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1,4-Addition of Triorganozincates and Silyldiorganozincates to α,β-Unsaturated Ketones

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Lithium and magnesium triorganozincates, prepared by combination of $ZnCl_2$(TMEDA) with 3 molar equivalents of RLi or RMgX, or from dialkylzinc and 1 molar equivalent of RLi or RMgX, react with 2-cyclohexen-1-one (**1**) under mild conditions to produce moderate to good yields of the 1,4-addition products **2**. The approximate reactivity order obtained from the product distribution using unsymmetrical zincates is tBuCH$_2$ $\ll$ tBu, Me < Ph, iBu < Et, nBu, iPr, CH=CH$_2$ $\ll$ Me$_2$PhSi. The latter groups are transferred with good selectivity from mixed reagents derived from Me_2Zn. This sequence differs strikingly from that exhibited by unsymmetrical cuprates which transfer neopentyl very easily, and also *tert*-butyl more easily than the corresponding zincates. The methylation with Me_3ZnLi is catalyzed by cobalt complexes. Other enones (**7** – **13**) generally give poor yields, and the cobalt-catalyzed methylation of isophorone (**3**) is complicated by a Kharasch-type deconjugation. Mixed silyldialkylzincates, $Me_2PhSiZnR_2Li$, produce the β-silyl ketones from a variety of unhindered or moderately hindered enones in practically useful yields; one example of an α,β-unsaturated ester (**12**) is also included.

1,4-Addition von Triorganozinkaten und Silyldiorganozinkaten an α,β-ungesättigte Ketone

Lithium- und Magnesiumtriorganozinkate, die aus $ZnCl_2$(TMEDA) oder Dialkylzink und RLi oder RMgX (3 bzw. 1 Moläquivalent) erhalten werden, reagieren mit 2-Cyclohexen-1-on (**1**) unter milden Bedingungen in mäßigen bis guten Ausbeuten zu den 1,4-Additionsprodukten **2**. Aus der Produktverteilung bei Verwendung unsymmetrischer Zinkate ergibt sich die ungefähre Reihenfolge der Reaktivität: tBuCH$_2$ $\ll$ tBu, Me < Ph, iBu < Et, nBu, iPr, CH=CH$_2$ $\ll$ Me$_2$PhSi. Reagenzien auf der Basis von Me_2Zn übertragen die letzteren Gruppen mit guter Selektivität. Die Methylierung mittels Me_3ZnLi wird von Cobaltkomplexen katalysiert. Andere Enone (**7** – **13**) geben durchweg schlechte Ausbeuten, und die cobaltkatalysierte Methylierung von Isophoron (**3**) wird von einer Dekonjugierung im Sinne einer Kharasch-Reaktion begleitet. Gemischte Silyldialkylzinkate, $Me_2PhSiZnR_2Li$, ergeben ausgehend von ungehinderten oder mäßig gehinderten Enonen β-Silylketone in brauchbaren Ausbeuten; an einem Beispiel wird auch die Addition an einen α,β-ungesättigten Ester (**12**) belegt.

The 1,4-addition of hydrocarbon groups to α,β-unsaturated carbonyl compounds is conventionally achieved using organocuprate reagents$^{1)}$. Only little attention has been paid to the related reactions of diorganozinc compounds$^{2)}$ and triorganozincates$^{3)}$, and their scope remains to be established. We became interested in zincates in connection with our work on the silylmetalation of acetylenes$^{4)}$ and decided to reexamine their behaviour toward α,β-unsaturated ketones.

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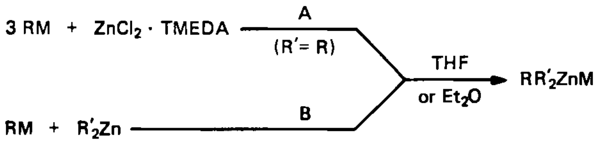
A. Preparation of the Reagents

THF or ether solutions of lithium- and magnesium triorganozincates were prepared by stirring a suspension of $ZnCl_2(TMEDA)$ or a solution of the $ZnCl_2$-diethyl ether complex with the threefold molar amount of the appropriate organolithium[3] or Grignard reagent at 0°C for 15 minutes (Scheme 1, path A), or by the equal treatment of a dialkylzinc solution (path B). The latter method allows the preparation of unsymmetrical zincates which were frequently used in this work. The reagent generally forms a clear colourless solution at 0°C, but in some cases a white precipitate appears on cooling to lower temperatures.

Scheme 1

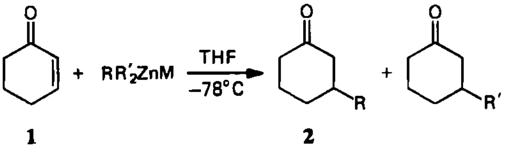


(M = Li, MgCl, MgBr, MgI)

B. Addition Reactions to 2-Cyclohexen-1-one

A 20% excess of various zincate reagents was allowed to react with 2-cyclohexen-1-one (**1**) in THF at −78°C for 1 hour; the results are summarized in Tables 1 and 2. 3-Substituted cyclohexanones **2a**–**l** (Scheme 2) were obtained in variable yields. In a control experiment, diethylzinc alone under otherwise identical conditions produced a 1% yield of **2c**, leaving 68% of the starting material unchanged. We generally observed partial decomposition of the substrate with insufficiently or moderately reactive reagents, accompanied by the appearance of diffuse polar zones in the thin layer chromatogram which do not contain substantial quantities of defined products (in particular, the 1,2-adduct). The combinations of diethylzinc and triethylaluminium, or 1-lithio-1-pentyne afforded **2c** in a poor 1 or 22% yield, respectively.

Scheme 2



1 **2**

	R		R
2a	H	**2g**	*i*Bu
b	Me	**h**	*t*BuCH$_2$
c	Et	**i**	Ph
d	*n*Bu	**j**	CH=CH$_2$
e	*i*Pr	**k**	C(Me)=CH$_2$
f	*t*Bu	**l**	Me$_2$PhSi

The results in Tables 1 and 2 demonstrate that unsymmetrical organozincates can exhibit a considerable selectivity for the transfer of only one of its different groups. The situation is, of course, complicated by the 1:2 ratio of the groups; thus, the comparison of $Me_2(tBu)ZnLi$ and $Me(tBu)_2ZnLi$ (Table 1, entry 8 B, and Table 2, entry 1 B) demonstrates different relative reactivities of Me vs. *t*Bu in both cases. Furthermore, the counterion exerts a strong influence on the selectivity as shown by the comparison of $Me_2(tBu)ZnM$ for M = Li vs. MgCl (Table 1, entries 7 B and 8 B), which differ by the respectable factor of 27. Nevertheless, the roughly qualitative order of reactivity can be established as $tBuCH_2 \ll tBu$, $Me < Ph$, $iBu < Et$, *n*Bu, *i*Pr, $CH=CH_2 \ll Me_2PhSi$. The lower reactivity of methyl as compared with *n*- and *sec*-alkyl groups allows the selective transfer of these groups; equally well, MeLi activates the corresponding dialkylzinc compounds for conjugate addition. Methyltrialkylborates have found a related use in borate chemistry[5]. Interestingly, although *tert*-butyl can be transferred in moderate yield, neopentyl is perfectly inert. Entry 10B (Table 1) demonstrates the potential synthetic utility of neopentyl-containing unsymmetrical zincates, the yield of **2b** being the best under the general conditions of Table 1. Even the lower degree of β-branching in the isobutyl group reduces the selectivity of its transfer vs. methylation considerably (Table 1, entry 9B).

Table 1. Reaction of 2-cyclohexen-1-one (**1**) with 1.2 molar equivalents of triorganozincates, R_3ZnM (A), RMe_2ZnM (B), and REt_2ZnM (C) in THF at −78 °C for 1 hour[a)]

Entry No.	RM	R_3ZnM (A)[b)] Products(Yield(%))[c)]	RMe_2ZnM (B) Products(Yield(%))[c)]	REt_2ZnM (C) Products(Yield(%))[c)]
1	$LiBHEt_3$		**1** (9) **2a** (21)	**1** (7) **2a** (30) **2c** (9)
2	MeLi	**1** (17) **2b** (37)	**1** (18) **2b** (55)	**2b** (<1) **2c** (92, $\underline{79}$[d)])
3	MeMgI	**1** (3) **2b** (65)	**1** (33) **2b** (8)	
4	EtMgBr	**1** (2) **2c** (70)		**2c** (94)
5	nBuLi	**2d** (90)[e)]	**2d** (92) **2b** (3)	**2d** (14) **2c** (77)
6	iPrMgBr	**2e** (81)	**1** (2) **2e** (65)	
7	tBuMgCl	**1** (4) **2f** (67)[f,g)]	**2f** (5) **2b** (68)	**2f** (6) **2c** (84)
8	tBuLi		**1** (38) **2f** (20) **2b** (10)	
9	iBuMgBr	**2g** (81, $\underline{63}$)	**2g** (67) **2b** (18)	
10	$tBuCH_2MgBr$	**1** (69)[g)]	**2b** (73)	
11	PhMgBr		**2i** ($\underline{62}$) **2b** ($\underline{4}$)[h)]	**2i** ($\underline{3}$) **2c** ($\underline{53}$)[h)]
12	$CH_2=CHMgBr$	**2j** (72, $\underline{48}$)	**2j** (87, $\underline{50}$)	**2j** (28) **2c** (31)
13	$CH_2=C(Me)MgBr$		**1** (3) **2k** (48, $\underline{42}$)	**1** (30) **2k** (7) **2c** (3)
14	$Me_2PhSiLi$	**2l** ($\underline{70}$)	**1** ($\underline{3}$) **2l** ($\underline{76}$)[i)]	**2l** ($\underline{85}$)

[a)] Reaction scale 0.5 – 1 mmol. – [b)] From $ZnCl_2(TMEDA)$ + 3 RM if not otherwise stated. – [c)] GC yield (isolated yield with underline). – [d)] Reaction scale 5 mmol. – [e)] 89% from $ZnCl_2(dppe)$; 85% from $ZnCl_2 \cdot Et_2O$. – [f)] Reaction time 3 h. – [g)] Zincate prepared from $ZnCl_2 \cdot Et_2O$. – [h)] Isolated as a mixture and analyzed by NMR. – [i)] 1.05 molar equivalents of the reagent were used.

Previous work on unsymmetrical cuprates[6)] has demonstrated a strong dependence of the selectivity on the substrate structure; we therefore undertook a few alkylations of cyclohexenone with unsymmetrical cuprates for the purpose of comparison (Table 3). Interestingly, neopentyl is now a very reactive group and can be transferred with good selectivity from a mixed methylneopentylcuprate.

Table 2. Reaction of 2-cyclohexen-1-one (**1**) with 1.2 molar equivalents of triorganozincates, $R(iPr)_2ZnM$ (A) and $R(tBu)_2ZnM$ (B) in THF at −78°C for 1 hour[a]

Entry No.	RM	$R(iPr)_2ZnM$ (A) Products (Yield(%))[b]	$R(tBu)_2ZnM$ (B) Products (Yield(%))[b]
1	MeLi	**2b** (3) **2e** (94)	**1** (20) **2b** (9) **2f** (32)
2	nBuLi	**2d** (19) **2e** (66)	
3	iPrMgBr	**2e** (78, $\underline{70}$[c])	
4	tBuMgCl		**1** (30) **2f** (48)
5	$Me_2PhSiLi$	**2l** ($\underline{79}$)	**2l** ($\underline{75}$) **2f** ($\underline{6}$)[d]

[a] Reaction scale 0.5 – 1 mmol. – [b] GC yield (isolated yield with underline). – [c] Reaction scale 5 mmol. – [d] Isolated as a mixture and analyzed by NMR.

Table 3. Reaction of 2-cyclohexen-1-one (**1**) with 1.2 molar equivalents of unsymmetrical dialkylcuprates, prepared from RM, R'M, and CuI in diethyl ether for 1 hour[a]

Entry No.	RM	R'M	temperature (°C)	Product/Yield(%)[b] R Transfer	Product/Yield(%)[b] R' Transfer
1	MeLi	EtMgBr	0	**2b**/25	**2c**/56
2	MeLi	$tBuCH_2MgBr$	0	**2b**/5	**2h**/90(66)
3	EtMgBr	$tBuCH_2MgBr$	0	**2c**/11	**2h**/63
4	MeLi	tBuMgCl	−20	**2b**/12	**2f**/90
5	MeLi	PhMgBr	0	**2b**/21	**2i**/49
6	MeLi	$Me_2PhSiLi$[c]	0	**2b**/(9)[d]	**2l**/(65)[d]

[a] Reaction scale 0.5 mmol. – [b] GC yield (isolated yield in parentheses). The starting material was consumed completely. – [c] As a solution in THF. – [d] Isolated as a mixture and analyzed by NMR.

Table 4. Reaction of 2-cyclohexen-1-one (**1**) with 1.2 molar equivalents of $Me_2(nBu)ZnLi$ in various solvents at −78°C for 1 hour[a]

Entry No.	Solvent[b]	Additive (molar equivalents)	Yield(%)[c] **1**	**2b**	**2d**
1	hexane	—	0	10	66
2	toluene	—	1	4	69
3	CH_2Cl_2[d]	—	5	2	75
4	diethyl ether	—	0	5	91
5	THF	—	0	3	92
6	DME	—	47	0	14
7	DMF/THF (4:1)[d]	—	31	0	0
8	THF	$BF_3 \cdot OEt_2$(1.2)	0	16	75
9	THF	$Co(acac)_3$(0.02)	3	4	70
10	DME	$Co(acac)_3$(0.02)	47	5	16

[a] Reaction scale 1 mmol. – [b] Hexane from BuLi and Me_2Zn was also present (approx. 25% of the total amount of solvent). – [c] GC yield. – [d] Added after formation of the zincate.

Conjugate reduction could be accomplished by the combination of $LiBHEt_3$ and Me_2Zn (Table 1, entry 1), but yields and selectivities are far from being synthetically useful. On the other hand, the reagents from $Me_2PhSiLi$ and various dialkylzinc derivatives silylate cyclohexenone in good yields and selectivities (Table 1, entry 14, and Table 2, entry 5). Only with $(t\mathrm{Bu})_2Zn$, a significant formation of alkylated byproduct was observed. This is unexpected from the otherwise low reactivity of *tert*-butyl, and one may speculate that the reason is the high degree of steric crowding in the reagent which can be diminished more efficiently by transfer of the *tert*-butyl rather than the silyl group.

Table 5. Methylation of 2-cyclohexen-1-one (1) with 1.2 molar equivalents of Me_3ZnLi in THF at −78 °C for 1 hour under the influence of additives[a]

Entry No.	Additive	(molar equivalents)	Yield (%)[b]	
			1	2b
1	none		18	55
2	none[c]		0	80
3	$BF_3 \cdot OEt_2$	(1.2)	26	59
4	LiOMe	(1.2)	60	20
5	TMEDA	(1.2)	47	28
6	$(C_5H_5)_2TiCl_2$	(0.02)	40	24
7	VCl_4	(0.02)	25	51
8	$Cr(acac)_3$	(0.02)	55	32
9	$MoO_2(acac)_2$	(0.02)	52	38
10	Li_2MnCl_4	(0.02)	37	36
11	$Fe(acac)_3$	(0.02)	37	23
12	$CoCl_2(PPh_3)_2$	(0.02)	0	79
13	$Co(acac)_3$	(0.02)	0	102
14	$NiCl_2(PPh_3)_2$	(0.02)	57	22
15	$Ni(acac)_2$	(0.02)	32	44
16	$RhCl(PPh_3)_2$	(0.02)	45	30
17	$PdCl_2(PPh_3)_2$	(0.02)	44	40
18	$PdCl_2(CH_3CN)_2$	(0.02)	0	82
19	CuCN	(0.02)	19	50
20	$CuBr \cdot SMe_2$	(0.02)	23	55
21	$AgNO_3$[d]		34	29

[a] Reaction scale 1 mmol. – [b] GC yield. – [c] Diethyl ether as the solvent. – [d] 0.02 molar equivalents were weighed into the reaction flask, but only a small part of the salt dissolved.

We briefly examined the applicability of other solvents for the addition of $Me_2(n\mathrm{Bu})ZnLi$ to cyclohexenone as shown in Table 4, entries 1 – 7. Hydrocarbon solvents, as well as methylene chloride, can be used, although with some sacrifice of yield and selectivity. DME and DMF suppress the reaction. All further experiments were therefore carried out in THF or diethyl ether.

C. Catalyzed Methylation of 2-Cyclohexen-1-one and Isophorone

We next examined the effect of various additives, predominantly transition metal salts and complexes, on the methylation of cyclohexenone with Me_3ZnLi. The results are summarized in Table 5. Although ether is a better solvent than THF for this individual reaction (entry 2), we consistently used THF because the lower yield in this solvent leaves more room for improvement.

The reactivity of ketones toward 1,2-addition of organolithium compounds has been reported[7] to be enhanced by $BF_3 \cdot$ ether; however, this additive showed little effect on the yield of the title reaction (entry 3). The selectivity of $Me_2(n\text{Bu})ZnLi$ is considerably reduced (Table 4, entry 8), the total yield being nearly the same as with the unmodified reagent. Added bases (Table 5, entries 4 and 5) reduce the yield.

Recent publications describe the catalysis of the addition of Et_2Zn to aromatic aldehydes by Co and Pd complexes[8] as well as the catalysis of the 1,4-addition of diarylzinc compounds and Me_2Zn to enones by $Ni(acac)_2$[2]. It was therefore desirable to know whether transition metal catalysis can also be applied to the title reaction. Ni complexes as well as most of the other potential catalysts proved ineffective or even decreased the yield. Among the Pd complexes, $PdCl_2(PPh_3)_2$ is not a catalyst whereas $PdCl_2(CH_3CN)_2$ is moderately effective. The latter is instantaneously reduced to a black Pd suspension on addition of Me_2Zn; therefore, the finely divided Pd metal must

Table 6. Methylation of isophorone (3) with Me_3ZnLi[a]

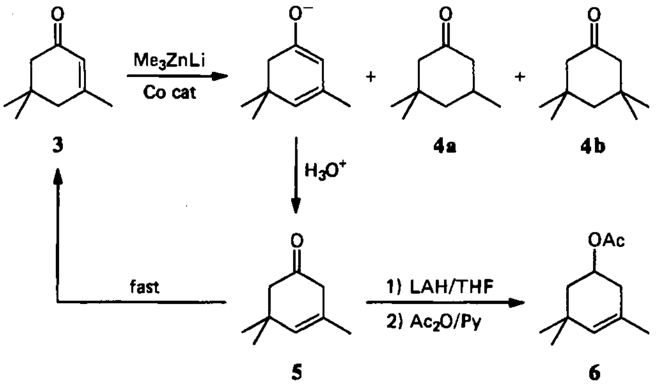
Entry No.	Molar equiv. of Reagent	Catalyst (Molar equiv.)	Solvent	Temp (°C)	Time (h)	Yields(%)[b]			
						3	4a	4b	5
1	1.2	none	ether	-78	1	93	0	0	0
2	1.2	$PdCl_2(CH_3CN)_2$ (0.02)	THF	-78	1	67	<1	<1	0
3	1.2	$CoBr_2$ (0.02)	THF	-78	1	87	2	0	+
4	1.2	$Co(acac)_3$ (0.02)	THF	-78	1	86	5	0	+
5	1.2	$Co(acac)_3$ (0.02)	ether	-78	1	94	0	0	0
6	1.5	$Co(acac)_3$ (0.1)	ether	-40	3	83	6	3	0
7	1.5	$CoCl_2(PPh_3)_2$ (0.1)	ether	-78	6	51	26	15	0
8	1.5	$CoCl_2(PPh_3)_2$ (0.1)	ether	-40	1	56	13	13	+
9	1.5	$CoCl_2(PPh_3)_2$ (0.1)	THF	-40	1	+	9	0	++
10	1.5	$CoCl_2(PPh_3)_2$ (0.1)	toluene	-40	1	72	5	<1	+
11	1.5	$CoCl_2(PPh_3)_2$ (0.1) $BF_3 \cdot OEt_2$ (1.2)	ether	-40	1	8	4	<1	+
12	1.5	$CoCl_2$(dppe) (0.1)	ether	-78	6	63	21	6	0
13	1.5	$CoCl_2$(dppe) (0.1)	ether	-40	1	60	26	6	+
14	1.5	$CoCl_2$(dppe) (0.1)	ether	0	1	+	8	3	++
15	3	$CoCl_2$(dppe) (0.2)	ether	-40	1	56	18	3	+
16	1.5	salcomin[c] (0.1)	ether	-40	1	62	14	4	+
17	1.5	salcomin[c] (1.0)	ether	-40	1	83	0	0	0

[a] Reaction scale 1 mmol. – [b] GC yield; + low to moderate yield; + + high yield. – [c] [*N,N'*-Bis(salicylidene)ethylenediamine]cobalt(II).

be the (heterogeneous) catalyst. The best results were obtained with Co complexes. $CoCl_2(PPh_3)_2$ is moderately, $Co(acac)_3$ highly effective, the latter producing a quantitative yield of 3-methylcyclohexanone (**2b**)[9].

Methylation of the sterically hindered enone isophorone (**3**) was found to be much more difficult, and in fact could not be achieved in a practically useful yield under any of the conditions of Table 6. The reaction is complicated by the formation of the 1,4-reduction product **4a**, and by enolization giving rise, after workup, to the deconjugated enone **5** which rapidly reverts to the starting material (Scheme 3). The deconjugation is especially important with the cobalt phosphane complex catalysts, when the solvent is THF (entry 9), or when the reaction temperature is too high (entry 14); it can be avoided by working at −78 °C. The resulting isomeric enone **5** can be detected by gas chromatography – it is obviously stable in the gas phase – but its reconversion to isophorone was found to be so fast that it could not be purified, and the yield not determined. Furthermore, for those reactions in Table 6 which produce it as the main product, the yield of recovered starting material is omitted because all of it may result from the reconversion of **5**. This reaction has previously been described to occur slowly at room temperature[10], therefore its increased rate as it is observed here must be due to impurities in the crude reaction mixture. To confirm its identity, **5** was converted into the acetate **6** by a literature procedure[11].

Scheme 3



The formation of **5** in this reaction closely resembles its only practical synthesis, namely the deconjugation of isophorone by $MeMgBr/FeCl_3$, the so-called Kharasch reagent[10]. It has recently been demonstrated that active iron metal is responsible for the deprotonation[12], the formation of which is rationalized through the intermediacy of a labile dimethyliron(II) species. In the light of the reported thermal instability of a Me_2Co-phosphane complex[13], the observed reaction may be explained by the formation of a low-valent cobalt species, probably complexed with phosphane ligands, which acts as the base. The mechanism for the formation of **4a**, especially the identity of the hydrogen source, remains unknown.

Table 7. Reaction of zincates with various enones[a]

Entry No.	Substrate	Reagent	Temp (°C)	Time (h)	Product Yield (%)[b]
1	**7**	Me$_3$ZnLi/Co(acac)$_3$[c]	-78	2	**14a** (10) **7** (30)[d]
2		Me$_3$ZnLi/CoCl$_2$(PPh$_3$)$_2$[c]	-78	2	**14a** (18) **7** (37)[d]
3		Et$_3$ZnMgBr	-78	2	**14b** (21) **7**(30)[d]
4		Me$_2$PhSiZnMe$_2$Li	-78	1.5	**14c** (67)
5	**8**	Me$_3$ZnLi/Co(acac)$_3$[c]	-78	2	**8** (64)
6		Me$_3$ZnLi[e]	0	1	**8** (24)
7		Et$_3$ZnMgBr	-78	2	**15b** (13) **8** (22)
8		Me$_2$PhSiZnEt$_2$Li	-78	1.5	**15c** (63)
9	**9**	Me$_3$ZnLi	0	2	**9**[f] **20**[d,g]
10		Me$_3$ZnLi/CoCl$_2$(PPh$_3$)$_2$[h]	-78	2	**9**[f]
11		Et$_3$ZnMgBr	0/25	1/0.5	**9**[f]
12	10	Me$_3$ZnLi/Co(acac)$_3$[c]	-78	2	**16a** (47) **10** (41)
13		Et$_3$ZnMgBr[d]	-78	1	**16b** (33) **10** (36)
14		Me$_2$PhSiZnEt$_2$Li	-78	1	**16c** (57) 10 (14)
15	**11**	Me$_3$ZnLi/Co(acac)$_3$[c]	-78	2	**21a**(48) **22**(7) **11**(13)
16		Me$_2$PhSiZnMe$_2$Li	-78	1	**17c** (85)
17	12	Et$_3$ZnMgBr[d]	-78	1.5	**21b**(8) **12**(60)
18		Me$_2$PhSiZnMe$_2$Li	-78	1	**18c**(48) **12**(15)[d]
19	13	Me$_2$PhSiZnMe$_2$Li	-78	1	**19c**(35) **23**(14)

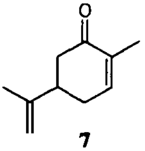
[a] 0.5 mmol of substrate and 0.6 mmol of zincate were employed. The solvent was ether for alkylations, if not otherwise noted, and THF for silylations. – [b] Isolated yield. – [c] 0.02 molar equivalents of catalyst was used. – [d] Unidentified byproducts were also formed. – [e] THF was used as a solvent. – [f] Plenty of starting material was recovered. – [g] Ref.[15]. – [h] 0.1 molar equivalents of catalyst was used.

D. Heterozincates

The use of heterozincates, R$_n$ZnX$_{3-n}$M, as 1,4-alkylating reagents was briefly examined. We did not obtain any alkylated product from cyclohexenone and a reagent prepared from Et$_2$Zn and (*n*Bu)$_4$NF (4% of unreacted starting material was detected after 1 hour at −78°C). The combinations Zn(CN)$_2$/*n*BuLi and Zn(CN)$_2$/2 *n*BuLi equally failed to produce **2d**. Finally, when cyclohexenone was reacted with Zn(OMe)$_2$ (from Et$_2$Zn and 2 MeOH)/*n*BuLi for 1 hour at −78°C, only 64% of starting material could be detected.

E. Other Substrates

The reactivity of Me$_3$ZnLi and Et$_3$ZnMgBr toward other enones **7**–**11** and methyl cinnamate (**12**) was found to be disappointingly low (Table 7). Not only were the desired products obtained in consistently low yields or not at all, but also were 1,2-adducts or products derived from their further reactions isolated from several experiments (Table 7, entries 9, 15, and 17). The reaction is obviously very sensitive to steric hindrance as well as to the electronic effect of a conjugated phenyl group. Attempts to catalyze the ethylation of carvone (7) with $Et_3ZnMgBr$ (Table 7, entry 3; a similar result was obtained when 5% of $CoCl_2(PPh_3)_2$ or $NiBr_2(PPh_3)_2$ were added) as well as the alkylation of cyclohexenone **1** with $Me_2(n\text{Bu})ZnLi$ (Table 4, entries 9 and 10) failed (the latter reaction works well without catalyst, but we did the experiment to test its compatibility with the butyl group).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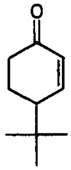
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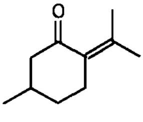
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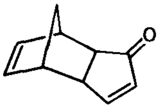
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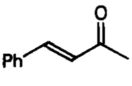
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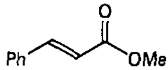
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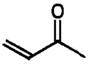
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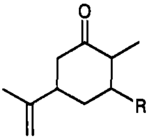
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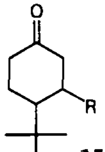
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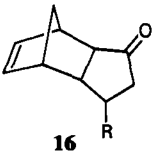
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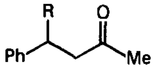
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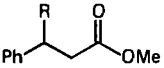
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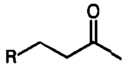
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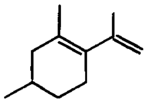
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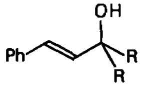
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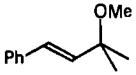
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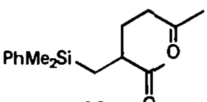
23

a: R = Me
b: R = Et
c: R = $SiMe_2Ph$

Silylations with $Me_2PhSiZnR_2Li$ (R = Me, Et; Table 7) are more effective and produce fair yields of the 3-silyl ketones even with moderately hindered substrates (entries 4 and 8). The high yield of **17c** stands in sharp contrast to the failure of **11** to undergo conjugate alkylations with Me_3ZnLi and $Et_3ZnMgBr$. With no other substrate than **1** (Table 1, entry 14), however, reached the yields those reported by *Fleming* et al.[14] for the addition of silylcuprates.

Financial support by the *Ministry of Education, Science, and Culture, Japanese Government* (Grant-in-Aid for Special Project Research No. 59104005) is acknowledged. We also thank *Toyo Stauffer Chemical Company* for a gift of Et_2Zn and Me_2Zn.

Experimental Part

All reactions were performed under argon. THF was distilled from sodium/benzophenone, ether stored over sodium. MeLi (in ether), *n*BuLi (in hexane), *t*BuLi (in pentane), Me_2Zn (in hexane), and Et_2Zn (in hexane or ether) were commercial products. Grignard reagents (in ether except for $H_2C=CHMgBr$ which was prepared in THF), $Me_2PhSiLi$[16] (in THF), iPr_2Zn[17], and tBu_2Zn[18] were prepared by reported procedures. Neopentyl bromide was obtained from the alcohol using PPh_3/Br_2 in DMF[19]. All organometallic reagents were assayed in due intervals, organolithium and Grignard reagents using the *s*BuOH/*o*-phenanthroline method[20], and dialkylzinc compounds after protonolysis by complexometric titration with disodium ethylenediaminetetraacetate/eriochrome black T[21]. The preparation of $ZnCl_2$(TMEDA)[3] and $ZnCl_2$(dppe)[22] was accomplished by known procedures. An ethereal solution of $ZnCl_2 \cdot$ diethyl ether was obtained by melting commercial anhydrous $ZnCl_2$ in vacuo and dissolving the cooled material in anhydrous ether under argon; it was assayed by complexometric titration[21]. $Co(acac)_3$ and [*N,N'*-bis(salicylidene)ethylenediamine]cobalt(II) (salcomin) were commercial products. Cobalt phosphane complexes were synthesized by the method of *Cotton* et al.[23]. All unsaturated carbonyl compounds were commercial products except for **8**[24] and **10**[25] which were prepared by published procedures. GC yields are corrected for response factors; the required product samples were in part commercially available (**2a**, **2b**, **4a**), in part isolated from the reaction mixtures; their purity was confirmed by ^1H NMR and GC. **2d** and **j** were obtained by the cyanocuprate method of *Lipshutz* et al.[26], and **4b** by the $Cu(OAc)_2$ catalyzed methylation of isophorone (**3**) with MeMgI[27].

IR spectra: Jasco IR-810 spectrometer. – Mass spectra: Hitachi M-80 machine. – ^1H NMR spectra: Varian EM-390 and XL-200 spectrometer (for **6**), TMS internal standard. – Analyses: Elemental Analyses Center of Kyoto University. – GC: Shimadzu Gas Chromatograph GC-4CPT; column A: 10% PEG 20M on Celite 545 60–80 mesh, 2 m; column B: 2% silicone OV-1 on Uniport HP 60–80 mesh, 2 m.

General Procedure for the Reaction of α,β-Unsaturated Carbonyl Compounds with Zincates and Cuprates: The following procedure applies to a reaction on a 1 mmolar scale, and is analogously followed for other reaction scales. Detailed parameters and yields for each reaction are indicated in the tables. If a catalyst is used, it is placed in the reaction flask before the exchange of the atmosphere, as are $ZnCl_2$(TMEDA) and $ZnCl_2$(dppe) if the zincate is to be made from them, or CuI for the reactions with cuprates. 4 ml of solvent is added by syringe, the flask cooled in an ice bath, and the diorganozinc or $ZnCl_2$-ether complex (if necessary) added by syringe, followed by the organolithium or Grignard reagent. The mixture is stirred for approx. 15 min at 0 °C, the flask cooled to the reaction temp., and the substrate (mixed with the GC standard if necessary) in 1 ml of solvent is added by syringe. After stirring for the indicated period, 1 N HCl is added (this should be done cautiously for larger scale reactions), and the product extracted into ether. The organic phases are dried over $MgSO_4$ and evaporated to leave the crude product, which is analyzed by GC and/or separated on a preparative scale, mostly by TLC (SiO_2, EtOAc/hexane 1 : 5, if not otherwise indicated). If $BF_3 \cdot OEt_2$ is to be added to the reaction mixture, this is done at –78 °C immediately before the addition of the substrate.

3-Ethylcyclohexanone (**2c**) *and 3-Isopropylcyclohexanone* (**2e**) (Table 1, entry 2C, and Table 2, entry 3A): Isolated by column chromatography (SiO_2, 15 × 2 cm, EtOAc/hexane 1 : 5) and kugelrohr distillation (aspirator, 90 and 115 °C, respectively).

3-tert-Butylcyclohexanone (**2f**) (Table 1, entry 7A): Isolated by TLC and GC (column A, 150 °C). No isolated yield determined.

3-Isobutylcyclohexanone (**2g**) (Table 1, entry 9A): Isolated by TLC and kugelrohr distillation (aspirator, 110–115 °C).

3-Neopentylcyclohexanone (**2h**) (Table 3, entry 2): Isolated by TLC; the analytical sample was further purified by GC (column A, 150 °C). – ^1H NMR (CCl_4): δ = 0.90 (s; 9H), 1.0–2.5 (m;

11 H). – IR (neat): 2952, 1713, 1364, 1226 cm^{-1}. – MS (70 eV): *m/z* 178 (3%, M^+), 153 (2), 97 (100), 57 (87).

$C_{11}H_{20}O$ (168.3) Calcd. C 78.51 H 12.28 Found C 78.66 H 11.98

Phenylation of **1** *with* $PhZnR_2MgBr$ (R = Me, Et) (Table 1, entry 11): The crude product was purified by TLC and then analyzed by ^1H NMR. From the reaction with R = Me, a pure sample of **2i** was obtained by kugelrohr distillation (aspirator, 200°C).

3-(Dimethylphenylsilyl)cyclohexanone (**2l**) (Table 1, entry 14, and Table 2, entry 5): Isolated by TLC, in the case of Table 2, entry 5B, as a mixture with **2f**.

Methylation of Isophorone (**3**) (Table 6): The general procedure as stated above was followed. From the crude product of entry 13, a mixture of **4a** and **4b** was isolated by TLC as the fraction running immediately before the starting material, and identified by comparison with the ^1H NMR spectra of authentic samples. Furthermore, pure **4a** could be isolated from the crude product of entry 6 by TLC as above, followed by GC (column A, 130°C).

5-Acetoxy-1,3,3-trimethyl-1-cyclohexene (**6**) (according to ref.[11]): After drying over $MgSO_4$, the crude product from entry 14 (Table 6) was without concentration added to 76 mg (2.0 mmol) of $LiAlH_4$ in 1 ml of ether at 0°C. After stirring at this temp. for 1.5 h hydrolysis was performed with saturated Na_2SO_4 solution at 0°C, the solid removed by filtration and washed, and the solution evaporated. The resulting oil was taken up in 2 ml of pyridine, 0.28 ml (3 mmol) of acetic anhydride added at 0°C, and the mixture stirred at 0°C for 20 min, then at room temp. for 3 h. Ice and excess 1 N HCl were added, the product taken up in ether, the organic phase washed with water, aq. $NaHCO_3$, and brine, and dried over $MgSO_4$. After evaporation, the main component of the resulting oil was isolated by GC (column B, 80°C). – IR (neat): 2956, 1734, 1377, 1239, 1033 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 1.01 (s; 6H), 1.43 (t, J = 12 Hz; 1 H), 1.64 (s; 3H), 1.72 (broad d, J = 12 Hz; 1 H), 1.92 (mc; 1 H; simplifies to a broad d, J = 16 Hz, on irradiation at δ = 5.10), 2.05 (s; 3H), 2.29 (dd, J = 6, 16 Hz; 1 H), 5.0–5.25 (m; 2H).

The products in Table 7 were isolated by TLC as colourless oils; only the following which have not been reported previously or the structure of which is not immediately obvious, are further described.

4-tert-Butyl-3-ethylcyclohexanone (**15b**): The analytical sample was obtained by GC (column A, 180°C). – IR (neat): 2958, 2868, 1720, 1462, 1367 cm^{-1}. – ^1H NMR (CCl_4): δ = 0.88 (t; 3H), 0.96 (s; 9H), 1.0–2.5 (m; 10H).

$C_{12}H_{22}O$ (182.3) Calcd. C 79.06 H 12.16 Found C 78.81 H 12.46

5-Ethyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (**16b**): The analytical sample was obtained by GC (column B, 110°C). – IR (neat): 3058, 2960, 2930, 1729, 1459, 1088, 730 cm^{-1}. – ^1H NMR (CCl_4): δ = 0.91 (t; 3H), 1.1–3.2 (m; 11 H), 6.02 (mc; 2H). – MS (70 eV): *m/z* 176 (0.2%, M^+), 147 (1), 111 (100), 66 (100).

$C_{12}H_{16}O$ (176.3) Calcd. C 81.77 H 9.15 Found C 81.74 H 9.41

1-Isopropenyl-2,4-dimethyl-1-cyclohexene (**20**): Isolated in low yield by GC (column A, 90°C). – ^1H NMR (CCl_4): δ = 0.93 (d, J = 6 Hz; 3H), 1.0–2.2 (m; 7H), 1.57 (s; 3H), 1.72 (s; 3H), 4.52 (mc; 1 H), 4.81 (mc; 1 H).

4-tert-Butyl-3-(dimethylphenylsilyl)cyclohexanone (**15c**): The analytical sample was obtained by kugelrohr distillation (155°C/0.2 Torr). – IR (neat): 3068, 2954, 1716, 1426, 1250, 1112, 824, 701 cm^{-1}. – ^1H NMR (CCl_4): δ = 0.29 (s; 6H), 0.83 (s; 9H), 1.2–2.1 (m; 6H), 2.17, 2.35 (AB system, J = 16 Hz, both parts split into doublets with J = 7.5 and 3.5 Hz, respectively, 2H), 6.8 – 7.1 (m; 5H). – MS (70 eV): *m/z* 288 (0.5%, M^+), 287 (1), 273 (32), 231 (100), 204 (33), 135 (99). $C_{18}H_{28}OSi$ (288.5) Calcd. C 74.94 H 9.78 Found C 74.97 H 9.76

5-(Dimethylphenylsilyl)tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (**16c**): Decomposes on attempted further purification by GC (column B, 150°C). – IR (neat): 3066, 2958, 1733, 1427, 1249, 1112, 832, 814, 731, 698 cm^{-1}. – ^1H NMR (CCl_4): δ = 0.24 (s; 3H), 0.27 (s; 3H), 0.9 – 3.1 (m; 9H), 6.03 (mc; 2H), 7.1 – 7.45 (m; 5H). – MS (70 eV): *m/z* 282 (0.05%, M^+), 267 (0.3), 217 (66), 216 (100, $M^+ - C_5H_6$), 135 (91). Exact mass of *m/z* 216: $C_{13}H_{16}OSi$ Calcd. 216.0966 Found 216.0970.

4-(Dimethylphenylsilyl)-4-phenyl-2-butanone (**17c**): The analytical sample was obtained by kugelrohr distillation (155°C/0.2 Torr). – IR (neat): 3066, 3022, 2956, 1716, 1427, 1249, 1113, 832, 811, 735, 699 cm^{-1}. – ^1H NMR (CCl_4): δ = 0.20 (s; 6H), 2.79 (s; 3H), 2.4 – 2.9 (m; 3H), 6.7 – 7.3 (m; 10H). – MS (70 eV): *m/z* 282 (1%, M^+), 267 (5), 204 (17), 135 (100).

$C_{18}H_{22}OSi$ (282.5) Calcd. C 76.54 H 7.85 Found C 76.08 H 7.85

Methyl 3-(Dimethylphenylsilyl)-3-phenylpropanoate (**18c**): Purified by TLC (SiO_2, C_6H_6). The analytical sample was obtained by kugelrohr distillation (160°C/0.2 Torr). – IR (neat): 3066, 3022, 2950, 1733, 1599, 1491, 1428, 1250, 1166, 1113, 834, 817, 735, 699 cm^{-1}. – ^1H NMR (CCl_4): δ = 0.19 (s; 3H), 0.22 (s; 3H), 2.5 – 2.8 (m; 3H), 3.33 (s; 3H), 7.8 – 8.4 (m; 10H). – MS (70 eV): *m/z* 298 (6%, M^+), 267 (2), 135 (100), 104 (57).

$C_{18}H_{22}O_2Si$ (298.5) Calcd. C 72.44 H 7.43 Found C 72.26 H 7.66

3-[(Dimethylphenylsilyl)methyl]-2,6-heptanedione (**23**): This product could not be further purified because of its thermal sensitivity which precluded distillation or GC. – IR (neat): 2952, 1712, 1426, 1356, 1249, 1112, 731, 700 cm^{-1}. – ^1H NMR (CCl_4): δ = 0.27 (s; 6H), 0.65 – 1.25 (m; 2H), 1.45 – 1.75 (m; 2H), 1.87 (s; 3H), 1.95 (s; 3H), 2.1 – 2.45 (m; 3H), 7.15 – 7.4 (m; 5H). – MS (70 eV): *m/z* 261 (8%, $M^+ - CH_3$), 233 (5), 203 (23), 141 (18), 135 (100).

CAS Registry Numbers

1: 930-68-7 / **2a**: 108-94-1 / **2b**: 591-24-2 / **2c**: 22461-89-8 / **2d**: 39178-69-3 / **2e**: 23396-36-3 / **2f**: 936-99-2 / **2g**: 5674-05-5 / **2h**: 100103-35-3 / **2i**: 20795-53-3 / **2j**: 1740-63-2 / **2k**: 6611-97-8 / **2l**: 67262-98-0 / **3**: 78-59-1 / **4a**: 873-94-9 / **4b**: 14376-79-5 / **5**: 471-01-2 / **6**: 22463-33-8 / **7**: 99-49-0 / **8**: 937-07-5 / **9**: 15932-80-6 / **10**: 15584-54-0 / **11**: 122-57-6 / **12**: 103-26-4 / **13**: 78-94-4 / **14a**: 50910-65-1 / **14b**: 61229-13-8 / **14c**: 80256-21-9 / **15b**: 100103-31-9 / **15c**: 100103-36-4 / **16a**: 63683-99-8 / **16b**: 100103-37-5 / **16c**: 100103-38-6 / **17c**: 100103-32-0 / **18c**: 94286-28-9 / **19c**: 18042-35-8 / **20**: 56763-60-1 / **21a**: 25625-21-2 / **21b**: 77722-59-9 / **22**: 100103-33-1 / **23**: 100103-34-2 / $\mathrm{Me_3ZnLi}$: 52196-05-1 / MeZnMgI: 100111-89-5 / $\mathrm{Et_3ZnMgBr}$: 100111-91-9 / $n\mathrm{Bu_3ZnLi}$: 63676-96-0 / $i\mathrm{Pr_3ZnMgBr}$: 100165-26-2 / $t\mathrm{Bu_3ZnMgCl}$: 100110-94-2 / $i\mathrm{Bu_3ZnMgBr}$: 100112-01-4 / $(t\mathrm{BuCH_2})_3\mathrm{ZnMgBr}$: 100112-05-8 / $\mathrm{(CH_2CH)_3ZnMgBr}$: 100112-11-6 / $\mathrm{(Me_2PhSi)_3ZnLi}$: 100165-31-9 / $\mathrm{HMe_2ZnLi}$: 26520-83-2 / $i\mathrm{PrMe_2ZnMgBr}$: 100165-28-4 / $n\mathrm{BuMe_2ZnLi}$: 100111-92-0 / $t\mathrm{BuMe_2ZnMgCl}$: 100111-96-4 / $t\mathrm{BuMe_2ZnLi}$: 100111-99-7 / $i\mathrm{BuMe_2ZnMgBr}$: 100165-30-8 / $t\mathrm{BuCH_2Me_2ZnMgBr}$: 100112-03-6 / $\mathrm{PhMe_2ZnMgBr}$: 100112-07-0 / $\mathrm{(CH_2CH)Me_2ZnMgBr}$: 100112-13-8 / $\mathrm{(CH_2CMe)Me_2ZnMgBr}$: 100112-17-2 / $\mathrm{(Me_2PhSi)Me_2ZnLi}$: 100112-20-7 / $\mathrm{HEt_2ZnLi}$: 26520-82-1 / $\mathrm{MeEt_2ZnLi}$: 100111-87-3 / $n\mathrm{BuEt_2ZnLi}$: 14240-66-5 / $t\mathrm{BuEt_2ZnMgCl}$: 100111-98-6 / $\mathrm{PhEt_2ZnMgBr}$: 100112-09-2 / $\mathrm{(CH_2CH)Et_2ZnMgBr}$: 100112-15-0 / $\mathrm{(CH_2CMe)Et_2ZnMgBr}$: 100112-19-4 / $\mathrm{(Me_2PhSi)Et_2ZnLi}$: 100112-21-8 / $\mathrm{Me}(i\mathrm{Pr})_2\mathrm{ZnLi}$: 100112-22-9 / $n\mathrm{Bu}(i\mathrm{Pr})_2\mathrm{ZnLi}$: 100112-24-1 / $\mathrm{(Me_2PhSi)}(i\mathrm{Pr})_2\mathrm{ZnLi}$: 100112-25-2 / $\mathrm{Me}(t\mathrm{Bu})_2\mathrm{ZnLi}$: 100112-23-0 / $\mathrm{(Me_2PhSi)}(t\mathrm{Bu})_2\mathrm{ZnLi}$: 100112-26-3 / $\mathrm{EtCuMe^-}$: 100112-27-4 / $t\mathrm{BuCH_2CuMe^-}$: 100112-28-5 / $t\mathrm{BuCH_2CuEt \cdot MgBr}$: 100112-30-9 / $t\mathrm{BuCuMe^-}$: 70196-76-8 / $\mathrm{PhCuMe^-}$: 70196-74-6 / $\mathrm{(Me_2PhSi)CuMe \cdot Li}$: 94140-67-7 / $\mathrm{ZnCl_2(TMEDA)}$: 28308-00-1 / $\mathrm{ZnCl_2(dppe)}$: 31322-63-1 / $\mathrm{ZnCl_2 \cdot Et_2O}$: 21512-92-5 / $\mathrm{Me_2Zn}$: 544-97-8 / $\mathrm{Et_2Zn}$: 557-20-0 / $i\mathrm{Pr_2Zn}$: 625-81-0 / $t\mathrm{Bu_2Zn}$: 16636-96-7 / CuI: 7681-65-4 / $\mathrm{LiBHEt_3}$: 22560-16-3 / MeLi: 917-54-4 / MeMgI: 917-64-6 / EtMgBr: 925-90-6 / nBuLi: 109-72-8 / iPrMgBr: 920-39-8 / tBuMgCl: 677-22-5 / tBuLi: 594-19-4 / iBuMgBr: 926-62-5 / $t\mathrm{BuCH_2MgBr}$: 33974-41-3 / PhMgBr: 100-58-3 / $\mathrm{(CH_2CH)MgBr}$: 1826-67-1 /

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