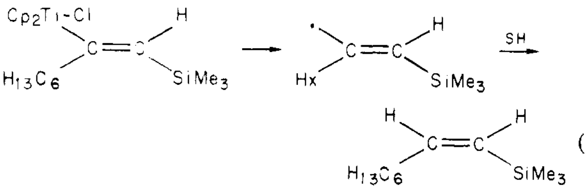

(14)

involved for both the bis(dialkylamino)alane[4] and the aluminate reactions is approximately the same. This indicates that the regiospecific step must be the same for both reactions. We suggest that the complexation of the intermediate titanium hydrido compound or the formation of the alkyltitanium compound is the rate-determining step, after which the subsequent steps of Scheme I follow.

Acknowledgment. We are indebted to the National Science Foundation (Grant No. MPS 7504127), Union Camp Corp., and the Alcoa Foundation for financial support of this work.

Registry No. 1-Octene, 111-66-0; octane, 111-65-9; 1-hexene, 592-41-6; hexane, 110-54-3; styrene, 100-42-5; ethylbenzene, 100-41-4; methylenecyclohexane, 1192-37-6; methylcyclohexane, 108-87-2; 2-ethyl-1-hexene, 1632-16-2; 2-ethylhexane, 589-81-1; neohexene, 558-37-2; 2,2-dimethylbutane, 75-83-2; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7; cyclohexene, 110-83-8; cyclohexane, 110-82-7; 1-methyl-1-cyclohexene, 591-49-1; 1-octyne, 629-05-0; phenylethyne, 536-74-3; 4-octyne, 1942-45-6; *cis*-4-octene, 7642-15-1; 2-hexyne, 764-35-2; 1-phenyl-1-propyne, 673-32-5; 1-phenylpropane, 103-65-1; 1-deuterio-*cis*-1-phenyl-1-propene, 72087-52-6; 2-deuterio-*cis*-1-phenyl-1-propene, 72090-05-2; 3-phenyl-1-propene, 300-57-2; 1-(trimethylsilyl)-1-octyne, 15719-55-8; 1-(trimethylsilyl)octane, 3429-76-3; *cis*-1-(trimethylsilyl)-1-octene, 57365-48-7; 1-iodooctane, 629-27-6; 2-iodo-*cis*-2-hexene, 72087-50-4; 3-iodo-*cis*-2-hexene, 72087-51-5; Cp_2TiCl_2, 1271-19-8; $LiAlH_4$, 16853-85-3; $NaAlH_4$, 13770-96-2; $LiAlMe_3H$, 62816-22-2; $NaAlMe_3H$, 66484-08-0; $NaAl(OCH_2CH_2OCH_3)_2H_2$, 22722-98-1; *cis*-2-octene, 7642-04-8; $LiAlH_2(NEt_2)_2$, 72749-21-4; $LiAlH_2(N\text{-}i\text{-}Pr_2)_2$, 72749-22-5; $NaAlH_2(NEt_2)_2$, 62259-84-1; $NaAlH_2(N\text{-}i\text{-}Pr_2)_2$, 72749-23-6.

Hydrometalation. 6. Evaluation of Lithium Hydride as a Reducing Agent and Hydrometalation Agent

Eugene C. Ashby* and Stephen A. Noding

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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The reactions of activated lithium hydride with carbonyl compounds (aldehydes, ketones, esters, and enones), alkenes, and alkynes in the presence of transition-metal halides were investigated. Significant reaction involving the above substrates was accomplished only when an equimolar amount of VCl_3 was used in conjunction with the lithium hydride. Aldehydes were reduced to their corresponding alcohols in high yield (95–97%), and esters were also reduced to their corresponding alcohols in high yield (93–95%) with a small amount (5–7%) of the corresponding aldehyde (of the carboxylic acid portion) formed. Reductions of cyclohexanones were highly stereoselective. In this connection, 4-*tert*-butylcyclohexanone was reduced to the axial alcohol in 96% yield and with 82% stereoselectivity. The only enone to be reduced was cinnamaldehyde, which gave the 1,2-reduction product in 90% yield. Terminal olefins were reduced to alkanes whereas internal olefins were completely unreactive. In this connection, 1-octene was reduced to octane in 95% yield. In this example, 30% deuterium incorporation of the product was observed when hydrolysis was effected with D_2O. Such a result indicates formation of the intermediate octyllithium in 30% yield. Since alkynes and internal olefins are not reduced at all with LiH and VCl_3 and terminal olefins are, reduction of enynes and dienes with LiH and VCl_3 could serve as a selective reduction method for the reduction of a terminal double bond in the presence of a triple bond and also for the selective reduction of a terminal double bond in the presence of an internal double bond.

Lithium, sodium, and potassium hydrides have been widely used as bases in synthetic organic chemistry, but have not been used as reducing agents. Some time ago we developed a simple method for the preparation of a very active form of lithium hydride.[1] This method involves the room-temperature hydrogenolysis of *tert*-butyllithium (eq 1). The resulting white solid is easily filtered from the

$$t\text{-}C_4H_9Li + H_2 \xrightarrow[1000\ \text{psi}]{\text{room temp}} i\text{-}C_4H_{10} + LiH \qquad (1)$$

reaction mixture but is most conveniently used as a slurry due to its high degree of pyrophoricity. This form of lithium hydride appears to be much more reactive than the lithium hydride that is commercially available and which is prepared at about 450 °C. A preliminary experiment[2] showed that benzophenone is reduced to benzhydrol in 6% yield when stirred with activated lithium hydride for 2 h, whereas no trace of benzhydrol was found when commercial lithium hydride was used under the same conditions.

Recently Caubere and co-workers showed that the reagent $NaH\text{–}RONa\text{–}MX_n$ is capable of reducing halides,[3,4] ketones, alkenes, and alkynes.[5,6] Although these reactions were not catalytic, they did provide a 75–95% yield of the corresponding alkanes, alcohols, alkanes, and alkenes, respectively.

In our continuing search for new stereoselective reducing agents and new hydride systems to effect hydrometalation of alkenes and alkynes, we investigated the reactions of activated LiH with various carbonyl compounds, alkenes, and alkynes in the absence and presence of catalysts. The

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[1] E. C. Ashby and R. D. Schwartz, *Inorg. Chem.*, 10, 355 (1971).

[2] E. C. Ashby and R. Boone, unpublished results.

[3] G. Guillaumet, L. Mordentia, and P. Caubere, *J. Organomet. Chem.*, **92**, 43 (1975).

[4] G. Guillaumet, L. Mordentia, and P. Caubere, *J. Organomet. Chem.*, **102**, 353 (1977).

[5] J. J. Brumet, L. Lordenti, B. Loubinaux, and P. Caubere, *Tetrahedron Lett.*, 1069 (1977).

[6] J. J. Brumet and P. Caubere, *Tetrahedron Lett.*, 3947 (1977).

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results are quite interesting in light of previous notions about the lack of reactivity of LiH as a reducing agent and provide some information about the ease of transfer of hydrogen from lithium to a transition metal.

Experimental Section

Apparatus. Reactions were performed under nitrogen or argon at the bench by using Schlenk-tube techniques or in a glovebox equipped with a recirculating system using manganese oxide columns to remove oxygen and dry ice–acetone traps to remove solvent vapors.[7] Calibrated syringes equipped with stainless-steel needles were used for transfer of reagents. Glassware and syringes were flamed or heated in an oven and cooled under a flow of nitrogen or argon prior to use. All inorganic and organic compounds, including internal standard solutions, were prepared by weighing the reagent in a tared volumetric flask and diluting with the appropriate solvent.

Proton NMR spectra were determined at 60 MHz with a Varian Model A-60 or Model T-60 spectrometer or at 100 MHz with a JEOL Fourier transform spectrometer, Model PFT-100. The chemical shift values are expressed in ppm (δ values) relative to a Me_4Si internal standard. The mass spectra were obtained with a Hitachi Perkin-Elmer Model RMU-7 or a Varian Model M-66 mass spectrometer. GLC analyses were carried out on an F&M Model 700 or Model 720 gas chromatograph. The IR spectra were determined with a Perkin-Elmer Model 621 or Model 256 infrared recording spectrophotometer. High-pressure reactions were carried out in an autoclave rated to 15000 psi obtained from the Superpressure Division of the American Instrument Co.

Analytical Methods. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[8] Lithium reagents were analyzed by the standard Gilman double-titration method (titration of total base and then titration of total base after reaction with benzyl chloride).[9] The amount of active C–Li was determined by titrating the active reagent with dry 2-butanol in xylene with 2,2′-diquinoline as an indicator.

Analyses of all products arising from the quenching of reactions of alkenes and carbonyl compounds with hydride reagents with H_2O or D_2O were identified by GLC and/or NMR, isolated by GLC techniques, and compared to authentic samples obtained commercially or synthesized by proven methods. All NMR spectra were obtained in $CDCl_3$ or benzene-d_6 by using Me_4Si as the internal standard.

Materials. Solvents. Fisher reagent-grade tetrahydrofuran (THF) was dried over $NaAlH_4$ and distilled under nitrogen with diphenylmethane as a drying indicator.

Fisher reagent-grade benzene was stirred over concentrated H_2SO_4, washed with Na_2CO_3 and then distilled water, dried over anhydrous $MgSO_4$, and distilled from $NaAlH_4$ under nitrogen or argon.

Alkenes. 1-Octene, 1-methyl-1-cyclohexene, *cis*-2-hexene, *trans*-2-hexene, methylenecyclohexane, 2-ethyl-1-hexene, and cyclohexene were obtained from Chemical Samples Co. or Aldrich Chemical Co. The liquids were distilled and stored over 4A molecular sieves.

Alkynes. 1-Hexyne, 2-hexyne, 1-phenyl-1-propyne, diphenylethyne, and 1-octyne were obtained from Chemical Samples Co. or Aldrich Chemical Co. and distilled and stored over 4A molecular sieves.

Ketones and Aldehydes. Fisher certified ACS grade acetone was dried over $MgSO_4$, filtered, distilled from P_2O_5, and stored over 4A molecular sieves. Finton 4-*tert*-butylcyclohexanone was sublimed under nitrogen. Eastman benzophenone and Aldrich benzaldehyde were distilled under vacuum and stored under argon in the dark.

Metal Salts. The following transition-metal halides were obtained from Fisher: $TiCl_3$, $TiCl_4$, $CrCl_3$, $MnCl_2$, and $ZnBr_2$. Alfa Inorganics supplied the following transition-metal halides: VCl_3, $FeCl_3$, $FeCl_2$, $CoCl_2$, $NiCl_2$, Cp_2TiCl_2. All transition-metal halides were opened only in the drybox and used without further purification.

Table I. Reactions of LiH and Transition-Metal Halide with 4-*tert*-Butylcyclohexanone[a]

halide	rel alcohol yield, % Ax[b]	rel alcohol yield, % Eq[b]	yield, %
none	45	55	6
$CrCl_3$	83	17	8
$MnCl_2$	0	0	0
$FeCl_2$	0	0	0
$CoCl_2$	0	0	0
$NiCl_2$	0	0	0
$TiCl_3$	61	39	41
VCl_3[d]	82	18	86
$FeCl_3$	74	26	68
Cp_2TiCl_2	65	35	27
VCl_3[c]	80	20	3

[a] In a 1:1:1 ratio at room temperature for 24 h in THF. [b] Yields were determined by GLC on the basis of internal standard. Ax = axial and Eq = equatorial. [c] Only 5 mol % of VCl_3 was added. [d] When this reaction was allowed to take place in benzene, an 80% yield of the alcohols was obtained, with the axial alcohol constituting 79% of the total.

Hydrides. Activated LiH was prepared by the hydrogenolysis of *t*-BuLi or *n*-BuLi at 4000 psi of hydrogen for 12 h at room temperature in hexane.[1] The resulting LiH slurry was transferred via syringe under argon in a drybox.

Sodium hydride as a 50% dispersion in oil was obtained from Alfa Inorganics. The oil was removed by repeated washing and decantation using freshly distilled hexane.

General Reactions of Alkenes, Alkynes, and Carbonyl Compounds. A 10 × 18 mm test tube with a Teflon-coated magnetic stirring bar was flamed and cooled under a flow of argon or nitrogen. The transition-metal halide was transferred to a tared test tube in the drybox. The tube was sealed with a rubber serum cap, removed from the drybox, reweighed, and connected by means of a syringe needle to a nitrogen- or argon-filled manifold equipped with a mineral oil filled bubbler. A 1- or 2-mL sample of THF or benzene was introduced into the reaction vessel and then the organic substrate added. The mixture was stirred for 2 to 3 min before the hydride was added. The reaction mixture was then stirred at room temperature or at higher temperatures, depending upon the reactants (for up to 40 h in some cases). The reactions were quenched by either H_2O or D_2O and worked up by conventional methods (addition of water, followed by extraction with THF, diethyl ether, or hexane and drying over $MgSO_4$). Most products were separated by GLC using a 6-ft, 10% Apiezon L 60-80 column with a helium flow rate of 45 mL/min: 1-octene (110 °C, oven temperature), 1-methyl-1-cyclohexene (50 °C), 2-ethyl-1-hexene (50 °C), cyclohexene (50 °C). A 20-ft, 10% TCEP column with a helium flow rate of 45 mL/min was used for *cis*-2-hexene (45 °C), *trans*-2-hexene (45 °C, flow rate 25 mL/min), 2-hexyne (70 °C), 1-octyne (70 °C), 1-hexyne (70 °C), and 1-phenyl-1-propyne (125 °C). A 10-ft, 5% Carbowax 20M column was used for diphenylethyne (200 °C, flow rate 60 mL/min). The yield was calculated by using a suitable hydrocarbon internal standard for each case (n-$C_{12}H_{26}$, n-$C_{14}H_{30}$, or n-$C_{16}H_{34}$), and the products were identified by comparing the retention times of authentic samples with the products under similar conditions and/or by coinjection of products and authentic samples obtained commercially or synthesized by proven methods.

General Quenching Techniques. Quenching with H_2O. After the desired reaction time, the reaction mixture was quenched with water or a saturated solution of ammonium chloride to produce the protonated species. The amounts of recovered starting material and products were determined by the methods described above.

Quenching with D_2O. The same procedure for quenching with H_2O was followed. Each product collected by GLC was subjected to mass spectral analysis. The amount of the deuterated species observed in the mass spectrum was compared to that observed in the mass spectrum of the protonated species and calculated as percent deuterium incorporation.

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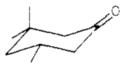
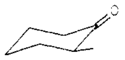
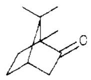
(8) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, 1969.
(9) H. Gilman and A. H. Harbein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

Table II. Reactions of Carbonyl Compounds with LiH and VCl_3[a]

substr	% recovd substr	rel alcohol yield, % Ax or exo[b]	 Eq or endo[b]	yield, %
	11	82	18	86
	3	90	10	90
	0	92	8	90
	3	95	5	95
PhC(O)H	0			97[c]
$C_5H_{11}C(O)H$	0			95[d]
$PhC(O)OC_2H_5$	0	7[e]	93[c]	95
$C_3H_7C(O)OC_2H_5$	0	5[f]	95[g]	95

[a] In a 1:3:3 molar ratio in THF. [b] All reactions were carried out at 45 °C for 36 h, and yields were determined by GLC on the basis of an internal standard. Ax = axial and Eq = equatorial. [c] $PhCH_2OH$. [d] $C_6H_{13}OH$. [e] PhC(O)H. [f] $C_3H_7C(O)H$. [g] C_4H_9OH.

Results and Discussion

Table I lists the results of reactions of activated LiH with 4-*tert*-butylcyclohexanone in the presence of a series of transition-metal halides in a 1:1:1 ratio. Without any transition-metal halide present, only a 5% yield of alcohols was obtained, with 45% being the axial alcohol. However, when an equimolar amount of VCl_3 was added to the LiH, an 86% yield of alcohols was obtained, with 82% being the axial alcohol. $FeCl_3$ was the next most effective transition-metal halide, producing the alcohols in 68% yield, with 74% being the axial alcohol. A catalytic amount of VCl_3 (5 mol %) was added, but under these conditions, only a 3% yield of the alcohols was obtained with basically the same stereoselectivity observed for the stoichiometric reaction. It is clear from the results (Table I) that VCl_3 is the most effective transition-metal halide used in conjunction with LiH for reduction purposes both from a conversion and from a stereospecificity standpoint.

Table II represents the reactions of LiH-VCl_3 in a 1:1 ratio with other carbonyl substrates. The ketones (4-*tert*-butylcyclohexanone, 3,3,5-trimethylcyclohexanone, 2-methylcyclohexanone, and camphor) were reduced in high yield (86–95%) with the axial or exo alcohols formed predominantly (82, 90, 92, and 95%, respectively). The aldehydes (benzaldehyde and hexanal) and esters (ethyl benzoate and ethyl *n*-butyrate) were also reduced to their respective alcohols in high yield (97, 95, 95, and 95%). In the case of the ester reductions, small amounts of the corresponding aldehydes were also observed.

When a series of seven alkenes was allowed to react under similar conditions (Table III), only the terminal alkenes reacted to form the corresponding alkanes in high yield. For example, 1-octene, 2-ethyl-1-hexene, and methylenecyclohexane were reduced to the corresponding alkane in 93–95% yield. The same olefins, when reduced, however, did not produce high percentages (~30%) of deuterium incorporation product when the reaction mixture was quenched with D_2O. Changing solvents from THF to benzene had no effect on the outcome of these reactions. In any event, these results show that terminal olefins are reduced to the corresponding alkanes in high yield and that a significant amount of the corresponding organolithium compound is formed as an intermediate.

Table III. Reactions of Alkenes with LiH and VCl_3 in THF[a]

substr	% recovd substr	alkane (% yield)[b]	D incorp, %
1-octene	0	octane (95)	30
cis-2-hexene	100	hexane (0)	
trans-2-hexene	100	hexane (0)	
2-ethyl-1-hexene	5	3-methylheptane (95)	29
cyclohexene	100	cyclohexane (0)	
1-methyl-1-cyclohexene	100	methylcyclohexane (0)	
methylenecyclohexane	7	methylcyclohexane (93)	30

[a] At 45 °C for 36 h in a molar ratio of 1:3:3. [b] Yields were determined by GLC on the basis of internal standard.

Table IV. Reactions of LiH and NaH with 1-Octene in the Presence of Catalytic Amounts (5 mol %) of Transition-Metal Halides[a]

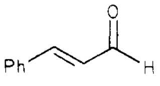
metal hydride	catalyst[c]	recovd yield,[b] % 1-octene	 octane	D incorp, %
LiH	VCl_3	94	trace	
	Cp_2TiCl_2	18	77	50
	$TiCl_4$	33	59	45
	$FeCl_3$	74	25	<5
	$NiCl_2$	70	27	<5
	$CoCl_2$	65	32	<5
NaH	VCl_3	97	0	
	Cp_2TiCl_2	94	5	
	$TiCl_4$	97	trace	
	$FeCl_3$	97	0	
	$NiCl_2$	97	trace	
	$CoCl_2$	97	trace	

[a] In benzene at room temperature for 24 h. [b] Yields were determined by GLC on the basis of hexane as the internal standard. [c] All 5 mol %.

In an attempt to improve on the above reducing system involving an alkali metal hydride and stoichiometric amounts of a transition-metal halide, we decided to explore the possibility of catalytic (5 mol %) hydrometalation using LiH or NaH. Table IV summarizes the results of this study. Of all the transition-metal halides surveyed, Cp_2TiCl_2 produced the most encouraging results when allowed to react with activated LiH and a representative olefin such as 1-octene. When LiH in the presence of a catalytic amount (5 mol%) of Cp_2TiCl_2 was allowed to react with 1-octene in benzene, octane was formed in 77% yield. Even more encouraging is the fact that quenching with D_2O resulted in the formation of a product exhibiting 50% deuterium incorporation. It was somewhat disappointing that NaH did not produce yields of octane larger than 5% since NaH is much less expensive than LiH and is easier to handle. Our work continues on this point with various forms of activated NaH.

Because of the success observed in the reactions of terminal alkenes with LiH in the presence of an equimolar amount of VCl_3, a similar reaction involving alkynes was studied. In this connection, 1-octyne, 1-hexyne, 2-hexyne, 1-phenyl-1-propyne, diphenylethyne, and phenylethyne were allowed to react with LiH and VCl_3 in a 1:3:3 ratio in benzene at 45 °C for 36 h. In each case the alkyne was recovered quantatively. This result could be used to great advantage in the reduction of compounds containing olefinic double bonds in the presence of triple bonds.

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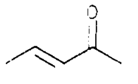
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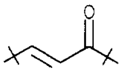
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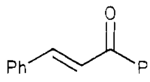
IV

Acknowledgment. The authors wish to thank the National Science Foundation (Grant No. MPS 6504127), Union Camp, and Alcoa for financial support of this work.

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.

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

Received September 3, 1979

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.

$$\begin{tikzcd} \mathrm{Ar{-}Te{-}Te{-}Ar} + \mathrm{CN^-} \arrow[r, shift left] & \mathrm{ArTe^-} \arrow[l, shift left] \arrow[l, bend left=40, "O_2"] + \mathrm{ArTeCN} \end{tikzcd} \qquad (1)$$

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.

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

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