Nickel-Catalysed 1,4-Addition of Aryl Groups to Enones Using Aryldialkylaluminum Compounds

Jürgen Westermann*, Ute Imbery, Anh Thu Nguyen, and Klaus Nickisch

Schering AG Berlin,
Müllerstraße 178, D-13342 Berlin, Germany
Fax: (internat.) + 49(0)30/468-18008
E-mail: juergen.westermann@schering.de

Received November 5, 1996

Keywords: Conjugate addition / Enones / Steroids

The transmetallation of arylmagnesium halides or aryllithium with Me_2AlCl results in the formation of aryldimethylaluminum compounds. These arylaluminum compounds are useful reagents for conjugate additions to enones in the presence of $Ni(acac)_2$ as a catalyst. 3-Aryl ketones are obtained in good yields in these catalytic reactions. Starting from the 3-oxo-$\Delta^{1,4}$-steroids this method gives access to 1α-arylsteroids.

The addition of organometallic compounds to enones is one of the most important reactions in organic synthesis for C−C bond formation, and various synthetic methods which focus on this problem have been developed[1]. Organocuprates are widely explored in stochiometric as well as in catalytic reactions[2]. In connection with the conjugate addition reactions of organoaluminum compounds to enones we have reported the following: (a) the 1,4-addition reaction can be catalysed by copper salts for the transfer of alkyl groups[3a]; (b) under the catalysis of nickel the method is efficient for the transfer of a methyl group, even in the case of highly sterically hindered enones[3b]. To investigate the transition metal catalysed transfer of an aryl group we have studied the possibility of using mixed aryldialkylaluminum compounds in the conjugate addition of an aryl group to α,β-unsaturated enones.

Organoaluminum compounds are useful reagents for organic syntheses[4a] in both catalysed and non-catalysed reactions. Amongst these the triarylaluminum compounds are reported to react in a conjugate addition with nitroalkenes[4b][4c], diarylaluminum chlorides exhibit conjugate addition to acrylamides when irradiated[4c], and arylaluminum halides add to enones in the absence of a catalyst[4d]. Triarylaluminum compounds react with aryl iodides in the presence of a palladium catalyst to produce unsymmetrical diaryl ketones[5a], and are also useful for the synthesis of aryl-substituted *o*-allylphenols[5b]. Arylaluminum complexes are helpful in the oxirane ring opening of *trans*-2,3-epoxy alcohols as described by K. H. Ahn[5c][5d].

The conjugate addition of aryl groups to enones can be achieved in general by molar and catalytic copper reactions[1][2], or by arylzinc compounds in sonication reactions[6a][6b]. In a recent paper we studied the nickel-catalysed 1,4-arylation of enones by aryltitanate complexes[7].

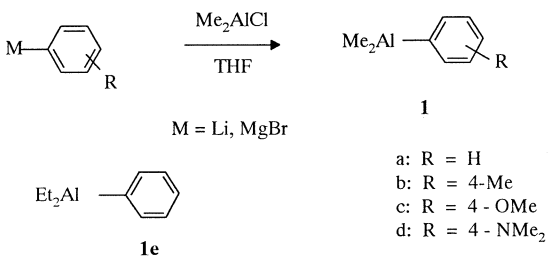
Nickel salts catalyse not only the addition of trimethylaluminum to enones[8a][8b], but also, as reported by J. Schwartz[8c], the transfer of an alkinyl group from dialkyl(alkynyl)aluminum to enones in good yields. The conjugate addition of an aryl group of mixed dialkyl(aryl)alanes has not so far been reported.

Results

In 1,4-addition reactions the use of molar organocopper reagents is often necessary, or the assistance of Lewis acids is required to give good results[9]. Cuprates are "softer" reagents than aryllithium or arylmagnesium halides, which are the reagents in transition metal catalysed reactions in the Kharasch procedure. The latter reagents lead mainly to a carbonyl attack when the enones are sterical hindered or when the cross-conjugated dienone **12** is the substrate, which results in undesired 1,2-adducts.

The authors were looking for a general catalytic method for the transfer of an aryl group to an enone in a simple manner, and therefore tested mixed aryldimethylaluminum compounds. Dialkyl(aryl)aluminum compounds are prepared by transmetallation of organolithium compounds with dimethylaluminum chloride in tetrahydrofuran[5a][5c].

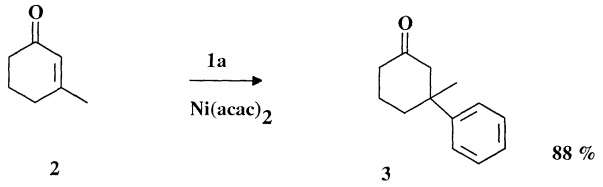
Surprisingly it was found that the dialkyl(aryl)alanes **1a−e** are suitable reagents for the transfer of an aryl group to enones.



In the presence of 5 mol-% of the catalyst $Ni(acac)_2$ a clean conversion of the alane **1a** with the enone **2** was ob-

  1434−1948/98/0202−0295 $ 17.50+.50/0

served. After workup, the β-aryl ketone **3** could be isolated in 88% yield.



2 3

Furthermore, in the addition of the alane **1a** to 3,5,5-trimethylcyclohex-1-en-3-one (**4**) the yield of the product **5a** was 83%. The alanes **1c** and **1d**, with different substituents at the aryl group, were used in the addition to carvone **4**. It is promising that the addition to sterically hindered enones is possible. Also the conversion of 4-methylpent-2-ene-3-one (**6**) gave high yields of the products **7a−b**. In general, the aryl group is selectively transferred and no alkyl transfer has been observed[10].

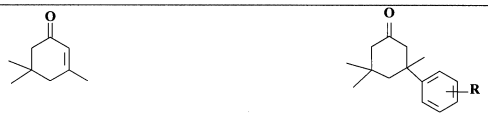
The alanes **1a** and **1b** were prepared from commercially available aryllithium compounds. **1c** was prepared from 4-methoxyphenylmagnesium bromide. **1d** was prepared from 4-dimethylaminophenyllithium which was prepared from 4-dimethylaminophenyl bromide and *sec*-butyllithium by halogen/metal exchange. The reaction of the alanes **1d** with **4** gave **5d** in a yield of 65%. This shows that the method is sucessful for the addition to sterically hindered enones. The addition of an aryl group to the less hindered enone **6** gave the products **7** in high yields. The conversion of pulegone **8** with **1a** resulted in the formation of the ketone **9a** in a 85:15 ratio of two diastereomers. When **1e** (prepared from Et_2-AlCl and PhLi) was tested in the reaction with **4** the formation of **5a** was observed in a yield of 85%. Further examples are given in Table 1.

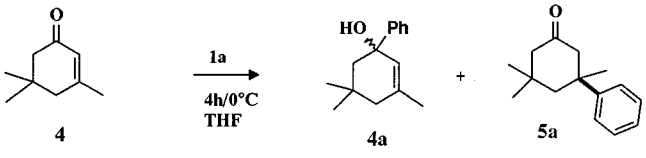
In testing the nucleophilic properties of mixed aryldimethylaluminum compounds versus a carbonyl group it was found that the alane **1a** gave, in the reaction with isophorone (**4**) under typical conditions (4 h, 0°C) without a catalyst, less than 1% of the 1,2-addition product **4a**. This indicates that the solvent THF has a reduced tendency for a 1,2-addition of a methyl or a phenyl group to the carbonyl group. This low 1,2-addition rate is a good assumption to make for a catalytic process. In comparison with the $Ni(acac)_2$-catalysed reaction the conversion was low, the main compound identified (98%) was the starting material **4**.

J. Y. Satoh et. al. report the introduction of a 1-phenyl group to a Δ^1-steroid by a copper-catalysed reaction in a yield of only 49%[11]. In our experiments the steroidal enone **10** reacted with the alane **1a** to give the product **11**, in a yield of 81%, without cleavage of the 17-acetate group. This is an example of the selective reaction conditions.

Less is known in the literature about conjugate additions of arylmetals to 3-oxo-$\Delta^{1,4}$-steroids of type **12,** in either stochiometric or catalytic reactions[3a]. The introduction of a phenyl group to position 1 of the steroid **12** was attempted in our laboratory using common catalytic methods. The result was a simple carbonyl attack; phenylmagnesium bromide in the presence of catalytic copper bromide yielded

Table 1. $Ni(acac)_2$-catalysed 1,4-arylations of enones with $ArAlMe_2$

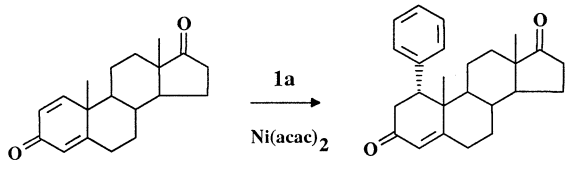
Enone	$ArAlMe_2$	Cond.	Product	Yield	Ref.
					
	1a	4 h, 0 °C	**5a**: R = H	83 %	[7]
4	**1c**	2 h, 0 °C	**5c**: R = 4-MeO	79 %	[12a]
	1d	4 h, 0 °C	**5d**: R = 4-Me_2N	65 %	–
	1e	4 h, 0 °C	**5a**: R = H	85 %	[7]
					
6	**1a**	1 h, 0 °C	**7a**: R = H	95 %	[12b]
	1b	1 h, 0 °C	**7b**: R = 4-Me	96 %	[12c]
					
8	**1a**	1 h, 0 °C	**9a**: R = H	95 %	[12d]
					
10	**1a**	2 h, 0 °C	**11**	81 %	–
					
12	**1a**	4 h, 0 °C	**13a**: R = H	90 %	–
	1b	4 h, 0 °C	**13b**: R = Me	77 %	–
	1c	3 h, 0 °C	**13c**: R = 4-MeO	89 %	–
	1d	3 h, 0 °C	**13d**: R = 4-Me_2N	78 %	–



4 4a 5a

	4a	5a	4
no catalyst	< 1%	-	98 %
5 mol-% $Ni(acac)_2$	<1 %	83 %	<2%

only the 1,2-addition product. In contrast to this the reaction of **12** with two equivalents of high-order cuprate ArThCuCNLi[9] was sucessful with molar copper reagent, and gave the 1,4-adduct **13a** in a yield of 65%.



12 13a

The experiments using the enone **12** and the alanes **1a−d** in the nickel-catalysed reaction gave the products **13a−d** in good to excellent yields. This is similar to the PhLi/Me_2-AlCl system in the nickel-catalysed reaction, and shows that Et_2AlCl is also useful. In the reaction of **1a** with **12** only 3% of 5β-methylandrost-4-ene-3,17-dione, which originates in the methylation of **12** in a side reaction, were produced. In the reactions of the alane **1d**, prepared from the Grignard reagent (*p*-Me_2N-ArMgBr), the yield was somewhat lower than in the experiment where **1d** was derived from 4-dimethylaminophenyllithium. This was prepared from the bromo compound by metal exchange with *n*-butyllithium in THF (see Experimental Section).

In the absence of the catalyst $Ni(acac)_2$ no reaction was observed. Optimal yields of conjugate addition product were obtained when 1.2−1.3 equivalents of aryldimethylaluminum was used. A small excess of arylalane was necessary to produce optimal yields, otherwise the unreacted starting material is methylated in a side reaction. When the aryl groups in the reagent are consumed, it seems that the starting compound is methylated by the dimethylaluminum enolates as methyl source under the catalysis of a nickel salt.

In the experiments the catalyst [$Ni(acac)_2$] was used in the commercial form without initial activation, similar to the use of DIBAH[8c]. It was found that the alane **1d** from phenylmagnesium bromide reacts faster with the enones **4** and **12** than the alane **1d** prepared from aryllithium, and that it also gives a better yield. A small amount of biaryl is usually isolated in the reactions. This comes from the biaryls in the aryllithium or arylmagnesium solutions.

5 mol-% of the catalyst gave a satisfactory yield, the optimal amount of the catalyst is in the range 2−5%. There were no advantages in the use of [$Ni(PPh_3)_4$] and [$Ni(PPh_3)_2Cl_2$] over the less expensive catalyst [$Ni(acac)_2$]. The alane **1a** and the enone **4** did not show a selective aryl transfer with the catalysts CuBr, CuCN and CuCl. The result was a statistical mixture of methylated and arylated product in the copper-catalysed reactions.

Conclusion

These experiments have demonstrated that dimethylaluminum chloride is a versatile carrier for aryl groups in transmetallation reactions, from arylmagnesium or -lithium compounds to arylalanes. This can be exploited for a chemoselective 1,4-aryl transfer to enones and cross-conjugated steroidal dienones catalysed by Ni^{II} salts.

Experimental Section

All reactions were carried out in capped vials under nitrogen. The products were isolated from the reaction mixture by preparative chromatography on silica gel (Merck F 254s) with ethyl acetate/hexane as eluent. The analysis of the products was carried out on a gas chromatograph, fitted with a 25 m × 0.2 mm CP Sil 19 CB fused capillary column. The detector signal was integrated. The column temp. was programmed to rise from 150 to 250°C at 10°C/min. Phenyllithium, *p*-tolyllithium, $Ni(acac)_2$ (95%), and the ketones **2**, **4**, **6**, **8**, were purchased from Aldrich. Dimethylaluminum chloride was used as a 1 M solution in hexane from Aldrich. 4-Dimethylaminophenyllithium was prepared from *p*-dimethylaminophenyl bromide by transmetallation with a *n*-butyllithium solution (1.6 M in hexane) in THF at 0°C/30 min, *p*-methoxyphenylmagnesium bromide was prepared from *p*-bromoanisol and magnesium in THF in a standard procedure[5c]. All solvents were used in commercial grade without any further purification.

General Procedure: 13 mmol [6.5 ml of a 2 M solution of phenylmagnesium bromide (or phenyllithium)] was added to 12 mmol of dimethylaluminum chloride (12 ml of a 1 M solution in hexane) at −20°C. The mixture was stirred for 10 min at −20°C. Then 10 mmol of the enone in 15 ml of THF was added at −20°C, followed by 0.5 mmol (0.128 g) of [$Ni(acac)_2$]. The reaction mixture was then stirred for 1−4 h at 0°C, during this time the solution was allowed to warm up to the temp. shown in Table 1. The reaction mixture was quenched with aqueous NH_4Cl solution and stirred for 15 min. The product was then extracted using ethyl acetate and dried with Na_2SO_4. Chromatography of the reaction product on silica gel and elution of the product with ethyl acetate/hexane gave the 3-aryl ketones in the yields shown in Table 1. All reactions described in the text and in Table 1 were performed on a 10-mmol scale.

3-Methyl-3-phenylcyclohexan-1-one (**3**)[12e]: From 1.3 ml (1.1 g, 10 mmol) of **2**, yield 1.65 g (88%) of **3**. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 1.33 (s, 3 H, 3-CH_3), 1.55−2.24 (m, 4 H), 2.34 (t, *J* = 3.25 Hz, 2 H), 2.45 (d, *J* = 7.5 Hz, 2 H), 7.19−7.33 (m, 5 H).

3,5,5-Trimethyl-3-phenylcyclohexan-1-one (**5a**)[7]: From 1.54 ml [97%, 1.38 g (10 mmol)] of isophorone (**4**), yield 1.79 g (83%) of **5a**. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.4 (s, 3 H, 3-CH_3), 1.03 (s, 3 H), 1.04 (s, 3 H), 1.88−2.45 (m, 5 H), 3.0−3.1 (m, 1 H), 7.1−7.4 (m, 5 H).

3,5,5-Trimethyl-3-(4-methoxyphenyl)cyclohexan-1-one (**5c**)[12a]: From 1.54 ml [97%, 1.42 g (10 mmol)] of isophorone (**4**), yield 1.86 g (79%) of **5c,** colourless oil. **5c**. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.39 (s, 3 H, 3-CH_3), 1.02 (s, 3 H), 1.33 (s, 3 H), 1.5−2.5(m, 5 H), 3.0−3.1 (d, 1 H), 3.77 (s, 3 H), 6.8−7.3 (m, 4 H).

3,5,5-Trimethyl-3-(4-dimethylaminophenyl)cyclohexan-1-one (**5d**): From 1.54 ml [97%, 1.42 g (10 mmol)] of **4**, yield 1.68 g (65%) of **5d**: colourless crystals, m.p. 113.6°C. − $C_{17}H_{25}NO$ (259.4): calcd. C 78.8, N 5.39, H 8.88; found C 78.45, N 5.6, H 9.53. − MS CI (70 eV): *m/z* = 260 $[M - H]^+$ (98%). − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.45 (s, 3 H, 3-CH_3), 1.042 (s, 3 H), 1.35 (s, 3 H), 1.65−2.4 (m, 5 H), 2.9 (t, 3 H), 2.95−3.05 (m, 1 H), 6.65−7.2 (m, 4 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.36, 33.08, 35.07, 36.01, 42.05, 51.50, 51,60, 54.43, 55.15, 113.52, 126.88, 139.88, 157.63, 211.63.

4-Methyl-4-phenylpentan-2-one (**7a**)[12b]: From 0.99 g (10 mmol) of **6**, yield 1.63 g (95%) of **9a**. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 1.32 (s, 6 H, 4-CH_3), 1.8 (s, 3 H), 2.75 (s, 2 H), 7.15−7.5 (m, 5 H).

4-Methyl-4-(4-methylphenyl)pentan-2-one (**7b**)[12c]: From 0.99 g (10 mmol) of **6**, yield 1.78 g (96%) of **9b**. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 1.4 (s, 6 H, 4-CH_3), 1.82 (s, 3 H), 2.33 (s, 3 H, Ar-CH_3), 2.72 (s, 2 H), 7.1−7.3 (m, 4 H).

2-(1-Methyl-1-phenylethyl)-5-methylcyclohexanone (**9a**)[12c]: From 1.52 g (10 mmol) of **8**, yield 2.18 g (95%) of **9a**. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.91/0.98 (d, 3 H, 5-CH_3), 1.42 (d, 6 H), 1.0−2.75 (m, 8 H), 7.15−7.4 (m, 5 H).

17β-Acetoxy-1α-phenylandrostan-3-one (**11**): From 3.3 g (10 mmol) of **10**, yield 3.3 g (81%) of **11**, colourless crystals, m.p. 197°C. − $C_{27}H_{36}O_3$ (408.6): calcd. C 79.36, H 8.88; found C 79.45,

H 8.71. − MS CI/NH_3 (70 eV): *m/z* = 409 $[M - H]^+$ (10%), 426 $[M - NH_4]^+$ (90%). − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.82 (s, 3 H, 18-CH_3), 1.25 (s, 3 H, 19-CH_3), 0.4−2.5 (m, 16 H), 2.05 (s, 3 H), 2.8−2.9 (m, 1 H), 3.3 (d, 1 H), 4.5−4.6 (m, 1 H, 17-H), 7.02−7.35 (m, 5 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.68, 14.32, 20.34, 20.73, 22.51, 26.59, 27.96, 29.39, 35.09, 35.71, 37.15, 38.48, 42.07, 43.36, 43.97, 47.78, 49.43, 49.76, 81.64, 125.78, 127.26, 128.15, 141.26, 170.24, 211.25.

1α-Phenylandrost-4-ene-3,17-dione (**13a**): From 2.84 g (10 mmol) of **12**, yield 3.25 g (90%) of **13a,** colourless crystals, m.p. 189.6°C. − $C_{25}H_{30}O_2$ (362.5): calcd. C 82.82, H 8.34; found C 83.05, H 8.26. − MS CI/NH_3 (70 eV): *m/z* = 363 $[M - H]^+$ (97%). − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.91 (s, 3 H, 18-CH_3), 1.47 (s, 3 H, 19-CH_3), 0.8−2.1 (m, 16 H), 2.35−2.6 (m, 1 H), 2.95−3.1 (m, 1 H), 5.98 (s, 1 H, 4-H), 7.1−7.3 (m, 5 H, Ar-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.70, 20.02, 21.02, 21.72, 21.96, 29.27, 30.89, 33.20, 35.51, 35.59, 41.97, 42.21, 47.20, 47.41, 50.64, 125.51, 126.81, 128.61, 128.76, 142.69, 168.90, 197.68, 220.049. The less polar fraction (90 mg, 2.7% yield) is *5β-methylandrost-1-ene-3,17-dione*[12f].

1α-(4-Methylphenyl)androst-4-ene-3,17-dione (**13b**): From 2.84 g (10 mmol) of **12**, yield 2.90 g (77%) of **13b,** colourless crystals, m.p. 212°C. − $C_{26}H_{32}O_2$ (376.5): calcd. C 83.55, H 8.56; found C 83.7, H 8.4. − MS CI/NH_3 (70 eV): *m/z* = 377 $[M - H]^+$ (99%).− ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.9 (s, 3 H, 18-CH_3), 1.4 (s, 3 H, 19-CH_3), 0.8−2.1 (m), 2.3 (s, 3 H, Ar-CH_3), 2.35−2.60 (m, 4 H), 2.95 (d, *J* = 7.5 Hz, 1 H), 3.05 (d, *J* = 9 Hz, 1 H), 5.95 (s, 1 H, 4-H), 6.9−7.15 (m, 4 H, Ar-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.98, 19.20, 20.11, 20.78, 21.14, 28.47, 30.05, 32.40, 34.69, 34.79, 41.27, 41.38, 46.88, 46.62, 49.46, 49.78, 124.61, 127.75, 128.42, 135.36, 138.71, 168.08, 197.00, 219.31.

1α-(4-Methoxyphenyl)androst-4-ene-3,17-dione (**13c**): From 2.84 g (10 mmol) of **12**, yield 3.4 g (89%) of **13c,** colourless crystals, m.p. 196°C. − $C_{26}H_{32}O_3$ (392.5): calcd. C 79.55 H 7.94; found C 79.82, H 8.17. − MS CI/NH_3 (70 eV): *m/z* = 393 $[M - H]^+$ (90%), 410 $[M - NH_4]^+$ (98%). − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.89 (s, 3 H, 18-CH_3), 1.48 (s, 3 H, 19-CH_3), 0.8−2.1 (m, 12 H), 2.35−2.6 (m, 3 H), 2.95−3.06 (m, 1 H), 3.2−3.25 (m, 1 H), 3.75 (s, 3 H), 5.5 (s, 1 H, 4-H), 6.7−7.2 (m, 4 H, Ar-H). − ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.99, 19.21, 20.81, 21.16, 28.48, 30.09, 32.42, 34.74, 34.80, 41.34, 41.49, 46.36, 46.64, 49.02, 49.85, 54.28, 113.08, 124.63, 133.82, 157.35, 167.97, 197.08, 219.25.

1α-(4-Dimethylaminophenyl)androst-4-ene-3,17-dione (**13d**): From 2.84 g (10 mmol) of **12**, yield 3.145 g (78%) of **13d,** colourless crystals, m.p. 202°C. − $C_{27}H_{35}NO_2$ (405.6): calcd. C 79.55, H 7.94, N 3.45; found C 79.82, H 8.17, N 3.56. − MS CI/NH_3 (70 eV): *m/z* = 406 $[M - H]^+$ (95%). −^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.91 (s, 3 H, 18-CH_3), 1.46 (s, 3 H, 19-CH_3), 0.8−2.1 (m, 12 H), 2.35−2.55 (m, 3 H), 2.89 (s, 6 H), 2.95−3.06 (m, 1 H), 3.15 (m, 1 H), 5.95 (s, 1 H, 4-H), 6.55−7.1 (m, 4 H, Ar-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.77, 20.33, 21.58, 21.58, 21.96, 29.25, 30.88, 33.24, 35.56, 40.43, 42.19, 42.36, 47.11, 49.63, 50.61, 112.59, 125.35.

[1] P. Perlmutter in *Conjugate Addition Reactions in Organic Synthesis*, Pergamon Press, Oxford, **1992**.
[2] B. H. Lipshutz, *Synthesis* **1987**, 325−341.
[3] [3a] J. Westermann, K. Nickisch, *Angew. Chem.* **1993**, *105*, 1429; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1368. − [3b] J. Westermann, S. Flemming, J. Kabbara, K. Nickisch, H. Neh, *Synthesis* **1995**, 317−320.
[4] [4a] K. Maruoka, H. Yamamoto, *Tetrahedron* **1988**, *44*, 5001. − [4b] I. Fleming, R. C. Moses, M. Tercel, J. Ziv, *J. Chem. Soc., Perkin Trans. 1* **1991**, 617. − [4c] A. Pecunioso, R. Menicagli, *J. Org. Chem.* **1988**, *53*, 45−49. − [4d] K. Rück, H. Kunz, *Synlett* **1992**, 343. − [4e] E. C. Ashby, S. A. Noding, *J. Org. Chem.* **1979**, *44*, 4792−4797.
[5] [5a] N. A. Bumagin, A. B. Ponomaryov, I. P. Beletskaya, *Tetrahedron Lett*. **1985**, *26*, 4819−4822. − [5b] A. Alberola et al., *Synthesis* **1984**, 238−240. − [5c] K. H. Ahn, J. S. Kim, C. S. Jin, D. H. Kang, D. S. Han, Y. S. Shin, D. H. Kim, *Synlett* **1992**, 306. − [5d] K. H. Kim et al., *J. Heterocycl. Chem.* **1993**, *90*, 825−827.
[6] [6a] C. Petrier, J. C. de Souza Barbosa, C. Dupuy, J.-P. Luche, *J. Org. Chem.* **1985**, *50*, 5761−5765. − [6b] J. L. Luche, C. Petrier, J.-P. Lansard, A. E. Greene, *J. Org. Chem*. **1983**, *48*, 3837−3839.
[7] S. Flemming, J. Kabbara, K. Nickisch, H. Neh, J. Westermann, *Tetrahedron Lett*. **1994**, *35*, 6075−6078.
[8] [8a] J. A. Jeffery, A. Meisters, T. Mole, *J. Organomet. Chem*. **1974**, *74*, 365. − [8b] E. C. Ashby, G. Heinsohn, *J. Org. Chem*. **1974**, *39*, 3297−3299. − [8c] J. Schwartz, D. B. Carr, R. T. Hansen, F. M. Dayrit, *J. Org.Chem*. **1980**, *45*, 3053−3061.
[9] B. H. Lippshutz, D. A. Parker, J. A. Kozlowski, S. L. Nguyen, *Tetrahedron Lett.* **1984**, *25*, 5959.
[10] The aryl group from mixed alkylarylzinc compounds seems also to be faster transferred than an alkyl group, see ref.[6a], see also: W. Tückmantel, K. Oshima, H.Nozaki, *Chem. Ber.* **1986**, *119*, 1581.
[11] T. T. Takahashi, J. Y. Satoh, *Bull. Chem. Soc. Jpn*. **1976**, *49*, 1089−1072.
[12] [12a] B. L. Shapiro, M. D. Johnston, M. J. Shapiro, *Org. Magn. Reson.* **1973**, *5*, 21−27. − [12b] M. Suzuki, T. Suzuki, T. Kawagashi, R. Noyori, *Tetrahedron Lett*. **1980**, *21*, 1247. − [12c] C. Pichat, *Bull. Soc. Chim. Fr*. **1949**, *177*, 183−184. − [12d] D. Pottin, J. Maddaluno, F. Dumas, *Synth. Commun*. **1990**, *20*, 2805−2813. − [12e] H. O. House, J. M. Wilkins, *J. Org. Chem.* **1978**, *43*, 2443−2454; G. Cahiez, M. Alami, *Tetrahedron Lett.* **1989**, *27*, 3541−3544. − [12f] J. Westermann, H. Neh, K. Nickisch, *Chem. Ber.* **1996**, *129*, 963−966.

[97260]