

# Substitution Reactions toward 2-Nitrobenzyl Pseudohalides. The Crystal Structure of 2-Nitrobenzyl Tellurocyanate

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The reactions between 2-nitrobenzyl pseudohalides, 2-NO<sub>2</sub>-PhCH<sub>2</sub>XCN, and pseudohalide ions, NCX<sup>-</sup> (X = S, Se or Te) have been studied kinetically in acetonitrile at 25.0°C. The reactions proceed through nucleophilic attack at the methylene carbon atom, forming exclusively the exchange products. The average nucleophilicity order, NCTe<sup>-</sup> >> NCSe<sup>-</sup> > NCS<sup>-</sup>, and the average leaving group order, NCTe<sup>-</sup> ≥ NCSe<sup>-</sup> ≥ NCS<sup>-</sup>, lead to a carbon basicity order NCTe<sup>-</sup> > NCSe<sup>-</sup> ≥ NCS<sup>-</sup>, which is confirmed with equilibrium studies.

A crystal structure determination of 2-nitrobenzyl tellurocyanate at ca. 135°C has revealed that the TeCN group is *syn*-clinal (*gauche*) to the C(CH<sub>2</sub>)–C(Ar) bond with a torsion angle of –48.5(5)°. The TeCC plane forms an angle of 103.4(5)° with the phenyl ring plane. In this conformation the steric influence of the 2-NO<sub>2</sub> group in substitution reactions at the methylene carbon atom will be negligible except for bulky nucleophiles. The tellurium atom forms two fairly strong intermolecular bonds to nitrogen atoms from neighbouring tellurocyanate groups, viz. 2.889(6) Å *trans* to the cyano group and 3.382(6) Å *trans* to the methylene group. In the crystalline state the compound may be considered both as a tellurium(II) complex and as an organic pseudohalide. No intermolecular tellurium–oxygen contacts could be observed.

A nucleophilic substitution reaction may be described by eqn. (1), where Y is the nucleophile and X is the leaving group:



The equilibrium constant, *K*, defined as the ratio between the forward and reverse rate constants, *k<sub>f</sub>* and *k<sub>r</sub>*, may serve as a measure of the possible yield of the product, AY.<sup>1</sup> When A represents an organic group R, the term carbon basicity applies.<sup>2</sup> According to Hine and Weimar<sup>3</sup> this term is analogous to the more familiar concept of hydrogen basicity.<sup>4</sup> Each carbon atom, however, will have its own basicity scale, depending upon its hybridization and the properties of the substituents.

The design and performance of experiments leading to carbon basicity determination are generally difficult; only reaction systems undisturbed by side reactions can be examined. Furthermore, for a complete description of a series of reactions according to eqn. (1), the equilibria must be approached with suitable rapidity to allow at least two of the three parameters for each reaction, *k<sub>f</sub>*, *k<sub>r</sub>*, and *K*, to be determined. Phenacyl compounds, PhC(O)CH<sub>2</sub>X, and benzyl compounds, Z-PhCH<sub>2</sub>X, satisfy several of these demands, and it has been possible to obtain a reasonable estimate of the *sp*<sup>3</sup>-carbon basicity of Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NCS<sup>-</sup> and NCSe<sup>-</sup> in acetonitrile.<sup>5</sup>

In view of the potential of organotellurium compounds in synthesis<sup>6</sup> it was of interest to consider the tellurocyanate ion, NCTe<sup>-</sup>. However, the notorious instability of solutions of the few known organic tellurocyanates<sup>7–11</sup> has so far prevented reliable kinetic and equilibrium studies.<sup>1</sup> We now report on 2-nitrobenzyl tellurocyanate, 2-NO<sub>2</sub>-PhCH<sub>2</sub>TeCN, a compound which is easily prepared from the commercially available chloride.<sup>7</sup> Solutions of this tellurocyanate are stable for days in several organic solvents and can be handled without taking precautions to exclude molecular oxygen provided direct sunlight is avoided. Together with the readily available thiocyanate and selenocyanate, RSCN and RSeCN, and non-hygroscopic sources of NCS<sup>-</sup>, NCSe<sup>-</sup> and NCTe<sup>-</sup> (<sup>12</sup>C and <sup>13</sup>C), the desired exchange reactions [eqn. (1)] could be studied. Similar experiments involving the 3- and 4-nitrobenzyl compounds were also investigated, but the results were, however, of lower accuracy due to the limited stability of the tellurocyanates. Still, it was possible to obtain sufficient kinetic data to compare the three series of substrates. Since 2-nitrobenzyl tellurocyanate crystallizes nicely it was possible to determine its crystal structure, in an attempt to obtain some idea of the steric influence of the 2-nitrobenzyl group in substitution reactions. The results from a structural study of 4-nitrobenzyl tellurocyanate have previously been reported.<sup>9</sup>

## Experimental

**Materials. Solvents.** Acetonitrile and dimethyl sulfoxide (Baker Analyzed Reagents) were distilled under argon from calcium hydride. The purified solvents were stored over Linde 4 Å molecular sieves in the dark. The hydrocarbons were treated with sodium metal.

**Starting materials for benzyl compounds.** 2-Nitrobenzyl chloride (Fluka puriss.) was crystallized from acetonitrile/diethyl ether and dried in vacuum prior to use. 3-Nitrobenzyl chloride, m.p. 45–47 °C (diethyl ether/pentane), was prepared from the corresponding iodide and silver chloride in methanol. The iodide was prepared from the bromide (from 3-nitrotoluene and bromine) and potassium iodide in acetone. All attempts to convert the bromide directly into the chloride by means of silver chloride led to a mixture of halides as indicated by the NMR spectra in MeCN. [–CH<sub>2</sub>Cl: δ 4.80(<sup>1</sup>H) and 45.1(<sup>13</sup>C); –CH<sub>2</sub>Br: 4.69(<sup>1</sup>H) and 32.1(<sup>13</sup>C)].

**Benzyl thiocyanates and benzyl selenocyanates.** These compounds were prepared from the corresponding chlorides and carefully dried potassium thiocyanate and selenocyanate in acetone. The compounds were crystallized from cyclohexane and acetonitrile and dried in vacuum. 3-Nitrobenzyl selenocyanate, m.p. 86–87 °C, appears to be a new compound. [IR: 2154 cm<sup>-1</sup>, –CH<sub>2</sub>SeCN: 31.1(<sup>13</sup>C)]. 2-Nitrobenzyl thiocyanate: 2163 cm<sup>-1</sup>, δ 4.53(<sup>1</sup>H) and 36.0(<sup>13</sup>C). 2-Nitrobenzyl selenocyanate: 2160 cm<sup>-1</sup>, δ 4.54(<sup>1</sup>H) and 30.1(<sup>13</sup>C). The 4-nitrobenzyl pseudohalides were prepared from the chloride as described:<sup>1</sup> –CH<sub>2</sub>Cl: δ 4.76(<sup>1</sup>H), 45.0(<sup>13</sup>C); –CH<sub>2</sub>SCN: δ 4.61(<sup>1</sup>H), 36.7(<sup>13</sup>C); –CH<sub>2</sub>SeCN: δ 4.37(<sup>1</sup>H), 31.1(<sup>13</sup>C); –CH<sub>2</sub>TeCN: δ 4.37(<sup>1</sup>H), 13.5(<sup>13</sup>C). (NMR-spectra in MeCN; shifts in p.p.m. rel. to TMS).

**2-Nitrobenzyl tellurocyanate.** This compound was prepared in 69 % yield from the chloride and an *in situ* solution of KTeCN in dimethyl sulfoxide.<sup>7,10,12,13</sup> The tellurocyanate was first crystallized from benzene/pentane and then twice from acetonitrile, m.p. 87–89 °C (dec.). [I.R. 2153 cm<sup>-1</sup> (TeCN); –CH<sub>2</sub>TeCN: δ 4.51(<sup>1</sup>H) and 11.6(<sup>13</sup>C)].

**3-Nitrobenzyl tellurocyanate.** Prepared as the 2- and 4-nitrobenzyl tellurocyanates but in considerably lower yield, ~20–30 %. The yellow crystals, from benzene/pentane, are stable in the dark. A solution in acetonitrile rapidly deposits black tellurium. M.p. ~81 °C (dec.), IR 2151 cm<sup>-1</sup> (TeCN), δ 22.6(<sup>13</sup>C). A minute amount of a red crystalline product, presumably the ditelluride, (3-NO<sub>2</sub>PhCH<sub>2</sub>Te)<sub>2</sub>, coprecipitated with the tellurocyanate. This compound was not further characterized.

**[PNP]<sup>+</sup> salts.** The [(Ph<sub>3</sub>P)<sub>2</sub>N]<sup>+</sup> salts, abbreviated [PNP]<sup>+</sup> salts, were prepared and purified as described.<sup>1</sup> The <sup>13</sup>C-enriched salts were prepared from potassium <sup>13</sup>C-cyanide (90.5 % enriched; Prochem, British Oxygen Co. Ltd.).

**Rate and equilibrium studies.** The reactions were followed by IR using liquid cells. For experimental details and calculations see Ref. 1.

**Addition compound from 2-nitrobenzyl tellurocyanate and [PNP]Cl.** A solution of 2-nitrobenzyl tellurocyanate in acetonitrile was treated with an equivalent amount of [PNP]Cl as described for the preparation of [PNP][4-NO<sub>2</sub>-PhCH<sub>2</sub>Te(CN)Cl].<sup>13</sup> Yellow crystals were obtained from acetone/diethyl ether in 62 % yield, m.p. 131–133 °C (dec.). IR showed no residual absorption in the 2100–2200 cm<sup>-1</sup> region.

**Oxygenation reaction.** A 0.02 M solution of 2-NO<sub>2</sub>-PhCH<sub>2</sub>TeCN in acetonitrile, kept in the dark at room temperature, was flushed with a slow stream of dry oxygen. After 24 h the solution had become slightly turbid, but an IR spectrum of the solution showed that the tellurocyanate was virtually unchanged. The solution was then irradiated with a Hanovia lamp (λ<sub>max</sub> = 264 nm). Elemental tellurium, and possibly some tellurium dioxide, precipitated immediately. After 20 min the solution was filtered. An IR spectrum of the colourless solution, from which no further tellurium precipitated, showed a strong peak at ~2150 cm<sup>-1</sup>, far stronger than anticipated for the organic tellurocyanate at 2153 cm<sup>-1</sup>. Additionally, two new strong peaks at ~1700 cm<sup>-1</sup> and at ~3400 cm<sup>-1</sup> had appeared. The products from the reaction were not subjected to further analyses.

Table 1. Crystal and experimental data for 2-nitrobenzyl tellurocyanate, 2-NO<sub>2</sub>-PhCH<sub>2</sub>TeCN (C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>Te).

|  |  |
|--|--|
| Crystal system   | Orthorhombic   |
| <i>a</i> /Å  | 5.280(1)   |
| <i>b</i> /Å  | 6.101(1)   |
| <i>c</i> /Å  | 29.053(6)  |
| <i>V</i> /Å <sup>3</sup>   | 935.9(3)   |
| Temp./°C   | –135   |
| Space group  | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19) |
| <i>M</i>   | 289.74   |
| <i>Z</i>   | 4  |
| <i>F</i> (000)   | 544  |
| <i>D</i> <sub>x</sub> /gcm <sup>-3</sup>   | 2.056  |
| μ (MoKα)/cm <sup>-1</sup>  | 31.5   |
| Scan mode  | ω  |
| Scan speed (ω)/° min <sup>-1</sup>   | 3  |
| Scan range (ω)/°   | 1.2  |
| Stability monitoring   | 3 Test refl./100 observ.                                       |
| Maximum sin θ/λ/Å <sup>-1</sup>  | 0.81   |
| No. of indep. meas.  | 1657   |
| No. with <i>I</i> > 3.σ( <i>I</i> )  | 1635   |
| Correction for absorption  | Empirical  |
| No. of parameters refined  | 118  |
| Weighting scheme   | ω = [σ <sup>2</sup> ( <i>F</i> )] <sup>-1</sup>                |
| <i>R</i> = Σ  <i>F</i> <sub>o</sub> – <i>F</i> <sub>c</sub>  /Σ <i>F</i> <sub>o</sub>  | 0.036  |
| <i>R</i> <sub>w</sub> = [Σ <i>w</i> ( <i>F</i> <sub>o</sub> – <i>F</i> <sub>c</sub> ) <sup>2</sup> /Σ <i>wF</i> <sub>o</sub> <sup>2</sup> ] <sup>1/2</sup> | 0.044  |
| <i>S</i> = [Σ <i>w</i> ( <i>F</i> <sub>o</sub> – <i>F</i> <sub>c</sub> ) <sup>2</sup> /( <i>n</i> – <i>m</i> )] <sup>1/2</sup>                             | 1.89   |

Table 2. Fractional atomic coordinates.  $U_{eq}$  is defined by  $\frac{1}{3} \sum u_{ii}$ .

| Atom | x           | y           | z          | $U_{eq}$ |
|------|-------------|-------------|------------|----------|
| Te1  | 0.75361(10) | 0.09388(5)  | 0.96197(1) | 0.020    |
| O1   | 0.8899(11)  | 0.3289(8)   | 0.8653(2)  | 0.036    |
| O2   | 1.0349(12)  | 0.2182(9)   | 0.8001(2)  | 0.049    |
| N1   | 0.8887(11)  | 0.2002(9)   | 0.8328(2)  | 0.027    |
| N2   | 0.6925(12)  | -0.4356(9)  | 0.9600(2)  | 0.035    |
| C1   | 0.5241(12)  | -0.0095(10) | 0.9669(2)  | 0.025    |
| C2   | 0.7106(11)  | 0.0157(9)   | 0.8327(2)  | 0.021    |
| C3   | 0.7417(16)  | -0.1308(9)  | 0.7965(2)  | 0.030    |
| C4   | 0.5851(15)  | -0.3094(11) | 0.7936(2)  | 0.034    |
| C5   | 0.3979(16)  | -0.4314(11) | 0.8255(3)  | 0.038    |
| C6   | 0.3692(13)  | -0.1934(11) | 0.8617(2)  | 0.028    |
| C7   | 0.4800(12)  | 0.1341(10)  | 0.9071(2)  | 0.026    |
| C8   | 0.7134(14)  | -0.2476(8)  | 0.9600(2)  | 0.026    |

**X-Ray data and structure determination.** A suitable crystal of 2-nitrobenzyl tellurocyanate,  $0.1 \times 0.3 \times 0.3$  mm, was grown from an acetonitrile solution. Data for unit cell determination and intensity data were collected using a SYNTEX P1 diffractometer with crystal monochromated MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å). Crystal and experimental data are given in Table 1.

The atomic coordinates of all non-hydrogen atoms were determined by direct methods (MITHRIL<sup>14</sup>). Refinements were performed by least-squares calculations; hydrogen positions were calculated and included in the structure factor calculations but they were not refined. An empirical absorption correction was applied;<sup>15</sup> minimum absorption correction was 0.714, maximum absorption correction was 1.394. Computer programs employed are described in Ref. 16. Final figures of merit based on the refinement of 118 parameters are included in Table 1. Positional parameters are given in Table 2. Anisotropic thermal parameters and the structure factor listing may be obtained from the authors upon request.

## Results and discussion

*The crystal structure of 2-nitrobenzyl tellurocyanate.*

**1. Description of the structure.** An ORTEP drawing of 2-NO<sub>2</sub>-PhCH<sub>2</sub>TeCN is shown in Fig. 1. In this drawing the tellurium atom, Te, the cyano carbon atom, C8, and the ipso carbon atom, C1, are in the plane of the paper. Fig. 1 also shows the two intermolecular contacts between the tellurium atom and the nitrogens (N2' and N2'') in neighbouring tellurocyanate groups, with lengths of 2.889(6) Å *trans* to the cyano group and 3.382(6) Å *trans* to the methylene group. The bond lengths and bond angles are listed in Table 3.

Fig. 2 shows Newman projections along the Te-C7 bond (left), the C7-C1 bond (center) and the N1-C2 bond (right). The left figure shows that the TeCN group is *syn-clinal* to the C1-C7 bond. The distance between the tellurium atom and one of the oxygens, O1, is 3.235 Å, significantly less than the van der Waals contact distance,

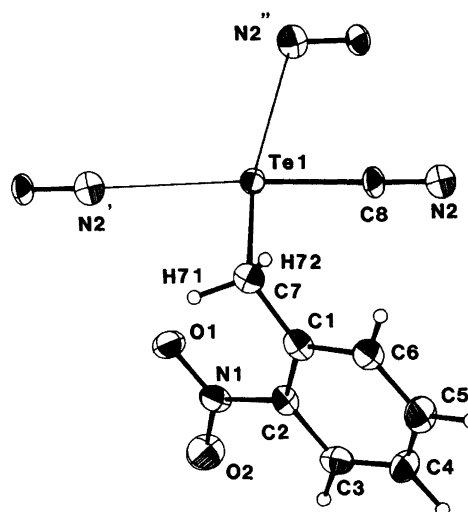


Fig. 1. ORTEP drawing of 2-nitrobenzyl tellurocyanate. The tellurium atom, Te1, the ipso carbon atom, C1, and the cyano carbon atom, C8, are in the plane of the paper. The weak lines from Te1 to N2' and N2'' represent intermolecular Te-N contacts.

Table 3. Bond lengths (Å), bond angles (°) and torsion angles (°).

| Distance      |            | Distance     |           |
|---------------|------------|--------------|-----------|
| Te1-C7        | 2.165(7)   | Te1-C8       | 2.095(6)  |
| O1-N1         | 1.228(7)   | O2-N1        | 1.228(8)  |
| N1-C2         | 1.466(8)   | N2-C8        | 1.152(8)  |
| C1-C2         | 1.406(9)   | C1-C6        | 1.397(10) |
| C1-C7         | 1.480(9)   | C2-C3        | 1.391(8)  |
| C3-C4         | 1.370(10)  | C4-C5        | 1.368(11) |
| C5-C6         | 1.394(10)  | Te1-N2'      | 2.889(6)  |
| Te1-N2''      | 3.382(7)   |              |           |
| Angle         |            | Angle        |           |
| Te1-C8-N2     | 178.5(6)   | O1-N1-O2     | 122.2(6)  |
| C7-Te1-C8     | 91.5(3)    | O2-N1-C2     | 118.1(6)  |
| O1-N2-C2      | 119.7(6)   | C2-C1-C7     | 127.1(6)  |
| C2-C1-C6      | 114.9(6)   | C6-C1-C7     | 117.9     |
| N1-C2-C1      | 122.1(6)   | C1-C2-C3     | 123.1(6)  |
| N1-C2-C3      | 114.8(6)   | C2-C3-C4     | 119.1(7)  |
| C3-C4-C5      | 120.6(7)   | C1-C6-C5     | 122.6(7)  |
| C4-C5-C6      | 119.7(7)   | C7-Te1-N2'   | 78.4(6)   |
| Te1-C7-C1     | 114.2(5)   | C8-Te1-N2''  | 78.7(6)   |
| C7-Te1-N2''   | 169.4(7)   | N2'-Te1-N2'' | 111.9(6)  |
| C8-Te1-N2'    | 167.7(7)   |              |           |
| Torsion angle |            |              |           |
| C8-Te1-C7-C1  | -48.5(5)   |              |           |
| O1-N1-C2-C1   | 5.6(6)     |              |           |
| O1-N1-C2-C3   | -174.3(8)  |              |           |
| O2-N1-C2-C1   | -175.3(9)  |              |           |
| O2-N1-C2-C3   | 4.8(6)     |              |           |
| C6-C1-C2-N1   | 179.7(9)   |              |           |
| C2-C1-C7-Te1  | -75.4(7)   |              |           |
| C7-C1-C2-N1   | -1.3(6)    |              |           |
| C7-C1-C2-C3   | 178.5(10)  |              |           |
| C6-C1-C7-Te1  | 103.4(7)   |              |           |
| C7-C1-C6-C5   | -178.7(10) |              |           |
| N1-C2-C3-C4   | 179.6(9)   |              |           |

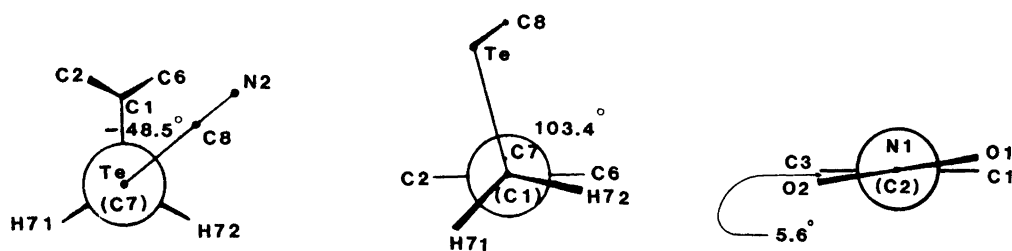


Fig. 2. Newman projections along the Te–C7 bond (left), the C7–C1 bond (center) and the N1–C2 bond (right).

3.6 Å. The position of this oxygen, however, more than 2 Å away from the Te–C8–N2'–N2'' plane, does not indicate contact between O1 and Te (Fig. 1). Since no intermolecular Te–O contacts were observed and the inter-tellurium distances were longer than 3.935 Å, one may conclude that the crystal lattice is essentially the result of a network of tellurium–nitrogen contacts with C8–N2–Te angles of 168.0° at N2' and 110.4° at N2''.

**2. The 2-nitrobenzyl group.** The phenyl ring carbon atom and the nitrogen atom of the nitro group form a perfect plane. The methylene carbon atom, C7, is slightly (0.036 Å) out of this plane. This type of non-planarity in benzyl compounds appears to be quite general.<sup>17</sup> The nitro group is twisted 5.6° from the phenyl ring plane. Relative to this plane, C7, O1 and the tellurocyanate group are located say, above, while O2 and the methylene hydrogen atoms, H71 and H72, are below.

The distance between O1 and H71 is 2.33 Å. The question arises whether the oxygen atom has sufficient donor properties to engage in an intramolecular contact with the weakly acidic hydrogen atom. Such a contact would undoubtedly influence the C–Ph dihedral angle [Fig. 2 (center)] and thus the conformation of the molecule; cf. the structure of 2-nitrobenzenesulfonyl chloride<sup>18</sup> and related compounds.<sup>19,20</sup> The twist of the nitro group from the phenyl ring plane, however, moves O1 away from H71. A similar increase in the O–H distance due to the twist angle of the nitro group has been observed in 2-nitrobenzaldehyde.<sup>21</sup> The nearly complete symmetry of the nitro groups [N–O lengths 1.228(4) Å, C–N–O angles 119.7(4)° and 118.1(4)°] gives no indication of the oxygens being involved in interactions with electron-accepting elements. Actually, the C1–C2–N1 angle, 122.1(4)°, significantly larger than the C3–C2–N1 angle, 114.8(6)°, indicates repulsion between the methylene hydrogen atoms and the nitro group.<sup>22,23</sup> The distinct difference in the external bond angles at the *ipso* carbon atom, C1 [ $\angle$ C2C1C7, 127.1(4)° and  $\angle$ C6C1C7, 117.9(4)°], is in agreement with this suggestion. In 4-NO<sub>2</sub>-PhCH<sub>2</sub>XCN (X = Te, Se and S) the corresponding bond angles are in the 118–122° range.<sup>9</sup> The large C1–C2–N1 and C2–C1–C7 bond angles further demonstrate the absence of a contact between Te and O1.

Although the aromatic carbon atoms form a perfect plane, the phenyl ring is distorted. The bond angle at the

carbon bearing the nitro group, C2, is 123.1(4)°, as observed in numerous nitroaromatic compounds.<sup>24</sup> The bond angle at the *ipso* carbon, C1, is only 115.0(4)°. Bond angles of this magnitude, ~115°, are usually observed only at carbon atoms linked to weakly electronegative atoms, as in Ph<sub>4</sub>B<sup>-</sup><sup>26</sup> and in Ph<sub>4</sub>Si.<sup>27</sup> Characteristic for this class of compounds are distinctly non-planar *ipso* carbon atoms. In 2-nitrobenzyl tellurocyanate the benzyl group is close to being planar; cf. the small distance between C7 and the aromatic plane. Presumably, the size of the C2–C1–C6 angle is due to an additive effect of the nitro group at C2 and the methylene group linked to C1, each group causing a decrease of the internal bond angle at C1 of ~2°. <sup>9,17</sup>

The bond angle at C7, 114.2(2)°, is significantly larger than expected for an *sp*<sup>3</sup> hybridized atom. This increase in the *s*-character of the methylene carbon atom appears to be general for benzyl compounds and is probably related to the electronegativity of the substituents. The larger C7 bond angle in the present compound than in the 4-nitrobenzyl tellurocyanate, 112.4(2)°, may therefore suggest that the 2-nitro group is a more electron-attracting substituent than is the 4-nitro group. The lack of structural studies of other 2-nitrobenzyl compounds prevents this conclusion from being substantiated.

**3. The tellurium-carbon bonds.** The available surveys on Te–C single-bond lengths suggest that 2.14 Å is a reasonable estimate for Te–C(aliph.).<sup>27,28</sup> The Te–C(CH<sub>2</sub>) bond length in the present compound, 2.165(7) Å, may appear to be rather long, but is as observed in the 4-nitro compound.<sup>9</sup> The long Te–C(CH<sub>2</sub>) bond in the two tellurocyanates accords with a trend toward longer C–X bonds in benzyl compounds than in the corresponding methyl compounds when descending the VI and VII main groups. This bond-lengthening may explain the facile substitution of benzyl compounds.<sup>7</sup>

The Te–C(CN) bond, 2.095(6) Å, is significantly shorter than the Te–C(CH<sub>2</sub>) bond. This shortening by ~0.07 Å is expected from the difference in the single bond radii of *sp*<sup>3</sup>-C and *sp*-C, viz. 0.077 Å. In the 4-nitro derivative the Te–C(CN) bond is only 2.060(4) Å.<sup>9</sup> This difference between the two Te–C(CN) bond lengths may not be real, however, because it is known that the position of a small carbon atom is difficult to determine accurately when linked to a large atom in a linear group.<sup>29</sup> The C–N bond

length, 1.152(3) Å, confirms that this bond length in pseudohalide groups, XCN, is independent of the size and charge of the heteroatom, X, and of the X–C bond length. The TeCN group is essentially linear, with a Te–C8–N2 angle of 178.5(5)°.

**4. Coordination around the tellurium atom.** The tellurium atom forms two intermolecular "secondary bonds" to nitrogen atoms in neighbouring tellurocyanate groups: one short bond *trans* to the cyano group and one long bond *trans* to the methylene group. The C7–Te–C8 bond angle, 91.5(3)°, is at the low end of the range for R<sub>2</sub>Te.<sup>28</sup> Strong intermolecular contacts seem to decrease the C–X–C angle in divalent main group VI species.<sup>13</sup> The sum of the bond angles around the tellurium atom is 360.5(2.1)°. 2-Nitrobenzyl tellurocyanate may therefore be considered as being a distorted square-planar Te(II) complex in the crystalline state.<sup>30</sup> The intermolecular contacts (Fig. 1) show that the tellurocyanate group in RTeCN contains an electron-accepting tellurium atom and an electron-donating nitrogen atom. No dipole moment studies on RTeCN have so far been performed, but from purely electronegativity considerations one may assume that the donor ability of the nitrogen atom in RXCN will increase with increasing size of X. The group moment of SeCN in RSeCN exceeds that of SCN in RSCN by some 0.5 D.<sup>31,32</sup> A comparison of the structures of 2- and 4-nitrobenzyl tellurocyanate, I and II, may indicate that the former compound has the larger contribution from the pseudo-ionic structure, RTe<sup>δ+</sup>=C=N<sup>δ-</sup>. While the contacts *trans* to the cyano group in the two compounds are rather similar, viz. 2.889(4) Å (Te–N in I) and 2.949(1) Å (Te–O in II), the contacts *trans* to the methylene group [3.382(4) Å (Te–N in I) and 3.182(2) Å (Te–O in II)] do not substantiate this conclusion. It is apparent from these two structural studies that the tellurium atom in RTeCN does not exhibit any particular preference for oxygen donors rather than nitrogen donors, or vice versa, when completing its coordination sphere. This lack of preference for the two types of donor atoms has also been observed for Te(IV); cf. the structure of Ph<sub>3</sub>Te(NCO) · 1/2 CHCl<sub>3</sub>.<sup>33</sup> Presently, it is not possible to decide whether the preference of tellurium for nitrogen donors in 2-nitrobenzyl tellurocyanate is due to weaker donor properties of the oxygen atoms or to a larger contribution from the pseudo-ionic structure. It is notable that intermolecular contacts to one of the two oxygen atoms, O2, are not sterically hindered.

**5. Conformational considerations.** In a molecule like 2-NO<sub>2</sub>-PhCH<sub>2</sub>TeCN, free rotation is possible around two bonds, viz. C(Ph)–C(CH<sub>2</sub>) and C(CH<sub>2</sub>)–Te. Due to the tendency of the nitro group to become coplanar with the aromatic ring, the C2–N1 twist angle is expected to be small.<sup>24</sup> Twist angles significantly larger than ~10° are only observed when conjugation is sterically impeded.<sup>34</sup>

Fig. 2 (left) shows that 2-nitrobenzyl tellurocyanate in the crystalline state exists in the expected *syn*-clinal

(*gauche*) conformation. Exceptions to this conformational rule for organic pseudohalides have only been observed when the heteroatom, X, is locked in a particular position by a strong intramolecular contact.<sup>17</sup> A model of the present pseudohalide shows that such a contact, i.e. a Te–O1 contact *trans* to the cyano group, is possible, but only when the nitro group is distinctly out of the aromatic ring plane and the TeCN group is *anti*-clinal to the C1–C7 bond. The present structural study shows clearly that the usual *syn*-clinal conformation without an intramolecular Te–O bond represents a distinct energy minimum. The torsion angle, –48.5°, is smaller than observed in most organic pseudohalides.<sup>9</sup> This angle is probably largely determined by the lattice forces through the intermolecular Te–N8' contact *trans* to the cyano group.

The C–Ph dihedral angle [Fig. 2 (center)], 103.4(4)°, is as observed in several 4-nitrobenzyl pseudohalides.<sup>9</sup> The position of the substituent apparently does not influence the dihedral angle; in benzyl halides and in benzyl pseudohalides the CH<sub>2</sub>–X bond usually lies in a plane almost perpendicular to the aromatic plane. Notable exceptions are benzyl fluorides and benzyl alcohols, with C–Ph dihedral angles ranging from 0 to ~60°, depending upon the substituents.<sup>35–38</sup> A C–Ph dihedral angle larger than 90° will cause an increase in the distance between H71 and O1. This observation strengthens the conclusion that the interaction between these two atoms is of repulsive nature.<sup>22,23</sup>

**Reaction rates and equilibria.** Table 4 gives a summary of second-order rate constants,  $k_t$ , and equilibrium constants,  $K$ , for the substitution reactions toward the various 2-nitrobenzyl compounds. The relative rate constants,  $k_{rel}$ , are defined as  $k_t(RX)/k_t(RSCN)$ . Several of the rate constants, and especially some of the equilibrium constants, are of modest accuracy. Rate constants for reactions with  $K \ll 1$  were particularly difficult to determine and were usually estimated by means of the rate constant for the reverse reaction,  $k_r$ , and the equilibrium constant (see footnote *b* in Table 4). Some of the equilibrium constants could not be determined with certainty due to their magnitude ( $K$  being  $>10^2$  or  $<10^{-2}$ ) or due to insufficient differences in the IR, UV and NMR spectra of reactants and products. These equilibrium constants were estimated by an internal consistency analysis according to Hine and Weimar.<sup>3</sup> All experimentally determined equilibrium constants were found to be in accordance with this analysis.

Apart from a slow decomposition of the reaction mixtures containing 2-nitrobenzyl tellurocyanate, no significant amounts of by-products could be detected. Lack of colorization of reaction mixtures containing RSeCN, RTeCN, NCSe<sup>-</sup> or NCTe<sup>-</sup> indicated that, at most, traces of diselenides or ditellurides could have been formed as products of nucleophilic attack at the hetero-atoms. Compounds of this type are known to have a distinct yellow or orange colour. Generally, when both products and reactants could be quantitatively determined, the sum of their concentrations did not vary with time and was equal to the

Table 4. Second order rate constants,  $k_f$ , relative rate constants,  $k_{rel}$  (rate constants for RSCN are unity), and equilibrium constants,  $K$ , for reactions between 2-NO<sub>2</sub>-PhCH<sub>2</sub>X and Y<sup>-</sup> in acetonitrile at 25.0°C.

| X    | Y <sup>-</sup>    | $k_f/M^{-1} s^{-1}$         | $k_{rel}$            | $K^a$                |
|------|-------------------|-----------------------------|----------------------|----------------------|
| Cl   | NCTe <sup>-</sup> | $3.5(7) \times 10^{-2}$     | 8                    | $>10^4$              |
| SCN  | NCTe <sup>-</sup> | $4.2(7) \times 10^{-3}$     | 1                    | 16(20)               |
| SeCN | NCTe <sup>-</sup> | $2.9(8) \times 10^{-2}$     | 6                    | 50(20)               |
| TeCN | NCTe <sup>-</sup> | $\sim 5.0 \times 10^{-2}$   | 12                   | 1                    |
| Br   | NCSe <sup>-</sup> | $\sim 1.5 \times 10^{-1}$   | $\sim 9 \times 10^2$ | $\sim 10^3$          |
| Cl   | NCSe <sup>-</sup> | $2.9(3) \times 10^{-3}$     | $1.7 \times 10$      | 4.6                  |
| SCN  | NCSe <sup>-</sup> | $1.7(3) \times 10^{-4}$     | 1                    | 1                    |
| SeCN | NCSe <sup>-</sup> | $4.1(2) \times 10^{-4}$     | 2.4                  | $\sim 1$             |
| TeCN | NCSe <sup>-</sup> | $\sim 5.9 \times 10^{-4 b}$ | 3.5                  | $2 \times 10^{-2 c}$ |
| I    | NCS <sup>-</sup>  | $6.9(5) \times 10^{-1}$     | $3 \times 10^4$      | $3 \times 10^3$      |
| Br   | NCS <sup>-</sup>  | $1.9(4) \times 10^{-2}$     | $8 \times 10^2$      | $4.4 \times 10^2$    |
| Cl   | NCS <sup>-</sup>  | $4.0(5) \times 10^{-4}$     | $1.7 \times 10$      | 2.8                  |
| SCN  | NCS <sup>-</sup>  | $2.4(5) \times 10^{-5}$     | 1                    | 1                    |
| SeCN | NCS <sup>-</sup>  | $1.7(3) \times 10^{-4 b}$   | 7                    | 1                    |
| TeCN | NCS <sup>-</sup>  | $5.9(5) \times 10^{-4 b}$   | 25                   | $6 \times 10^{-2 c}$ |
| I    | Cl <sup>-</sup>   |                             |                      | $\sim 10^3$          |
| Br   | Cl <sup>-</sup>   |                             |                      | $\sim 10^2$          |
| Cl   | Cl <sup>-</sup>   |                             |                      | 1                    |
| SCN  | Cl <sup>-</sup>   | $1.7(3) \times 10^{-4}$     | 1                    | 0.4                  |
| SeCN | Cl <sup>-</sup>   | $5.6(8) \times 10^{-4}$     | 3.3                  | 0.3                  |
| I    | Br <sup>-</sup>   |                             |                      | $\sim 6^a$           |
| Br   | Br <sup>-</sup>   |                             |                      | 1                    |
| Cl   | Br <sup>-</sup>   |                             |                      | $6 \times 10^{-3}$   |
| SCN  | Br <sup>-</sup>   | $3.4(7) \times 10^{-5}$     |                      | $6 \times 10^{-3}$   |
| SeCN | Br <sup>-</sup>   | $1 \times 10^{-3 b}$        |                      | $5 \times 10^{-3}$   |
| Br   | I <sup>-</sup>    |                             |                      | $2 \times 10^{-1}$   |
| Cl   | I <sup>-</sup>    |                             |                      | $5 \times 10^{-3}$   |
| SCN  | I <sup>-</sup>    | $2.4 \times 10^{-4 b}$      |                      | $3.4 \times 10^{-4}$ |

<sup>a</sup>Minimum uncertainty  $\pm 30\%$ . <sup>b</sup>Calculated from  $k_f$  for the reverse reaction and  $K$ . <sup>c</sup>Calculated from  $k_f$  and  $k_r$ .

initial concentration of the reactants. One may therefore conclude that all rate constants in Table 4 refer to reactions occurring via nucleophilic attack at the methylene carbon atom only.

Table 5 lists some rate and equilibrium constants for the 3-nitrobenzyl compounds. While the reactions involving the halides, thiocyanates and selenocyanates appeared to be clean, the instability of 3-nitrobenzyl tellurocyanate prevented detailed studies involving this compound, and studies of the reactions between ionic tellurocyanate and other 3-nitrobenzyl compounds. The trend in the rate and equilibrium data are in general agreement with the data for the 2-nitrobenzyl compounds (Table 4) and for the 4-nitrobenzyl compounds (Ref. 1).

From reactions between RX (X = Cl, Br, I<sup>-</sup>) and NCTe<sup>-</sup>, and similarly between RTeCN and Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>, no substitution products were obtained. The IR absorption due to RTeCN or NCTe<sup>-</sup> at  $\sim 2100 \text{ cm}^{-1}$  disappeared, indicating that the only products were salts of [RTe(CN)X]<sup>-</sup> (cf. Experimental for the preparation of [PNP][2-NO<sub>2</sub>-PhCH<sub>2</sub>Te(CN)Cl]). For the reactions between RX (X = SCN, SeCN or TeCN) and TeCN<sup>-</sup>, and from the reverse

reactions, only substitution reactions took place. Similarly, for RX (X = Cl, Br, I<sup>-</sup>) reacting with NCS<sup>-</sup> (NCSe<sup>-</sup>), only substitution products were obtained. Apparently, [RTe(CN)XCN]<sup>-</sup> (X = S, Se or Te) and [RX(CN)Y]<sup>-</sup> (X = S, Se and Y = Cl, Br, I, SCN, SeCN or TeCN) are of very low stability in acetonitrile. In general, the substitution pattern for the 2-nitrobenzyl compound is quite comparable to that in the 4-nitrobenzyl series.<sup>9</sup>

Shiavon<sup>39</sup> has shown that benzyl selenocyanates and ionic selenocyanate in acetonitrile give a minute amount ( $\sim 1\%$ ) of RSeSeCN from nucleophilic attack at the selenium atom [eqn. (2)]:



Reactions of this type could not, however, be detected in reaction mixtures after five to ten half-lives. Admittedly, the corresponding reaction between RTeCN + NCTe<sup>-</sup> was difficult to follow accurately due to formation of elemental tellurium. Nevertheless, no evidence of formation of ditellurides could be obtained. Although the Te-C(CN) bond in RTeCN is weak,<sup>9</sup> the tellurium basicity of NCTe<sup>-</sup>, NCSe<sup>-</sup> and NCS<sup>-</sup> has to be significantly lower than that of NC<sup>-</sup>. The weak tellurium basicity of these three ions is further demonstrated by the lack of Te-XCN contacts, allowing complex anions [RTe(CN)XCN]<sup>-</sup>, to be formed.

Regardless of the accuracy of some of the rate constants listed in Table 4, it is apparent that the nucleophilicity order is NCTe<sup>-</sup>  $\gg$  NCSe<sup>-</sup>  $>$  NCS<sup>-</sup>.<sup>40</sup> The leaving group ability follows the same order, but is less marked for the three anions. The net effect is that the carbon basicity order in acetonitrile is NCTe<sup>-</sup>  $>$  NCSe<sup>-</sup>  $\geq$  NCS<sup>-</sup>. In other words, RTeCN is kinetically the least stable but is thermodynamically the most stable of the three organic pseudo-

Table 5. Second order rate constants,  $k_f$ , and equilibrium constants,  $K$ , for reactions between 3-NO<sub>2</sub>-PhCH<sub>2</sub>X and Y<sup>-</sup> in acetonitrile at 25.0°C.

| X    | Y <sup>-</sup>    | $k_f/M^{-1} s^{-1}$     | $K$                     |
|------|-------------------|-------------------------|-------------------------|
| SCN  | NCTe <sup>-</sup> | $1.6(9) \times 10^{-3}$ | 40                      |
| SeCN | NCTe <sup>-</sup> | $7.5(2) \times 10^{-3}$ | 30                      |
| TeCN | NCTe <sup>-</sup> | Not measurable          | 1                       |
| Br   | NCSe <sup>-</sup> | $2.7(2) \times 10^{-1}$ | $1.5 \times 10^2$       |
| Cl   | NCSe <sup>-</sup> | $3.0(4) \times 10^{-3}$ | $\sim 2$                |
| TeCN | NCSe <sup>-</sup> | $1.5 \times 10^{-4}$    | $\sim 2 \times 10^{-2}$ |
| SeCN | NCSe <sup>-</sup> |                         | 1                       |
| SCN  | NCSe <sup>-</sup> |                         | $\sim 1$                |
| Br   | NCS <sup>-</sup>  | $1.7(1) \times 10^{-2}$ | $1.2 \times 10^1$       |
| Cl   | NCS <sup>-</sup>  | $9 \times 10^{-4}$      | $\sim 1.2$              |
| TeCN | NCS <sup>-</sup>  | $4.4 \times 10^{-5}$    | $2.8 \times 10^{-2}$    |
| SeCN | NCS <sup>-</sup>  |                         | $\sim 10$               |
| SCN  | NCS <sup>-</sup>  |                         | 1                       |
| SCN  | Cl <sup>-</sup>   | $1.6(9) \times 10^{-4}$ | 0.8                     |
| SeCN | Cl <sup>-</sup>   | $1.2(3) \times 10^{-3}$ | 0.5                     |

Table 6. Average nucleophilicity, average leaving group ability and average carbon basicity of  $\text{NCTe}^-$ ,  $\text{NCSe}^-$ ,  $\text{NCS}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$  and  $\text{Cl}^-$  in reactions with 2- and 3-nitrobenzyl substrate in acetonitrile at 25.0 °C. (data for 4-nitrobenzyl and phenacyl substrates from Refs. 1 and 19, respectively).

|  | $\text{NCTe}^-$ | $\text{NCSe}^-$ | $\text{NCS}^-$ | $\text{I}^-$       | $\text{Br}^-$        | $\text{Cl}^-$ |
|--|-----------------|-----------------|----------------|--------------------|----------------------|---------------|
| <b>Nucleophilicity</b>                     |                 |                 |                |                    |                      |               |
| 2- $\text{NO}_2$ - $\text{PhCH}_2\text{X}$ | ~170            | ~7              | 1              | 8                  | 5                    | 5             |
| 3- $\text{NO}_2$ - $\text{PhCH}_2\text{X}$ | ~160            | ~4              | 1              |                    | ~7                   | ~8            |
| 4- $\text{NO}_2$ - $\text{PhCH}_2\text{X}$ |                 | 8               | 1              | 6                  | 4                    |               |
| $\text{PhC(O)CH}_2\text{X}$                |                 | 10              | 1              |                    | 15                   | 7             |
| <b>Leaving group ability</b>               |                 |                 |                |                    |                      |               |
| 2- $\text{NO}_2$ - $\text{PhCH}_2\text{X}$ | 6               | 4               | 1              | $3 \times 10^4$    | $9 \times 10^2$      | 17            |
| 3- $\text{NO}_2$ - $\text{PhCH}_2\text{X}$ | ~5              | ~5              | 1              |                    | $\sim 1 \times 10^3$ | ~10           |
| 4- $\text{NO}_2$ - $\text{PhCH}_2\text{X}$ |                 | 3               | 1              | $1 \times 10^4$    | $1.5 \times 10^3$    | 6             |
| $\text{PhC(O)CH}_2\text{X}$                |                 | 10              | 1              |                    | $2 \times 10^4$      | 75            |
| <b>Carbon basicity</b>                     |                 |                 |                |                    |                      |               |
| 2- $\text{NO}_2$ - $\text{PhCH}_2\text{X}$ | ~30             | 2               | 1              | $8 \times 10^{-4}$ | $3 \times 10^{-3}$   | 0.5           |
| 3- $\text{NO}_2$ - $\text{PhCH}_2\text{X}$ | ~30             | ~1.5            | 1              |                    | $7 \times 10^{-3}$   | 0.8           |
| 4- $\text{NO}_2$ - $\text{PhCH}_2\text{X}$ |                 | 2.8             | 1              | $6 \times 10^{-4}$ | $2.5 \times 10^{-3}$ | 0.9           |
| $\text{PhC(O)CH}_2\text{X}$                |                 | 1.2             | 1              |                    | $1.4 \times 10^{-3}$ | 0.14          |

halides,  $\text{RXCN}$ . The reputed instability of  $\text{RTeCN}$  is therefore not due to the  $\text{Te}-\text{C(R)}$  bond but seems rather to be caused by the low tellurium basicity of the cyanide ion, i.e. by the weakness of the  $\text{Te}-\text{C(CN)}$  bond.

Based upon the data in Tables 4 and 5 one can calculate the average nucleophilicity, the average leaving group ability and the average carbon basicity of the anions. The results are summarized in Table 6, where the thiocyanate ion has been used as a reference. The data in Table 6 show a remarkable similarity to the corresponding data for the 4-nitrobenzyl series (Ref. 1). Apparently, the position of the nitro substituent has no distinct effect. This observation seems to suggest that benzyl compounds, except benzyl fluorides and benzyl alcohols, will attain a conformation in solution in which the  $\text{CH}_2-\text{X}$  bond lies in a plane approximately perpendicular to the aromatic plane,<sup>35,36</sup> as observed in the crystalline state. In this conformation the steric influence of a 2-substituent on substitution reactions will be negligible [cf. Fig. 2 (center)]. Although 2- and 4-nitrobenzyl tellurocyanate show a distinctly different pattern in the intermolecular contacts in the crystalline state, it is reasonable to assume that in a solvent like acetonitrile the hetero-atom will satisfy its electron demand similarly, i.e.

by coordination to the nitrogen atom of the solvent molecules. Rate differences for the 2- and 4-nitrobenzyl series are presumably due to electronic effects rather than specific solvent effects.

Table 7 presents a comparison between rate constants for some reactions of 2- and 4-nitrobenzyl substrates in acetonitrile. The rate data show clearly that for Finkelstein reactions,<sup>41</sup> i.e. reactions with charged nucleophiles, 2-nitrobenzyl compounds are twice as reactive as the 4-nitro-substituted compounds. In the case of Menshutkin reactions,<sup>42</sup> i.e. reactions with uncharged nucleophiles, the opposite is often observed.<sup>43</sup> Since this difference can hardly be of steric origin, the present results confirm the general conclusion by Charton<sup>44</sup> that no equality exists between electronic effects due to *ortho* and *para* substituents. Due to the fact that Hammett rate plots for reactions of benzyl compounds are generally non-linear,<sup>45</sup> no universal substituent constants can be arrived at for reactions of this kind. Since Finkelstein and Menshutkin reactions of benzyl compounds respond differently to the position of a nitro substituent, one may conclude that the 2-nitro group is the better stabilizer of a "tight" transition state,<sup>46</sup> i.e.  $\sigma^-(2-\text{NO}_2) > \sigma^-(4-\text{NO}_2)$  and  $\sigma^+(2-\text{NO}_2) < \sigma^+(4-\text{NO}_2)$ .<sup>47</sup>

Table 7. A comparison of rate constants for reactions of 2-, 3- and 4-nitrobenzyl substrates.

|  | $k_2(2-\text{NO}_2)/k_2(4-\text{NO}_2)$ | $k_2(2-\text{NO}_2)/k_2(3-\text{NO}_2)$ |
|--|---|---|
| $\text{NO}_2\text{PhCH}_2\text{Cl} + \text{NCS}^-$   | 2.2                                     | 0.5                                     |
| $\text{NO}_2\text{PhCH}_2\text{Cl} + \text{NCSe}^-$  | 2.2                                     | 1.0                                     |
| $\text{NO}_2\text{PhCH}_2\text{Cl} + \text{NCTe}^-$  | 2.2                                     |   |
| $\text{NO}_2\text{PhCH}_2\text{SCN} + \text{NCTe}^-$ | ~3.2                                    | ~2.6                                    |
| $\text{NO}_2\text{PhCH}_2\text{Br} + \text{NCS}^-$   |   | 1.2                                     |

Table 8. A comparison between second order rate constants,  $k_f$ , at 25.0 °C in dichloromethane and in acetonitrile.

|   | $k_f(\text{CH}_2\text{Cl}_2) / \text{M}^{-1} \text{s}^{-1}$ | $k_f(\text{CH}_3\text{CN}) / \text{M}^{-1} \text{s}^{-1}$ | $\frac{k_f(\text{CH}_2\text{Cl}_2)}{k_f(\text{CH}_3\text{CN})}$ |
|---|---|---|---|
| 2-NO <sub>2</sub> PhCH <sub>2</sub> Cl + NCS <sup>-</sup> | 1.2(1) × 10 <sup>-3 a</sup>                                 | 4.0 × 10 <sup>-4</sup>                                    | 3   |
| 2-NO <sub>2</sub> PhCH <sub>2</sub> Br + NC5              | 3.5(1) × 10 <sup>-2 b</sup>                                 | 1.9 × 10 <sup>-2</sup>                                    | 1.8   |
| 2-NO <sub>2</sub> PhCH <sub>2</sub> I + NC5               | 5.6(5) × 10 <sup>-1 c</sup>                                 | 6.9 × 10 <sup>-1</sup>                                    | 0.8   |

<sup>a</sup> $K \approx 120$ . <sup>b</sup> $K \approx 110$ . <sup>c</sup> $K > 10^4$ .

The suggestion that Finkelstein reactions with 2-nitrobenzyl substrates go through a "tight" transition state is strengthened by a comparison of some rate constants for reactions in dichloromethane and in acetonitrile (Table 8). [PNP]<sup>+</sup> salts were used as the source of the anions. While these salts are extensively dissociated in acetonitrile at  $\sim 10^{-2}$  M, the concentration at which the rate studies were performed, the association constants in CH<sub>2</sub>Cl<sub>2</sub> are  $\sim 1-2 \times 10^3$ .<sup>48</sup> The data in Table 8 have not been corrected for this association. Nevertheless, 2-nitrobenzyl chloride and 2-nitrobenzyl bromide react distinctly more rapidly with NCS<sup>-</sup> and NCSe<sup>-</sup> in dichloromethane ( $\epsilon = 8.9$ ) than in acetonitrile ( $\epsilon = 36.7$ ); 2-nitrobenzyl iodide reacts slightly slower. Reactions involving RTeCN and NCTe<sup>-</sup> could not be studied in dichloromethane owing to the high rate of the CH<sub>2</sub>Cl<sub>2</sub>-TeCN<sup>-</sup> reaction.<sup>49</sup> It is notable that while the carbon basicity of NCS<sup>-</sup> in acetonitrile equals that of Cl<sup>-</sup>, NCS<sup>-</sup> is a far better base in dichloromethane, presumably due to solvation of Cl<sup>-</sup> in this solvent.<sup>49</sup> Thus, when RSCN and RSeCN are to be prepared from RCl and onium pseudohalides, the use of dichloromethane instead of acetonitrile leads to more rapid reactions and to products less contaminated by the reactants.

*Comments on the stability of RTeCN.* Falcone and Cava<sup>50</sup> have concluded from a study on 4-substituted phenyl tellurocyanates that electron-donating substituents stabilize this class of compounds. Apparently, due to the electron deficiency of the tellurium atom, the stability of organic tellurocyanates can be increased by electron-donating substituents, by inter- and intramolecular contacts to donor atoms,<sup>51,52</sup> and by employing solvents of some donicity. The limited stability of this class of compounds, however, leads to some interesting applications in synthesis.<sup>6,7,53,54</sup> Despite the length of the Te-C(R) bond and the leaving group ability of the TeCN group, homolytic or heterolytic scission of the Te-C(CN) bond seems to be the predominant first step in reactions of RTeCN.

Cava and co-workers<sup>7</sup> showed that benzyl tellurocyanate reacted with molecular oxygen provided the solution was irradiated. The results from the present study show clearly that organic tellurocyanates react only extremely slowly with oxygen in the dark, but rapidly in UV light. This result substantiates the conclusion by Cava<sup>7</sup> that singlet oxygen is the reactant. The reaction appears to be highly complicated. In addition to the formation of an aldehyde and an

alcohol, as reported by Cava,<sup>7</sup> a significant amount of ionic cyanate is also formed. In this respect RTeCN differ from TeCN<sup>-</sup>; starting from an ionic tellurocyanate and molecular oxygen no ionic cyanate can be detected.<sup>55</sup>

3-Nitrobenzyl tellurocyanate appears to be rather unstable as compared with the 2- and 4-substituted compounds. This may be due to the facility with which 3-nitrobenzyl compounds undergo reactions by the S<sub>RN</sub>1 mechanism,<sup>56</sup> a mechanism promoting the homolytic scission of the Te-C(CN) bond. In <sup>13</sup>C NMR the methylene carbon of the 3-nitro compound is  $\sim 10$  ppm further downfield than in the 2- and 4-analogues. For all other nitrobenzyl compounds (RCl, RBr, RI, RSCN and RSeCN) the shift is essentially independent of the position of the nitro group. This may suggest that the 3-nitro substituent is superior to the 2-nitro and the 4-nitro substituent as regards conjugation with a methylene group containing a very polarizable group. The net effect will be a dilution of the electron density in the Te-C(CN) bond which will favour both homolytic and heterolytic scission of this bond. The heavy atom effect,<sup>57</sup> however, may obscure conclusions based upon NMR data.

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