Reaction of phenyllithium with *E*-cinnamaldehyde: survey of several variables and their influence on the mechanism of reaction and in organic synthesis

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ABSTRACT: The reaction of phenyllithium (PhLi) with *E*-cinnamaldehyde (**1**) has been fully examined. Besides the main product *E*-1,3-diphenyl-2-propen-1-ol (**2**), three other by-products were detected: *E*-cinnamyl alcohol (**3**), *E*-chalcone (**4**) and *E*-1,3-diphenylpropanone (**5**). The effect of several variables on the nature and relative yields of products was examined. In all the solvents studied, the selectivity of the reaction was higher at higher temperatures, probably owing to aggregation effects; at lower temperatures the reaction is slower and the amount of by-products increases. The addition is complete in 1 h at 0 °C in THF for a [PhLi]:[**1**] ratio of 1:1, and longer reaction times have almost no effect, while for the reaction in toluene the amount of by-products increases when the reaction mixture is allowed to stand. The concentration of the reagents has no important effect on the reaction as long as the ratio is kept equal to 1:1. The influence of light was examined and a marked decrease in the selectivity of the reaction was observed. When the reaction was carried out in the presence of radical traps, no by-products were detected. Finally, for a [PhLi]:[**1**] ratio of 3:1 the main product is the dihydrochalcone **5**, especially for long reaction times. All the above results could be interpreted in a reaction scheme involving electron transfer from PhLi to **1**, and further reaction of the radical ions formed as well as reaction of dimeric PhLi without previous deaggregation when the ratio is 3:1. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: phenyllithium; *E*-cinnamaldehyde; organolithium; addition; mechanism

INTRODUCTION

It is well known that in the solid state as well as in hydrocarbon solutions organolithium compounds are more or less aggregated.[1,2] The reactivity and in many cases also the regio- and stereochemistry of their reactions are strongly dependent on the solution structure of the organolithium reagent.[3] The ever-increasing knowledge in this field is very helpful to the synthetic chemist, since it helps to choose the right organolithium–solvent combination more suitable for leading the reaction to the desired synthetic goal.[4] The organolithium compound aggregates are generally dimers, tetramers and hexamers, the degree of aggregation depending on several factors: lower aggregation numbers are favoured by bulkier alkyl groups, delocalization of charge, polar solvents[5] and lower temperatures.[6,7]

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Numerous efforts have been made to uncover the structure of PhLi in the solid state as well as in solution. X-ray investigations have characterized the tetramer crystallized from Et$_2$O,[8] the dimer which crystallizes as a complex with TMEDA from the same solvent[9] and the monomer stabilized through complexation with the tridentate ligand pentamethyldiethylenetriamine (PMDTA).[10] In solution the aggregation number can be derived from chemical shift considerations but more clearly from the multiplicity of the ^{13}C NMR signals of the lithiated C atom and the magnitude of the ^{13}C, ^{6}Li scalar spin–spin coupling. Published results[11,12] lead to the conclusion that PhLi forms a tetramer in Et$_2$O. Only at low concentration and in the presence of toluene are indications of the coexistence of dimers found. From freezing point depression values in dilute solutions at −108 °C, Bauer and Seebach[13] have found that PhLi in ether varies its aggregation grade between $n = 1.64$ (0.070 M) and $n = 2.17$ (0.35 M), while in THF $n = 1.6$ for concentrations between 0.1 and 0.7 M. Schleyer and co-workers[14] have found that PhLi in THF solution exists in a dimer–monomer equilibrium.

On the other hand, although the reactions of organolithiums with carbonyl compounds are among the most

elementary synthetic reactions, little detailed mechanistic information on the role of aggregation is yet available. Yamataka *et al.*[15] have demonstrated that the reactions of PhLi with aromatic carbonyl compounds proceed via a mechanism in which the rate-determining step is an initial electron transfer. The mechanism of the reaction of alkyllithiums with esters has been investigated in cyclohexane and benzene.[16] Kaufmann and Schleyer[17] reported an *ab initio* examination of the mechanisms of model reactions of formaldehyde with the monomers CH_3Li and LiH as well as with their dimers, and recently Nakamura *et al.*[18] have shown the importance of open dimers in the same reaction. The observation of an appreciable kinetic isotope effect (KIE) in the reactions of methyllithium with substituted arylketones has been interpreted as an indication of a pre-equilibrium between an aggregate and a reactive monomer.[19]

This paper describes an investigation of the reaction of PhLi with *E*-cinnamaldehyde (**1**). The effects of solvent, temperature, concentration and [PhLi]:[**1**] ratio were examined as a contribution to elucidating their influence on the mechanisms of the reaction and its use in organic synthesis.

RESULTS AND DISCUSSION

The reactions between PhLi and *E*-cinnamaldehyde (**1**) were carried out in tetrahydrofuran, toluene and ether at several temperatures between −78 and 25 °C, with a concentration of both reagents of 0.07 M and a reaction time of 3 h. *E*-1,3-Diphenyl-2-propen-1-ol (**2**) was the main reaction product, accompanied by various amounts

of the by-products *E*-cinnamyl alcohol (**3**), *E*-chalcone (**4**) and *E*-1,3-diphenylpropanone (**5**).

Since the variation in the distribution of the minor products was considered essential to the purpose of this work, and in many cases the reproducibility was not very good, the reactions under each set of reaction conditions were repeated at least five times. The values shown in the tables are average results, % variation ± 5%.

Table 1 gathers the results for the reaction in THF at several temperatures. It is shown that production of the 1,2-addition product **2** is high at 0 and 20 °C, while at the lower temperatures a substantial amount of **1** was recovered unreacted and formation of some by-products was observed. It was previously reported that PhLi exists as a dimer–monomer equilibrium in THF solution[14] and that lower temperatures favour less aggregation,[5,6] but the high yields of **2** observed at $T \geq 0 \,^{\circ}C$ would suggest that the reaction is insensitive to aggregation effects or, more likely, that the dimer could add without previous deaggregation as observed in some other reactions of BuLi.[20] This observation is in agreement with the lower % reaction yield at −78 °C, which could also be partly due to the decrease in the reaction rate. It is unlikely that the temperature effect was only due to the high activation energy, since the results at 0 and 20 °C are very similar. At these temperatures the addition in THF is highly selective: only small amounts of by-products are formed and very good yields of the addition product are obtained with retention of the geometry as expected.

When the reaction was carried out in toluene (see Table 2), less sensitivity of the 1,2-addition product yield to the temperature was observed. It is likely that in toluene most of the PhLi exists as a dimer at all the
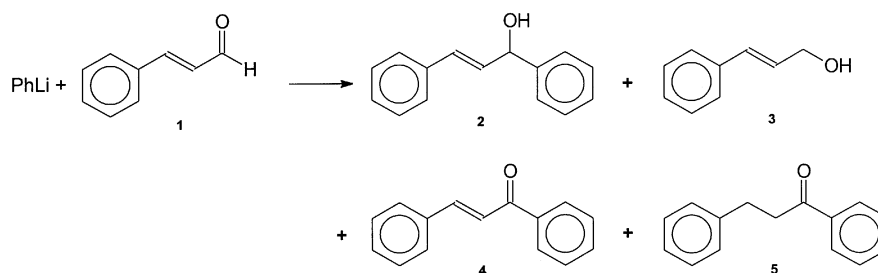

Table 1. Addition of PhLi to *E*-cinnamaldehyde, **1**, in THF at several temperatures

| Temperature (°C) | % Yields[a] | | | % **1** recovered | % Total reaction products |
	2	**3**	**4**		
−78	58	7	8	19	73
−20	76	8	3	14	87
0	94	0	6	0	100
20	95	0	5	0	100

[a] Determined by quantitative GC analysis using decalin as internal standard. $[PhLi]_0 = [\mathbf{1}]_0 = 0.07$ M. All the reactions were carried out protected from light.

Table 2. Addition of PhLi to *E*-cinnamaldehyde, **1**, in toluene at several temperatures

Temperature (° C)	% Yields[a]				% 1 recovered	% Total reaction products
	2	**3**	**4**	**5**		
−78	86	5	9	0	0	100
−20	85	5	9	1	0	100
0	75	0	13	8	0	96
20	81	0	13	0	0	94

[a] Determined by quantitative GC analysis using decalin as internal standard. $[PhLi]_0 = [1]_0 = 0.07$ M. All the reactions were carried out protected from light.

Table 3. Addition of PhLi to *E*-cinnamaldehyde, **1**, in ether at several temperatures

Temperature (° C)	% Yields[a]				% 1 recovered	% Total reaction products
	2	**3**	**4**	**5**		
−78	72	7	14	3	0	96
−20	68	0	6	7	0	81
0	52	19	15	2	1	88
20	76	0	6	4	1	86

[a] Determined by quantitative GC analysis using decalin as internal standard. $[PhLi]_0 = [1]_0 = 0.07$ M. All the reactions were carried out protected from light.

Table 4. Addition of PhLi to *E*-cinnamaldehyde, **1**: concentration effects

Solvent	$[PhLi]_0 = [1]_0$ (M)	Temperature (° C)	% Yields[a]				% 1 recovered	% Total reaction products
			2	**3**	**4**	**5**		
THF	0.20	−20	84	4	3	0.5	3	92
	0.07	−20	76	8	3	0	14	87
	0.20	20	91	0	3	0	0	94
	0.07	20	95	0	5	0	0	100
Toluene	0.20	−20	85	2	3	3	8	93
	0.07	−20	86	5	9	1	0	101
	0.20	20	72	2	2	0	0	76
	0.07	20	81	0	13	0	0	94
Ether	0.20	−20	60	0	7	11	0	78
	0.07	−20	68	0	6	7	0	81
	0.20	20	70	5	2	3	1	80
	0.07	20	76	0	6	4	1	86

[a] Determined by quantitative GC analysis using decalin as internal standard. All the reactions were carried out protected from light; reaction time 3 h.

studied temperatures and the reaction was complete in all cases. The production of by-products is more sensitive to temperature changes: the most important by-product is the chalcone **4**, whose yield increases slightly with temperature, while the yields of the reduction product of **1** (compound **3**) and the unusual product **5** were smaller. In ethyl ether solution (Table 3) the selectivity is even lower than in toluene and a considerable distribution of products is observed. The lower yields of **2** cannot be ascribed to a lower reactivity in this solvent, since the reaction of **1** was almost complete. By-products **3** and **4** appeared in appreciable amounts, but no clear relationship of the product distribution with temperature is observed.

The possible influence of concentration was then examined in the three solvents at −20 and 20 °C. Comparison of [PhLi] = 0.2 M with [PhLi] = 0.07 M is shown in Table 4. Essentially no effects were detected and again the formation of by-products was higher in ether.

The reactions of PhLi with **2** and **4** in 3:1 ratio at 20 °C have been carried out in order to observe if **4** and **5** are the result of reaction of PhLi with **2** and not **1**. The reaction of **2** with PhLi produces 79% of **5** and 21% of **4**, while in the reaction with **4** only the products expected for the 1,2- and 1,4-addition were obtained.

The effects of variation in the time of reaction are shown in Table 5. For the reaction carried out in THF at 1:1 ratio no diminution in the yield of **2** was observed on exposing the reaction mixture to longer reaction times:

Table 5. Addition of PhLi to *E*-cinnamaldehyde, **1**, at 0 °C: effect of reaction time

Solvent	Time (h)	% Yields[a]				% 1 recovered	% Total reaction products
		2	**3**	**4**	**5**		
THF	1	100	0	0	0	0	100
	3	94	0	0	0	0	94
	4	94	0	6	0	0	100
Toluene	1	84	0	0	0	5	84
	2	75	5	16	3	3	99
	4	69	0	13	8	0	90

[a] Determined by quantitative GC analysis using decalin as internal standard. $[PhLi]_0 = [1]_0 = 0.07$ M. All the reactions were carried out protected from light.

Table 6. Addition of PhLi to *E*-cinnamaldehyde, **1**: effect of light[a]

Solvent	Temperature (°C)	% Yields[b]				% **1** recovered	% Total reaction products
		2	**3**	**4**	**5**		
THF	0	45	10	9	0	24	64
	20	53	6	14	0	17	75
Toluene	−78	58	13	14	3	0	88
	0	53	17	20	5	1	95
Ether	−20	24	30	20	0	10	74
	0	46	18	16	0	0	80
	20	52	4	12	0	0	68

[a] $[PhLi]_0 = [1]_0 = 0.07$ M and reaction time 3 h.
[b] Determined by quantitative GC analysis using decalin as internal standard.

Table 7. Effect of addition of radical traps[a] in reaction of PhLi with *E*-cinnamaldehyde, **1**, in THF at 0 °C

[PhLi]: [**1**][b]	[Hydroquinone]: [**1**]	[Quinhydrone]: [**1**]	% Yields[c]				% **1** recovered	% Total reaction products
			2	**3**	**4**	**5**		
1	0	0	88.3	0	11.1	0.9	0	100.3
1	1	0	52.8	0	0	0	48	52.8
1	0	1	26.2	0	0	0	62.5	26.2
3	0	0	59.4	0	8.4	33.2	0	101.0
3	1	0	67.6	0	1.6	21.2	0	90.4
3	0	1	76.9	0	10.5	0	0	87.4

[a] Blanks of PhLi with each radical trap were performed in THF, recovering unreacted benzene in high yields.
[b] $[1]_0 = 0.2$ M; PhLi was added over the *E*-cinnamaldehyde; reaction time 2 h.
[c] Determined by quantitative GC analysis using decalin as internal standard. The reactions were carried out without protection from light.

only 6% of **4** appeared when the mixture was allowed to stand for 4 h. In toluene the yield of **2** decreased and some side products were formed for reaction times higher than 1 h. This seems to indicate that **2** is partially undergoing further reaction to produce mainly **4**, its oxidation product.

The influence of light on the selectivity of the reaction was then examined by carrying out the reaction in colourless flasks unprotected from light. It can be observed in Table 6 that there is a marked decreased in the selectivity of the reaction in the three solvents at several temperatures. The sensitivity of the reaction to light suggests that radical processes might be involved, especially in those pathways leading to by-products **3** and

4. In these cases, as well as in the previous one, the [**3**]:[**4**] ratio was not 1:1.

The effect of added radical traps at the beginning of the reaction in THF was then examined. Two different kinds of experiments were carried out. In the first case the ratio [PhLi]:[**1**] was 3:1, while in the second a 1:1 ratio was used. The known radical traps *m*-dinitrobenzene and TEMPO reacted with PhLi under the present reaction conditions, while hydroquinone and quinhydrone seemed to be unreactive against PhLi in the presence of **1** in the time the addition reaction takes place. Hydroquinone and quinhydrone were previously found to be effective radical traps in the reaction of naphthyllithium with CO.[21,22] The results of the reaction in the presence of

Table 8. Addition of PhLi to *E*-cinnamaldehyde, **1**, in THF at 20 °C: influence of [PhLi]:[**1**] ratio and reaction time[a]

[PhLi]:[**1**]	Time (h)	[PhLi] (M)	% Yields[b]			% Total reaction products
			2	**4**	**5**	
1	3	0.07	95	5	0	100
2	2	0.04	84	6	4	94
2	24	0.04	82	3	15	100
3	2	0.07	18	7	75	100
3	3	0.06	0	8	88	96
3	6	0.06	0	6	94	100
3	24	0.07	0	0	100	100
6	24	0.09	0	0	83	83

[a] The reaction was carried out protected from light.
[b] Determined by quantitative GC analysis using decalin as internal standard.
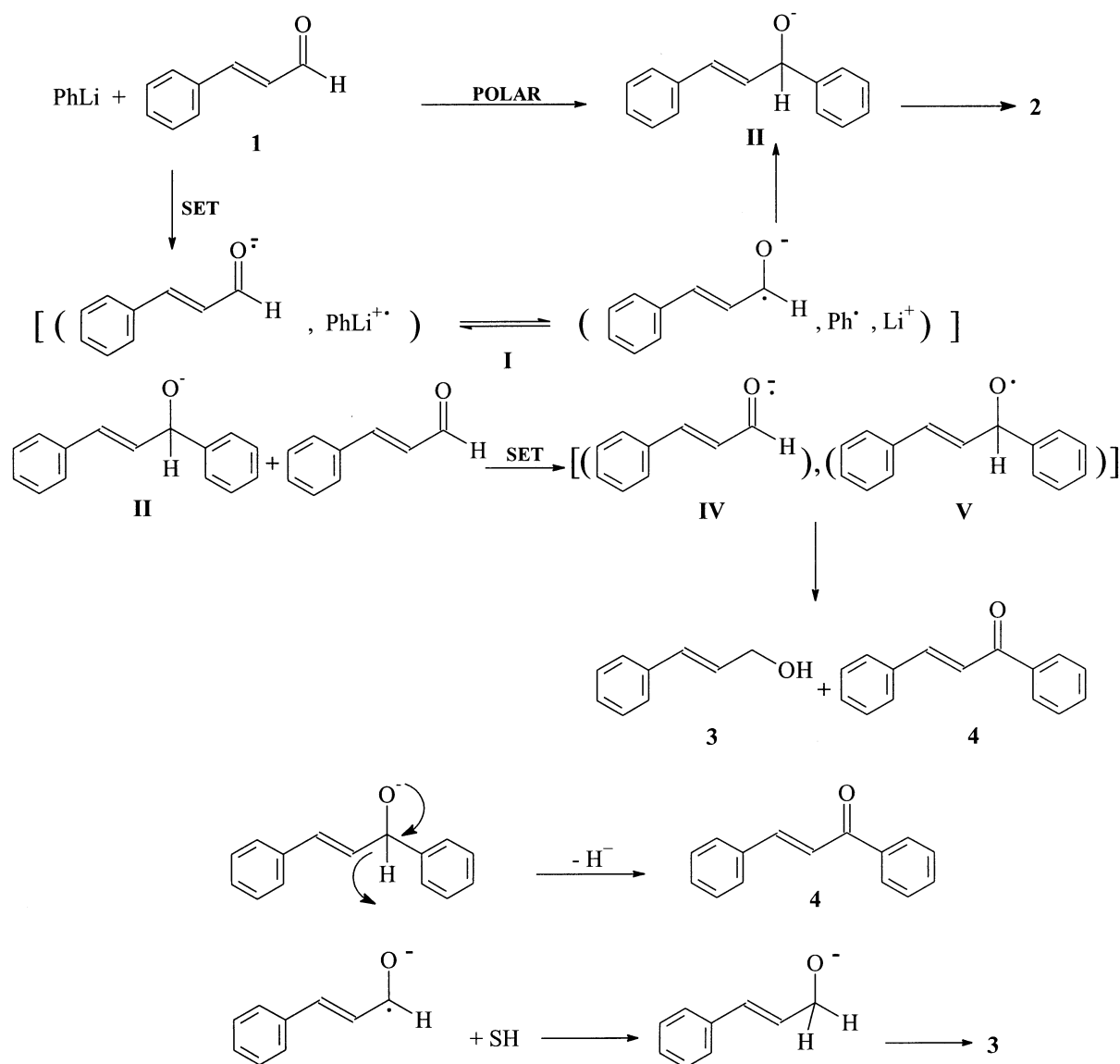
Scheme 1. Reaction of PhLi with *E*-cinnamaldehyde, **1**, in 1:1 ratio

these radical traps can be observed in Table 7. When the reaction was carried out with a [PhLi]:[**1**] = 1:1 ratio, a considerable recovery of **1** was observed in the presence of both compounds and no by-products were observed. This is in agreement with the mechanism proposed, in which the formation of **3** and **4** occurs by a radical way.
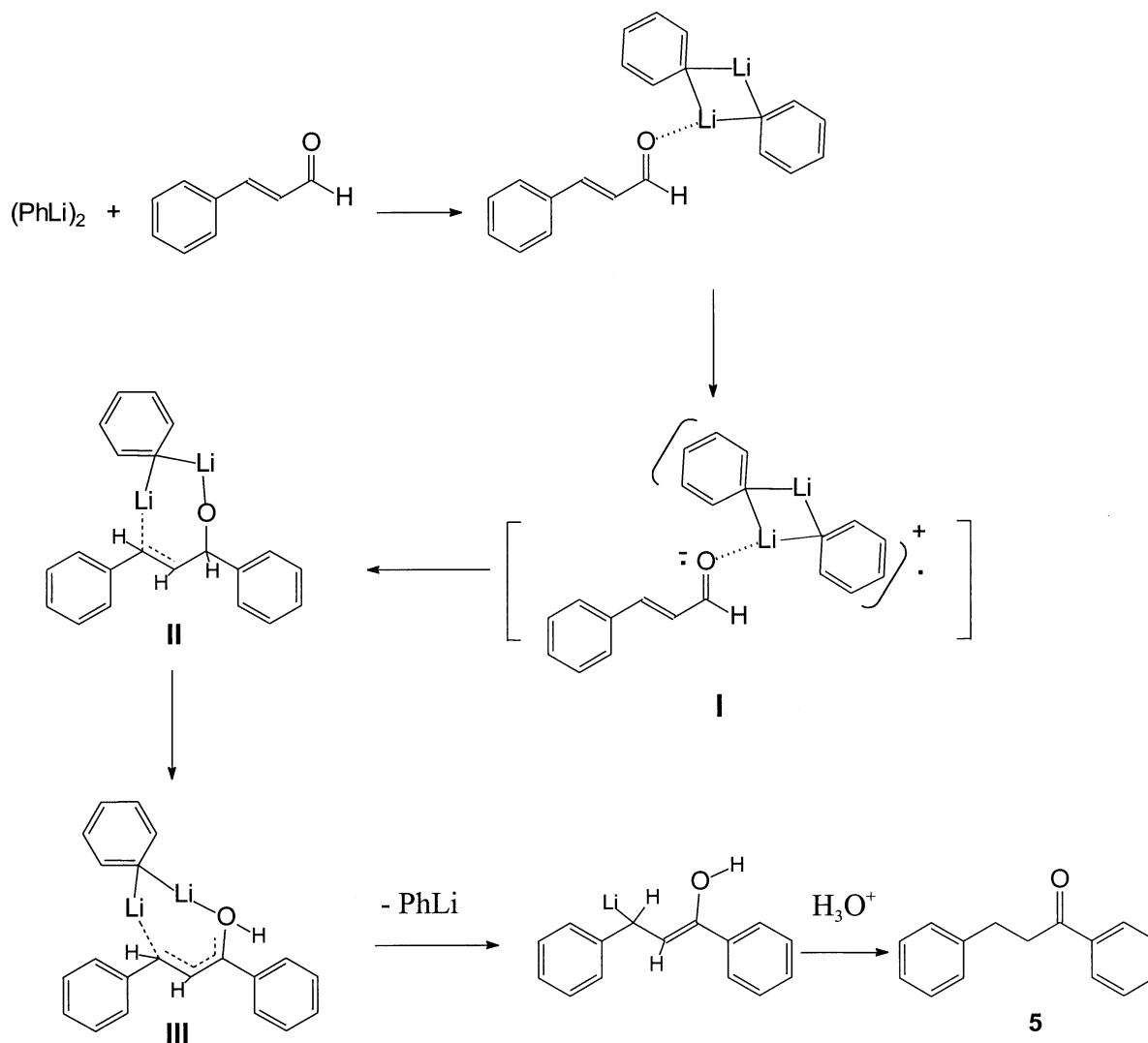
Scheme 2. Reaction of PhLi with *E*-cinnamaldehyde, **1**, in 3:1 ratio

Nevertheless, when PhLi was in excess (3:1 ratio), **1** was completely consumed and an unusually high production of **5** was observed in the absence of radical traps, which decreases in the presence of hydroquinone and is nil in the presence of quinhydrone, while the yield of **2** *increases.* The yield of **4** is lower when hydroquinone is present.

By-product **3** is a reduction product of **1.** To prove that its formation involves a radical intermediate and hydrogen abstraction from the solvent, the reaction was carried out unprotected from light in ether at −20 °C and quenched with deuterium oxide. Undeuterated product **3** in the C1 was obtained as well as the -OD group, as expected from an intermediate leading to **3** that takes an H from the solvent before quenching.

A final study was carried out to examine the influence of the [PhLi]:[**1**] ratio and the reaction time on the reaction carried out in THF at 20 °C. Table 8 shows that the production of **5** increases with longer reaction times, which could indicate that this compound is formed *after*

the first intermediate leading to **2** is produced. The effect of the [PhLi]:[**1**] ratio is more interesting: using a [PhLi]:[**1**] = 3:1 ratio and [PhLi] = 0.07 M, a quantitative conversion of **1** to **5** can be afforded in a 24 h reaction. Similar results (not shown) were observed for the reaction carried out in toluene. The scope of these reactions for the production of other related compounds is currently under study.

In the light of all the above results the mechanism shown in Scheme 1 is proposed for the 1,2-addition and the formation of by-products **3** and **4.** (Although PhLi is written as a monomer for the sake of clarity, it is likely that the dimer reacts also without previous deaggregation especially in THF and toluene, as was observed in other cases.[20]) The first step is electron transfer from the phenyllithium to **1**, giving the radical anion–radical cation pair **I**, as was previously reported for the reactions of PhLi with arylketones[15] and with CO.[23] Reaction of **I** within the solvent cage leads to the 1,2-addition intermediate anion **II**, which by hydrolysis renders **2**.

The formation of **3** and **4** could be described by an SET mechanism in which the adduct **II** could react with **1**, giving its radical anion **IV** and the radical of the adduct, **V**. The transference of a hydrogen radical from **V** to **IV** would yield **3** and **4**. Light stimulates electron transfer, and when the reaction is carried out in the presence of light (Table 6), the yields of **3** and **4** increase and are very similar.

On the other hand, under other reaction conditions not always [**3**] ≈ [**4**], usually [**4**] > [**3**] and sometimes **3** is not detected (Tables 7 and 8). This suggests the existence of an alternative pathway for the formation of **4**. Intermediate **II** could alternatively eliminate an H$^-$ ion, giving the oxidation product **4**; although the oxidation reagent is difficult to envisage under the present reaction conditions, oxidation of radical anion intermediates was also observed in the reaction of PhLi with CO[23] and of naphtyl- and xylyllithium with CO[24,25] under similar reaction conditions. That **4** is formed by oxidation of intermediate **I** is consistent with the increase in the yield of **4** observed in toluene at the expense of **2** for long reaction times (see Table 5).

The reaction carried out using a [PhLi]:[**1**] = 3:1 ratio affords a new method of preparation of compound **5** and the mechanism proposed for its formation is depicted in Scheme 2. In this case, taking into account the ratio effect, the reaction is formulated as occurring with dimeric PhLi. Coordination to **1** through the lithium atom without deaggregation is proposed, followed by an electron transfer forming the new radical anion–radical cation pair intermediate **I**. Addition of phenyl radical to the carbonyl carbon, as well as addition of the second lithium atom to the β-carbon, would give the complex intermediate **II** (both additions could be concerted or stepwise; not enough information is yet available, although the fact that the yield of **5** increases with time favours a stepwise addition). Rearrangement of **II** to **III** and separation of a molecule of PhLi give the organolithium precursor of compound **5**. That the lithium atom is bonded to the β-carbon was confirmed by quenching the reaction with D$_2$O: 100% deuteration on the β-carbon (but no α-carbon) was observed. Since intermediate **III** is a lithium carbanion, the scope of this reaction to synthesize 3-alkyl-substituted 1,3-diphenyl-propanones is under study; preliminary results with several electrophiles showed good yields of the β-alkyl-substituted products.

Although similar results could be reached by assuming monomeric PhLi and stepwise addition of each PhLi, semiempirical calculations carried out on several reaction intermediates with the AMPAC 5.0[26] program favour attack by dimeric PhLi. It has been shown[27] that the current MNDO lithium parameters accurately reproduce lithium interactions with nitrogen and oxygen through comparisons with experimental results and *ab initio* calculations.[28,29] In the present work it can be observed that the C1-C2 bond is shortened while the C2-C3 bond is lengthened on going from **II** to **III**. The intermediate **III** was calculated to be more stable than **II** by almost 20 kcal mol^{-1}; the transition state for the rearrangement **II–III** was searched and its geometry optimized. Calculations show that it is a real transition state, having only one negative vibrational frequency corresponding to the reaction coordinate.[30]

EXPERIMENTAL

Materials and methods

Tetrahydrofuran (THF) was purified and made anhydrous as previously described;[31] it was freshly distilled from lithium benzophenone ketyl under an N$_2$ atmosphere immediately prior to use. Hexane was purified by refluxing with sulphuric acid (conc.) for 2 h, then distilled, stored for 2–3 days over sodium hydroxide lentils and distilled under N$_2$. Toluene was stored over sodium strings for 2–3 days, then distilled. Diethyl ether was purified similarly. All solvents were redistilled over sodium benzophenone ketyl immediately prior to use. *E*-cinnamaldehyde (Aldrich, 99%) was distilled prior to use. Solid phenyllithium was prepared as described previously.[32] The concentration of PhLi was determined by reaction with diphenyl acetic acid.[33] All glassware, syringes and needles were dried in a vacuum oven and cooled in a desiccator. The reactions of PhLi with **1** were carried out by the general procedure reported previously,[34] using techniques described for the manipulation of these air-sensitive compounds.[35]

Mass spectra were recorded using a gas chromatograph coupled to a BG Trio-2 mass spectrometer. The GLC analyses were carried out on a 5890 + HP gas chromatograph using an HP-5 column (conditions: $T_i = 70$ °C, $T_f = 250$ °C, rate 10 °C min^{-1}). NMR spectra were determined with a Brucker 200 MHz NMR spectrometer. IR measurements were performed on a Nicolet 510 P FT-IR spectrometer. Isolation of the reaction products was carried out by preparative TLC using silica gel G. The isolated compounds were fully characterized by spectroscopy and by their GC retention times against standards independently prepared.

(E)-1,3-Diphenyl-2-propen-1-ol, **2**, was prepared by standard procedures, m.p. 56–58 °C (lit. 55–57 °C[36]). IR (KBr) (cm^{-1}): 700 (s), 750 (s), 970 (s), 1450 (s), 1500 (s), 1600 (w), 3030 (s), 3060 (m), 3350 (br s). ^{1}H NMR (CDCl$_3$) (ppm): 2.32 (br s, 1H), 5.40 (d, 1H, $J = 6.5$ Hz), 6.41 (dd, 1H, $J = 6.5$ and 15.9 Hz), 6.72 (d, 1H, $J = 15.9$ Hz), 7.38 (m, 10H). ^{13}C NMR (CDCl$_3$) (ppm): 75.18, 126.44, 126.71, 127.17, 127.85, 128.65, 128.71, 130.65, 131.65, 136.63, 142.88. MS *m/e* (I_{rel}): 210 (24), 105 (100), 91 (16), 77 (32), 51 (10).

(E)-Cinnamyl alcohol, **3**, b.p. 249–250 °C. IR (KBr) (cm^{-1}): 685 (s), 730 (s), 740 (s), 963 (w), 1065 (m), 1090 (m), 1450 (m), 1480 (m), 2850 (m), 3000 (m), 3350 (s).

^{1}H NMR (CDCl$_3$) (ppm): 4.27 (d, 2H, $J = 5.6$ Hz), 6.31 (dt, 1H, $J = 5.6$ and 15.9 Hz), 6.57 (d, 1H, $J = 15.9$ Hz), 7.27 (m, 5H). ^{13}C NMR (CDCl$_3$) (ppm): 63.78, 126.53, 127.75, 128.65, 131.20. MS m/e (I_{rel}): 134 (85), 133 (23), 115 (43), 105 (46), 103 (22), 92 (100), 91 (76), 79 (25), 78 (50), 77 (39), 55 (19), 51 (23).

(E)-1,3-Diphenyl-2-propen-1-one (chalcone), **4**. To 20 ml of 3 M sodium hydroxide and 12.5 ml of 96% ethanol contained in a 50 ml round-bottomed flask provided with a magnetic stirrer, 5.2 g of distilled acetophenone were added with rapid stirring. The mixture was cooled in a cracked ice water bath and 4.6 g of benzaldehyde were added at once. The temperature was maintained between 15 and 30 °C during the reaction. After 2–3 h the mixture was cooled for about 10 h at 0 °C. The product was filtered through a Buchner funnel, washed with water until the washings were neutral, and finally washed with 2 ml of 96% ethanol which had previously been cooled to 0 °C. After drying, the crude product was crystallized from 96% ethanol, m.p. 57–58 °C (lit. 58 °C[37]). ^{1}H NMR (CDCl$_3$) (ppm): 6.70 (d, 1H, $J = 13.2$ Hz), 6.95 (d, 1H, $J = 13.2$ Hz), 7.56 (m, 10H). ^{13}C NMR (CDCl$_3$) (ppm): 122.16, 128.47, 128.53, 128.66, 128.98, 130.57, 132.81, 134.97, 138.28, 144.83. MS m/e (I_{rel}): 208 (85), 207 (100), 179 (17), 131 (33), 105 (30), 103 (32), 77 (68), 51(20).

(E)-1,3-Diphenylpropanone (dihydrochalcone), **5**. To a solution of 210 mg (1 mmol) of **4** in 10 ml of THF contained in a 50 ml round-bottomed flask provided with a magnetic stirrer, 100 mg of lithium aluminium hydride in 5 ml of THF were added in several portions. The mixture was heated in a water bath at 40 °C for 1 h. The excess of hydride was destroyed with 3 ml of ethyl acetate and 0.2 ml of water. The salt was separated and the solvents were distilled under vacuum. The resulting oil was dissolved in ether, dried with sodium sulphate and then the solvent was distilled again. The crude product was crystallized from 96% ethanol, m.p. 70 °C (lit. 71–72 °C[38]). ^{1}H NMR (CDCl$_3$) (ppm): 3.09 (t, 2H, $J = 7.8$ Hz), 3.33 (t, 2H, $J = 7.8$ Hz), 7.29 (m, 4H), 7.52 (m, 4H), 7.98 (dd, 2H, $J = 1.4$ and 8.3 Hz). ^{13}C NMR (CDCl$_3$) (ppm): 30.19, 40.45, 126.14, 128.05, 128.43, 128.54, 128.61, 133.06, 141.33, 199.21. MS m/e (I_{rel}): 210 (35), 106 (11), 105 (100), 91 (16), 78 (8), 77 (61), 65 (9), 51 (30), 50 (9).

General reaction procedure

In a typical experiment, 1 ml of a 1 M solution of PhLi in dry THF, contained in a septum-capped round-bottomed reaction flask under a nitrogen atmosphere, was cooled at the desired temperature. Then 14 ml of the desired solvent and 126 μl of *E*-cinnamaldehyde were added to the stirred solution all at once. By this procedure, both reagents have a final concentration of 0.07 M.

The reaction was worked up by treating the reaction mixture with 0.2 ml of NH$_4$Cl saturated solution. The organic layer was dried over MgSO$_4$ and the mixture was quantitatively analysed by gas chromatography using an HP-5 capillary column.

Reaction in presence of radical inhibitors

The reaction was carried out similarly to the general procedure already described, in a reaction flask containing a weighed amount of the radical inhibitor. Suitability of the radical inhibitor was controlled by determining the % benzene recovered after treating with it a solution of PhLi. The almost quantitative recovery using hydroquinone or quinhydrone as radical traps indicated that these inhibitors were appropriate under the reaction conditions used in this work.

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