Condensation of **8** with benzaldehyde in the presence of $TiCl_4$ gave the syn isomer **9** predominantly (93:7) in 90% yield. The optical purity of **9** was 94.5% ee.[12] The absolute configuration of **9** was determined by transformation of **9** into dimethyl ether **10** ($[\alpha]^{24}_D$ -83.8°; *c* 0.370, EtOH). (-)-**10** could be assigned as the *R,R* form in comparison with the authentic sample ($[\alpha]^{24}_D$ +101.0°; *c* 0.015, EtOH) derived from the *S,S* diol.[12] Accordingly, it is clear that the $TiCl_4$-mediated reaction of **8** proceeds through retention.

We are now in a position to prepare 1,2-diols in a stereodivergent and enantioselective way via the newly developed α-methoxy organolead reagents. Further, the S_E2-retention mechanism is established. We are actively pursuing research of the Pb-mediated new synthetic reactions.

Acknowledgment. We thank Professor M. Hirama of our department for providing us with an authentic sample of the *S,S* diol.

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(12) The optical purity was determined by ^1H NMR (270 MHz) analysis of the corresponding MTPA ester. The optical purity of **9** does not correlate to the rotational data given for **10**. This is due to the difference in concentration, and thus the purity determined by ^1H NMR analysis is more reliable than that by the rotation.

Ready Access to α-(Triorganosilyl)methylene β-Lactones by Means of Rhodium-Catalyzed Cyclocarbonylation of Substituted Propargyl Alcohols

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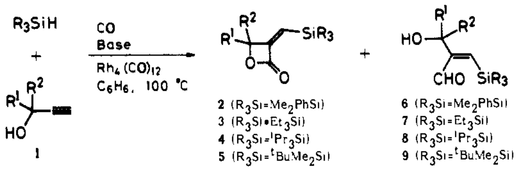
The incorporation of carbon monoxide in the synthesis of α-methylene γ-lactones has been of interest because it is one of the most elegant examples of the synthetic application of transition-metal complexes.[1] In particular, palladium-catalyzed cyclocarbonylation of homopropargyl alcohols is attractive because of the easy access to starting materials and the mildness of reaction conditions.[1a,b] α-Methylene β-lactones, however, are not formed by an analogous carbonylation of propargyl type alcohols.[2] Despite their simple structure it is astonishing that these compounds are constructed by an extremely limited number of methods.[3] Recently, we reported a rhodium-catalyzed silylformylation of alkynes.[4] The efficacy of the catalyst prompted us to apply this reaction to lactone formation. We report herein a successful cyclocarbonylation of acetylenic alcohols to form α-(triorganosilyl)methylene β-, γ-, and δ-lactones with the assistance of an appropriate base and $Rh_4(CO)_{12}$.

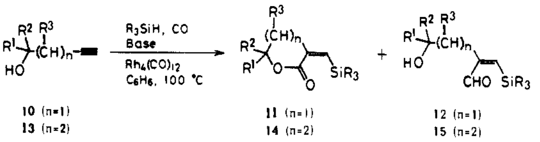
Carbonylation of a mixture of 1 equiv each of 2-methyl-3-butyn-2-ol (**1c**), Me_2PhSiH, and Et_3N gave α-silylmethylene β-lactone **2c**[5] (43%) and 3-silylpropenal **6c**[5] (52%) in the presence of a catalytic amount of $Rh_4(CO)_{12}$. The structure of the β-lactones is unambiguously confirmed by the IR spectrum, which showed a strong $\nu_{C=O}$ absorption at 1820 cm^{-1}. In the absence of Et_3N, however, **6c** was the sole product (94%). On the other hand, 2-propyn-1-ol (**1a**) gave **6a** (83%) selectively even in the presence of Et_3N. This preliminary finding suggests that the propensity for β-lactone formation depends on both steric and electronic factors. In fact, the ratio of β-lactone to 3-silylpropenal was remarkably affected by the silane and base employed in the carbonylation of **1c** (entries 5–9 in Table I). A dramatic improvement of the selectivity for β-lactone was attained by the use of either a bulkier silane, such as $^tBuMe_2SiH$, or a stronger base, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). On the basis of this information, suitable conditions to form **5b** (R_3Si = $^tBuMe_2Si$) from the less substituted **1b** were found by the combined use of $^tBuMe_2SiH$ and 0.1 equiv of DBU. Spiro type β-lactones were also obtained by this method. These results are summarized in Table I.



(1)

γ-Lactone **11** is derived from homopropargyl type alcohols **10** by a similar operation even more easily than **2**. A γ-lactone **11a**[5] (R^1 = R^2 = R^3 = H, R_3Si = Me_2PhSi) (90%) was obtained selectively with the aid of $Rh_4(CO)_{12}$ in the carbonylation of a mixture of 1 equiv each of 3-butyn-1-ol (**10a**), Me_2PhSiH, and Et_3N. 1-(2-Propynyl)cyclohexan-1-ol (**10b**) and *trans*-2-ethynylcyclohexan-1-ol (**10c**) were converted to the corresponding lactones, **11b** (87%)[5] and **11c** (87%),[5,8] respectively, under analogous conditions. This simple operation is also applicable to the synthesis of six-membered α-silylmethylene lactones, although a combined use of $^tBuMe_2SiH$ and Et_3N is again required for the selective formation of δ-lactone **14**[5] (R^1 = R^2 = R^3 = H, R_3Si = $^tBuMe_2Si$) (84%) in the carbonylation of 4-pentyn-1-ol **13**.

Carbonylation of **1** without a base, however, results in the formation of **6** selectively. The trimethylsilyl ether of **1** is converted to the trimethylsilyl ether of **6** by a similar carbonylation, which is an alternative method to give **6** as the sole product. The latter is the route of choice for selective synthesis of **12** or **15**. The results suggest that the presence of the adjacent hydroxyl group is crucial and silylation[6] of the hydroxyl group prior to carbonylation should be strictly avoided for the selective cyclocarbonylation of **1**, **10**, and **13**.



(2)

It should be stressed that the present modified silylformylation provides an effective route to strained α-silylmethylene β-lactones **2–5** by means of the carbonylation of **1**. The result is quite different from the previous reports that butenolides are formed by the reaction of the acetylenic triple bond with 2 equiv of CO in the presence of $Rh_4(CO)_{12}$.[9] In fact, the carbonylation of **1f**

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(7) The isolated lactones (**2–5**, **11**, and **14**) show the *Z* geometry in the exocyclic double bond unless otherwise noted. The assignment of *Z* and *E* geometry is based on the chemical shift value of the vinyl proton. An appreciable low-field shift is observed in the *E* isomer (e.g., δ 6.47 and 7.05 for (*Z*)- and (*E*)-**11c**, respectively).

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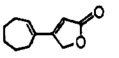
Table I. Silylative Cyclocarbonylation of **1**[a]

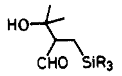
	acetylenic alcohol					product			
						β-lactone[c]		propenal[d]	
entry	no.	R^1	R^2	silane	base[b]	no.	yield, %	no.	yield, %
1	**1a**	H	H	Me_2PhSiH	Et_3N	**2a**	0	**6a**	83
2	**1b**	H	Me	Me_2PhSiH	Et_3N	**2b**	15	**6b**	76
3	**1b**	H	Me	Me_2PhSiH	DBU	**2b**	54	**6b**	26
4	**1b**	H	Me	$^tBuMe_2SiH$	DBU	**5b**	79	**9b**	6
5	**1c**	Me	Me	Me_2PhSiH	none	**2c**	0	**6c**	94
6	**1c**	Me	Me	Me_2PhSiH	pyridine	**2c**	0	**6c**	67
7	**1c**	Me	Me	Me_2PhSiH	Et_3N	**2c**	43	**6c**	52
8[e]	**1c**	Me	Me	Me_2PhSiH	DABCO	**2c**	52[f]	**6c**	0[g]
9	**1c**	Me	Me	Me_2PhSiH	DBU	**2c**	81	**6c**	0
10[h]	**1c**	Me	Me	Et_3SiH	Et_3N	**3c**	64	**7c**	6
11	**1c**	Me	Me	$^iPr_3SiH$	Et_3N	**4c**	33	**8c**	0
12	**1c**	Me	Me	$^tBuMe_2SiH$	Et_3N	**5c**	86	**9c**	0
13	**1d**	$-(CH_2)_4-$		Me_2PhSiH	Et_3N	**2d**	0	**6d**	71
14	**1d**	$-(CH_2)_4-$		$^tBuMe_2SiH$	DBU	**5d**	68	**9d**	0
15	**1e**	$-(CH_2)_5-$		Me_2PhSiH	DBU	**2e**	85	**6e**	0
16	**1f**	$-(CH_2)_6-$		Me_2PhSiH	DBU	**2f**	86	**6f**	2

[a] Reactions were conducted in a pressure bottle containing benzene, an acetylenic alcohol (1 equiv), a silane (1 equiv), a base (1 equiv), and $Rh_4(CO)_{12}$ (0.001 equiv) at 100 °C for 2 h under CO pressure (15–40 kg/cm^2) on a scale of 1–2 mmol. [b] DABCO: 1,4-diazabicyclo[2.2.2]octane. The quantity of DBU was reduced to 0.1 equiv. [c] References 5 and 7. [d] Reference 5. The ratio of isomers was evaluated for entries 1 (Z:E = 37:63), 2 (Z:E = 65:35), 5 (Z:E = 97:3), 6 (Z:E = 100:0), and 13 (Z:E = 97:3). [e] The reaction time is 17 h. [f] Z:E = 79:21. [g] Compund **19a** (R_3Si = Me_2PhSi, 32%) was isolated. [h] The reaction time is 25 h. Compound **19b** (R_3Si = Et_3Si, 20%) was also isolated.

under water gas shift conditions gave butenolide **16**[5] in 44% yield with the concomitant formation of some unidentified materials.



16



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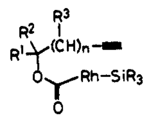

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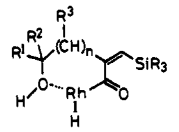

18

In the absence of precise mechanistic details, the formation of lactones through the intermediacy of an alkoxycarbonyl complex **17** reminiscent of the palladium-catalyzed cyclocarbonylation[1a,b] of **10** is presumed. In the rhodium case, however, **18** may be proposed as the common intermediate to give both lactone and propenal derivatives on the bases of the following observations: (i) the isolated propenal **6c** was not transformed to the β-lactone **2c** under the carbonylation conditions, (ii) the presence of R_3SiH is crucial for smooth carbonylation, and (iii) the presence of methanol or 2-methyl-2-propanol does not cause an intermolecular alkoxycarbonylation in the silylformylation of 1-pentyne. A conformation such as that of **18** seems to be advantageous for lactone formation and for the release of severe steric repulsion caused by a bulkier silyl group and rhodium metal. Hydrogen gas accompanying the lactones was detected by mass spectroscopic analysis[10] of the gas recovered after the formation of **2c**. Hydrogen formation was also supported by the fact that an appreciable amount of a saturated aldehyde **19** was isolated after a lengthy reaction time (entries 8 and 10 in Table I).

The silyl-protected *exo*-methylene group linked to the α-position of lactones could be transformed to the methylene group by a known procedure.[11] The triorganosilyl group located at the *exo*-methylene carbon serves to stabilize these structures and to direct the regioselectivity in successive reactions. Further studies are in progress.

Supplementary Material Available: Experimental details for typical cyclocarbonylations and characteristic boiling or melting point, IR, and ^1H and ^{13}C NMR data for the products (4 pages). Ordering information is given on any current masthead page.

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New, Rational Molecular Design for Chiral Recognition Involving Application of Dual Hydrogen Bond Association

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The recognition of molecular chirality is a very important aspect of the field of molecular recognition. For small molecules, the association mode provides a basis for molecular design of the chiral selector. Thus, to date, various modes of association have been developed for attaining enantioselectivity.[1,2] We recently found a unique mode of dual hydrogen bonds in the crystal structure[3] of a 1:1 complex of (R,R)-N,N'-diisopropyltartramide (DIPTA)[4] and (S,S)-9,10-dimethyl-9,10-dihydrophenanthrene-9,10-diol (**1**). The observed mode has led to a new concept of "complementary twist" for molecular design in quest of chiral recognition. In the

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