

# Reactions of Benzylic Compounds. Nucleophilicity, Leaving Group Ability and Carbon Basicity of some Ionic Nucleophiles in Acetonitrile. Comments on the Utility of the Finkelstein Reaction in Synthesis

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The reactions of some 4-substituted benzylic compounds, 4-Z-PhCH<sub>2</sub>X, with various ionic nucleophiles, Y<sup>-</sup>, (Z=NO<sub>2</sub>, H and Me; X and Y = Cl, Br, I, SCN and SeCN) have been studied under homogeneous conditions in acetonitrile at 25.0 °C. All the reactions have been found to proceed through nucleophilic attack at the methylene carbon atom. Isothiocyanates, 4-Z-PhCH<sub>2</sub>NCS, and isoselenocyanates, 4-Z-PhCH<sub>2</sub>NCSe, are not formed. The reactions obey second-order kinetics, first order in each of the reactants. The halide ions and the selenocyanate ion show similar nucleophilic strength and are five to ten times as reactive as the thiocyanate ion. The average leaving group ability is I<sup>-</sup> > Br<sup>-</sup> ≫ Cl<sup>-</sup> > NCSe<sup>-</sup> > NCS<sup>-</sup>. From the equilibrium constants the average carbon basicity order is NCSe<sup>-</sup> ~ NCS<sup>-</sup> ~ Cl<sup>-</sup> ≫ Br<sup>-</sup> > I<sup>-</sup>. The relative basicity of NCSe<sup>-</sup>, NCS<sup>-</sup> and Cl<sup>-</sup> is slightly dependent upon Z; in 4-Me-PhCH<sub>2</sub>X the order is NCS<sup>-</sup> ≥ NCSe<sup>-</sup> > Cl while in 4-NO<sub>2</sub>-PhCH<sub>2</sub>X the order is NCSe<sup>-</sup> > NCS<sup>-</sup> ~ Cl.

The tellurocyanate ion, NCTe<sup>-</sup>, is ten times as reactive as NCSe<sup>-</sup> toward 4-NO<sub>2</sub>-PhCH<sub>2</sub>Cl and no equilibrium is established ( $K > 10^4$ ). The reaction product is an addition compound from the first formed organic tellurocyanate and the displaced chloride ion, the [4-NO<sub>2</sub>-PhCH<sub>2</sub>TeCN(Cl)]<sup>-</sup> anion, a Te(II)-tellurate. The results from an X-ray structure determination of [(Ph<sub>3</sub>P)<sub>2</sub>N][4-NO<sub>2</sub>-PhCH<sub>2</sub>TeCN(Cl)] is presented in brief. In the adduct Cl is *trans* to the cyano group and the Te–Cl bond, 2.923(2) Å, is more than 1 Å shorter than the sum of the van der Waals' radii.

A nucleophilic substitution reaction may be illustrated by the general equation, eqn. (1), where Y



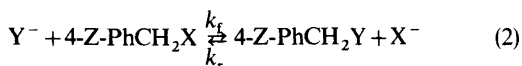
is the nucleophile, X is the leaving group and A is the substrate. In many cases the leaving group X exhibits some nucleophilic strength toward the product AY and an equilibrium will be established.<sup>1</sup> The ratio of the forward rate constant,  $k_f$ , and the reverse rate constant,  $k_r$ , is the equilibrium constant,  $K$ .

To be able to describe in some detail a reaction system as depicted by eqn. (1), it appears necessary to consider a number of factors: 1. The nucleophilicity of Y toward the reaction center. 2. The leaving group ability of X which is in some way related to the energy of the bond to be broken and is dependent upon the structure of the transition state and the nature of the nucleophile Y.<sup>2,3</sup> 3. The relative element basicity of Y and X as given by the equilibrium constant  $K$  which serves as a measure of the possible yield of products. For organic reactions, *i.e.*, when A represents an organic group R, the term carbon basicity applies.<sup>4</sup>

To obtain AY in high yield and of high purity, reaction time and temperature have to be controlled to avoid undesirable by-products due to side-reactions of higher activation energies and from decomposition. A favourable equilibrium constant will first of all be obtained by choosing a leaving group, X, of modest nucleophilicity, but also by experimental conditions by which the nucleophilicity of Y is enhanced<sup>5</sup> and that of X is suppressed or by deactivation or removal of X from the phase in

which the reaction takes place.

In order to get information about the various factors determining  $k_f$ ,  $k_r$  and thus  $K$  for a reaction system the reaction must be well defined, *i.e.* undisturbed by side reactions, and its equilibrium approached with suitable rapidity to allow determination of the rate constants. In the present study we report on some Finkelstein reactions<sup>6</sup> involving various 4-substituted benzylic compounds, eqn. (2).



$Y^- = I^-, Br^-, Cl^-, NCS^-, NCSe^-$  and  $NCTe^-$

$X = I, Br, Cl, SCN$  and  $SeCN$

$Z = NO_2, H$  and  $Me$

Using acetonitrile as solvent and bis(triphenylphosphine)iminium salts,  $[(Ph_3P)_2N]Y$ , abbreviated  $[PNP]Y$ , the reactions are homogeneous. The reactions are sufficiently slow for kinetic measurements and have  $K$ -values of suitable magnitude. The use of  $^{13}C$ -pseudohalide ions and the IR-technique allowed exchange reactions involving organic pseudohalides and pseudohalide ions to be studied. A comparable study of 2-substituted-1-phenyl-ethanones (phenacyl compounds) has recently been published.<sup>7</sup>

## EXPERIMENTAL

**Materials. Solvents.** Acetonitrile, Baker Analyzed Reagent, was first distilled from phosphorus pentoxide and then from calcium chloride in an argon atmosphere. The purified solvent was stored over Linde 4 Å molecular sieves in darkness. All the hydrocarbons and diethyl ether were treated with metallic sodium. Acetone, Baker Analyzed Reagent, was used as received. Dichloromethane was fractionated after the usual treatment with concentrated sulfuric acid. All solvents used for reactions involving the tellurocyanate ion were carefully flushed with argon prior to use.

**Benzyl compounds.** 4-Nitrobenzyl chloride and 4-nitrobenzyl bromide, Fluka *purum*, were crystallized from acetonitrile–diethyl ether and finally from cyclohexane. Benzyl chloride and benzyl bromide, Fluka *puriss*, were flushed for several hours with nitrogen to remove traces of HCl and HBr, then distilled in vacuum with an argon leak. A mid-fraction was used for the kinetic studies. 4-Methylbenzyl bromide, Fluka *purum*, was twice crystallized from cyclohexane.

4-Nitrobenzyl iodide was prepared according to Finkelstein,<sup>6</sup> crystallized from acetone, dried at 0.1 mmHg and stored in darkness. Benzyl iodide was made according to Kumpf,<sup>8</sup> m.p. 25 °C (diethyl ether–pentane) (24 °C<sup>8</sup>). This compound was only used for the recording of its  $^1H$  NMR spectrum, *cf.* Table 1.

4-Nitrobenzyl thiocyanate was prepared according to Bennet and Berry<sup>9</sup> from 4-nitrobenzyl bromide and dry potassium thiocyanate in acetone. After two crystallizations from benzene–diethyl ether the compound was dried at 0.1 mmHg. M.p. 85–86 °C (85.5 °C<sup>9</sup>).  $M^+ 194(15)$ ;  $m/e 136(100)$ . 4-Nitrobenzyl selenocyanate was prepared and purified in a similar way, m.p. 122 °C (122.5 °C<sup>10</sup>).  $M^+ 240(6)$  and  $242(12)$ ,  $m/e 136(100)$ . 4-Nitrobenzyl tellurocyanate was prepared as previously described<sup>11</sup> and crystallized twice from acetone–diethyl ether and finally from dichloromethane, m.p. 123 °C (dec).  $M^+ 292(13)$ ,  $290(11)$ ,  $288(7)$ ;  $m/e 136(100)$ ,  $401(3)$ .

Benzyl thiocyanate was made in the same way as 4-nitrobenzyl thiocyanate. After two crystallizations from diethyl ether–pentane the m.p. was 42 °C (41 °C<sup>12</sup>).  $M^+ 149(14)$ ;  $m/e 91(100)$ . Benzyl selenocyanate was prepared in a similar way, m.p. 72 °C (diethyl ether) (70–71 °C<sup>13</sup>).  $M^+ 195(8)$ ,  $197(17)$ ;  $m/e 91(100)$ .

4-Methylbenzyl chloride was made from the commercially available bromide and tetraphenylarsonium chloride in acetonitrile: To 13.2 g  $Ph_4AsCl$ , 0.03 mol, dried at 70 °C for 4 h at 0.1 mm Hg, dissolved in a minimum quantity of acetonitrile, was added 4.6 g 4-methylbenzyl bromide, 0.025 mol, in 25 ml acetonitrile. The mixture was stirred at room temperature for 3 h and left for 1 h at 0 °C. The least soluble salt, tetraphenylarsonium bromide, together with some unreacted chloride was removed by filtration whereupon the solvent was removed in vacuum. The residue was treated with five 50 ml portions of diethyl ether and the combined diethyl ether extracts distilled in vacuum. Yield 2.1 g (60%), b.p. 92 °C/19 mmHg, (95 °C/20 mmHg<sup>14</sup>).  $M^+ 140(42)$ ,  $142(14)$ ;  $m/e 105(100)$ .

4-Methylbenzyl thiocyanate was made as the 4-nitro-substituted compound. This compound was crystallized from cyclohexane–pentane and purified by sublimation. M.p. 24 °C.  $M^+ 163(7)$ ;  $m/e 105(100)$ . The corresponding selenocyanate, a new compound, was obtained in a similar way and crystallized from cyclohexane. The yield was 57%. M.p. 56 °C. The compound was further purified by sublimation. (Found: C 51.64; H 4.23; N 6.62. Calc. for  $C_9H_9NSe$ : C 51.14; H 4.32; N 6.67).  $M^+ 213, 211(\sim 1)$ ,  $209, 208, 207$ ;  $m/e 105(100)$ .

$[PNP]^+$ -salts. These salts were prepared as previously described<sup>7,15</sup> and dried at ~75 °C at 0.1

mmHg to constant weight prior to use. [PNP]Cl m.p. 272–273 °C (273–274 °C<sup>15</sup>), [PNP]Br m.p. 254–255 °C (253–255 °C<sup>15</sup>), [PNP]I m.p. 253–254 °C (252–254 °C<sup>15</sup>), [PNP]SCN m.p. 186–187 °C, (187–188 °C<sup>15</sup>), [PNP]SeCN m.p. 196–197 °C, (182–185 °C<sup>15</sup>), [PNP]TeCN m.p. ~190 °C (dec) (190–193 °C (dec)<sup>15</sup>). The <sup>13</sup>C-enriched salts were made from potassium <sup>13</sup>C-cyanide,<sup>15</sup> 90.5 % enriched, used as received from Prochem, British Oxygen Co. Ltd.

[PNP]-chlorocyano-4-nitrobenzyltellurate(II). To 0.05 g 4-nitrobenzyl chloride, 0.003 mol, in 40 ml acetone was added 1.73 g [PNP]-tellurocyanate, 0.0025 mol, in 20 ml acetone. The reaction mixture was stirred for 24 h at room temperature. After filtration (to remove traces of Te and TeO<sub>2</sub>) the yellow-green solution was evaporated nearly to dryness. Upon addition of a small amount of diethyl ether traces of the white [PNP]-chloride first precipitated and was removed by filtration. The very soluble [PNP]-tellurate, precipitated in close to quantitative yield after 2 days at ~-10 °C after addition of a considerable amount of diethyl ether. This purification procedure was repeated once to remove traces of [PNP]Cl whereupon a yield of 1.7 g (76%) of yellow-brownish needles was obtained. M.p. ~120 °C (dec). (Found: C 61.61; H 4.34; N 4.95. Calc. for C<sub>44</sub>H<sub>36</sub>ClN<sub>3</sub>O<sub>2</sub>P<sub>2</sub>Te: C 61.18; H 4.20; N 4.86). U.V.: Shoulder to the NO<sub>2</sub>-peak at ~350 nm, log ε ~3.3. I.R.: The spectrum (KBr-

pellet) in the 400–4000 cm<sup>-1</sup> range appeared as a superposition of the spectra of [PNP]Cl and of 4-nitrobenzyl tellurocyanate except for the peak at ~2100 cm<sup>-1</sup> due to the C–N group in nitrobenzyl tellurocyanate which had disappeared.

*Crystal structure determination of [PNP][4-NO<sub>2</sub>PhCH<sub>2</sub>TeCN(Cl)].* Elongated prisms, suitable for the X-ray study were obtained from acetone–diethyl ether. A crystal with dimensions 0.25 × 0.07 × 0.08 mm was selected. Space group P1̄ (No. 2), Z=2, a=9.833(2), b=14.435(2) and c=16.307(2) Å; α=66.09(1)°, β=78.63(1) and γ=71.77(1)°; V=2003 Å<sup>3</sup>, d(calc.)=1.432 g cm<sup>-3</sup>. Intensity data were collected on a CAD4 Enraf-Nonius diffractometer using monochromated MoKα radiation (λ=0.71073 Å). The number of reflections recorded at room temperature was 7051 of which 3589 with I > 2.0σ(I) were retained for the structure determination. No decomposition could be observed during X-ray exposure. The structural parameters were determined with the Enraf-Nonius Structure Determination Pack revised in 1980. Full-matrix least squares refinement led to a final conventional R-value of 0.048 (R<sub>w</sub>=0.046). The estimated standard deviation of the intensity, E.S.D., was 1.136. Tables of observed and calculated structure factors and atomic coordinates etc. are available from the authors.

*Determination of rate and equilibrium constants.* In Table 1 are listed some IR, UV and NMR data for

Table 1. IR, UV and NMR data for benzyl compounds, RX, and some anions, X<sup>-</sup>, in acetonitrile.

X <sup>-</sup> , RX	ν <sub>NCX</sub> (cm <sup>-1</sup> )	ε <sub>320 nm</sub>	ε <sub>350 nm</sub>	δ <sub>CH<sub>2</sub></sub> (Rel. TMS)
N <sup>12</sup> CS <sup>-</sup>	2058			
N <sup>13</sup> CS <sup>-</sup>	2011			
N <sup>12</sup> CSe <sup>-</sup>	2067			
N <sup>13</sup> CSe <sup>-</sup>	2021			
N <sup>12</sup> CTe <sup>-</sup>	2081			
4-NO <sub>2</sub> PhCH <sub>2</sub> Cl		493	236	4.75
4-NO <sub>2</sub> PhCH <sub>2</sub> Br		754	293	4.66
4-NO <sub>2</sub> PhCH <sub>2</sub> I			727	4.58
4-NO <sub>2</sub> PhCH <sub>2</sub> SCN	2159			4.28
4-NO <sub>2</sub> PhCH <sub>2</sub> SeCN	2150			4.30
4-NO <sub>2</sub> PhCH <sub>2</sub> TeCN	2157			4.36
[4-NO <sub>2</sub> PhCH <sub>2</sub> TeCN(Cl)] <sup>-</sup>		(Shoulder at ~340 nm, log ε ~3.3)		4.36
[PNP]Cl		2	0	
PhCH <sub>2</sub> Cl				4.65
PhCH <sub>2</sub> Br				4.62
PhCH <sub>2</sub> I				4.54
PhCH <sub>2</sub> SCN	2165			4.20
PhCH <sub>2</sub> SeCN	2158			4.28
4-MePhCH <sub>2</sub> Cl				4.64
4-MePhCH <sub>2</sub> SCN	2158			4.28
4-MePhCH <sub>2</sub> SeCN	2149			4.26

Table 2. Second-order rate constants,  $k_f$ , relative rate constants,  $k_{rel}$ , (rate constants for RSCN are unity) and equilibrium constants,  $K$ , for reactions between 4-Z-PhCH<sub>2</sub>X and Y<sup>-</sup> in acetonitrile at 25.0 °C.

Z	X	Y <sup>-</sup>	$k_f/M^{-1} s^{-1}$	$k_{rel}$	K
NO <sub>2</sub>	Br	NCSe <sup>-</sup>	2.1(8) × 10 <sup>-1 a</sup>	8.5 × 10 <sup>2</sup>	1.4(5) × 10 <sup>3 b</sup>
NO <sub>2</sub>	Cl	NCSe <sup>-</sup>	1.3(3) × 10 <sup>-3</sup>	3.4	2.6(5)
NO <sub>2</sub>	SeCN	NCSe <sup>-</sup>	0.9(1) × 10 <sup>-3</sup>	2.4	1
NO <sub>2</sub>	SCN	NCSe <sup>-</sup>	3.8(6) × 10 <sup>-4</sup>	1	2.6(5) <sup>b</sup>
NO <sub>2</sub>	Br	NCS <sup>-</sup>	4.5(5) × 10 <sup>-2 c</sup>	2.1 × 10 <sup>3</sup>	3.2(1.2) × 10 <sup>2 b</sup>
NO <sub>2</sub>	Cl	NCS <sup>-</sup>	1.8(3) × 10 <sup>-4</sup>	8.6	1.4(2)
NO <sub>2</sub>	SeCN	NCS <sup>-</sup>	1.2(3) × 10 <sup>-4</sup>	5.7	0.38(7)
NO <sub>2</sub>	SCN	NCS <sup>-</sup>	2.1(4) × 10 <sup>-5</sup>	1	1
NO <sub>2</sub>	I	Cl <sup>-</sup>	1.2(2)	1.0 × 10 <sup>4</sup>	1.0(3) × 10 <sup>3 d</sup>
NO <sub>2</sub>	Br	Cl <sup>-</sup>	2.1(4) × 10 <sup>-1</sup>	1.8 × 10 <sup>3</sup>	3.0(7) × 10 <sup>2 b</sup>
NO <sub>2</sub>	Cl	Cl <sup>-</sup>	5.8 × 10 <sup>-4</sup>	~7 <sup>f</sup>	1
NO <sub>2</sub>	SeCN	Cl <sup>-</sup>	4.7(5) × 10 <sup>-4</sup>	3.9	0.38(6)
NO <sub>2</sub>	SCN	Cl <sup>-</sup>	1.2(2) × 10 <sup>-4</sup>	1	0.8(1)
NO <sub>2</sub>	I	Br <sup>-</sup>	1.8(3)	1.4 × 10 <sup>4</sup>	3.3(5) <sup>b</sup>
NO <sub>2</sub>	Cl	Br <sup>-</sup>	6.3(1.4) × 10 <sup>-4</sup>	4.8	3.3(7) × 10 <sup>-3 d</sup>
NO <sub>2</sub>	SeCN	Br <sup>-</sup>	2.5(1.0) × 10 <sup>-4 g</sup>	1.9	3.1(1.1) × 10 <sup>-3</sup>
NO <sub>2</sub>	SCN	Br <sup>-</sup>	1.3(0.6) × 10 <sup>-4</sup>	1	3.1(1.1) × 10 <sup>-3</sup>
NO <sub>2</sub>	Br	I <sup>-</sup>	0.5(0.2) <sup>g</sup>	4.2 × 10 <sup>2 h</sup>	0.30(0.04) <sup>d</sup>
NO <sub>2</sub>	Cl	I <sup>-</sup>	1.2(0.4) × 10 <sup>-3 g</sup>	1 <sup>h</sup>	1.0(0.3) × 10 <sup>-3 b</sup>
NO <sub>2</sub>	Cl	NCTe <sup>-</sup>	1.6(2) × 10 <sup>-2</sup>		> 1 × 10 <sup>4</sup>
H	I	Cl <sup>-</sup>	6 × 10 <sup>-1 i</sup>	~ × 10 <sup>3 j</sup>	10 <sup>3 i</sup>
H	Br	Cl <sup>-</sup>	1.2 × 10 <sup>-1 i</sup>	~ 1.6 × 10 <sup>3 j</sup>	2.4 × 10 <sup>2 i</sup>
H	Cl	Cl <sup>-</sup>	6.5 × 10 <sup>-4 i</sup>	~ 10 <sup>j</sup>	1
H	SeCN	Cl <sup>-</sup>	2.4(0.4) × 10 <sup>-4</sup>	4.9	0.40(0.05)
H	SCN	Cl <sup>-</sup>	4.9(0.6) × 10 <sup>-5 k</sup>	1	0.48(0.06)
H	Cl	I <sup>-</sup>	6.0 × 10 <sup>-3 i</sup>		1 × 10 <sup>-3 i</sup>
H	Cl	Br <sup>-</sup>	6.0 × 10 <sup>-3 i</sup>		1.4 × 10 <sup>-1 i</sup>
H	Cl	NCSe <sup>-</sup>	6.0(0.7) × 10 <sup>-4</sup>		2.4(0.4)
H	Cl	NCS <sup>-</sup>	1.2(0.3) × 10 <sup>-4</sup>		2.3(0.3)
Me	Cl	Cl	4.6 × 10 <sup>-4 e</sup>		1
Me	Cl	NCSe <sup>-</sup>	9.5(1) × 10 <sup>-4</sup>		2.4(4)
Me	Cl	NCS <sup>-</sup>	2.1(0.3) × 10 <sup>-4</sup>		3.0(5)
Me	SeCN	Cl <sup>-</sup>	3.8(0.4) × 10 <sup>-4</sup>	5.3	0.42(0.06)
Me	SCN	Cl <sup>-</sup>	7.2(0.9) × 10 <sup>-5</sup>	1	0.36(0.05)

<sup>a</sup> 3.2(2) × 10<sup>-1</sup> M<sup>-1</sup> s<sup>-1</sup> in Ref. 16. <sup>b</sup> Calculated from K for the reverse reaction. <sup>c</sup> 5.4(3) × 10<sup>-2</sup> M<sup>-1</sup> s<sup>-1</sup> in Ref. 16. <sup>d</sup> Determined by <sup>1</sup>H NMR. <sup>e</sup> At 20.0 °C, Ref. 17. <sup>f</sup> Assuming the rate constant at 25.0 °C to be 50% higher than at 20.0 °C. <sup>g</sup> Calculated from K and  $k_r$ . <sup>h</sup> Rate constant of RCl defined as unity. <sup>i</sup> At 30.0 °C, Ref. 18. <sup>j</sup> Assuming the rate constant at 25.0 °C to be 30% lower than at 30.0 °C. <sup>k</sup>  $k_f = 5.4 \times 10^{-5}$  M<sup>-1</sup> s<sup>-1</sup> at 30.0 °C, Ref. 18. <sup>l</sup> From rate constant at 20.0 °C,  $k_f = 3.1 \times 10^{-4}$  M<sup>-1</sup> s<sup>-1</sup> + 50%, Ref. 17.

the various compounds which formed the basis for the analytical methods applied for the determination of rate and equilibrium constants. The rate of the reactions between the organic halides and the halide ions were determined by UV; for reactions involving the pseudohalide ions the IR technique was used throughout. For the majority of the reactions the equilibrium constants,  $K$ , were determined from the ratio between the forward and

the reverse rate constants,  $k_f$  and  $k_r$ , and checked by UV and IR of kinetic runs at infinite time or by NMR of more concentrated solutions. Some rate constants could only be determined by the ratio between  $K$  and  $k_f$  or between  $K$  and  $k_r$ , cf. footnotes in Table 2.

The rate constants were calculated from kinetic runs performed under pseudo first-order or second-order conditions, depending upon rate and

equilibrium constants. The concentration of the ionic nucleophiles was in the  $(2-10) \times 10^{-3}$  range. When calculating the equilibrium constants the activity coefficients of the two competing anions were assumed to be the same. No decomposition could be observed during any of the studied reactions and the linearity of the rate plots was generally satisfactory for several half-lives suggesting the reactions to be clean second-order reactions, first order in each of the reactants. For further details with regard to the experimental procedures, cf. Ref. 7.

*Calculations.* From the general equation, eqn. (3),



where  $k_f$  and  $k_r$  are the second-order rate constants, one obtains the integrated rate equations (4)–(7) when  $K_r = k_r/k_f$ ,  $a$  and  $b$  are the initial concentrations of the reactants and  $x$  is the concentration of product at time  $t$ .

$$a \neq b, \quad K_r \neq 0:$$

$$Z^{-\frac{1}{2}} \ln \frac{2ab - x(a+b - Z^{\frac{1}{2}})}{2ab - x(a+b + Z^{\frac{1}{2}})} = k_f t \quad (4)$$

$$\text{where } Z = (a-b)^2 + 4abK_r$$

$$a = b, \quad K_r \neq 0:$$

$$(2aK_r)^{-1} \ln \frac{a-x(1-K_r^{\frac{1}{2}})}{a-x(1+K_r^{\frac{1}{2}})} = k_f t \quad (5)$$

$$a = b, \quad K_r \ll 1:$$

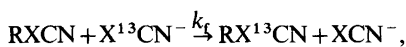
$$\frac{x}{a(a-x)} = k_f t \quad (6)$$

$$a \gg b, \quad K_r \neq 0$$

$$M^{-1} \ln \frac{2ab - x(a - M^{\frac{1}{2}})}{2ab - x(a + M^{\frac{1}{2}})} = k_f t \quad (7)$$

$$\text{where } M = a^2 + 4abK_r$$

For the isotope exchange reactions, *i.e.*



employing  $\text{X}^{13}\text{CN}^-$  of 90.5% isotopic purity in  $^{13}\text{C}$ , the rate equation (8) is valid since  $K$  is necessarily

$$\frac{1}{a+b} \ln \frac{0.905ab}{(a+b)x - 0.905b^2} = k_f t \quad (8)$$

$$\frac{1}{2a} \ln \frac{0.905a}{2ax - 0.905a} = k_f t \quad (9)$$

unity. For equal concentrations of reactants,  $a=b$ , this equation reduces to eqn. (9). A general program was written and used for the evaluation of the rate constants according to eqns. (4)–(9).

*Instrumental.* The UV measurements were performed with a Perkin Elmer 555 Spectrophotometer employing 1 and 0.1 cm quartz cells. A Perkin Elmer 399B Infrared Spectrophotometer and 0.05 cm liquid cells were used for the IR measurements. A Varian EM 360 A NMR Spectrometer was used for the determination of the  $^1\text{H}$  NMR data.

All rate and equilibrium constants determined by IR and UV were calculated from measurements performed at 25.0(1)°C. Up to 10 aliquots were withdrawn periodically for each kinetic run. The NMR experiments were performed at ambient temperature, 25(2)°C.

## RESULTS

In Table 2 are listed the second-order rate constants,  $k_f$ , the equilibrium constants,  $K$ , and the relative rate constants,  $k_{rel}$ , obtained in the present study. (The rate constants for RSCN are defined as unity.) Table 2 also includes some rate constants of  $\text{RCl} + \text{X}^-$  and of  $\text{RX} + \text{Cl}^-$  at 20.0°C and at 30.0°C determined by Hayami and co-workers using  $^{36}\text{Cl}$ .<sup>17,18</sup> Their rate constants are in general agreement with the present data with the exception of the rate of the reactions between benzyl chloride and ionic bromide and iodide which tend to be far too high as compared with the rate constants for the corresponding reactions of 4-nitrobenzyl chloride determined in the present study. We cannot offer a satisfactory explanation for this discrepancy. In order to make a comparison with our rate constants at 25.0°C the rate constants at 20.0°C<sup>17,18</sup> were given an increment of 50% while the rate constants at 30.0°C<sup>17,18</sup> were reduced with 30%.

Admittedly, some of the rate constants and especially some of the equilibrium constants are of rather modest accuracy. Equilibrium constants outside the  $10^{-2}$ – $10^2$  range were particularly difficult to determine accurately. Likewise, rate constants for reactions which progressed only to a small extent ( $K \ll 1$ ) could only be determined with very limited accuracy. (Example:  $\text{RSCN} + \text{Br}^- \xrightarrow{k_f} \text{RBr} + \text{NCS}^-$ .)

In none of the reactions studied could any significant amounts of by-products be detected by IR or by NMR, even after prolonged reaction times. Owing to the large extinction coefficients of RNCS and RNCSe in the 2000–2200  $\text{cm}^{-1}$  region even trace amounts of these compounds should be possible to detect by IR. Previously it has been shown that both in the benzyl<sup>18,21</sup> and in the phenacyl series<sup>7</sup> only esters of the thiocyanic acid, RSCN, and of the selenocyanic acid, RSeCN, are formed by substitution reactions in acetonitrile. Toward benzyl halides in acetonitrile the sulfur end of the potentially ambident thiocyanate ion is known to be three orders of magnitude more reactive than is the nitrogen end.<sup>22</sup> No data are presently available for the Se/N ratio for the selenocyanate ion but in view of the high reactivity of the selenium atom, *cf.* Table 2, this ratio may actually be even higher than  $10^3$  as observed for the S/C ratio in the case of the thiocyanate ion.

Benzylic compounds are also known to act as ambident species, *i.e.* other atoms than the methylene carbon atom may be attacked by nucleophilic species. Of special interest are the sulfur and the selenium atoms in reactions as depicted by eqn. (10) (in the case of Se). No such



products could be detected in any significant amounts by IR and the anticipated yellow colourization of the reaction solution due to RSeSeCN could not be observed. Schiavon<sup>22</sup> has shown by isotopic exchange studies in acetonitrile that the rate of the reaction according to eqn. (10) is only ~1% of the rate of the reaction which proceeds through attack at the methylene carbon atom. The sulfur atom in RSCN is an even less reactive electrophilic atom.<sup>23</sup>

The majority of the experiments in the present study were performed with 4-nitro-substituted compounds ( $Z = \text{NO}_2$ ). This choice was governed by the fact that all 4-nitro-substituted benzyl compounds are well-crystalline and most stable substances and thus simple to purify by crystallization. Furthermore, these compounds are known to be the classic substrates with regard to the  $\text{S}_{\text{N}}2$  mechanism without contributions from  $\text{S}_{\text{N}}1$ -like mechanisms. The high reactivity of the methylene carbon atom<sup>16</sup> causes side-reactions as the one depicted by eqn. (10) to be kinetically of negligible importance.<sup>22</sup> However, the fairly high acidity of the

methylene protons in this class of compounds<sup>24</sup> prevents the use of nucleophiles of some hydrogen basicity in this type of study, particularly in dipolar aprotic solvents.<sup>5</sup>

As a final test of the equilibrium constants determined in the present study and thus also of the rate constants listed in Table 2, the equilibrium constants were the subject of an internal consistency analysis as described by Hine and Weimar.<sup>25</sup> From an equilibrium constant  $K_{\text{A/B}}$  for a reaction  $\text{RB} + \text{A} \rightleftharpoons \text{RA} + \text{B}$  and  $K_{\text{B/C}}$  for  $\text{RC} + \text{B} \rightleftharpoons \text{KB} + \text{C}$ ,  $K_{\text{A/C}}$  for  $\text{RC} + \text{A} \rightleftharpoons \text{KA} + \text{C}$  is given by the ratio between  $K_{\text{A/B}}$  and  $K_{\text{B/C}}$  and can be compared with the experimentally determined value of  $K_{\text{A/C}}$ . When taking the estimated uncertainties into account, no discrepancies between calculated and experimentally determined equilibrium constants could be observed.

The listed equilibrium constant for the reaction between the tellurocyanate ion and 4- $\text{NO}_2$ - $\text{PhCH}_2\text{Cl}$ ,  $K > 10^4$ , is only a crude estimate. No trace of ionic tellurocyanate could be detected by IR from the reaction between the tellurate ion,  $[\text{4-NO}_2\text{-PhCH}_2\text{TeCN}(\text{Cl})]^-$ , and a large excess of ionic chloride. Fig. 1 shows the structure of this tellurate anion from the X-ray study of the [PNP]-salt; the Cl

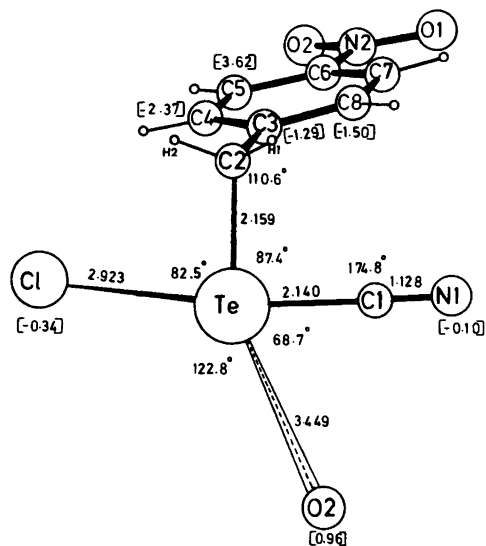


Fig. 1. The structure of the anion in  $[\text{Ph}_3\text{P}]_2\text{N}^+[\text{4-NO}_2\text{-PhCH}_2\text{Te}(\text{CN})\text{Cl}]^-$  as determined by X-ray crystallography. The C2, Te and C1 atoms are in the plane of the paper. The numbers in brackets indicate the distance of the various atoms from this plane.

—Te—C2 part of the ion is in the plane of the paper. The Te—Cl bond in the adduct is approximately *trans* to the Te—C(CN) bond. The Te—Cl bond distance is 2.923(2) Å and is somewhat longer than a Te—Cl single bond, 2.36 Å, but is considerably shorter than the sum of the van der Waals' radii of Te and Cl, 4.00 Å.<sup>25</sup> The Te—Cl bond formation causes a significant elongation of the Te—C(CN) bond length from 2.060(4) Å in 4-nitrobenzyl tellurocyanate<sup>11</sup> to 2.140(10) in the Te(II)anion. The short Te—Cl bond distance and the elongation of the Te—C(CN) bond length suggest that the anion may be considered as yet another example of a three-center two-electron Te-complex.<sup>26</sup> The [PNP]-cation has the expected non-linear form with a P—N—P bond angle of 137.1(4)°. A detailed structural report on [PNP][4-NO<sub>2</sub>-PhCH<sub>2</sub>TeCN(Cl)] and the corresponding bromo and iodo compounds will be published shortly. No evidence for the formation of similar selenium complexes could be observed.

## DISCUSSION

It has become increasingly clear in recent years that the classical organic reactions of the Finkelstein type<sup>6</sup> (charged nucleophiles) and of the Menschutkin type<sup>27</sup> (uncharged nucleophiles) are reversible reactions. Since equilibrium constants are in principle measurable quantities, a number of studies have appeared attempting to relate the kinetics and the thermodynamics of these alkyl transfer reactions in the same manner as the Brønsted equation treats protolysis; for recent surveys Refs. 28 and 29. Unfortunately, the relatively high activation barriers for these reactions is a serious obstacle to obtaining data of both rates and equilibria of sufficient accuracy to allow reliable comparisons to be made between the kinetic property, carbon nucleophilicity, and the thermodynamic property, carbon basicity.

Since benzylic compounds undergo substitution reactions with a number of nucleophiles fairly rapidly<sup>16,30</sup> with clean second-order kinetics; this class of compounds is well-suited for this type of study. Furthermore, by the use of substituents, rates and equilibria may be correlated with Hammett substituent constants. However, it should be emphasized that conclusions derived from studies using ionic nucleophiles as in the present study may not be valid for Menschutkin reactions and *vice versa*

since the structure of the transition state for these two reactions is apparently quite dissimilar. For Finkelstein reactions the transition state is "tight" and fairly symmetrical<sup>31</sup> while for the latter reactions the transition state is fairly product-like.<sup>29,30</sup> Furthermore, it is well known that charged and uncharged nucleophiles are responding most differently to donor and acceptor substituents in the vicinity of the reacting carbon atom.<sup>16,33</sup>

The choice of acetonitrile as the solvent in the present study was governed by the fact that several relevant studies have been performed in this solvent<sup>7,17,18,34-38</sup> and thus allowing valid comparisons to be made.<sup>4,5,39</sup> By using the very soluble and well-dissociated [PNP]-salts as the source of the nucleophiles, experimental difficulties caused by precipitation or variations in the degree of dissociation were eliminated. Unfortunately, when using charged nucleophiles attention cannot be focused on the kinetics—thermodynamics relationship since the nucleophilic atom will be altered from one nucleophile to another which is not necessarily the case in Menschutkin reactions.<sup>29,40</sup>

*The nucleophilicity of the anions.* The data in Table 2 indicate that I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup> and NCSe<sup>-</sup> exhibit approximately the same nucleophilicity and these ions are slightly but significantly more nucleophilic than is the thiocyanate ion, NCS<sup>-</sup>. The tellurocyanate ion, NCTe<sup>-</sup>, is by far the more nucleophilic one being ten times as reactive as is the selenocyanate ion. This observation agrees with the results from a previous kinetic study employing benzyl bromide as the substrate.<sup>41</sup>

Table 3 presents some ratios between second-order rate constants for the various reactions studied. For comparison the range of these ratios from a similar study on 2-substituted-1-phenylethanones (phenacyl compounds), PhC(O)CH<sub>2</sub>X, is included in the Table. It is apparent that none of the nucleophiles show any preference for any of the leaving groups, even though the reactivity of the various substrates spans over several powers of ten, *cf.* Table 2. These rate ratios are also, as can be seen from Table 3, quite independent upon the substituents in the 4-position. The  $k_r(\text{NCSe}^-)/k_r(\text{Br}^-)$  ratios may suggest that the selenocyanate ion prefers a benzylic carbon atom to a phenacylic carbon atom as compared with the bromide ion, but the effect is not very pronounced.

When comparing the rates of the various substrates as a function of the 4-substituents, Me, H

Table 3. The ratio between second-order rate constants for various nucleophiles reacting with 4-Z-PhCH<sub>2</sub>X in acetonitrile at 25.0 °C.

Z	X	$\frac{k_f(\text{NCSe}^-)}{k_f(\text{NCS}^-)}$	$\frac{k_f(\text{NCSe}^-)}{k_f(\text{Cl}^-)}$	$\frac{k_f(\text{NCSe}^-)}{k_f(\text{Br}^-)}$	$\frac{k_f(\text{Br}^-)}{k_f(\text{Cl}^-)}$	$\frac{k_f(\text{I}^-)}{k_f(\text{Br}^-)}$
NO <sub>2</sub>	I				1.5	
NO <sub>2</sub>	Br	7	1.5			
NO <sub>2</sub>	Cl	7	1.5 <sup>a</sup>	2.1	0.7 <sup>a</sup>	~2
NO <sub>2</sub>	SeCN	7	1.9	3.6	0.5	
NO <sub>2</sub>	SCN	18	3.2	2.9	1.1	
H	Cl	5	1.5 <sup>b</sup>		(9) <sup>c</sup>	1 <sup>c</sup>
Me	Cl	5	2			
PhC(O)CH <sub>2</sub>	X <sup>d</sup>	8–20	0.6–2.5	0.3–1.1	~2.2	

<sup>a</sup>Rate constant for Cl<sup>-</sup> exchange at 20.0 °C, cf. Table 2. <sup>b</sup>Rate constant for Cl<sup>-</sup> exchange at 30.0 °C, cf. Table 2. <sup>c</sup>From rate constants at 30.0 °C, Refs. 17 and 18. <sup>d</sup>Range observed for reactions with phenacyl compounds, X = Br, Cl, SeCN and SCN from Ref. 7.

and NO<sub>2</sub>, the usual V-shaped Hammett plot is observed as for numerous other Finkelstein reactions.<sup>16,42</sup> The small variations in the rate ratios with substituents as listed in Table 3 may imply that the form of the Hammett plot is not very dependent upon either the nucleophile or the leaving group.

Hayami and co-workers<sup>37,38</sup> have concluded from NMR-studies that benzylic halides and related substances form addition compounds *via* the methylene protons to halide ions in acetonitrile. These authors have suggested that the formation of these adducts may be part of the mechanism for the substitution process and thus to be taken into account when calculating the rate constants. However, since the ions used in the present study

differ considerably in hydrogen basicities and as the acidities of the methylene protons in the benzylic compounds are well known to be significantly dependent upon the substituents,<sup>24</sup> the small variations in the ratios in Table 3 point against a pre-equilibrium step in the substitution process to be of any kinetic significance.

In Table 4 a summary is made of the average nucleophilicities of the various ions as observed in the present study and a comparison is made with data obtained on 2-substituted-1-phenyl ethanones. The values are given as relative to the thiocyanate ion. As can be seen from the data, only small variations are observed; the bromide ion is apparently somewhat less nucleophilic toward 4-

Table 4. A comparison between the average nucleophilicity, the average leaving group ability and the carbon basicity of I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, NCSe<sup>-</sup> and NCS<sup>-</sup> for reactions with 4-NO<sub>2</sub>-PhCH<sub>2</sub>X (this study) and for reactions with Ph(O)CH<sub>2</sub>X (Ref. 7) in acetonitrile at 25.0 °C.

	I <sup>-</sup>	Br <sup>-</sup>	Cl <sup>-</sup>	NCSe <sup>-</sup>	NCS <sup>-</sup>
Nucleophilicity					
4-NO <sub>2</sub> -PhCH <sub>2</sub> X	6	4	4	8	1
PhC(O)CH <sub>2</sub> X		15	7	10	1
L group ability					
4-NO <sub>2</sub> -PhCH <sub>2</sub> X	1 × 10 <sup>4</sup>	1.5 × 10 <sup>3</sup>	6	3	1
PhC(O)CH <sub>2</sub> X		2 × 10 <sup>4</sup>	75	10	1
Carbon basicity					
4-NO <sub>2</sub> -PhCH <sub>2</sub> X	6 × 10 <sup>-4</sup>	2.5 × 10 <sup>-3</sup>	0.9	2.8	1
PhC(O)CH <sub>2</sub> X		1.4 × 10 <sup>-3</sup>	0.14	1.2	1



nitrobenzylic compounds than toward phenacyl compounds. A similar comparison for the average leaving group ability and the carbon basicity is also presented in Table 4.

*The leaving group ability.* The iodides are clearly the most reactive among the 4-nitrobenzylic compounds. This observation is in general agreement with all other alkyl halides undergoing substitution reactions by the  $S_N2$  mechanism.<sup>4,3</sup> Likewise, the bromides are far more reactive than are the chlorides; the average rate ratio between RBr and RCl being  $\sim 200$  which is of the expected order of magnitude.<sup>7</sup> It is notable from the data in Table 4 that relative to the thiocyanate ion, the leaving group ability of  $\text{NCSe}^-$  and especially the halide ions is far less in the benzyl series than in the phenacyl series. Apparently, in 2-thiocyanato-1-phenylethanone the carbon-sulfur bond is exceptionally strong.

*The carbon basicity.* The iodide ion is the least basic one, but the difference between the iodide ion and the bromide ion is somewhat less than could be concluded from the leaving group ability of these two ions owing to the slightly higher nucleophilicity of the iodide ion. The chloride ion is far more basic and is comparable with the thiocyanate ion. As in the phenacyl series<sup>7</sup> the selenocyanate ion is both a better leaving group and a better nucleophile than is the thiocyanate ion; the net effect causes the selenocyanate ion to be a better carbon base than is the thiocyanate ion. Since the leaving group ability of the selenocyanate ion relative to that of the thiocyanate ion is somewhat less in the benzyl series than in the phenacyl series the result is a slight increase in the carbon basicity of the selenocyanate ion.

In Table 5 a comparison between the carbon basicity of  $\text{Cl}^-$ ,  $\text{NCSe}^-$  and  $\text{NCS}^-$  for various benzylic substrates is made. In the case of the 4-methyl substituted compounds the basicity order is  $\text{NCS}^- > \text{NCSe}^- > \text{Cl}^-$  while in the compounds containing the electron-attracting  $\text{NO}_2$ -group in the 4-position the order is  $\text{NCSe}^- > \text{NCS}^- \sim \text{Cl}^-$ ; the

Table 5. The carbon basicity of  $\text{Cl}^-$ ,  $\text{NCSe}^-$  and  $4\text{-Z-NCS}^-$  ( $\text{NCS}^- = 1$ ) for reactions of  $4\text{-Z-PhCH}_2\text{X}$  in acetonitrile at  $25.0^\circ\text{C}$ .

Z	$\text{Cl}^-$	$\text{NCSe}^-$	$\text{NCS}^-$
$\text{CH}_3$	0.35	0.8	1
H	0.46	1.1	1
$\text{NO}_2$	0.9	2.8	1

order being intermediate in the unsubstituted compounds. The data in Table 2 reveal that this change in basicity order with substituents is due to a slight preference of the thiocyanate ion for substrates with electron-donating substituents relative to  $\text{NCSe}^-$  and  $\text{Cl}^-$  with regard to nucleophilicity which is not sufficiently compensated by a similar effect upon the leaving group ability of  $\text{NCS}^-$ . Such variations in carbon basicity with changes in substrate are highly expected and it has previously been argued that no absolute order of carbon basicity of nucleophiles can be arrived at.<sup>7</sup> In Table 6 is listed some equilibrium constants for reactions between some organic iodides and ionic bromide in acetonitrile. When making such comparisons it is obvious that only results from studies in one solvent and preferably at one temperature can be used,<sup>4,35</sup> cf. Table 7 for the effect of the solvent upon the equilibrium constant for the methyl iodide-bromide ion reaction. Specific effects of cations may also exert a profound influence

Table 6. The equilibrium constants for the reaction between organic iodides and ionic bromide,  $\text{RI} + \text{Br}^- \xrightleftharpoons{K} \text{RBr} + \text{I}^-$  in acetonitrile.

R	4-Nitrobenzyl	Methyl	Ethyl
K	3.3(5) <sup>a</sup>	3.7 <sup>b</sup>	17.7 <sup>c</sup>

<sup>a</sup>This study,  $25.0^\circ\text{C}$ . <sup>b</sup>From Ref. 35,  $30.0^\circ\text{C}$ . <sup>c</sup>From Ref. 36,  $30^\circ\text{C}$ .

Table 7. The equilibrium constants for the reaction between methyl iodide and ionic bromide in various solvents.

	MeCN	Acetone	$\text{H}_2\text{O}$	MeOH	EtOH	2-PrOH	<i>t</i> -AmOH
K	3.7 <sup>a</sup>	12 <sup>b</sup>	0.08 <sup>b</sup>	0.08 <sup>c</sup>	0.1 <sup>c</sup>	0.14 <sup>c</sup>	0.25 <sup>c</sup>

<sup>a</sup>Ref. 35,  $30.0^\circ\text{C}$ . <sup>b</sup>Ref. 4,  $25.0^\circ\text{C}$ . <sup>c</sup>Ref. 36,  $30^\circ\text{C}$ .

upon carbon basicities, even for reactions which apparently are completely homogeneous. Schiavon<sup>22</sup> has found the rate constant for the exchange reaction between 4-nitrobenzyl selenocyanate and potassium [<sup>14</sup>C]-selenocyanate in acetonitrile at 25.0°C to be  $1.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  which is nearly 20 times as high as the one determined in the present study, *cf.* Table 2, even though KSeCN is extensively associated in acetonitrile.<sup>44</sup> Presumably, the leaving group ability of the selenocyanate ion is enhanced in the presence of potassium ions through interaction between the potassium ion and the nitrogen end of the selenocyanate group in RSeCN.<sup>44</sup>

It has become customary to use the thiocyanate ion as a reference ion when making comparisons of carbon basicity in various solvents, *cf.* Refs. 4 and 7 and Tables 2, 4 and 5. However, the data, especially in the two latter tables, may indicate that this choice of reference ion may not be a good one. It is highly possible that the strength of the sulfur-carbon(CH<sub>2</sub>) bond is more dependent upon the organic group than is any of the other X-C(CH<sub>2</sub>) bonds owing to the presence of some double-bond character of the sulfur-carbon(CN) bond as represented by the following canonical structure:

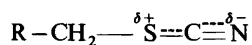


Table 8 summarizes some data from a recent X-ray structural investigation on 4-NO<sub>2</sub>-PhCH<sub>2</sub>XCN (X = Te, Se and S).<sup>45</sup> The results from this study indicate a distinct shortening of the X-C(CN) bond when ascending the VI main group. This is in agreement with the suggestion of some double-bond character of the S-C(CN) bond.

The tellurocyanate ion is by far the most basic

Table 8. A comparison between the X-C(CN) and the X-C(CH<sub>2</sub>) bond lengths in 4-NO<sub>2</sub>-PhCH<sub>2</sub>XCN.<sup>45</sup> (X = Te, Se and S) (Bond lengths in Å).

	RTeCN	RSeCN	RSCN
X-C(CH <sub>2</sub> )	2.167(3)	1.972(3)	1.822(2)
X-C(CN)	2.060(4)	1.844(3)	1.680(2)
Difference	0.107	0.128	0.142
Σ Rcov. X-C <sup>a</sup>	2.14	1.94	1.81

<sup>a</sup> Based upon values from Ref. 25.

one of the ions examined which is highly surprising in view of the reputed weakness of the tellurium-carbon bond.<sup>46,47</sup> However, this observation is entirely due to the fact that the displaced halide ion is trapped by the tellurium atom in the first formed organic tellurocyanate forming a Te(II) complex ion, *cf.* Fig. 1, and thus preventing the reverse reaction to take place.

*Comments on the utility of the Finkelstein reaction in synthesis.* Although the data on rates and equilibria for Finkelstein reactions made available in recent years suggest considerable dependence of nucleophilicity, leaving group ability and carbon basicity upon the structure of the organic group and also the cation present, some general conclusions can still be made. Together with suitable information on solubilities of alkali and onium salts in both protic and aprotic solvents, these data allow a closer scrutiny on the utility of the Finkelstein reaction in synthesis.

First of all, all rate constants, and not to be disregarded, also all rate constants for the reverse reactions, are considerably higher in dipolar aprotic solvents than in protic ones. Since small nucleophilic atoms are discriminating far more between protic and aprotic solvents than large ones, dipolar aprotic solvents are levelling carbon basicities.<sup>4</sup> Variations in equilibrium constants of several orders of magnitude may therefore be experienced; *cf.* Table 7 for a case where only modest variations are observed since the two competing anions, the bromide ion and the iodide ion, are fairly similar in size.

The Finkelstein reaction is usually applied for the preparation of RY from the commercially available chlorides and bromides, RX, eqn. (11). Both from a

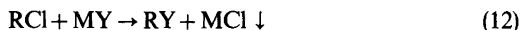


X = Cl, Br, Y<sup>-</sup> = I<sup>-</sup>, NCS<sup>-</sup>, NCSe<sup>-</sup>, NCTe<sup>-</sup>, F<sup>-</sup>, N<sub>3</sub><sup>-</sup>, ROO<sup>-</sup>, RS<sup>-</sup> etc.

kinetic and a thermodynamic point of view it is apparent that the bromides are superior to the chlorides, *cf.* Table 4 for acetonitrile as solvent and Ref. 48 for water as solvent. Thus, any RY, where Y<sup>-</sup> exhibits a higher carbon basicity than the bromide ion may in principle be prepared in homogeneous reactions, particularly in a dipolar aprotic solvent to avoid parallel or consecutive solvolysis reactions. However, the limited solubility of most alkali salts

(MY) in dipolar aprotic solvents often necessitates the use of onium salts as the source of the anion. Furthermore, the considerable hydrogen basicity of many anions in dipolar aprotic solvents, notably  $\text{NC}^-$ ,  $\text{N}_3^-$ ,  $\text{OCN}^-$ ,  $\text{OR}^-$  and  $\text{F}^-$ , may promote undesirable elimination reactions.<sup>49,50</sup> Substitution reactions with these nucleophiles may therefore better be performed in protic solvents but at a high kinetic price.<sup>5</sup> Alternatively, one has to apply various synthetic procedures based upon phase transfer catalysis.<sup>51</sup> The carbon basicity of all these ions are known to be superior to  $\text{Br}^-$  in all solvents and in most cases to  $\text{Cl}^-$ <sup>18,48</sup> preventing the reverse reactions to take place. It should be emphasized that RF cannot be prepared in good yield from RCl, even in dipolar aprotic solvents, without allowing the product to escape, owing to the fairly similar carbon basicity of  $\text{F}^-$  and  $\text{Cl}^-$ .<sup>18,48</sup> The fluoride ion is well solvated also in dipolar aprotic solvents preventing this ion to exhibit the anticipated powerful nucleophilicity in this class of solvents.<sup>52</sup>

The data in Tables 4 and 5 indicate that RSCN and RSeCN cannot be prepared from the corresponding chlorides in good yield and of high purity in homogeneous reactions in dipolar aprotic solvents. Thus, either the bromides, RBr, are to be used or, in the case of the chlorides, RCl, alkali salts, MY, have to be the source of  $\text{NCS}^-$  and  $\text{NCSe}^-$  whereby the displaced chloride ions are trapped as their fairly insoluble alkali salts in both protic and aprotic solvents, eqn. (12).



Eqn. 12 forms the basis for the preparation of organic tellurocyanates,  $\text{RTeCN}$ , in dimethyl sulfoxide as outlined by Cava and co-workers.<sup>47</sup> In the presence of small alkali ions the displaced chloride ion is trapped by the alkali ion allowing the organic tellurocyanate to be isolated. In the presence of onium cations in a homogeneous reaction the chloride ion is trapped by the organic tellurocyanate and the  $\text{Te(II)}$ -complex anion is formed,<sup>46</sup> cf. Fig. 1.

Both from a kinetic and a thermodynamic point of view, organic iodides, RI, are better reagents than are the corresponding bromides, cf. Table 4. However, it should be emphasized that the data readily suggest that the advantage of the iodides to the bromides is generally greatly overestimated.

Both in protic and in aprotic solvents the gain in rate is only 5 to 10-fold, cf. Table 4 and Refs. 16, 43, 48 and 53 for Finkelstein reaction; the same applies to Menschutkin type reactions.<sup>43</sup> When considering their cost and, in most cases, their limited availability, their thermic and photolytic instability and their susceptibility to undergo elimination reactions and to be attacked at the iodine atom by strongly halophilic reagents,<sup>54,55</sup> it is doubtful that the slight increase in rate from the bromides justifies any extensive use of alkyl iodides in either Finkelstein or Menschutkin reactions. Furthermore, owing to the high solubility of most alkali iodides in both protic and aprotic solvents an increase in yield cannot be accomplished by precipitation as outlined in eqn. 12 for the chlorides. Admittedly, toward weakly basic nucleophiles as  $\text{Me}_2\text{S}$  and related compounds,<sup>56</sup> alkyl iodides are to be preferred to the alkyl bromides, particularly in aprotic solvents, the preference being due to the lower basicity of the iodide ion, cf. Table 7. Alkyl iodides are also well known to be superior to the corresponding bromides in insertion reactions and in many-center reactions.<sup>27</sup>

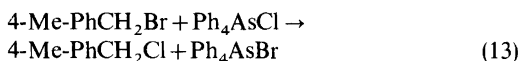
Alkyl iodides present a particular problem owing to their generally difficult preparation. From Table 4 it is seen that RI cannot be prepared from RCl in homogeneous reactions; only when applying alkali salts is the equilibrium shifted in the desired direction, according to eqn. (12); cf. Experimental. In the case of RBr being the substrate, the problem is more complex since alkali bromides and alkali iodides have fairly comparable solubilities in most solvents preventing the reaction according to eqn. (12) to take place. According to equilibrium constants listed in Table 7 the equilibrium is shifted in the right direction in protic solvents. The considerably lower rate constant in this class of solvents combined with the unavoidable solvolysis reactions, particularly when the alkyl group is a secondary or a tertiary one, leads quite often to a less amenable reaction mixture than desired. Organic iodides can, therefore, in practice only be prepared from the corresponding chlorides in heterogeneous reactions in dipolar aprotic solvents or in homogeneous reactions from compounds with leaving groups of very low carbon basicity as  $\text{ROSO}_2\text{F}$ ,  $\text{R}_3\text{O}^+\text{X}^-$  and related compounds. Recently some entirely new methods for the preparation of RI have been described<sup>59,60</sup> which are not based upon the Finkelstein reaction.

As outlined above, the bromides and the chlorides

appear to be the most convenient starting compounds in substitution reactions. However, for many organic groups only one of the organic compounds is commercially available or is conveniently synthesized in the laboratory. In order to increase rate and yield, the bromides are to be preferred to the chlorides, *cf.* Table 4. For reactions with very powerful nucleophiles the chlorides may be sufficiently reactive. Furthermore, the chlorides are generally more stable compounds and less susceptible to undergo solvolysis reactions and to be attacked at the halogen atom by halophilic nucleophiles. Thus, for practical purposes one needs simple and clean procedures for the conversion of chlorides to bromides and *vice versa*.

Organic bromides may, in principle, be prepared from the chlorides by heterogeneous Finkelstein reactions taking advantage of the low solubility of alkali chlorides in most solvents, *cf.* eqn. (12). The yields are generally low, the maximum conversion reported is 84% when varying the substrate, the cation and the solvent.<sup>61</sup> However, by adding ethyl bromide to the reaction mixture whereby the competing ions are removed from the reaction by forming the very volatile ethyl chloride the conversion is close to being quantitative.<sup>61</sup>

When converting bromides to chlorides the procedure is based upon the significantly higher carbon basicity of the chloride ion in homogeneous reactions in dipolar aprotic solvents, *cf.* Table 4. The high nucleophilicity of the chloride ion in this class of solvents<sup>5,33</sup> causes these reactions to be kinetically favourable. Since high molecular weight onium chlorides are necessary for this reaction in order to maintain the ionic chloride soluble, this reaction is hardly recommendable for large scale synthesis of organic chlorides. However, for the preparation of small quantities of organic chlorides this reaction appears as a valuable method. In the present study 4-methylbenzyl chloride was readily obtained from the commercially available bromide using tetraphenylarsonium chloride as the source of the chloride ions, eqn. (13), *cf.* Experimental. Owing



to the lower solubility of  $\text{Ph}_4\text{AsBr}$  than of  $\text{Ph}_4\text{AsCl}$  in acetonitrile the equilibrium is forced in the desired direction by cooling of the reaction mixture.  $[\text{PNP}]\text{Cl}$ , being non-hygroscopic,<sup>15</sup> is an even more convenient source of chloride ions than is  $\text{Ph}_4\text{AsCl}$

for the reaction.<sup>62</sup> Any trace of water present will reduce the nucleophilicity of the chloride ions and thus the rate of the reaction and invariably lower the yield since the equilibrium will be shifted in the undesired direction.

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