Protonation and Alkylation of 1-Arylpropenyl-lithium

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The protonation and alkylation of 1-arylpropenyl-lithium (**1a**—**c**) in ether was undertaken systematically; the regio- and stereo-chemistry being influenced by various factors. The characteristic features are as follows. (*a*) Protonation occurs predominantly at C-3, whereas the sterically more crowded C-1 is the more favoured site for alkylation, and (*b*) although 1-arylpropenyl-lithium (**1**) seems to exist mainly as the *E*-isomer, in some cases the product (**3**) or (**5**) having the *Z*-configuration is produced from attack at C-3 in a significant amount together with the *E*-isomer, *e.g.* protonation by oxygen acids in the presence or absence of tetramethylethylenediamine and methylation of the *p*-methoxy derivative (**1a**).

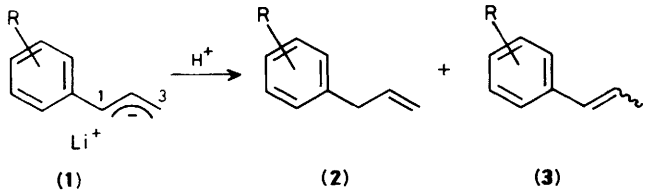
Allylic organometallics have two reaction sites and their reactions with electrophiles often give a mixture of two products. The product composition is a function of various factors[1] including substituent effects (both electronic[2] and steric),[3] the electrophiles used,[4] the nature of the cation,[5] the solvent,[6] and the presence of strongly co-ordinating additives, [*e.g.* tetramethylethylenediamine (TMEDA), hexamethylphosphoric triamide (HMPA), and crown ethers[6,7]].

We report herein the protonation and alkylation of 1-arylpropenyl-lithium (**1a**—**c**; R = OMe-*p*, H, Cl-*m*). The lithium compounds (**1a**—**c**) could be prepared under a variety of conditions, and we carried out a systematic survey for the factors affecting the product regiochemistry. Also of interest was the stereochemistry of the products (**3**) and (**5**), produced by electrophilic attack at the 3-position. In connection with this, it has been well established that 1-phenylpropenyl-lithium exists mainly as the *E*-isomer.[8]

Results and Discussion

Protonation of 1-Arylpropenyl-lithium.—Protonation of 1-arylpropenyl-lithium (**1a**—**c**) in ether was undertaken under three conditions; (*a*) in the absence of additive, (*b*) in the presence of TMEDA, and (*c*) in the presence of HMPA (Scheme 1). 3-Arylpropene (**2**) and 1-arylpropene (**3**) were isolated by column chromatography on silica gel; the regio- and stereo-chemistry of compound (**3**) were determined by ^{1}H n.m.r. spectroscopy and g.l.p.c. analysis.

The data in Table 1 reveal the following. (*a*) In the reaction of (**1b,c**) in the presence or absence of TMEDA, the product ratio was significantly influenced by the nature of the proton donor; the carbon acids phenylacetylene and 3-phenylindene (3-PI) favoured attack at the 3-position to give the 1-arylpropene (**3**)



(**1**) (**2**) (**3**)

a; R = OMe-*p* **b**; R = H **c**; R = Cl-*m*

Scheme 1.

Table 1. Protonation of 1-arylpropenyl-lithium[a]

Lithium compound	Reagent	Additive	Products[c] % Yield	(2):(3)	*E*:*Z* for (3)
(**1a**)	PhC≡CD	TMEDA	66	13:87	86:14
(**1a**)	D_2O	TMEDA	60	11:89	68:32
(**1a**)	Bu^{t}OD	TMEDA	67	7:93	45:55
(**1a**)	PhC≡CD	HMPA	67	5:95	82:18
(**1a**)	D_2O	HMPA	78	1:99	82:18
(**1a**)	Bu^{t}OH	HMPA	58	0:100	89:11
(**1a**)	AcOH	HMPA	78	3:97	82:18
(**1b**)	PhC≡CD		70	26:74	96:4
(**1b**)	D_2O		75	47:53	83:17
(**1b**)	Bu^{t}OH		65	50:50	83:17
(**1b**)	AcOH		67	51:49	82:18
(**1b**)	PhC≡CD	TMEDA	72	8:92	93:7
(**1b**)	3-PI[b]	TMEDA	70	9:91	94:6
(**1b**)	D_2O	TMEDA	75	31:69	44:56
(**1b**)	Bu^{t}OH	TMEDA	65	39:61	44:56
(**1b**)	AcOH	TMEDA	60	42:58	44:52
(**1b**)	PhC≡CD	HMPA	72	8:92	98:2
(**1b**)	D_2O	HMPA	75	3:97	98:2
(**1b**)	Bu^{t}OH	HMPA	70	2:98	93:7
(**1b**)	AcOH	HMPA	65	9:91	93:7
(**1c**)	PhC≡CD		65	9:91	98:2
(**1c**)	D_2O		60	42:58	86:14
(**1c**)	Bu^{t}OH[d]		56	48:52	84:16
(**1c**)	AcOH[d]		51	46:54	85:15
(**1c**)	PhC≡CD	TMEDA	60	6:94	94:6
(**1c**)	3-PI[b]	TMEDA	55	26:74	94:6
(**1c**)	D_2O	TMEDA	59	32:68	62:38
(**1c**)	Bu^{t}OH	TMEDA	58	44:56	58:42
(**1c**)	AcOH	TMEDA	63	37:63	61:39
(**1c**)	PhC≡CD	HMPA	60	3:97	95:5
(**1c**)	D_2O[d]	HMPA	56	3:97	96:4
(**1c**)	Bu^{t}OH[d]	HMPA	62	2:98	97:3
(**1c**)	AcOH[d]	HMPA	60	12:88	94:6

[a] The protonation in the presence or absence of TMEDA was undertaken at 0 °C for 1 min, while the reaction in the presence of HMPA was performed at −45 °C for 1 min unless otherwise noted. [b] 3-Phenylindene. [c] The average values of duplicated runs; the error in the (**2**):(**3**) ratio was of the order of 2%, as was the error of *E*:*Z* ratio in (**3**). The error of the overall yields of products was of the order of 7%. [d] The reaction temperature was −70 °C.

almost exclusively, whereas oxygen acids, deuterium oxide, t-butyl alcohol, and acetic acid, led to the 3-arylpropene (**2**). From the protonation of *p*-methoxy derivative (**1a**) with oxygen

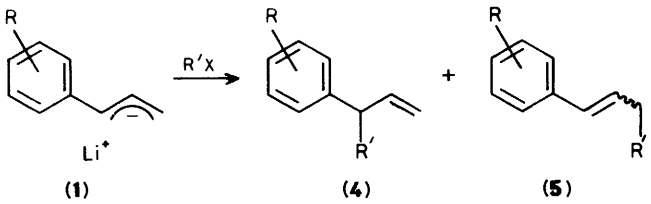
acids, however, 1-(*p*-methoxyphenyl)propene (**3a**) was obtained almost exclusively. The reaction in the presence of HMPA followed a different trend. Three lithium compounds (**1a—c**) gave *predominantly* the C-3-attack products (**3a—c**) irrespective of the identity of the proton donors. Perhaps in accordance with this, protonation of 1-phenylpropenylsodium with methanol in liquid ammonia has been found to give a mixture of (**2b**) and (**3b**) in a ratio of 7:93, whereas the protonation in a less polar solvent, pentane, resulted in the formation of (**2b**) (74%) and (**3b**) (26%).[9]

(*b*) The stereochemistry of the 1-arylpropene (**3**) was also markedly dependent on the nature of the proton donor and additives. The reaction in the presence of HMPA afforded predominantly *E*-1-arylpropenes (*E*)-(**3a—c**). Protonation with phenylacetylene in the presence or absence of TMEDA also showed the same trend. In contrast, protonation by oxygen acids in the presence of TMEDA provided the thermodynamically less stable *Z*-isomer in an amount much the same as that of the *E*-isomer. In the reaction in the absence of an additive, the relatively smaller but significant difference in the *E*:*Z* ratio was observed between the oxygen acids and phenylacetylene.

Thus, the nature of the proton donor and additive exerted a notable influence on the product regio- and stereo-chemistry. The difference in the pK_a values of the proton donors did not seem likely to be the cause (the pK_a values of phenylacetylene,[10] 3-phenylindene,[11] water,[12] t-butyl alcohol,[12] and acetic acid[12] being 28.7, 17.3, 15.7, 19.0, and 4.5, respectively). Consequently, we considered the difference in ion-pairing between the 1-arylpropenyl-lithium in the presence or absence of TMEDA and also in the presence of HMPA. To obtain information about the extent ion-pair formation, the electronic spectra of 1-phenylpropenyl-lithium (**1b**) were recorded. In ether in the presence or absence of TMEDA (**1b**) had $\lambda_{max.}$ at 390 and 384 nm respectively, while in ether and tetrahydrofuran in the presence of HMPA the spectra exhibited $\lambda_{max.}$ 423 and 439 nm, respectively.[13] These results imply that (**1b**) exists as a tight ion pair in the presence or absence of TMEDA, while the contribution of solvent-separated ion pair was important in the presence of HMPA.[14] This conclusion is supported by ^1H and ^{13}C n.m.r. spectra.[8] Also worthy of note is that (*a*) oxygen proton donors can co-ordinate to lithium cations, whilst carbon proton donors are unlikely to, and (*b*) the lithium cation co-ordination to oxygen proton donors is important in the absence of strongly co-ordinating additives.[15] Therefore, if the 1-arylpropenyl-lithium (**1**) exists mainly as an *E*-isomer under all the conditions we investigated, the proton donor-dependent regio- and stereo-chemistry of the products would be interpreted as follows. The first step of protonation of (*E*)-(**1**) by oxygen acids in ether in the presence or absence of TMEDA would involve co-ordination of the oxygen acids toward the lithium cation, followed by proton transfer to yield an *E*/*Z* mixture of the 1-arylpropene (**3**) together with the 3-arylpropene (**2**). This implies the requirement of C–C bond rotation in (**1**) in the transition state of the protonation. In contrast, proton transfer by carbon acids would occur without pre-co-ordination to the lithium cation, to give mainly (*E*)-(**3**), as does the protonation by oxygen acids in the presence of HMPA.

Alternatively, in the presence of TMEDA the *Z*-isomer of (**1**) would also exist in a small but significant amount (*ca.* 20%). Since protonation with oxygen acids is almost diffusion controlled,[16] the *E*:*Z* ratio of (**3**) would reflect the isomer ratio in the lithium compound (**1**). On the other hand, the rate of protonation with carbon acids would be comparable with that of the C–C bond rotation in (**1**)[17] and as a result, protonation with carbon acids would give predominantly the thermodynamically more stable (*E*)-(**13**).*

Alkylation of 1-*Arylpropenyl-lithium.*—The alkylation of 1-arylpropenyl-lithium (**1a—c**) gave a mixture of 3-substituted 3-arylpropenes (**4**) and 3-substituted 1-arylpropenes (**5**) (Scheme 2). The data in Table 2 reveal the following. (*a*) In all of the



(**1**) (**4**) (**5**)

a; R=OMe-*p*
b; R=H
c; R=Cl-*m*

a; R = OMe-*p*, R' = Me
b; R = H, R' = Me
c; R = Cl-*m*, R' = Me
d; R = OMe-*p*, R' = Et
e; R = H, R' = Et

f; R = Cl-*m*, R' = Et
g; R = OMe-*p*, R' = Pr^i
h; R = H, R' = Pr^i
i; R = Cl-*m*, R' = Pr^i

Scheme 2.

alkylations, the 3-substituted 3-arylpropene (**4**), produced by attack at the more hindered C-1 position, was obtained in greater yield. This is in marked contrast to the protonation which occurs mainly at C-3. The same trend has been observed for the reaction of 1-phenylpropenylsodium with methyl bromide in liquid ammonia, where the (**4b**):(**5b**) ratio was as high as 97:3.[9]

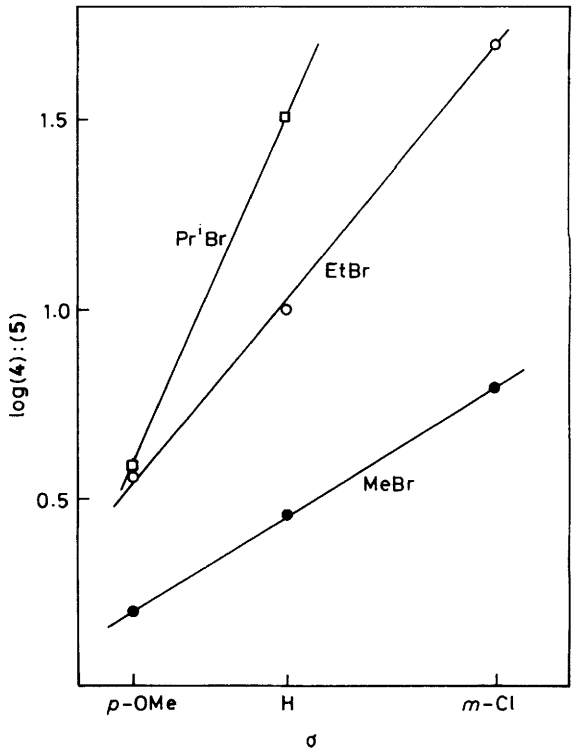


Figure. The plot of the (**4**):(**5**) ratio against σ for the reaction of the 1-arylpropenyl-lithiums (**1a—c**) with alkyl bromides in the presence of TMEDA

* This possibility was kindly suggested by a referee.

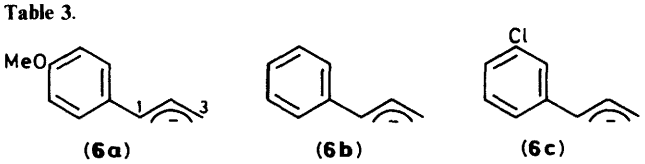
Table 2. Alkylation of 1-arylpropenyl-lithiums

Lithium compound	Reagent	Additive	Reaction temp./°C	Reaction time/min	Products[a] % Yield	(4):(5)	E:Z for (5)
(1a)	MeBr	TMEDA	−70	1	72	61:39	40:60
(1a)	EtBr	TMEDA	20	60	69	78:22	87:13
(1a)	EtI	TMEDA	−70	10	82	59:41	51:49
(1a)	Pr^{i}Br	TMEDA	20	60	86	79:21	100:0
(1a)	Pr^{i}I	TMEDA	0	60	64	49:51	100:0
(1a)	MeOTs	HMPA	−45	10	65	88:12	63:37
(1a)	MeBr	HMPA	−45	10	69	83:17	60:40
(1a)	MeI	HMPA	−45	10	66	77:23	67:33
(1a)	EtBr	HMPA	20	60	79	79:21	87:13
(1a)	EtI	HMPA	20	60	77	67:33	86:14
(1a)	Pr^{i}Br	HMPA	20	60	60	92:8	84:16
(1a)	Pr^{i}I	HMPA	20	60	82	83:17	82:18
(1b)	MeOTs		0	30	48[b]	82:18	91:9
(1b)	MeBr		0	30	42[b]	71:29	90:10
(1b)	MeI		0	30	62	54:46	92:8
(1b)	EtBr		20	60	79	89:11	89:11
(1b)	EtI		0	60	82	71:29	96:4
(1b)	Pr^{i}Br		20	60	62	94:6	96:4
(1b)	Pr^{i}I		0	60	84	83:17	97:3
(1b)	MeOTs	TMEDA	−70	30	59	89:11	83:17
(1b)	MeBr	TMEDA	−70	30	59	74:26	92:8
(1b)	MeI	TMEDA	−70	30	70	53:47	92:8
(1b)	EtBr	TMEDA	0	30	59	91:9	87:13
(1b)	EtI	TMEDA	0	60	81	71:29	95:5
(1b)	Pr^{i}Br	TMEDA	20	60	60	97:3	100:0
(1b)	Pr^{i}I	TMEDA	0	60	57	86:14	97:3
(1b)	MeOTs	HMPA	−70	10	56	93:7	85:15
(1b)	MeBr	HMPA	−70	10	57	89:11	78:22
(1b)	MeI	HMPA	−70	10	54	83:17	81:19
(1b)	EtBr	HMPA	20	60	62	85:15	95:5
(1b)	EtI	HMPA	20	60	79	73:27	95:5
(1b)	Pr^{i}Br	HMPA	20	60	73	96:4[c]	
(1b)	Pr^{i}I	HMPA	20	60	85	89:11	91:9
(1c)	MeOTs		−70	30	62	93:7	90:10
(1c)	MeBr		−70	30	59	90:10	100:0
(1c)	MeI		−70	30	65	83:17	91:9
(1c)	EtBr		20	60	62	95:5	100:0
(1c)	EtI		0	60	57	83:17	100:0
(1c)	Pr^{i}Br		20	60	54	97:3	100:0
(1c)	Pr^{i}I		0	60	65	89:11	100:0
(1c)	MeOTs	TMEDA	0	30	56	94:6	89:11
(1c)	MeBr	TMEDA	−70	30	58	86:14	90:10
(1c)	MeI	TMEDA	−70	30	67	74:26	94:6
(1c)	EtBr	TMEDA	20	60	50	98:2	100:0
(1c)	EtI	TMEDA	0	60	60	84:16	100:0
(1c)	Pr^{i}Br	TMEDA	20	60	55	100:0	
(1c)	Pr^{i}I	TMEDA	0	60	55	94:6	100:0
(1c)	MeOTs	HMPA	−45	10	93	97:3	100:0
(1c)	MeBr	HMPA	−45	10	82	94:6	100:0
(1c)	MeI	HMPA	−45	10	82	93:7	100:0
(1c)	EtBr	HMPA	20	60	51	90:10	100:0
(1c)	EtI	HMPA	20	60	81	82:18	100:0
(1c)	Pr^{i}Br	HMPA	20	60	62	96:4	100:0
(1c)	Pr^{i}I	HMPA	20	60	70	93:7[c]	

[a] The average values of duplicated runs; the error of the (4):(5) ratio as of the order of 2%, as was the error of the *E*:*Z* ratio in (5). The error of the overall yield of products was of the order of 7%. [b] A considerable amount of oligomeric products were also produced. [c] The *E*:*Z* ratio in (5) was not determined.

(*b*) The product regiochemistry was influenced by several factors. In the reaction in the presence or absence of TMEDA the (4):(5) ratio increased as the steric bulk of alkyl halides increased (Me < Et < Pr^i). In the presence of HMPA, however, the (4):(5) ratio decreased in the order Pr^i > Me > Et. The leaving group of MeX also affected the product composition, the (4):(5) ratio decreasing in the order OTs > Br > I. The substituent electronic effects were also important: The (4):(5) ratio increased as the substituent became increasingly electron-withdrawing. It was also noted that the reaction in the presence of TMEDA is subject to a significantly larger substituent effect than the reaction in the presence of HMPA. For the alkylation with alkyl bromides in the presence of TMEDA, the plot of (4):(5) ratio against σ gave a straight line; the ρ values were 0.9 for Me, 1.8 for Et, and 3.5 for Pr^i, respectively (see Figure). Reflecting the accumulated effects

Table 3.



(6a) (6b) (6c)

	C-1	C-3	C-1	C-3	C-1	C-3
Charge densities	−0.215	−0.298	−0.214	−0.296	−0.209	−0.286
Coefficient in HOMO	0.598	−0.678	0.598	−0.679	0.595	−0.673

of the substituent of (**1**) and the nature of alkylating agent, the reaction of the *m*-chloro derivative (**1c**) with the bulky isopropyl bromide in the presence of TMEDA gave exclusively the product of C-1 attack (**4i**).

In order to understand the substituent electronic effects on the product regiochemistry, the charge densities of the 1-arylpropenyl anion (**6**) were calculated by an *ab initio* SCF-MO method at the HF/STO-3G level.[18] The data revealed that (*a*) the charge density at C-3 is significantly larger than that at C-1,* and (*b*) the substituent exerts a considerable influence on the charge densities at C-1 and C-3. The electron-donating *p*-methoxy group increases the charge density at both positions and, in direct contrast, the electron-withdrawing *m*-chloro substituent decreases the charge densities. Moreover, the substituent effect is more important at the position away from the substituent, C-3.† From this we deduce that the ratio of C-1 attack *vs.* C-3 attack (if the substituent does affect the ratio) would increase with increased electron-withdrawing ability of the substituent. This expectation is in good agreement with the results for alkylation of (**1a**—**c**). Protonation of (**1a**—**c**) with oxygen acids in the presence of TMEDA would, however, demonstrate that the relative charge density at C-1 and C-3 is not the sole factor in determining the product composition. Certainly, the (**2a**):(**3a**) ratio is significantly smaller than the (**2b**):(**3b**) ratio. However, this ratio is much the same as the (**2c**):(**3c**) ratio.‡

With regard to the stereochemistry of 3-alkylation products (**5**), the *E*-isomer was obtained almost exclusively. The exceptions were the reactions of the relatively less stable *p*-methoxy derivative (**1a**) with MeBr or EtI in the presence of TMEDA and the reaction of (**1a**) with MeOTs, MeBr, or MeI in the presence of HMPA, where the thermodynamically less stable *Z*-isomer was also produced in a significant amount. In extreme case, *i.e.* the reaction with MeBr in the presence of TMEDA, (*Z*)-(**5a**) was the major product.

As the regio- and stereo-chemistries of protonation and alkylation of the 1-arylpropenyl-lithiums (**1a**—**c**) are complicated and are influenced by many factors, it is difficult to rationalize the results.

* For the 1-phenylpropenyl anion, the calculation by ω-technique shows, however, the reverse trend. The reason for this discrepancy is obscure, see H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, 1974, **93**, 215.

† This is in agreement with the substituent electronic effects on the relative charge densities of 1,3-diarylpropenyl-lithium at the two allylic sites as determined by ^{13}C n.m.r. spectroscopy.[2]

‡ It would be expected that the reaction of the lithium compound (**1**) with alkyl halides—soft electrophiles—is controlled by the frontier electron densities of the lithium compound (**1**) instead of the charge densities and consequently, the observed substituent effects on the (**4**):(**5**) ratio would be rationalized in terms of the substituent effects on the frontier electron densities (see T. L. Ho, 'Hard and Soft Acids and Bases Principles in Organic Chemistry,' Academic Press, New York, 1977). However, the MO calculations could not substantiate this hypothesis; for carbanions (**6a**) and (**6b**) the substituent effects on the HOMO coefficients are negligibly small (Table 3).

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 electronic spectra with a Hitachi 220A spectrometer. G.l.p.c. analysis was carried out on a Hitachi 164 gas chromatograph.

The 3-arylpropenes (**2a**—**c**) were prepared by treating allyl bromide with the corresponding arylmagnesium bromide in ether for 2 h under reflux.[19] (**2a**): b.p. 88—90 °C at 10 mmHg, δ 3.25 (2 H, d, *J* 7.0 Hz), 3.67 (3 H, s), 4.70—5.15 (2 H, m), 5.49—6.20 (1 H, m), and 6.50—7.10 (4 H, m); (**2b**): b.p. 68—70 °C at 40 mmHg, δ 3.30 (2 H, d, *J* 7.0 Hz), 4.73—5.21 (2 H, m), 5.50—6.22 (1 H, m), and 6.79—7.29 (5 H, m); (**2c**): b.p. 78—79 °C at 10 mmHg, δ 3.30 (2 H, d, *J* 7.0 Hz), 4.78—5.38 (2 H, m), 5.48—6.20 (1 H, m), and 6.81—7.54 (4 H, m).

Preparation of the 1-*Arylpropenyl-lithiums* (**1a**—**c**).—(*a*) *In the absence of an additive.* To a 50-ml flask, equipped with a magnetic stirrer and maintained under argon, was added an ethereal solution of the 3-arylpropene (4.2 mmol) *via* syringe. To this was added a hexane solution of BuLi (8.4 mmol) also *via* syringe at 0 °C, and the mixture was stirred for 2 h under reflux.

(*b*) *In the presence of TMEDA.* To an ethereal solution of the 3-arylpropene (4.2 mmol) and TMEDA (5.0 mmol) was added a hexane solution of BuLi (5.0 mmol) *via* syringe at 0 °C, and the mixture was stirred at 20 °C for 1 h. In the case of the *p*-methoxy derivative (**1a**), the mixture was stirred at 20 °C for 2 h.

(*c*) *In the presence of HMPA.* To an ether solution of the 3-arylpropene (4.2 mmol) and HMPA (42 mmol) was added a hexane solution of BuLi (5.0 mmol) *via* syringe at −45 °C, and the mixture was stirred at −45 °C for 10 min.

Protonation of 1-*Phenylpropenyl-lithium* (**1b**) *with* Bu^{t}OH.—Into an ether–hexane solution of (**1b**) containing TMEDA (5.0 mmol) [prepared from (**2b**) (4.2 mmol)] was injected an ether solution of Bu^{t}OH (21 mmol) at 0 °C in one portion. After 1 min the mixture was quenched with water. The ether layer was then separated and dried (Na_2SO_4). After the ether had been evaporated, the crude products were column chromatographed on silica gel to give a mixture of (*Z*)-(**3b**) (8%), (*E*)-(**3b**) (42%), and (**2b**) (50%). The composition of the products was determined by ^1H n.m.r. spectroscopy and g.l.c. (the data in Tables 1 and 2 show the average value of duplicate runs). It was found that these products did not change during column chromatography and g.l.p.c. analysis. Consistent with this, the composition determined after column chromatography was exactly the same as that before column chromatography. The prolonged reaction (1 min⟶1 h) also did not affect the product composition.

To ascertain if the product composition was affected by sunlight, the preparation and reaction of the lithium compound (**1b**) was undertaken in the dark. The product composition was found to be the same as that observed in the reaction under sunlight, suggesting that the photoisomerization of (**1b**) is not important under the reaction conditions.[20]

Treatment of the lithium compound (**1b**) with Bu^{t}OD gave the corresponding mono-deuteriated products, [$^2H_1$]-(*Z*)-(**3b**), [$^2H_1$]-(*E*)-(**3b**), and [$^2H_1$]-(**2b**), the deuterium content as determined by mass spectroscopy being in excess of 98%.

Repeated column chromatography on silica gel afforded the pure products (*Z*)-(**3b**), (*E*)-(**3b**), and (**2b**). (*Z*)-(**3b**): b.p. 45 °C at 10 mmHg, δ 1.85 (3 H, dd, *J* 7.0 and 1.5 Hz), 5.62 (1 H, dq, *J* 11.1 and 7.0 Hz), 6.36 (1 H, dq, *J* 11.1 and 1.5 Hz), and 6.93—7.32 (5 H, m);[21] (*E*)-(**3b**): b.p. 76 °C at 18 mmHg, δ 1.83 (3 H, d, *J* 5.4 Hz), 6.00 (1 H, dq, *J* 15.0 and 5.4 Hz), 6.33 (1 H, d, *J* 15.0 Hz), and 6.90—7.32 (5 H, m).[22]

Reaction of 1-(p-*Methoxyphenyl*)*propenyl-lithium* (**1a**) *with* MeBr *in the Presence of TMEDA.*—Into an ether–hexane

solution of (**1a**) containing 5.0 mmol of TMEDA [prepared from (**2a**) (4.2 mmol)] was injected an ethereal solution of methyl bromide at −70 °C for 1 min. After a conventional work-up, the products were chromatographed on silica gel. The product composition determined after column chromatography was found to be the same as that before column chromatography. (*Z*)-(**5a**): b.p. 123—125 °C at 13 mmHg, δ 1.06 (3 H, t, *J* 7.0 Hz), 2.30 (2 H, d quintet, *J* 1.5 and 7.0 Hz), 3.76 (3 H, s), 5.42 (1 H, dt, *J* 11.5 and 7.0 Hz), 6.22 (1 H, dd, *J* 11.5 and 1.5 Hz), and 6.60—7.25 (4 H, m);[23] (*E*)-(**5a**): m.p. 22—24 °C, δ 1.02 (3 H, t, *J* 7.0 Hz), 2.20 (2 H, quintet, *J* 7.0 Hz), 3.67 (3 H, s), 5.59—6.37 (2 H, m), and 6.55—7.32 (4 H, m);[23] (**4a**): b.p. 118—120 °C at 13 mmHg (Found: C, 81.3; H, 8.7. $C_{11}H_{14}O$ requires C, 81.48; H, 8.64%); *m/z* 160 (M^+); δ 1.26 (3 H, d, *J* 7.0 Hz), 3.32 (1 H, quintet, *J* 7.0 Hz), 3.61 (3 H, s), 4.70—5.14 (2 H, m), 5.60—6.22 (1 H, m), and 6.50—7.30 (4 H, m). The preparation and methylation of the lithium compound (**1a**) was undertaken in the dark also. This change in the reaction conditions, however, did not exert a significent influence on the product composition.

Reaction of 1-*Phenylpropenyl-lithium* (**1b**) *with* EtI *in the Presence of HMPA*.—Into an ether–hexane solution of (**1b**) containing HMPA (42 mmol) [prepared from 4.2 mmol of (**2b**)] was injected an ether solution of ethyl iodide (21 mmol) in one portion and the mixture was kept with stirring at 20 °C for 1 h. Column chromatography of the crude products on silica gel afforded the pure compounds (*Z*)-(**5e**), (*E*)-(**5e**), and (**4e**). (*Z*)-(**5e**): b.p. 79—80 °C at 12 mmHg, δ 0.92 (3 H, t, *J* 7.0 Hz), 1.24—1.68 (2 H, m), 2.12—2.40 (2 H, m), 5.64 (1 H, dt, *J* 11.5 and 7.0 Hz), 6.40 (1 H, dt, *J* 11.5 and 1.5 Hz), and 7.40—7.50 (5 H, m);[24] (*E*)-(**5e**): b.p. 86—87 °C at 10 mmHg, δ 0.95 (3 H, t, *J* 7.0 Hz), 1.46 (2 H, sextet, *J* 7.0 Hz), 2.12 (2 H, q, *J* 7.0 Hz), 6.04 (1 H, dt, *J* (16.0 and 7.0 Hz), 6.28 (1 H, d, *J* 16.0 Hz), and 7.05—7.41 (5 H, m);[25] (**4e**): b.p. 79—80 °C at 20 mmHg (Found: C, 90.6; H, 9.3. $C_{11}H_{14}$ requires C, 90.41; H, 9.59%); δ 0.82 (3 H, t, *J* 7.0 Hz), 1.67 (2 H, quintet, *J* 7.0 Hz), 3.04 (1 H, q, *J* 7.0 Hz), 4.79—5.10 (2 H, m), 5.65—6.27 (1 H, m), and 6.88—7.37 (5 H, m).

Reaction of 1-*Phenylpropenyl-lithium* (**1b**) *with* Pr^{i}I *in the Presence of TMEDA*.—Into an ether–hexane solution of (**1b**) containing TMEDA (5.0 mmol) [prepared from (**2b**) (4.2 mmol)] was injected an ethereal solution of Pr^{i}I (21 mmol) in one portion and the mixture was kept with stirring at 0 °C for 1 h. Column chromatography of the crude products on silica gel afforded the pure compounds (*Z*)-(**5h**), (*E*)-(**5h**),[26] and (**4h**).[26] (*Z*)-(**5h**): an oil, *m/z* 160 (M^+); δ 0.92 (6 H, d, *J* 6.0 Hz), 1.40—1.80 (1 H, m), 2.18 (2 H, td, *J* 7.0 and 1.5 Hz), 5.60 (1 H, dt, *J* 11.5 and 7.0 Hz), 6.37 (1 H, dd, *J* 11.5 and 1.5 Hz), and 6.95—7.30 (5 H, m). The physical properties of (*Z*)-(**5h**) were identical with those of an authentic sample prepared from benzaldehyde and 3-methylbutylidenetriphenylphosphorane.

Physical Properties of Products.—(*Z*)-(**3c**): b.p. 76—78 °C at 7 mmHg, δ 1.80 (3 H, dd, *J* 7.0 and 1.8 Hz), 5.55—5.94 (1 H, m), 6.12—6.36 (1 H, m), and 6.87—7.32 (4 H, m); (**4c**): b.p. 98—100 °C at 15 mmHg, δ 1.29 (3 H, d, *J* 7.0 Hz), 3.36 (1 H, quintet, *J* 7.0 Hz), 4.81—5.22 (2 H, m), 5.66—6.25 (1 H, m), and 6.86—7.21 (4 H, m); (*E*)-(**5c**): b.p. 108—110 °C at 15 mmHg, δ 1.06 (3 H, t, *J* 7.0 Hz), 2.02—2.39 (2 H, m), 5.99—6.22 (2 H, m), and 7.05—7.32 (4 H, m); *Z*-(**5c**): b.p. 104—105 °C at 15 mmHg, δ 1.05 (3 H, t, *J* 7.0 Hz), 2.28 (2 H, d quintet, *J* 7.0 and 2.4 Hz), 5.49—5.79 (1 H, m), 6.18—6.39 (1 H, m), and 6.96—7.38 (4 H, m); (**4d**): b.p. 125—127 °C at 13 mmHg, δ 0.82 (3 H, t, *J* 7.0 Hz), 1.63 (2 H, quintet, *J* 7.0 Hz), 2.98 (1 H, q, *J* 7.0 Hz), 3.66 (3 H, s), 4.79—5.16 (2 H, m), 5.57—6.08 (1 H, m), and 6.57—7.25 (4 H, m); (**4f**): b.p. 120—122 °C at 18 mmHg, δ 0.84 (3 H, t, *J* 7.0 Hz), 1.67 (2 H, quintet, *J* 7.0 Hz), 3.06 (1 H, q, *J* 7.0 Hz), 4.78—5.12 (2 H, m), 5.58—6.03 (1 H, m), and 6.83—7.28 (4 H, m); (**4g**): b.p. 126—129 °C at 13 mmHg, δ 0.74 (3 H, d, *J* 7.0 Hz), 0.92 (3 H, d, *J* 7.0 Hz), 1.85 (1 H, d heptet, *J* 1.8 and 7.0 Hz), 2.77 (1 H, t, 7.0 Hz), 3.64 (3 H, s), 4.79—5.08 (2 H, m), 5.65—6.10 (1 H, m), and 6.56—7.24 (4 H, m); *Z*-(**5g**): b.p. 131—134 °C at 13 mmHg, δ 0.92 (6 H, d, *J* 6.0 Hz), 1.40—1.80 (1 H, m), 2.18 (2 H, td, *J* 7.0 and 1.5 Hz), 3.65 (3 H, s), 5.60 (1 H, dt, *J* 11.5 and 7.0 Hz), 6.37 (1 H, dd, *J* 11.5 and 1.5 Hz), and 6.95—7.30 (4 H, m); (**4i**): b.p. 114—116 °C at 15 mmHg, δ 0.74 (3 H, d, *J* 7.0 Hz), 0.92 (3 H, d, *J* 7.0 Hz), 1.87 (1 H, d heptet, *J* 2.1 and 7.0 Hz), 2.79 (1 H, t, *J* 7.0 Hz), 4.82—5.12 (2 H, m), 5.64—6.08 (1 H, m), and 6.86—7.20 (4 H, m); (*E*)-(**5i**): b.p. 118—120 °C at 15 mmHg, δ 0.94 (6 H, d, *J* 7.0 Hz), 1.46—1.98 (1 H, m), 2.06 (2 H, t, *J* 7.0 Hz), 5.70—6.38 (2 H, m), and 6.90—7.41 (4 H, m).

The physical properties of the following products have been reported in the literature: (*E*)-(**3a**),[22,27] (*Z*)-(**3a**),[21] (*E*)-(**3c**),[21] (**4b**),[28] *E*-(**5b**),[29] *Z*-(**5b**),[29] (*E*)-(**5d**),[23] (*Z*)-(**5d**),[23] (*E*)-(**5f**),[30] and (*E*)-(**5g**).[31]

The Retention Times in G.l.p.c. Analysis.—The column used was 20% SE-30 on Aeropak 30, 3 ft × 0.125 in; R_t, min (oven temp, °C). (**2a**): 4.5 (120); (*Z*)-(**3a**): 6.0 (120); (*E*)-(**3a**): 7.5 (120); (**2b**): 2.7 (90); (*Z*)-(**3b**): 3.6 (90); (*E*)-(**3b**): 4.6 (90); (**2c**): 3.5 (120); (*Z*)-(**3c**): 4.1 (120); (*E*)-(**3c**): 5.3 (120); (**4a**): 10.7 (110); (*Z*)-(**5a**): 14.5 (110); (*E*)-(**5a**): 19.2 (110); (**4b**): 3.2 (100); (*Z*)-(**5b**): 4.4 (100); (*E*)-(**5b**): 6.1 (100); (**4c**): 4.9 (120); (*Z*)-(**5c**): 6.3 (120); (*E*)-(**5c**): 8.6 (120); (**4d**): 5.6 (140); (*Z*)-(**5d**): 7.8 (140); (*E*)-(**5d**): 10.2 (140); (**4e**): 3.9 (110); (*Z*)-(**5e**): 5.7 (110); (*E*)-(**5e**): 7.6 (110); (**4f**): 8.0 (120); (*E*)-(**5f**): 14.9 (120); (**4g**): 7.3 (140); (*Z*)-(**5g**): 10.4 (140); (*E*)-(**5g**): 17.0 (140); (**4h**): 5.5 (110); (*Z*)-(**5h**): 8.6 (110); (*E*)-(**5h**): 10.6 (110); (**4i**): 10.5 (120); (*E*)-(**5i**): 19.8 (120).

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