

142.7°. The W-Si bond length of 2.606 (2) Å is within the range of various estimates of the Si and W covalent radii (2.47-2.77 Å).^{13,14} The experimental range for W-Si and Mo-Si bonds in seven structurally characterized silyl complexes is 2.389-2.669 Å (2.562-Å average).^{15,16}

The Si-Si bond distance in **1b** is 2.260 (2) Å, a value that falls midway between the expected values for a single bond¹⁷ (2.35 Å) and a double bond¹⁸ (2.14 Å). However, unusual Si-Si distances have also been observed in other ESi₂ ring systems: E = O [2.227 (2) Å],¹⁹ NR (2.232 Å),²⁰ CH₂ [2.272 (2) Å],²¹ S [2.289 (2) Å],²² Te (2.32 Å),²⁰ and SiR₂ (2.40 Å).²³ Among these main-group rings, however, the Si-Si distance decreases with increasing electronegativity and smaller size of the non-silicon atom. The extremely short Si-Si bond in **1b**, which contains a large electropositive tungsten atom, does not fit this trend and most probably results from partial Si-Si double bond character as described by the Dewar-Chart-Duncanson model.

Another measure of disilene character in **1b** is the extent of pyramidalization at silicon. The angles subtended at each silicon by the methyl groups and the other silicon total 348.3°, between the 360° and 329.1° values expected for sp² and sp³ hybridization. The planes containing the SiMe₂ fragments are bent away from the tungsten center by 30.2° from the "olefin" plane containing the two silicon atoms and perpendicular to the WSi₂ plane. Thus the silicons are somewhat pyramidal, but less so than found for carbon in ethylene complexes of low-valent early-transition metals (Cp*₂Ti(C₂H₄), 35°; Cp*Ta(CHCMe₃)(PMe₃)(C₂H₄), 34°).²⁴ Adverse nonbonded interactions with the Cp rings may increase the degree of nonplanarity at the silicon atoms. The C7-C3 (Cp-Me) separation is 3.30 Å, within the sum of the van der Waals radii (3.40 Å),²⁵ and the calculated closest H-H contact is ~2.0 Å. Steric interactions with the Cp rings may also be responsible for the small C7-Si-C8 angle of 104.0 (4)°.

Although **1b** is the first structurally characterized complex of its type, there have been two previous reports of mononuclear transition-metal disilene complexes. In 1987, West briefly described a compound formed by reaction of the stable disilene Mes₂Si=SiMes₂ (Mes ≡ 2,4,6-trimethylphenyl) with (R₃P)₂Pt-

(CH₂=CH₂).^{7a} More recently, Pham and West have reported the synthesis and spectroscopic characterization of two (R₃P)₂Pt(R'₂SiSiR'₂) complexes (R = Ph, C₆H₁₁; R' = *i*-Pr, Ph).^{7b} In addition, Youngs and co-workers have prepared several binuclear platinum complexes in which the two metals are bound to opposite faces of a planar R₂SiSiR₂ fragment.²⁶

In summary, the new complexes of the Si₂Me₄ ligand described in this report exhibit properties intermediate between disilene complex and disilametallacycle formalisms, analogous to the situation found in transition-metal complexes of organic olefins. The reaction chemistry of **1a** and **1b** is currently under investigation and will be described in future publications.

Acknowledgment. Financial support for this work was provided by the National Science Foundation and the Pew Science Program. D.H.B. also thanks the University of Pennsylvania Natural Science Association for a Young Faculty Award.

Supplementary Material Available: Description of synthetic procedures, X-ray data collection and refinement, and tables of positional parameters, anisotropic thermal parameters, and intramolecular bond angles and distances for **1b** (7 pages); table of final structure factor amplitudes for **1b** (6 pages). Ordering information is given on any current masthead page.

(26) (a) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068-4070. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1989**, 577-578.

Oligonucleotides Containing Flexible Nucleoside Analogues

K. Christian Schneider and Steven A. Benner*

Laboratory for Organic Chemistry
ETH Zurich, CH-8092 Switzerland

Received September 6, 1989

In all forms of modern life, genetic information is stored in macromolecules having a pentose (ribose or deoxyribose) as the repeating unit. Because RNA molecules are the most plausible candidates for the first catalytic molecules,¹ and (entirely unrelatedly) as "antisense" oligonucleotides (both DNA and RNA) are potentially valuable for treating a wide range of intractable human diseases,² considerable effort has been devoted to the study of these molecules and their analogues.

Two conclusions are evident. First, ribose and deoxyribose ring systems are difficult to synthesize from simple precursors, especially under abiotic conditions.³ Second, natural oligonucleotides are easily degraded biologically and, in the case of RNA, chemically. The first is problematical for models for the origin of life that postulate that RNA was the first self-replicating molecule; known abiotic reactions seem unable to produce sufficient ribose to permit the assembly of a self-replicating RNA molecule.⁴ The second makes externally added antisense oligonucleotides largely unsuitable for controlling the expression of unwanted genes in vivo.

If carbon 2 is removed from the ribose ring system, an isosteric oligonucleotide analogue derived from glycerol can be envisioned (Scheme I, 4).⁵ This "flexible" structure is attractive for several reasons. First, glyceronucleosides are (presumably) simpler to prepare than ribonucleosides under prebiotic conditions, and they

(13) The covalent radius of silicon is 1.17-1.18 Å.^{14a} The radii of tungsten and molybdenum have been variously estimated as 1.30-1.60 Å.^{14a-d} It is assumed in the discussion that the radii of Mo and W are virtually identical.

(14) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (b) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3799-3801. (c) Chisolm, M. H.; Corning, J. F.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 38. (d) Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1968**, *5*, 953-959.

(15) (a) Bennett, M. J.; Simpson, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 7156-7160. (b) Barron, A. R.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 837-846. (c) Hseu, T. H.; Chi, Y.; Liu, C. S. *Inorg. Chem.* **1981**, *20*, 199-204. (d) Chisolm, M. H.; Chiu, H. T.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 4097-4102.

(16) Cp₂W(H)(SiMe₂) [D(W-Si) = 2.560 (1) Å]; Cp₂Mo(H)(SiMe₂Cl) [D(Mo-Si) = 2.513 (2) Å]; and (MeCp)₂Mo(H)[Si(*t*-Bu)₂H] [D(Mo-Si) = 2.604 (1) Å]; Berry, D. H.; Jiang, Q.; Koloski, T. S.; Carroll, P. J. Manuscript in preparation.

(17) Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605.

(18) (a) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793-800. (b) Masamune, S.; Murakami, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Organometallics* **1984**, *3*, 333-334.

(19) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865.

(20) West, R. Personal communication.

(21) Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 7776.

(22) West, R.; DeYoung, D. J.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 4942.

(23) Average of three Si-Si distances in seven complexes: (a) Masamune; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. (b) Schafer, A.; Weidenbruch, M.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302. (c) Watanabe, H.; Kato, M.; Okawa, T.; Nagai, Y.; Goto, M. *J. Organomet. Chem.* **1984**, *271*, 225. (d) Dewan, J. C.; Murakami, S.; Snow, J. T.; Collins, S.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1985**, 892. (e) Jones, R.; Williams, D. J.; Kabe, Y.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 173. (f) Weidenbruch, M.; Thom, K. L.; Pohl, S.; Saak, W. *J. Organomet. Chem.* **1987**, *329*, 151.

(24) (a) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136-1143. (b) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.

(25) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441-451.

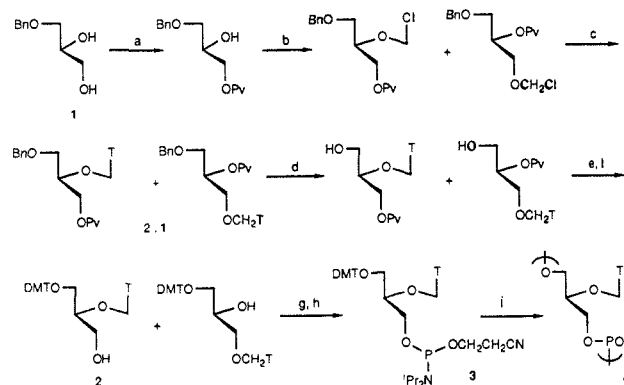
(1) Orgel, L. E. *J. Theor. Biol.* **1986**, *123*, 127-149.

(2) *Antisense RNA and DNA*; Melton, D. A., Ed.; Cold Spring Harbor Laboratory: Cold Spring Harbor, NY, 1988.

(3) Mizuno, T.; Weiss, A. H. *Adv. Carbohydr. Chem.* **1974**, *29*, 173-227.

(4) (a) Joyce, G. F. *Nature* **1989**, *338*, 217-224. (b) Joyce, G. F.; Schwartz, A. W.; Miller, S. L.; Orgel, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 4398-4402.

(5) Elion, G. B. *Science* **1989**, *244*, 41-47.

Scheme I^a

^a (a) Pivaloyl chloride (1.2 equiv), pyridine, -15°C , 3 h, 75%. (b) Paraformaldehyde (2.0 equiv); $\text{HCl}(\text{g})$, dichloromethane.¹³ (c) Bis-(trimethylsilyl)thymine (1.2 equiv). Bu_4NI (0.1 equiv), dichloroethane, 50°C , 1 h, 60% from 2.¹⁴ (d) $\text{Pd}(\text{OH})_2/\text{C}$, 2:1 ethanol/cyclohexene, 80°C , 20 h.¹⁴ (e) Dimethoxytrityl (DMT) chloride (1.5 equiv), (dimethylamino)pyridine (cat.), Et_3N (2.0 equiv), pyridine, 12 h.¹⁵ (f) NaOH (2 N), MeOH , 25°C , 5 h, 90% for three steps. (g) Separation (silica gel, 19:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$). (h) 2-Cyanoethyl diisopropylchlorophosphoramidite, $\text{Et}^i\text{Pr}_2\text{N}$ (2.0 equiv), CH_2Cl_2 , 25°C , 15 min, 56% after two precipitations from toluene/hexane.¹⁵ (i) Applied Biosystems automated DNA synthesizer.

are achiral, eliminating some of the potential problems that arise when one attempts to oligomerize a mixture of antipodes of a nucleoside building block.⁴ Second, oligonucleotides built from flexible nucleoside analogues might be stable to nucleases,⁶ improving their bioavailability as antisense drugs. Therefore, it is not surprising that information-containing oligomers having glycerol as a repeating unit have been proposed as the first living molecules derived from the prebiotic world⁴ and (again entirely unrelatedly) as antisense nucleoside analogues.

These proposals imply that oligonucleotide analogues incorporating flexible bases hybridize to complementary natural oligonucleotides.⁷ We report here the synthesis of oligonucleotide analogues containing one or more building blocks constructed, for the first time, from an optically active glycerol derivative (a "flexible nucleoside"), incorporation of the oligonucleotide into duplex DNA, and measurements of the strength of the duplex formed between flexible and natural oligonucleotides.

Optically active flexible nucleoside analogues bearing thymine were prepared from (*S*)-3-(benzyloxy)-1,2-propanediol (Fluka) by the route shown in Scheme I, which yielded **2** with $[\alpha]_{546}^{20} = -4.4^{\circ}$ ($c = 1.76$, acetone). The pivaloyl protecting group used to protect selectively the primary hydroxyl group was only partly satisfactory, as it undergoes migration during chloromethylation. However, considerations of cost and synthetic flexibility made it the optimal solution to the synthetic problem. Spectroscopic data on detritylated **2** were identical with those reported in the literature.⁸

The melting temperatures of a series of duplexes of oligonucleotides incorporating the flexible nucleoside analogue complementary to the sequence 5'-CAAAAAAAG-3' and 5'-CTTTATTTG-3' were determined (Table I).⁹ The melting temperature of duplex DNA is lowered by 9–15 $^{\circ}\text{C}$ for each flexible nucleoside incorporated into a strand (Table I). The effect is not precisely additive; the melting temperature of a strand containing two adjacent residues is slightly lower than the melting

Table I. Melting Temperatures of Duplexes Containing Flexible Analogues^a

	T_m , $^{\circ}\text{C}$		T_m , $^{\circ}\text{C}$
5' CTTTTTTTGG 3' 3' GAAAAAAC5'	40	5' CAAATAAG3' 3' GTTTATTTC5'	37
5' CTTTtTTTGG 3' 3' GAAAAAAC5'	25	5' CAAAtAAG3' 3' GTTTATTTC5'	25
5' CTTTtTTTGG 3' 3' GAAAAAAC5'	13	5' CAAtAtAAG3' 3' GTTTATTTC5'	12
5' CTTTtTTTGG 3' 3' GAAAAAAC5'	11	5' CAAttAAG3' 3' GAAAAAAC5'	11
5' CTTTTTTTGG 3' 3' GAAAGAAC5'	21	5' CTTTtTTTGG 3' 3' GAAAGAAC5'	12
5' CTTTTTTTTTTTGG 3' 3' GAAAAAAAAAAC5'	55	5' CtttttttttttGG 3' 3' GAAAAAAAAAAC5'	<0

^a Upper-case letters refer to deoxyribonucleotides, while lower-case letters refer to glyceronucleosides. Melting temperature (T_m) were determined⁹ by measuring change in absorbance at 260 nm (cuvette, 1-mm path length) as a function of temperature at 0.050 mM of each strand in sodium phosphate buffer (10 mM, pH 7.0) containing NaCl (1 M) and EDTA (10^{-4} M). For the duplex of CTTTTTTTGG and CAAAAAAAAAAG, and additional measurement was performed in Tris buffer (10 mM, pH 7.0) containing MgCl_2 (100 mM); no transition was observed under these conditions. When a base line at low temperatures was observed, the T_m was calculated by using sloping base lines. For duplexes with $T_m < 20^{\circ}\text{C}$, such a base line could not be observed in water, and T_m values were calculated by using a flat base line.

temperature of a strand containing the two separated by a natural nucleoside. However, the destabilization is similar to that created by a GT mismatch.

First principles suggest that incorporation of flexible nucleoside analogues into an oligonucleotide chain decreases its ability to form duplex structures, as the entropy lost upon going from two oligonucleotides to a duplex is larger in a system containing flexible nucleosides than in one containing natural oligonucleotides. We did not, however, anticipate that the decrease in stability would be so great. From these results, it seems unlikely that oligonucleotides of moderate length (shorter than 15 bases) composed entirely of flexible nucleosides will form stable duplex structures with complementary natural oligonucleotides in aqueous solution.

This result is disappointing for those hoping to use flexible oligonucleotide analogues as antisense compounds or as probes. Further, this result diminishes the likelihood that the first self-replicating systems used flexible oligonucleotide analogues. However, it should be emphasized that it is not yet known what amount of stability in duplex structures is desirable to create a primitive self-replicating system.^{7,10}

The ubiquity of ribose in modern biochemistry¹¹ strongly suggests a central role for ribose at the time in natural history when modern metabolism was emerging. However, modern biochemistry cannot be extrapolated back to organisms more ancient than the first that contained a genetically encoded messenger RNA.¹² Thus, the question as to whether RNA was *first* can be resolved only by chemical experiments such as those reported here. By raising doubts about the suitability of flexible

(6) Ogilve, K. K.; Nguyen-Ba, N.; Gillen, M. F.; Radatus, B. K.; Cheriyan, U. O.; Hanna, H. R.; Smith, S. M.; Galloway, K. S. *Can. J. Chem.* **1984**, *62*, 241–252.

(7) Of course, these results do not exclude the possibility that an oligonucleotide composed entirely of flexible building blocks will not form a stable duplex with a second strand also entirely composed of flexible building blocks.

(8) Beauchamp, L. M.; Serling, B. L.; Kelsey, J. E.; Biron, K. K.; Collins, P.; Selway, J.; Lin, J.-C.; Schaeffer, H. J. *J. Med. Chem.* **1988**, *31*, 144–149.

(9) Borer, P. N.; Dengler, B.; Tinoco, I., Jr. *J. Mol. Biol.* **1974**, *86*, 843–853.

(10) We are indebted to L. Orgel for making this point clearly.

(11) Benner, S. A.; Allemann, R. K. *Trends Biochem. Sci.* **1989**, *14*, 396–397.

(12) Benner, S. A.; Ellington, A. D.; Tauer, A. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 7054–7058.

(13) Hill, A. J.; Keach, D. T. *J. Am. Chem. Soc.* **1926**, *48*, 257.

(14) Ogilve, K. K.; Hamilton, R. G.; Gillen, M. F.; Radatus, B. K.; Smith, K. O.; Galloway, K. S. *Can. J. Chem.* **1984**, *62*, 16–21.

(15) *Oligonucleotide Synthesis*; Gait, M. J., Ed.; IRL Press: Oxford, 1985.

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.

(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

Tomoki Hiroy, Yoshiyuki Morita, Toru Inoue, Nobuaki Kambe,* Akiya Ogawa, Ilhyong Ryu, and Noboru Sonoda*

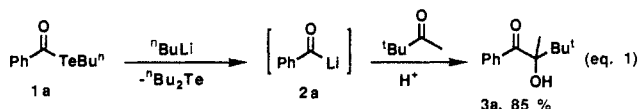
Department of Applied Chemistry, Faculty of Engineering
Osaka University, Suita, Osaka 565, Japan

Received August 15, 1989

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-

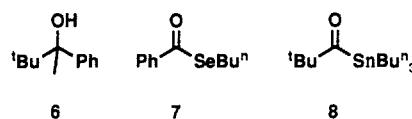
tellurium exchange^{6,7} of telluroesters **1**, which are easily accessible from the corresponding acid chlorides and telluroate anions.⁸

When butyllithium was added to *Te*-butyl tellurobenzoate (**1a**) in THF/Et₂O (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}



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/Et₂O 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



(1) For a recent review for synthetic equivalents of acyl and aroyl anions, see: Ager, D. J. In *Unpoled 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) Jutzki, P.; Schröder, F.-W. *J. Organomet. Chem.* **1970**, *24*, 1. (d) Trzupke, 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) Hiroy, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187. (b) Hiroy, 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) Telluroesters **1** were prepared by the reaction of lithium (**1a,d,e**) or sodium (**1b,c**) butanetelluroates 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.