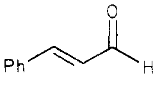
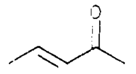
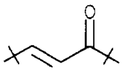
In an attempt to study the regioselectivity of the new reagent (LiH–$VCl_3$) in the reduction of $\alpha,\beta$-unsaturated carbonyl compounds, the compounds I–IV were allowed



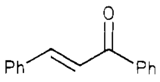
I



II



III



IV

to react at 45 °C for 36 h in a 1:3:3 ratio. Only in the case of cinnamaldehyde did a reaction take place; i.e., the 1,2-reduction product was formed in 90% yield with 10% recovered enone and no trace of 1,4-reduction product observed. The reduction of enones by LiH–$VCl_3$ may offer some promise as a regioselective reducing agent.

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**Registry No.** LiH, 7580-67-8; NaH, 7646-69-7; 4-*tert*-butylcyclohexanone, 98-53-3; 3,3,5-trimethylcyclohexanone, 873-94-9; 2-methylcyclohexanone, 583-60-8; 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one, 76-22-2; PhC(O)H, 100-52-7; $C_5H_{11}C(O)H$, 66-25-1; PhC(O)-$OC_2H_5$, 93-89-0; $C_3H_7C(O)OC_2H_5$, 105-54-4; 4-*tert*-butylcyclohexanol, 98-52-2; 3,3,5-trimethylcyclohexanol, 116-02-9; 2-methylcyclohexanol, 583-59-5; *exo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 124-76-5; *endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 507-70-0; $PhCH_2OH$, 100-51-6; $C_6H_{13}OH$, 111-27-3; $C_3H_7C(O)H$, 123-72-8; $C_4H_9OH$, 71-36-3; 1-octene, 111-66-0; 2-ethyl-1-hexene, 1632-16-2; methylenecyclohexane, 1192-37-6; octane, 111-65-9; 3-methylheptane, 589-81-1; methylcyclohexane, 108-87-2.

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# Organotellurium Chemistry. 4. Synthesis of Phenyl, 4-Methoxyphenyl, and 2-Nitrophenyl Tellurocyanates

Samuel J. Falcone and Michael P. Cava*

*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

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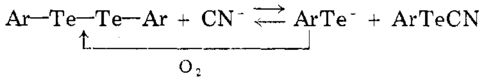
The previously unreported phenyl tellurocyanate and 4-methoxyphenyl tellurocyanate were prepared in low yields from potassium cyanide and the diaryl ditellurides and in high yields through reductive cyanation of the aryltellurium trihalides. The highly stabilized (2-nitrophenyl)tellurenyl bromide reacted directly with potassium cyanide to give *o*-nitrophenyl tellurocyanate.

The chemistry of organic thiocyanates and selenocyanates[1] is extensive and well studied. In contrast, little is known about organic tellurocyanates. Benzyl tellurocyanate, the first example of an alkyl tellurocyanate, was described in 1977.[2] Several aryl tellurocyanates with a carbonyl-containing group in the position ortho to the tellurium atom have been prepared in recent years by the action of silver cyanide on tellurenyl bromides.[3] Unfortunately, this method is of quite limited applicability because aryltellurenyl halides (ArTeX),[4] unless stabilized by an *o*-carbonyl-containing function[3] or by an *o*-nitro group,[5] are unstable polymeric species.

The objective of the work reported here was to find a practical method for the synthesis of simple aryl tellurocyanates. Such compounds are of interest as potential reagents for the introduction of aryltellurenyl groups into other organic molecules.

## Results and Discussion

Our first aryl tellurocyanate synthesis was based upon the idea that cyanide ion might be capable of nucleophilic attack upon one of the tellurium atoms of a diaryl ditelluride, producing an aryl tellurocyanate and an aryl tellurolate ion. In the presence of air, however, the tellurolate ion should be oxidized to the ditelluride, which can again react with potassium cyanide. This general scheme is illustrated in eq 1.



$$\mathrm{Ar{-}Te{-}Te{-}Ar} + \mathrm{CN^-} \rightleftarrows \mathrm{ArTe^-} + \mathrm{ArTeCN} \tag{1}$$

In fact, diphenyl ditelluride[6] was partially converted to phenyl tellurocyanate on stirring with potassium cyanide in dimethyl sulfoxide solution at room temperature. Phenyl tellurocyanate had to be separated from unchanged ditelluride by silica chromatography. The yield never surpassed 20%. Under similar conditions, bis(4-methoxyphenyl) ditelluride[7] was converted in 18% yield to 4-methoxyphenyl tellurocyanate. Attempts to increase these yields by varying the reaction conditions (e.g., cyanide concentration, temperature, or addition of acetic acid) were unsuccessful.

The phenyl and 4-methoxyphenyl tellurocyanates are white crystalline compounds which appear to be stable indefinitely when stored under refrigeration. Like benzyl tellurocyanate,[2] they are somewhat labile to heat and light, especially in solution, decomposing to the ditellurides, probably by homolytic cleavage of the Te–CN bond.

Our second aryl tellurocyanate synthesis was based upon the assumption that a simple aryltellurenyl halide, if it could be generated in situ from a suitable precursor, might react readily with cyanide ion to give an aryl tellurocyanate. We were encouraged in this approach by examining the action of potassium cyanide on the stable (*o*-nitrophenyl)tellurenyl bromide.[5] An immediate reaction

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(1) For a review of selenocyanate chemistry, see: "Organic Selenium Compounds; Their Chemistry and Biology"; Klayman, D. L., Gunther, W. H. H., Eds.; Wiley-Interscience: New York, 1973.

(2) Spencer, H. K.; Lakshmikantham, M. V.; Cava, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 1470.

(3) (a) Piette, J. L.; Lysy, R.; Renson, M. *Bull. Soc. Chim. Fr.* **1972**, 3359. (b) Talbot, J. M.; Piette, J. L.; Renson, M. *Ibid.* **1976**, 294. (c) Piette, J. L.; Thibaut, P.; Renson, M. *Tetrahedron* **1978**, *34*, 655.

(4) For a complete survey of the literature on this subject, see: (a) Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1974. (b) Irgolic, K. J. *J. Organomet. Chem.* **1975**, *103*, 91. (c) Irgolic, K. J. *Ibid.* **1977**, *130*, 441. (d) Irgolic, K. J. *Ibid.* **1978**, *158*, 235, 267.

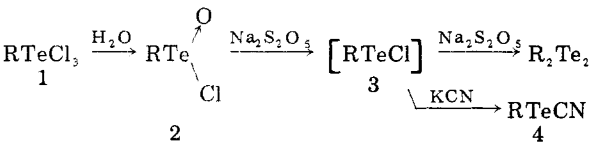
(5) Wiriyachitra, P.; Falcone, S. J.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 3957.

(6) (a) Seebach, D.; Beck, A. K. *Chem. Ber.* **1975**, *108*, 314. (b) Gunther, W. H. H.; Nepywoda, J.; Chu, J. Y. C. *J. Organomet. Chem.* **1974**, *74*, 79.

(7) Morgan, G. T.; Drew, H. D. K, *J. Chem. Soc.* **1925**, 2307.

took place, and 2-nitrophenyl tellurocyanate was isolated in 65% yield.

(4-Methoxyphenyl)tellurium trichloride (1) was chosen as an attractive starting material for this approach, because it is easily prepared in high yield from anisole and tellurium tetrachloride.[8] It is well-known that the trichloride 1 can be converted smoothly to the ditelluride by stirring with cold aqueous sodium bisulfite[7] (eq 2). The first



$$\underset{1}{RTeCl_3} \xrightarrow{H_2O} \underset{2}{RTe(\overset{O}{\uparrow})Cl} \xrightarrow{Na_2S_2O_5} \underset{3}{[RTeCl]} \xrightarrow{Na_2S_2O_5} R_2Te_2 \quad (2)$$

$$\underset{3}{[RTeCl]} \xrightarrow{KCN} \underset{4}{RTeCN}$$

$R = 4\text{-}OCH_3C_6H_4$

intermediate in this process is undoubtedly the rather stable (4-methoxyphenyl)tellurinyl chloride (2), which is produced from the trichloride 1 immediately upon contact with water.[4a] The second intermediate, formed by reduction of the tellurinyl chloride, is most likely the transient (4-methoxyphenyl)tellurenyl chloride 3. Strong support for this mechanism is found in the bisulfite reduction of (2-nitrophenyl)tellurium tribromide, in which case reduction to the corresponding ditelluride can be interrupted to yield the stable tellurenyl bromide in 90% yield.[5] We, therefore, attempted to carry out a partial reduction of the trichloride 1 (or tellurinyl chloride 2) to the unstable tellurenyl chloride 3 and to treat the crude product immediately with potassium cyanide. No tellurocyanate 4 was detected in any of these experiments, attesting to the lability of tellurenyl chloride 3.

It proved possible, however, to achieve the desired conversion to the tellurocyanate 4 in almost quantitative yield by using a reductive cyanation procedure in which the tellurenyl halide 3 is intercepted by cyanide ion as it is formed. The reaction conditions are critical, and the best results were obtained when the trichloride 1 was first stirred with 2 equiv of sodium bicarbonate to yield a white suspension of the tellurinyl chloride 2. About 4 equiv each of sodium metabisulfite and potassium cyanide was then added; after a few minutes, an additional 4 equiv of cyanide was added to the almost neutral solution. The resulting product was isolated by extraction with $CH_2Cl_2$ and crystallization. The tellurocyanate 4 was obtained in analytically pure condition in 93% yield.

In a similar manner, phenyltellurium tribromide, available in high yield by the action of bromine on diphenyl ditelluride, is converted to pure phenyl tellurocyanate in 86% yield.

A study of the behavior of these new tellurocyanates as synthetic reagents analogous to tellurenyl halides has been initiated in our laboratory.

## Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Mass, infrared (KBr, $cm^{-1}$), and ultraviolet spectra were determined by using Perkin-Elmer 270B, 137, and 202 spectrometers, respectively. All tellurium-containing mass spectral peaks are reported for $^{130}Te$. Elemental analyses were performed by Galbraith Laboratories.

**2-Nitrophenyl Tellurocyanate.** To a well-stirred solution of (2-nitrophenyl)tellurenyl bromide (0.100 g, 0.3 mmol)[5] in 3 mL of methanol was added potassium cyanide (0.020 g, 0.32 mmol). The deep red color of the tellurenyl bromide solution immediately changed to orange. After being gently warmed for 5 min, the solution was set aside at room temperature for 10 min. The solution was diluted with $H_2O$ and extracted with chloroform. Solvent removal followed by recrystallization from hexane afforded the red-brown 2-nitrophenyl tellurocyanate: 0.054 g (65%); mp 148–149 °C; IR 2400, 1600, 1580, 1500, 1320; mass spectrum, *m/e* 278 ($M^+$), 250 (M – CN, base). Anal. Calcd for $C_7H_4N_2O_2Te$: C, 30.49; H, 1.47; N, 10.16; Te, 46.28. Found: C, 30.36; H, 1.28; N, 10.11; Te, 46.20.

**4-Methoxyphenyl Tellurocyanate from Bis(4-methoxyphenyl) Ditelluride.** In an Erlenmeyer flask were placed bis(4-methoxyphenyl) ditelluride[7] (0.470 g, 1.0 mmol) and potassium cyanide (0.190 g, 3.0 mmol) in 10 mL of dimethyl sulfoxide. The solution was stirred for 3 h at room temperature and then diluted with 100 mL of water. The aqueous solution was extracted with diethyl ether. The ether extract was diluted with hexane, washed thoroughly with water, dried (sodium sulfate), filtered, and evaporated in vacuo. The resultant brown oil was chromatographed on silica gel. Elution with hexane removed unreacted ditelluride. Further elution with diethyl ether followed by recrystallization from $CHCl_3$/hexane afforded 4-methoxyphenyl tellurocyanate (0.100 g, 18%) as white needles: mp 75–77 °C; IR (Nujol) 2160, 1590, 1500, 1400, 1260, 1190; mass spectrum, *m/e* 263 ($M^+$), 237 (M – CN, base). Anal. Calcd for $C_8H_7NOTe$: C, 36.83; H, 2.71; N, 5.37; Te, 48.95. Found: C, 36.96; H, 2.84; N, 5.30; Te, 48.99.

**Phenyl Tellurocyanate from Diphenyl Ditelluride.** In an Erlenmeyer flask were placed diphenyl ditelluride[6] (0.414 g, 1.0 mmol) and potassium cyanide (0.190 g, 3.0 mmol) in 10 mL of dimethyl sulfoxide. The solution was stirred for 4 h at room temperature and then diluted with 100 mL of water. Workup in the preceding experiment, followed by recrystallization from $CHCl_3$/hexane afforded phenyl tellurocyanate (0.093 g, 20%) as off-white needles: mp 74–75 °C; IR (Nujol) 2170, 1400, 1170, 730, 690; mass spectrum, *m/e* 233 ($M^+$), 207 (M – CN, base). Anal. Calcd for $C_7H_5NTe$: C, 36.44; H, 2.18; N, 6.07; Te, 55.30. Found: C, 36.18; H, 2.22; N, 5.94; Te, 55.56.

**Phenyl Tellurocyanate from Phenyltellurium Tribromide by Reductive Cyanation.** To a well-stirred solution of $NaHCO_3$ (0.190 g, 2.2 mmol) in 20 mL of $H_2O$ and 1 mL of MeOH was added phenyltellurium tribromide[9] (0.500 g, 1.1 mmol). After the mixture had been stirred for 30 min, potassium cyanide (0.280 g, 4.4 mmol) was added, followed by sodium metabisulfite (0.840 g, 4.4 mmol). After stirring for ca. 7 min, additional potassium cyanide (0.280 g, 4.4 mmol) was added; the yellow color of the solution faded, and a white solid separated from the solution. The reaction mixture was diluted with water and extracted with $CH_2Cl_2$. The organic layer was dried (sodium sulfate), filtered, diluted with hexane, reduced in volume, and suction filtered to yield phenyl tellurocyanate (0.220 g, 86%) as analytically pure white needles, mp 74–75 °C. This material was indistinguishable from a pure sample prepared from diphenyl ditelluride.

**4-Methoxyphenyl Tellurocyanate from (4-Methoxyphenyl)tellurium Tribromide by Reductive Cyanation.** To a solution of $NaHCO_3$ (2.45 g, 29.2 mmol) in 50 mL of $H_2O$ and 3 mL of MeOH was added (4-methoxyphenyl)tellurium trichloride[8] (5.00 g, 14.16 mmol). After the mixture had been stirred for 0.5 h, potassium cyanide (3.70 g, 58.4 mmol) was added, followed by sodium metabisulfite (11.0 g, 58.4 mmol). After this mixture had been stirred for ca. 8 min, additional potassium cyanide (3.70 g, 58.4 mmol) was added when the yellow color of the solution was discharged and a white solid separated from the solution. Workup as in the preceding experiment afforded 4-methoxyphenyl tellurocyanate (3.60 g, 93%) as analytically pure white needles, mp 75–77 °C. This material was identical with a pure sample prepared from bis(4-methoxyphenyl) ditelluride.

**Acknowledgment.** We thank the National Science Foundation for a grant (CHE 76-83417) in support of this research.

**Registry No.** 2-Nitrophenyl tellurocyanate, 72726-15-9; 4-methoxyphenyl tellurocyanate, 72726-16-0; phenyl tellurocyanate, 72726-17-1; (2-nitrophenyl)tellurenyl bromide, 71129-55-0; bis(4-methoxyphenyl) ditelluride, 35684-37-8; diphenyl ditelluride, 32294-60-3; phenyltellurium tribromide, 36309-64-5; (4-methoxyphenyl)tellurium trichloride, 36309-68-9.

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(9) McWinnie, W. R.; Thavornyutikarn, P. *J. Chem. Soc., Dalton Trans.* **1972**, 551.