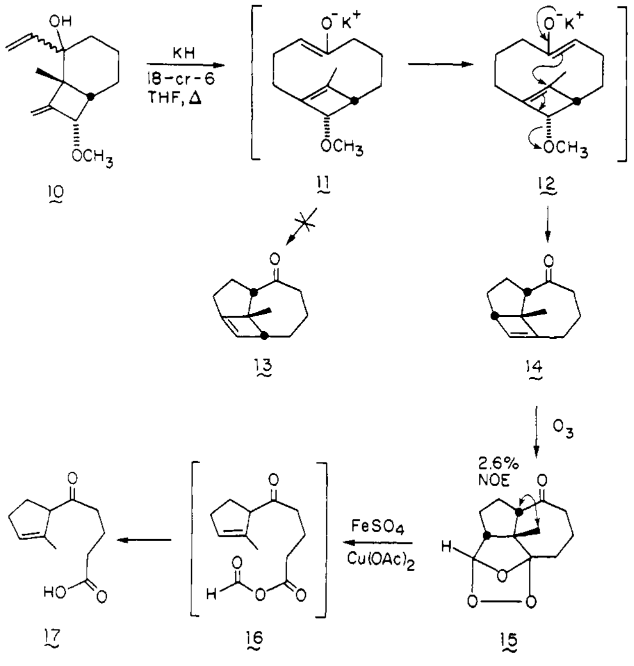
exo-boat transition state.[9] Since the methoxyl substituent in the initially generated enolate anion is consequently α-oriented, i.e., positioned nearly orthogonal to the π electrons, further transannular C–C bond formation is now stereoelectronically disfavored and does not operate.

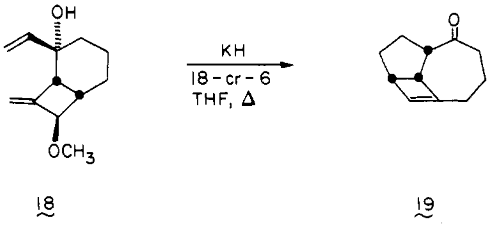
In yet another fascinating reaction, heating of **10** with potassium hydride and 18-crown-6 in dry tetrahydrofuran afforded **14** (40%).



Because detailed spectroscopic analysis of this tricyclic ketone did not allow for definitive determination of the position of its cyclobutene double bond, suitable degradation was undertaken. Thus, ozonolysis of **14** and subsequent treatment of stable ozonide **15** with $FeSO_4/Cu(OAc)_2$[10] in methanol gave the cyclopentene derivative **17**. The formation of **17** unequivocally establishes the site of unsaturation to be as in **14** rather than **13**.

This transformation is believed to originate from enolate anion **11** as the first-formed intermediate. Due to the large amount of strain associated with the bicyclo[3.2.0]hept-1(6)-ene part structure of **13**, intramolecular displacement of methoxide in **11** is energetically disfavored. Instead, enolate isomerization of **11** to **12** operates, with tetrahydrofuran or 18-crown-6 perhaps acting as the proton source, followed by S_N' transannular "scaffolding" to deliver the observed tricyclic product.

In order to scrutinize the kinetic consequences of methoxyl stereochemistry, alcohol **18** was also heated as its potassium salt. Under the same conditions, **19** was isolated in ca. 60% yield.



Charge annihilation within the intermediate enolate anion by $S_{N'}$ ejection of methoxide must consequently also be facile. This is because modest conformational flexing within cyclobutenes conveniently permits attainment of the necessary stereoalignment from either π face.

Among the many interesting facets of these reactions is their mixed stereochemical course. Whereas the **5** → **6** and **18** → **19** processes involve a trans-antiplanar arrangement of the entering and leaving groups, the conversion of **12** to **14** occurs in syn fashion (as does **2** → **3**). Further, the preceding observations show the $S_{N'}$ displacement of methoxide by enolate ions to proceed with reasonable efficiency and to constitute an exceptionally powerful synthetic method.

Acknowledgment. This investigation was supported by NIH Grants CA-12115 (to L.A.P.) and GM-32527 (to S.L.S).

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[9] The various mechanistic pathways open to these alcohols will be discussed in detail at a later date.

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An Efficient Silylformylation of Alkynes Catalyzed by $Rh_4(CO)_{12}$

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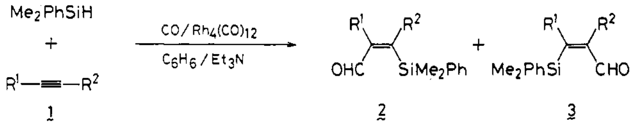
A combination of transition-metal complexes and hydrosilanes is a useful tool for highly selective transformations of alkenes, alkynes, and carbonyl groups.[1] In particular, cobalt-catalyzed incorporation of carbon monoxide is interesting as a unique method for the homologation of alkenes, aldehydes, and cyclic ethers, in which $R_3Si–Co(CO)_4$ plays an important role.[2] On the other hand, while hydroformylation is one of the most useful processes for the practical synthesis of aldehydes,[3] no analogous operation toward acetylenic compounds has been developed because of the concomitant formation of undesired products.[4] An excellent precedent is the selective acylation of 1-alkynes at the terminal carbon with the assistance of $Rh_4(CO)_{12}$,[5] or with a stoichiometric amount of $R–Mn(CO)_5$,[6] to give α,β-unsaturated enones. A formal silylformylation of 1-alkynes to give 3-silyl-2-alkenals **2**[7] can represent a useful synthetic approach to these valuable building blocks, due to the ready accessibility and elaboration of alkynes. We have designed a simple formylation reaction of alkynes in the presence of carbon monoxide, employing dimethylphenylsilane (Me_2PhSiH) instead of H_2, and $Rh_4(CO)_{12}$ as catalyst and have found a novel and selective formylation pattern of alkynes to give **2**. We report here the scope and limitations of this new catalytic silylformylation of alkynes.



When an alkyne **1** was allowed to react with 1 equiv each of Me_2PhSiH and Et_3N, using a catalytic amount (1 mol %) of $Rh_4(CO)_{12}$ in benzene solution under CO (30 kg/cm^2) at 100 °C

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Table I. Silylformylation of Alkynes with Me_2PhSiH[a]

entry		alkyne 1 R^1	R^2	product 2[b] yield[c] (%)	Z:E[d]
1	**a**	H	H	73	0:100
2	**b**	Me	H	99	80:20
3	**c**	C_2H_5	H	91	100:0
4	**d**	$^nC_3H_7$	H	93	95:5
5	**d**	$^nC_3H_7$	H	62[e]	90:10
6	**e**	Me_3Si	H	55	100:0
7	**f**	Ph	H	89	88:12
8	**g**	Me_3SiCH_2	H	93	91:9
9	**h**	$CH_2{=}CHCH_2$	H	90	48:52
10	**i**	$^cC_6H_{11}$	H	96	100:0
11	**j**	$HOCH_2$	H	83	37:63
12	**j**	$HOCH_2$	H	73[e]	77:23
13	**k**	Me	Me	93	100:0
14	**l**	$^nC_3H_7$	Me	85	(70:30)
15	**m**	Ph	Ph	90	95:5
16	**n**	Ph	Me	95	(89:11)
17	**o**	Ph	CO_2Et	43	100:0
18	**p**	Me	CO_2Me	67	100:0

[a] Reactions were conducted on a scale of 2–10 mmol in benzene solution including 1 mol % of $Rh_4(CO)_{12}$ and equimolar amounts of **1**, Me_2PhSiH, and Et_3N under CO pressure (10–30 kg/cm^2) for 2 h at 100 °C. [b] All products were identified by ^1H NMR, ^{13}C NMR, and IR spectra. All new compounds gave satisfactory combustion analyses. [c] Isolated yield. [d] The values in parentheses show the ratio of **2**:**3**. [e] The reaction was carried out in the absence of Et_3N.

for 2 h, a new compound **2** was obtained in excellent yield after purification of the reaction mixture by column chromatography. The most interesting feature of this result is the survival of the formyl group under the reaction conditions.[8] Analogous reactions proceeded smoothly with both of the terminal or internal alkynes. The results are summarized in Table I. The presence of an extremely small quantity of $Rh_4(CO)_{12}$ was sufficient for complete conversion; for example, a turnover number of catalyst greater than 12000 was observed in the case of **1d**. Catalysis by rhodium was demonstrated by control experiments for the case of **1f**, in which the incorporation of carbon monoxide was not observed either in the absence of catalyst or the presence of $Co_2(CO)_8$ or $Ru_3(CO)_{12}$ instead of $Rh_4(CO)_{12}$. Although the role of triethylamine is ambiguous at present, its inclusion improved yields of **2** and Z-selectivity in **2** as shown in entries 4 and 5. By contrast, the Z:E ratio for **2j** was greater in the absence of Et_3N (entries 11 and 12). The isomerization of (Z)-**2** to (E)-**2** under the reaction conditions is a possible explanation for entries 1, 9, and 11.

It should be noted that the terminal carbon of 1-alkynes is silylated specifically to give **2** (R^2 = H, entries 1–12) and that the olefinic part of **1h** and the hydroxy group of **1j** remained intact under the reaction conditions (entries 9, 11, and 12). A bulky substituent on the acetylenic carbon seems to prevent such silylformylation. 3,3-Dimethyl-1-butyne, 1-phenyl-2-trimethylsilylethyne, and 1-trimethylsilylpropyne did not give any attractive products. Our results contrast those of a recent report on the reactions of alkynes in the presence of $Rh_4(CO)_{12}$.[5,9] We therefore carried out the reaction of **1d** with Me_2PhSiH under a pressure of both CO (25 kg/cm^2) and ethene (15 kg/cm^2) in the presence of $Rh_4(CO)_{12}$. Aldehyde **2d** (95%) was again the sole product, and ethene was not incorporated at all.

The regioselectivity toward internal alkynes seems to depend on the steric effect of the substituent (entries 14 and 16). However, an alkoxycarbonyl group consistently contributes to the formation of **2** (entries 17 and 18), although the yields of formylated products are rather low; this point is quite separate from the observation that a steric effect seems to be more important than electronic effects in determining the product distribution.[5]

Unfortunately, any clear information to rationalize the catalytic sequence has not been obtained from the results of control experiments and the spectroscopic observation of an equimolar mixture of $Rh_4(CO)_{12}$ and Me_2PhSiH in the presence of CO.[10] The oxidative addition of Me_2PhSiH to form $Me_2PhSiRh$ species may be an important step at the first stage as shown in hydrosilylations.[11] Mechanistic aspects aside, however, the present novel reaction composed of an alkyne, hydrosilane, and carbon monoxide should prove to be a simple and efficient approach to form **2**. The structure of **2** is of interest as a versatile building block for the synthesis of complex molecules via a Peterson olefination,[12] a Nazarov type cyclopentenone annelation,[13] or a Trost type cyclopentane annelation.[14]

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Asymmetric Synthesis with Chiral Ferrocenylamine Ligands: The Importance of Central Chirality

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The development of synthetic methodology for the diastereo- and enantioselective formation of C–C bonds derived through the use of catalytic quantities of chiral transition-metal catalysts is today a topic of fundamental importance.[1–6] In 1986 Ito and Hayashi reported an elegant synthesis of oxazolines utilizing a gold(I)-catalyzed aldol reaction in the presence of chiral ferrocenylamine ligands that possess both planar and central chirality.[7] For example, the reaction of **1** with **2** catalyzed by bis(cyclohexyl isocyanide)gold(I) tetrafluoroborate, **3**,[8] in the presence of the chiral ferrocenylamine ligand (R)-(S)-**4** gave a mixture of the *trans*- and *cis*-oxazolines **5** and **6**, respectively (Scheme I). The trans isomer **5** illustrated was the dominant isomer formed in 91% enantiomeric excess (ee).[9]

Kumada et al. investigated the effect of the central chirality of the stereogenic carbon atom of **4** on the diastereo- and enantioselectivity of transition-metal-catalyzed Grignard cross-coupling reactions.[10,11] Kumada came to the reasonable conclusion from the experimental data obtained that the planar chirality of **4** plays

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