of Yb(III), is direct unambiguous evidence of interaction between the lanthanide ion and the antibiotic molecule. The number, energy spacings, and relative intensities of the bands can, in principle, give detailed information about the Yb(III) coordination site. Unfortunately, relationships between the near-IR-CD spectra and the structure of lanthanide complexes are not yet available, so well-defined structural information can not be obtained: however, even a qualitative analysis can offer some interesting suggestions.[12] According to a recent report,[13] strong lanthanide CD will be observable only when a chiral ligand is linked directly to the Ln(III) ion and there is some Ln(III)-ligand multidentate chelation. It is generally accepted that the preferred binding sites for the lanthanide ions will be those containing negatively charged groups (oxygen atoms, for instance); so it appears reasonable to assume that the acid function at the 8-position in **1** provides the strongest binding site. Experimental support for this hypothesis has been obtained by carrying out the measurement on the un-ionized form at pH $\simeq 2$ in the presence of Yb(III) ions. Under this condition there is no CD signal detectable between 1100 and 700 nm. Other donor groups that can promote the multidentate coordination enhancing the CD intensity are the hydroxyl groups in the ansa ring, which are directly linked to chiral centers. The remaining coordination positions of the ion may be reasonably assumed to be occupied by solvent molecules.

In conclusion, while further study has to be carried out on chiral Yb(III) compounds in order to relate the CD of f-f transitions and structure, the present communication shows that the above ions constitute a suitable probe for the interactions of "transparent" divalent alkaline-earth metal ions and biological molecules.

Acknowledgment. This investigation was partially supported by a grant from Ministero della Pubblica Istruzione, Roma.

Registry No. Rifampicin, 13292-46-1; Yb^{3+}, 18923-27-8.

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(12) Richardson, F. S. *Inorg. Chem.* **1980**, *19*, 2806.
(13) Richardson, F. S.; Das Gupta, A. *J. Am. Chem. Soc.* **1981**, *103*, 5716.

Acyllithium to Lithium Enolate Conversion by a 1,2-Silicon Shift. A Shortcut to Acylsilane Enolates

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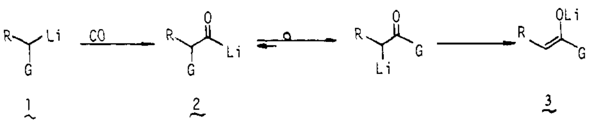
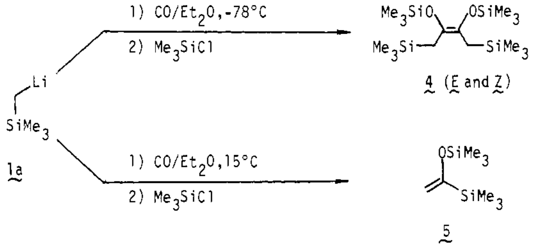
One of the key organic intermediates that heretofore has rarely been utilized in practical synthetic reactions is the negatively charged carbonyl species, carbonyl anion (acyl- or aroyllithium) **2**. They have long been suggested as the first intermediate in the reaction of organolithium **1** with carbon monoxide. The reactions are quite complex and give various products in a nonselective manner. Incorporation of at least two aryl or alkyl moieties into the products is usually inevitable.[1,2] However, Seyferth et al. have very recently succeeded in the efficient in situ trapping of acyllithium with electrophiles (Me_3SiCl[3a] or carbonyl compounds[3b-d], using extremely careful reaction conditions (a controlled, slow-rate addition of RLi at -110 °C). The commonly observed complex results of the reaction of alkyllithium with carbon monoxide could be attributed to the exceedingly reactive nature of acyllithium and alkyllithium, and, therefore, the development of a method for the immediate conversion of the highly reactive acyllithium to a more stable but still reactive synthetic intermediate seemed desirable. Thus, our strategy involves acyllithium to lithium enolate conversion.[4] We wish to report here the realization of this concept by utilizing the well-known 1,2-silicon shift[5] (eq 1, $G = R_3Si$).[6]



(1)

When silylmethyllithium **1a**[7] was exposed to carbon monoxide (1 atm) at -78 °C in ether, gradual absorption of carbon monoxide over a period of 2 h was observed. Quenching with Me_3SiCl gave an enediol disilyl ether **4** as a major product (eq 2) (33%, *E*/*Z* = 50/50),[8] and no desired product that was envisioned in eq 1 was detected. A dramatic change occurred when this reaction was conducted at 15 °C: the (1-siloxyvinyl)silane **5** was produced in 86% yield.[9] This indicates that the lithium enolate **3** (R = H, G = Me_3Si) has been formed as the result of the silicon shift (eq 1). Further examples of the reaction of α-silylalkylithium **1**[5c,10] with carbon monoxide at 15 °C are given in Table I. By quenching with H_2O or Me_3SiCl, acylsilanes or their enol silyl ethers were conveniently obtained, respectively, in good yields. Interestingly, the formation of these enolates took place in highly stereoselective manner to give *E* enolates exclusively or predominantly, as shown by the structures of products in runs 4, 6, 8, and 11.[11] The enolates undergo standard enolate reactions such



(2)

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(1) See, for example: (a) Wittig, G. *Angew. Chem.* **1940**, *53*, 241. (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. An excellent review of previous works is given in ref 3.

(2) Recent efforts for synthesis via aryllithium and CO, see: (a) Nudelman, N. S.; Vitale, A. A. *J. Org. Chem.* **1981**, *46*, 4625; (b) *Org. Prep. Proced. Int.* **1981**, *13*, 144. (c) Nudelman, N. S.; Outumuro, P. *J. Org. Chem.* **1982**, *47*, 4347. (d) Nudelman N. S.; Vitale, A. *J. Organomet. Chem.* **1983**, *241*, 143.

(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) *Ibid.* **1983**, *48*, 3367. (d) Seyferth, D; Weinstein, R. M.; Wang, W.-L.; Hui, R. C. *Tetrahedron Lett.* **1983**, *24*, 4907.

(4) The Δ*E* value between **2** and **3** where R,G = H (not lithium salt) has been estimated as ca. 28 kcal/mol; see: Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5612.

(5) (a) West, R. *Adv. Organomet. Chem.* **1977**, *16*, 1. (b) Brook, A. G.; Bassindale, A. R. "Rearrangement in Ground and Excited States"; Mayo, P. de, Ed.; Academic Press: New York, 1980; Vol. 2, pp 149-227. (c) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, **1980**. (d) Eisch, J. J.; Tsai, M.-R. *J. Am. Chem. Soc.* **1973**, *95*, 4065.

(6) A portion of this work has been taken from: Iriguchi, J. B. S. Thesis Osaka Univesity Suita, Osaka, Japan, 1982. Also presented at the 47th Annual Meeting of Chemical Society of Japan, Kyoto, Japan, April 1, 1983; abstract Vol. II, p 820.

(7) Prepared from Me_3SiCH_2Cl and Li dispersion containing 1% Na (Ventron Co.) in ether (-15 °C, 4 h)[a,b] and titrated by *N*-benzylidenebenzylamine/PhCOOH/THF.[c] (a) Sommer, L. H.; Murch, R. M.; Mitch, F. A. *J. Am. Chem. Soc.* **1954**, *76*, 1619. (b) Connoly, J. W.; Urry, G. *Inorg. Chem.* **1963**, *2*, 645. (c) Duhamel, L.; Plaquevent, J. C. *J. Org. Chem.* **1979**, *44*, 3404.

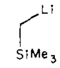
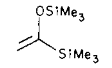
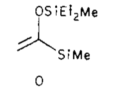
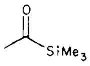
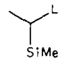
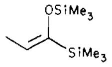
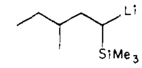
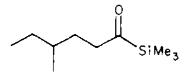
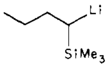
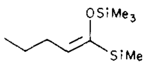
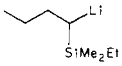
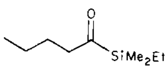
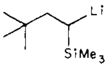
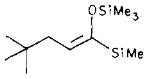
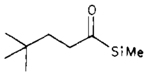
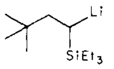
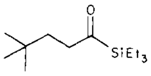
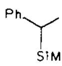
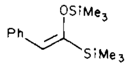
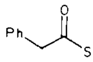
(8) The authentic sample of **4** was separately prepared from ethyl (trimethylsilyl)acetate ($Na/Me_3SiCl/Et_2O$, 35 °C, 17 h, 30% yield, *E*/*Z* = 18/82). See: Cookson, C. M.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1975**, 806.

(9) Representative procedure: the ethereal solution of Me_3SiCH_2Li (5 mmol, 4.5 mL of a 1.1 mol/L solution in ether) was degassed and exposed to carbon monoxide from a CO baloon (1 atm) at 15 °C. Gradual CO absorption was observed and after 1.5 h Me_3SiCl (5 mmol) was added. The product **5** was distilled directly from the mixture (75% yield). **5**: bp 73-80 °C (90 mm); ^1H NMR (CCl_4) δ 0.06 (s, 9 H, $CSi(CH_3)_3$), 0.17 (s, 9 H, $OSi(CH_3)_3$), 4.43 (d, $J = 4$ Hz, 1 H, HC=), 4.71 (d, $J = 4$ Hz, 1 H, HC=); IR (neat) ν 1590 cm^{-1} (C=C); mass spectrum, *m*/*e* 188 (M^+, 20), 173 ($M^+ - 15$, 24), 147 (100), 73 (100). **5** is a known compound, see: Bourgeois, P.; Dunogues, J.; Duffaut, N. *J. Organomet. Chem.* **1974**, *80*, C25. All new compounds have been fully characterized; see the supplementary material.

(10) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer Verlag: Berlin, 1983.

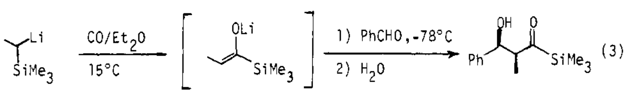
0002-7863/84/1506-2440$01.50/0

Table I. Preparation of Acylsilanes and Their Enol Silyl Ethers[a]

run	substrate	solvent	electrophile	product	yield, %[b]
1[c]	 **1a**	Et_2O	Me_3SiCl	 **5**	86 (75)
2			$Et_2MeSiCl$		80
3			H_2O		72
4[c]	 **1b**	Et_2O	Me_3SiCl		88 (E = ~100)[d]
5[e]	 **1c**	Et_2O	H_2O	 **7**	68
6[e]	 **1d**	THF	Me_3SiCl		(63) (E = ~100)[d]
7[e]	 **1e**	THF	H_2O	 **8**	(66)
8[e]	 **1f**	Et_2O	Me_3SiCl		96 (E = ~100)[d]
9			H_2O		(80)
10[e]	 **1g**	Et_2O	H_2O		73 (61)
11[f]	 **1h**	TMEDA	Me_3SiCl		92 (E/Z = 89/11)[d]
12			H_2O		94

[a] Unless otherwise stated, all reactions were performed at 15 °C for 1-1.5 h on a 5-mmol scale using concentration of 0.2-1.1 M of lithium compounds. [b] Determined by GLC. Isolated yields are in the parentheses. [c] Prepared from silylmethyl chlorides and Li dispersion; see ref 7. [d] Determined by ^1H NMR of vinylic hydrogen; generally, the vinylic H of E isomers resonate at higher fields. [e] Prepared from vinylsilanes and RLi (Et_2O or THF, −20 °C, 1-4 h); see: Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* 1975, *97*, 1464. Mulvaney, J. E.; Gardlund, Z. G. *J. Org. Chem.* 1965, *30*, 917. [f] Prepared from benzylsilane and n-BuLi (TMEDA, 0 °C, 0.5 h); see: Chan, T. H.; Chang, E. *J. Org. Chem.* 1974, *22*, 3264.

as aldol condensation. The propionylsilane enolate **3b**, generated in the stereochemically pure E form, reacted with benzaldehyde to afford erythro adduct **6** predominantly (eq 3) (52% yield, *erythro/threo* = 93/7).[12]

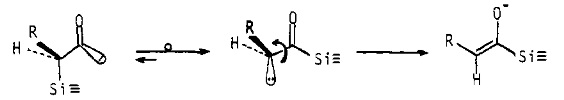


(3)

1b **3b** **6**

The intramolecularity of the silicon shift was verified by a crossover experiment. The admixture of α-silylalkyllithiums **1c** and **1e** was treated with carbon monoxide at 15 °C for 1 h. The resultant solution was quenched with aqueous NH_4Cl to afford **7** (64%) and **8** (61%) with no crossover products.

The preferential formation of E enolates may deserve comments. The silicon shift (**9** → **10**) would leave the negative charge in the plane perpendicular to that of the π-orbital of the carbonyl group, as depicted in the formula **10**. Subsequent 90° rotation around the C–C axis, avoiding steric congestion between the organosilicon group and R, would bring the negative charge into conjugation with the carbonyl π-orbital to form the E enolates **11** (eq 4).[13]



(4)

9 **10** **11**

The present reaction provides efficient and operationally simple access to acylsilane enolates, versatile synthetic intermediates.[5c,10,14] Further study on the conversion of acyllithium via *intramolecular* processes is in progress.[15]

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[11] Formation of the enol silyl ether of **3b** in a E/Z ratio of 38/62 by deprotonation of propionylsilane with LiN(i-Pr)$_2$ has been reported. See: Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066.

[12] Opposite selectivity has been achieved with the corresponding boron enolate (erythro/threo = 19/81); see: Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 3099. See also ref 11.

[13] It is not clear how significant the lithioxycarbene character of **9** is.

[14] Ager, D. J. *Chem. Soc. Rev.* **1982**, *11*, 493.

Acknowledgment. This work was supported in part by Grant-in-Aid for Special Project Research (No. 57118002) provided by the Ministry of Education, Science, and Culture, Japan. We thank Shin-Etsu Chemical Industries Co. Ltd. for the gift of chlorosilanes.

Registry No. **1a**, 1822-00-0; **1b**, 79158-44-4; **1c**, 74956-22-2; **1d**, 89165-09-3; **1e**, 89165-10-6; **1f**, 61540-28-1; **1g**, 89165-11-7; **1h**, 37820-39-6; (*E*)-**4**, 89165-12-8; (*Z*)-**4**, 89165-13-9; **5**, 54655-54-8; *erythro*-**6**, 61878-71-5; *threo*-**6**, 72658-20-9; **7**, 89165-14-0; **8**, 89165-15-1; Me$_3$SiCl, 75-77-4; Et$_2$MeSiCl, 17680-28-3; (1-((diethylmethylsilyl)oxy)-1-ethenyl)trimethylsilane, 89165-16-2; acetyltrimethylsilane, 13411-48-8; (*E*)-(1-((trimethylsilyl)oxy)-1-propenyl)trimethylsilane, 72658-07-2; (*E*)-(1-((trimethylsilyl)oxy)-1-pentenyl)trimethylsilane, 89165-17-3; (*E*)-(1-((trimethylsilyl)oxy)-4,4-dimethyl-1-pentenyl)trimethylsilane, 89165-18-4; (4,4-dimethyl-1-oxopentyl)trimethylsilane, 89165-19-5; (4,4-dimethyl-1-oxopentyl)triethylsilane, 89165-20-8; (*E*)-(1-((trimethylsilyl)oxy)-1-styryl)trimethylsilane, 89165-21-9; (*Z*)-(1-((trimethylsilyl)oxy)-1-styryl)trimethylsilane, 89165-22-0; (phenylacetyl)trimethylsilane, 56583-94-9.

Supplementary Material Available: Spectral and analytical data for all compounds prepared (7 pages). Ordering information is given on any current masthead page.

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(15) Incidentally, a similar silicon shift has been observed with organoactinides. See: Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112.

Role of Solvation in the Ultrafast Nonradiative Deactivation of Porphyrin–Quinone Exciplex Systems. Picosecond Laser Photolysis Studies

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Received December 13, 1983

Although the singlet excited state (S$_1$) of chlorophyll-*a*[1a] or bacteriopheophytin[1b] in polar solvents is quenched by benzoquinone due to electron transfer (ET), the formation of solvated radical ions or an exciplex has not been detected, in a marked contrast to the efficient charge separation (CS) that takes place on a picosecond (ps) time scale in a photosynthetic reaction center in vivo.[2]

Mechanisms of photoinduced ET have been studied in detail for some typical exciplex systems such as pyrene–dimethylaniline (DMA) or –dicyanobenzene (DCNB) by means of nanosecond (ns) and ps laser photolysis.[3,4] These exciplex systems and excited states of some weak electron donor–acceptor (EDA) complexes show CT fluorescence in nonpolar or less polar solvents.[3,4] However, the fluorescence is largely quenched in strongly polar solvents, and dissociated ion radicals are formed with a quantum yield of 50–80%.[3,4] This is again in marked contrast to the practically zero quantum yield of photoinduced CS from the singlet excited state of porphyrin–quinone systems in polar solvents. We have established a common mechanism underlying different behaviors of excited porphyrin–quinone systems, typical exciplexes, and excited EDA complexes by means of the ps laser photolysis studies of environmental effects upon these systems.

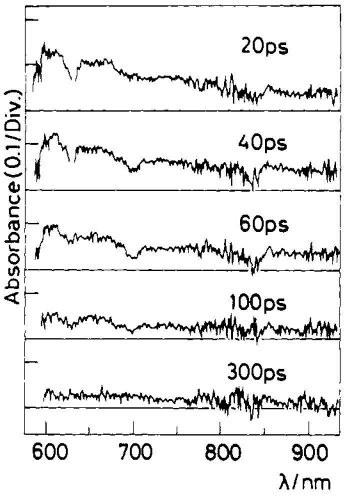

Figure 1. Time-resolved transient absorption spectra of the EEP–TQ system in acetone. The delay times from the exciting ps pulse are indicated in the figure. [TQ] = 0.59 M.

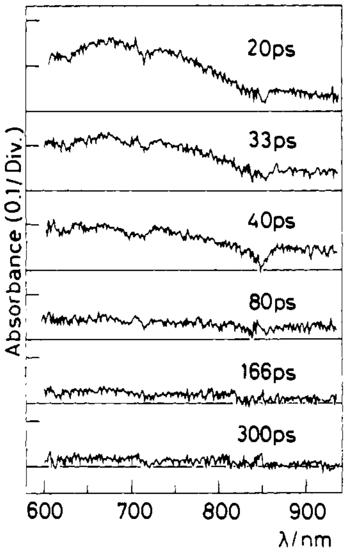

Figure 2. Time-resolved transient absorption spectra of the EEP–TQ system in benzene. The delay times from the exciting ps pulse are indicated in the figure. [TQ] = 0.62 M.

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(1) (a) Holten, D.; Gouterman, M.; Parson, W. W.; Windsor, M. W.; Rockley, M. G. *Photochem. Photobiol.* **1976**, *23*, 415. (b) Huppert, D.; Rentzepis, P. M.; Tollin, G. *Biochim. Biophys. Acta* **1976**, *440*, 356.

(2) See: Alfano, R. R., Ed. "Biological Events Probed by Ultrafast Laser Spectroscopy"; Academic Press: New York, 1982.

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