-$ or $CuBrCl^-$). Acetone or chloroform as solvent gave identical results. Buckson[15] has investigated ¹H NMR spectra for tetrabutylammonium chloride, bromide and iodide (0.005 to 0.25 M) in nitrobenzene at 35 °C and noticed, that the resonance position for the α protons of the cation was sensitive to both the concentration and the nature of the anion and concluded, that a closely associated cation and anion were involved. These results are in agreement with our ¹H NMR spectra of the tetrabutylammonium halides in chlorobenzene.

We have observed only small differences in the chemical shift of the tetrabutylammonium dihalocuprates(I) by varying the concentration.

The solvating power of various aprotic solvents does not depend on their relative permittivities alone, but also on their ability to donate electrons in cation solvation, or accept electrons from anions in anion solvation.[13a] A solvent may act as donor and acceptor simultaneously. The failure of the solvent permittivities to represent solute−solvent interactions has led to the definition of polarity in terms of empirical parameters. Dimroth and co-workers have proposed a solvent

polarity parameter, $E_T(30)$, based on the transition energy for the longest wavelength solvatochromic absorption band on the pyridinium-*N*-phenoxide betaine dye.[16–17a] $E_T(30)$ at 25 °C: acetone 176.6, chloroform 163.6 and chlorobenzene 156.9 kJ/mol.

The shifts in the ¹H NMR spectra for tetrabutylammonium dihalocuprates(I) and for the aromatic compounds are in accord with this solvent polarity scale.

The observed upfield shift in NMR for the protons of a dipolar solute in going from an inert solvent, *e.g.* chloroform, to an aromatic solvent, have been investigated in numerous cases.[17b–18]

These shifts, aromatic solvent-induced shifts (ASIS), are characteristic for the position of the nucleus in question with respect to the various polar groups in the solute molecule.

The observed upfield shift of the ¹H NMR signals for the α- and β-protons of the tetrabutylammonium cation in chlorobenzene at low temperatures can be caused by an increase of the solvation of cation and anion and of the distance to opposite ion.[19] See Fig. 4.

A negative salt effect is noticed in the substitution reaction of 2,3-dibromonitrobenzene and tetrabutylammonium dichlorocuprate(I) (see

Table 1), which can be explained by a dispersal of the negative charge in the transition state in the S_N2-like reaction, but can also be due to incomplete dissociation of the ammonium salts. As a consequence, the reaction rate will decrease as the concentration increases.[17c]

The rate constant for the halogen exchange reaction of 2,3-dibromonitrobenzene with the $CuCl_2^-$ ion in aqueous medium, studied in a previous work,[2] was five times greater than for the corresponding reaction with tetrabutylammonium dichlorocuprate(I), studied in chlorobenzene in the present work. This result was unexpected, but may be interpreted as solvation effects. The solvation of both the initial state and the activated complex must be taken into consideration in a change from protic to aprotic solvent. Solvation of the activated complex will tend to bring about an increase in the reaction rate, while solvation of one or more of the reactants will result in an increase of the activation energy and the reaction will be retarded.[12b]

The large negative entropy of activation, -119 J $K^{-1}mol^{-1}$, obtained for the substitution reaction of 2,3-dibromonitrobenzene with tetrabutylammonium dichlorocuprate(I) in chlorobenzene, indicates a greater degree of ordering in the transition state than in the initial state. The tetrahedral $CuCl_2^-$–aryl halide complex, proposed as an intermediate in aqueous medium,[2] could also justify the large negative entropy of activation for the present reaction in chlorobenzene. A change from protic to aprotic solvent in the substitution reactions in question reflects changes in the activation enthalpies rather than activation entropies; compare 51 kJ/mol in aqueous medium to 71 kJ/mol in chlorobenzene. The reactivity of the aromatic compounds is ArI>ArBr>ArCl as seen from Table 1.

The extent of ion pairing decreases with increasing ionic size, which means that the reactivity of the nucleophilic anions is $CuBr_2^-$ >$CuCl_2^-$. This is the traditional order of halogen nucleophilicity in aqueous medium, $I^->Br^->Cl^-$. Buckson[15] has estimated the ion pair dissociation constants for the tetrabutylammonium halides in nitrobenzene at 35.9 °C; $2.2 \cdot 10^{-2}$ for the chloride, $4.4 \cdot 10^{-2}$ for the bromide and $6.8 \cdot 10^{-2}$ for the iodide. Ion pairing must be relatively unimportant for the larger tetrabutylammonium dihalocuprates(I) in our investigations.

The slow initial step in the substitution reaction of the 2,3-dibromonitrobenzene with the dimeric tetrabutylammonium diiodocuprate(I) could originate from an attack on *one* of the terminal iodines of the trigonal dimer in the formation of an intermediate copper(I)–aryl halide complex, accompanied by bond breaking of the dimer, thus making all of the iodine available. Alternatively dissociation of $Cu_2I_4^{2-}$ could be slow.

Halogen exchange reactions of halobenzenes and tetrabutylammonium dihalocuprates(I) have hitherto never been described. Muscio, *et al.*[20] have described the rearrangement of 3-chloro-3-phenyl-1-propyne to 1-chloro-3-phenyl-1,2-propadiene with tetrabutylammonium dichlorocuprate(I) in acetone in an *anti* 1,3 S_N2' substitution. Axelrad, *et al.*[21] have reported the formation of vinylic chlorides in high yield in the reaction of vinylic bromides with triphenyl phosphine complexes of copper(I) chloride.

The results obtained in the present investigations of halogen exchange of 2-halo-3-bromonitrobenzenes with tetrabutylammonium dihalocuprates(I), available in a crystalline state, support the proposal[1-2] that dihalocuprate(I) ions are the relevant nucleophiles for the exchange reaction of halonitrobenzenes with copper(I) chloride in aqueous hydrochloric acid medium, where only a rough estimation of the concentration of the catalyzing dichlorocuprate(I) ion was feasible.[1] The highly negative entropy of activation, now observed also in chlorobenzene solution, points to a highly ordered transition state.

EXPERIMENTAL

The reactions between the halonitrobenzenes and tetrabutylammonium dihalocuprate(I) in chlorobenzene were performed in an argon atmosphere. The GLC analyses of the aryl halides were performed on a Perkin Elmer 3920-B instrument with Hot Wire Detector and equipped with a Hewlett Packard 3380 A integrator. A 3 mm×2 m SE-30 column was used. Carrier gas was He. Calibration curves were obtained from known mixtures of pure aryl halides.

The ^{1}H NMR analyses were performed on a Bruker WH 270 spectrometer with TMS as internal standard. The mass spectra were recorded on a Finnigan 1020 instrument and the UV spectra on a Cary 15 spectrophotometer. All

the calculations were made on a Compucorp 625 G desktop computer.

The chlorobenzene was distilled before use. 2,3-Dibromonitrobenzene, 3-bromo-2-chloronitrobenzene and 3-bromo-2-iodonitrobenzene were available from previous kinetic investigations.[1,22]

2,3-Dibromonitrobenzene. ^{1}H NMR (270 MHz, CDCl$_3$), δ 7.63 (H-4, q), 7.34 (H-5, q), 7.84 (H-6,q) J_{4-5}=7.95 Hz, J_{5-6}=7.90 Hz, J_{4-6}=1.40 Hz, (C$_6$D$_5$Cl): δ 7.12 (H-4,q) 6.7 (H-5,q), 7.28 (H-6,q), $J_{4-5,5-6}$=8.0 Hz, J_{4-6}=1.50 Hz. (CD$_3$COCD$_3$): δ 8.0 (H-4,q), 7.72 (H-5,q), 8.15 (H-6,q). $J_{4-5,5-6}$=8.0 Hz, J_{4-6}=1.40 Hz. Ms: A 1:2:1 triplet at *m/e* 279, 281 and 283.

3-Bromo-2-chloronitrobenzene. ^{1}H NMR (270 MHz, CDCl$_3$): δ 7.70 (H-4,q), 7.28 (H-5,q), 7.85 (H-6,q). J_{4-5}=7.95 Hz, J_{5-6}=7.80 Hz, J_{4-6}=1.40 Hz, MS: A 3:4:1 triplet at *m/e* 235, 237 and 239.

3-Bromo-2-iodonitrobenzene. ^{1}H NMR (270 MHz, CDCl$_3$): δ 7.54 (H-4,q), 7.36 (H-5,q), 7.84 (H-6,q). J_{4-5}=7.90 Hz, J_{5-6}=7.80 Hz, J_{4-6}=1.40 Hz. (C$_6$D$_5$Cl): δ 7.01 (H-4,q), 6.72 (H-5,q), 7.28 (H-6,q), $J_{4-5,5-6}$=7.8 Hz, J_{4-6}=1.50 Hz. (CD$_3$COCD$_3$): δ 7.85 (H-4,q), 7.70 (H-5,q), 8.10 (H-6,q). $J_{4-5,5-6}$=7.95 Hz, J_{4-6}=1.35 Hz. MS: A 1:1 doublet at *m/e* 327 and 329.

The syntheses of the tetrabutylammonium dihalocuprates(I) have been described previously.[6,8b]

Tetrabutylammonium dibromocuprate(I). ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.28 (α H, m), 1.69 (β H, m), 1.49 (γ H, m): 1.04 (δ H, t). (C$_6$D$_5$Cl): δ 2.97 (α H, m), 1.44 (β H, m), 1.30 (γ H, m), 0.92 (δ H, t). (CD$_3$COCD$_3$): δ 3.45 (α H, m), 1.83 (β H, m), 1.45 (γ H, m), 0.98 (δ H, t). UV (abs.ethanol): λ_{max} at 234 nm.

Tetrabutylammonium diiodocuprate(I). ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.32 (α H, m), 1.70 (β H, m), 1.50 (γ H, m), 1.03 (δ H, t). (C$_6$D$_5$Cl): δ 2.99 (α H, m), 1.45 (β H, m), 1.33 (γ H, m), 0.90 (δ H, t). (CD$_3$COCD$_3$): δ 3.45 (α H, m), 1.82 (β H, m), 1.45 (γ H, m), 0.96 (δ H, t). UV (abs.ethanol): λ_{max} at 218 nm.

Tetrabutylammonium dichlorocuprate(I). ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.26 (α H, m), 1.67 (β H, m), 1.47 (γ H, m), 1.02 (δ H, t). (C$_6$D$_5$Cl): δ 3.00 (α H, m), 1.46 (β H, m), 1.30 (γ H, m), 0.92 (δ H, t). UV (abs. ethanol): λ_{max} at 228 nm.

Tetrabutylammonium bromochlorocuprate(I). ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.26 (α H,m) 1.68 (β H, m), 1.47 (γ H, m), 1.02 (δ H, t). (C$_6$D$_5$Cl): δ 2.97 (α H, m) 1.44 (β H, m), 1.29 (γ H, m), 0.91 (δ H, t). UV (abs. ethanol): λ_{max} at 232 nm.

The exchange reactions between the halonitrobenzenes and tetrabutylammonium dihalocuprates(I) in chlorobenzene were performed in an argon atmosphere and with the apparatus described in Ref. 1. Aliquots were taken from the reaction mixtures at proper time intervals, quenched in ice-water, made alkaline with sodium hydroxide and then extracted with ether. The concentrated ether solutions, containing the arylhalides, were analyzed by GLC.

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