Hz); 5.30 (m; 1 H; C*H*=C(CH$_3$)$_2$); 7.05-7.40 (m; 4 H; C$_6$*H*$_4$).

(*Z*)-**PhC≡CCH=CHCH$_3$**: 1.95 (dd; 3 H; C*H*$_3$; ^3J = 6.8 Hz; ^4J = 1.7 Hz); 5.75 (m; 1 H, PhC≡CC*H*); 6.05 (dq; 1 H; CH$_3$C*H*; J = 10.0, 6.8 Hz); 7.2-7.5 (m; 5 H; C$_6$*H*$_5$).

(*E*)-**PhC≡CCH=CHCH$_3$**: 1.85 (dd; 3 H; C*H*$_3$; ^3J = 6.8 Hz; ^4J = 1.8 Hz); 5.65 (m; 1 H; PhC≡CC*H*); 6.25 (dq; 1 H; CH$_3$C*H*; J = 16.0, 6.8 Hz); 7.2-7.5 (m; 5 H; C$_6$*H*$_5$).

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this research.

Registry No. CH$_3$CH$_2$CH(CH$_3$)C≡CCH$_2$CH=CH$_2$, 139016-26-5; *n*-C$_4$H$_9$C≡CCH$_2$CH=CH$_2$, 31508-12-0; *n*-C$_5$H$_{11}$C≡CCH$_2$CH=CH$_2$, 24948-66-1; *n*-C$_8$H$_{17}$C≡CCH$_2$CH=CH$_2$, 130670-04-1; HC≡C(CH$_2$)$_6$C≡CCH$_2$CH=CH$_2$, 139016-27-6; [CH$_2$=CHCH$_2$C≡C(CH$_2$)$_3$]$_2$, 139016-28-7; Ph(CH$_2$)$_3$C≡CCH$_2$CH=CH$_2$, 139016-29-8; Ph(CH$_2$)$_3$C≡CCH$_2$CH=C(CH$_3$)$_2$, 139016-30-1; PhCH$_2$CH$_2$C≡CCH$_2$CH=CH$_2$, 139016-31-2; PhCH$_2$CH$_2$C≡CCH$_2$CH=C(CH$_2$)$_2$, 139016-32-3; Ph(CH$_2$)$_3$C≡CC(CH$_3$)$_2$CH=CH$_2$, 139016-33-4; PhCH$_2$CH$_2$C≡CC(CH$_3$)$_2$CH=CH$_2$, 139016-34-5; PhC≡CCH$_2$CH=CH$_2$, 4289-20-7; (*Z*)-PhC≡CCH=CHCH$_3$, 31552-04-2; (*E*)-PhC≡CCH=CHCH$_3$, 31552-03-1; PhCH=C=CHCH=CH$_2$, 31508-14-2; PhC≡CCH$_2$CH=C(CH$_3$)$_2$, 115584-90-2; PhC≡CC(CH$_3$)$_2$CH=CH$_2$, 34600-27-6; *p*-CH$_3$C$_6$H$_4$C≡CCH$_2$CH=CH$_2$, 139016-35-6; *p*-CH$_3$C$_6$H$_4$C≡CCH=CHCH$_3$, 139016-36-7; *p*-CH$_3$C$_6$H$_4$CH=C=CHCH=CH$_2$, 139016-38-9; *p*-CH$_3$C$_6$H$_4$C≡CCH$_2$CH=C(CH$_3$)$_2$, 139016-37-8; *p*-CH$_3$C$_6$H$_4$C≡CC(CH$_3$)$_2$CH=CH$_2$, 139016-39-0; 2-methyl-3-bromo-2-propene, 3017-69-4; 3-methyl-1-pentyne, 922-59-8; 1-hexyne, 693-02-7; 1-heptyne, 628-71-7; 1-decyne, 764-93-2; 1,9-decadiyne, 1720-38-3; 5-phenyl-1-pentyne, 1823-14-9; 4-phenyl-1-butyne, 16520-62-0; phenylacetylene, 536-74-3; *p*-tolylacetylene, 766-97-2; allyl bromide, 106-95-6; tetrahexylammonium bromide, 4328-13-6; tetraethylbenzylammonium chlorides, 56-37-1; copper(I) chloride, 7758-89-6.

Supplementary Material Available: NMR spectra for the obtained compounds (24 pages). Ordering information is given on any current masthead page.

Effect of Coordinating Solvent on Higher Order Organocyanocuprates

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The composition of organocyanocuprates has been a topic of recent controversy.[1a,b] Cuprates generated from the addition of 1 equiv of RLi (R = alkyl, aryl) and 1 equiv of CuCN are assumed to be addition products of these two species (RCu(CN)Li). In agreement with this formulation, Bertz has recently reported that cuprates derived from 1 equiv each of methyl-, ethyl-, or phenyllithium and copper cyanide exhibit ^{13}C-^{13}C coupling between C-1 of the alkyl or aryl residue and the cyanide carbon when in THF below -78 °C or in ether below -100 °C.[2]

Cuprates prepared from 2 equiv of RLi (R = alkyl, aryl) and 1 equiv of CuCN are generally assumed to be dianionic salts with three ligands coordinated to copper ($R_2Cu(CN)Li_2$).[3] However, alternative formulations in which these reagents possess Gilman-like compositions (R_2CuLi) and are coordinated with LiCN have been proposed.[1a,2] In support of the latter formulation (R_2CuLi·LiCN) Bertz reported that when prepared in the THF (R = Me, Et, and Ph) there were no differences in the ^{13}C-1 resonances of cuprates prepared from CuCN or CuI. In this solvent neither were there differences between the ^{13}C chemical shifts of the cyanide carbons of the various cyanocuprates. Further support for the Gilman formulation comes from the report of Bertz that for R = Et no ^{13}C-^{13}C coupling between C-1 of the alkyl residue and the cyanide carbon was observed in ether or THF with or without added HMPA at temperatures down to -120 °C.

In support of the formulation $R_2Cu(CN)Li_2$, Lipshutz et al. reported that although the ^{13}C-1 resonances of Me_2CuLi/LiI and $Me_2Cu(CN)Li_2$ appear very close to one another when examined in THF solution, if spectra were examined in DMS the former gave a signal at -9.65 ppm while the latter gave a signal at -8.53 ppm. Lipshutz further confirmed the bound nature of cyanide in $R_2Cu(CN)Li_2$ through infrared studies in which he demonstrated that LiCN or Bu_4NCN when added to Me_2CuLi/LiI in THF/HMPA or DMS/HMPA gave absorptions at 2138 and 2118 cm^{-1} that are identical to those obtained from preparations of $Me_2Cu(CN)Li_2$.[1b]

We report infrared and NMR spectroscopic evidence that the composition of cuprates prepared from the addition of 2 equiv of alkyllithium and 1 equiv of CuCN is dramatically affected by the addition of strongly coordinating solvents to the cuprate solution.[4] Present evidence suggests that $[R_2Cu(CN)Li_2]_x$ is the preferred formulation for these cuprate solutions in THF, DMS, or DMS/HMPA. However, R_2CuLi/LiCN and $[R_2Cu(CN)Li_2]_x$ together are representative formulations for cuprates prepared in THF/HMPA solutions.

Results and Discussion

Low-Temperature Infrared Experiments. Infrared measurements enable one to distinguish between equilibrating species with a time scale 10^4-10^{12} times faster than for ^{1}H or ^{13}C NMR.[5] The IR spectrum at -30 °C (low-temperature cell) of the cuprate prepared from mixing CH$_3$Li and CuCN in a 2:1 molar ratio in THF displayed an intense nitrile stretch at 2130 cm^{-1} with a shoulder near 2109 cm^{-1} (Figure 1a). Addition of HMPA to this solution causes an emergence of minor absorptions at 2109 and 2090 cm^{-1}. As the amount of HMPA to this solution is increased from 1.7% (v/v, 1 equiv) to 5% (v/v), the absorptions appearing at 2109 and 2090 cm^{-1} grow in intensity and a new absorption at 2068 cm^{-1} appears (Figures 1b and 1c). When the amount of HMPA is increased to 10% (v/v), 25% (v/v), and 50% (v/v) (Figures 1d, 1e, and 1f), the nitrile stretch due to the original cuprate species decreases as these three new nitrile stretches increase and a fourth at 2101 cm^{-1} appears. The absorption at 2068 cm^{-1} was confirmed to be LiCN by independent experiments in which this salt (0.10 M) was dissolved in THF/HMPA solutions varying in composition from 1.7% (v/v) to 50% (v/v) HMPA. At -30 °C LiCN exhibited a nitrile absorption at 2068 cm^{-1} for all concentrations of HMPA in THF examined (Figure 2f).

Thus, in the presence of appreciable amounts of HMPA in THF (>10% (v/v)) the cyanide ligand of $Me_2Cu(CN)Li_2$ is partly dissociated from the copper and is spectroscopically identical to free LiCN in solution. This observation leaves $[Me_2Cu(CN)Li_2]_x$ and Me_2CuLi/LiCN as the most reasonable formulations for the cuprate species existing in THF solutions containing >10% (v/v) HMPA. The

(1) (a) Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031. (b) Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 4032.
(2) Bertz, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 5470.
(3) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005 and references cited therein.
(4) See reference 11 in ref 1b above.
(5) Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 769.

0022-3263/92/1957-2192$03.00/0

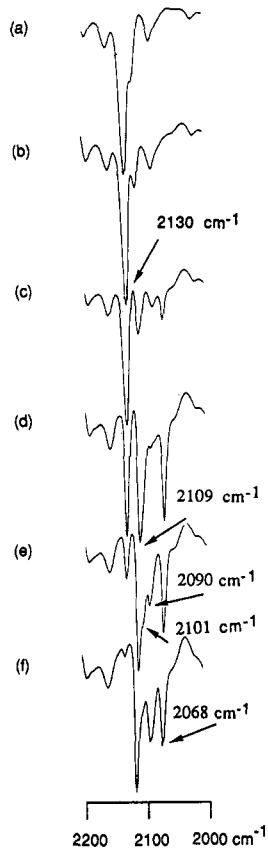

Figure 1. Low-temperature FT-IR spectra of (a) $Me_2Cu(CN)Li_2$ in THF at −30 °C; (b) $Me_2Cu(CN)Li_2$ in THF 1.7% v/v HMPA at −30 °C; (c) $Me_2Cu(CN)Li_2$ in THF 5.0% v/v HMPA at −30 °C; (d) $Me_2Cu(CN)Li_2$ in THF 10.0% v/v HMPA at −30 °C; (e) $Me_2Cu(CN)Li_2$ in THF 25.0% v/v HMPA at −30 °C; (f) $Me_2Cu(CN)Li_2$ in THF 50.0% v/v HMPA at −30 °C.

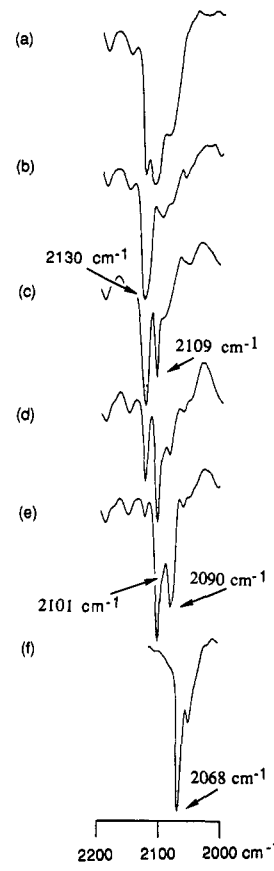

Figure 2. Low-temperature FT-IR spectra of (a) $Me_2Cu(CN)Li_2$ in DMS at −30 °C; (b) $Me_2Cu(CN)Li_2$ in DMS 5.0% v/v HMPA at −30 °C; (c) $Me_2Cu(CN)Li_2$ in DMS 10.0% v/v HMPA at −30 °C; (d) $Me_2Cu(CN)Li_2$ in DMS 25.0% v/v HMPA at −30 °C; (e) $Me_2Cu(CN)Li_2$ in DMS 50.0% v/v HMPA at −30 °C; (f) LiCN in DMS 50.0% v/v HMPA at −30 °C.

formulation $[Me_2Cu(CN)Li_2]_x$ represents the aggregated forms of the higher order cuprate present in THF/HMPA solutions containing a cyanide ligand bonded to copper[6] whereas $Me_2CuLi/LiCN$ represents the cuprate species also present in THF/HMPA solutions that has no cyanide ligand bonded to the copper.

The IR spectrum at −30 °C (low-temperature cell) of the cuprate prepared from mixing CH_3Li and CuCN in a 2:1 molar ratio in DMS displayed three intense nitrile stretches at 2130, 2109, and 2090 cm^{-1} (Figure 2a). Addition of 5% (v/v) HMPA to this solution caused the absorptions at 2109 and 2090 cm^{-1} to decrease markedly while the absorption at 2130 cm^{-1} remained as a single intense nitrile stretch (Figure 2b). As the amount of HMPA added to this solution is increased from 5% (v/v) to 10%, 25%, and 50% (v/v) (Figures 2c, 2d, and 2e), the nitrile stretch due to the cuprate species at 2130 cm^{-1} decreases while absorptions at 2109 and 2090 cm^{-1} reappear and a third absorption appears as a shoulder at 2101 cm^{-1}. Thus, in the presence of appreciable amounts of HMPA in DMS (up to 50% (v/v)) the cyanide ligand remains associated with the copper and no absorption attributable to free LiCN in solution is observed. This observation leaves $[Me_2Cu(CN)Li_2]_x$ as the most reasonable formulation for the aggregated cuprate species existing in DMS solutions containing up to 50% (v/v) HMPA.

To establish that the presence of DMS in solutions of cuprates prepared from mixing CH_3Li and CuCN in a 2:1 molar ratio prevents the dissociation of the cyanide ligand from the copper by HMPA, the IR spectra of cuprates prepared in ternary solvent mixtures were obtained. Hence, the IR spectrum of the cuprate prepared from mixing CH_3Li and CuCN in a 2:1 molar ratio in THF/HMPA 50% (v/v) followed by the addition of excess DMS displayed an identical spectrum to that cuprate prepared in DMS/HMPA 50% (v/v) followed by addition of excess THF. These spectra displayed intense nitrile stretches at 2125 and 2119 cm^{-1} and weak nitrile stretches at 2145 and 2138 cm^{-1}. No absorption due to free LiCN in solution was observed in either of these two cases.

^{13}C NMR Experiments. If, as demonstrated in Figure 1, parts d–f, the HMPA displaces the nitrile moiety as a ligand on the copper atom to afford $Me_2CuLi/LiCN$ in THF/HMPA solution, then a Gilman-like reagent could be present in this solution. Indeed, the methyl region of the ^{13}C NMR spectrum (−30 °C) of the cuprate prepared as in Figure 1f displayed a single resonance at −8.38 ppm which is very near to the position exhibited by Me_2CuLi/LiI (−8.32 ppm)[7a] prepared by the addition of

(6) There is much precedent for the aggregated nature of cuprates: (a) Lorenzen, N. P.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 300. (b) Olmstead, M. M.; Power, P. P. *Organometallics* **1990**, *9*, 1720. (c) Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 3197. (d) Lipshutz, B. H.; Kozlowski, J. A.; Wilhelm, R. S. *J. Org. Chem.* **1984**, *49*, 3943. (e) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312. (f) Filippo, Jr. *Inorg. Chem.* **1978**, *17*, 275. (g) Ashby, E. C.; Lin, J. J.; Watkins, J. J. *J. Org. Chem.* **1977**, *42*, 1099. (h) Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098.

(7) (a) This value is very close to that obtained by Bertz (see ref 1a); the slight difference is likely due to differences in the amount of HMPA present as well as the absence of 12-C-4 crown ether in our solutions. (b) This value is close to that obtained by Lipshutz et al. (see ref 1b); the difference appears to be a result of solvent reference (α = 68.6 for our solutions in THF whereas α = 67.4 for those of Lipshutz et. al.).

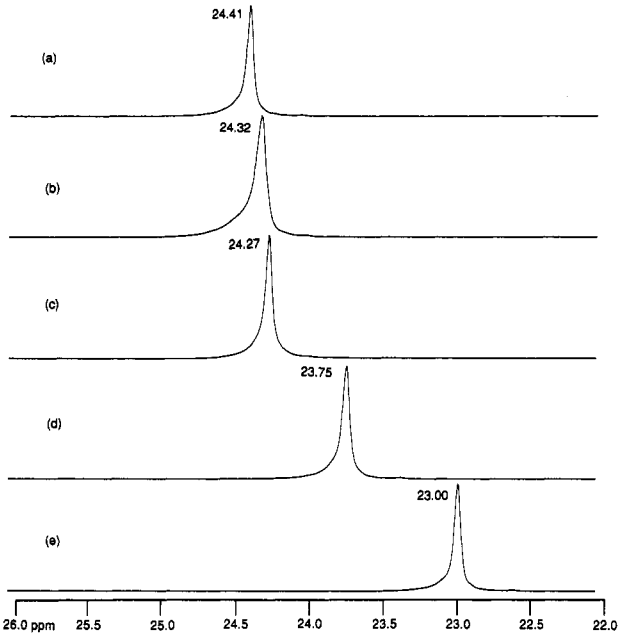

Figure 3. Low-temperature ^{31}P NMR spectra of (a) $Me_2Cu(CN)Li_2$ + 0.5 equiv of HMPA (0.85% (v/v)) in THF at −30 °C; (b) $Me_2CU(CN)Li_2$ + 1.0 equiv of HMPA (1.7% (v/v)) in THF at −30 °C; (c) $Me_2Cu(CN)Li_2$ + 2.0 equiv of HMPA (3.4% (v/v)) in THF at −30 °C; (d) $Me_2Cu(CN)Li_2$ + 4.0 equiv of HMPA (6.8% (v/v)) in THF at −30 °C; (e) 0.10 M HMPA in THF at −30 °C.

2 equiv of MeLi to 1 equiv of CuI in THF/HMPA (1:1). $Me_2CuCNLi_2$ prepared in THF without added HMPA gave a single signal at −9.76 ppm.[7b]

Conversely, as demonstrated in Figure 2, the HMPA does not displace the nitrile moiety as a ligand on the copper atom in DMS/HMPA solutions, and therefore no Gilman-like reagent should be present in this solution. Hence, the methyl region of the ^{13}C NMR spectrum (−30 °C) of the cuprate prepared as in Figure 2e displayed a single resonance at −10.29 ppm whereas the cuprate prepared by the addition of 2 equiv of MeLi to 1 equiv of CuI in THF/DMS 50% (v/v) displayed a single resonance of −6.27 ppm.

^{31}P NMR Experiments. The presence of a phosphorus in the HMPA molecule allows investigation of the interaction of this atom with organocyanocuprates in THF/HMPA solutions using ^{31}P NMR. As expected, the ^{31}P NMR spectrum (−30 °C) of cuprates prepared from the addition of 2 equiv of CH_3Li and 1 equiv of CuCN or 1 equiv of CuI in THF/1.7% HMPA (i.e. 1 equiv) displayed only one signal at essentially the same chemical shift (δ 24.2 ppm and 24.3 ppm, respectively). This signal is attributed to the averaged signal between HMPA coordinated to copper and uncoordinated HMPA (δ 23.0 ppm). The downfield shift of the ^{31}P signal is due to deshielding of the ^{31}P nucleus in HMPA through coordination of the oxygen atom in HMPA to the copper atom.[8]

That a dynamic equilibrium exists between coordinated and uncoordinated HMPA was demonstrated by varying the amount of HMPA in the solution (Figure 3). As the amount of HMPA is increased the chemical shift of the average signal moves toward that of HMPA alone.[9] If an equilibrium had not existed, then there would be no observed effect as HMPA was added to the solution. Cooling of the NMR sample did not slow the equilibrium sufficiently to allow signals to be observed for both coordinated and uncoordinated HMPA.

Scheme I

$$[(CH_3)_2Cu(CN)Li_2]_x \underset{\text{THF or DMS}}{\overset{\text{HMPA}}{\rightleftharpoons}} [(CH_3)_2Cu(CN)Li_2 \cdot \text{HMPA}]_y \underset{\text{THF}}{\overset{\text{HMPA}}{\rightleftharpoons}} (CH_3)_2CuLi \cdot \text{HMPA} + \text{LiCN}$$

$y < x$

Conclusions

Low-temperature IR, ^{13}C NMR, and ^{31}P NMR spectroscopic studies demonstrate that addition of a coordinating solvent such as HMPA alters the composition of organocyanocuprates in THF or DMS solutions. Higher order cuprates exist as aggregates in THF or DMS alone whereas they exist as lower aggregates and "lower order" Gilman-like cuprates (in the case of THF/HMPA) in the presence of HMPA; hence, multiple nitrile stretches are observed on the low-temperature IR spectra. The coordination of HMPA molecules to these cuprate species is in a rapid equilibrium process with uncoordinated HMPA (Scheme I) which has been partially characterized by low-temperature IR and ^{31}P NMR spectroscopy.[10]

Experimental Section

General Methods. All glassware and syringes were dried in an oven overnight at 120 °C, and glassware was flame-dried and flushed with argon immediately prior to use. Syringes were flushed with argon and kept under positive argon pressure until use. Transfer of reagents was performed with syringes equipped with stainless steel needles. All reactions were carried out under argon. Transfer of CuCN took place in a glovebag. All alkyllithiums were freshly titrated before use.[11] Tetrahydrofuran was freshly distilled over potassium benzophenone ketyl. Unless otherwise stated, other chemicals obtained from commercial sources were used without further purification.

Low-temperature FT-IR spectra were recorded at a 4-cm^{-1} resolution on a Perkin-Elmer 1600 Series FT-IR plotting percent transmittance vs wavenumber with background solvent subtraction. The spectra were recorded on THF/HMPA solutions in a variable-temperature cell modified with attached cannulae. The cell was flushed with argon and dry THF before transfer of solution via cannula to cell. The cell was equipped with CaF_2 windows, and all spectra were recorded at −30 °C unless otherwise stated.

Low-temperature ^{13}C and ^{31}P NMR spectra were recorded at 100.62 and 161.98 MHz, respectively. The spectra were recorded on THF solutions in 5-mm NMR tubes and were referenced to THF, α = 26.7 ppm, β = 68.6 ppm for the ^{13}C NMR spectra and in 10-mm NMR tubes, with an external reference of trimethyl phosphite, 140.2 ppm ($P(OMe)_3$), for the ^{31}P NMR spectra.

Sample Preparation. To CuCN (0.089 g, 1.0 mmol) in THF under argon was added HMPA (1.7, 5.0, 10.0, 25.0, or 50.0% v/v, respectively, unless otherwise stated) followed by dropwise addition of CH_3Li (1.43 mL, 2.0 mmol, 1.4 M in Et_2O) via syringe at −30 °C. After stirring at this temperature for 1 h, the 0.10 M homogeneous solution was transferred via cannula to an IR cell or an NMR tube equipped with septa, under argon, at −30 °C before recording spectra.

Preparation of Cuprates in Ternary Solvent Systems. To CuCN (0.089 g, 1.0 mmol) in THF under argon was added HMPA (50.0% v/v) followed by dropwise addition of CH_3Li (1.43 mL, 2.0 mmol, 1.4 M in Et_2O) via syringe at −30 °C. After stirring at this temperature for 1 h DMS was slowly added dropwise via syringe at −30 °C. After stirring at this temperature for an

(8) It can be concluded that the oxygen atom in HMPA is coordinated to the copper atom based on corroborating evidence between the IR study and the ^{31}P NMR study. It cannot be ruled out, however, that the oxygen atom in HMPA is not also coordinating to lithium atoms present in the system and that this aids in the deaggregation.

(9) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, New York, 1982.

(10) It is probable that LiCN is separated from the cuprate complex in THF/HMPA and not in DMS/HMPA due to greater stability/solubility of the HMPA complex in THF than in DMS. For example, CuCN remains solubilized in THF/HMPA whereas it forms a heterogeneous solution in DMS/HMPA.

(11) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

additional 30 min the 0.07 M homogeneous solution was transferred via cannula to the IR cell under argon at −30 °C before recording the IR spectrum.

Acknowledgment. We acknowledge the Natural Sciences and Engineering Research Council of Canada for support of this work through an operating grant to A.C.O. and a postgraduate fellowship to R.D.S.

Registry No. $Me_2Cu(CN)Li_2$, 80473-70-7.

A Facile Procedure for Producing γ-Halo Butyraldehyde Acetals

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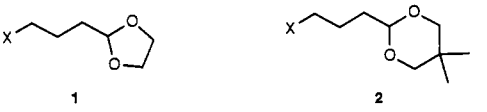
Received October 20, 1991

Four-carbon homologating agents are important in many syntheses. The acetals of 4-halobutanals have been used as alkylating agents to extend molecules by four carbons, while providing an aldehyde function at the new terminus. They have also been converted to Grignard and organolithium reagents and used to prepare 1,5-difunctionality. 1,1-Diethoxy-4-halobutanes[1] and 2-(3-halopropyl)-1,3-dioxolanes, **1a**,[2,3] **1b**,[4] and **1c**,[5] have seen frequent use. 2-(3-Chloropropyl)-5,5-dimethyl-1,3-dioxane, **2a**,[6] has also been used.

Early syntheses of 4-halobutanals began with tetrahydrofurfural and included such intermediates as 5-chloro-1,2-pentanediol, 1,2,5-pentanetriol, and 1,2-epoxy-5-chloropentane.[7,8] In 1961, Pleshakov and co-workers prepared **1a** in 64% yield by hydrogenolysis of 4-chlorobutanoyl chloride, followed by treatment with ethylene glycol in acid.[5e] They also prepared **1c** from **1a** with sodium iodide in acetone in 62% yield. Vedejs and coworkers prepared 4-bromobutanal in 24% overall yield by cleavage of tetrahydrofuran to 4-bromo-1-butanol with HBr, followed by pyridinium chlorochromate oxidation.[9] Kreif and Denis prepared 4-iodobutanal in 46% yield by treating cyclopropanecarboxaldehyde with P_2I_4.[10] Tius and Trehan reduced 4-chlorobutanonitrile with diisobutylaluminum hydride to the aldehyde in 50% yield.[11] Recently, the Pleshakov and Vedejs routes have been used most often, but all of these methods require expensive or less readily available reagents and involve demanding procedures.



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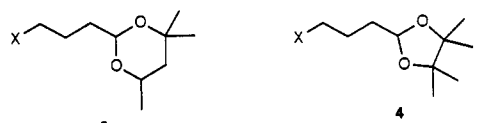


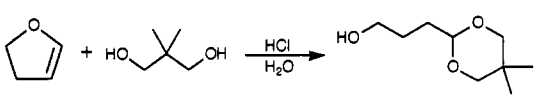
3 4

a, X = Cl
b, X = Br
c, X = I
d, X = OH

The readily available 2,3-dihydrofuran, **5**, is the cyclic enol ether of 4-hydroxybutanal. We proposed that treatment of **5** with an alcohol or diol under appropriate acid conditions might provide acetals of that aldehyde via rearrangement of a 2-alkoxytetrahydrofuran. Solutions of **5** in dry ethanol with a small amount of sulfuric acid gave 2-ethoxytetrahydrofuran or black polymer, but no hydroxy acetal. We then treated **5** with 1,3-propanediol and acid, hoping that the (hydroxypropyl)dioxane would be favored over the alkoxytetrahydrofuran, but only black polymeric material was obtained.

5

Dihydropyran is known to be hydrolyzable in aqueous HCl to the corresponding 5-hydroxypentanal,[12] so we decided to try concurrent hydrolysis of **5** and acetal formation in a substantial amount of water using HCl as catalyst. Although water may seem an unlikely medium for making acetals, we found that **5** and 1,3-propanediol gave about equal amounts of the desired acetal and 2-(3-hydroxypropyl)tetrahydrofuran. It is well-known that methyl groups favor ring formation under equilibrium circumstances;[13] therefore, we treated **5** with 2,2-dimethyl-1,3-propanediol (10% excess) in water with catalytic HCl. We were pleased to find only 2-(3-hydroxypropyl)-5,5-dimethyl-1,3-dioxane, **2d**, in 83% distilled yield (eq 1). In



(eq 1)

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