studies employing mass spectrometry were done in selected ion monitoring (SIM) mode, observing the molecular ion peaks 108, 109, and 110. The abundances of the M − 1, M, M + 1, and M + 2 peaks for the authentic samples were obtained before the kinetic runs, and appropriate corrections were made to the observed intensities in the kinetic analyses using the following general equation

$$[\mathbf{1}]/[\mathbf{1} - d_i] = \left[1 - \left(\frac{108+i}{108}\right)\left(\frac{108}{108+i}\right)_{\mathrm{D}}\right] \Big/ \left[\left(\frac{108+i}{108}\right) - \left(\frac{108+i}{108}\right)_{\mathrm{H}}\right]$$

where 108 and (108 + *i*) refer to mass spectral ion intensities at *m/e* 108, 109, or 110; subscripts H and D refer to unlabeled **1** or $\mathbf{1} - d_i$, respectively; and (108 + *i*)/108 gives the observed ion intensity ratio for a mixture of **1** and $\mathbf{1} - d_i$.

The kinetic results are summarized in Tables I–III above.

Acknowledgment. We are indebted to the National Science Foundation for support of our work on hydrocarbon rearrangements.

Carbon-Carbon Bond-Forming Reactions of Zinc Homoenolate of Esters. A Novel Three-Carbon Nucleophile with General Synthetic Utility

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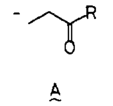
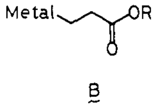
Abstract: In the presence of suitable catalysts and additives, the zinc homoenolate of alkyl propionate and its congeners undergo a variety of carbon–carbon bond-forming reactions, e.g., addition onto carbonyl compounds, allylation, arylation, vinylation, and acylation, to produce diverse kinds of alkanoates and cyclopropane derivatives. The moderately reactive zinc homoenolate exhibited a very high degree of chemoselectivity in these reactions. Me_3SiCl has been found to greatly accelerate 1,2- or 1,4-addition and the allylation reaction of the zinc reagent.

Homoenolate anion (A) represents an archetypal synthon in the concept of Umpolung (inversion of polarity)[1] and is important probably next to the ubiquitous acyl anion synthon.[2] The virtue



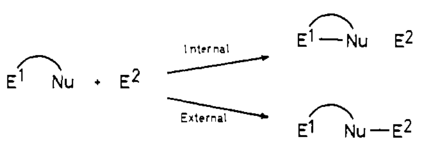
A



B

of the homoenolate is derived from its function as an inverse-polarity Michael acceptor. Despite such conceptual importance, homoenolate anion has gained very limited success in actual application.[3] In the present work, we describe the versatile reactivities of zinc homoenolate of propionate (B) and its congeners to demonstrate for the first time the great potential of homoenolate chemistry in organic synthesis[4] (cf. Scheme I).

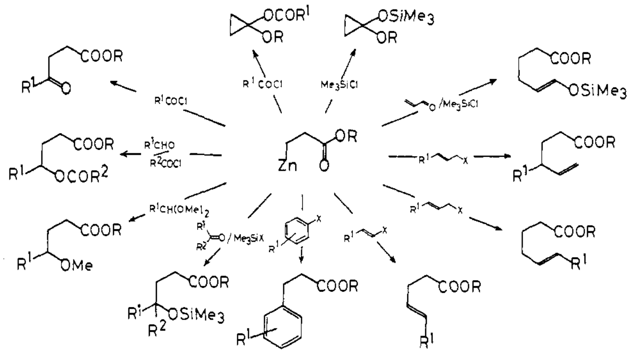
The inherent difficulty in using homoenolates for nucleophilic reactions is associated with the problem of competition between internal and external electrophilic sites (eq 1), in which an entropy



(1)

factor represents a major obstacle. The anionic site of the homoenolate A therefore cannot be too reactive, and the metal homoenolates so far reported undergo only limited types of reactions.[5] Any attempts to challenge such a difficult internal/external problem must achieve very fine control over the nucleophilicity of the anionic center, and research along these lines would also realize a high level of chemoselectivity among external electrophiles, which has been a constant recent concern of synthetic organic chemists.

Scheme I



The reaction of siloxycyclopropane **1** and $ZnCl_2$ in ether produces in over 80% yield zinc homoenolate **2**,[6] which exists as

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(1) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239. Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

(2) Groebel, B. T.; Seebach, D. *Synthesis* **1977**, 357.

(3) (a) For the cause and the solution to the problem, see: Werctiuk, N. H. *Tetrahedron* **1983**, *39*, 205. Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 932. (b) Review on metal homoenolate: Ryu, I.; Sonoda, N. *Yuki Gosei Kagaku Kyokaishi* (*J. Org. Synth. Chem. Jpn.*) **1985**, *43*, 112. See also references in ref 5a.

(4) Preliminary reports: (a) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 3368. (b) Oshino, H.; Nakamura, E.; Kuwajima, I. *J. Org. Chem.* **1985**, *50*, 2802. (c) Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 83. (d) A group at Kyoto also reported some of the reactions that we have described in these papers: Tamaru, Y.; Ochiai, H.; Nakamura, T.; Tsubaki, K.; Yoshida, Z. *Tetrahedron Lett.* **1985**, *26*, 5559. Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Tetrahedron Lett.* **1986**, *27*, 955.

(5) (a) Carbonyl addition: Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 7360. Nakamura, E.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1986**, *108*, 3745. (b) Conjugate addition: Giese, B.; Horler, H.; Zwick, W. *Tetrahedron Lett.* **1982**, *23*, 931. (c) Carbonylation: Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Synth. Commun.* **1984**, *14*, 1175. (d) Dimerization: Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192.

(6) (a) Nakamura, E.; Shimada, J.; Kuwajima, I. *Organometallics* **1985**, *4*, 641. (b) For experiments to isolate pure solvent-free zinc homoenolate **4**, use of excess $ZnCl_2$ should be avoided. Otherwise homoenolate **2** forms a complex with $ZnCl_2$, which either does not dissolve in a nonpolar solvent or tends to carry zinc-complexed ether into the extract. (c) Standardization of the homoenolate solution by iodine described previously[34] tends to give much lower concentration than actual and should be avoided.

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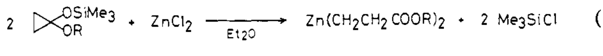
etherate **3** (eq 2). Upon removal of the solvent in vacuo, the coordinated solvent molecule is replaced by the internal ester ligand to form an oily, solvent-free chelate **4**.[6] Reduction of 3-iodopropionate by zinc/copper couple in a mixture of an amide solvent and benzene also provides a (rather ill-defined) species which exhibits chemical reactivities very similar to those of **2**.[4d] Despite their lower reactivities than the Grignard reagents or even simple zinc alkyls, we have been able to develop conditions where the zinc homoenolate reacts with a variety of electrophiles to undergo synthetically important carbon–carbon bond-forming reactions (Scheme I) without interference by the internal ester group. The zinc homoenolate thus created an entirely new synthetic route to substituted alkanoates. In addition, conditions have been found to effect also an internal nucleophilic addition to obtain cyclopropanone derivatives.

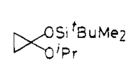


(2)

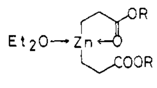
1a: R = ^{i}Pr

b: R = Et

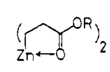
2a,b



1c



3



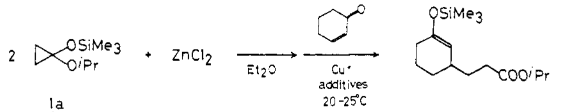
4

(A) Homoenolate as a Carbon Nucleophile: New Synthetic Routes to Substituted Alkanoates. Preliminary studies provided confirmation of the moderate nucleophilicity of homoenolate **2**, which had been expected in light of standard organozinc chemistry.[7] Since zinc alkyls are known to undergo transmetalation with metal halides,[8] we first studied transition metal catalyzed reactions of **2**.[9,10]

(1) Copper-Catalyzed Conjugate Addition Reaction. As we started the present series of studies, we became particularly attracted by the conjugate addition, since such a reaction has special heuristic value with respect to the concept of polarity inversion (eq 3). Being aware of the fact that dimethylzinc readily transfers its methyl group to copper(I) halide[8] and that organocopper species readily undergo conjugate addition to unsaturated carbonyl compounds,[11] we studied the copper-catalyzed reaction of **2** that corresponds to the scheme in eq 3.

(3)

Cyclohexenone was chosen as a prototype substrate for the search of optimum conditions (eq 4). During this early stage, we generally used, for the sake of experimental simplicity, the crude ethereal solution of the homoenolate (eq 2) *that contains 2 equiv of* Me_3SiCl. This fortuitous presence of the chlorosilane led to the unexpected finding of its extraordinary effect on the conjugate addition, which gave a lead to the later developments in a generalized form.[12]

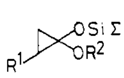


(4)

1a

Initial reactions designed after conventional copper-mediated conditions (CuI, −78 °C to room temperature, ether or tetrahydrofuran (THF)) resulted in >90% recovery of the enone (Table I, entry 1), suggesting the low reactivity of the copper homoenolate. We then examined the effect of various catalysts (CuI, $CuBr \cdot Me_2S$, CuCN), ligands (tributylphosphine, dimethyl sulfide, and tetramethyleneethylenediamine), solvents (ether, THF, and hexamethylphosphoric triamide (HMPA)), and Lewis acid additives (excess $ZnCl_2$, $MgBr_2$,[11c] and $BF_3 \cdot Et_2O$). Under a variety of conditions using most of the possible combinations of these additives, the reactions failed to give more than 10% conversion of the starting enone (room temperature, 2–15 h). *One combination of additives,* Me_3SiCl *and HMPA, resulted in a dramatic rate acceleration.*[12a] The first four entries in Table I illustrate *rate enhancement* by Me_3SiCl/HMPA. Most pleasing was that a catalytic amount of the copper catalyst gave as good a yield as a stoichiometric amount (entries 4 and 5) and much better (ca. 99.5% vs ca. 95%) regioselectivity of the double bond in the product. A note of caution is that the regioselectivity was lowered by prolonged exposure of the product to the reaction conditions. The reaction was considerably slower than the copper-catalyzed reaction of the Grignard reagents but tolerates much higher temperature (e.g., room temperature). The high thermal stability of the copper homoenolate species[13] is not unexpected in light of our previous experience with other metal homoenolates.[6] The reaction in THF gave a slightly better yield than that in ether.

Table II summarizes the results of the conjugate addition for various unsaturated carbonyl compounds in the presence of $CuBr \cdot Me_2S$. The reaction proceeded very cleanly at 0–35 °C in 1–4 h with as small as 0.5 mol % of the catalyst and produced no significant amount (<3%) of 1,2-adduct. 3-Methylcyclohexenone (entry 4), being unreactive, needed excess homoenolate due to competitive Cu/HMPA-catalyzed regeneration of cyclopropane **1** (vide infra). It is noteworthy that the addition reaction proceeded cleanly for methyl vinyl ketone and unsaturated aldehyde (entries 5 and 7). The enal in entry 7 produced an enol silyl ether of high (91%) geometrical purity. We found later that Me_3SiCl-assisted conjugate addition of organocopper reagents onto enals generally produces *E* isomers of >90% geometrical purity.[12] The homoenolate shows poor stereoselectivity in the reaction with substituted cyclohexenones (entries 3 and 6), behaving as if it had a smaller steric bulk (entries 3 and 6) than normal alkylcopper.[14,15] The reaction of acetylenic ketone produced allenic enol ether, which upon hydrolysis gave the corresponding enone as a 3:2 *E*/*Z* mixture. Acetylenic ester gave *cis*-olefinic adduct as a major product, in consonance with the general behavior of organocopper reagents.[11] Methyl-substituted homoenolate prepared from methylcyclopropane **5a** also underwent clean addition reaction (entry 2). Application of the conjugate addition reaction to the synthesis of cortisone and adrenosterone has recently been disclosed.[15]



5a: R^1 = Me, R^2 = Me, Σ = Me_3

5b: R^1 = Ph, R^2 = Et, Σ = Me_3

5c: R^1 = Me, R^2 = Me, Σ = ^{t}BuMe$_2$

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[7] Review: Boersma, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 2, p 823.

[8] Hofstee, H. K.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1978**, *144*, 255. Thiele, K.-H.; Köhler, J. *J. Organomet. Chem.* **1968**, *12*, 225.

[9] β-Hydride elimination is a prominent side reaction in the organic synthesis using transition-metal alkyls, and the internal ester function in **2** appeared to assist this side reaction. However, except in a single case in the palladium-catalyzed reaction, no significant trace this reaction was detected (cf. ref 10). Cf.: Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978.

[10] Cf.: Negishi, E.; Matsushita, H.; Kobayashi, M.; Rand, C. L. *Tetrahedron Lett.* **1983**, *24*, 3823.

[11] (a) Posner, G. H. *Organic Reactions* **1972**, *19*, 1. Taylor, R. J. K. *Synthesis* **1985**, 364. (b) Review on organocopper/Lewis acid reagents: Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.*, in press. (c) Metal salts such as $MgBr_2$ assists the conjugate addition of organocopper reagents. House, H. O.; Fischer, W. F., Jr. *J. Org. Chem.* **1968**, *33*, 949.

[12] (a) *Acceleration* of the conjugate addition by Me_3SiCl was first reported in ref 4a and then followed by reports of generalized cases by several groups: Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6015, 6019. Alexakis, A.; Berlan, J.; Besace, Y. *Tetrahedron Lett.* **1986**, *27*, 1047. Nakamura, E.; Matsuzawa, S.; Horiguchi, Y.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 4029. Johnson, C. R.; Marren, T. *Tetrahedron Lett.* **1987**, *28*, 27. (b) *E* selectivity in the Me_3SiCl-accelerated conjugate addition: Horiguchi, Y.; Matsuzawa, S.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 4025. (c) $BF_3 \cdot Et_2O$ also accelerates the conjugate addition of the homoenolate. The stereoselectivity of this reaction is different from that under Me_3SiCl assistance.[15]

[13] The internal ester ligand is known to endow high thermal stability to the metal–carbon bond.[6] In addition, an organocopper reagent generated from zinc alkyls appears generally more stable than the Grignard-based organocopper reagents.

[14] Blumenkopf, J. A.; Heathcock, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 2354.

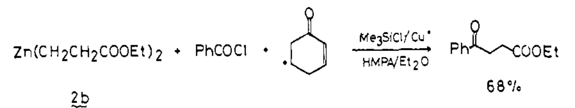
[15] Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *J. Org. Chem.* **1986**, *51*, 4323.

Table I. CuBr·Me_2S-Catalyzed Conjugate Addition of Zinc Homoenolate with Cyclohexenone[a]

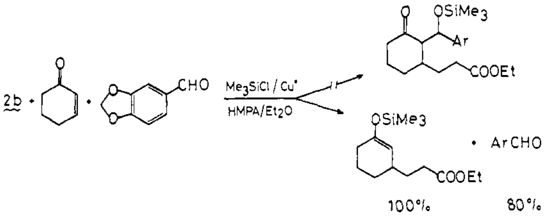
entry	cyclopropane **1a**, equiv	Cu^+, equiv	Me_3SiCl, equiv	HMPA, equiv	solv	% yield after 20 min	% yield after 8 h
1	3.6	1.5	0	0	ether	<5	<5
2	3.6	1.5	0	3.6	ether	<5	ca.5
3	3.6	1.5	3.6	0	ether	<5	ca.5
4	3.6	1.5	1.1	3.6	ether	80[b]	
5	2.4	0.12	2.4	2.4	ether/THF	71	100

[a] Homoenolate **2a** prepared from cyclopropane **1a** was used either as such or after being freed of Me_3SiCl. The reaction was performed at 0–25 °C, and the yield was determined by quantitative GLC analysis of the aliquot withdrawn from the mixture at the time indicated. [b] The product contained a few percent of the regioisomer of the enol double bond.

Acid chloride reacts much faster than enone (eq 5). An attempted three-component coupling reaction (eq 6a) failed and left the aldehyde intact (eq 6b), indicating that the silyl trapping of an intermediate of the conjugate addition is extremely fast. Separate experiments indicated that aldehydes are inert to the conditions of the conjugate addition (vide infra).



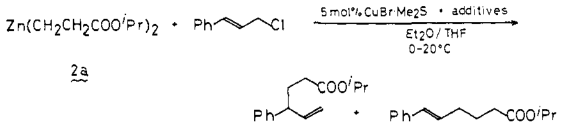
(5)



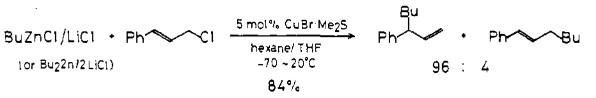
(6a)

(6b)

(2) Allylation Reaction. Despite its importance as a carbon–carbon bond-forming reaction, little is known about the substitution reaction of the homoenolate chemistry, while examples of additions onto polarized double bonds have been recorded.[5] We thus examined the CuBr·Me_2S-mediated reaction of allylic halides and found that homoenolate **2** (and notaby Bu_2Zn also) undergoes highly selective S_N2' reaction. The level of selectivity found was much higher than that of organocopper reagents prepared from lithium or magnesium alkyls.[16,17]



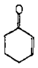
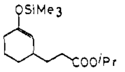
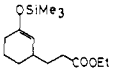
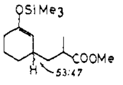
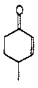
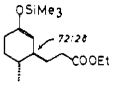
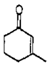
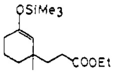
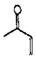
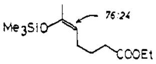
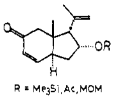
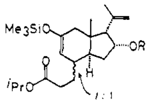
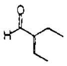
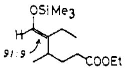
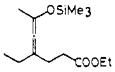
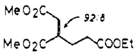
(7)



(8)

The reaction of cinnamyl chloride was examined first (eq 7). As seen in Table III, polar additives such as HMPA, or dimethylformamide (DMF), are needed to obtain high yield. *These additives also greatly improved the S_N2' selectivity of the* reaction. Thus, in an HMPA (2 equiv)/THF or a DMF/THF (1:4–1:1) mixture, the yield was quantitative and the ratio of the S_N2'/S_N2 reactions was as high as 96:4 (entries 4 and 5). We also found (eq 8) that Bu_2Zn ($2BuLi + ZnCl_2$) cleanly alkylates in an S_N2' fashion (97% S_N2') even in the absence of HMPA. Such a high degree of S_N2' selectivity stands in contrast to the reported S_N2-favoring reaction of lithium- and magnesium-based butylcopper reagents. $BF_3·Et_2O$, which enhances S_N2' selectivity of the RCu-type reagents,[17] lowered the selectivity (entry 3). Me_3SiCl showed no favorable effects in this reaction. No plausible explanation is available for the decreased S_N2' selectivity under stoichiometric conditions (entry 6). The reaction in the presence of excess cinnamyl chloride at room temperature afforded only about 120% yield based on the homoenolate **2** used, indicating that only one of the homoenolate moieties is practically available for the reaction under the present conditions as in the conjugate addition.

Table II. Conjugate Addition of Homoenolate

entry	enone	cyclopropane	product	%yield[b]
1		1a		93 (100)
1a		1b		76
2		5a		91[c]
3		1b		78[d]
4		1b		92
5		1b		75[e]
6		1a		85–95[f]
7		1b		75[g]
8		1b		73
9		1b		63[h]

[a] Zinc homoenolates were prepared in ether from the cyclopropanes indicated and used as such (yield was assumed to be 85%). The reactions (0.75–5-mmol scale) were performed with ca. 1.2 equiv of the homoenolates except in entries 1, 2, and 4, where 2 equiv was used. The reaction in entry 2 was conducted on a 0.1-mol scale. [b] Isolated yield. GLC yield in parentheses. [c] The ratio was determined by GLC analysis. [d] The ratio was determined by GLC, and the assignment by transformation into an authentic material (Experimental Section). [e] The ratio was determined by GLC analysis, and the assignment was based on the predominance of the higher field olefinic proton in the ^1H NMR spectrum. [f] Epimeric ratio determined by reversed-phase HPLC and by 200-MHz NMR analysis of the angular methyl signals.[15] [g] The ratio was determined by GLC, and the stereochemical assignment was based on the precedent.[19] [h] The assignment is based on the predominance of the higher field signal of the olefinic proton.

Under conditions optimized for cinnamyl chloride, the homoenolate smoothly reacted with a variety of allylating reagents in an S_N2' fashion. Various substitutions at both ends of the allylic

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(16) Posner, G. H. *Organic Reactions* **1975**, *22*, 253.

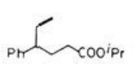
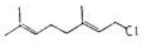
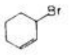
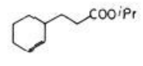
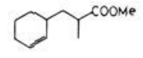
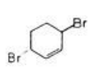
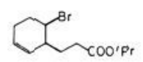
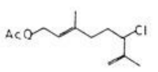
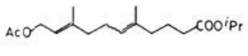
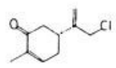
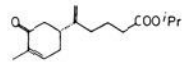
(17) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 2318.

Table III. CuBr·Me_2S-Catalyzed Reaction with Cinnamyl Chloride[a]

entry	Cu^+, equiv	$BF_3 \cdot Et_2O$, equiv	HMPA, equiv	DMF, vol %	% yield	S_N2':S_N2
1					trace	
2	5				18	67:33
3	5	2			14	71:29
4	5		2		100	97:3
5	5			50	100	96:4
6	100		2		78	86:14

[a] The reagent stoichiometry is based on cinnamyl chloride. About 1.5 equiv of the homoenolate was used and the reaction was run at room temperature till completion (>2 h).

Table IV. S_N2' Allylation of Homoenolate

entry	electrophile	1a,b	S_N2'product	%yield[b] (S_N2':S_N2)
1		1a		97[c,d] (96: 4)
2		1a		81[e] (88:12)
3		1a		93[e] (-)
4		5a		59[e] (-)
5		1a		79[e,f] (85:15)
6		1a		72[c,d] (100: 0)
7		1a		87[e] (-)
8		1a		48[c,d] (-)

[a] For preparation of the homenolate, see footnote *a* in Table II. The reaction was carried out at room temperature for 14–24 h using 0.5–1.1 equiv of homoenolate **1** either in the presence or absence of Me_3SiCl. Solvents are indicated in footnotes *c–e*. [b] Yield is based on pure isolated products. [c] DMF/ether (1:3–1:1). [d] In the presence of ca. 2 equiv of Me_3SiCl. [e] HMPA (2–5 equiv to **1**) in ether/THF. [f] The cis stereochemistry in the product was assigned by assuming anti stereochemistry of the S_N2' reaction.

system are found among the examples listed in Table IV. The S_N2'/S_N2 ratio was particularly high when the alkylated carbon bears no substituents (entries 6 and 8). The reaction of *trans*-1,4-dibromo-2-cyclohexene (entry 5) gave the S_N2' product as a single stereoisomer, which is presumably due to anti substitution.[18]

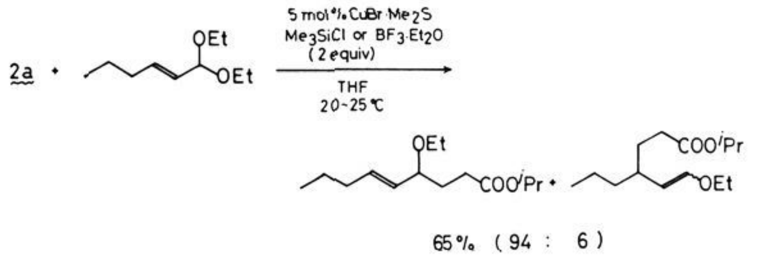
The chlorinated carvone (entry 7) illustrates an extremely interesting aspect of the chemoselectivity of the copper-catalyzed reactions described above. The allylation and the conjugate addition proceed under essentially the same conditions except that the latter needs Me_3SiCl as well. Due to this subtle difference, *we could selectively perform the allylation in the presence of an enone function in the same molecule (entry 7). In the presence of Me_3SiCl, the allylation and the conjugate addition competed.* Diene monoepoxide (entry 8) afforded an S_N2' product having an *E*-trisubstituted olefin of >98% geometrical purity,[19] whereas the substrate that gives a differently substituted olefin (entry 6) reacted much less selectively (*E*:*Z* = 2:1). A detailed study of the latter substrate showed that both the *E*/*Z* ratio and the product yield (70–90%) are insensitive to the nature of the bulk solvent (i.e., a mixture of HMPA (2 equiv) and hexane, benzene, CH_2Cl_2, or butyronitrile was examined). We could not alkylate the homoenolate with allylic acetates or carbonates, *n*-alkyl halides, epoxides, or even benzyl bromide. In summary, the catalytic copper reagent generated from the zinc homoenolate (or Bu_2Zn) is much less reactive toward alkylating agents but showed very much higher regio- and chemoselectivities than common organocopper reagents.

Table V. Phenylation of the Homoenolate with PhBr and PhI[a]

ArX	catalyst	additive	% yield (% recovery of PhBr)	
			30 min	22–28 h
PhBr	$PdCl_2(o\text{-}Tol_3P)_2$		35	81 (0.6)
		Me_3SiCl	9	41
	$PdCl_2(dppf)$		0	3 (95)
PhI	$PdCl_2(o\text{-}Tol_3P)$		90	
	$PdCl_2(dppf)$		13	37
PhBr	$NiCl_2(dppf)$		28	76 (22)
	$NiCl_2(Ph_3P)_2$		3	57 (40)
	$NiCl_2(o\text{-}Tol_3P)_2$		5	15 (78)
	$Ni(acac)_2$		0	10

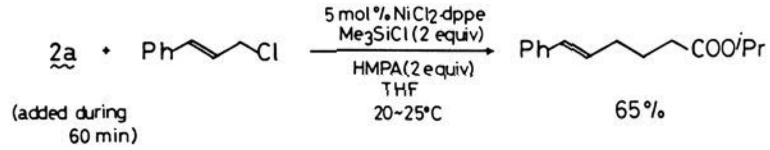
[a] The homoenolate prepared from the cyclopropane (3 equiv) and $ZnCl_2$ (1.5 equiv) was used as a THF solution after removal of Me_3SiCl. An ether/THF mixture was used in the run where Me_3SiCl was present in the reaction mixture.

Finally two examples of S_N2 reactions of the homoenolate are briefly described. Simple copper alkyls derived from organolithium reagents react with acetals of α,β-unsaturated aldehydes with varying degrees of regioselectivity. The zinc homoenolate in the presence of Cu(I) catalyst was found to react in an S_N2 fashion (eq 9). *The presence of Me_3SiCl or $BF_3 \cdot Et_2O$ was mandatory in this reaction* (otherwise no reaction was observed): The reaction in the presence of a reaction promoter (2 equiv) in THF gave the S_N2 product in 94% selectivity.[20] A significant controlling effect of the chlorosilane was evident from the fact that the regioselectivity dropped to 84% when the amount of Me_3SiCl was decreased to 1 equiv.



(9)

Nickel-catalyzed allylation proceeded in an S_N2 manner. $NiCl_2$ complexed with a bidentate ligand (e.g., ferrocenylphosphine (dppf)[21] or 1,2-bis(diphenylphosphino)ethane) effected a highly selective (>99%) S_N2 allylation (eq 10).[22] Slow addition of a solution of **6a** to a mixture containing the substrate, Me_3SiCl, and HMPA maximized the yield, and the selectivity afforded the S_N2 product in 65% yield together with diisopropyl adipate (29%). Geranyl chloride gave the desired product in no higher than 30% yield. Palladium catalysts were ineffective.



(10)

(3) Arylation and Vinylation Reactions. The work initiated by Kumada and Corriu[24] has established conditions for carrying out group 10 metal-catalyzed coupling reactions of organomagnesium

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[18] Cf.: Goering, H. L.; Singleton, V. D., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 7854. Claesson, A.; Olsson, L. I. *J. Chem. Soc., Chem. Commun.* **1978**, 621.

[19] The assignment is based on a precedent: Cahiez, C.; Alexakis, A.; Normant, J. F. *Synthesis* **1978**, 528.

[20] Ghribi, A.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1984**, *25*, 3079.

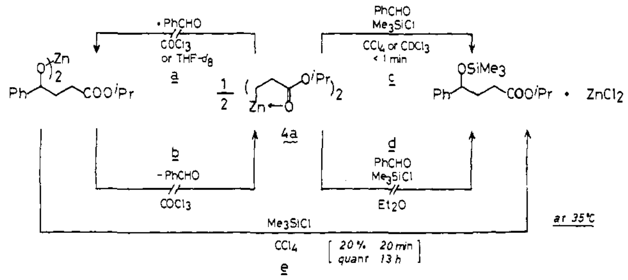
[21] Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

[22] The behavior of the nickel-catalyzed reaction of organometallics with an allylic system is quite complex: Matsushita, H.; Negishi, E. *J. Org. Chem.* **1982**, *47*, 4161. Chuit, C.; Felkin, H.; Frajerman, C.; Roussi, G.; Swierczewski, G. *J. Chem. Soc., Chem. Commun.* **1968**, 1604. Felkin, H.; Swierczewski, G. *Tetrahedron Lett.* **1972**, 1433; *Tetrahedron* **1975**, *31*, 2735.

[23] Chuit, C.; Foulon, J. P.; Normant, J. F. *Tetrahedron* **1980**, *36*, 2305.

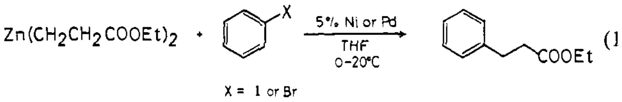
[24] Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374. Corriu, R. J. P.; Masse, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 144.

Scheme II



and zinc reagents with sp^2 organic halides. During the course of the present investigation, it was reported that organozinc compounds serve better as a nucleophile than Grignard reagents in such reactions.[21] The same report described the superiority of $PdCl_2(dppf)$ to conventional catalysts such as $NiCl_2(Ph_3P)_2$.

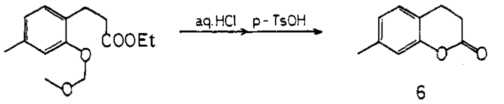
We first examined phenylation of the (Me_3SiCl-free) homoenolate in THF with bromobenzene in the presence of various catalysts (eq 11, Table V). To our surprise, $PdCl_2(dppf)$ afforded



(11)

a very poor yield in our case, and $PdCl_2(o\text{-}Tol_3P)_2$ proved highly effective.[26] In nickel-catalyzed reactions, dppf was found to be superior to $o\text{-}Tol_3P$. This reaction did not require HMPA or Me_3SiCl, and their presence even reduced the product yield in some reactions.

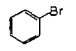
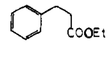
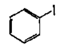
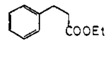
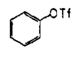
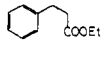
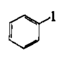
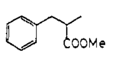
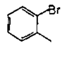
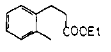
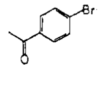
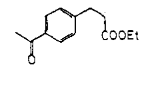
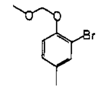
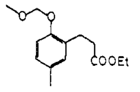
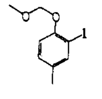
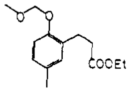
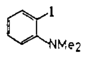
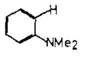
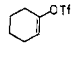
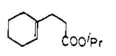
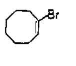
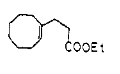
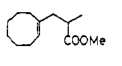
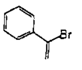
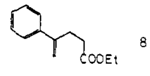
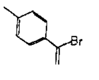
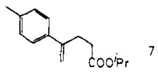
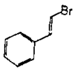
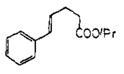
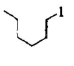
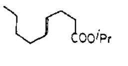
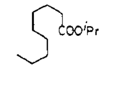
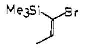
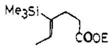
Table VI summarizes the results of the reaction that were conducted in THF in the presence of $PdCl_2(o\text{-}Tol_3P)_2$. Though 1–2 mol % of the catalyst was routinely used, as little as 0.1 mol % of the catalyst was tried successfully in a few runs. Iodides reacted much faster than bromides. While phenyl trifluoromethanesulfonate (triflate) (entry 3) did not react even in a refluxing HMPA/THF mixture, quantitative conversion of vinyl triflate occurred rapidly at room temperature in dimethylacetamide (DMA)/THF, giving the desired product (entry 10) together with a diene due to homocoupling of the triflate. The reaction slows down when an aryl halide has an ortho substituent (entries 5 and 7). High chemoselectivity is illustrated in entry 6 where p-bromoacetophenone reacted only at the halide portion and did not show any complication due to the ketone function. The reaction of vinyl halides is stereospecific (entries 11–15). N,N-Dimethyl-2-iodoaniline was dehalogenated in good yield, presumably due to the decomposition of the intermediary palladium homoenolate induced by the amine function in the ortho position. This was the only case which suggested the occurrence of β-eliminative decomposition of the palladium intermediate. The following equation, preparation of dihydrocoumarin **6**, illustrates the utility of the arylated products.



6

(4) Carbonyl Addition: Homo-Reformatsky Reaction. The zinc homoenolate is virtually inert either to benzaldehyde or to acetophenone in a variety of solvents, e.g., CH_2Cl_2, $CDCl_3$, CCl_4, benzene, ether, and THF (Scheme II, eq a). Control experiments indicated the kinetic nature of this failure of addition (Scheme II, eq b). Even in the presence of a most powerful solvating agent, HMPA in THF-d_8, only very slow reaction occurred (ca. 20% after 1 h, and 40% after 3.5 h at 35 °C). It was however found that *the homoenolate rapidly (<1 min, 35 °C) adds to benzaldehyde*

Table VI. Arylation and Vinylation Reaction[a]

entry	electrophile	cyclopropane	product	%yield[b]
1		1b		67 [81]
2		1b		79 [91]
3		1b		0
4		5b		79
5		1b		83
6		1b		49 (68)
7		1b		5
8		1b		73
9		1b		68
10		1a		55
11		1b		79
12		5a		85
13		1b		85
14		1b		76
15		1b		76[c]
16		1b		90[d]
17		1b		76[e]
18		1b		87[f]

[a] For the preparation of the homoenolate, see footnote a in Table II. The reaction was performed with ca. 1.5 equiv of the homoenolate and 5 mol % of $PdCl_2(o\text{-}Tol_3P)_2$ in THF at room temperature except in entry 5, where 2.5 equiv was used. [b] Isolated yield: ^1H NMR yield in parentheses; quantitative GLC yield in brackets. [c] Starting halide, 90% E; product, 90% E. [d] Halide, >97% E; product, 100% E. [e] Halide, 89% Z; product, 86% Z. [f] Halide, >99% E; product, 99% E.

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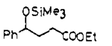
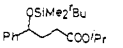
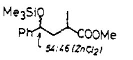
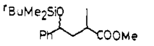
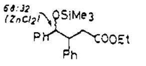
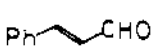
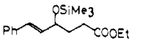
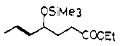
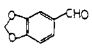
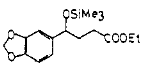
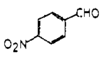
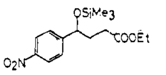
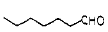
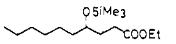
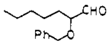
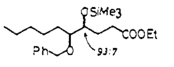
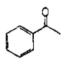
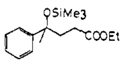
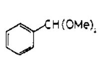
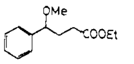
(25) Ziegler, C. B.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941.

(26) The observed inferiority of bidentate dppf may be related to the reported importance of a coordinatively unsaturated intermediate in the reductive elimination stage: Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181.

Table VII. Catalytic Homo-Reformatsky Reaction[a]

entry	carbonyl compd	cyclopropane	product	Catalyst, %yield[b] ZnCl$_2$	ZnI$_2$
1	PhCHO	1b		84	B9
2		1c		0	86
3		5a		56	72
4		5c		88	0
5		5b		83	76
6		1b		94	84
7		1b		54 (77)	72
8		1b		91	95
9		1b		--	84
10		1b		51 (74)	44 (50)
11		1b		79	--
12		1b		0	77
13		1b		0	9:

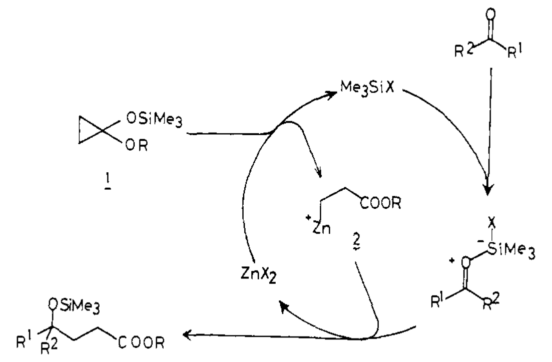
[a] The reactions were performed with 0.2–1.1 equiv of the cyclopropanes. [b] Isolated yield. The values in parentheses refer to the quantitative NMR yield.

in the presence of 1 equiv of Me_3SiCl in $CDCl_3$ to give 3-siloxy ester in quantitative yield (Scheme II, eq c). Silylation of the 4-oxido ester (separately prepared; see Experimental Section) with Me_3SiCl (Scheme II, eq e) is too slow to be involved as a step to the 4-siloxy ester. Interestingly, *the accelerating effect of Me_3SiCl disappears in ether*, in which the alkoxide is expected to be more nucleophilic than in chloroform. $ZnCl_2$ did not cause any acceleration of the rate either in ether or in chloroform.

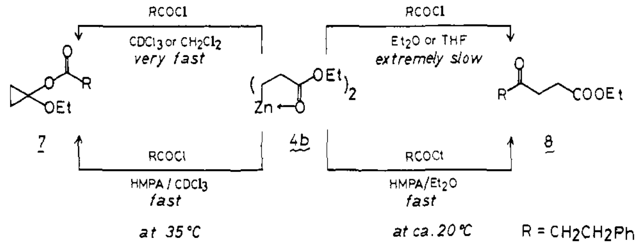
Since $ZnCl_2$ is regenerated in the Me_3SiCl-mediated addition (Scheme II, eq c), a catalytic amount of $ZnCl_2$ makes possible direct coupling of cyclopropane **1** with aldehydes. When a mixture of **1** and an aldehyde was treated with 30–50 mol % of $ZnCl_2$ in CH_2Cl_2 at room temperature, the 4-siloxy ester was obtained in good yield (Table VII). Addition of the homoenolate onto β-alkoxy aldehyde (Table VII, entry 11) proceeds with a reasonably high selectivity (93:7), giving a chelation-controlled product as a major diastereomer. ZnI_2 was then found more effective than $ZnCl_2$, and *as little as 1/1000 equiv of ZnI_2 realized direct coupling of cyclopropane 1 and aldehydes* at room temperature (Table VII). ZnI_2, but not $ZnCl_2$, promoted the addition reaction of (*tert*-butyldimethylsiloxy)cyclopropane **1c** (entry 4). ZnI_2 also catalyzed the reaction of acetophenone or benzaldehyde dimethyl acetal, which fail to react under $ZnCl_2$ catalysis (entries 12 and 13).

Pieces of evidence described above strongly support the Me_3SiX-mediated mechanism shown in Scheme III. Activation of a carbonyl or acetal function by Me_3SiI has been well documented,[27] while the Lewis acid assistance of 1,2-addition by Me_3SiCl has not been recognized thus far.[28]

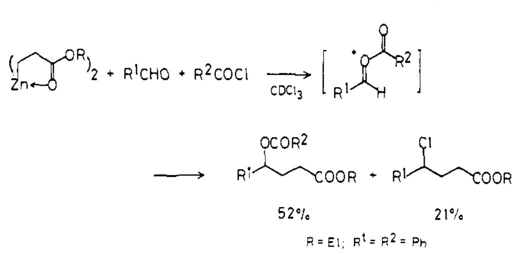
Scheme III



Scheme IV



It was a rather curious finding that *acid chloride also exercises strong accelerating effects.* The homoenolate in $CDCl_3$ is inert to benzaldehyde (vide supra) and is reactive to benzoyl chloride (vide infra). On the other hand, the reaction of the homoenolate with a mixture of these two electrophiles proceeded very rapidly at 35 °C to give an adduct due to the coupling of the aldehyde with the homoenolate (eq 12). A reaction pathway that involves activation of the aldehyde by an acyl cation is reasonable in analogy to the Me_3SiX-assisted addition. The formation of a small amount of the 4-chloro ester is no doubt due to $ZnCl_2$-assisted decomposition of an initial adduct.



(12)

(B) Reactions on Oxygen: Cyclopropane Formation. In the reactions described above, the zinc homoenolate reacted as a carbon nucleophile without interference by the internal ester group. In the following examples was found a remarkable ambident behavior of the homoenolate such as the one found frequently documented in enolate chemistry.

(1) Acylation Reaction. Inasmuch as acylation of zinc alkyls makes a straightforward ketone synthesis,[29] that of the zinc homoenolate turns out to be unexpectedly more complex, revealing the most intriguing chemical behavior of the zinc homoenolate.

The reaction of homoenolate **2b** with an acyl chloride in ethereal solvents (Scheme IV), being extremely slow without additives, proceeded very rapidly in the presence of 2 equiv of HMPA to

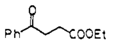
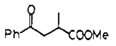
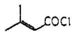
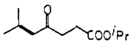
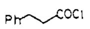
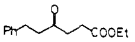
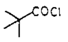
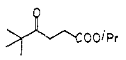
---

(27) Cf.: Sakurai, H.; Sasaki, K.; Hosomi, A. *Tetrahedron Lett.* **1981**, *22*, 745. Review: Hosomi, A. *Yuki Gosei Kagaku Kyokaishi* (*J. Synth. Org. Chem. Jpn.*) **1982**, *40*, 545.

(28) Cf.: RajanBabu, T. V. *J. Org. Chem.* **1984**, *49*, 2083.

(29) (a) Jorgensen, J. J. *Organic Reactions* **1970**, *18*, 1. (b) Negishi, E.; Bagheri, V.; Chatterjee, S.; Luo, F.-T.; Miller, J. A.; Stoll, A. T. *Tetrahedron Lett.* **1983**, *24*, 5181.

Table VIII. C-Acylation Reaction[a]

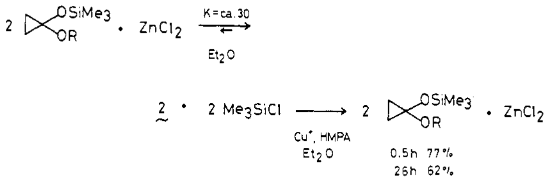
acid chloride	cyclopropane	product	catalyst	%yield
PhCOCl	1a		HMPA[b] Pd[c] Cu/HMPA[d]	76 93 76
	5a		Pd	93
	1a		Pd	81
	1b		HMPA[b] Pd[c] Cu/HMPA[d]	79 83 89
	1a		Pd	50

[a] Crude ethereal solution of the homoenolate (1.2–2.0 equiv) was allowed to react with acid chlorides at room temperature. [b] The reaction was performed in the presence of 2 equiv of HMPA. [c] $PdCl_2(Ph_3P)_2$ (5 mol %) was used as a catalyst; 0.5 equiv of the homoenolate was required for complete conversion. [d] $CuBr{\cdot}Me_2S$ (5 mol %) and HMPA (2 equiv) were used to promote the reaction.

give 4-keto ester **8** as a single product (76–79% yield). This reaction is subject to Me_3SiCl acceleration and is also catalyzed by transition metals (e.g., with particular efficiency by palladium) (Table VIII).

Surprisingly, when the acylation reaction of purified homoenolate ***4b*** *was conducted in $CDCl_3$, it proceeded via a totally different pathway to give O-acylation product* ***7*** *(single product, 56% isolated yield) due to internal nucleophilic addition.* The reaction, otherwise being quite rapid ($t_{1/2}$ = 8 min at 35 °C), slowed down upon addition of 1 equiv of HMPA and stopped on addition of excess ether.

(2) Silylation Reaction. The method of the synthesis of **2** (eq 3) deceptively suggests the inertness of Me_3SiCl toward the zinc homoenolate. Detailed examination revealed that this reaction is in fact an equilibrium with an equilibrium constant of ca. 30 in 0.2 M solution (eq 13). Addition of nonpolar compounds such



(13)

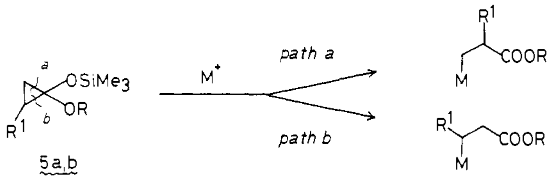
as hexane or *tert*-butyldimethylsilyl chloride (2 equiv) to the reaction mixture regenerated as much as 7–20% of the siloxycyclopropane. A large amount (ca. 60%) of the siloxycyclopropane was regenerated also in HMPA/ether, where the forward reaction is negligibly slow (eq 13).

Discussion

(A) Regioselectivity of the Homoenolate Forming Reaction. The mechanism of the siloxycyclopropane ring cleavage, the key reaction in the development of the present homoenolate chemistry, has been the constant subject of our concern.[4,5a,6a] We have already presented evidence that the metal halide mediated cleavage of siloxycyclopropane **1** is initiated not by the cleavage of the silicon–oxygen bond, but by direct interaction between the metal and the strained σ bond.[5a,b] Investigation of the regiochemistry of the ring cleavage of substituted cyclopropanes by various metals was expected to give further insights into the nature of such interaction.

We studied the reaction of cyclopropanes **5a**,**c** and **5b**,[5a] for methyl and phenyl groups are known to exert contrasting electronic and steric effects on the cleavage of cyclopropanol derivatives.[30] In Scheme V are shown two possible modes of ring cleavage (paths a and b).

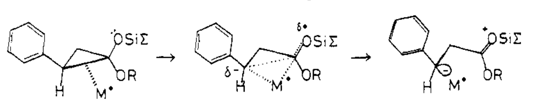
Scheme V



M+	path a : path b		13C NMR (ppm)
	R^1 = Me	R^1 = Ph	CH_3M
MeOLi/MeOD	100 : 0	0 : 100	<-10
$ZnCl_2$/PhCHO	>98 : 2	2 : >98	- -4
$Hg(OAc)_2$/EtOH	>95 : 5	22 : 78	1-10
$TiCl_4$/PhCHO	61 : 39	22 : 78	-40

Both (trimethylsiloxy)- and (*tert*-butyldimethylsiloxy)-methylcyclopropanes **5a**,**c** reacted exclusively (>98%) via path a to give 2-methyl-substituted adducts (Table VII, entries 3 and 4). In contrast, path b was the exclusive pathway for phenylcyclopropane **5b** to give the 3-substituted isomer (Table VII, entry 5). In the latter reaction, the diastereomeric ratio in the recovered cyclopropane (67:33) was very similar to that of the starting one (62:38). Thus, the attack of the metal atom onto the cyclopropane ring is very sensitive to the C-2 substituent, but insensitive to the change around C-1. While the 2-methylpropionate homoenolate could be isolated and purified, the 3-phenyl homoenolate suffered in situ protonation (no deuterium incorporation upon D_2O quench) and could not be characterized.

In order to obtain further information, the regiochemistry of the MeOLi/MeOD- and the mercury-induced reactions was also examined, and the results are compared with those of the ZnX_2- and the $TiCl_4$-mediated[5a] reactions (Scheme V). The lithium- and zinc-mediated cleavage proceeded in such a way that the anionically more stable homoenolates are formed. Such a trend is less obvious for the mercury and titanium cases that generate more covalent metal–carbon bonds. The decreased selectivity in the latter cases must mainly be due to the steric effect of the phenyl ring overriding its electronic effect. The transition state leading to a less ionic product as in the mercury and titanium cases would be less polarized than that leading to a more ionic product (eq 14; the side-one attack indicated is just for the sake of illustration),



(14)

and consequently the resonance stabilization of path b by the phenyl group becomes less important. Information provided by ^{13}C NMR spectroscopy, which gives a rough estimate of the environment of the carbon being measured, provided support to such a contention; namely, the downfield shift of the signal of the carbon bound to the metal, as we go from Li to Ti,[31] showed a very strong correlation to the observed loss of the regioselectivity as the metal changes from Li to Ti.

(B) Role of Me_3SiCl and HMPA. During the present studies, we recognized the very unexpected effects of Me_3SiCl and HMPA on the reactivities of the homoenolate. Me_3SiCl, which has been deemed as an innocuous electrophile, exhibited a strongly positive participation in nucleophilic reactions such as conjugate addition (eq 4), allylation (eq 9 and 10), and 1,2-addition (Scheme II). The best explanation of the synergetic effect of Me_3SiCl and HMPA involves a dual role of HMPA in activation of both the chlorosilane and the copper homoenolate. Before the present studies,[4a] the function of Me_3SiCl in *accelerating* nucleophilic reaction had been totally unrecognized. Four research groups, including ours, have subsequently confirmed this effect in the

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[30] Gibson, D. H.; DePuy, C. H. *Chem. Rev.* **1974**, *74*, 605.

[31] Cf. MeLi (<~10 ppm), Me_2Zn (−4 ppm), MeHgX (1–10 ppm), and $MeTi(O^iPr)_3$ (43 ppm). Data were taken from: Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: London, 1981.

Table IX. Effects of Solvent and Complexing Reagent on the ^{1}H NMR of Homoenolate **1b**

solvent	additive (equiv)	chem shift,[a] ppm C-3	chem shift,[a] ppm C-2	C/O acyln
$CDCl_3$	none	δ 0.35	δ 2.62	100:0
	HMPA (0.92)	$\Delta\delta$ −0.11	$\Delta\delta$ −0.02	
	HMPA (2.00)	$\Delta\delta$ −0.15	$\Delta\delta$ −0.07	100:0
Et_2O	none	δ 0.36	δ 2.56	7:1–1:3[b]
	HMPA (1.00)	$\Delta\delta$ −0.10	$\Delta\delta$ −0.02	
	HMPA (2.00)	$\Delta\delta$ −0.16	$\Delta\delta$ −0.03	0:100
THF-d_8	none	δ 0.25	δ 2.46	
	HMPA (0.88)	$\Delta\delta$ −0.03	$\Delta\delta$ −0.00	
	HMPA (2.00)	$\Delta\delta$ −0.08	$\Delta\delta$ +0.01	

[a] $\Delta\delta = \delta_{HMPA/solvent} - \delta_{solvent}$. Thus, a negative value indicates an upfield shift. [b] Ratios obtained under $PdCl_2(Ph_3P)_2$ catalysis in the presence of different amounts of added $ZnCl_2$ (see text).

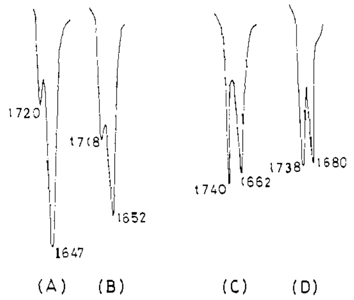


Figure 1. IR spectra of homoenolate **2b** in a 0.06 M solution of $CDCl_3$ or ether: (A) in $CDCl_3$; (B) in $CDCl_3$ with 2.0 equiv of HMPA; (C) in ether; (D) in ether with 2.0 equiv of HMPA.

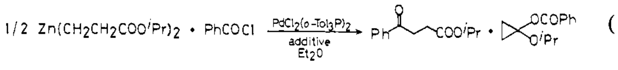
generalized conjugate additions.[12] One plausible mechanism of the Me_3SiCl participation where the chlorosilane may react with the substrate during an early stage in the conjugate addition has already been advanced.[12a] It remains only to stress that the possible Lewis acid interaction of Me_3SiCl with the substrates cannot be discounted and that this may be a more common phenomenon than has been recognized thus far. Important in this respect is the acceleration of 1,2-addition of the zinc homoenolate in halomethane (Scheme II), in which a single electron transfer mechanism is most unlikely to operate.

HMPA (or other polar solvents) is needed in many of the above reactions. In the copper-mediated reactions, especially in the allylation reaction, it must be activating the intermediary copper species.[33] Most puzzling, yet intriguing, is its control over the reaction sites in the acylation reactions (Scheme V). The solvent effect on the spectroscopic properties of the homoenolate indicated that the gross structure of the homoenolate is not affected by the solvent. In the following paragraphs, we will briefly discuss the function of HMPA in such a control.

The NMR chemical shift values (δ) of the C-2 and C-3 methylene protons of the homoenolate were recorded in the solvents used for the preparative reactions, i.e., $CDCl_3$, ether, and THF (THF-d_8), with 0, 1, and 2 equiv each of HMPA, and are shown in Table IX together with the ratio of C/O-acylation products in the respective solvent mixtures. None of these data showed meaningful correlation to the selectivity, indicating that the basic structural features of the homoenolate are retained in a variety of solvents.

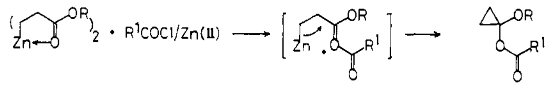
A clearer change was observed in the IR spectra (Figure 1). In $CDCl_3$ the homoenolate exists mainly in a tetracoordinated form **4** as indicated by the predominance of the absorption at 1647 cm^{-1} due to the chelated carbonyl groups.[6a] Increase of the solvent basicity (A to D) not only induces a shift of the chelated carbonyl band to higher wavenumber but also gradually intensifies the carbonyl absorption (1720–1740 cm^{-1}) due to the nonchelated ester group. Such a change is in full accord with the weaker acidity of the metal in polar solvents and consequently indicates that HMPA enhances the carbanionic activity of the homoenolate. The propionate moieties would therefore behave like a simple zinc alkyl to acylate on the carbon in HMPA/ether mixture, and this is indeed what was observed for the acylation in HMPA/ether mixture.

On the other hand, the higher Lewis acidity of the metal in a nonpolar solvent accounts for the O-acylation reaction (cf. Scheme IV). Particularly informative is the effect of added $ZnCl_2$ in the palladium-mediated benzoylation of homoenolate **1a** in ether (eq 15): The 1:1 O/C-acylation ratio being a standard value, O-acylation was enhanced by $ZnCl_2$ and effectively suppressed by a basic solvent. It is important to recognize the close similarity between the O-acylation reaction and the acylative addition (eq 12), which is most likely an external version of the former reaction. A possible rationale for the O-acylation reaction is therefore as shown in eq 16.



(15)

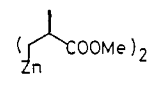
additive	ratio	%yield
20 vol%DMF	100: 0	93
none	54:46	78
1 equiv $ZnCl_2$	28:72	46



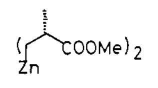
(16)

Conclusion

The studies detailed above demonstrate the diverse synthetic utility of the homoenolate species. The high chemoselectivity observed in such combinations as enone/acid chloride, enone/aldehyde, enone/allyl halide, allyl halide/nitrile, etc. is unique and may apply also for simpler zinc reagents. The utility of the present new approach to ester synthesis has been strengthened by the recent development of chiral homoenolates, e.g., (*R*)- and (*S*)-**9**.[34]



S-9



R-9

The present work also presents an important guideline for the future use of functionalized organozinc compounds and gives a strong indication that this class of nucleophiles, combined with appropriate activators, would become a viable species for the construction of highly functionalized molecules.

Experimental Section

General. All the reactions dealing with air- and moisture-sensitive compounds were carried out in a dry reaction vessel under nitrogen. Liquid samples were introduced either neat via a microsyringe or in an organic solvent via a hypodermic syringe. Solid samples were weighed into a vessel in a nitrogen-filled bag. Routine flash chromatographic purification was achieved with purified (by sedimentation) Wako C-300 silica gel using hexane/AcOEt as eluent. Medium-pressure liquid chromatography (MPLC) was performed on a Merck Lobar column under pressure (around 2 kbar) using the same solvent mixture.

^{1}H NMR spectra taken at 60 MHz (unless indicated as 200 MHz) were recorded on a Hitachi R24B spectrometer and at 200 MHz on a JEOL FX-200 instrument, which was also used for ^{13}C NMR spectra at 50 MHz. Spectra are reported in parts per million from internal tetramethylsilane. IR spectra were recorded on a Hitachi 260-10 instrument; absorptions are reported in cm^{-1}. Gas chromatographic analysis was performed on a Hitachi 063 or on a Shimazu 4BM machine equipped with a glass capillary column (0.25 mm × 25 m). GC–MS analysis was performed on a Shimazu 9020-DF equipped with an OV-1 (7 m) capillary column.

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(33) For the role of HMPA in organocopper chemistry, see: House, H. O.; Lee, T. V. *J. Org. Chem.* **1978**, *43*, 4369 and references therein.

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Table X. Conjugate Addition

acceptor mg, mmol	cyclopropane mg, mmol	$ZnCl_2$ mg, mmol	$CuBr \cdot Me_2S$ mg, mmol	HMPA mL, mmol	product mg, %
cyclohexenone	**1a**				
34, 035	263, 1.4	93, 0.68	95, 0.46	244, 1.4	93, 93
cyclohexenone	**5a**				
34. 0.35	244, 1.40	99, 0.73	144, 0.70	244, 1.4	78, 82
4-methylcyclohexenone	**1b**				
336, 3.05	1380, 7.35	489, 3.66	3.5, 0.02	1313, 7.33	718, 78
3-methylcyclohexenone	**1b**				
27.5, 0.25	261, 1.50	108, 0.79	162, 0.79	261, 1.5	64, 89
1-buten-3-one	**1b**				
52.5, 0.75	522, 3.00	288, 2.11	10, 0.05	261, 1.5	147, 80
2-ethylcrotonaldehyde	**1b**				
74, 0.75	261, 1.5	131, 1.00	6, 0.03	261, 1.5	153, 75
3-butyn-2-one	**1b**				
72, 0.75	261, 1.5	131, 1.00	6, 0.03	261, 1.5	198, 73
dimethyl acetylenedicarboxylate	**1b**				
107, 0.75	261, 1.5	131, 1.00	6, 0.03	261, 1.5	115, 63

Material. Ethereal solvents were distilled from benzophenone ketyl immediately before use. CH_2Cl_2 and $CDCl_3$ were distilled successively from P_2O_5 and K_2Cl_3 under nitrogen and stored over molecular sieves. Hexane was distilled from $LiAlH_4$ under nitrogen and stored over potassium mirror. $CuBr \cdot Me_2S$ complex was prepared as described and handled with caution as recently reported.[35]

Siloxycyclopropanes were prepared as previously described.[5a] All commercially available reagents were either distilled or recrystallized before use. Allylic halides were prepared by standard halogenation procedures either from allylic alcohol or from simple olefins. Isoprene oxide was prepared via a bromohydrin.[19] Chlorinated terpenes were prepared by the Yamamoto procedure[36] as described below.

10-Chlorocarvone. To a mixture of (+)-carvone (0.16 mL, 1.0 mmol), silica gel (0.5 g), and hexane (4 mL) was added dropwise *tert*-butyl hypochlorite (0.1258 mL, 1.1 mmol) at 0 °C, and the mixture was stirred for 3 h at room temperature. After reductive workup (aqueous Na_2SO_3) and chromatography (15% EtOAc in hexane), the title compound (140 mg, 76%) was obtained: IR (neat) 2950 (m), 2825 (m), 1670 (s), 1450 (m), 1430 (m), 1365 (m), 1255 (m), 1105 (m), 900 (m), 750 (m); ^{1}H NMR (200 MHz, $CDCl_3$) 1.79 (s), 2.10–2.74 (m), 2.89–3.10 (m), 4.11 (s), 5.07 (s), 5.27 (s), 6.78 (m); ^{13}C NMR ($CDCl_3$) 15.58 (d), 31.33 (t), 37.83 (q), 42.97 (t), 46.85 (t), 114.96 (t), 135.38 (s), 143.84 (d), 146.44 (s), 197.71 (s).

Anal. ($C_{10}H_{13}ClO$): C, H.

6-Chloro-3,7-dimethyl-2,7-octadienyl Acetate. Geranyl acetate (0.43 mL, 2.0 mmol) was chlorinated (0.5 g of silica gel) as above by *tert*-butyl hypochlorite (0.25 mL, 2.2 mmol) to obtain 382 mg (83%) of the title chloride: IR (neat) 2980 (m), 1740 (s), 1440 (m), 1370 (m), 1235 (s), 1020 (m), 960 (m), 905 (m); ^{1}H NMR (200 MHz, $CDCl_3$) 1.71 (s, 3 H), 1.79 (s, 3 H), 1.86–2.29 (m, 13 H, involving a singlet at 2.03 ppm), 4.31 (t, $J = 7$ Hz, 1 H), 4.57 (d, $J = 7$ Hz, 2 H), 4.88 (bs, 1 H), 4.99 (bs, 1 H), 5.36 (bt, $J = 7$ Hz, 1 H).

Anal. ($C_{12}H_{19}ClO_2$): C, H.

Aryl bromides were prepared by bromination of suitable aromatic compounds, and commercially unavailable iodides were prepared from bromides via lithiation/iodine quench.[37] Aryl and vinyl triflates were prepared as reported.[38] Stereoselective preparation of vinyl halides was achieved by the reaction of catechol boranes.[39] Acid chlorides were prepared by the action of thionyl chloride on the parent acids.

Conjugate Addition: Optimization Studies. To a weighed amount of $ZnCl_2$ (1.1 mmol) were added ether (3 mL) and isopropoxycyclopropane **1a** (2 mmol), and the mixture was sonicated under nitrogen for 3 h. A minimal 85% yield of the homoenolate (determined by isolation[6] in representative runs) was assumed in all runs. $CuBr \cdot Me_2S$, additives, cyclohexenone, and a hydrocarbon internal standard were added in this sequence at 0 °C with ca. 1-min intervals. The mixture was stirred at ca. 25 °C, and aliquots were removed and analyzed by capillary GLC.

Typical Procedure for the Copper-Catalyzed Conjugate Addition:[40] **3-[2-(Ethoxycarbonyl)ethyl]-1-(trimethylsiloxy)cyclohex-1-ene.** To a solution of $ZnCl_2$ (16.4–17.0 g), freshly fused under vacuum, in 500 mL of ether was added 1-(trimethylsiloxy)-1-ethoxycyclopropane[41] (**1b**: 41.80 g, 0.24 mol) during 5 min. The cloudy mixture was stirred at room temperature for 1 h and then refluxed for 30 min. The clear colorless solution of the zinc homoenolate **2b** and chlorotrimethylsilane was cooled with an ice bath, and to this was added $CuBr \cdot Me_2S$ (0.4 g, 2 mmol). Cyclohexenone (9.62 g, 0.1 mol) and then hexamethylphosphoramide (34.8 mL, 0.2 mol) were added during 5 min. (HMPA may be replaced by *N,N*-dimethylpropyleneurea at the expense of a slight decrease of the yield.[40]) A slightly exothermic reaction occurs initially and the bath is removed after 20 min. After 3 h at room temperature, 40 g of silica gel and 300 mL of dry hexane were added while the mixture was stirred vigorously. The supernatant was decanted, and the residue was extracted twice with a mixture of ether and hexane. Hexamethylphosphoramide is collected as a low-boiling fraction (about 50–80 °C), and after about 1 g of forerun, the desired product (18.9–20.5 g, 70–76%) was obtained as a fraction boiling at 122–125 °C/2.40 mmHg): IR (neat) 1730 (s), 1655 (s), 1445, 1365, 1245, 1180 (vs), 840 (vs); ^{1}H NMR (CCl_4) 0.06 (s, 9 H), 1.13 (t, 3 H, $J = 7$ Hz), 1.3–2.2 (m), 3.96 (q, 2 H, $J = 7$ Hz), 4.54 (br s, 1 H); MS (relative intensity) *m/z* 270 (M^+, 3), 225 (8), 219 (8), 182 (40), 169 (100), 75 (36), 73 (92); high-resolution MS 270.1659 (calcd for $C_{14}H_{26}O_3Si$: 270.1652). This product contains 0.2% of the double-bond regioisomer (OV-101, 120 °C), with retention times of 4.96 and 6.13 min for the major (99.8%) and the minor (0.2%) isomer, respectively.

As long as the reaction is conducted below room temperature with less than a few percent of the catalyst over a period of several hours, the reproducibility of the reaction (yield and selectivities) is very high. In small-scale runs, product was purified by column chromatography (10% EtOAc in hexane).

Details of the reaction conditions for various runs are listed in Table X. Physical properties of the addition products are listed in the Supplementary Material.

Typical Procedure for Allylation of the Zinc Homoenolate: Reaction with Cinnamyl Chloride. To a mixture of cinnamyl chloride (144 μL, 1.0 mmol), $CuBr \cdot Me_2S$ (10 mg, 0.05 mmol), and dimethylacetamide (4.5 mL) was added a 0.37 M ethereal solution of homoenolate **2a** (1.7 mmol, 4.5 mL; containing 2 equiv of Me_3SiCl), and the solution was stirred for 16 h at room temperature. The reaction mixture was diluted with ether and washed 5 times with water. After washing with saturated NaCl, drying, and concentration, the crude product was purified by chromatography (2% ethyl acetate in hexane) to obtain 148 mg (97%) of the allylated product as a 96:4 mixture of the S_N2' and the S_N2 isomers (GLC retention times on OV-1, 23 m 194 °C: 5.4 and 8.1 min, respectively). The isomers were separated by medium-pressure chromatography for analysis. **Isopropyl 4-phenyl-5-hexenoate**: bp 80 °C/0.3 mmHg; IR (neat) 2975 (s), 2925 (m), 1720 (s), 1490 (m), 1450 (m), 1370 (m), 1240 (m), 1175 (m), 750 (m), 700 (s); ^{1}H NMR (200 MHz, $CDCl_3$) 1.21 (d, 6 H, $J = 6$ Hz), 1.91–2.33 (m, 4 H), 3.26 (q, $J = 8$ Hz, 1 H), 4.89–5.14 (m, 3 H), 5.96 (ddd, $J = 17, 10, 8$ Hz, 1 H), 7.13–7.37 (m, 5 H).

Anal. ($C_{15}H_{20}O_2$): C, H.

Isopropyl *trans*-6-phenyl-4-hexenoate: bp 80 °C/0.3 mmHg; ^{1}H NMR (200 MHz, $CDCl_3$) 1.22 (d, $J = 6$ Hz, 6 H), 1.80 (tt, $J = 7, 7$

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(42) Cf.: Wehrli, F. W.; Nishida, T. *Prog. Chem. Org. Nat. Prod.* **1979**, *36*, 1.

Table XI. Arylation and Vinylation[a]

halide	cyclopropane mmol	$PdCl_2(o\text{-}Tol_3P)_2$ mg, mmol	product mg, %
bromobenzene	**1b**		
1.57, 10	16	79, 0.1	1183, 67
2-bromotoluene	**1b**		
171, 1.00	2.5	39, 0.05	160, 83
4-bromoacetophenone	**1b**		
199, 1.00	1.5	30, 0.04	109, 49
3-bromo-4-methoxy-toluene	**1b**		
278, 1.00	1.5	14, 0.02	185, 73
1-bromocyclooctene	**1b**		
189, 1.00	1.5	15, 0.02	166, 79
α-bromostyrene	**1b**		
183, 1.00	1.5	15, 0.02	171, 85
1-(1-bromoethenyl)-4-methylbenzene	**1a**		
393, 2.00	3	23, 0.03	355, 76
β-bromostyrene	**1a**		
55, 0.30	0.4	8, 0.01	54, 76
(*E*)-1-iodopentene	**1a**		
276, 0.82	0.95	8, 0.01	179, 90
(*Z*)-1-bromopentene	**1a**		
82, 0.50	0.75	8, 0.01	75, 76
(*E*)-1-bromo-1-trimethyl-siloxy)propene	**1b**		
125, 0.65	0.97	10, 0.01	121, 87

[a] The homoenolate was prepared from the cyclopropane indicated, concentrated, and redissolved in THF for the palladium-catalyzed reaction.

Hz, 2 H), 2.20–2.36 (m, 4 H), 5.01 (qq, *J* = 6, 6 Hz), 6.41 (d, *J* = 16 Hz, 1 H), 7.17–7.36 (m, 5 H).

Anal. ($C_{15}H_{20}O_2$): C, H.

Details of specific examples and physical properties of the products are listed in the Supplementary Material. Chromatographic purification was achieved on silica gel using 2–15% EtOAc in hexane as eluent.

Copper-Catalyzed Reaction with Hexenal Diethyl Acetal. A mixture of $CuBr{\cdot}Me_2S$ (5.1 mg, 0.025 mmol), the title acetal (100 μL, 0.5 mmol), chlorotrimethylsilane (125 μL, 1.0 mmol), and the zinc homoenolate (0.76 mmol) in 1.7 mL of ether was stirred for 24 h to obtain a 93:7 mixture of isopropyl (5*E*)-3-ethoxy-5-nonenoate (S_N2) and isopropyl 4-(2-ethoxy-1-ethenyl)heptanoate (S_N2') (79 mg, 65%). The ratio was estimated from ^1H NMR signals at 5.25, 5.57, and 6.15 ppm. **Isopropyl (5*E*)-3-ethoxy-5-nonenoate**: IR (neat) 2960 (m), 2920 (m), 2860 (m), 1720 (s), 1450 (w), 1370 (m), 1250 (m), 1175 (m), 1100 (m), 960 (m), 840 (w); ^1H NMR (200 MHz, $CDCl_3$) 0.88 (t, *J* = 6 Hz, 3 H), 1.15 (t, *J* = 6 Hz, 3 H), 1.22 (d, *J* = 6 Hz, 6 H), 1.40 (dt, *J* = 6 Hz, 2 H), 1.80 (m, 2 H), 2.02 (dt, *J* = 6 Hz, 2 H), 2.34 (t, *J* = 6 Hz, 2 H), 3.28 (dt, *J* = 9, 6 Hz, 1 H), 3.56 (q, *J* = 6 Hz, 2 H), 5.00 (qq, *J* = 6 Hz, 1 H), 5.25 (dd, *J* = 9, 17 Hz, 1 H), 5.57 (dt, *J* = 6, 17 Hz, 1 H), with peaks due to the minor S_N2' product at 4.40 (dd, *J* = 10, 13 Hz) and 6.15 (d, *J* = 13 Hz).

Anal. ($C_{14}H_{26}O_3$): C, H.

Nickel-Catalyzed S_N2 Allylation. To a mixture of cinnamyl chloride (14.4 μL, 0.1 mmol), Me_3SiCl (25 μL, 0.2 mmol), HMPA (35 μL, 0.2 mmol), and $NiCl_2(dppe)$ (2.6 mmol) was added dropwise a 0.41 M THF solution of homoenolate **2a** (0.36 mL, 0.15 mmol) during 1 h, and the mixture was stirred for 16 h to obtain the S_N2 allylated product (65% yield by GLC with pentadecane as an internal standard) as an exclusive product (GLC analysis), which was identical with the one obtained as the side product of the copper-catalyzed S_N2' reaction (vide supra).

General Procedure for the Arylation and Vinylation Reactions. A crude ca. 0.3 M ethereal solution of the zinc homoenolate (vide supra) is concentrated in vacuo (1 mmHg) at 30–40 °C. The yield is assumed to be ca. 80%. The residue is dissolved in THF to make a 0.5 M solution. A halide and $PdCl_2(o\text{-}Tol_3P)_2$ (0.1–2%) are weighed into another flask under nitrogen, and to it is added 1.5 equiv of the homoenolate at 0 °C. The mixture is stirred overnight at room temperature. About 5 equiv each of powdered KF and water is added, the suspension is stirred for 3 h, and the organic phase is separated. The desired product is obtained either by chromatography (3–10% EtOAc in hexane as eluent) or by distillation under reduced pressure.

Experimental details are summarized in Table XI and the physical properties of the products are listed in the Supplementary Material.

General Procedure for $ZnCl_2$-Catalyzed Homo-Reformatsky Reaction. About 0.3–0.5 equiv of freshly fused $ZnCl_2$ is suspended in methylene chloride (1–2 mL/mmol). A siloxycyclopropane (1.2–1.5 equiv) is added, and after 5 min an aldehyde (1 equiv) is added. After stirring for 1–5 h at 20–27 °C, the reaction mixture is diluted with ether. TLC analysis (30% ethyl acetate in hexane) usually indicates a very clean reaction. If TLC analysis indicates the formation of 4-hydroxy ester as a side product, triethylamine (1 mmol) and Me_3SiCl (0.5 mmol) are added at this point. The mixture is filtered and washed with water. The desired adduct may be isolated either by distillation or by chromatography on silica gel using 10–15% EtOAc in hexane as eluent.

Table XII. Catalytic Homo-Reformatsky Reaction (CH_2Cl_2, 20–25 °C)

aldehyde mg, mmol	cyclopropane mg, mmol	ZnX_2 mg, mmol	time h	product mg, %
benzaldehyde	**1b**	X = Cl		
63, 0.59	129, 0.74	39, 0.29	1	138, 84
benzaldehyde	**1c**	X = I		
58, 0.55	140, 0.61	3.5, 0.011	1	159, 86
benzaldehyde	**5a**	X = Cl		
106, 1.00	175, 1.00	65, 0.474	3	159, 56
benzaldehyde	**5b**	X = Cl		
21, 0.21	55, 0.22	16, 0.12	17	58, 76
cinnamaldehyde	**1b**	X = Cl		
78, 0.59	129, 0.74	21, 0.15	0.5	168, 91
cinnamaldehyde	**1b**	X = I		
50, 0.38	79, 0.45	2.4, 0.008	1	99, 84
crotonaldehyde	**1b**	X = Cl		
21, 0.29	77, 0.44	12, 0.09	0.5	38, 54
crotonaldehyde	**1b**	X = I		
1110, 15.8	3100, 17.8	51, 0.16	1	2780, 72
piperonal	**1b**	X = Cl		
81, 0.54	91, 0.52	39, 0.29	1	178, 91
piperonal	**1b**	X = I		
59, 0.39	81, 0.46	2.5, 0.008	1	121, 95
hexanal	**1b**	X = Cl		
102, 1.02	361, 2.07	69, 0.50	18	141, 51
hexanal	**1b**	X = I		
115, 1.15	404, 2.32	7.3, 0.023	18	139, 44
benzaldehyde dimethyl acetal	**1b**	X = I		
193, 1.27	258, 1.48	7.9, 0.025	4	256, 91

Typical Procedure for the ZnI_2-Catalyzed Addition Reaction: Ethyl 4-Phenyl-4-(trimethylsiloxy)butanoate. To a flask containing ZnI_2 (94 mg, 0.3 mmol) is added a solution of ethoxycyclopropane **1b** (20.9 g, 0.12 mol) and benzaldehyde (10.6 g, 0.10 mol) in 60 mL of methylene chloride cooled with a water bath. A slightly exothermic reaction continues for a while and the clear solution is stirred for 4 h. Dry pyridine (0.05 mL, 0.06 mmol) is added, the mixture is concentrated, and the crude product is distilled under vacuum. After a ca. 1.5-g forerun, the title ester (23.8–24.7 g, 85–88%) is obtained: bp 122–125 °C/2.3 mmHg; IR (neat) 1725 (s), 1250 (s), 840 (s); ^1H NMR (CCl_4) 0.0 (s, 9 H), 1.19 (t, *J* = 7 Hz, 3 H), 1.6–2.05 (m, 2 H), 2.05–2.4 (m, 2 H), 3.94 (q, *J* = 7 Hz, 2 H), 4.55 (t, *J* = 6 Hz, 1 H), 7.02 (s, 5 H).

Anal. ($C_{15}H_{24}O_3Si$): C, H.

Experimental details are summarized in Table XII, and the physical properties of the homo-Reformatsky products are listed in the Supplementary Material.

Me_3SiCl-Mediated Addition of the Homoenolate onto Benzaldehyde (Scheme III). To a solution of bis[2-(isopropoxycarbonyl)ethyl]zinc (**4a**, 0.18 mmol) in 0.4 mL of CCl_4 or $CDCl_3$ at 35 °C was added benzaldehyde (0.20 mmol). ^1H NMR analysis for a period of 1 h indicated less than 5% reaction. Analysis of the mixture after addition of 0.20 mmol of Me_3SiCl indicated quantitative formation of isopropyl 4-phenyl-4-(trimethylsiloxy)butanoate after about 1 min in $CDCl_3$ and after 5 min in CCl_4.

Preparation and Silylation of Ethyl 4-Oxido-4-phenylbutanoate. To a CCl_4 solution (ca. 0.2 mol) of ethyl 4-hydroxy-4-phenylbutanoate (0.365 mmol) in an NMR sample tube was added a solution of the solvent-free homoenolate, bis[2-(isopropoxycarbonyl)ethyl]zinc (**4a**, 0.18 mmol) in 0.3 mL of CCl_4. Deprotonation was instantaneous, giving the 4-oxido ester (as a dialkoxyzinc) in quantitative yield. Important changes of the spectrum involved the downfield shift of the signal due to the benzylic position from 4.53 (br t) to 5.33 ppm and the change of the OCH_2CH_3 signal at 3.97 ppm (q) to a very broad one.

After 15 min, 0.4 mmol of Me_3SiCl was added to this solution, and the progress of the reaction was monitored by ^1H NMR at 35 °C. The 4-siloxy ester formed in 20% yield after 20 min and in quantitative yield after 13 h. TLC analysis of the final reaction mixture indicated the formation of a very small amount of butyrolactone due to cyclization of the starting material. The reaction rate of the Me_3SiCl-mediated addition of the homoenolate onto benzaldehyde (vide supra) is overwhelmingly faster than the silylation of the zinc alkoxide.

4-(Benzyloxy)-4-phenylbutanoate. To a solution of the ether-free zinc homoenolate (0.069 mmol) in $CDCl_3$ (0.3 mL) was added a mixture of benzaldehyde (14 μL, 0.138 mmol) and benzoyl chloride (16 μL, 0.138 mmol). The reaction was monitored by 60-MHz NMR at 35 °C and was found to be complete after 30 min. The mixture was diluted with ether and washed with saturated NaCl. Purification of the crude product gave the title compound (20 mg, 52%) and ethyl 4-chloro-4-phenylbutanoate (6 mg, 21%), which was identical with an authentic sample. Treatment of the benzoylated adduct with aqueous NaOH and then *p*-toluenesulfonic acid gave a known γ-lactone.[5a]

The title compound showed the following spectra: IR (neat) 1720 (vs), 1600 (w), 1445 (m), 1260 (s), 1105 (m), 1020 (m), 750 (m), 705 (s), 695 (s); ^{1}H NMR (CCl_4) 1.17 (t, J = 7 Hz, 3 H), 1.7–2.5 (m, 4 H), 3.97 (q, J = 7 Hz, 2 H), 5.95 (m, 1 H), 7.0–7.5 (m, 8 H), 7.8–8.15 (m, 2 H).

C-Acylation of the Homoenolate: Ethyl 4-Oxo-6-phenylhexanoate. To a crude solution of the zinc homoenolate prepared from $ZnCl_2$ (88 mg, 0.65 mmol) and ethoxycyclopropane **1b** (226 mg, 1.30 mmol) were added at 0 °C HMPA (233 mg, 1.30 mmol) and 3-phenylpropionyl chloride (73 mg, 0.43 mmol). After 2 h at 0 °C, the reaction was almost complete (TLC). After 6 h, 0.5 g of silica gel was added and the mixture was filtered. The crude product was distilled to give 80 mg (79%) of the title 4-oxo ester, which was homogeneous by TLC (10% EtOAc in hexane): bp 100–102 °C/0.6 mmHg; IR (neat) 1715 (vs), 1602 (w), 1495 (w), 1450 (m), 1410 (m), 1370 (s), 1180 (vs), 1095 (s), 1028 (m), 748 (s), 700 (s); ^{1}H NMR (CCl_4) 1.23 (t, J = 7 Hz, 3 H), 2.2–3.1 (m, 8 H), 4.07 (q, J = 7 Hz, 2 H), 7.15 (s, 5 H).

Anal. ($C_{14}H_{18}O_3$): C, H.

O-Acylation of the Homoenolate: 1-Ethoxy-1-[(3-phenylpropanoyl)oxy]cyclopropane. A crude solution of zinc homoenolate prepared from $ZnCl_2$ (104 mg, 0.76 mmol) and ethoxycyclopropane (387 mg, 2.22 mmol) was concentrated in vacuo at room temperature. After addition of ca. 0.5 mL of methylene chloride, followed by 3 mL of hexane, a portion of the supernatant was transferred to another reaction vessel. The solvent was removed in vacuo to leave 0.124 mmol of the solvent-free homoenolate. To a $CDCl_3$ solution of this product 0.22 mmol (34 mg) of 3-phenylpropionyl chloride was added and allowed react for 50 min at 35 °C under NMR monitoring (56% NMR yield). Purification by chromatography (10% EtOAc in hexane) gave the title cyclopropane (25 mg, 47%): bp 67–68 °C/0.4 mmHg; IR (neat) 1750 (vs), 1600 (w), 1450 (m), 1315 (s), 1180 (s), 1130 (s), 1115 (s), 1055 (s), 1038 (s), 795 (s), 760 (s); ^{1}H NMR (CCl_4) 0.75–1.0 (m, 4 H, cyclopropane), 1.05 (t, J = 7 Hz, 3 H), 2.3–2.65 (m, 2 H), 2.65–3.0 (m, 2 H), 3.44 (q, J = 7 Hz, 2 H), 6.93 (s, 5 H).

Anal. ($C_{14}H_{18}O_2$): C, H.

1-Ethoxy-1-(benzoyloxy)cyclopropane: bp 62–63 °C/1.1 mmHg; IR (neat) 1730 (s), 1600 (w), 1450 (m), 1320 (s), 1278 (s), 1195 (s), 1150 (m), 1088 (s), 1055 (s), 902 (m), 708 (s); ^{1}H NMR (CCl_4) 1.10 (s, 4 H, cyclopropane), 1.15 (t, J = 7 Hz, 3 H), 3.76 (q, J = 7 Hz, 2 H), 7.2–7.6 (m, 3 H), 7.9–8.1 (m, 2 H).

Anal. ($C_{12}H_{14}O_3$): C, H.

MeOLi-Induced Ring Cleavage of Siloxycyclopropanes. To a ca. 0.3 M solution MeOLi (0.1 mmol) in MeOD/hexane (prepared by addition of *n*-butyllithium in hexane to MeOD) was added cyclopropane **5a** or **5b** (neat, 0.3 mmol), and the mixture was stirred overnight at room temperature. GLC analysis indicated completely regioselective conversion to the 2-methyl- or 3-phenylpropionate. Mass spectral analysis of 2-methylpropionate indicated a high degree of deuterium incorporation and an NMR analysis of the 3-phenylpropionate indicated a high level of deuterium incorporation only at the 3-position.

Acetoxy[2-(methoxycarbonyl)propyl]mercury. To a suspension of mercuric acetate (159 mg, 0.5 mmol) in 1 mL of methylene chloride at room temperature was added methylcyclopropane **5a** (100 μL, 0.5 mmol). After 16 h, quantitative NMR analysis indicated 93% of the title product. Bulb-to-bulb distillation gave the title product (164 mg, 91%) as an oil which solidified on cooling: mp 43–44 °C (hexane/ethyl acetate); bp 125–130 °C/0.08 mmHg; IR (CCl_4) 1718 (m), 1571 (vs); ^{1}H NMR ($CDCl_3$) 1.28 (d, J = 6.5 Hz, 3 H), 1.9–2.1 (m, involving a singlet at 2.01, 5 H), 2.95 (unresolved tq, J = 6, 7 Hz, 2 H), 3.68 (s, 3 H); ^{1}H NMR (1:1 benzene/$CDCl_3$) 1.10 (d, 3 H), 1.45, 1.75 (m, 2 H), 1.97 (s, 3 H), 2.71 (unresolved tq, J = 7 Hz), 3.62 (s, 3 H).

Anal. Calcd for $C_7H_{12}O_4Hg$: C, 23.31; H, 3.36. Found: C, 23.21; H, 3.15.

Spectral Studies of the Homoenolate Structure. The zinc homoenolate was prepared and purified as previously reported[6] and dissolved in a specified solvent to make a 0.50 M solution for the NMR studies and a 0.06 M solution for the IR studies. Although several times more dilute conditions were desirable for IR studies for elimination of intramolecular coordination, such conditions tended to give much less reproducible results due probably to water contamination.

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Supplementary Material Available: General data from the experiments, physical properties of products, and experimental details of allylation (12 pages). Ordering information is given on any current masthead page.