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Alkylation Reactions of the Tellurocyanate Ion

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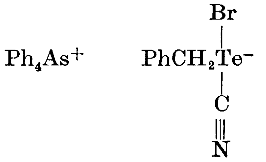
This paper reports a study on the reaction between a primary alkyl halide and the tellurocyanate ion in acetonitrile. Methyl iodide and methyl tosylate were first used as substrates, but because of the obnoxious odour of the product(s) from these reactions a primary alkyl halide of higher molecular weight was chosen. Benzyl bromide was found to be ideal for several reasons. The product obtained was a crystalline compound, sufficiently stable for elemental analysis and only slightly malodourous. Furthermore, the reaction was rapid and the experimental difficulties due to the reaction between the tellurocyanate ion and traces of oxygen and moisture[1] were thus negligible. Although the rate of the reaction is high at room temperature, a kinetic study was possible and the rate of the reaction was determined. As the rates of the reactions between benzyl bromide and the selenocyanate ion and between benzyl bromide and the thiocyanate ion could be determined as well, a picture of the relative nucleophilicity of the tellurocyanate ion could be obtained.

Benzyl halides have been known for a long time to form exclusively benzyl thiocyanate[2] and benzyl selenocyanate[3] when they react with ionic thiocyanate and selenocyanate, respectively. From the reaction between equivalent amounts of benzyl bromide and tetraphenylarsonium tellurocyanate in acetonitrile, a slightly yellowish crystalline compound was obtained in high yield. This compound was insoluble in diethyl ether while readily soluble in acetonitrile and acetone. An IR spectrum of the product did not show a peak due to the tellurocyanate ion at 2081 cm^{-1}.[1] As the characteristic peaks of the tetraphenylarsonium ion were present, the product from the reaction necessarily had to be a salt.

The product decomposed slowly in water and protic solvents with the formation of elemental tellurium. The usual qualitative tests for nitrogen and bromine were positive. Elemental analysis suggested the product to be considered as an adduct between tetraphenylarsonium bromide and benzyl tellurocyanate, tetraphenylarsonium bromocyanobenzyltellurate(II).

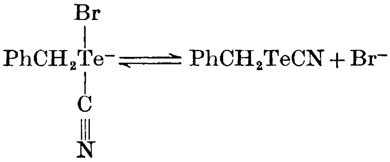


$$\mathrm{Ph_4As^+}\qquad \mathrm{PhCH_2}\overset{\displaystyle \mathrm{Br}}{\underset{\displaystyle \mathrm{C{\equiv}N}}{\mathrm{Te^-}}}$$

The compound, crystallized from acetonitrile, is nearly colourless. The prism-shaped crystals are extended along the a axis. Unit cell parameters were calculated from 89 high-order reflections read from Weissenberg $0kl$ and $h0l$ films, employing Ni-filtered Cu$K\alpha$ radiation. Refinement by a least squares program gave final values of $a = 9.471(4)$ Å, $b = 26.345(9)$ Å, $c = 12.899(5)$ Å and $\beta = 114.63(4)°$. There are four formula units per unit cell. (Density, found by flotation 1.60; calc. 1.61 g/cm^3.) From systematic absences, $h0l$ for $l = 2n+1$ and $0k0$ for $k = 2n+1$, the space group is $C_{2h} - P2_1/c$.

The compound is probably an example of a four-electron three-center tellurium compound with a close to linear (N)C–Te–Br bond. The exceptional ability of the tellurium atom to be the central atom in four-electron three-center systems is well documented.[4,5] Recently, several salts of anions of the general type $PhTeX_2^-$ have been isolated.[6]

Freshly prepared samples of the compound have no odour, but on storage at room temperature an unpleasant odour is produced though no significant decomposition was observed. On recrystallization of pure samples, tetraphenylarsonium bromide crystallized as a minor recrystallization product. It is therefore probable that the following equilibrium exists,



$$\mathrm{PhCH_2}\underset{\underset{\mathrm{N}}{\overset{|||}{\mathrm{C}}}}{\overset{\mathrm{Br}}{\mathrm{Te}}}{}^{-} \rightleftharpoons \mathrm{PhCH_2TeCN} + \mathrm{Br}^-$$

and that the unpleasant odour is due to traces of benzyl tellurocyanate or subsequent products. No yield of dibenzyl telluride or dibenzyl ditelluride could be detected.

The reaction between tetraphenylarsonium tellurocyanate and benzyl bromide in acetonitrile was found to be strictly second order, first order in each reactant, and one equivalent of benzyl bromide consumed one equivalent of the tellurocyanate ion. As the rate of the reaction is high, $t_{\frac{1}{2}} \approx 2$ min for concentrations of reactants of 0.01 M, the accuracy of the rate measurements was limited. Benzyl chloride was found to react at least three orders of magnitude slower than benzyl bromide, but as severe decomposition of the tellurocyanate ion was observed for such long reaction times, the rate of this reaction could not be accurately determined. A $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ ratio of $> 10^3$, however, for a non-transition metal nucleophile, is unusual. The results of the kinetic studies are listed in Table 1.

The observed reactivity sequence is thus $NCTe^- > NCSe^- > NCS^-$. This reactivity sequence appears to be the same as when the ions act as electrophiles toward polarizable nucleophiles.[5,7]

Further studies on alkylation reactions of the tellurocyanate ion are in progress in this laboratory.

Table 1. Second order rate constants at 21.0°C for nucleophiles reacting with benzyl bromide in acetonitrile. Concentrations of reactants, 6.0×10^{-3} M.

	k_2 M^{-1} sec^{-1}
$NCTe^-$	1.20
$NCSe^-$	1.95×10^{-1}
NCS^-	3.24×10^{-2}

Experimental. Acetonitrile was purified as previously reported [1] and carefully flushed with nitrogen prior to use. Tetraphenylarsonium tellurocyanate, thiocyanate, and selenocyanate were synthesized and purified as reported.[1] Benzyl bromide, Fluka *puriss.*, was distilled in vacuum and stored in a dark bottle in the refrigerator.

Tetraphenylarsonium bromocyanobenzyltellurate(II). To 1.343 g tetraphenylarsonium tellurocyanate, 2.5×10^{-3} mol, in 30 ml acetonitrile, was slowly added a solution of an equivalent amount of benzyl bromide, 0.428 g, in 20 ml acetonitrile. A slight increase of the yellow colour of the solution could be observed. The reaction mixture was stirred for 15 min at room temperature and traces of tellurium dioxide was removed by filtration. Due to the high solubility of the product in acetonitrile, the volume had to be reduced in vacuum to 15 ml. On addition of a small amount of diethyl ether, the product, slightly yellowish, crystallized. Yield of crude product, 1.624 g, 92 %. IR of the product showed no peak at 2081 cm^{-1} due to ionic tellurocyanate while a very weak peak at 2162 cm^{-1} could be observed. The mother liquor from the crystallization was evaporated to dryness and a minute amount of residue was obtained. No known compounds, however, could be isolated from the residue, which, on standing, deposited traces of elemental tellurium.

The product was dissolved in a minimum of luke-warm acetonitrile, filtered, and the solution allowed to cool in the refrigerator. The first crystals which deposited, less than 0.1 g, mainly consisting of tetraphenylarsonium bromide, were discarded. After 12 h in the refrigerator, 1.28 g, 73 %, of pure product, slightly yellowish, was obtained. M.p. 118°C. The compound decomposed in the melting point capillary at ≈160°C. (Found: C 54.63; H 3.62; N 2.06. Calc. for $C_{32}H_{27}AsBrNTe$: C 54.28; H 3.84; N 1.98). The compound, dissolved in acetonitrile, appeared stable in the presence of lithium perchlorate, while water slowly deposited elemental tellurium.

Kinetic study. The rate constants were determined by measuring the disappearance of the peaks at 2081 cm^{-1} ($TeCN^-$), 2068 cm^{-1} ($SeCN^-$), and 2059 cm^{-1} (SCN^-) at varying concentration of the pseudohalide ions and benzyl bromide in the $4-10\times 10^{-3}$ M concentration range. The rate constants in Table 1 refer to measurements with initial concentrations of reactants of 6×10^{-3} M. When the thiocyanate ion and the selenocyanate were the nucleophiles, 0.1 cm liquid cells were used. Due to the considerably lower extinction coefficient of the tellurocyanate ion at 2081 cm^{-1},[1] 0.15 cm liquid cells were used in these reactions. The rate constants for the selenocyanate ion and the thiocyanate ion are probably good to ± 3 % while the rate constant for the reaction between the tellurocyanate ion and benzyl bromide is probably of considerably lower accuracy, $\approx \pm 5$ %, due to the high rate of this reaction. A very weak peak at ~ 2162 cm^{-1} could be observed in completed reaction mixtures. For all examined reactions, the rate plots were linear up to two or three half-lives. Due to traces of oxygen in the applied solvent, the rate constant for the very slow reaction between tetraphenylarsonium tellurocyanate and benzyl chloride could not be accurately determined.

The stoichiometry of the reaction between tetraphenylarsonium tellurocyanate and benzyl bromide was determined in more concentrated solutions by measuring the reduction of the peak due to the tellurocyanate ion as a function of added benzyl bromide. All measurements confirmed the reaction to be a 1:1 reaction.

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Reactions of Diphenylditelluride with Halogens in Presence of Ligands Containing Sulphur or Selenium as Donor Atoms

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Phenyltellurium trichloride dissolved in methanol reacts with aqueous thiourea (tu) to give thiourea complexes of divalent tellurium, $C_6H_5Te(tu)Cl$ and $C_6H_5Te(tu)_2Cl$.[1]

It has now been found that diphenylditelluride dissolved in methanol reacts with halogen (chlorine or bromine) and ligands containing sulphur or selenium to form complexes of divalent tellurium:

$$C_6H_5TeTeC_6H_5 + X_2 + 2\,L = 2C_6H_5TeLX \quad (1)$$

or

$$C_6H_5TeTeC_6H_5 + Br_2 + 4\,L^- = 2\,C_6H_5TeL_2^- + 2\,Br^- \quad (2)$$

In the first case L is thiourea, selenourea, triphenylphosphineselenide, or trimorpholylphosphineselenide. In the second case L^- is thiocyanate or selenocyanate. The anionic complexes formed have been isolated as tetramethylammonium salts.

By use of 4 mol of selenourea (su) and 1 mol chlorine the complex $C_6H_5Te(su)_2Cl$ was formed:

$$C_6H_5TeTeC_6H_5 + Cl_2 + 4\,su = 2\,C_6H_5Te(su)_2^+ + 2\,Cl^-$$

The analogous complex with thiourea is known.[1]

When potassium selenocyanate instead of tetramethylammonium selenocyanate was used in reaction (2) a blue-violet compound separated from the solution. The compound was shown to be bis(benzenetellurenyl) selenide, $C_6H_5TeSeTeC_6H_5$. A possible mechanism may be that benzenetellurenyl selenocyanate is formed first, and then ($Ar = C_6H_5$):

$$ArTeSeCN + SeCN^- = Se(CN)_2 + ArTeSe^-$$

$$ArTeSeCN + ArTeSe^- = ArTeSeTeAr + SeCN^-$$

The same compound, bis(benzenetellurenyl) selenide, was isolated from a reaction between selenourea-benzenetellurenyl chloride, $C_6H_5Te(su)Cl$, and potassium selenocyanate. The reaction is probably