sugars as building blocks for replicating systems, these results direct thinking once again toward ribose itself, and chemical work seeking an improved abiotic synthesis of ribose would be most desirable.

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(16) **Note Added in Proof**: In the synthesis of these oligomers, coupling yields were ca. 90% for glycerothymine and >99% for natural nucleosides. The product oligonucleotides were purified by reversed phase HPLC (Nucleosil C-4 column, gradient from 15% to 30% acetonitrile in 0.1 M triethylammonium acetate) prior to the removal of the 5′-trityl groups and detritylated (80% acetic acid). Samples of the oligonucleotides containing the flexible base were digested with spleen phosphodiesterase, snake venom phosphodiesterase, and bacterial alkaline phosphatase. HPLC of the digests showed the expected nucleosides in their expected ratios.

A New Access to Acyl- and Aroyllithiums via Lithium–Tellurium Exchange

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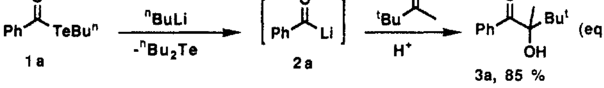
The most straightforward method for nucleophilic introduction of acyl and aroyl groups into organic molecules is the use of carbonyl anions, represented by acyl- and aroyllithiums, as nucleophiles.[1] Their synthetic utility, however, has been severely limited for a long time because of difficulty both in their generation and in control of their reaction courses.[2,3] Notable advances in this chemistry appeared in the 1980s.[3,4] In 1982, Seyferth et al. succeeded in an efficient intermolecular trapping of acyllithiums under carefully controlled reaction conditions.[3a–f] Shortly after, Murai and we disclosed a unique intramolecular conversion of acyllithiums into lithium enolates based on 1,2-silicon shift.[3g] As for the methodology for generation of acyl- and aroyllithiums, there are only two methods available so far.[5] One is the reaction of organolithiums with carbon monoxide,[2,3] and the other is the direct lithiation of carbonyl carbon by abstraction of a formyl hydrogen.[4] In this paper we report a novel and practically useful entry to acyl- and aroyllithiums **2** based on efficient lithium–tellurium exchange[6,7] of tellurolesters **1**, which are easily accessible from the corresponding acid chlorides and tellurolate anions.[8]

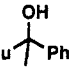
When butyllithium was added to *Te*-butyl tellurobenzoate (**1a**) in THF/Et$_2$O (10/8) at −105 °C in the presence of pinacolone as an electrophile, α-hydroxy ketone **3a** was obtained in 85% yield together with dibutyl telluride (82%) (entry 1 in Table I).[9] This simple benzoyllithium cannot be trapped efficiently by the PhLi/CO method.[3d]



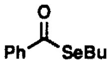
(eq. 1)

Under similar conditions, [*p*-(trifluoromethyl)benzoyl]lithium and (2,6-difluorobenzoyl)lithium (**2b**,**c**) can be generated from the corresponding tellurides (**1b**,**c**) in good yields (entries 3 and 4). Efficient generation of acyllithiums bearing no α-hydrogen, e.g., pivaloyllithium and (1-adamantylcarbonyl)lithium (**2d**,**e**), has been attained also (entries 5–11). In the case of acyllithiums, reactions at −78 °C using *tert*-butyllithium gave favorable results when pinacolone was used as an electrophile (entries 5–7 and 11). Chlorotrimethylsilane is also a suitable electrophile, and the desired product, acylsilane **4**, was formed in good yield by using butyllithium at −105 °C (entry 8). Use of pivalaldehyde as an electrophile afforded a poor yield of α-hydroxy ketone **5** due to rapid addition of *tert*-butyllithium to the aldehyde (entry 10). Although *Te*-butyl octanetelluroate gave octanoyltrimethylsilane in only ca. 10% yield under conditions similar to those of entry 8, the exchange reaction might have proceeded efficiently because an almost quantitative amount of dibutyl telluride was obtained from the resulting mixture.

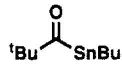
In order to test the stability and the reactivity of benzoyllithium, we subsequently added pinacolone to the mixture obtained by the reaction of **1a** with butyllithium performed at −105 °C in THF/Et$_2$O for 1 min. The result that **3a** (16%), benzoin [34%, via dimerization of in situ formed benzoyllithium (**2a**)],[2] and benzil (21%, probably derived by the reaction of **2a** with **1a**) were formed, together with 81% of dibutyl telluride, indicates that benzoyllithium is extremely reactive, having a lifetime much shorter than 1 min, even at −105 °C. The fact that benzene and alcohol **6** were not detected from the resulting mixture suggests that elimination of carbon monoxide from **2a** leading to phenyllithium may be ruled out under these conditions.[10]



6



7



8

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(1) For a recent review for synthetic equivalents of acyl and aroyl anions, see: Ager, D. J. In *Umpoled Synthons*; Hase, T. A., Ed.; Wiley-Interscience: New York, 1987; Chapter 2 and references cited therein.

(2) (a) Wittig, G. *Angew. Chem.* **1940**, *53*, 241, footnote 58. (b) Ryang, M.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1121. (c) Jutzi, P.; Schröder, F.-W. *J. Organomet. Chem.* **1970**, *24*, 1. (d) Trzupek, L. S.; Newirth, T. L.; Kelly, E. G.; Sbarbati, N. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 8118. (e) Nudelman, N. S.; Vitale, A. A. *J. Organomet. Chem.* **1983**, *241*, 143. For a review, see: (f) Narayana, C.; Periasamy, M. *Synthesis* **1985**, 253.

(3) (a) Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534. (b) Seyferth, D.; Weinstein, R. M.; Wang, W.-L. *J. Org. Chem.* **1983**, *48*, 1144. (c) Weinstein, R. M.; Wang, W.-L.; Seyferth, D. *Ibid.* **1983**, *48*, 3367. (d) Seyferth, D.; Wang, W.-L.; Hui, R. C. *Tetrahedron Lett.* **1984**, *25*, 1651. (e) Seyferth, D.; Hui, R. C. *J. Org. Chem.* **1985**, *50*, 1985. (f) Seyferth, D.; Hui, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 4551. (g) Murai, S.; Ryu, I.; Iriguchi, J.; Sonoda, N. *Ibid.* **1984**, *106*, 2440.

(4) Shiner, C. S.; Berks, A. H.; Fisher, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 957.

(5) Heathcock et al. suggested that aroyl anions might be formed by the reaction of acylsilanes with fluoride ion, where corresponding adducts were obtained in the presence of electrophiles. Alternative mechanisms have been also postulated. (a) Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881. (b) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201. (c) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385. (d) Page, P. C. B.; Rosenthal, S.; Williams, R. V. *Tetrahedron Lett.* **1987**, *28*, 4455.

(6) For our previous papers on lithium–tellurium exchange, see: (a) Hiiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187. (b) Hiiro, T.; Mogami, T.; Kambe, N.; Fujiwara, S.-I.; Sonoda, N. *Synth. Commun.*, in press.

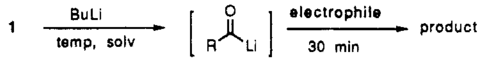
(7) Reich et al. suggested that the lithium–tellurium exchange reaction proceeds via ate complexes: (a) Reich, H. J.; Green, D. P.; Phillips, N. H. *Proceedings of Pre-Ichac Ube Conference Held at Ube*; July 16–18, 1987; pp 24–34. For recent reports on the intermediacy of ate complexes in lithium–metal and lithium–metalloid exchange, see: (b) Reich, H. J.; Phillips, N. H.; Reich, I. L. *J. Am. Chem. Soc.* **1985**, *107*, 4101. (c) Reich, H. J.; Phillips, N. H. *Ibid.* **1986**, *108*, 2102. (d) Reich, H. J.; Phillips, N. H. *Pure Appl. Chem.* **1987**, *59*, 1021. (e) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444.

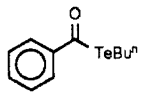
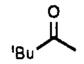
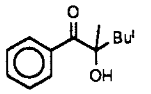
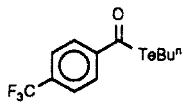
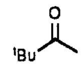
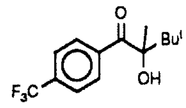
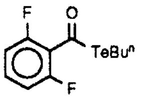
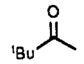
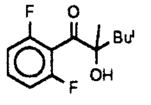
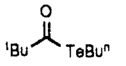
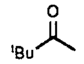
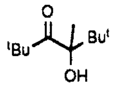
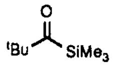
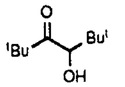
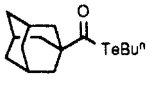
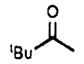
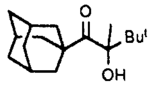
(8) Tellurolesters **1** were prepared by the reaction of lithium (**1a**,**d**,**e**) or sodium (**1b**,**c**) butanetellurolates with the corresponding acid chlorides according to the following literature: (a) Piette, J. L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 383; *Chem. Abstr.* **1970**, *73*, 66201. (b) Piette, J. L.; Debergh, D.; Baiwir, M.; Llabres, G. *Spectrochim. Acta* **1980**, *36A*, 769. (c) Gardner, S. A.; Gysling, H. J. *J. Organomet. Chem.* **1980**, *197*, 111.

(9) The result clearly indicates that butyllithium attacked Te atom exclusively affording benzoyllithium (**2a**), which then reacted with pinacolone to give **3a**. For other byproducts formed, see supplementary material.

0002-7863/90/1512-455$02.50/0

Table I. Trapping of Acyllithiums and Aroyllithiums Generated by Lithium–Tellurium Exchange



entry	substrate	electrophile (1.5 equiv)	product	BuLi (equiv)	temp, °C	solv	yield,[a] %
1	 **1a**		 **3a**	^{n}BuLi (1.2)	-105	THF/Et_2O	85
2					-78	THF	45[b]
3	 **1b**		 **3b**	^{n}BuLi (1.2)	-105	THF/Et_2O	60
4	 **1c**		 **3c**	^{n}BuLi (1.2)	-105	THF/Et_2O	74
5	 **1d**		 **3d**	^{n}BuLi (1.2)	-105	THF/Et_2O	trace[c]
6				^{t}BuLi (1.6)	-105	THF/Et_2O	27
7					-78	THF	66
8		Me_3SiCl	 **4**	^{n}BuLi (1.2)	-105	THF/Et_2O	65[b] (70)[b,d]
9					-78	THF	10[b]
10		^{t}BuCHO	 **5**	^{t}BuLi (1.6)	-78	THF	25[e]
11	 **1e**		 **3e**	^{t}BuLi (1.6)	-78	THF	57

[a] Isolated yield based on tellurolesters. [b] GLC yield. [c] Addition of ^{n}BuLi to pinacolone predominated. [d] HMPA (3 equiv) was added. [e] 2,2,4,4-Tetramethyl-3-pentanol was obtained in ca. 40% yield based on pivalaldehyde used.

Although corresponding selenolesters and acylstannanes can also be the candidates for precursors of carbonyl anions, reactions of **7** and **8** under similar conditions did not give desired adducts **3a** and **3d**.[11]

In summary, a novel method for generation of acyl- and aroyllithiums has been established by the use of a lithium-tellurium exchange reaction.[12] This success may be based on the extremely high reactivity of organotellurium compounds toward alkyllithiums. Since tellurolesters **1** are stable and easily accessible, the present method is practically quite useful for generation of a variety of acyl- and aroyllithiums which are thermodynamically somewhat stable but kinetically quite reactive.

Acknowledgment. We thank the Computer Center of the Institute for Molecular Science for the use of the HITAC M-680H and S-820/80 computer and the library program GAUS82[13] and Professor K. Morokuma and Dr. N. Koga for their fruitful help in ab initio calculations. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (No. 01607004) from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: A typical experimental

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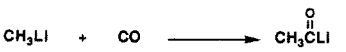
(10) Ab initio calculations showed that the following reaction was exothermic. The optimized structure of the acyllithium has one of the C–H bonds eclipsed with the carbonyl group. Li has an intramolecular interaction with oxygen (∠O–C–Li = 61.3°), as demonstrated in the case of formyllithium: Kaufmann, E.; Schleyer, P. v. R.; Gronert, S.; Streitwieser, A., Jr.; Halpern, M. *J. Am. Chem. Soc.* **1987**, *109*, 2553.


$$CH_3Li + CO \longrightarrow CH_3\overset{\overset{O}{\|}}{C}Li$$

basis set	ΔE (kcal/mol)
3-21G//3-21G	-24.1
6-311+G*//3-21G	-11.2
MP2/6-311+G*//3-21G	-15.7

(11) Under the same conditions as in entry 1, **7** gave only a trace amount of dibutyl selenide (<1%). In this case, reaction of **7** with the lithium enolate of pinacolone predominated. In the case of **8**, considerable amounts of tetrabutylstannane (up to 30%) were obtained. This result may suggest that lithium-tin exchange might proceed to some extent.

(12) The actual acylating and aroylating species would probably be free acyl- and aroyllithiums rather than their tellurium ate complexes, which are likely to be the transient intermediates in lithium-tellurium exchange,[7] because product ratios of 1,2-addition over 1,4-addition to methyl vinyl ketone in the present system using *Te*-butyl 2,2-dimethylpropanetelluroate (2.2 at -110 °C in THF/Et_2O and 5.0 at -78 °C in THF) were quite similar to those in a ^{t}BuLi/CO system (1.9 and 5.5, respectively). For details and discussion, see the supplementary material.

(13) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, PA, 1984.

procedure, full characterization of tellurolesters, α-hydroxy ketones, and an acylsilane obtained, and a discussion on actual acylating species and main side reactions (8 pages). Ordering information is given on any current masthead page.

Effects of Metal and Ligand Substitutions on Gas-Phase Acidities of Transition-Metal Hydrides

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Received September 22, 1989

Gas-phase chemistry and spectroscopy of negative ions have provided important data on thermochemistry and reactivity for a wide variety of transition-metal organometallic complexes.[1-6] Despite this, since the work of Stevens Miller and Beauchamp,[7] who determined the gas-phase acidities of $HMn(CO)_5$, $H_2Fe(CO)_4$, and $HCo(CO)_4$, no further acidities for transition-metal hydride complexes have been reported. This is particularly surprising since hydrides are very important in reactive and catalytic chemistry.[8] We report here the determination of the gas-phase acidity of $HRe(CO)_5$, a refinement in the value for the gas-phase acidity of $HMn(CO)_5$, and experiments identifying $HMn(CO)_3(PF_3)_2$, $HMn(CO)_2(PF_3)_3$, $HCo(PF_3)_4$, and $HIr(PF_3)_4$ as extremely strong gas-phase acids.

The hydrides were synthesized as described in the literature.[11-16] $HIr(PF_3)_4$ showed an unidentified low-mass contaminant in some of the samples we prepared, but all other compounds gave pure samples. The ion-molecule reactions were studied at the Geophysics Laboratory, using a selected-ion flow tube described elsewhere.[17] Proton abstraction reactions by the metal anions were not studied since the metal compounds decompose in the ion source.

The hydride $HMn(CO)_5$ proton transfers to F^-, Cl^-, Br^-, and $CCl_3CO_2^-$, at rates near the collision frequency.[18] No reaction is observed with I^-. $HRe(CO)_5$ reacts rapidly by proton transfer to F^-, HCO_2^-, NO_2^-, and Cl^-. In the reaction with F^-, ligand displacement also occurs, with ion products $(CO)_5Re^-$ (65%) and $HRe(CO)_3F^-$ (35%). $HRe(CO)_5$ reacts by proton transfer with $CHF_2CO_2^-$, but at a rate about a factor of 3 less than collisional. No reaction is observed with $CF_3COCHCOCH_3^-$, $CHCl_2CO_2^-$, Br^-, or I^-.

Table I. Gas-Phase Acidity Scale Used for This Work, with the Relative Positions of the Transition-Metal Hydrides Given[a]

acid	ΔH_{acid}	ΔG_{acid}
HF	371.5 ± 0.2	365.7 ± 0.5
HCO_2H	345.2 ± 2.3	338.2 ± 2.0
HNO_2	338.2 ± 4.3	330.5 ± 4.6
HCl	333.4 ± 0.2	328.0 ± 0.5
$HRe(CO)_5$	position according to this work	
CHF_2CO_2H	330.0 ± 2.3	323.5 ± 2.0
$CF_3COCH_2COCH_3$	328.4 ± 4.1	322.0 ± 2.0
$CHCl_2CO_2H$	327.3 ± 2.6	320.8 ± 2.0
HBr	323.5 ± 0.1	318.2 ± 0.4
CCl_3CO_2H	319.9 ± 2.9	312.8 ± 2.0
$HMn(CO)_5$	position according to this work	
HI	314.4 ± 0.1	309.3 ± 0.4
HPO_3	311 ± 3[b]	
$HMn(CO)_3(PF_3)_2$, $HMn(CO)_2(PF_3)_3$	positions according to this work	
FSO_3H	*b*	
$HIr(PF_3)_4$	position according to this work	
CF_3SO_3H	*b*	
$HCo(PF_3)_4$	position according to this work	

[a] The acidity data, in kilocalories per mole, are from refs 9 and 10 except as noted. [b] Reference 19.

A mixture of $HMn(CO)_3(PF_3)_2$ and $HMn(CO)_2(PF_3)_3$ reacts rapidly with Br^-, I^-, and PO_3^-, and a factor of 30 more slowly with FSO_3^-. Proton transfer occurs to all the ions, but the mixture also shows product masses 455 ± 10 amu and 475 ± 10 amu from reaction with PO_3^-, and ion products of mass 325 ± 10 amu and 403 ± 10 amu from reaction with FSO_3^-. No reaction occurs with $CF_3SO_3^-$.

$HCo(PF_3)_4$ proton transfers at collision frequency to I^-, PO_3^-, FSO_3^-, and $CF_3SO_3^-$. $HIr(PF_3)_4$ proton transfers rapidly to Br^-, I^-, PO_3^-, and FSO_3^-, and a factor of 1000 more slowly to $CF_3SO_3^-$.

Table I gives the gas-phase acidity scale[9,10,19] used for this work. The positions of the hydride acidities are determined by assuming that the reaction is exothermic if the proton-transfer rate is equal to the ion-molecule collision rate,[18] and endothermic if the rate is much smaller than the collisional rate.[20]

The acidity of $HMn(CO)_5$ was previously bracketed between the acidities of HI and CF_3CO_2H.[7] The present work confirms that result, but narrows the bracketing slightly, to between HI and CCl_3CO_2H (ΔH_{acid} = 314-320 kcal/mol). The third-row complex $HRe(CO)_5$ has an acidity, ΔH_{acid}, between 330 and 333 kcal/mol, or about 10-19 kcal/mol less acidic than $HMn(CO)_5$. Meckstroth and Ridge[21] presented evidence that the electron affinities of $(CO)_5Mn$ and $(CO)_5Re$ are equal. The acidity difference between $HMn(CO)_5$ and $HRe(CO)_5$ therefore is a result of the homolytic bond energy $D[(CO)_5Re{-}H]$ being 10-19 kcal/mol stronger than $D[(CO)_5Mn{-}H]$. Using $D[(CO)_5Mn{-}H]$ = 60 kcal/mol[22] gives $D[(CO)_5Re{-}H]$ = 70-79 kcal/mol. These energetics are in keeping with the less acidic

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