Use of Magnesium Anthracene · 3 THF in Synthesis: Generation of Grignard Compounds and Other Reactions with Organic Halides[1)]

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The course (a), (b), (c) (Scheme 1) of the reaction of magnesium anthracene · 3 THF (**1**) with organic halides (RX) is dependent on the nature of RX. With alkyl halides in THF **1** reacts as a nucleophile, whereby primary as well as secondary alkyl halides produce dialkyldihydroanthracenes (**4**–**4″**) and tertiary alkyl halides yield primarily monoalkyl-substituted dihydroanthracenes (**2**, **2′**). With bromo- and iodobenzene in THF **1** reacts predominantly as a radical with H atom abstraction from the solvent affording benzene and **9**. The formation of Grignard compounds (**5**) and anthracene (**6**), originating from primary and secondary alkyl and aryl halides and **1** in toluene or ether at elevated temperatures, is not caused by the reaction of **1** but by the "active magnesium" (Mg*) formed by decomposition of **1** in these solvents. In contrast, allyl, propargyl, and benzyl halides react with **1** independently of the solvent under mild conditions to produce **5** and **6**. Allyl- and the difficultly accessible allenylmagnesium chloride can be prepared in THF at −78 and 0°C, respectively, from the corresponding halides and ordinary Mg powder via catalytic amounts of **1**.

Magnesium anthracene · 3 THF (**1**) has been used to activate magnesium powder for the preparation of γ- or δ-unsaturated 2-substituted allylmagnesium chlorides between −78 and −65°C. These Grignard compounds undergo intramolecular magnesium-ene reaction, as reported by Oppolzer et al.[2)] **1** has been employed stoichiometrically by Raston et al.[3)] to generate bi- or polyfunctional benzylic-type Grignard compounds. A remarkable recent achievement in this field is the first direct synthesis of polymeric Grignard compounds from *p*-(chloromethyl)polystyrene and **1** by Fréchet et al.[4)] and Raston et al.[5)]

Within the scope of our work on magnesium/anthracene systems and their application in synthesis and catalysis[6)] we report here on the results of our investigations concerning the reaction of **1** with some representative organic halides and its use as a stoichiometric reagent, and in some cases also as a promoter, for the generation of Grignard compounds[7)].

Stoichiometric Reactions of Magnesium Anthracene · 3 THF (1) with Organic Halides

With oxygen-containing electrophiles (THF[6,8)], acetone, ethyl acetate, CO_2[6,7b)]), and ethene[6,9)] **1** reacts as a nucleophile, as expected for (di)organomagnesium compounds, to afford 9-mono- or 9,10-disubstituted 9,10-dihydroanthracenes. However, with organic halides (RX) **1** can react in three different ways (Scheme 1): (a) as a nucleophile yielding mono- and disubstituted dihydroanthracenes (**2**, **2′**, **4**–**4″**), (b) as a source of "soluble zerovalent magnesium"[10)] to produce Grignard compounds (**5**) and anthracene (**6**), and (c) as a single-electron donor with reduction of the halide to RH (**8**) and formation of the tetrahydrofuran derivative **9**[11)].

The pathway [reaction (a), (b) or (c)] involving treatment of **1** with RX depends on the nature of RX, the dependence on solvent and temperature is only an apparent one and is caused by the instability of **1** in solvents of low coordinating ability[1)].

The results of stoichiometric reactions of **1** with organic halides are summarized in Tables 1–5. Except for MeI (see below), **1** reacts with primary and secondary alkyl halides in THF as a nucleophile (molar ratio 1:2) to yield mainly **4** and to a lesser extent **4′** and **4″** (Table 1, entries 2, 3, 5, 6, 8). No Grignard compounds are formed under these conditions. The same reaction products are also obtained with a 1:1 molar ratio; in this case ca. 50% of **1** does not react (entries 4, 7). On the other hand, tertiary butyl halides, both in the molar ratio 1:1 and 2:1 produce **2** and **2′** preferentially (entries 9–11). Upon prolonged reaction of *t*BuBr with **1** in THF (entry 12) the formation of an unexpected cleavage product of THF, 10-*tert*-butyl-9,10-dihydro-9,9-bis(4-hydroxybutyl)anthracene (**3**, Scheme 1), is observed[7b)]. The ^{1}H-NMR spectrum of the diol **3** (Experimental) exhibits the remarkable high-field shift of the signals of the β-H atoms of one hydroxybutyl group ($\Delta\delta$ = 0.16 ppm) which is found in the least trisubstituted 9,10-dihydroanthracenes in the 9,10-positions[13,14)].

An exception in the reactivity of alkyl halides toward **1** is observed with MeI (entry 1). During the reaction MgI_2-$(THF)_6$ precipitates quantitatively from the THF solution[15)], and CH_4 and C_2H_6 are evolved (molar ratio 2:1, overall yield 24% with respect to MeI). Hydrolysis of the reaction

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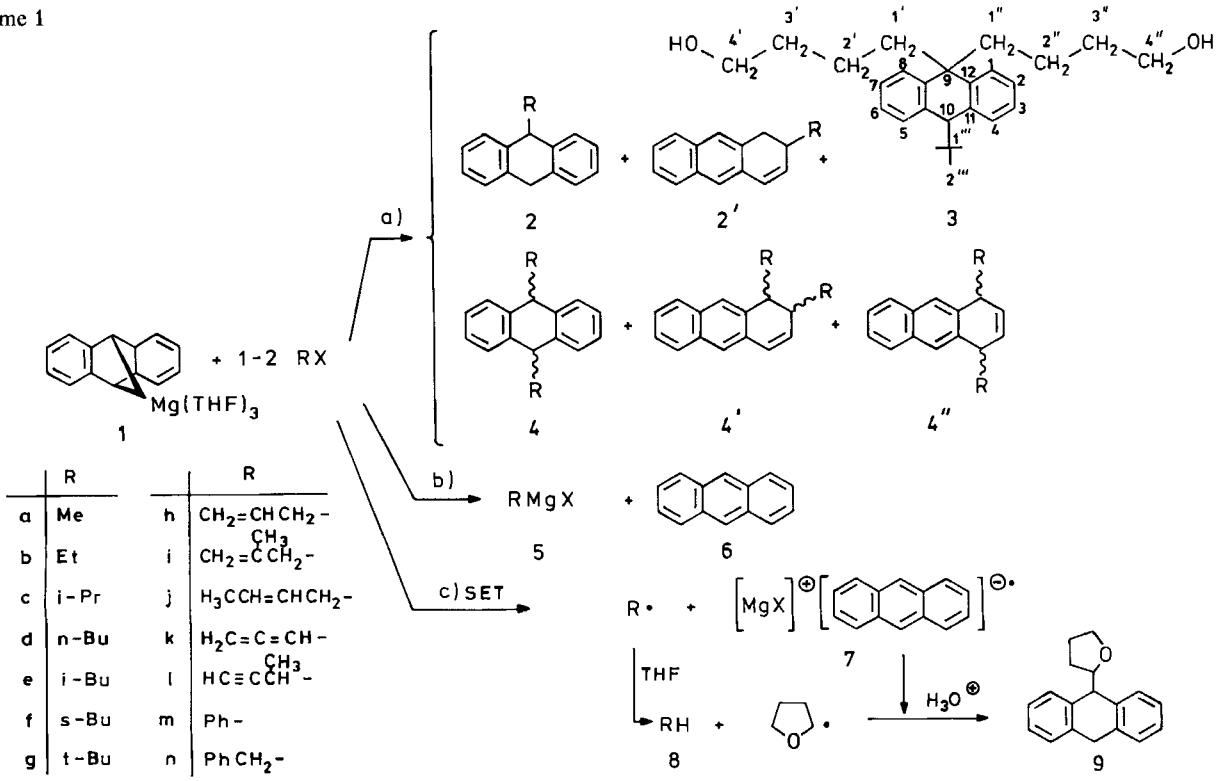
Scheme 1



	R		R
a	Me	h	$CH_2=CHCH_2-$
b	Et	i	$CH_2=C(CH_3)CH_2-$
c	i-Pr	j	$H_3CCH=CHCH_2-$
d	n-Bu	k	$H_2C=C=CH-$
e	i-Bu	l	$HC\equiv CCH(CH_3)-$
f	s-Bu	m	Ph-
g	t-Bu	n	$PhCH_2-$

Table 1. Reaction of magnesium anthracene · 3 THF (**1**) with alkyl halides (RX) in THF (r.t. = room temperature)

Entry	RX	g(mmol)	Molar ratio RX/1	THF[a] [ml]	React. temp. [°C]	React. time [h]	Raw[b] product [g]	Conv.[c] of 1 [%]	Reaction 2	2'	4 [%][d]	Products 4'	4''	other
1	MeI	6.72(47.3)	2.10	125	r.t.	2	4.45	100	–		23	18	3	CH_4,C_2H_6 Me_2Mg **6**[e]
2	EtCl	1.44(22.3)	2.19	105	30	2	2.42	99	–		61	15	9	
3	EtBr	10.66(97.8)	2.58	280	r.t.	3	8.66	99	–		57	24	11	f)
4	EtBr	1.10(10.1)	1.04	140	r.t.	2	2.00	47	–		60	18	12	
5	iPrBr	6.36(51.7)	2.37	150	r.t.	2	5.97	98	3		46	21	12	
6	nBuCl	3.63(39.3)	2.07	130	40	2	5.10	97	3		56	12	9	3[g]
7	nBuCl	3.81(41.2)	1.00	70	r.t.	24	9.64	51	5		48	10	6	3[g]
8	sBuCl	6.71(72.5)	2.27	140	40	2	9.10	96	–		51	12	11	
9	tBuCl	3.45(37.3)	2.16	125	40	2	4.63	99	30	19	–	Σ27	–	
10	tBuBr	4.64(33.9)	2.39	80	r.t.	15	3.67	97	44	17	–	Σ23	–	21(iC_4H_8)[h]
11	tBuBr	2.08(15.6)	1.03	70	r.t.	2	3.57	93	39	20		–		0 (**3**)
12	tBuBr	3.30(24.1)	1.01	60	r.t.	24	6.64	99	6	14	–	Σ 2	–	21 (**3**)[e]

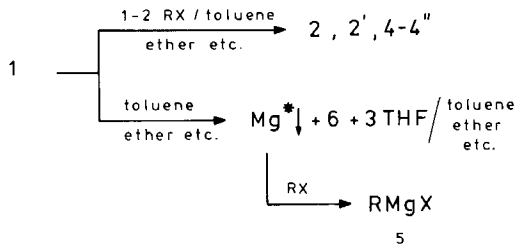
[a] Total amount. – [b] Total amount of nonvolatile organic reaction products. – [c] On the basis of 9,10-dihydroanthracene obtained by hydrolysis of the reaction mixture. – [d] Yield of reaction products based on converted **1**. – [e] See exp. part. – [f] No gas was evolved upon protolysis of the reaction mixture. – [g] Trialkylated dihydroanthracenes. – [h] During the reaction 6.5 mmol of i-C_4H_8 and 0.5 mmol of i-C_4H_{10} were evolved.

mixture yields 20% additional CH_4 from the dimethylmagnesium produced in the reaction. **6** (33%), and dihydrodimethylanthracenes (**4a**–**4a''**, the main product being *cis*-**4a**) have also been identified in the reaction mixture. The production of CH_4 and C_2H_6 before hydrolysis shows that the reaction follows the radical pathway (c). The primary step of the reaction can be assumed to be the transfer of a single electron from **1** to MeI in analogy to the mechanism of the reaction of alkyl halides with sodium naphthalene[16]. The lower reduction potential of alkyl iodides in comparison to bromides and chlorides leads to an increased concentration of methyl radicals in solution which then dimerize to produce ethane[17].

A drastic change in the reaction products from primary and secondary alkyl halides and **1** can be achieved by performing the reaction in toluene instead of THF, since the major products are then Grignard compounds (**5**) and anthracene (**6**) (pathway b), with only minor amounts of al-

kylated dihydroanthracenes (**2**, **2'**, **4**–**4''**, pathway a) being formed (Table 2, entries 1–6)[7a,b]. A closer inspection of the results of Table 2 reveals that higher yields of **5** and **6** and lower amounts of **2**, **2'** and **4**–**4'** result when the reaction is performed at a higher temperature or in boiling toluene (entries 4, 5) than at 0 °C or room temperature (entries 1–3, 6). The fact that in toluene the rate of the decomposition of **1** to **6**, *active magnesium* (Mg*), and THF increases with increasing temperature[1] suggests that the distribution of the reaction products depends on the competition between the reaction of **1** with RX to produce **2**, **2'**, and **4**–**4''** (as shown above for THF, pathway a) and the decomposition of **1**; the resulting Mg* reacts then rapidly with RX to yield Grignard compounds (**5**, Scheme 2)[7a,b]. Indeed, as described in the following publication[18], Grignard compounds can be prepared under mild conditions in various solvents in which **1** is unstable, by *first* decomposing it in the desired solvent by gentle heating or ultrasonic irradiation, and *subsequently* treating the Mg* thus generated with RX.

Scheme 2



The fact that *tert*-butyl halides react with **1** in toluene at room temperature to give exclusively **2**, **2'**, and **4**–**4''** and no Grignard compounds (Table 2, entries 7, 8) can be explained by their higher reactivity toward **1** in comparison to that of primary and secondary alkyl halides, so that alkylation of **1** (Scheme 2, upper pathway) takes place before any substantial amounts of **1** are decomposed.

The results of the reaction of primary, secondary, and tertiary alkyl halides with **1** in ether (Table 3) can be explained by considering the same arguments as presented for the toluene reactions above. The moderate yields of Grignard compounds from the reaction of primary and secondary alkyl halides in ether (entries 1–5) reflect the moderate decomposition rate of **1** in ether between 0 °C and room temperature[1].

The reaction of phenyl radicals formed by single-electron transfer[19] from **1** to RX [Scheme 1 (c)] appears to be the major pathway in the reaction of **1** with bromo- or iodobenzene in THF, since benzene (**8**) and **9** are the major products and either phenylmagnesium bromide (**5**) and **6** or diphenylmagnesium, MgI_2[15], and **6** are produced only as side products (Table 4, entries 1–4). In the first step of this reaction the phenyl radical and an anthracene radical anion complex **7** [similar to $Mg_2Cl_3(THF)_6^{\oplus}$ anthracene$^{\ominus\bullet}$[20]] are probably formed. The abstraction of a hydrogen atom from the solvent by the phenyl radical produces benzene, while the resulting tetrahydro-2-furanyl radical recombines with the anthracene radical anion from **7** to give **9** after protolysis. This reaction course is further supported by the deuterolysis of the reaction products from C_6H_5I and **1** (Table 4, entry 3) with the formation of C_6H_6 and C_6H_5D in the molar ratio of 90:10 and D_1-**9**[7b]. An analogous radical reaction product, 1-ethoxy-7-(tetrahydro-2-furanyl)norbornane, has been obtained in 1.5% yield by Bickelhaupt et al.[21] by the treatment of 7-bromo-1-ethoxynorbornane with Mg in THF.

In contrast to bromo- and iodobenzene, chlorobenzene reacts with **1** in THF only sluggishly up to the boiling point. In toluene at 60 °C or ether at reflux phenylmagnesium chloride can be obtained in 85–90% yield from **1** and chlorobenzene (entries 5, 8) by decomposition of **1** and generation of Mg*, as discussed above for alkyl halides (Scheme 2). With bromo- or iodobenzene in toluene, due to the competition between radical reduction of halobenzenes [Scheme 1 (c)] and phenylation an decomposition of **1**, a mixture of benzene, **2**, **2'**, and **5** (entries 6, 7) is obtained[7b].

Allyl, propargyl, and benzyl chlorides react in THF with **1** to give mainly Grignard compounds (**5**) and anthracene (**6**) (Scheme 1, pathway b) and only minor amounts of **2**, **2'**

Table 2. Reaction of **1** with alkyl halides (RX) in the molar ratio 1:1 in toluene (r.t. = temperature)

Entry	RX	g(mmol)	Tol.[a] [ml]	React. temp. [°C]	React. time [h]	Raw[b] product [g]	Conv.[c] of **1** [%]	Reaction products Σ **2**,**2'** [%][e]	Σ **4**–**4''** [%][e]	$RMgX^{d}$ (**5**)	**6**
1	EtBr	1.39(12.7)	60	r.t.	1	2.50[f]	99	23	3	80	65
2	nBuCl	1.51(16.3)	50	0	24	3.38	98	17	10	44	52
3	nBuCl	1.44(15.5)	60	r.t.	24	3.19[f]	95	25	3	62	57
4	nBuCl	1.06(11.5)	50	50–80	2	2.17	98	9	1	79	82
5	iBuCl	1.14(12.4)	50	reflux temp.	1	2.19	99	3	6	77	84
6	sBuCl	1.49(16.1)	50	r.t.	2	g)	g)	g)	g)	38	g)
7	tBuCl	1.94(20.9)	60	r.t.	3	4.21	93	75	–	0	12
8	tBuBr	2.44(17.8)	70	r.t.	18	4.32	97	68	14	0	15

[a] Total amount. – [b] Total amount of nonvolatile organic reaction products. – [c] On the basis of 9,10-dihydroanthracene obtained by hydrolysis of the reaction mixture. – [d] On the basis of gaseous hydrocarbons evolved upon hydrolysis of the reaction mixture (MS analysis). – [e] Yield of reaction products based on converted **1**. – [f] From the raw product **6** (1.50 g) was separated by crystallization (see exp. part); the soluble part was analyzed by gas chromatography. – [g] Not determined.

Table 3. Reaction of **1** with alkyl halides (RX) in ether at room temperature

Entry	RX	g(mmol)	Molar ratio RX/1	Ether[a] [ml]	React. time [h]	Raw[b] product [g]	Conv.[c] of **1** [%]	Reaction products Σ 2,2' [%][e]	Σ 4–4'' [%][e]	RMgX[d] (**5**)	**6**
1	EtBr	1.46(13.4)	1	40	16	2.82	98	25	15	40	42
2	nBuCl	2.75(29.7)	1	50	24	6.00[f]	95	21	3	62	54
3	nBuCl	7.27(78.5)	2	60	48	9.79	99	3	51		37
4	sBuCl	5.24(56.6)	1	120	48	12.14[g]	97	39[g]	12	26	26
5	sBuCl	5.94(64.1)	2	120	48	9.70[g]	99	6	59[g]	h)	24
6	tBuCl	1.85(20.0)	1	60	3	4.39[g]	90	77[g]	–	h)	11
7	tBuBr	3.66(26.7)	1	60	15	6.02	94	72	–	h)	17
8	tBuBr	11.60(84.6)	2	140	48	10.17	100	72	10	–	13

[a] Total amount. – [b] Total amount of nonvolatile organic reaction products. – [c] On the basis of 9,10-dihydroanthracene obtained by hydrolysis of the reaction mixture. – [d] On the basis of gaseous hydrocarbons evolved upon hydrolysis of the reaction mixture (MS analysis). – [e] Yield of reaction products based on converted **1**. – [f] From the raw product **6** (2.64 g) was separated by crystallization (see exp. part); the soluble part was analyzed by gas chromatography. – [g] See text, exp. part. – [h] Not determined.

Table 4. Reaction of **1** with halobenzenes (PhX) in THF, toluene and ether (r.t. = room temperature)

Entry	PhX	g(mmol)	Molar ratio PhX/1	Solvent[a] [ml]	React. temp. [°C]	React. time [h]	Conv.[b] of **1** [%]	Reaction products Σ 2,2'	Σ 4–4''	PhMgX[c] (**5**)	**6** [%][d]	C_6H_6[c]	**9**
1	PhBr	2.99(19.0)	1	THF 140	0	2	99	–		23	33	69	30
2	PhBr	5.53(35.2)	2.6	THF 140	0	2	99	–	–		30		30
3	PhI	4.94(24.2)	1	THF 200	0	2	99	–	–	15	22	82	45
4	PhI	7.69(37.7)	2	THF 120	r.t.	2	100	–	–		19		29
5	PhCl	1.66(14.7)	1	tol. 80	60	2	100	–	–	85	90	8	–
6	PhBr	1.94(12.4)	1	tol. 85	60	2	93	35	4	19	50	28	–
7	PhI	3.57(17.5)	1	tol. 80	r.t.	2	91	39	3	11	49	35	–
8	PhCl	1.44(12.8)	1	ether 80	reflux temp.	6	100	–	–	90	87	6	–

[a] Total amount. – [b] On the basis of 9,10-dihydroanthracene obtained by hydrolysis of the reaction mixture. – [c] For the determination of PhMgX and C_6H_6 in the mixture see exp. part. – [d] Yield of reaction products based on converted **1**.

and **4–4''** (Table 5, entries 1, 3–5, 8–10), which are the major products in the alkyl halide reactions. In these cases Grignard compounds are probably formed by direct attack of the electrophiles on **1** rather than by decomposition of **1** to Mg* (Scheme 2) since under these conditions **1** is stable. With reference to the generally accepted ideas on the pathways for the formation of Grignard compounds[19], the higher stability and rate of formation of allyl, propargyl, and benzyl chloride radical anions and/or of their respective radicals R· relative to alkyl chloride radicals may be the reason for this behavior. For the formation of allylmagnesium chloride in toluene and ether (entries 6, 7) and benzylmagnesium chloride in benzene and ether (entries 11, 12)[7a,b] both the pathways in Scheme 1(b) and Scheme 2 are possible.

The generation of allyl-, methallyl-, and crotylmagnesium chlorides from **1** in THF is possible at temperatures as low as −78°C (entries 3–5)[7a,b]. In contrast to the reaction at 0°C (entries 1, 2), the reaction mixture has an intense blue color at −78°C, probably due to the presence of magnesium anthracene radical anion complex $Mg(THF)_6^{\oplus}$ $(anthracene^{\ominus\bullet})_2$[20] which is stable only at low temperatures.

A notable example offered by this novel method is the preparation of allenylmagnesium chloride (**5k**) from propargyl chloride and **1** in THF (Scheme 3, Table 5, entry 8)[7c]. The preparation of the Grignard compound from propargyl chloride has previously been only possible by using amalgamated magnesium in combination with the application of the dilution technique[22]. The Grignard reagent prepared by this method is proposed, on the basis of its IR spectrum (absorption at 1878 cm^{-1} [22a]), to exist in the allenyl form (**5k**)[22]. However, IR and NMR spectra of the related Grignard reagent prepared from propargyl bromide suggest that the presence of a minor proportion of the acetylenic form cannot be excluded[22d]. The reaction of propargyl chloride with Mg* generated from **1** or catalytically prepared MgH_2[7a] has also failed to produce this Grignard reagent[7c,18].

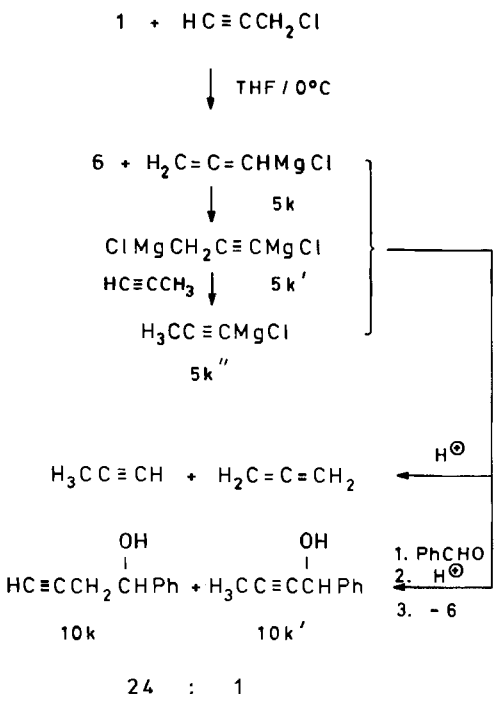
The Grignard reagent **5k** (Table 5, entry 8) reacts with benzaldehyde to give 4-hydroxy-4-phenyl-1-butyne (**10k**)[23] admixed with 4% of 4-hydroxy-4-phenyl-2-butyne (**10k'**)

Table 5. Reaction of **1** with allyl, propargyl, and benzyl halides in various solvents in the molar ratio 1:1

Entry	RX	g(mmol)	Solvent[a] [ml]	React. temp. [°C]	React. time [h]	Raw[b] product [g]	Conv.[c] of **1** [%]	Reaction products Σ 2,2'	Σ 4–4''	RMgX[d] (5) [%][e]	6	8	R–R
1		1.92(25.1)	THF 60	0	2		91			91			–
2		1.54(12.7)	THF 50	0	2	2.55	77	–	4	70	76		30
3		1.78(23.3)	THF 140	–78	12	3.89	85	5	–	87	90		3
4		3.16(34.9)	THF 160	–78	12	6.00	86	–	8	66	80		4
5		2.69(29.8)	THF 155	–78	12	5.74	72	–	24	40	64		7
6		1.59(20.8)	tol. 60	0	2		81			81			
7		0.75(9.8)	ether 60	0	2		98			98			
8	$HC{\equiv}CCH_2Cl$	1.21(16.3)	THF 45	0	0.17		97	2	~1	76.6	91		
9	$HC{\equiv}C\underset{\displaystyle CH_3}{\underset{|}{C}}HCl$	1.51(17.1)	THF 40	r.t.	15	2.91	80	5		46[f]	72	7	–
10	$PhCH_2Cl$	2.64(20.9)	THF 80	r.t.	3		99	8	3	67	81	3	1
11	$PhCH_2Cl$	1.63(12.9)	benz. 70	r.t.	2		96	4	3	68	68	5	2
12	$PhCH_2Cl$	1.85(14.6)	ether 70	r.t.	1		93	4	3	73	93	3	1

[a] Total amount. – [b] Total amount of nonvolatile organic reaction products. – [c] On the basis of 9,10-dihydroanthracene, obtained by hydrolysis of the reaction mixture. – [d] On the basis of gaseous hydrocarbons or toluene produced by hydrolysis of the reaction mixture (see exp. part). – [e] Yield of reaction products based on converted **1**. – [f] Mixture of 1-butyne and 1,2-butadiene.

Scheme 3



(total yield 86%). The latter is probably formed by reaction of the rearranged Grignard reagent, **5k'** and/or **5k''** [22d], with benzaldehyde. The reaction of 3-chloro-1-butyne with **1** affords the Grignard compound **5l** in 46% yield (Table 5, entry 9)[7c].

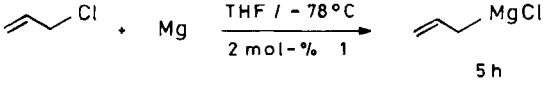
The generation of allyl- and allenylmagnesium chloride can also be carried out be using ordinary magnesium powder and with only catalytic amounts of **1** (cf. next section).

Generation of Allyl- and Allenylmagnesium Chloride Promoted by 1

The ability of **1** to act as a source of soluble zerovalent magnesium with the liberation of anthracene (**6**), which will regenerate **1** in the presence of magnesium in THF, can be utilized to catalyze phase-transfer reactions[24] of metallic magnesium[6]. For such purposes **1** can be conveniently prepared in situ in the presence of an excess of metallic magnesium (cf. Experimental); ultrasound treatment of the system can improve the efficiency of the catalytic reaction[6].

In view of the stoichiometric reactions of **1** with organic halides described in the previous section, it can be expected that the application of **1** (or **6**) to the catalysis of Grignard compound formation, in the sense of Scheme 4, should be limited to those halides which in THF react with **1** according to pathway (b) (Scheme 1) (i.e. allyl, propargyl, and benzyl halides). If the halide in question also partially reacts with **1** according to pathway (a) or (c), the catalytic effect of **1** (or **6**) will be limited to a certain number of catalytic cycles until **1** has been completely consumed. If, finally, the particular halide reacts with **1** exclusively according to (a) or (c), the beneficial effect of generating in situ a small amount of **1** before the addition of the halide, will just be that of facilitating the start of the reaction with the halide by cleaning the solvent and the magnesium surface, comparable to the effect of iodine or the entrainment method[26].

In accordance with the previous discussion, allylmagnesium chloride (**5h**) has been prepared from commercial magnesium powder and allyl chloride in THF at –78 °C in 71% yield by generating in situ 2 mol-% of **1** prior to the addition of the allyl chloride[7b].



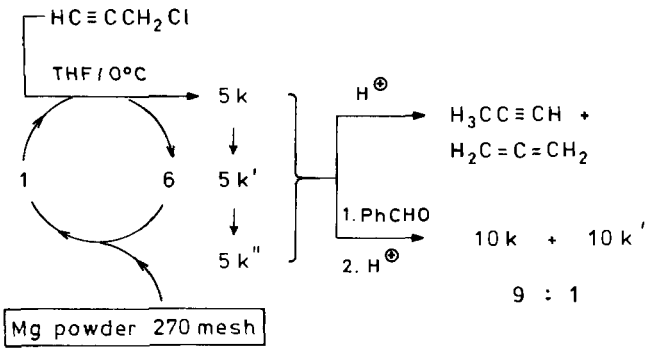
In view of the difficulties that arise in the preparation of the Grignard reagent from propargyl chloride (cf. previous section), it is of interest to catalyze the reaction of propargyl chloride with magnesium by means of **1** (or **6**)[27]. The reaction is complicated by the fact that the primary product of the reaction, **5k**, is unstable and rearranges to **5k'** and/or **5k''** (cf. previous section and ref.[22]).

In the presence of 8 mol-% of **1** propargyl chloride reacts with commercial Mg powder in THF between 0 and +20°C to give **5k** admixed with **5k'** and/or **5k''** in a total yield of 81–83%, as determined by their hydrolysis to a mixture of allene and propyne. The formation of side (**2k**, **4k**) and rearrangement products (**5k'**, **5k''**) can be minimized by slow addition (8 h) of propargyl chloride to a well stirred suspension of Mg powder and **1** in THF at 0°C. Under such conditions **5k** is obtained together with **5k'** and **5k''** in a 9:1 molar ratio, as determined by their subsequent reaction with benzaldehyde to produce **10k** and **10k'** (Scheme 4). Performing the reaction at room temperature leads to higher percentages of rearranged products[7c].

Since propargyl chloride reacts neither with ordinary[22] nor with active magnesium[7c,18], but with **1** in THF to give **5k** and **6** (cf. previous section), it is likely that the generation of **5k** takes place via intermediate **1**, as indicated in Scheme 4. The blue color of the reaction mixture observed during the addition of propargyl chloride, which disappears suddenly after each drop of propargyl chloride is stirred into the solution, suggests that an anthracene radical anion complex, analogous to $[Mg_2Cl_3(THF)_6]^{\oplus}$ anthracene$^{\ominus\bullet}$[20], could also be formed as an intermediate in this reaction. After the completion of the reaction, the presence of **6** has been detected in the reaction mixture by gas chromatography (cf. discussion p. 1511).

In summary, according to our investigations **1** can be used stoichiometrically to generate allyl-, propargyl-, and benzyl-type Grignard compounds and catalytically to generate allyl- and propargylmagnesium chloride under mild conditions. The preparation of these and other types of Grignard compounds using Mg* generated from **1**, or from the catalytically formed MgH_2, is discussed in the following publication[18].

Scheme 4



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Experimental

^1H NMR: Varian EM 360, WP 80 FT, or AM 200, Bruker WH 400 FT. – ^{13}C NMR: Bruker WM 300 or Varian XL 100 FT. – IR: Nicolet 7000. – MS: Varian MAT CH 5, CH 7, or Finnegan MAT 8230. – GC/MS coupling analyses: combination of an F 22 Perkin-Elmer gas chromatograph with a Varian CH 7 A spectrometer. – Gas analyses: CEC 103 mass spectrometer. – GC analyses: glass capillary columns with different stationary phases, commercial instruments, H_2 as the carrier gas, FID detection. – Elemental analyses: Dornis & Kolbe, Mülheim-Ruhr.

Starting Materials: Mg powder (Eckart-Werke PK-31, 270 mesh, or Ventron, 50 mesh) and anthracene (99%, Rütgerswerke AG) were used without further purification. **1** was prepared according to the refs.[12a,28]. Organic halides were dried over P_2O_5, distilled, and stored over molecular sieves (4 Å) under argon. 3-Chloro-1-butene was prepared according to ref.[29] THF was refluxed over $MgEt_2$ and distilled under argon.

All the reactions and operations with organometallic compounds were performed under argon using air- and water-free solvents. The gas volume measurements were executed at 20°C and 1 bar of pressure.

General Procedure for the Stoichiometric Reaction of **1** *with Organic Halides:* All the data concerning amounts of starting materials and amounts and composition of reaction products in the experiments are collected in Tables 1–5. A weighed amount of **1** is suspended in the respective solvent and the organic halide (RX), dissolved in 1/3 of the total amount of the solvent, is dropped into the stirred suspension at 0°C (exceptions: Table 5, entries 3–5) for 0.5–1 h. The reaction mixture is stirred at the temperature and for the period of time given in Tables 1–5. To determine the yield of Grignard compound an aliquot of the reaction mixture is evaporated in vacuo (0.2 mbar) and the residue hydrolyzed by the addition of H_2O. The gases liberated are collected in a gas buret and analyzed by mass spectrometry. The solvent is removed in vacuo (0.2 mbar), and ether is added to the residue and subsequently H_2O and diluted HCl. The ether layer is neutralized with a $NaHCO_3$ solution, dried with Na_2SO_4, and the ether is then removed in vacuo to give the "raw product" which is weighed. For the isolation of **6** and 9,10-dihydroanthracene (DHA) the raw product is dissolved in toluene/pentane (1:2) and the solution cooled to −78°C for 1 h. The crystals are filtered off at −78°C, washed with cold pentane, and dried in vacuo. For GC and GC/MS analysis a weighed amount (40–60 mg) of the raw product is dissolved in 2–5 ml of a standard solution (toluene/CH_3OH 50:1) containing analytically weighed amounts (6–8 mg/ml) of *n*-C_8H_{18} and/or *n*-$C_{16}H_{34}$ as standards. The conversion of **1** is calculated on the basis of DHA (the hydrolysis product of **1**) as ascertained by the GC analysis. The compounds *cis*-**4a**, *cis*- and *trans*-**4b**, *trans*-**4b'**, *cis*- and *trans*-**4b''**, *cis*/*trans*-**4c**, **2f**, **4f**, **2g**, **2g'**, **3**, and **9** were isolated from the raw product by means of preparative gas chromatography or crystallization and identified by means of their NMR spectra (see text below); the remaining dihydroanthracene derivatives **2**, **2'**, and **4**–**4''** were identified by GC/MS coupling analyses and comparison of their gas chromatograms with those of analogous known compounds (e.g. **2g**, **2g'**, **4b**–**4b''**).

Reaction of **1** *with MeI (Molar Ratio 1:2) in THF* (Table 1, Entry 1): During the reaction 93 ml of a mixture of CH_4 and C_2H_6

(93:7) evolved. From the THF solvent an additional 38 ml of a mixture of CH_4 and C_2H_6 (3:97) was isolated by condensation of the THF and gases intraps at −78 and −196 °C, respectively, in vacuo. Upon hydrolysis of the residue obtained after evaporation of the solution, 116 ml of CH_4 were evolved. For the isolation of *cis*-**4a** the raw product (4.45 g) was dissolved in 50 ml of pentane, the solution stirred at 30 °C for 1 h, and the insoluble part (**6**, 33%) was filtered off. The pentane solution was concentrated to 20 ml, filtered again, and cooled to −78 °C for 12 h. **4a** was isolated by filtration at −78 °C, washed with cold pentane, and dried in vacuo. Further purification of **4a** was achieved by flash chromatography[30] (silica, 40−63 μm, 0.4 bar, hexane). Crystallization from ethanol produced pure **4a**, m.p. 130−131 °C (ref.[31] 131 °C). The preparation and isolation of **4a** according to this method on a larger scale (0.2 mol) is described in communication 8 of this series[32]. The ^{1}H-NMR spectrum of **4a** was in accordance with that of described in ref.[31].

Reaction of **1** *with EtBr (Molar Ratio 1:2.58) in THF* (Table 1, Entry 3): From the raw product (8.66 g) *cis*- and *trans*-**4b**, *trans*-**4b′** (98% purity), (presumably) *cis*-**4b″** (79% purity) and (presumably) *trans*-**4b″** (69% purity) were isolated by means of preparative gas chromatography. The ^{1}H-NMR spectra of *cis*- and *trans*-**4b** were in agreement with those reported in ref.[31] − ^{1}H NMR of *trans*-**4b′** (80 MHz, $CDCl_3$): δ = 0.87−0.90 (m, 2′,2″-H), 1.56−1.34 (m, 1′,1″-H), 2.21 (m, 2-H), 2.64 (t, *J* = 7 Hz, 1-H), 6.05 (dd, *J* = 6 Hz, 3-H), 6.56 (d, *J* = 10 Hz, 4-H), 7.46 (m, 9,10-H), 7.37 (m, 6,7-H), 7.74 (m, 5-H). − ^{1}H NMR of (presumably) *cis*-**4b″** (80 MHz, $CDCl_3$): δ = 0.79 (t, *J* = 7 Hz, 2′-H), 1.86 (m, 1′-H), 3.49 (m, 1,4-H), 5.94 (d, *J* = 1.5 Hz, 2,3-H), 7.41 (m, 6,7-H), 7.70 (s, 9,10-H), 7.82 (m, 5-H). − ^{1}H NMR of (presumably) *trans*-**4b″** (80 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7 Hz, 2′-H), 1.38, 1.87 (m, 1′-H), 3.47 (m, 1,4-H), 6.05 (d, *J* = 3 Hz, 2,3-H), 7.40 (m, 6,7-H), 7.60 (s, 9,10-H), 7.77 (m, 5-H).

Reaction of **1** *with iPrBr (Molar Ratio 1:2.37) in THF* (Table 1, Entry 5): The workup of the reaction mixture was carried out as described for the reaction of **1** with MeI. The main product, **4c**, was isolated as a 4:1 *trans/cis* mixture. The ratio and the structure of the stereoisomers of **4c** were determined by a comparison of the ^{1}H-NMR spectrum of the mixture with the spectra reported for the components[33].

Reaction of **1** *with tBuBr (Molar Ratio 1:1; 24 h) in THF* (Table 1, Entry 12): The raw product (6.64 g) was dissolved in toluene/pentane (1:2) and the solution cooled to −30 °C for 1 h, whereby 1.90 g (21%) of **3** (m.p. 110 °C) crystallized. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.16 (m, 2″-H), 0.84 (s, 2‴-H), 1.20 (m, 3″-H), 1.50−1.64 (m, 2′,3′-H, OH), 2.13, 2.15 (m, 1′,1″-H), 3.22 (t, 4″-H), 3.57 (t, 4′-H), 3.87 (s, 9-H), 7.19 (m, 2,3-H), 7.27 (m, 4-H), 7.49 (m, 1-H). − ^{13}C NMR (25.2 MHz, $CDCl_3$): δ = 19.9 (t, C-2′), 22.3 (t, C-2″), 29.9 (2, C-2‴), 32.7 (t, C-3′), 33.5 (t, C-3″), 36.6 (s, C-1‴), 43.4 (t, C-1′), 44.9 (t, C-1″), 46.0 (s, C-9), 54.5 (d, C-10), 62.3 (t, C-4′), 62.6 (t, C-4″), 124.1 (d, C-1), 126.1 (d, C-2), 126.9 (d, C-3), 130.9 (d, C-4), 136.9 (s, C-11), 141.6 (s, C-12).

$C_{26}H_{36}O_2$ (380.6) Calcd. C 82.06 H 9.53
Found C 81.96 H 9.03

Reaction of **1** *with sBuCl (Molar Ratio 1:1) in Ether* (Table 3, Entry 4): From the raw product (12.14 g) 2.53 g of **6** (95.1% purity) was isolated by crystallization (see General Procedure). From the soluble part (8.90 g) **2f** was separated by preparative GC. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.87 (d, *J* = 6.5 Hz, 1″-H), 0.98 (t, *J* = 6.5 Hz, 3′-H), 1.20, 1.60 (m, 2′-H), 1.80 (m, 1′-H), 3.87 (d, 9-H), 3.91 (d, 10-H), 4.24 (d, *J* = −18.4 Hz, 10-H), 7.29 (m, 1-H), 7.37 (m, 2,3-H).

Reaction of **1** *with sBuCl (Molar Ratio 1:2) in Ether* (Table 3, Entry 5): From the raw product (9.70 g) 1.40 g of **6** (93% purity) was isolated by crystallization (see General Procedure). From the soluble part (7.56 g) **4f** was separated by preparative GC. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.88 (d, *J* = 6.5 Hz, 1″-H), 0.97 (t, *J* = 6.5 Hz, 3′-H), 1.36, 1.56 (m, 2′-H), 2.10 (m, 1′-H), 3.95 (d, *J* = 5 Hz, 9,10-H), 7.20 (m, 1-H), 7.37 (m, 2,3-H).

Reaction of **1** *with tBuCl (Molar Ratio 1:1) in Ether* (Table 3, Entry 6): From the raw product (4.39 g) **2g** and **2g′** were isolated by preparative GC. Their ^{1}H-NMR spectra were in agreement with those reported in the literature[34].

Reaction of **1** *with PhBr (Molar Ratio 1:1) in THF* (Table 4, Entry 1): An aliquote of 1.00 ml of the reaction mixture was protolyzed by addition of 3.00 ml of the standard solution (see General Procedures) and analyzed by gas chromatography. On the basis of the GC analysis the following yields of the hydrolysis products of the reaction mixture were calculated: 1.35 g (17.3 mmol) of C_6H_6, 0.040 g (0.2 mmol) of DHA, 1.12 g (6.3 mmol) of **6**, and 1.42 g (5.70 mmol) of **9**. A 50.0-ml aliquote of the reaction mixture was filtered, the filtrate evaporated in vacuo (0.2 mbar) and the distillate and the residue analyzed separately by gas chromatography. An analysis of the respective distillate and residue revealed that the reaction mixture contained 1.03 g (13.2 mmol) of C_6H_6 and 0.35 g (4.4 mmol) of C_6H_6 (after protolysis of the residue by adding 25 ml of ether and 1 ml of CH_3OH).

Reaction of **1** *with PhBr (Molar Ratio 1:2.6) in THF* (Table 4, Entry 2): From the raw product 3.00 g of **9** was isolated in 93.4% purity by preparative GC. − ^{1}H NMR (80 MHz, CD_2Cl_2): δ = 1.68 (m, 4H, 5′-H), 3.65−4.18 (m, 6H, 10,9,3′,4′-H), 7.30 (s, 8H, 2,3-H). − ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 26.1 (t, C-4′), 29.8 (t, C-3′), 36.2 (t, C-10), 52.4 (d, C-9), 68.3 (t, C-5′), 83.3 (d, C-2′), 125.8 (d, C-4), 126.1 (d, C-3), 126.4 (d, C-2), 126.7 (d, C-1), 126.8 (d, C-5), 128.0 (d, C-6), 129.4 (d, C-7), 129.9 (d, C-8), 137.1 (s, C-11), 137.7 (s, C-12), 138.0 (s, C-14), 138.3 (s, C-13). − MS (70 eV): *m/z* = 179 (M^+), 178, 71, 43.

Reaction of **1** *with PhI (Molar Ratio 1:1) in THF* (Table 4, Entry 3): The $MgI_2(THF)_x$[15] precipitated (5.38 g) was filtered off, washed with THF, and dried in vacuo. According to the acidimetric titration, the filtrate contained a total of 10.6 mmol of Mg^{2+} but no iodide ions. The analysis of the organic hydrolysis products in the filtrate was performed as described for the reaction of **1** with PhBr (molar ratio 1:1).

Reaction of **1** *with PhI (Molar Ratio 2:1) in THF* (Table 4, Entry 4): The workup and analysis were performed as described for the reaction with a 1:1 molar ratio.

Reaction of **1** *with PhCl (Molar Ratio 1:1) in Toluene* (Table 4, Entry 5): The precipitate formed during the reaction was filtered off, washed with toluene, and dried in vacuo to give 2.20 g of solid. Hydrolysis of the solid yielded 0.45 g (5.6 mmol) of THF, 0.12 g (1.5 mmol) of C_6H_6, and 1.33 g (7.5 mmol) of **6** (GC analysis). Further workup and analysis of the filtrate were performed as described for the reaction of **1** with PhBr (molar ratio 1:1) in THF.

Reaction of **1** *with PhBr and PhI (Molar Ratio 1:1) in Toluene* (Table 4, Entries 6 and 7): The analysis of the reaction mixture was performed as described for the reaction of **1** with PhBr in a 1:1 molar ratio in THF.

Reaction of **1** *with PhCl (Molar Ratio 1:1) in Ether* (Table 4, Entry 8): The precipitate formed during the reaction was filtered off, washed with ether, and dried in vacuo to give 2.43 g of solid. Hydrolysis of the solid gave 0.40 g (5.5 mmol) of THF, 0.11 g (1.4

mmol) of C_6H_6, and 1.30 g (7.3 mmol) of **6** (GC analysis). Further workup and analysis of the filtrate were performed as described for the reaction of **1** with PhBr in a 1:1 molar ratio in THF.

Reaction of **1** *with Allyl, Methallyl, and trans-Crotyl Chloride (Molar Ratio 1:1) in THF at −78°C* (Table 5, Entries 3−5): The reaction mixtures were protolyzed at −78°C by the addition of 5 ml of CH_3OH, the volatiles evaporated in vacuo (0.2 mbar) and condensed in two cold traps (−78 and −196°C) in series. The volatiles condensed in the −78°C cold trap were analyzed by gas chromatography, and the gas condensed in the −196°C cold trap was determined by mass spectrometry.

Reaction of **1** *with Propargyl Chloride (Molar Ratio 1:1) in THF* (Table 5, Entry 8): To a stirred cooled (ice bath) suspension of 6.82 g (16.3 mmol) of **1** in 35 ml THF a solution of 1.21 g (1.20 ml; 16.3 mmol) of propargyl chloride in 5 ml of THF was added over a period of 20 min. The mixture was stirred for an additional 10 min at 0°C. Hydrolysis of a 15.0-ml aliquot of the total of 40 ml of the suspension afforded 120 ml of gas composed of 93.6% of C_3H_4 (mixture of allene and propyne) and 6.4% of THF (MS analysis). Yield of the Grignard compound **5k** (including **5k′**, **5k″**): 76.6%.

10k (**10k′**) *from* **5k** (**5k′**, **5k″**) *and Benzaldehyde:* To the rest of the stirred solution of C_3H_4MgCl described above (7.8 mmol of C_3H_4MgCl), 1.08 g, (1.10 ml; 10.2 mmol) of C_6H_5CHO (molar ratio C_3H_4MgCl/C_6H_5CHO = 1:1.3) was added dropwise at 0°C. The mixture was allowed to warm to room temp. and stirred for 17 h. The residue, after removal of the solvent in vacuo, was treated with H_2O and dilute HCl. The organic products were extracted with ether and the ether extracts dried with Na_2SO_4. Evaporation of the ether gave 3.29 g of a partly crystalline oil. To separate **6** the latter was dissolved in 10 ml toluene at 50°C, 10 ml of pentane was added and the mixture cooled to −78°C whereby 1.65 g of **6** (m.p. 210°C) crystallized. The solution was evaporated in vacuo to yield 1.39 g of an oil of the following composition (GC analysis): **10k** 68.0, **10k′** 2.7 (yield of **10k** + **10k′** 86%, based on C_3H_9MgCl), DHA 2.8, 6 5.8, **2k** 3.2, **4k** 2.1%.

^{1}H NMR of **10k** (**10k′**) (200 MHz, $CDCl_3$): δ = 1.80 (d, CH_3), 1.97 (t, HC≡), 2.52 (dd, CH_2), 2.87 (s, OH), 4.72 [t, HC (**10k**)], 5.30 [m, HC (**10k′**)], 7.38 (m, aromatic H). − IR of **10k** (**10k′**) (neat): $\tilde{\nu}$ = 3538 cm^{-1}, 3375 (OH), 3290 (HC≡), 3060, 3025, 2975, 2930, 2910, 2880, 2815, 2223 (−C≡C−), 2118 (HC≡C−).

Reaction of **1** *with $PhCH_2Cl$ (Molar Ratio 1:1) in THF* (Table 5, Entry 10): A small amount of the precipitate formed during the reaction was separated by filtration and washed with THF. A 5.0-ml aliquot of the filtrate (total volume 101 ml) was evaporated in vacuo (0.2 mbar), and the distillate and the residue were analyzed separately by gas chromatography. The distillate contained a total of 0.06 g (0.6 mmol) toluene determined by the addition of 5.0 ml of a standard solution with ≈7 mg/ml of *n*-C_8H_{18} in THF). The residue was protolyzed by the addition of 20.0 ml of a standard solution (THF containing 7−8 mg/ml of *n*-C_8H_{18} and *n*-$C_{16}H_{34}$) and consisted of a total of 1.23 g (13.4 mmol) of toluene, 0.01 g (0.1 mmol) of $PhCH_2Cl$, 0.05 g (0.3 mmol) of bibenzyl, 0.02 g (0.1 mmol) of DHA, 2.91 g (16.3 mmol) of **6**, 0.42 g (1.6 mmol) of **2n**, and 0.23 g (0.6 mmol) of **4n**.

Reaction of **1** *with $PhCH_2Cl$ (Molar Ratio 1:1) in Benzene* (Table 5, Entry 11): The precipitate formed during the reaction was filtered off, washed with benzene, and dried in vacuo to give 1.69 g of a solid. Hydrolysis of the solid produced 0.23 g (2.5 mmol) of toluene and 0.43 g (2.4 mmol) of **6** (GC analysis). Further workup and analysis of the filtrate were performed as in the THF reaction.

Reaction of **1** *with $PhCH_2Cl$ (Molar Ration 1:1) in Ether* (Table 5, Entry 12): The precipitate formed during the reaction was filtered off, washed with ether, and dried in vacuo to give 3.77 g of a solid. Hydrolysis of the solid produced 0.35 g (3.8 mmol) of toluene, 0.12 g (0.7 mmol) of DHA, and 1.71 g (9.6 mmol) of **6** (GC analysis). Further workup and analysis of the filtrate were performed as in the THF reaction.

5h *from Allyl Chloride and Mg at −78°C in the Presence of* **1**: To a suspension of 0.71 g (29.2 mmol) of Mg powder (50 mesh, Ventron) and 0.11 g (0.6 mmol) of **6** in 50 ml of THF was added a drop of EtBr, and the mixture was stirred for 2−3 h during which time **1** was produced. A solution of 2.25 g (29.4 mmol) of C_3H_5Cl in 25 ml of THF was dropped into the stirred suspension at −78°C over 1 h, and the mixture was further stirred for 15 h at −78°C. The protolysis was performed at −78°C by addition of 2 ml of CH_3OH; the volatiles were evaporated in vacuo (0.2 mbar) and condensed into two cold traps (−78 and −196°C) in series. The −196°C cold trap contained 481 ml of C_3H_6 (MS analysis) and the −78°C cold trap 36.5 mg (0.9 mmol) of C_3H_6 and 0.42 g (5.1 mmol) of biallyl (GC analysis).

5k (**5k′**, **5k″**) *from Propargyl Chloride and Mg Catalyzed by* **1**: A mixture of 1.00 g (41.1 mmol) of Mg powder (270 mesh), 0.53 g (3.1 mmol) of **6**, and 0.04 ml of EtBr in 20 ml of THF was stirred for 2−3 h to complete the formation of **1**. To the suspension a solution of 3.10 g (3.00 ml; 42 mmol) of propargyl chloride in 25 ml of THF was added dropwise at 0°C with constant stirring for 8 h. During the addition of the propargyl chloride solution the reaction mixture was blue, but the blue color faded suddenly after the addition of each drop of the solution. However, by the time the next drop was added, the blue color reappeared. Hydrolysis of a 10.0-ml aliquot of the solution (total volume 45 ml) caused evolution of 195 ml of gas composed of C_3H_4 (mixture of allene and propyne, 93.1%), THF (4.4%), and H_2 (2.5%) (MS analysis). Based on the amount of C_3H_4 found, the total yield of the Grignard compounds **5k** (**5k′**, **5k″**) was 83%.

10k (**10k′**) *from* **5k** (**5k′**, **5k″**) *and Benzaldehyde:* To the rest of the stirred solution of C_3H_4MgCl described above (26.5 mmol of C_3H_4MgCl), 3.5 ml (33 mmol) of C_6H_5CHO (molar ratio C_3H_4MgCl/C_6H_5CHO = 1:1.25) was added dropwise at 0°C for 20 min. The mixture was allowed to warm to room temp. and stirred for 17 h. It was worked up as described above for the reaction of **1** with propargyl chloride. Composition of the raw product (5.59 g; GC analysis): **10k** 61.0, **10k′** 6.8 (yield of **10k** + **10k′** 98%, based on C_3H_4MgCl), **6** 4.8, and **2k** 8.0%.

CAS Registry Numbers

1: 86901-19-1 / **2b**: 605-82-3 / **2d**: 10394-60-2 / **2f**: 13387-48-9 / **2g**: 13387-48-9 / **2h**: 84332-59-2 / **2l**: 126695-06-5 / **2m**: 13577-28-1 / **2n**: 2294-89-5 / **2′b**: 126694-96-0 / **2′d**: 126694-91-5 / **2′f**: 62337-62-6 / **2′g**: 62337-62-6 / **2′h**: 126695-01-0 / **2′l**: 126695-07-6 / **2′m**: 126695-00-9 / **2′n**: 126695-08-7 / **3**: 126694-95-9 / *cis*-**4a**: 13417-34-0 / **4b**: 46868-29-5 / *cis*-**4b**: 20826-55-5 / *trans*-**4b**: 23660-32-4 / *cis*-**4c**: 24316-21-0 / *trans*-**4c**: 25340-82-3 / **4d**: 47205-57-2 / **4e**: 126694-97-1 / **4f**: 126694-92-6 / **4i**: 95164-05-9 / **4j**: 126695-04-3 / **4′a**: 54271-79-3 / **4′b**: 94960-49-3 / *trans*-**4′b**: 126694-85-7 / **4′c**: 94578-27-5 / **4′d**: 126694-89-1 / **4′e**: 126694-98-2 / **4′f**: 126694-93-7 / **4′g**: 95129-03-6 / **4′i**: 126695-02-1 / **4′j**: 126695-05-4 / **4″b**: 126694-84-6 / *cis*-**4″b**: 126694-86-8 / *trans*-**4″b**: 126694-87-9 / **4″c**: 126694-88-0 / **4″d**: 126694-90-4 / **4″e**: 126694-99-3 / **4″f**: 126694-94-8 / **4″i**: 126695-03-2 / **4″j**: 126752-54-3 / **5b** (X = Br): 925-90-6 / **5d** (X = Cl): 693-04-9 / **5e** (X = Cl): 5674-02-2 / **5h** (X = Cl): 2622-05-1 / **5h** (X = Br): 1730-25-2 / **5i** (X = Cl): 5674-01-1 / **5j** (X = Cl): 6088-88-6 / **5k**: 75854-80-7 / **5l** (X = Cl): 21020-24-6 / **5m** (X = Br): 100-58-3 / **5m** (X = Cl): 100-59-4 / **5m** (X = I): 16002-63-4 / **5n** (X = Cl): 6921-34-2 / **5′k**: 126695-09-8 / **5″k**: 104085-63-4 / **6**: 120-12-7 / **9**: 110079-20-4 / **10k**: 1743-36-8 / **10′k**:

32398-66-6 / MeH: 74-82-8 / EtH: 74-84-0 / Me_2Mg: 2999-74-8 / $Me_2C=CH_2$: 75-28-5 / PhH: 71-43-2 / PhBr: 108-86-1 / PhI: 591-50-4 / PhCl: 108-90-7 / $CH_2=CHCH_2Cl$: 107-05-1 / $CH_2=CHCH_2Br$: 106-95-6 / $CH_2=C(Me)CH_2Cl$: 563-47-3 / $MeCH=CHCH_2Cl$: 591-97-9 / $CH\equiv CCH_2Cl$: 624-65-7 / $CH\equiv CCHMeCl$: 21020-24-6 / $PhCH_2Cl$: 100-44-7 / $(CH_2=CH)_2$: 590-19-2 / PhMe: 108-88-3 / $CH\equiv CEt$: 107-00-6 / $(CH_2=CHCH_2)_2$: 592-42-7 / $(MeCH=CHCH_2)_2$: 4974-27-0

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