Reaction of 1-Aryl-3-chloropropenes with Grignard Reagents. Nucleophilic Substitution *versus* Single-electron Transfer

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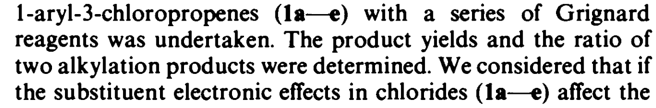
The reactions of ambident 1-aryl-3-chloropropenes (**1a**—**e**) with a series of Grignard reagents, R′MgY (R′ = Me, Pr, Ph, Pr^i, Bu^t; Y = Br, I), were carried out in diethyl ether (EE) and tetrahydrofuran (THF). The products were a mixture of two alkylation products (**2**) and (**3**), and three dimerization products (**4**)—(**6**). The alkylation:dimerization ratio and the composition of the two alkylation products were a marked function of substituent electronic effects in the chlorides (**1a**—**e**), R′ or Y of R′MgY, and solvent. On the basis of the stereochemistry of alkylation, cyclizable probe experiments, and the effect of the addition of $FeCl_3$ on product composition, the following conclusions were obtained. First, dimers (**4**)—(**6**) are most likely to be produced by a mechanism involving single-electron transfer (SET). Second, for the formation of alkylation products (**2**) and (**3**), three alternative pathways contribute depending on the nature of R′MgY and solvent, (a) competitive S_N2–S_N2' pathways in the reaction of R′MgBr in EE, (b) a process involving SET in the reaction with R′MgI in EE, and (c) S_N2 pathways in the reaction of R′MgBr in THF.

The reaction of alkyl halides with magnesium reagents has received attention lately with regard to mechanism.[1] Using stereochemistry and CIDNP as the most definitive indicators of mechanism, it has been confirmed that at least two reaction mechanisms, *i.e.*, electron transfer [equation (1)] and direct nucleophilic substitution [equation (2)], are possible. Evidence



is available for both mechanisms in individual cases. However, a delicate balance must exist between these mechanistic alternatives, and a minor change of reaction conditions may alter the extent of each path.[†]

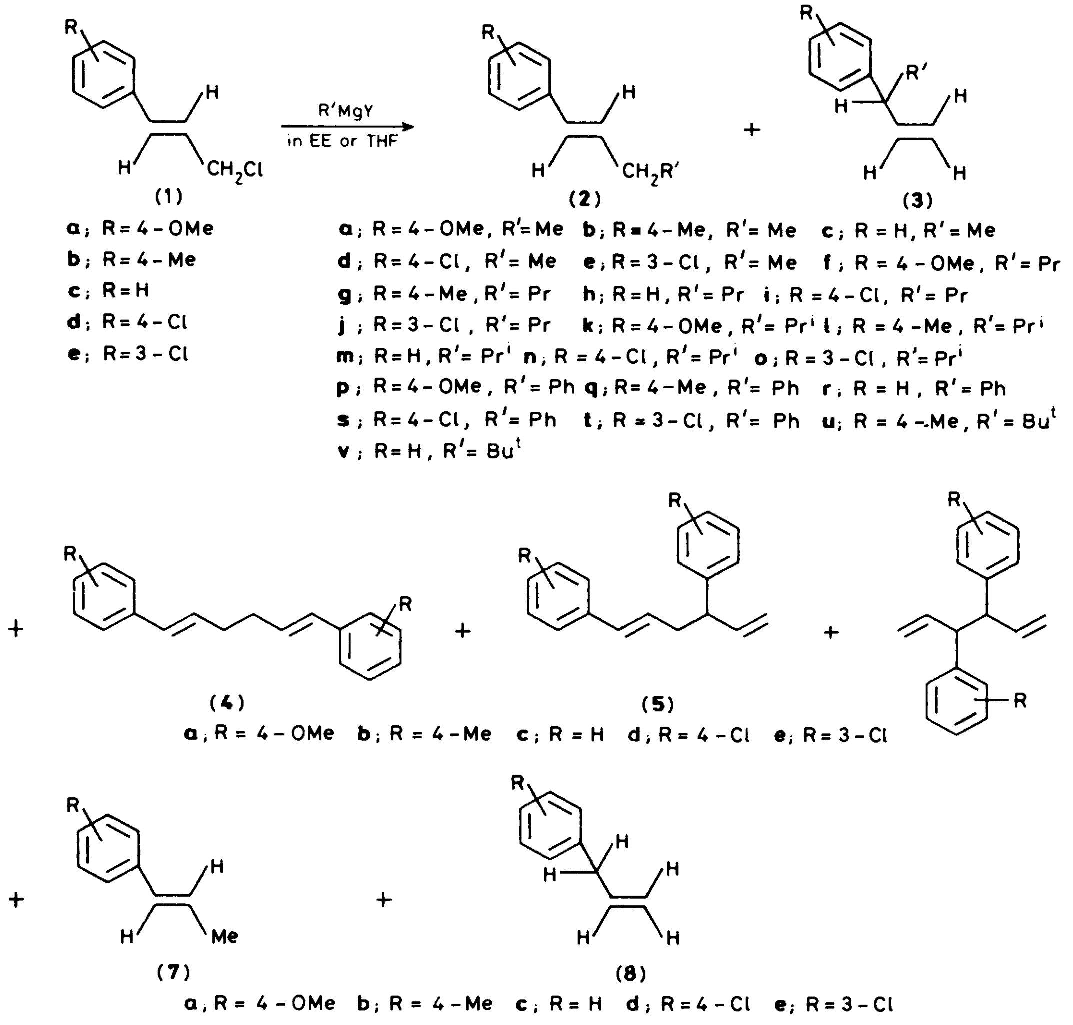
As an approach to this complicated but important reaction of alkyl halides with Grignard reagents, the reaction of ambident 1-aryl-3-chloropropenes (**1a**—**e**) with a series of Grignard reagents was undertaken. The product yields and the ratio of two alkylation products were determined. We considered that if the substituent electronic effects in chlorides (**1a**—**e**) affect the composition of the alkylation products in a significantly different fashion depending on the mechanism, this would serve to elucidate the reaction paths participating in these reactions and the factors affecting the extent of each process.[1e]

Results

Reaction of (E)-1-*Aryl*-3-*chloropropenes with Grignard Reagents in Diethyl Ether.*—The reaction of chlorides (**1a**—**e**) with R′MgBr (R′ = Me, Pr, Ph, Pr^i) at 30 °C for 1 h gave in each case a mixture of two alkylation products, 3-substituted 1-arylpropene (**2**) and 3-substituted 3-arylpropene (**3**), together with three dimerization products (**4**)—(**6**) (Scheme 1 and Table 1). In the case of t-butylmagnesium bromide, dimers (**4**)—(**6**) were the major products, accompanied by small amounts of the reduction products, 1-arylpropene (**7**) and 3-arylpropene (**8**) (Table 2). Examination of the data reveals the following. (a) The (**2**):(**3**) ratios were markedly influenced by the substituent electronic effects, the (**2**):(**3**) ratio being increased with the increase of electron-withdrawing ability of the substituent R. In connection with this, it is noted that the (**2**):(**3**) ratios observed in the reactions of 1-arylpropenyl-lithiums with alkyl halides are also markedly affected by the substituent electronic effects, the (**2**):(**3**) ratio being, however, increased with the increase of electron-donating ability of the substituent.[3] This clearly indicates that in the reaction of chlorides (**1**) with Grignard reagents, metal–chlorine exchange prior to cross-coupling is not important. The alkyl group of R′MgBr also affected the (**2**):(**3**) ratio, the proportion of C-3 attack product (**2**) being increased with the decrease of steric bulk of R′: Pr^i < Ph < Pr < Me. (b) The yields of dimers (**4**)—(**6**) increased in the order Ph ≃ Me < Pr < Pr^i < Bu^t. The composition of dimers (**4**):(**5**):(**6**) (*ca.* 3:6:1) were almost insensitive to the substituent electronic effects and the structure of alkyl groups of R′MgBr. The addition of $FeCl_3$, a probable accelerator of a single-electron transfer (SET) process,[2] resulted in an increase in the yield of dimers (**4**)—(**6**) (Table 3). The ratio (**4**):(**5**):(**6**) was much the same as that from the reaction in the absence of $FeCl_3$. The composition of reduction products (**7**) and (**8**), obtained from the reaction with t-butylmagnesium bromide, was also substituent-independent, the (**7**):(**8**) ratio being *ca.* 1:1 (Table 2).

In marked contrast to the reaction with R′MgBr, the reaction of chlorides (**1b**—**e**) with R′MgI (R′ = Me, Pr) gave in each case a substituent-independent mixture of two alkylation products (**2**) and (**3**), the (**2**):(**3**) ratios being 9:1 for MeMgI and 7:3 for PrMgI (Table 1). Another characteristic feature was the dimer yield. The proportion of dimers (**4**)—(**6**) in the reaction with MeMgI was as high as 60%, whereas the reaction with MeMgBr provided mainly alkylation products (**2**) and (**3**).

[†] The extensive study by Ashby and his co-workers has revealed the existence of a delicate balance between nucleophilic addition and single-electron transfer in the reaction of Grignard reagents with carbonyl compounds.[2]



Scheme 1.

Reaction of (E)-1-*Aryl-3-chloropropenes with Grignard Reagents in Tetrahydrofuran.*—Tetrahydrofuran (THF) as a solvent exerted remarkable effects on the reaction rate and product composition. The reaction of 1-phenyl-3-chloropropene (**1c**) with MeMgBr in THF at 30 °C for 1 h resulted in the recovery of the starting chloride (**1c**), whereas the same reaction in diethyl ether (EE) lead to complete consumption of chloride (**1c**). In the case of PrMgBr also, the reaction in THF was much slower than that in EE. Similar trends were observed in the reaction of (9-anthryl)arylmethyl chloride.[1e] Consequently, the reaction of (**1**) in THF was undertaken at 30 °C for 2 h (Table 4). The reaction of chlorides (**1b**—**e**) with phenyl- or propylmagnesium bromide, yielded exclusively the corresponding C-3 attack product (**2**). From the highly ionizable *p*-methoxy derivative (**1a**), however, a considerable amount of C-1 attack product (**3**) was obtained together with (**2**). Exactly the same trends were observed for the reductions of (**1a**—**e**) with lithium aluminium hydride in EE (Figure 1), whilst lithium triethylborohydride reductions in THF resulted in exclusive formation of 1-arylpropenes (**7a**—**e**).[4] This fact suggests that the reagents having high nucleophilicity prefer to attack the leaving group site of chloride (**1**). Although the reaction with isopropylmagnesium bromide afforded a mixture of (**2**) and (**3**), the observed (**2**):(**3**) ratio was, however, much higher than that from the reaction in EE. From the reaction of chlorides (**1c**—**e**) with t-butylmagnesium bromide, dimers (**4**)—(**6**) were obtained exclusively (Table 2).

Stereochemistry of the Reaction of 1-*Aryl-3-chloropropenes with Grignard Reagents.*—In all the reactions of (*E*)-1-aryl-3-chloropropenes (**1**) with Grignard reagents in EE or THF, the corresponding 3-substituted 1-arylpropene (**2**) with *E*-configuration was obtained, together with 3-substituted 3-arylpropene (**3**) and dimers (**4**)—(**6**). When the reaction of (*Z*)-1-phenyl-3-chloropropene (*Z*)-(**1c**) with phenylmagnesium bromide was undertaken in EE or THF, (*Z*)-1,3-diphenylpropene was obtained in a considerable amount. The reaction of (*Z*)-(**1c**) with isopropylmagnesium bromide in EE also gave (*Z*)-1-phenyl-4-methylpent-1-ene, together with 3-phenyl-4-methylpent-1-ene and dimers (**4**)—(**6**). From the reaction in THF, however, only dimers (**4**)—(**6**) were obtained, in 53% yield.*

In marked contrast, the reaction of (*Z*)-(**1c**) with propylmagnesium iodide resulted in the formation of an *E*–*Z* mixture of 1-phenylhex-1-ene (**2**) (*E*/*Z* = 3:2), together with 3-phenylhex-1-ene (**3**) and dimers (**4**)—(**6**) (Scheme 2 and Table 5). It is

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* Compared with (*E*)-1-phenyl-3-chloropropene, the reaction of the *Z*-isomer is very slow and, moreover, the alkylation products are obtained in a relatively lower yield.

worth nothing that (a) sodium borohydride reduction of (*Z*)-(**1c**) in aqueous diglyme, which is known to proceed by 1-phenylpropenyl cation,[5] gave a mixture of (*E*)- and (*Z*)-1-phenylpropenes (**7c**) in a ratio of *ca.* 1:1, together with 3-phenylpropene (**8c**) and (b) tributyltin hydride reduction of (*Z*)-1-phenyl-3-bromopropene *via* 1-phenylpropenyl radical[6] also afforded an *E*–*Z* mixture of 1-phenylpropene (**7c**) in a ratio of *ca.* 1:1, suggesting that the reaction of (*Z*)-1-phenyl-3-halogenopropene, if it proceeds by prior carbon–halogen cleavage, provides an *E*–*Z* mixture of the corresponding 3-substituted 1-phenylpropene. As might be expected, lithium aluminium hydride reduction of (*Z*)-(**1c**) in EE or THF. in which an S_N2 pathway should predominate, gave exclusively (*Z*)-(**7c**).[4]

Table 1. Reaction of 1-aryl-3-chloropropenes (**1a**—**e**) with Grignard reagents in diethyl ether[a]

	R′MgY		Products	
Chloride	R′	Y	% Alkylation[b,c] [(**2**):(**3**)]	% Dimerization[b,c] [(**4**):(**5**):(**6**)]
(**1a**)	Me	Br	100 [65:35]	
(**1b**)	Me	Br	93 [87:13]	7[d]
(**1c**)	Me	Br	94 [96:4]	6[d]
(**1d**)	Me	Br	84 [100:0]	16[d]
(**1e**)	Me	Br	100 [100:0]	
(**1b**)	Me	I	41 [91:9]	59 [30:50:20]
(**1c**)	Me	I	41 [86:14]	59 [30:55:15]
(**1d**)	Me	I	40 [87:13]	60 [21:64:15]
(**1e**)	Me	I	36 [89:11]	64 [27:59:14]
(**1a**)	Pr	Br	100 [52:48]	
(**1b**)	Pr	Br	58 [67:33]	42 [25:61:14]
(**1c**)	Pr	Br	50 [83:17]	50 [26:62:12]
(**1d**)	Pr	Br	52 [86:14]	48 [24:62:14]
(**1e**)	Pr	Br	44 [94:6]	56 [30:60:10]
(**1b**)	Pr	I	38 [68:32]	62 [22:63:15]
(**1c**)	Pr	I	21 [70:30]	79 [32:54:14]
(**1d**)	Pr	I	43 [66:34]	57 [25:62:13]
(**1e**)	Pr	I	45 [70:30]	55 [30:58:12]
(**1a**)	Pr^i	Br	48 [53:47]	52 [25:61:14]
(**1b**)	Pr^i	Br	49 [56:44]	51 [28:66:6]
(**1c**)	Pr^i	Br	26 [64:36]	74 [25:70:5]
(**1d**)	Pr^i	Br	36 [65:35]	64 [26:62:12]
(**1e**)	Pr^i	Br	33 [67:33]	67 [28:69:3]
(**1a**)	Ph	Br	100 [63:37]	
(**1b**)	Ph	Br	100 [70:30]	
(**1c**)	Ph	Br	89 [72:28]	11 [25:75:0]
(**1d**)	Ph	Br	78 [74:26]	22 [26:74:0]
(**1e**)	Ph	Br	76 [85:15]	24 [25:61:14]

[a] The reaction with 3 mol equiv. of a Grignard reagent in diethyl ether at 30 °C for 1 h. [b] The total yield was *ca.* 70%, normalized; 100% = % alkylation + % dimerization. [c] The ratio of products was determined by ^1H n.m.r. spectroscopy; average values of duplicate runs. The errors were *ca.* 2% for alkylation products and 6% for dimerization products. [d] The composition was not determined.

Reaction with Hex-5-enylmagnesium Halides, Radical Probe Compounds.—Since it is known that hex-5-enyl radical cyclizes to cyclopentylmethyl radical, hex-5-enylmagnesium halides (Y = Br, I) could serve as probes for the detection of single-electron transfer (SET) in the reaction of 1-aryl-3-chloropropenes (**1**) with Grignard reagents.[2] When the reaction of chloride (**1**) with hex-5-enylmagnesium bromide was performed in EE, a mixture of only non-cyclized products, 1-arylnona-1,8-diene (**9**) and 3-arylnona-1,8-diene (**10**), was obtained together with dimers (**4**)—(**6**) (Scheme 3 and Table 6). The reaction in THF afforded preferentially 1-arylnona-1,8-diene (**9**). These results suggest that a radical–radical coupling process is not important for the formation of alkylation products (**2**) and (**3**) from the reaction of chloride (**1**) with primary Grignard reagents.

Unfortunately, the reaction of chloride (**1c**) with hex-5-enylmagnesium iodide in EE resulted in the formation of only dimers (**4**)—(**6**) and reduction products (**7**) and (**8**). From the reaction of chloride (**1c**) with 1-methylhex-5-enylmagnesium bromide, a secondary cyclizable probe compound, dimers (**4**)—(**6**) were obtained exclusively.

An Ab Initio *Study.*—As an approach to the reactions of ambident 1-aryl-3-chloropropenes (**1a**—**e**) with Grignard reagents, the spin- and charge-densities of the possible intermediates, 1-arylpropenyl radicals (**11a**,**c**,**e**) and 1-arylpropenyl cations (**12a**,**c**,**e**), were calculated by an *ab initio* SCF MO method at the HF/STO-3G level (Table 7).[7]

Table 3. Reaction of 1-aryl-3-chloropropenes with Grignard reagents in the presence of $FeCl_3$ in diethyl ether[a]

		Products	
Chloride	R′MgBr R′	% Alkylation[b,c] [(**2**):(**3**)]	% Dimerization[b,c] [(**4**):(**5**):(**6**)]
(**1b**)	Me	41 [96:4]	59 [27:56:17]
(**1c**)	Me	47 [100:0]	53 [27:59:14]
(**1d**)	Me	45 [100:0]	55 [29:59:12]
(**1e**)	Me	44 [100:0]	56 [28:54:18]
(**1c**)	Pr		100 [33:55:12]
(**1c**)	Pr^i		100 [30:54:16]
(**1c**)	Bu^t	2[d]	98 [29:59:12]

[a] Reaction with 3 mol equiv. of a Grignard reagent in the presence of $FeCl_3$ (0.1 mol equiv.) in diethyl ether at 30 °C for 1 h. [b—d] See footnotes in Table 1.

Table 2. Reaction of 1-aryl-3-chloropropenes with t-butylmagnesium bromide[a]

			Products		
Chloride	Solvent	Reaction time (h)	Alkylation % yield [(**2**):(**3**)][b]	Dimerization % yield [(**4**):(**5**):(**6**)][b]	Reduction % yield [(**7**):(**8**)][b]
(**1b**)	EE	1	26 [53:47]	42 [27:63:10]	5 [56:44]
(**1c**)	EE	1	2 [69:31]	43 [16:74:10]	3 [60:40][c]
(**1d**)	EE	1		37 [22:70:8]	10 [50:50]
(**1e**)	EE	1		27 [25:70:5]	23 [45:55]
(**1c**)	THF	2		65 [28:72:0]	
(**1d**)	THF	2		42 [30:59:11]	
(**1e**)	THF	2		52 [32:58:10]	

[a] Reaction with 3 mol equiv. of t-butylmagnesium bromide. [b] Isolated yield. The composition was determined by ^1H n.m.r. spectroscopy. [c] The composition was determined by g.l.c.

Table 4. Reaction of 1-aryl-3-chloropropenes with Grignard reagents in tetrahydrofuran[a]

		Products	
Chloride	R'MgBr R'	% Alkylation[b,c] [(**2**):(**3**)]	% Dimerization[b,c] [(**4**):(**5**):(**6**)]
(**1a**)	Pr	100 [67:33]	
(**1b**)	Pr	78 [100:0]	22 [31:52:17]
(**1c**)	Pr	64 [100:0]	36 [34:54:12]
(**1d**)	Pr	68 [100:0]	32 [31:60:9]
(**1e**)	Pr	70 [100:0]	30 [33:53:14]
(**1a**)	Pr^i	75 [87:13]	25 [33:67:0]
(**1b**)	Pr^i	50 [89:11]	50 [32:65:3]
(**1c**)	Pr^i	47 [96:4]	53 [30:64:6]
(**1d**)	Pr^i	50 [97:3]	50 [31:60:9]
(**1e**)	Pr^i	58 [100:0]	42 [30:60:10]
(**1a**)	Ph	100 [80:20]	
(**1b**)	Ph	62 [100:0]	38 [59:41:0]
(**1c**)	Ph	60 [100:0]	40 [65:35:0]
(**1d**)	Ph	65 [100:0]	35 [54:46:0]
(**1e**)	Ph	75 [100:0]	25 [39:56:5]

[a] Reaction with 3 mol equiv. of a Grignard reagent in tetrahydrofuran at 30 °C for 2 h. [b,c] See footnotes in Table 1.

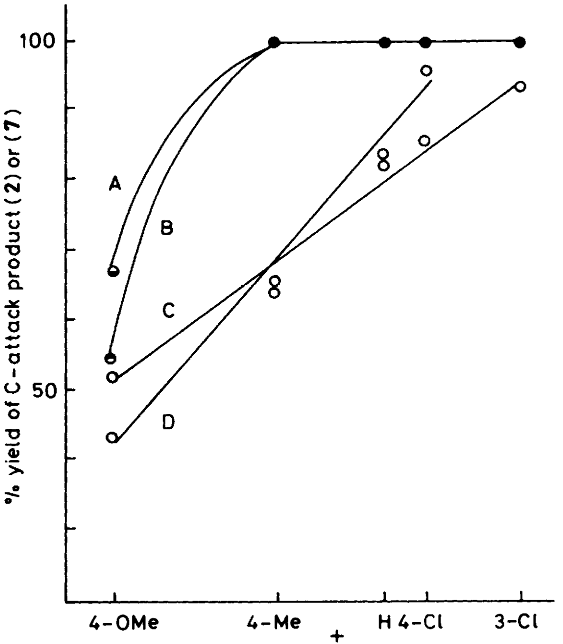
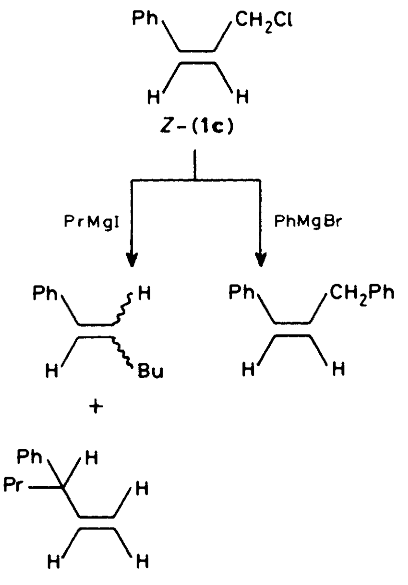


Figure 1. A, Reaction of (**1**) with PrMgBr in THF; B, of (**1**) with $LiAlH_4$ in EE; C, of (**1**) with PrMgBr in EE; D, of (**1**) with $NaBH_4$ in aqueous diglyme

Table 5. Stereochemistry of the reaction of (*Z*)-1-phenyl-3-chloropropene

		Products	
Reagent	Solvent	% Yield [(**2**):(**3**)] or [(**7**):(**8**)]	*Z*:*E* ratio
PhMgBr[a]	EE	67 [99:1]	100:0
Pr^{i}MgBr[a]	EE	10 [83:17][e]	100:0
PhMgBr[a]	THF	20 [200:0][e]	100:0
PrMgI[a]	EE	6 [72:28][e,f]	40:60
$NaBH_4$[b]	Aqueous diglyme	60 [42:58]	50:50
Bu_3SnH[c,g]	Benzene	40 [100:0]	50:50
$LiAlH_4$[d]	EE	90 [100:0]	100:0
$LiAlH_4$[d]	THF	85 [100:0]	100:0

[a] Reaction with 3 mol equiv. of a Grignard reagent at 30 °C for 3 h. [b] Reaction with 5 mol equiv. of $NaBH_4$ in aqueous diglyme at 30 °C for 1 h. [c] Reaction with 3 mol equiv. of Bu_3SnH in the presence of benzoyl peroxide (0.1 mol equiv.) in benzene at 80 °C for 10 h. [d] Reaction with 10 mol equiv. of $LiAlH_4$ at 30 °C for 1 h. [e] Dimeric products (**4**)—(**6**) were also produced in *ca.* 50% yield. [f] Chloride (*Z*)-(**1c**) was recovered (10%). [g] Reaction of (*Z*)-1-phenyl-3-bromopropene.



Scheme 2.

For a series of 1-arylpropenyl radicals (**11a**,**c**,**e**), the substituents R exert no meaningful influence on the spin densities at C-1 and -3. This would imply that if alkylation products are produced by cross-coupling of 1-arylpropenyl radical (**11**) and the alkyl radical produced from a Grignard reagent, then the (**2**):(**3**) ratio would be substituent-independent.

For a series of 1-arylpropenyl cations (**12a**,**c**,**e**), the substituents R show a significant influence on the charge densities at C-1 and -3. The electron-donating 4-methoxy group decreases the charge densities at both C-1 and -3 and in direct contrast, the electron-withdrawing 3-chloro substituent increases the charge densities at the same positions. More important is that the carbon far from the substituent (C-3) is more susceptible to the substituent electronic effects than C-1 attached directly to the aryl group. Thus, if reaction proceeds *via* a carbonium ion intermediate (**12**), then the product regiochemistry would be influenced by the substituent R such that the increase in electron-withdrawing ability increases the proportion of C-3 attack product. This prediction is in good agreement with the fact that the $NaBH_4$ reduction of chlorides (**1a**—**e**) in aqueous diglyme provided a mixture of 1-aryl- (**7**) and 3-aryl-propene (**8**), the ratio being increased with the increase in electron-withdrawing ability of the substituent R (Figure 1).[4]

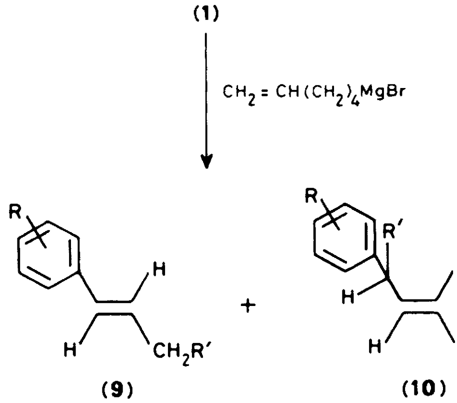
Discussion

Dimers (**4**)—(**6**) are most likely to be produced by coupling of 1-arylpropenyl radicals (Scheme 4).[1] As the MO study for

Table 6. Reaction of 1-aryl-3-chloropropenes with hex-5-enylmagnesium bromide[a]

Chloride	Solvent	Reaction time (h)	Products % Alkylation [(**9**):(**10**)]	 % Dimerization [(**4**):(**5**):(**6**)]
(**1a**)	EE	1	53 [31:69]	10 [25:55:20]
(**1c**)	EE	1	34 [55:45]	35 [30:60:10]
(**1e**)	EE	1	35 [60:40]	40 [28:58:14]
(**1c**)	THF	2	26 [100:0]	54 [32:58:10]
(**1e**)	THF	2	30 [100:0]	40 [28:62:10]

[a] Reaction with 3 mol equiv. of hex-5-enylmagnesium bromide at 30 °C. [b] Isolated yield. The composition was determined by ^{1}H n.m.r. spectroscopy.



a; R = 4-OMe, R' = $(CH_2)_4CH{=}CH_2$

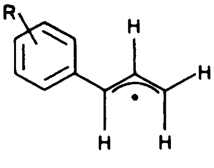
c; R = H, R' = $(CH_2)_4CH{=}CH_2$

e; R = 3-Cl, R' = $(CH_2)_4CH{=}CH_2$

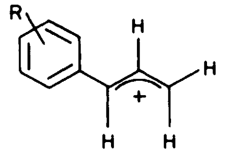
Scheme 3.

1-arylpropenyl radical (**11**) suggests, the substituent-independent composition of dimers (**4**)—(**6**) is not inconsistent with this hypothesis.* The effect of the alkyl group of Grignard reagents on the product composition would be interpreted as that the Grignard reagents having a relatively higher donicity favour an SET process, with the dimers (**4**)—(**6**) being produced in greater percentage.[8] The most probable pathway for the formation of reduction products (**7**) and (**8**), obtained exceptionally from the reaction of chloride (**1**) with t-butylmagnesium bromide, is hydrogen abstraction of 1-arylpropenyl radical (**11**) from t-butyl radical. The (**7**):(**8**) ratio is also substituent-independent (Table 2).

The reaction of chloride (**1**) with R'MgBr in THF leads to preferential formation of the C-3 attack product (**2**). The observed stereospecificity clearly demonstrates that this is an S_N2 reaction. Exclusive formation of non-cyclized product (**9**) from the reaction with hex-5-enylmagnesium bromide supports this. For the reaction of chloride (**1**) with R'MgBr in EE, the following facts require explanation. (a) The (**2**):(**3**) ratios are a marked function of the substituent R, the ratios increasing with the increase in electron-withdrawing ability of the substituent R.

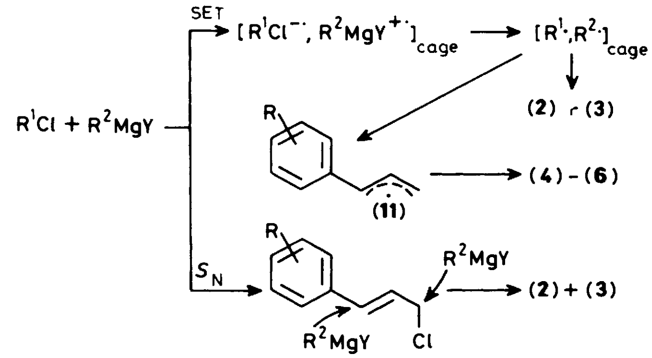


(**11**)



(**12**)

a; R = 4-OMe, b; R = H, c; R = 3-Cl



Scheme 4.

The (**2**):(**3**) ratios correlate well with substituent constants σ^+ (Figure 2). (b) The nucleophilicity of a Grignard reagent in a less polar EE would be significantly smaller than that in THF[1c] but, nevertheless, the reaction in the former solvent is much faster than that in the latter. (c) The reactions are stereospecific, suggesting that C–C bond formation occurs prior to C–Cl bond cleavage. The solvent effect on rate would be rationalized in terms of external assistance of C–Cl bond cleavage in EE by co-ordination of electropositive magnesium to electronegative chlorine of (**1**), with the electrophilicity of chloride (**1**) being significantly increased.[1c] Then the stereospecificity in alkylation and notable substituent electronic effects on the (**2**):(**3**) ratio lead us to deduce that the reaction of chloride (**1**) with Grignard reagents would proceed by a charge-developed species (**13**), in which the C–Cl bond is still retained; the Grignard reagent co-ordinated to chloride (**1**) would attack the chloride at C-1 to provide (**3**), whilst external attack of a Grignard reagent on chloride (**1**) at the 3-position would lead to the formation of (**2**).† A similar mechanism has been postulated for the reaction of allylic halides and amine.[9] In THF, in which a Grignard reagent is strongly solvated, such external assistance to C–Cl bond cleavage would not be expected.‡ Consequently, in this solvent Grignard reagents favour attack on the most polarized carbon attached directly to the leaving group, as do highly nucleophilic lithium aluminium hydride or lithium triethylborohydride.[4]

The reaction or chloride (**1**) with R'MgI seems to proceed by a different pathway. The observed non-stereospecificity in the alkylation suggests that C–Cl bond cleavage would occur prior to cross-coupling. Then, the substituent-independent composition of alkylation products would imply that a mechanism

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* The reaction of chloride (**1**) with phenylmagnesium bromide in THF exerts a very different trend for the composition of dimers (**4**)—(**6**) (Table 4). The reason is obscure.

† The reaction of Grignard reagents with optically active halides, if it proceeds by an S_N2 pathway, gives an inversion product.[1a]

‡ As a referee has kindly suggested, the observed solvent effects would be due to the difference in the Schlenk equilibrium between EE and THF. In EE the mixed species RMgX is prevalent, whilst in THF a more random distribution of three components, RMgX, R_2Mg, and MgX_2, is observed.[1c] Since R_2Mg is more nucleophilic than RMgX,[1c] consequently, S_N2 processes are more favoured in THF than EE.

Table 7. An *ab initio* study for radical (**11**) and cation (**12**)

	1-Arylpropenyl radical spin density		1-Arylpropenyl cation charge density	
Substituent	C-1	C-3	C-1	C-3
4-OMe	0.904	1.130	0.086	0.058
H	0.905	1.130	0.092	0.069
C-Cl	0.904	1.130	0.095	0.076

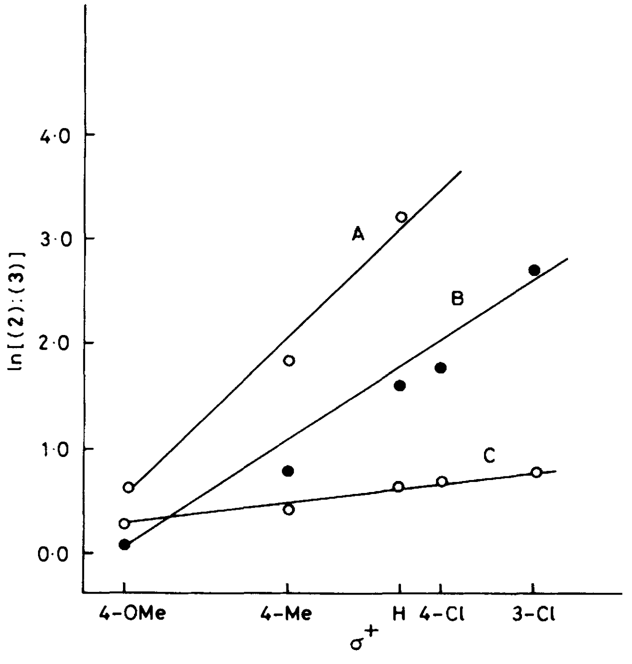
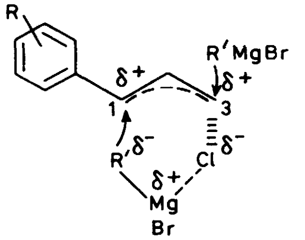


Figure 2. Reaction of A, (**1**) with MeMgBr in EE; B, (**1**) with PrMgBr in EE; C, (**1**) with Pr^iMgBr in EE



(13)

involving 1-arylpropenyl radical (**11**) is important.* It is reasonable to expect that alkylmagnesium iodide, having probably a lower ionization potential than the corresponding alkylmagnesium bromide,† favours an SET pathway. The relatively higher yield of dimers (**4**)—(**6**) would be consistent with this hypothesis.

Experimental

^1H N.m.r. spectra were obtained with a JNM-PS-100 spectrometer in CCl_4. Mass spectral data were obtained with a Hitachi RMU-6H spectrometer and i.r. spectra with a Hitachi 215 spectrometer. G.l.p.c. analysis was carried out on a Hitachi 164 gas chromatograph.

Materials.—Grignard reagent solutions were prepared by a standard procedure from Wako Grignard grade turnings (99.5%), and were analysed by hydrolysing a portion with distilled water, adding excess of standard HCl, and back-titrating standard NaOH to a phenolphthalein end point. The procedures of preparation of (*E*)-1-aryl-3-chloropropenes (**1a**—**e**) are described elsewhere.[4] (*Z*)-1-Phenyl-3-chloropropene[12] and (*Z*)-1-phenyl-3-bromopropene[13] were prepared from (*Z*)-3-phenylbut-2-en-1-ol[14] by reported methods. By means of lithium aluminium hydride reduction in THF, the content of the *E*-isomer was confirmed to be < 2%. Hex-5-enyl bromide,[15] hex-5-enyl iodide,[16] and 6-bromohept-1-ene[17] were prepared by reported methods. $FeCl_3$ was commercial grade and used without purification.

General Reactions.—The following procedure for the reactions of chlorides (**1a**—**e**) with Grignard reagents is representative. Into a flask (50 ml), equipped with a magnetic stirrer and maintained under N_2, a solution of a Grignard reagent was syringed. A solution of chloride was dropped into the solution, and the mixture was stirred at 30 °C under N_2. The mixture was then hyrolysed with aqueous NH_4Cl solution. The ether layer was separated, dried (Na_2SO_4), and the solvent was removed under vacuum. The crude products were chromatographed on silica gel to give two fractions (elution with hexane). The first fraction was composed of a mixture of two alkylation products. The second fraction contained dimers (**4**)—(**6**). In the case of t-butylmagnesium bromide, however, three fractions were obtained. The first fraction contained reduction products (**7**) and (**8**), followed by alkylation products (**2**) and (**3**), and then dimers (**4**)—(**6**). The composition of the products was determined by ^1H n.m.r. spectroscopy and g.l.p.c.

Reaction of (E)-1-*phenyl*-3-*chloropropene with phenylmagnesium bromide in diethyl ether.* To phenylmagnesium bromide (5.90 mmol) in EE (10 ml) was added a solution of chloride (**1c**) (300 mg, 1.97 mmol) in EE (10 ml). After 1 h, the mixture was decomposed with aqueous NH_4Cl and extracted with EE. The crude products were chromatographed on silica gel to give two fractions. The first fraction contained 1,1-diphenylprop-2-ene (**3r**) (18%) and 1,3-diphenylpropene (**2r**) (45%). The second fraction consisted of 1,4-diphenylhexa-1,5-diene (**5c**) (6%) and 1,6-diphenylhexa-1,5-diene (**4c**) (2%).

By column chromatography and fractional distillation of the first fraction, were isolated (*E*)-(**2r**), m.p. 17.5 °C (lit.,[18] 18 °C), *m/e* 194 (M^+), δ 3.48 (2 H, d, *J* 5.0 Hz), 6.25—6.40 (2 H, m), and 6.90—7.50 (10 H, m), and (**3r**), m.p. 14—15 °C (lit.,[19] 14.5—16 °C), δ 4.50—5.22 (3 H, m), 6.00—6.50 (1 H, m), and 7.00—7.40 (10 H, m). Column chromatography of the second fraction on silica gel gave pure (**4c**), m.p. 70—72 °C (lit.,[20] 70—72 °C), *m/e* 234 (M^+), δ 2.40 (4 H, t, *J* 7.0 Hz), 5.80—6.51 (4 H, m), and 7.02—7.22 (10 H, m) and (**5c**), an oil, *m/e* 234 (M^+), δ 2.60 (2 H, t, *J* 7.2 Hz), 3.20—3.50 (1 H, m), 4.90—5.20 (2 H, m), 5.80—6.50 (3 H, m,), and 7.00—7.20 (10 H, m).[20]

Reaction of (E)-1-*phenyl*-3-*chloropropene with isopropylmagnesium bromide in THF.* The reaction of (**1c**) (300 mg, 1.97 mmol) with isopropylmagnesium bromide (5.90 mmol) was performed in THF at 30 °C for 2 h. After conventional work-up, the products were isolated by column chromatography on silica gel. Physical properties of (*E*)-1-phenyl-4-methylpent-1-ene (*E*)-(**2m**), 3-phenyl-4-methylpent-1-ene (**3m**), and 3,4-diphenylhexa-1,5-diene (**6c**) were as follows: (**2m**), an oil, *m/e* 160 (M^+), δ 0.95

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* We have postulated that alkylation products are most likely to be produced by cross-coupling between 1-arylpropenyl radical and the radical from R'MgY. An $S_{RN}1$ mechanism involving coupling of 1-arylpropenyl radical and R'MgY could be, however, an alternative one.[10]

† There are reliable data for ionization potentials of RMgY and R_2Mg. However, first vertical ionization potentials of binary mercury(II) derivatives are known to follow the sequence MeHgCl (10.88 eV) > MeHgBr (10.16) > Me_2Hg (9.33) > MeHgI (9.25) and therefore, it may be reasonable to expect that the same sequence holds for MeMgBr, Me_2Mg, and MeMgI.[11]

(6 H, d, *J* 6.0 Hz), 1.70 (1 H, heptet, *J* 6.0 Hz), 2.06 (1 H, t, *J* 6.0 Hz), 5.90—6.38 (2 H, m), and 6.97—7.35 (5 H, m); (**3m**), an oil, *m*/*e* 160 (M^+), δ 0.70 (3 H, d, *J* 6.0 Hz), 0.93 (3 H, d, *J* 6.0 Hz), 1.65—2.12 (1 H, m), 2.80 (1 H, t, *J* 8.0 Hz), 4.80—5.20 (2 H, m), 5.66—6.24 (1 H, m), and 6.95—7.38 (5 H, m), (**6c**), m.p. 35 °C (lit.,[21] 35.1—35.4 °C), δ 3.55—3.65 (2 H, m), 4.82—5.31 (4 H, m), 6.02—6.13 (2 H, m), and 7.01—7.09 (10 H, m).

Reaction of 1-(4-*chlorophenyl*)-3-*chloropropene with methylmagnesium bromide in the presence of ferric chloride.* A mixture of (**2d**) (500 mg, 2.67 mmol), MeMgBr (8.02 mmol), and $FeCl_3$ (43 mg, 0.27 mmol) in EE was kept with stirring at 30 °C for 1 h. The products were a mixture of 1-(4-chlorophenyl)but-1-ene (**2d**) (31%), 1.6-bis-(4-chlorophenyl)hexa-1,5-diene (**4d**) (11%), 1,4-bis-(4-chlorophenyl)hexa-1,5-diene (**5d**) (22%), and 3,4-bis-(4-chlorophenyl)hexa-1,5-diene (**6d**) (5%). The physical properties of these products were as follows: (**2d**), b.p. 110 °C at 11 mmHg (lit.,[22] 120 °C at 15 mmHg), *m*/*e* 166 and 168 (M^+), δ 1.05 (3 H, t, *J* 7.5 Hz), 2.10—2.15 (2 H, m), 6.05—6.20 (2 H, m), and 7.01—7.21 (4 H, m); (**4d**), an oil, δ 2.40 (4 H, t, *J* 7.2 Hz), 5.81—6.52 (4 H, m), 7.01—7.18 (8 H, m); (**5d**), an oil, *m*/*e* 302, 304, 306, and 308 (M^+), δ 2.50—2.71 (2 H, t, *J* 7.2 Hz), 3.21—3.53 (1 H, m), 4.90—5.20 (2 H, m), 5.79—6.52 (3 H, m), and 7.00—7.22 (8 H, m); (**6d**), an oil, δ 3.50—3.52 (2 H, m), 4.61—5.19 (4 H, m), 5.78—6.52 (2 H, m), and 7.03—7.21 (8 H, m).

Reaction of (Z)-1-*phenyl*-3-*chloropropene with phenylmagnesium bromide in THF.* Treatment of (*Z*)-(**1c**) (300 mg, 1.97 mmol) with PhMgBr (9.85 mmol) in THF at 30 °C for 3 h gave, together with dimers (**4**)—(**6**) (45% yield), (*Z*)-1,3-diphenylprop-1-ene in 20% yield, b.p. 120—122 °C (at 4 mmHg) (lit.,[18] 120—122 °C at 4 mmHg), *m*/*e* 194 (M^+), δ 3.51 (2 H, d, *J* 5.8 Hz), 5.54—5.80 (1 H, m), 6.40—6.57 (1 H, m), and 7.00—7.30 (10 H, m).

Reaction of (Z)-1-*phenyl*-3-*chloropropene with propylmagnesium iodide in EE.* The reaction of (*Z*)-(**1c**) (300 mg, 1.97 mmol) with propylmagnesium iodide (9.0 mmol) in EE gave a mixture of 1-phenylhex-1-ene (**2h**) (an *E*–*Z* mixture), 3-phenylhex-1-ene (**3h**), and dimers (**4**)—(**6**). The product compositions were determined by ^{1}H n.m.r. spectroscopy and g.l.p.c. analysis. The physical properties of the alkylation products were as follows: (*E*)-(**2h**), b.p. 84 °C at 6 mmHg (lit.,[23] 84 °C at 6.5 mmHg), *m*/*e* 160 (M^+), δ 0.90—0.95 (3 H, m), 1.28—1.50 (4 H, m), 2.03—2.20 (2 H, m), 6.00—6.31 (2 H, m), and 7.01—7.30 (5 H, m); (*Z*)-(**2h**), an oil, δ 0.88 (3 H, t, *J* 6.0 Hz), 1.10—1.03 (4 H, m), 2.02—2.55 (2 H, m), 5.55 (1 H, dt, *J* 11.5 and 6.7 Hz), 6.33 (1 H, dt, *J* 11.5 and 1.5 Hz), and 7.02—7.35 (5 H, m);[24] (**3h**), b.p. 82 °C at 7 mmHg, *m*/*e* 160 (M^+), δ 0.90—0.96 (3 H, m), 1.26—1.48 (4 H, m), 3.14 (1 H, q, *J* 7.0 Hz), 4.75—4.97 (2 H, m), 5.73—5.94 (1 H, m), and 7.00—7.12 (5 H, m).

Reaction of 1-(4-*methoxyphenyl*)-3-*chloropropene with hex*-5-*enylmagnesium bromide in EE.* A mixture of chloride (**1a**) (300 mg, 1.64 mmol) and hex-5-enylmagnesium bromide (4.92 mmol) in EE was kept with stirring at 30 °C for 1 h. By column chromatography on silica gel, two non-cyclized products, (**9a**) and (**10a**), were isolated in pure states: (**9a**), an oil, *m*/*e* 230 (M^+), δ 1.00—1.72 (6 H, m), 1.79—2.22 (4 H, m), 3.63 (3 H, s), 4.77—5.02 (2 H, m), 5.70—6.18 (3 H, m), and 6.60—7.20 (4 H, m); (**10a**), an oil, *m*/*e* 230 (M^+), δ 1.00—1.72 (6 H, m), 1.79—2.20 (2 H, m), 3.30 (1 H, q, *J* 6.0 Hz), 3.63 (3 H, s), 4.77—5.02 (4 H, m), 5.55—6.22 (2 H, m), and 6.60—7.20 (4 H, m).

Reaction of (E)-1-*phenyl*-3-*chloropropene with t-butylmagnesium bromide in EE.* The reaction of (*E*)-(**1c**) (300 mg, 1.97 mmol) with t-butylmagnesium bromide (5.90 mmol) in EE gave a mixture of (*E*)-1-phenyl-4,4-dimethylpent-1-ene (**2v**),[25] 3-phenyl-4,4-dimethylpent-1-ene (**3v**), 1-phenylpropene (**7c**), 3-phenylpropene (**8c**), and dimers (**4**)—(**6**). The product compositions were determined by ^{1}H n.m.r. spectroscopy and g.l.p.c. analysis. The physical properties of the alkylation products were as follows: (**2v**), an oil, *m*/*e* 174 (M^+), δ 0.92 (9 H, s), 1.90—2.15 (2 H, m), 5.85—6.55 (2 H, m), and 7.00—7.40 (5 H, m); (**3v**), an oil, *m*/*e* 174 (M^+), δ 0.88 (9 H, s), 2.94 (1 H, d, *J* 8.4 Hz), 4.82—5.10 (2 H, m), 5.94—6.42 (1 H, m), and 6.93—7.31 (5 H, m).

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