Reaction of Phenyl-substituted Allyl-lithiums with Secondary Alkyl Halides. A Polar Process *versus* Single-electron Transfer

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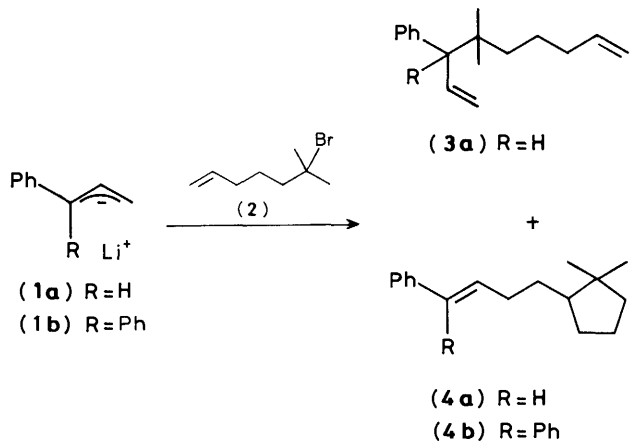
The reaction of 1-phenylallyl-lithium (**1a**) with optically active 2-halobutanes in ether in the presence of tetramethylethylenediamine or hexamethylphosphoramide gives exclusively 4-methyl-3-phenylhex-1-ene (**5a**) (coupling at the phenyl-substituted site) with essentially 100% inversion of configuration. In contrast, treatment of 1,1-diphenylallyl-lithium (**1b**) with (−)-2-halobutanes under the same conditions results in the formation of a mixture of 4-methyl-3,3-diphenylhex-1-ene (**5b**) (coupling at C-1) and 4-methyl-1,1-diphenylhex-1-ene (**6b**) (coupling at C-3). Moreover, C–C bond formation at the 1-position to provide (**5b**) is also found to proceed with complete inversion of configuration, while a small but significant loss of stereochemical integrity is observed in the case of the C-3 attack product (**6b**). These results suggest that a polar pathway should predominate for the formation of the C-1 attack products (**5a**, **b**), while competition between polar and single-electron-transfer processes occurs for the formation of the C-3 attack product (**6b**).

The reaction of organometallic compounds with alkyl halides has received attention lately with regard to mechanism.[1] Using stereochemistry as the most definitive indicator, the reaction of organometallic compounds (metal = Li, Na, or K) is known to proceed by two different pathways, a polar pathway and single-electron transfer (SET), the extent of each path being markedly dependent on various factors. Recently we reported that the reaction of 1-phenylallyl-lithium (**1a**) with 6-bromo-6-methylhept-1-ene (**2**), a tertiary cyclizable probe, gives a mixture of (**3a**) (a straight-chain product formed by coupling at the more hindered C-1) and (**4a**) (a cyclized product formed by coupling at C-3). The (**3a**)/(**4a**) ratio increases as the donicity of the solvent system is increased and the following order is observed: ether/tetramethylethylenediamine (TMEDA) < ether/hexamethylphosporamide (HMPA) < tetrahydrofuran (THF)/HMPA.[2] This would imply that a polar pathway favours coupling at the phenyl-substituted site (C-1), while in the case of SET C–C bond formation occurs predominantly at the site far from the phenyl-substituent (C-3). Moreover, the increase in donicity of the medium increases the contribution of a polar pathway. In the case of 1,1-diphenylallyl-lithium (**1b**), however, the cyclized product (**4b**) formed by coupling at C-3 was the sole alkylation product, irrespective of the nature of the medium, demonstrating that the contribution of an SET process is very important in the case of the lithium compound (**1b**), in which attack by an electrophile at the 1-position is disfavoured for steric reasons (Scheme 1).[2]

It would be, therefore, instructive to see if an SET pathway can competitively participate, even in the reaction of the lithium compounds (**1a**, **b**) with less hindered and more reactive secondary alkyl halides. A question may arise as to whether the regiochemistry of the products obtained by an SET pathway is significantly different from that obtained by a polar pathway. We therefore carried out a systematic investigation of the reactions of 1-phenyl- and 1,1-diphenylallyl-lithiums (**1a**, **b**) with secondary alkyl halides.

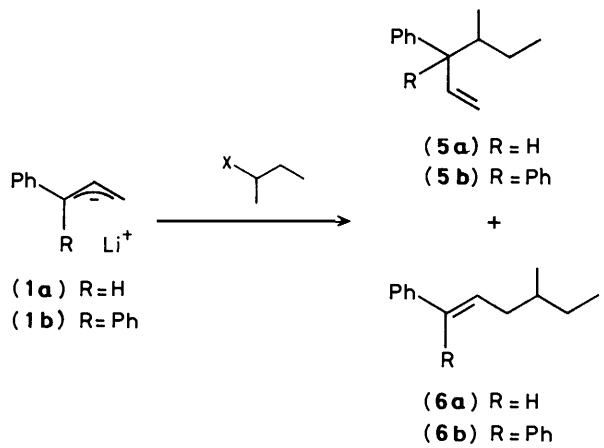


Scheme 1.

Results and Discussion

Reaction with 2-Halobutanes.—The reaction of 1-phenylallyl-lithium (**1a**) with 2-bromobutane in ether in the presence of TMEDA or HMPA yielded the C-1 attack product (**5a**) almost exclusively. The same trend was observed in the reaction with 2-iodobutane and 2-butyl toluene-4-sulphonate (Scheme 2 and Table 1). This is in marked contrast with the fact that treatment of 1,1-diphenylallyl-lithium (**1b**) with 2-halobutanes or 2-butyl toluene-4-sulphonate gave a mixture of two alkylation products, (**5b**) (coupling at C-1) and (**6b**) (coupling at C-3), the (**5b**)/(**6b**) ratio being a marked function of both the identity of the leaving group and the donicity of the additives, TMEDA and HMPA. The (**5b**)/(**6b**) ratio decreased in the order OTs > Br ≃ I and TMEDA > HMPA. As a result of the accumulated effects of these variables, the (**5b**)/(**6b**) ratio observed in the reaction of (**1b**) with 2-butyl toluene-4-sulphonate in ether/TMEDA was as high as 64:36, while the (**5b**)/(**6b**) ratio observed in the reaction with 2-bromobutane in THF/HMPA was as low as 2:98. In order to understand the difference in behaviour between these two lithium compounds (**1a**, **b**), we then undertook the reaction with 6-halohept-1-ene, a secondary cyclizable probe.[3]

Reaction with 6-Halohept-1-ene, a Secondary Cyclizable Probe.—The reaction of 1-phenylallyl-lithium (**1a**) with 6-iodohept-1-ene in ether in the presence of TMEDA or HMPA gave 4-methyl-3-phenylnona-1,8-diene (**7a**), a straight-chain



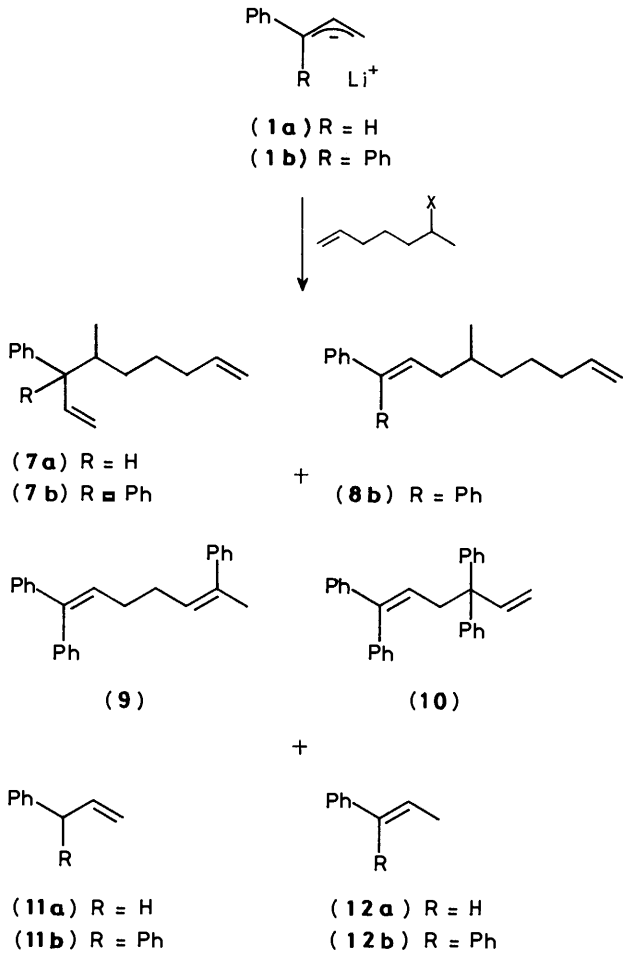
Scheme 2.

Table 1. Reaction of the lithium compound (**1**) with 2-halobutanes (RX).[a]

X	Solvent	Additive[b]	Products Yield (%)	Products (5):(6)
Compound (**1a**)				
OTs	Et_2O	TMEDA	88	98:2
OTs	Et_2O	HMPA	82	97:3
Br	Et_2O	TMEDA	80	94:6
Br	Et_2O	HMPA	72	96:4
I	Et_2O	TMEDA	72	96:4
I	Et_2O	HMPA	75	91:9
Compound (**1b**)				
OTs	Et_2O	TMEDA	77	64:36
OTs	Et_2O	HMPA	73	22:78
Br	Et_2O	TMEDA	82	60:40
Br	Et_2O	HMPA	79	2:98
Br	THF	HMPA	85	2:98
I	Et_2O	TMEDA	62	29:71
I	Et_2O	HMPA	73	5:95
I	THF	HMPA	69	7:93

[a] Reaction of lithium compound (**1**) with 2-halobutane (2.5 mol equiv.) at 20 °C for 1 h. [b] TMEDA (1.2 equiv.); HMPA (10 mol equiv.).

product formed by coupling at C-1, in around 40% yield (Scheme 3 and Table 2). The same trend was observed for the reaction of (**1a**) with 6-bromohept-1-ene and hept-6-en-2-yl toluene-4-sulphonate. When the reaction of 1,1-diphenylallyl-lithium (**1b**) was performed in ether/TMEDA, ether/HMPA or THF/HMPA, however, a mixture of two straight-chain products, (**7a**) (coupling at C-1) and (**8b**) (coupling at C-3), was obtained. The (**7b**)/(**8b**) ratio decreased with an increase in the softness of the leaving group of the secondary cyclizable probes and an increase in donicity of the additives. This trend was exactly the same as that observed in the reaction with 2-halobutanes. Dimers (**9**) and (**10**) were also obtained in around 15% yield from the reaction of (**1b**) with 6-iodohept-1-ene in ether. The absence of the corresponding cyclized product would imply that the reaction of phenyl-substituted allyl-lithiums (**1a**, **b**) with secondary alkyl halides proceeds mainly by a polar process. However, since the cyclized product would result only after diffusion of the phenyl-substituted allyl radical (**15**) and hept-6-en-2-yl radical (**16**) from the solvent cage, rapid geminate coupling of the radicals inside the cage would also lead to exclusive formation of the straight-chain products, (**7**) and/or (**8**) (Scheme 4).[3] To differentiate these mechanistic alternatives, we then undertook the reaction of the lithium compounds (**1a**, **b**) with optically active 2-halobutanes. A chiral centre would lose its stereochemical integrity inside the solvent cage at a rate much faster than that for geminate coupling and consequently, the extent of loss of stereochemical integrity would then be a measure of the extent of radical formation in the solvent cage.[4]



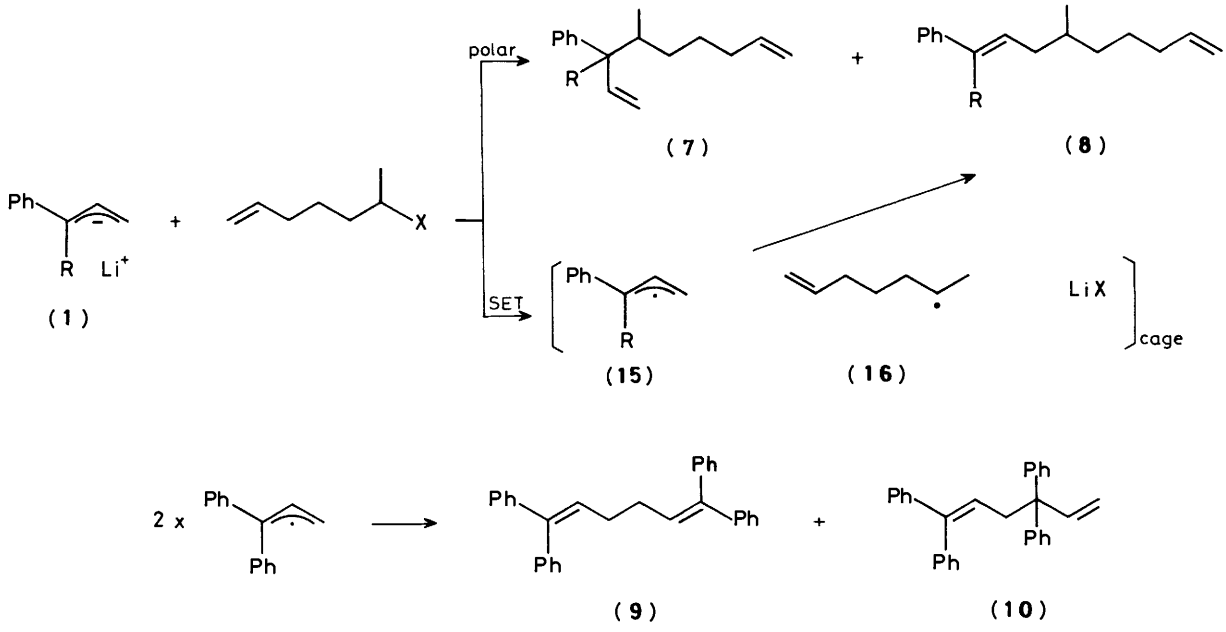
Scheme 3.

Reaction with Optically Active 2-Halobutanes.—The reaction of 1-phenylallyl-lithium (**1a**) with optically active 2-halobutanes or 2-butyl toluene-4-sulphonate was performed under various conditions (Table 3). Since alkyl halides RX are more easily reduced in the order X = I > Br > OTs,[5] reactions of toluene-4-sulphonates are more likely to proceed by an S_N2 pathway, whereas iodides are more likely to react by SET.[4] Thus, when (**1a**) was allowed to react with (+)-2-butyl toluene-4-sulphonate in ether in the presence of TMEDA or HMPA, (−)-4-methyl-3-phenylhex-1-ene [(−)-(**5a**)] was obtained in good yield. Because of the unfavourable reduction potential of the toluene-4-sulphonate, the reactions are believed to proceed with 100% inversion of configuration.[4,5] Thus, the value of −14.3° was assumed to be the specific rotation of the optically pure (**5a**) obtained from the toluene-4-sulphonate. If this assumption is correct, the values +13.8 ⟶ +14.7° observed in the reactions with (−)-2-halobutanes (X = Br or I) in ether in the presence of TMEDA or HMPA would then imply that the reaction of (**1a**) with 2-halobutanes proceeds with almost complete inversion of configuration. In other words, a polar process is important in the reaction of 1-phenylallyl-lithium (**1a**) with secondary alkyl halides to yield the corresponding C-1 attack product. This is apparently in agreement with the fact that in the reaction with

Table 2. Reaction of the lithium compound (**1**) with 6-halohept-1-ene.[a]

				Products					
				Alkylation		Dimerization		Reduction	
X	Solvent	Additive	Reaction time/h	Yield (%)	(**7**):(**8**)	Yield (%)	(**9**):(**10**)	Yield (%)	(**11**):(**12**)
Compound (**1a**)									
OTs	Et_2O	TMEDA	2	45	100:0			20	20:80
Br	Et_2O	TMEDA	4	32	100:0			35	15:85
I	Et_2O	TMEDA	2.5	30	100:0			40	15:85
I	Et_2O	HMPA	2.5	48	100:0			30	17:83
Compound (**1b**)									
OTs	Et_2O	TMEDA	2	68	60:40			20	30:70
Br	Et_2O	TMEDA	2	24	40:60			50	30:70
Br	Et_2O	HMPA	2	16	0:100			52	0:100
I	Et_2O	TMEDA	4	41	29:71	14	68:32	30	25:75
I	Et_2O	HMPA	4	60	5:95	16	70:30	16	0:100
I	THF	HMPA	2	64	11:89			25	0:100

[a] The reaction with a secondary cyclizable probe (2.5 mol equiv.). For experimental conditions, see footnotes in Table 1.



Scheme 4.

tertiary alkyl bromides the C-1 attack product is produced by a polar pathway, although SET is important for the formation of the C-3 attack product (Scheme 1).[2]

A remarkably different trend was observed for the reaction of 1,1-diphenylallyl-lithium (**1b**) with optically active 2-halobutanes (Table 3). The reaction of (**1b**) with (+)-2-butyl toluene-4-sulphonate was undertaken in ether in the presence of TMEDA. The specific rotations of the C-1 coupling product (**5b**) and the C-3 coupling product (**6b**) were −46.8 and −25.1°, respectively. On the same basis described above, these values were assumed to be the specific rotations of optically pure 4-methyl-3,3-diphenylhex-1-ene (**5b**) and 4-methyl-1,1-diphenylhex-1-ene (**6b**), respectively. The reaction with (+)-2-butyl toluene-4-sulphonate in ether/HMPA yielded only (**6b**), the values of −24.4° being much the same as those obtained from the reaction in ether/TMEDA, as expected. Treatment of (**1b**) with (−)-2-bromobutane gave a mixture of (**5b**) and (**6b**). It is worth noting that the absolute value of 48.3° for the specific rotation of the C-1 attack product (**5b**) was the same as that obtained from the reaction with (+)-2-butyl toluene-4-sulphonate, indicating that this product (**5b**) is also a result of direct nucleophilic substitution. In marked contrast, the enantiomeric excess (ee) value of the C-3 attack product (**6b**) was as low as 72%. The reaction of (**1b**) with (−)-2-bromobutane in various solvent systems revealed that the nature of the medium exerts a notable influence on the ee values of (**6b**); 72% (ether/TMEDA), 89% (ether/HMPA), and 94% (THF/HMPA). The same trend was also observed in the reaction with (−)-2-iodobutane.

The small but significant loss of stereochemical integrity in (**6b**) would imply that for the formation of (**6b**) an alternative process can compete. Since the carbenium ion is not likely to be formed from 2-halobutanes under the reaction conditions, we believe the alternative pathway is an SET process from the lithium compound (**1b**) to the lowest lying anti-bonding orbital of 2-halobutanes. Subsequent departure of X^- from $RX^{-\bullet}$, followed by rapid geminate coupling of the 1,1-diphenylallyl radical (**15b**) and s-butyl radical in a solvent cage, would yield

Table 3. Reaction of the lithium compound (**1**) with optically active 2-halobutanes (RX).[a]

RX					(5)			(6)		
X	obs$[\alpha]_D^{20}$	ee (%)[b]	Solvent	Additive	obs$[\alpha]_D^{20}$	corr$[\alpha]_D^{20}$	ee (%)[c]	obs$[\alpha]_D^{20}$	corr$[\alpha]_D^{20}$	ee (%)[c]
OTs	+10.54°	81.0	Et_2O	TMEDA	−11.5°	−14.2°	99			
OTs	+10.54°	81.0	Et_2O	HMPA	−11.6°	−14.3°	100[e]			
Br	−29.50°	74.9	Et_2O	TMEDA	+10.3°	+13.8°	97			
Br	−29.21°	74.1	Et_2O	TMEDA[d]	+10.9°	+14.7°	102			
Br	−29.50°	74.9	Et_2O	HMPA	+10.8°	+14.4°	101			
I	−15.10°	47.0	Et_2O	TMEDA	+6.5°	+13.8°	97			
OTs	+10.54°	81.0	Et_2O	TMEDA	−37.6°	−46.4°	99	−20.3°	−25.1°	100[e]
OTs	+10.54°	81.0	Et_2O	TMEDA[d]	−37.9°	−46.8°	100[e]	−20.3°	−25.1°	100
OTs	+10.54°	81.0	Et_2O	HMPA				−19.8°	−24.4°	97
Br	−29.21°	74.1	Et_2O	TMEDA	+35.8°	+48.3°	103	+13.3°	+17.0°	72
Br	−29.50°	74.9	Et_2O	HMPA				+16.5°	+22.0°	89
Br	−29.00°	73.6	THF	HMPA				+17.1°	+23.2°	94
I	−15.10°	47.0	Et_2O	TMEDA				+8.8°	+18.7°	76
I	−15.10°	47.0	THF	HMPA				+9.6°	+20.4°	83

[a] For experimental conditions, see footnotes in Table 1. [b] The following maximum rotations ($[\alpha]_D^{20}$) for 2-halobutanes were used: OTs, −13.2°[15]; Br, +39.4°[10]; I, +32.1°.[12] [c] In some cases the specific rotations of the minor product were not determined. [d] The reaction in the presence of 1.2 equiv. of $MgBr_2$. [e] The values of +14.3°, +46.8°, and +25.1° were assumed to be the rotations of optically pure (+)-(**5a**), (+)-(**5b**), and (+)-(**6b**), respectively. The errors were around 2%.

exclusively (**6b**) (Scheme 1). The medium effect on the ee value of (**6b**) leads us to deduce therefore that the ability of the species in the reaction medium to co-ordinate the counter-ion plays a significant role in determining the mechanistic competition between polar and SET processes, the contribution of an SET pathway being increased with the decrease in donicity of the solvent system.[1f,6] This is also in the reaction of (**1a**) with tertiary alkyl bromides.[2]

The remarkable effects of the additives on the regiochemistry of alkylation of 1,1-diphenylallyl-lithium (**1b**) can be rationalized in terms of the effects of the additives on the ion-pair states of (**1b**).* In this respect, the electronic spectra have revealed that in ether/TMEDA the lithium compound (**1b**) exists mainly as a contact ion-pair, while contribution of a solvent-separated ion-pair is important in the case of ether/HMPA and THF/HMPA.[2] If (**1b**) exists in the form of a contact ion-pair in which there is a significant covalent bonding contribution, then the lithium ion would be co-ordinated at the less-hindered C-3 position. This would block this position from attack by an electrophile relative to the 'free' 1-position. Consequently, the reaction of (**1b**) with secondary alkyl halides in ether/TMEDA, if it proceeds by a polar process, provides mainly the C-1 attack product. In ether/HMPA or THF/HMPA, in which (**1b**) exists mainly as a solvent-separated ion-pair, such a counterion effect would not be important, thereby facilitating the formation of the C-3 attack product. It is noted, however, that in the case of the lithium compound (**1a**), in which the phenyl-substituted site is less congested relative to (**1b**), the C-1 attack product is produced predominantly, even in the reactions in ether/HMPA and THF/HMPA.

Steric and electronic effects probably play complex roles in determining the regiochemistry of alkylation of phenyl-substituted allyl-lithiums (**1a**, **b**).[8],† In addition, we have to consider the possibility of a remarkable difference in regiochemistry between polar and SET processes. Certainly, although most of the reactions of well-delocalized carbonions with s-alkyl halides should proceed by a polar process,[1] we can not ignore the contribution of SET in some cases. For example, Korte found that the reaction of allyl-lithiums with bulky α-methylbenzyl chloride resulted in significant loss of stereochemical integrity.

Conclusion.—This study on stereochemistry reveals that in the reaction of 1,1-diphenylallyl-lithium (**1b**) with secondary alkyl halides the C-1 attack product is produced by a polar pathway, while competition between polar and SET processes occurs for the formation of C-3 attack product. The contribution of an SET pathway increases with a decrease in donicity of the medium. The fact that the reaction with 6-halohept-1-ene yields only straight-chain products, (**7**) and (**8**), leads us to deduce that stereochemistry would be more sensitive in the detection of the contribution of an SET pathway.[3]

Exerimental

General.—^{1}H N.m.r. spectra were recorded in carbon tetrachloride at 100 MHz using a JNM-PS-100 spectrometer. G.l.c. analysis was carried out on a Hitachi 164 gas chromatograph. Optical rotations were measured in ethanol using a JASCO DIP-181 electronic polarimeter at 589 nm. Ether and THF were dried by distillation from lithium aluminium hydride (ether refers to diethyl ether throughout). BuLi and (*S*)-(+)-butan-2-ol were purchased from Aldrich. TMEDA and HMPA were distilled over calcium hydride and sodium, respectively. (−)-2-Bromobutane,[10] (+)-2-butyl toluene-4-sulphonate,[11] (−)-2-iodobutane,[12] 6-bromohept-1-ene,[13] 6-iodohept-1-ene,[1i] and hept-6-en-2-yl toluene-4-sulphonate,[1i] were prepared by the reported methods. This method of preparation of the lithium compounds (**1a**, **b**) has been described elsewhere.[2]

Reaction of 1-*Phenylallyl-lithium* (**1a**) *with* 6-*Bromohept*-1-*ene.*—To a solution of (**1a**) is ether–hexane (3:1, 20 cm^3) [prepared from 4 mmol of (**11a**), 4.8 mmol of BuLi, and 4.8 mmol of TMEDA) was injected a solution of 6-bromohept-1-ene (10 mmol) in ether (10 cm^3), and the mixture was kept for 4 h with stirring at 20 °C. The reaction mixture was then quenched with water, and the ether layer was separated and dried over

* A similar mechanism has been proposed to explain the counter-ion effect on the regiochemistry for the reaction of 1,1-dihaloallyl-lithiums with carbonyl compounds [7a] and the reaction of alkyl-lithiums with α,β-unsaturated carbonyl compounds.[7b]

† To explain the notable leaving group effects on the regiochemistry of alkylation of (**1a**, **b**), an alternative hard/soft-acid/base approach has been proposed.[9] See, however, ref. 7*a*.

anhydrous sodium sulphate. After evaporation of the ether layer, the crude products were column chromatographed on silica gel (elution with benzene–hexane, 3:97). The first fraction contained 6-bromohept-1-ene. From the second fraction was isolated 4-methyl-3-phenylnona-1,8-diene (**7a**), oil; δ_H 0.72 (1.5 H, d, *J* 7 Hz), 0.90 (1.5 H, d, *J* 7 Hz), 1.0–2.3 (7 H, m), 2.9–3.1 (1 H, m), 4.8–5.4 (4 H, m), 5.5–6.3 (2 H, m), 7.0–7.3 (5 H, m) (Found: C, 90.0; H, 10.2. $C_{16}H_{22}$ requires C, 89.7; H, 10.3%). The final fraction contained a mixture of (**11a**) and (**12a**).

Reaction of 1,1-*Diphenylallyl-lithium* (**1b**) *with* 6-*Iodohept*-1-*ene*.—To a solution of (**1b**) in ether–hexane (3:1, 20 cm^3) [prepared from 4 mmol of (**11b**), 4.8 mmol of BuLi, and 4.8 mmol of TMEDA], was added, using a syringe, a solution of 6-iodohept-1-ene (10 mmol) in ether (10 cm^3) in one portion, and the reaction was allowed to continue for 2 h at 20 °C. After conventional work-up, the products were isolated by column chromatography on silica gel (elution with benzene–hexane, 4 : 96). The first fraction contained 6-iodohept-1-ene. From the second fraction was isolated 4-methyl-1,1-diphenylnona-1,8-diene (**8b**), oil (Found: C, 90.8; H, 8.9. $C_{22}H_{26}$ requires, C, 91.0; H, 9.0%); δ_H 0.88 (3 H, d, *J* 7.0 Hz), 1.0–2.3 (9 H, m), 4.7–5.1 (2 H, m), 5.5–5.9 (1 H, m), 6.02 (1 H, t, *J* Hz), 7.0–7.4 (10 H, m). The third fraction contained a mixture of (**11b**) and (**12b**).[2] From the fourth fraction was isolated 4-methyl-3,3-diphenylnona-1,8-diene (**7b**), oil (Found: C, 91.0; H, 9.0. $C_{22}H_{26}$ requires C, 91.0; H, 9.0%); δ_H 0.87 (3 H, d, *J* 7 Hz), 1.1–2.8 (7 H, m), 4.7–5.4 (4 H, m), 5.5–6.0 (1 H, m), 6.35 (1 H, dd, *J* 10 and 17 Hz), 7.0–7.5 (10 H, m). The final fraction contained a mixture of (**9**) and (**10**).[2]

Reaction of 1-*Phenylallyl-lithium* (**1a**) *with* (+)-2-*Butyl Toluene*-4-*sulphonate*.—To a solution of (**1a**) in ether–hexane (3:1, 20 cm^3) [prepared from 4 mmol of (**11a**), 4.8 mmol of BuLi, and 4.8 mmol of TMEDA], was injected an ether solution of (+)-2-butyl toluene-4-sulphonate (10 mmol), and the mixture was kept at 20 °C for 2 h. After conventional work-up, the crude products were chromatographed on silica gel (elution with benzene–hexane, 3:97). The first fraction contained 4-methyl-1-phenylhex-1-ene (**6a**), oil; δ_H 0.8–1.0 (3 H, m), 0.92 (3 H, d, *J* 6 Hz), 1.1–1.7 (3 H, m), 1.8–2.3 (2 H, m), 5.9–6.4 (2 H, m), 6.9–7.4 (5 H, m). The physical properties, including the retention time in g.l.c. analysis, were identical with those of the authentic sample prepared from the reaction of chloro-3-1-phenylprop-1-ene with 2-butylmagnesium bromide.[14] Since the yield was very low, (**6a**) was not isolated in sufficient quantity to measure the specific rotation. From the second fraction was isolated 4-methyl-3-phenylhex-1-ene (**5a**), b.p. 81–82 °C (6 mmHg) (Found: C, 89.9; H, 10.3. $C_{13}H_{18}$ requires C, 89.7; H, 10.4%); $[\alpha]_D^{20}$ −11.5°; δ_H 0.74 (3 H, t, *J* 6.9 Hz), 0.87 (3 H, d, *J* 6.9 Hz), 1.0–1.9 (3 H, m), 2.97 (1 H, td, *J* 9.0 and 3.0 Hz), 4.8–5.1 (2 H, m), 5.7–6.3 (1 H, m), 6.6–7.3 (5 H, m). As the alcohol used {$[\alpha]_D^{20}$ + 11.0° (neat)} was 81% optically pure,[15] the rotation of optically pure (**5a**) is calculated to be −14.2°.

Reaction of 1,1-*Diphenylallyl-lithium* (**1b**) *with* (+)-2-*Butyl Toluene*-4-*sulphonate*.—To a solution of (**1b**) in ether–hexane (3:1, 20 cm^3) [prepared from 4 mmol of (**11b**), 4.8 mmol of BuLi, and 4.8 mmol of TMEDA], was added by syringe a solution of (+)-2-butyl toluene-4-sulphonate (10 mmol) in ether and the mixture was kept at 20 °C for 2 h. Column chromatography on silica gel (elution with benzene–hexane, 4 : 96) afforded first 4-methyl-1,1-diphenylhex-1-ene (**6b**), b.p. 123–125 °C (1 mmHg) (Found: C, 91.2; H, 8.8. $C_{19}H_{22}$ requires C, 91.1; H, 8.9%); $[\alpha]_D^{20}$ −20.3°; δ_H 0.89 (3 H, t, *J* 6.9 Hz), 0.89 (3 H, d, *J* 6.9 Hz), 1.0–2.3 (5 H, m), 6.03 (1 H, t, *J* 6.9 Hz), 7.0–7.5 (10 H, m). The second fraction gave a mixture of (**11b**) and (**12b**).[2] From the final fraction was isolated 4-methyl-3,3-diphenylhex-1-ene (**5b**), b.p. 120–122 °C (1 mmHg) (Found: C, 91.1; H, 8.9. $C_{19}H_{22}$ requires C, 91.1; H, 8.9); $[\alpha]_D^{20}$ −37.6°; δ_H 0.87 (3 H, d, 6.9 Hz), 0.96 (3 H, t, *J* 6.9 Hz), 0.6–1.1 (2 H, m), 1.4–1.8 (1 H, m), 2.3–2.6 (1 H, m), 4.81 (1 H, d, *J* 17.4 Hz), 5.14 (1 H, d, *J* 9.9 Hz), 6.36 (1 H, dd, *J* 17.4 and 9.9 Hz), 6.9–7.5 (10 H, m). As the alcohol used was 81% optically pure,[15] the rotations of optically pure (**5b**) and (**6b**) are calculated to be −46.4 and −25.1°, respectively.

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