

Isocyanides from Alkyl Halides and Onium Dicyanoargentates.

Scope and Mechanism

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Alkyl halides and tetramethylammonium dicyanoargentate give, when a reaction takes place, exclusively the corresponding alkyl isocyanide in nearly quantitative yield. The reactivity sequence of the alkyl halides is shown to be very dependent upon the alkyl group: tertiary > secondary > primary, and the displaced halide ion: $I^- > Br^- > Cl^-$. Acyl halides and activated aromatic iodides are found to be unreactive toward the dicyanoargentate ion.

From a kinetic study in acetonitrile employing some substituted benzhydryl halides, the reactions have been found to be second order, first order in each reactant. The Br/Cl ratio of the rates was found to be highly dependent upon the substrate, being 100 for 4,4'-dimethylbenzhydryl halides but $>10^5$ for unsubstituted benzhydryl halides.

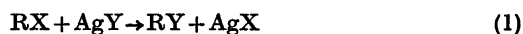
Various possible reaction mechanisms are evaluated and discussed.

A large number of reactions are known where metal compounds, either ionic or neutral ones, are employed as catalysts in replacement reactions. Generally, the HSAB principle¹ may be applied as a useful guide when selecting the appropriate metallic catalyst.^{2,3}

The catalytic properties of silver compounds in various reactions and the application of silver salts in synthesis has been examined for more than a century. The driving force in reactions where silver salts are employed is the ability of silver ions to complex with polarizable atoms; the stability constants of the various complexes formed is in accordance with Pearson's classification;¹ $I > Br > Cl > F$ ^{4,5} and $Se > S > O$.^{6,7} Silver cations are thus valuable as catalysts whenever a polarizable atom is to be displaced, for example in the oxidation of aldehydes⁸ (H-Ag interaction) and in the aminolysis of *S*-alkyl

thiobenzoates⁹ (S-Ag interaction). Copper(II) ions, on the other hand, are known to catalyze the hydrolysis of esters and amides.¹⁰ The rather recently observed catalysis of strained σ -bond rearrangements by silver ions¹¹ has initiated further studies of the chemistry of the silver ion.

The most extensively studied reactions where silver compounds are employed as reagents are the replacement reactions on alkyl halides:

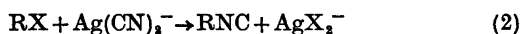


where soluble or slightly soluble silver compounds are employed and where the driving force in the reactions is the formation of less soluble silver compounds, AgX , or in some cases, the formation of silver complexes of high stability.

With regard to the mechanism of these reactions, several kinetic studies have appeared,¹²⁻¹⁷ but the mechanism appears far from settled. In numerous reactions, the anion of the applied silver salt may assist nucleophilically, and the order of the reaction may thus be dependent upon the anion attached to the silver cation. The majority of the reactions following eqn. 1 are thus not strictly second order, but, being first order in the applied alkyl halide, the order in the silver compound varies, usually from 1.5 to 2, depending upon the alkyl halide, the solvent, the concentration and, especially, the applied silver compound. Furthermore, the pronounced dependence of the rate of reaction upon the alkyl halide and the leaving group: $tert-RX \gg sec-RX \gg prim-RX$ and $RI \gg RBr \gg RCl$, has made the interpretation of kinetic results difficult.

Generally, the reactions following eqn. 1 are believed to go via a quadruple ion intermediate, $Y\delta^- - R\delta^+ - X\delta^- - Ag\delta^+$,¹² to a varying extent prior to product formation.¹⁴ Kornblum^{18,19} has argued convincingly in favour of this electrophilic pull-nucleophilic push mechanism, and has suggested that the rather erratic stereochemical results obtained in his studies on the reaction between 2-bromooctane and silver nitrite and silver nitrate in various solvents is due to the relative importance of the electrophilic pull of silver and the nucleophilic push of the anion.

Recently,²⁰ it was shown that by applying onium dicyanoargentates instead of silver cyanide, alkyl isocyanides could be obtained in high yields in homogeneous reactions in aprotic solvents:



No trace of alkyl cyanides was found in the products of these reactions even after repeated analyses directed towards this end. When concentrated solutions of the reactants were applied, the reactions became heterogeneous due to the limited solubility of the onium dihaloargentates. Tetramethylammonium dichloroargentate and dibromoargentate in acetonitrile started to

precipitate at concentrations above 5×10^{-3} M.

We now wish to report an extended study of this reaction to explore the possible generality of this route to organic isocyanides. In Table 1 are collected a number of successful and unsuccessful reactions employing different organic halides, together with obtained yields of isocyanides and semi-quantitative rates of reactions at 25°C in acetonitrile.

For the reactions where no yields of isocyanide could be detected after work-up of the reaction mixture, no precipitation of slightly soluble salts of dihaloargentate ions could be observed, and the applied organic halides were recovered in quantitative yields except for mechanical losses. The yields of 4,4'-dimethylbenzhydryl isocyanide and benzhydryl isocyanide were probably higher than reported in Table 1, as these two isocyanides were quite difficult to purify due to their rather low melting points, their high solubilities in all organic solvents and, especially, to their tendency to polymerize at elevated temperatures which prevented these compounds from being crystallized from warm solution. For this latter reason, the reaction between tetramethylammonium dicyanoargentate and benzhydryl chloride was not examined at elevated temperature to see whether increased

Table 1. Survey of examined reactions with tetramethylammonium dicyanoargentate in acetonitrile in accordance with eqn. 2, with yields of isocyanides and apparent rates of reactions. Concentration of reagents in the $1 \times 10^{-2} - 5 \times 10^{-2}$ M range.

RX	Reaction condition	Yield of RNC in %	Apparent rate of reaction at 25°C
Ph ₃ CCl	Room temp., 90 min	97	Very rapid ^a
(4-MePh) ₃ CHBr	" 4 h	84	Rapid
(4-MePh) ₃ CHCl	" 20 h	77	Slow
Ph ₃ CHBr	" 15 h	92	Slow
Ph ₃ CHCl	" 48 h	0	No reaction
(4-NO ₂ Ph) ₃ CHBr	" 48 h	0	"
(4-NO ₂ Ph) ₃ CBr	" 6 h	0	No reaction
	81.5°C (reflux) 2 h	84	Very slow
MeI	80°C 30 min	> 80	Very slow ^b
MeBr	Room temp., 14 d	trace	Very slow ^c
4-NO ₂ PhCH ₂ Br	" 48 h	0	No reaction
4-NO ₂ PhI	81.5°C (reflux) 24 h	0	"
PhI	" "	0	"
PhCOCl	" "	0	"
4-NO ₂ PhCOBr	" "	0	"

^a Reaction appeared instantaneous; Ref. 21. ^b Nitrobenzene as solvent; Ref. 20. ^c Reaction just observable.

temperature would give a measurable quantity of benzhydryl isocyanide. In contrast to trityl isocyanide,²² 4,4'-dimethylbenzhydryl isocyanide and benzhydryl isocyanide were found to be perfectly stable in acetonitrile at room temperature (see experimental part).

As can be deduced from Table 1, the usual reactivity sequences for Ag(I) assisted reactions are followed for these reactions: *tert*-RX > *sec*-RX > *prim*-RX and RI > RBr > RCl. Acyl halides and aryl halides were found to be completely unreactive. This suggests that the present method for the synthesis of organic isocyanides is only useful for alkyl halides as substrates, and preferably S_N1 type alkyl halides and S_N2 type alkyl iodides.

For the successful reactions, with one exception, no colour was observed during the course of the reactions and the isocyanides isolated were nearly colourless, with a slightly yellowish taint. The reaction between tetramethylammonium dicyanoargentate and tris(4-nitrophenyl)methyl bromide at acetonitrile reflux temperature, however, was completely different. The reaction mixture went through a series of various intensive colours before becoming yellow. (See later discussion for a probable explanation).

In order to gain some insight into the mechanism of this silver-assisted reaction, which appears to be a rare case of a homogeneous one, a kinetic study in acetonitrile was attempted. As it turned out, only a few substrates were found to be useful, because the rates of the reactions were very dependent upon the substrates. Triphenylmethyl chloride was found to react too rapidly for standard analytical methods, while methyl iodide and other very unreactive substrates reacted too slowly, since concentrated solutions of the reactants had to be avoided due to the very limited solubility of the tetramethylammonium dihaloargentates. Some substituted and unsubstituted benzhydryl halides, however, were found to react with rate constants within an acceptable range. 4,4'-Dimethylbenzhydryl bromide and chloride, and benzhydryl bromide, were chosen as substrates.

The UV method, measuring the decrease in alkyl halide concentration, was used for the determination of rate constants. Since the extinction coefficients of the alkyl halides in the 230–260 nm region were considerably greater

than that of tetramethylammonium dicyanoargentate, rate constants could be determined from runs with greatly varying concentrations of tetramethylammonium dicyanoargentate. The UV method appeared to be the only method by which the rates of reaction could be determined. The IR method could not be applied because the dicyanoargentate ion and the formed isocyanides absorbed at nearly the same wavelength, $\approx 2130 \text{ cm}^{-1}$, with rather similar extinction coefficients. The very limited solubility of the tetramethylammonium dihaloargentates prevented the use of the NMR technique for the determination of accurate rate constants.

EXPERIMENTAL

Acetonitrile, "Baker Analyzed" reagent, was distilled from P₂O₅ and finally from CaH₂ prior to use. A midfraction from the final distillation was used both as solvent for the kinetic studies and for the various syntheses. During the kinetic studies, the distillation from CaH₂ was repeated every two weeks.

Benzene, cyclohexane, diethyl ether, and various fractions of light petroleum were dried with sodium.

Tetraphenylarsonium dicyanoargentate and perchlorate were purified as reported.^{20,22}

Tetramethylammonium chloride and bromide, both Fluka *purum*, were washed with acetonitrile and ether and dried in vacuum prior to use.

Tetramethylammonium dicyanoargentate, Me₄NAg(CN)₂. To 40 g of purified tetramethylammonium chloride in 250 ml acetonitrile was added 80 g freshly prepared and dried silver cyanide, and the reaction mixture was refluxed for 5 h. After filtration, diethyl ether was added to precipitate the product. The product was repeatedly dissolved in dry acetonitrile, filtered and precipitated with diethyl ether to remove traces of the sparingly soluble products from the reaction. Finally, the salt was crystallized from acetonitrile; the first crop of crystals was discarded and the midfraction was used for the kinetic studies. This purification was continued until the observed rate constants were reproducible to within 3% for a given concentration of benzhydryl bromide and tetramethylammonium dicyanoargentate. M.p. 194–195°C. (Found: C 31.1; H 5.3; N 17.6; Ag 46.0. Calc. for C₄H₁₂AgN₃: C 30.8; H 5.2; N 17.9; Ag 46.0).

Tetramethylammonium dibromoargentate was made from equivalent amounts of tetramethylammonium bromide and silver bromide in acetonitrile. M.p. 328–330°C. (Found: C 14.6; H 3.5; N 4.0. Calc. for C₄H₁₂AgBr₂N: C 14.4; H 3.5; N 4.1). Tetramethylammonium dichloroargentate was made likewise, m.p. 312–315°C.

These two salts were only sparingly soluble in acetonitrile.

Benzhydryl isocyanide. To 5.0 g benzhydryl bromide, 0.02 mol, crystallized from acetonitrile, in 150 ml acetonitrile was added 7.0 g, 0.03 mol, tetramethylammonium dicyanoargentate. A white precipitate slowly formed. The reaction mixture was stirred at room temperature for 15 h. After filtration, the mother liquor was evaporated to dryness in vacuum and the product extracted with diethyl ether. Crystallization from this solvent alone or by addition of light petroleum (40–60°C) proved unsuccessful. Two crystallizations from luke-warm light petroleum (40–60°C) gave a pure, slightly yellowish product. Yield 3.9 g, 92%, m.p. 48–49°C (47°C²⁰). (Found: C 86.9; H 5.9; N 7.2. Calc. for C₁₄H₁₁N: C 87.0; H 5.7; N 7.3). The white precipitate from the reaction was found to be tetramethylammonium dibromoargentate.

4,4'-Dimethylbenzhydryl isocyanide. To 5.0 g 4,4'-dimethylbenzhydryl bromide, 0.018 mol, m.p. 49–50°C (47.5–48.5°C²³), in 100 ml acetonitrile was added 7.0 g, 0.03 mol, tetramethylammonium dicyanoargentate. Tetramethylammonium dibromoargentate started to precipitate immediately. The reaction mixture was stirred for 4 h at room temperature, and the product was then isolated and purified as above. Yield 3.4 g, 84%, m.p. 57–58°C. (Found: C 87.0; H 6.9; N 6.1. Calc. for C₁₆H₁₅N: C 86.9; H 6.8; N 6.3). Upon reaction with HCl in acetone, this isocyanide gave the corresponding Passerini product,²⁰ *N*-(4,4'-dimethylbenzhydryl)-2-hydroxy-2-methylpropionamide, m.p. 146–147°C, in nearly quantitative yield.

From 4,4'-dimethylbenzhydryl chloride, m.p. 45°C (45–46°C²⁴), the isocyanide was obtained in 77% yield. As this reaction was considerably slower than when the bromide was used, the reaction mixture was stirred for 20 h at room temperature. The white precipitate from the reaction was crystallized from acetonitrile and shown to be tetramethylammonium dichloroargentate.

The reactions between 4,4'-dimethylbenzhydryl bromide, 4,4'-dimethylbenzhydryl chloride and benzhydryl bromide and tetramethylammonium dicyanoargentate were repeated in unpurified acetonitrile and in acetonitrile containing 1% water by volume. The isocyanides were isolated in yields which were not significantly different from the reactions when performed in dry and purified acetonitrile. The IR spectrum in carbon tetrachloride revealed that the formation of the corresponding benzhydrols from reactions performed in moist acetonitrile was negligible.

Tris(4-nitrophenyl)methyl isocyanide. Method A. To 0.5 g tetramethylammonium dicyanoargentate, 0.0027 mol, in 25 ml acetonitrile was added 0.5 g tris(4-nitrophenyl)methyl bromide, m.p. 195–195°C (190–191°C²⁵). No precipitate was formed when the reaction mixture was

stirred at room temperature. The reaction mixture was then refluxed for 2 h and tetramethylammonium dibromoargentate slowly started to precipitate. After the usual treatment of the reaction mixture, the product was extracted with benzene and precipitated with light petroleum. Yield 0.37 g, 84%, m.p. 167–169°C. IR_{NC} 2130 cm⁻¹. Elemental analysis of this compound gave too low values for nitrogen, even after repeated crystallizations from benzene–light petroleum (40–60°C) which did not alter the melting point.

To 0.060 g of tris(4-nitrophenyl)methyl isocyanide in 25 ml warm carbon tetrachloride was added 0.5 ml bromine and the mixture was kept at approximately 50°C for 30 min. After evaporation of the solvent and excess bromine in vacuum, the residue was crystallized from carbon tetrachloride–light petroleum (40–60°C). The product showed no absorbance in the 2100–2300 cm⁻¹ range, but a new, very strong band at 1660 cm⁻¹, due to C=N, suggested the product to be 2,2-dibromo-1-[tris(4-nitrophenyl)methyl]formimine. Yield 0.050 g, 63%, m.p. 162–163°C. (Found: C 43.1; H 2.6; N 9.2. Calc. for C₂₀H₁₂Br₂N₄O₆: C 42.5; H 2.2; N 9.9).

Method B. To 0.3 g tris(4-nitrophenyl)methyl bromide in 25 ml acetonitrile was added a five-fold excess of silver cyanide, and the mixture was stirred at room temperature for 18 h. After the usual work-up, 0.25 g of the product, 93% was isolated. M.p. and mixed m.p. 164–166°C. With excess bromine in carbon tetrachloride a product was obtained which was shown to be identical with that formed from the isocyanide synthesized according to method A using excess bromine.

Attempted isomerization studies of benzhydryl isocyanide, 4,4'-dimethylbenzhydryl isocyanide, and tris(4-nitrophenyl)methyl isocyanide were performed by measuring the peak in the 2130 cm⁻¹ region of 2.0 × 10⁻³ M solution using 0.1 cm liquid cells at approximately 25°C.²³ One solution of each isocyanide was kept in a dark-painted bottle, the other in daylight. No reduction in the intensities of the isocyanide peaks could be observed after 40 to 50 days. A Unicam SP 200 G Infrared Spectrometer was used for the experiments.

Attempted synthesis of methyl isocyanide from methyl bromide and tetramethylammonium dicyanoargentate. To 2.0 g methyl bromide, Fluka purum, 0.021 mol, in 25 ml acetonitrile was added 7.0 g, 0.03 mol, tetramethyl dicyanoargentate. After 14 days at room temperature no precipitate of tetramethylammonium dibromoargentate or change in the UV spectrum of the solution could be observed. The slightly obnoxious odour of the reaction mixture suggested that a minute amount of methyl isocyanide had been formed.

The unreacted methyl bromide was then slowly distilled into a concentrated solution of 10 g triphenyl phosphine in acetone. After 3 days at room temperature, 7.0 g methyl tri-

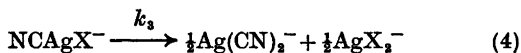
phenylphosphonium bromide, 93 %, precipitated upon addition of diethyl ether.

Benzhydryl chloride and 4,4'-dinitrobenzhydryl bromide, m.p. 93–94°C (92–93°C²⁶) did not give any precipitate with tetramethylammonium dicyanoargentate and no isocyanide could be isolated after stirring at room temperature for 48 h; neither was 4-phenylbenzoyl bromide found to be reactive. Solutions of 4-nitrobenzyl bromide, phenyl iodide, and 4-nitrophenyl iodide were refluxed with tetramethylammonium dicyanoargentate for 24 h without yielding any isocyanides or precipitates of dihaloargentates. From all these unsuccessful synthesis the alkyl halides, acyl halides and aryl halides were recovered in quantitative yields.

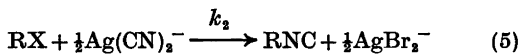
All melting points are corrected.

Chemical shifts of methine protons in benzhydryl compounds. The spectra were measured in carbon tetrachloride on a Jeol NMR C-60 H spectrometer and a Spin-decoupler Frequency Counter JNM-SD 30 was used to determine the resonance positions. The measurements were performed on 0.2 M solutions except for 4,4'-dimethylbenzhydryl where the shift at infinite dilution was obtained by extrapolation. The observed shifts in ppm, relative to TMS were: Ph₂CHBr 6.17; Ph₂CHNC 5.79; (4-MePh)₂CHBr 6.12; (4-MePh)₂CHCl 5.95; (4-MePh)₂CHOH 5.64; (4-MePh)₂CHNC 5.69.

Kinetic studies. Between an alkyl halide, RX, and an onium dicyanoargentate, the following reaction take place:



As no mixed complex silver anions of type NCAgX⁻ are known and as no salts of these anions could be isolated, k_3 is assumed to be far greater than k_2 . The net reaction will thus be:



or simplified for the further calculations:



For a second-order reaction, first order in each of the reactants, the following rate equation is obtained:

$$\left(b - \frac{a}{2}\right)^{-1} \ln \frac{a(2b-x)}{2b(a-x)} = k_2 t \quad (7)$$

where a and b are the concentrations of species A and B, respectively, at $t=0$.

When ϵ_A , ϵ_B , ϵ_C , and ϵ_D are the extinction coefficients of species A, B, C, and D, respectively, at a given wavelength, and x is the

amount of A reacted at time t , the absorption at this wavelength is given by

$$A_t = \epsilon_A(a-x) + \epsilon_B(b-\frac{1}{2}x) + \epsilon_C x + \frac{1}{2}\epsilon_D x \quad (8)$$

With an expression for x , calculated from eqn. 8, one obtains the following rate equation:

$$\left(b - \frac{a}{2}\right)^{-1} \ln \frac{a}{b} \frac{At + 2b\epsilon_A - a\epsilon_A - b\epsilon_D - 2b\epsilon_C}{2A_t + a\epsilon_B - 2b\epsilon_B - a\epsilon_D - 2a\epsilon_C} = k_2 t \quad (9)$$

As the calculations according to eqn. 9 were quite timeconsuming, a Fortran N program²⁷ for Watfor compiler was made whereby plots of the left side of eqn. 9 versus time were rapidly obtained.

In some of the runs there was a downward trend in the rate plots after one or two half-lives, in other runs the plots were completely linear up to five half-lives. No relation, however, between concentrations of reactants, substrates or leaving groups and the observed curvature could be found. Several calculations were performed to adjust the kinetics to rate equations using order of the reactants different from one, but in no case was this procedure found to be successful.

For the reaction between benzhydryl bromide and tetramethylammonium dicyanoargentate with equal concentrations of the reactants, 10⁻³ M, an isobestic point at 225 nm was obtained, and the rate constants were calculated from the change in absorbance at 238 nm. With 4,4'-dimethylbenzhydryl chloride as substrate, an isobestic point at 228 nm was observed; the rate constants were calculated from absorbances at 240 nm. Due to the lower extinction coefficient of this substrate in the 230–250 nm range, rate constants could not be accurately determined from runs where the initial concentration of the alkyl halide was lower than 5 × 10⁻⁴ M. The rate of reaction between 4,4'-dimethylbenzhydryl bromide and tetramethylammonium dicyanoargentate was calculated from the change of absorbance at 250 nm. In this latter reaction, no isobestic point > 220 nm could be observed.

The extinction coefficients of the compounds at the various wavelengths were determined from different batches and the purification of the compounds was continued until the extinction coefficients were reproducible to within the experimental error, ± 2 %. Beer's law was found to be valid for all compounds at the concentrations used for determination of the kinetic data. For all the reactions studied, the reduction in absorbance in the 230–300 nm range during the course of the reactions was due almost entirely to the disappearance of the benzhydryl halides. The neglect of the other species present in the reactions, however, was not found to be justified. The extinction coefficients were determined in 0.1 cm thermostated cells, except for the tetramethylammonium dihaloargentates

where, due to the limited solubility of these salts in acetonitrile, 1 cm cells were used.

The rate studies were performed on a Beckman DB Spectrophotometer using 0.1 cm cells. The thermostated compartments were kept at $\pm 0.05^\circ\text{C}$.

RESULTS

In Tables 2, 3, and 4 are listed the calculated rate constants in acetonitrile at 25.0°C for the various substrates.

In Table 5 are listed the rates of reaction of two of the three substrates at various temperatures together with calculated activation enthalpies and activation entropies. 4,4'-Dimethylbenzhydryl bromide reacted too rapidly at temperatures above 25°C to allow sufficiently accurate activation parameters to be determined.

Due to the dependence of the rates of reaction upon concentration, the rate constants in Table 5 are determined solely from one set of concentrations of the reactants, 5.00×10^{-4} M in

Table 2. Calculated second order rate constants for the reaction between benzhydryl bromide and tetramethylammonium dicyanoargentate in acetonitrile at 25.0°C .

$[\text{Ph}_2\text{CHBr}]_0 \times 10^4$ M	$[\text{Me}_4\text{NAg}(\text{CN})_2]_0 \times 10^4$ M	Number of runs	$k_2 \times 10^3$ $\text{M}^{-1} \text{s}^{-1}$
2.30	2.50	2	6.0 ± 0.1
4.60	5.00	2	5.1 ± 0.1
4.80	5.00	3	5.1 ± 0.2
5.00	100	2	5.3 ± 0.2
9.60	10.0	3	3.6 ± 0.2
11.0	100	3	3.8 ± 0.1
10.0	201	2	3.6 ± 0.1
10.2	200	2	3.6 ± 0.1
10.2	200 (0.5 vol % H_2O)	3	4.7 ± 0.2
10.1	200 (1.0 vol % H_2O)	2	6.5 ± 0.2

Table 3. Calculated second order rate constants for the reaction between 4,4'-dimethylbenzhydryl bromide and tetramethylammonium dicyanoargentate in acetonitrile at 25.0°C .

$[(4\text{-MePh})_2\text{CHBr}]_0 \times 10^4$ M	$[\text{Me}_4\text{NAg}(\text{CN})_2]_0 \times 10^4$ M	Number of runs	k_2 $\text{M}^{-1} \text{s}^{-1}$
5.03	5.03	3	5.0 ± 0.2
5.00	5.00	2	4.8 ± 0.2
4.90	5.00	2	5.0 ± 0.2
10.1	10.1	4	3.5 ± 0.2
10.0	10.0	2	3.8 ± 0.2
10.2	10.0	3	3.6 ± 0.2
9.9	10.1	2	3.4 ± 0.2
10.0	10.0	2	3.6 ± 0.2

Table 4. Calculated second order rate constants for the reaction between 4,4'-dimethylbenzhydryl chloride and tetramethylammonium dicyanoargentate in acetonitrile at 25.0°C .

$[(4\text{-MePh})_2\text{CHCl}]_0 \times 10^4$ M	$[\text{Me}_4\text{NAg}(\text{CN})_2]_0 \times 10^4$ M	Number of runs	$k_2 \times 10^3$ $\text{M}^{-1} \text{s}^{-1}$
4.80	5.00	2	3.7 ± 0.3
5.00	5.00	4	3.6 ± 0.3
5.05	5.00	2	3.9 ± 0.1
4.95	100	2	3.7 ± 0.2
5.05	5.00 (0.1 vol % H_2O)	2	14.0 ± 0.5

Table 5. Effect of temperature on the rates of reaction together with calculated ΔH^\ddagger and ΔS^\ddagger . Concentrations of benzhydryl halides and tetramethylammonium dicyanoargentate 5.00×10^{-4} M and 1.00×10^{-2} M, respectively.

RX	$k_2 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ 25.0°C	35.0°C	45.0°C	ΔH^\ddagger kcal mol ⁻¹	ΔS^\ddagger cal mol ⁻¹ K ⁻¹
Ph ₂ CHBr	5.3 ± 0.1	11.7 ± 0.3	23.2 ± 0.5	13.4	-19
(4-MePh) ₂ CHCl	3.7 ± 0.2	8.8 ± 0.1	20.7 ± 0.5	15.4	-13

Table 6. Rate constants for 4,4'-dimethylbenzhydryl bromide reacting with tetraphenylarsonium dicyanoargentate in acetonitrile at 25.0°C in the presence of tetraphenylarsonium perchlorate at a constant ionic strength of 1.00×10^{-3} M.

$[(4\text{-MePh})_2\text{CHBr}]_0 \times 10^3 \text{ M}$	$[\text{Ag}(\text{CN})_2^-]_0 \times 10^4 \text{ M}$	$[\text{ClO}_4^-]_0 \times 10^4 \text{ M}$	k_2 M ⁻¹ s ⁻¹
1.02	10.0	0	3.3 ± 0.2
1.02	5.0	5.00	8.8 ± 0.5
1.02	1.00	9.00	21.5 ± 1

alkyl halide and 1.00×10^{-2} M in ionic dicyanoargentate.

In Table 6 are listed the rates of reaction of 4,4'-dimethylbenzhydryl bromide in the presence of an ionic perchlorate at a constant ionic strength. Due to the dependence of the rates of reaction upon water, Tables 2 and 4, and since tetramethylammonium perchlorate was found to be most difficult to obtain completely dry, tetraphenylarsonium perchlorate and tetraphenylarsonium dicyanoargentate were used for these rate studies. The higher background absorption in the 220–260 nm region caused by the tetraphenylarsonium ions necessarily reduced the accuracy by which the rate constants could be determined, but the accuracy was clearly sufficient to show the catalytic effect of the perchlorate ions.

DISCUSSION

The very high rate of reaction of trityl chloride, moderate rates of benzhydryl halides and very low reactivity of typical S_N2 substrates (Table 1), suggest that the rates of these silver(I) assisted reactions are highly dependent upon the ability of the substrates to react by what is usually termed the S_N1 mechanism. The term S_N1Ag⁺ for this and related reactions thus appears to be well founded.

In accordance with the idea that the first and

rate-determining step in this S_N1Ag⁺ reaction, as for other reactions of similar type, is the partly or completely heterolytic fission of the carbon-halogen bond, as for usual S_N1 reactions, any factors affecting the rates of S_N1 reactions are expected to influence in a somewhat similar manner the rate of formation of isocyanides in the present reaction.

However, as has been recently pointed out,^{25,28} the mechanisms of S_N1 reactions are very complicated, and the factors determining the rates of these reactions are known to be a function of the substrate, the nucleophile, the leaving group, the ionic strength, the solvent, *etc.*, and depending on which species in the Winstein dissociation scheme is the kinetically most important one. Sneen and co-workers²⁷ have argued that even in classical S_N2 reactions, electrophilic species other than the alkyl halides in their ground state have to be considered. Koskikallio³⁰ has recently presented evidence for the "unified mechanism" or the "ion-pair mechanism" in the reaction between some charged nucleophiles and methyl benzenesulphonate, although this mechanism appears most unlikely for primary and secondary alkyl halides as substrates.³¹ In any event, factors increasing the amount of ion pairs or charged species from uncharged alkyl substrates will necessarily increase the rates of S_N1 reactions.

As water or protic solvents in dipolar aprotic

or non-polar solvent are known to catalyze S_N1 reactions by assisting the carbon-halogen bond fission by hydrogen bonding to the departing halide,^{24,22-24} the catalysis by water in the present reaction is readily understood. The more pronounced catalysis in the case of 4,4'-dimethylbenzhydryl chloride as substrate is thus as expected (Table 4). However, the last two entries in Table 2 indicate that the concentration of water should not be included in the rate equations. Furthermore, the quality of the kinetic runs in moist acetonitrile was not significantly lower than in dry acetonitrile, and more importantly, no yield of benzhydrols or reduction in the yield of the desired isocyanides could be detected when moist acetonitrile was used as solvent for the reactions.

The results listed in Tables 2 and 3 clearly indicate that the calculated second order rate constants are significantly dependent upon the concentration of the alkyl halides, the rates increasing slightly for decreasing concentrations of the alkyl halides. It appears conceivable that for low concentrations of the applied alkyl halides, $< 5 \times 10^{-4}$ M, where the increased rates are observed, the amount of water in the applied purified acetonitrile is of sufficient magnitude to exert a measurable catalytic effect. The second order rate constants were found to be independent, within experimental error, of the concentration of ionic dicyanoargentate for constant concentrations of the alkyl halides, suggesting the order of one for the dicyanoargentate ion in the rate equation to be a valid choice.

The observed catalysis by perchlorate ions (Table 6) is further evidence for the fundamental similarity between the S_N1 and the S_N1Ag^+ mechanism. Although salt effects on S_N1 reactions in aprotic solvents are not very well investigated,²² there appears presently to be no exception to the rule that salts of perchlorate ions and other indifferent ions exert a positive salt effect on S_N1 reactions in this class of solvents.²⁵

Although rates of reactions of only two alkyl bromides, 4,4'-dimethylbenzhydryl bromide and unsubstituted benzhydryl bromide, have been determined, a ρ^+ of -3.1 and a ρ of -5.9 may be calculated from σ^+_{Me} and σ_{Me} , respectively. (Accurate values of ρ^+ and ρ can hardly be determined due to the lack of additivity of σ^+_{Me} and σ_{Me} in benzhydryl substrates.²⁶) The

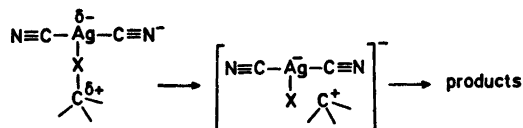
mere magnitudes of these ρ values, however, suggest that the rates of these reactions are highly dependent upon the formation of positive charge on the reacting carbon atom of the reacting alkyl halides.²⁷ As benzhydryl chloride was found not to react, an upper value of ρ^+ of -6 for the benzhydryl chlorides may be estimated.

The rate sequence $RI > RBr > RCl$, the extreme dependence of the ρ^+ -value upon the halogen atom, and likewise, the dependence of the ratio of the rates for corresponding bromo and chloro compounds upon the substrate, being ~ 100 for 4,4'-dimethylbenzhydryl halides and $> 10^5$ for benzhydryl halides, Tables 1 to 4, clearly indicate that the silver atom is playing an important role in the rate determining step. As the examined reactions are clearly second order, first order in the dicyanoargentate ion, a preformed quadruple intermediate²² reacting with a second dicyanoargentate ion is excluded as a mechanistic possibility on kinetic grounds. Thus, the formation of isocyanides in the present reactions must take place through an intramolecular collapse of a 1:1 transition state or intermediate of the reacting species. The lack of detectable amounts of benzhydrols when the reactions are performed in moist acetonitrile is further evidence for an intramolecular rearrangement without the formation of solvent-separated ion pairs or free ions.

The activation parameters determined in this work, Table 5, are in the range expected for typical S_N2 reactions, but this mechanism can be ruled out as the typical S_N2 substrates, methyl iodide, methyl bromide, and 4-nitrobenzyl bromide, are the least reactive ones. The dicyanoargentate ion must therefore necessarily be a very poor nucleophile. As there appears to be some similarities between the factors governing the halophilicity and the carbon nucleophilicity of a nucleophile, it is natural to assume that the dicyanoargentate ion is a poor nucleophile toward positive halogen as well. The very negative ρ -values observed substantiate the conclusion that the dicyanoargentate ion cannot possibly act as a nucleophile in the present reaction.²⁷

Due to the electrophilic nature of the silver atom and the low nucleophilicity of the dicyanoargentate ion, the reaction between an alkyl halide and the dicyanoargentate ion may basi-

cally be considered a typical silver(I) assisted reaction, the interaction between the silver atom and the halogen atom promoting ionization of the carbon halogen bond. The isocyanide may then be formed directly or preferably *via* a tight ion pair by expulsion of the unsymmetrical halocyanoargentate ion (Scheme A).



Scheme A.

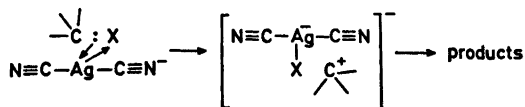
The observed increase in reactivity from unsubstituted benzhydryl halides to 4,4'-dimethylbenzhydryl halides is compatible with the mechanism suggested above and this mechanism readily explains the rate sequences observed: *tert*-RX > *sec*-RX > *prim*-RX and RI > RBr > RCl. It does not, however, satisfactorily explain the variations in the Br/Cl rate ratios upon the substituents in the benzhydryl halides. As pointed out by Kevill and Horwath¹⁶ in their study on 1-adamantyl halides, any reasonable mechanism for the so-called S_N1Ag⁺ reactions must account for the extremely large rate differences between bromides and chlorides. The negative entropies of activation observed in the present reaction, Table 5, may point to a mechanism which is different from the simple Ag⁺-catalyzed S_N1 mechanism depicted in Scheme A. In view of these difficulties a closer look at the reactivity pattern of silver(I) species appears necessary.

Silver(I) species, known to be powerful electrophiles, interact strongly with unsaturated organic molecules through a σ coordinate bond to the metal and the metal in turn donates a pair of *d* electrons to the organic molecule through a π bond.³⁸ The remarkable capability of silver(I) ions to promote σ -bond rearrangements,¹¹ however, suggest that these species are capable of interacting with saturated organic substrates containing only σ -bonds.

In silver(I) species, the *5sp* orbitals are unoccupied and it is therefore suggested that these orbitals interact with carbon-carbon or carbon-halogen σ -bonds. This interaction is facilitated by σ -bonds endowed with substantial *p* character,¹¹ since high levels of *p* character in

the σ -bond are necessary to bring the substrate into the metal coordination sphere. The *4d*-orbitals of silver(I) are filled and in the present reaction these interact with the halogen atoms and transmit electron density to them.

Applying the arguments outlined above, the first step in the reaction between alkyl halides and the dicyanoargentate ion is the ionization of the carbon-halogen bond through transfer of electrons from the carbon-halogen bond to the halogen atom *via* the *sp* and the *d*-orbitals of the silver atom as depicted in Scheme B.



Scheme B.

A reaction mechanism as suggested in Scheme B would imply that the silver atom must act both as an electrophile and as a nucleophile to be able to assist in the breaking of the carbon-halogen bond. The suggestion that the silver atom in the dicyanoargentate ion acts biphilically in the present reaction, a reaction which may be considered as a partly metal insertion reaction, requires some further comments. As this class of reactions of *d*¹⁰ metal complexes are not very well investigated,³⁹ the possible similarity with oxidative addition reactions of other species, notably *d*⁸ elements,^{39,40} may allow a comparison. Chock and Halpern⁴¹ noted the following reactivity sequence for Ir(I) complexes reacting with methyl iodide in benzene: (Ph₃P)₂IrCOCl > (Ph₃P)₂IrCOBr > (Ph₃P)₂IrCOI. Although better donors than triphenyl phosphine as ligands increase the reactivity of Ir(I) complexes,⁴¹ this reactivity sequence is compatible with the suggestion that the biphilic nature of the reacting metal complex plays an important role in determining the reactivity of this class of compounds toward certain substrates. Furthermore, Chock and Halpern³⁸ found that the activation energy for the reaction in benzene between methyl iodide and (Ph₃P)₂IrCOCl, the presumably most electrophilic Ir(I) complex, was only 5.6 kcal mol⁻¹, which is significantly lower than for any known nucleophilic displacement reaction toward methyl iodide in this solvent.⁴² This may be additional evidence for the initial weakening of the carbon-halogen bond

through interaction between the σ -bond orbitals of the carbon-halogen bond and the unoccupied orbitals of the transition metal.

The negative entropies of activation calculated from the rate data in this work, Table 5, accord with a highly constrained or ordered transition state in the rate determining step. The low k_H/k_D ratio, 1.22, found by Chatt and Davidson⁴⁸ for the hydrogenation reaction of $(Ph_3P)_2IrCOCl$, suggests little H-H bond breaking in the transition state, in conformity with the first step depicted in Scheme B.

The biphilic mechanism as suggested above may give a reasonable explanation for the variation in the Br/Cl rate ratios observed in this work. Apart from the fact that the bond energy of the C-X bonds decrease with increasing size of the halogen atom, which may be of rather equal importance to the mechanisms in Scheme A and Scheme B, the effect of a heavy halogen atom in S_N2 type alkyl halides appears to be two-fold when the mechanism in Scheme B is considered: to make the electron density of the carbon-halogen σ bond more available for interaction with the unoccupied $5sp$ orbitals of the silver atom and, simultaneously, to provide a better acceptor for the $4d$ electron density of the silver atom. $(Ph_3P)_2IrCOCl$ is known to react easily with methyl iodide while being quite unreactive toward methyl bromide.⁴¹ There appears to be only a very poor relationship between the bond energies of molecules into which a transition metal is to be inserted and the activation energy of the insertion reaction.⁴¹

For S_N1 alkyl halides, the interaction between the carbon-halogen bond electrons and the unoccupied orbitals of the transition metal may be of limited significance, and a simple electrophilic pull mechanism as indicated in Scheme A may appear satisfactory.

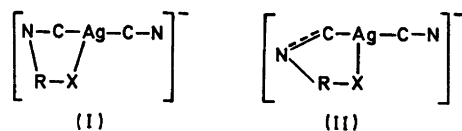
Recently, Halpern and co-workers⁴⁴ have proposed that the silver(I)-catalyzed rearrangement of cubane to cuneane goes *via* adducts of silver(III) prior to the reductive elimination of the observed products. The formation of a silver(III) adduct would necessarily imply that the silver atom becomes completely inserted into the carbon-carbon bond through an oxidative addition reaction prior to the consecutive steps. If a silver(III) species is formed in the present reaction between the dicyanoargentate ion and S_N2 type alkyl halides, the mechanism would in principle be similar to the one depicted in Scheme B, except that the ion pair is formed

via a silver(III) species. The strongly oxidizing character of silver(III)⁴⁴ would be expected to promote heterolysis to the carbonium ion in the tight ion pair, and the extra step of forming the silver(III) species would thus be kinetically insignificant.

Due to the high ionization potential of silver(I) to give silver(III) species,⁴⁵ one has so far hesitated to include species formally of silver(III) as conceivable intermediates or transition states in reactions where silver(I) compounds are used as reagents. In recent years, however, several stable silver(III) compounds have been synthesized.⁴⁶⁻⁵⁰ They are all diamagnetic in conformity with their dsp^3 electronic structure.⁵¹ It appears that compounds containing silver(III) ions fall into two groups: those with highly electronegative donors as ligands, and those containing biguanide frameworks, in which case the high charge of the Ag(III) ion is accommodated by extensive delocalization over the whole biguanide structure.⁵² Whether the two cyano groups in the present case satisfy these demands so as to allow the silver atom in the dicyanoargentate ion to attain a high oxidation state remains unknown. Since the reaction mechanism depicted in Scheme B seems reasonable, at the present stage, the introduction of silver(III) species appears to be an unnecessary complication.

A comparison with reactions of the dicyanoaurate(I) ion⁵³ is not valid due to the large difference in stability between gold(III) and silver(III) species, relative to gold(I) and silver(I).

Finally the following two cyclic transition states have to be considered (Scheme C).



Scheme C.

In (I), the isocyanide would have to be formed *via* a five-membered ring. As the Ag-C and Ag-N distances in the dicyanoargentate ion are 2.13 Å and 3.28 Å, respectively,⁵⁴ and the R-X distances lie in the 1.7 Å - 2.1 Å range,⁵⁵ depending upon which halide is employed, it is hard to imagine how a five-membered ring of this type, with linear N-C-Ag, should be completely favoured over a four-membered ring, in which case the alkyl cyanide would be the expected product. It appears safe to conclude that a cyclic transition state like (I) in Scheme C is a most improbable one.

Another possible reaction mechanism would be an interaction between the N-C triple bond and the alkyl moiety, and an interaction between the silver atom and the halogen atom *via* a cyclic alkylycyanium ion with sp^3 hybridized

carbon and a non-linear N—C—Ag bond (transition state II in Scheme C). Through a transition state of this type, the formation of isocyanides could readily be understood, but this transition state does not appear to be able to explain the large Br/Cl rate ratios observed and its dependence upon the substituents on the phenyl groups in the benzhydryl substrates. Neither are the very negative ρ values in accordance with this mechanism.

It has become increasingly evident in recent years that the classical S_N2 mechanism does not satisfactorily explain certain displacement reactions, particularly reactions of potentially biphilic nucleophiles with alkyl halides. In Scheme B outlined above, a biphilic reagent, through its valence orbitals is acting as an agent for the transfer of electron density from the bond to be broken to the leaving group, giving rise to exceptional high leaving group ratios.

When an oxidative addition product is stable, the reaction may conveniently be described as an insertion of the attacking biphilic nucleophile into the carbon-halogen bond. The exceptional ability of silver(I) species like the silver(I) ion to react by this mechanism appears to be connected with the silver(I) ion itself being a low-valent transition metal ion without the presence of bulky ligands, allowing it to interact with a minimum of steric hindrance with suitable σ -bonds.

The extreme dependence of rate upon the departing halide in substitution reactions of S_N2 type alkyl halides may be a valuable criterion for this mechanism. Furthermore, for reactions which can not possibly be of the S_N2 type, exceptionally low ΔH^\ddagger values and unfavourable entropies may be an additional criterion for this mechanism, in contrast to the typical S_N1 mechanism where the opposite is the case.

As mentioned earlier, the reaction between tris(4-nitrophenyl)methyl bromide and the dicyanoargentate ion appeared to be of a special nature as a series of intensive colours appeared during the reaction. The intensive colour observed may suggest that this reaction follows a radical mechanism as the tris(4-nitrophenyl)methyl radical is known to be stable.⁵⁶ The radical mechanism for reactions between metal complexes and alkyl halides is well substantiated.⁵⁷ Bilevitch and co-workers⁵⁸ have shown that potassium *tert*-butoxide and unsubstituted

trityl halides react *via* radicals. The reaction between trityl chloride and the dicyanoargentate ion, however, gave a near quantitative yield of trityl isocyanide. No yield of "hexaphenylethane", 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene,⁵⁹ could be detected.

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