910. *The Catalytic Action of Anionic Catalysts. Part I. The Interaction of Butyl-lithium with* 1,1-*Diphenylethylene.*

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Butyl-lithium with 1,1-diphenylethylene in benzene gives the ion pair $Bu \cdot CH_2 \cdot CPh_2^- Li^+$, which has an absorption peak at 428 mμ (ε 1·6 $\times$ 10^4). The order of this reaction is unity in 1,1-diphenylethylene, and 0·18 in butyl-lithium. Since it is known that butyl-lithium is highly associated (some six-fold) in benzene, we interpret the low order in this reagent by assuming (i) that equilibrium in this association lies well towards the associated side, and (ii) that only monomeric butyl-lithium reacts with 1,1-diphenylethylene.

Butyl-lithium does not react with 1,1,3,3-tetraphenylbut-1-ene or with tetraphenylethylene, although both these olefins give carbonium ions with dilute acids. We assume that steric hindrance here inhibits formation of an anion by addition of a butyl group.

THE action of cationic catalysts on 1,1-diphenylethylene was studied earlier;[1] we have extended this work to anionic catalysts. Following a preliminary communication[2] this paper gives a detailed account of the spectrophotometric part of this work.

EXPERIMENTAL

Apparatus.—The apparatus used was of all-glass construction, without taps. Contamination with tap grease or air was impossible. The glass was cleaned by soaking it for a few minutes in concentrated nitric acid, followed by a rinse with water and a soaking for some minutes in 5% aqueous sodium hydroxide; it was then washed in a stream of water for at least an hour, and after a final rinse with distilled water was dried in an oven at 120°. Each piece of apparatus was baked under a high vacuum for at least 3 hr. before contact with any of the reagents.

[1] Evans and E. D. Owen, *J.*, 1959, 4123.
[2] Evans and George, *Proc. Chem. Soc.*, 1960, 144.

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The optical cells used were of Pyrex glass and were cylindrical with optically flat ends separated by 1 cm.

Materials.—Benzene and 1,1,3,3-tetraphenylbut-1-ene were prepared and purified as described earlier.[3] 1,1-Diphenylethylene was purified by the rigorous treatment with stannic chloride described earlier.[4]

Tetraphenylethylene was prepared by the action of copper bronze on dichlorodiphenyl-methane and, recrystallised from dioxan, had m. p. 221°.

" AnalaR " diethyl ether was dried over sodium wire, distilled, then outgassed under a high-vacuum and stored over sodium–potassium alloy in vessels fitted with magnetically operated breakers.

Benzyl chloride, after being dried (P_2O_5) and distilled at atmospheric pressure, was outgassed and then distilled a number of times under a high vacuum. The first and last 5% were discarded in each distillation.

A solution of butyl-lithium in benzene was prepared by the method of Ziegler and Colonius[5] adapted to high-vacuum conditions in a manner similar to that described by Evans and Owen.[6]
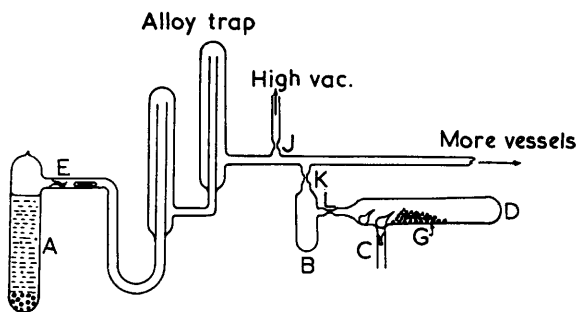

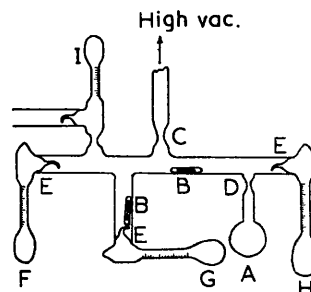FIG. 1. Apparatus for estimation of butyl-lithium.

FIG. 2. Apparatus for preparation of reaction solution.

A, Optical cell. F, Benzene. G, Benzene solution of butyl-lithium. H, Benzene solution of 1,1-diphenylethylene. I, Vessel to collect excess of solution.

Standardisation of the Butyl-lithium Solution.—The double-titration method of Gilman and Haubein[7] was adapted to high-vacuum conditions as follows. Fragile bulbs of known volume were filled with the butyl-lithium solution under a high vacuum. They were then broken under distilled water, and the lithium hydroxide formed was titrated with standard hydrochloric acid to phenolphthalein.

Further samples of the butyl-lithium solution were pretreated with benzyl chloride in dry ether in the apparatus shown in Fig. 1. After a thorough baking under a high vacuum, the apparatus was opened at the point D and two bulbs were introduced, one containing a known volume of the butyl-lithium solution and the other a known volume of benzyl chloride. Glass beads, G, were also introduced. The apparatus was resealed at D and after evacuation was sealed from the pumps at J. The fragile capillary E was next broken by operating the magnetic breaker, and ether was distilled from vessel A, where it was over sodium–potassium alloy, into vessel B by cooling the latter in ice-water. When sufficient had collected (about 20 ml.), the vessel was sealed off at the constriction K. The ether was then poured into the adjoining vessel containing the bulbs of butyl-lithium and benzyl chloride, which was then sealed at L. The bulbs containing the reactants were next completely shattered by vigorously shaking the vessel. As the substances mixed an exothermic reaction ensued and a fleeting yellow colour

[3] Evans and Price, *J.*, 1959, 2982.
[4] Evans and Lewis, *J.*, 1957, 2975.
[5] Ziegler and Colonius, *Annalen*, 1930, **479**, 135.
[6] Evans and G. D. T. Owen, *J.*, 1961, 1733.
[7] Gilman and Haubein, *J. Amer. Chem. Soc.*, 1944, **66**, 1515.

appeared, which was quickly followed by a white precipitate. The whole was set aside for several minutes and capillary C was then broken and the solution was hydrolysed with distilled water. The mixture, with copious washings, was transferred to a titrating flask and the lithium hydroxide present was estimated as before, vigorous shaking being maintained throughout the titration to ensure thorough mixing of the ether and water layers. In this way it was found that the butyl-lithium solution contained less than 3% of impurities (see Table 1), and that the solution gave the same analysis after several months' storage at 6—7°.

General Procedure.—Benzene solutions of butyl-lithium and of olefin were mixed in the manner described below, and the ultraviolet absorption, D, of the resulting solution was measured at various time intervals at 428 mμ. All citations of D hereafter also refer to 428 mμ.

Master solutions of the monomer, 1,1-diphenylethylene,[4] and the linear dimer (1,1,3,3-tetraphenylbut-1-ene)[3] in benzene were prepared under high-vacuum conditions as described in earlier papers. The solution of tetraphenylethylene in benzene was prepared in a manner similar to that of the butene solution. Known volumes of these master solutions and of the butyl-lithium solution were diluted with known volumes of benzene, under high-vacuum conditions, until the resulting solutions were sufficiently dilute for use in preparing the solutions for reaction.

The reactants were mixed and the optical cells filled with the solution by using the apparatus shown in Fig. 2. After being baked under a high vacuum the apparatus was sealed at C. The bulbs, each containing a known volume of solution, were next opened to the central part of the apparatus by breaking the fragile capillaries, E, by means of the iron-in-glass breakers, B, and the solutions of olefin and of butyl-lithium in benzene, and benzene itself were quickly but thoroughly mixed. The reaction solution was then poured into the optical cell which was sealed at the constriction D. Together with a similar cell containing pure benzene as control, it was placed in a thermostat bath fitting on the carriage of a Unicam S.P.500 spectrophotometer. This thermostat bath was fitted with silica windows, and water at a known temperature ($\pm 0.1°$) was circulated through it.

RESULTS

Interaction of Butyl-lithium with 1,1-Diphenylethylene.—Spectrum. When benzene solutions of 1,1-diphenylethylene and butyl-lithium were mixed, a yellow colour appeared which gradually

FIG. 3. A typical reaction rate plot.

Temp. 30·5°. [BuLi]$_i$ = 1·51 × 10^{-2} mole l.$^{-1}$. [CH$_2$:CPh$_2$]$_i$ = 1·01 × 10^{-4} mole l.$^{-1}$.
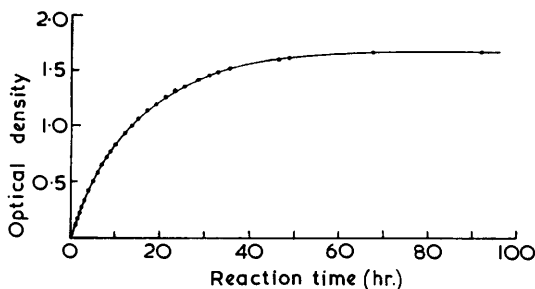
intensified until it became orange, or, if the solutions were very concentrated, a deep cherry-red. The optical density of such solutions increased with time to a value which remained constant for several days (see Fig. 3). The spectrum of a solution which has reached this steady state is given in Fig. 4, curve A. This curve is of the same shape as that given in our preliminary communication,[2] but the optical density is greater than that which we should expect from our earlier work. We believe this to be because in our earlier experiments the solution had been left for some time before dilution for spectroscopic measurement, and we now find a very slow decrease in optical density after the steady state has been reached. This decrease, however, is so slow that even after many months the reaction solutions are still coloured.

Order of reaction. Initial rates of formation of the coloured species were determined from tangents at the origin of the optical density–time plots. These tangents could be drawn with an accuracy of within 5%. The order of reaction in butyl-lithium was found from the dependence of the initial rate of reaction on the initial butyl-lithium concentration for a series of experiments in which the initial monomer concentration and the reaction temperature were

kept constant. These results (Table 2) show that an ~100-fold increase in the initial butyl-lithium concentration increases the initial rate only by about two-fold. The plot of $\log_{10}$ (initial rate $= R_i$) against $\log_{10}$ (initial butyl-lithium concentration $=$ [BuLi]$_i$) shows the order of the reaction in butyl-lithium to be 0.18 ± 0.02 (see also column 4, Table 2).

Since a large excess of butyl-lithium over 1,1-diphenylethylene was used in each experiment, the order of reaction in the latter reagent could be obtained from an analysis of the optical density–time curves. Each of these shows the order of reaction in 1,1-diphenylethylene to be 1.0. An example of such an analysis is given in Table 3.
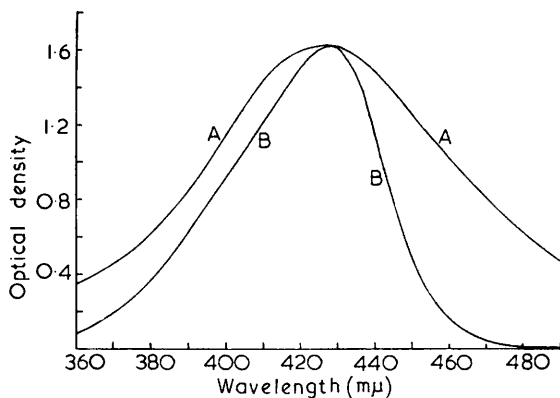

Fig. 4. (A) Benzene solution of LiBu (1.51×10^{-2} mole l.$^{-1}$) and CH_2:CPh_2 (1.01×10^{-4} mole l.$^{-1}$) at $20°$. (B) CH_2:CPh_2 in 98% H_2SO_4 (0.58×10^{-4} mole l.$^{-1}$) at $20°$.

The dependence of the initial rate of reaction on initial 1,1-diphenylethylene concentration is shown in Table 4. It is again seen that the order in diphenylethylene is 1.0 ± 0.05.

Thus we may write:

$$\text{Rate of production of coloured species} = k[CH_2\text{:}CPh_2]^1[BuLi]^{0.18}.$$

Irreversibility of reaction. The fact that first-order kinetics hold up to at least 96% reaction (see Table 3) shows that, as far as we can determine, the reaction is irreversible under these conditions.

Test of Beer's law. We allowed a reaction system to come to the steady state, and then diluted it with various quantities of benzene, measuring the optical density of the solution at each stage. The results (Table 5) show that Beer's law is accurately obeyed.

TABLE 1.

Typical analyses.

BuLi (ml.)	0·1N-HCl used in titrn. (ml.)	[Li]$_{total}$ (mole l.$^{-1}$)	BuLi (ml.)	0·1N-HCl used in titrn. (ml.)	[Li]$_{total}$ − [BuLi] (mole l.$^{-1}$)
	Hydrolysis with water			*Treatment with* CH_2PhCl *in* Et_2O, *then hydrolysis*	
1·82	28·2	1·55	4·90	2·42	0·049
1·44	22·5	1·567	5·91	1·98	0·034
2·25	35·15	1·563	3·85	1·50	0·039
		Av.: 1·56			Av.: 0·04

$\therefore$ [BuLi] $= 1.56 - 0.04 = 1.52$ mole l.$^{-1}$.

TABLE 2.

Dependence of the initial rate of reaction on butyl-lithium concentration, at 30·5°.

10^4[CH$_2$:CPh$_2$]$_i$ (mole l.$^{-1}$)	10^4[BuLi]$_i$ (mole l.$^{-1}$)	R_i (D hr.$^{-1}$)	R_i/[BuLi]$_i^{0.18}$
1·01	10·2	0·084	0·290
1·01	151	0·114	0·248
1·01	981	0·192	0·292

Extinction coefficient. Since the reaction is irreversible under the conditions used and Beer's law is obeyed, the extinction coefficient of the coloured species was found from the optical density at complete reaction. Its value is $1.6 \pm 0.2 \times 10^4$ at the wavelength of maximum absorption (428 mμ).

Temperature-dependence. The temperature-dependence of the initial rate of reaction at constant initial olefin and butyl-lithium concentrations is given in Table 6. The apparent activation energy, found by plotting $\log_{10} k$ against $1/T$ was 16.4 ± 0.7 kcal. mole^{-1}.

TABLE 3.

First-order dependence of reaction rate on 1,1-diphenylethylene, when butyl-lithium is in excess.

$[CH_2\!:\!CPh_2]_i = 1.01 \times 10^{-4}$ mole l.$^{-1}$. $[LiBu]_i = 151 \times 10^{-4}$ mole l.$^{-1}$. $a = 1.673$ (*i.e.*, the value of D at $t = \infty$).

Time (hr.)	Reaction (%)	D at time t ("x")	$\log_{10}\left(\dfrac{a}{a-x}\right)$	First-order rate constant (hr.$^{-1}$)	Time (hr.)	Reaction (%)	D at time t ("x")	$\log_{10}\left(\dfrac{a}{a-x}\right)$	First-order rate constant (hr.$^{-1}$)
1	6.87	0.115	0.0310	0.071	16	66.04	1.105	0.4692	0.068
2	13.45	0.225	0.0627	0.072	18	70.00	1.171	0.5228	0.066
3	19.43	0.325	0.0938	0.072	20	72.28	1.226	0.5732	0.066
4	24.99	0.418	0.1249	0.072	22	76.50	1.280	0.6291	0.066
5	30.00	0.502	0.1549	0.071	24	79.50	1.330	0.6882	0.066
6	34.66	0.580	0.1849	0.071	26	81.34	1.361	0.7392	0.066
7	38.92	0.650	0.2137	0.070	28	84.20	1.409	0.8019	0.066
8	42.62	0.713	0.2412	0.069	30	86.44	1.446	0.8675	0.067
9	46.62	0.780	0.2726	0.070	32	88.47	1.480	0.9379	0.068
10	50.02	0.837	0.3013	0.069	34	90.00	1.506	1.0008	0.068
12	56.48	0.945	0.3614	0.069	46	95.74	1.602	1.3722	0.069
14	61.67	1.032	0.4166	0.069					

TABLE 4.

$10^4[CH_2\!:\!CPh_2]_i$ (mole l.$^{-1}$)	$10^4[BuLi]_i$ (mole l.$^{-1}$)	R_i (D hr.$^{-1}$)	$R_i/[CH_2\!:\!CPh_2]_i{}^1[BuLi]_i{}^{0.18}$
2.39	30.46	0.22	2.6×10^3
1.01	10.2	0.084	2.87×10^3

TABLE 5.

Test of Beer's law: dilution of a solution containing 7.36×10^{-5} mole l.$^{-1}$ of $Bu\cdot CH_2\cdot CPh_2{}^- Li^+$ at 20°.

$10^5[Bu\cdot CH_2\cdot CPh_2{}^- Li^+]$ (mole l.$^{-1}$)	7.36	5.61	3.77	1.95
Optical density (D)	1.18	0.90	0.60	0.271
$10^{-4} D/[Bu\cdot CH_2\cdot CPh_2{}^- Li^+]$	1.6	1.6	1.6	1.4

TABLE 6.

Temperature-dependence.

$10^5 k$ (mole$^{-0.18}$ l.$^{0.18}$ sec.$^{-1}$)	8.91	4.17	2.51	1.75	0.6
Temp. (K)	313.4°	303.5°	298.2°	293.1°	284.4°

Interaction of Butyl-lithium with 1,1,3,3-Tetraphenylbut-1-ene and Tetraphenylethylene.— When butyl-lithium was mixed with either of these substances in benzene under rigorous high-vacuum conditions, no colour developed even after several weeks at 30°. This was true both at low concentrations, comparable with those used for 1,1-diphenylethylene, and at much higher concentrations, *e.g.*, 0.26 mole l.$^{-1}$ of butyl-lithium and 0.42 mole l.$^{-1}$ of 1,1,3,3-tetra-phenylbut-1-ene, and 0.035 mole l.$^{-1}$ of butyl-lithium and 0.082 mole l.$^{-1}$ of tetraphenylethylene. At these high concentrations the butene and tetraphenylethylene could be recovered unchanged from the solutions.
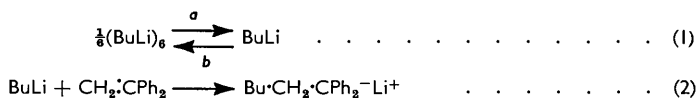
DISCUSSION

Spectrum of the Solution.—Our results show that butyl-lithium reacts with 1,1-diphenylethylene to give a coloured product having the spectrum given in Fig. 4, curve A. Since Ziegler *et al.*[8] showed by analysis of the product that when butyl-lithium adds to 1,1-diphenylethylene the butyl group is attached to the primary carbon atom we attribute this spectrum to the ion pair $Bu\cdot CH_2\cdot CPh_2^-Li^+$. The wavelength of maximum absorption of this ion is the same as that for the corresponding carbonium ion [9] (Fig. 4, curve B) but the shape of the spectrum is somewhat different; it is broader and extends further into the visible region.

The extinction coefficient of the ion pair at the wavelength of maximum absorption (428 mμ) was $1\cdot6 \times 10^4$, slightly less than that $(2\cdot8 \times 10^4)$ for the corresponding carbonium ion.

Mechanism of the Reaction.—We have found the order of reaction to be unity in 1,1-diphenylethylene and 0·18 in butyl-lithium.

There is much evidence that butyl-lithium is highly associated in benzene,[10] and the majority of results indicate that it is mainly present as the hexamer $(BuLi)_6$. If we assume (as was done [11] for the butyl-lithium-catalysed polymerisation of styrene in benzene) (i) that an equilibrium exists between associated and unassociated molecules of butyl-lithium which, under the conditions of our experiments lies well towards the associated side, and (ii) that only monomeric butyl-lithium reacts with 1,1-diphenylethylene, then the following reaction scheme is consistent with our results:

$$\tfrac{1}{6}(BuLi)_6 \underset{b}{\overset{a}{\rightleftharpoons}} BuLi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$BuLi + CH_2{:}CPh_2 \longrightarrow Bu\cdot CH_2\cdot CPh_2^-Li^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The rate of production of ion pairs would be given by the expression:

Rate of production of ion pairs $= k_2[BuLi][CH_2{:}CPh_2]$, and since $[BuLi]/[(BuLi)_6]^{\frac{1}{6}} = k_{1a}/k_{1b} = K_1$, we have:

Rate of production of ion pairs $= k_2K_1[(LiBu)_6]^{\frac{1}{6}}[CH_2{:}CPh_2]$.

The order of reaction would, from this equation, be unity in 1,1-diphenylethylene and $\tfrac{1}{6}$ (0·167) in butyl-lithium. These values are in good agreement with those we find experimentally. Thus our velocity constant k is equal to k_2K_1.

It is interesting to compare our results for the addition of butyl-lithium to 1,1-diphenylethylene in benzene with those obtained for the addition of butyl-lithium to styrene in benzene, *i.e.*, for initiation of the polymerisation of styrene by butyl-lithium. Bywater and Worsfold [11] found that the rate of initiation varies as [Styrene][1] and $[BuLi]^{0\cdot155}$, even down to butyl-lithium concentrations as low as 5×10^{-5} mole l.$^{-1}$. They account for this by suggesting that only monomeric butyl-lithium can initiate the polymerisation of styrene, and that within the concentration range they use the butyl-lithium is associated six-fold, the equilibrium lying heavily towards the associated form.

Welch [11] also studied the butyl-lithium-catalysed polymerisation of styrene in benzene, and concluded that above a concentration of 2×10^{-2} mole l.$^{-1}$ the butyl-lithium is six- or seven-fold associated, but that below this concentration it is monomeric. Our results agree with those of Bywater and Worsfold, and not with those of Welch, for we have observed first-order dependence on the olefin and a low order of 0·18 in butyl-lithium over a concentration range of butyl-lithium from 10^{-3} to 10^{-1} mole l.$^{-1}$ We disagree, however,

[8] Ziegler, Crossman, Kleiner, and Schafer, *Annalen*, 1929, **473**, 1.
[9] Evans, *J. Appl. Chem.*, 1951, **1**, 240.
[10] Rogers, *J. Phys. Chem.*, 1957, **61**, 366; Warhurst, *Discuss. Faraday Soc.*, 1947, **2**, 239; Coates, " Organo-Metallic Compounds," Methuen & Co., London, 1956, p. 7.
[11] Welch, *J. Amer. Chem. Soc.*, 1959, **81**, 1345; Bywater and Worsfold, *Canad. J. Chem.*, 1960, **38**, 1891.

with Ziegler *et al.*[8] who concluded that the reaction between butyl-lithium and 1,1-diphenyl-ethylene was of the first order in olefin and in butyl-lithium for reagent concentrations of 0·15 mole l.$^{-1}$.

Temperature-dependence.—Our results show an apparent activation energy for the reaction of 16·4 kcal. mole^{-1}. Since the concentration of monomeric butyl-lithium in reaction (2) depends on equilibrium (1), this value will equal the activation energy of reaction (2) plus the endothermicity of reaction 1(*a*), *i.e.*, $\Delta H^0_{1a} + \Delta H_2^{\ddagger} = 16\cdot4$ kcal. mole^{-1}. Bywater and Worsfold obtained a value of 18 kcal. mole^{-1} (velocity constant = $2\cdot3 \times 10^{-5}$ l.$^{0\cdot167}$ mole$^{-0\cdot167}$ sec.$^{-1}$ at 30°) for the addition of butyl-lithium to styrene. Our value of 16·4 kcal. mole^{-1} (velocity constant = $4\cdot17 \times 10^{-5}$ l.$^{0\cdot18}$ mole$^{-0\cdot18}$ sec.$^{-1}$ at 30°) for its addition to 1,1-diphenylethylene is less than this, indicating that introduction of a second phenyl group into styrene stabilises the negative ion to a greater extent than it does the olefin.

Steric Hindrance.—No colour is obtained when butyl-lithium is mixed with the linear dimer of 1,1-diphenylethylene, $CH_3\cdot CPh_2\cdot CH\colon CPh_2$, or with tetraphenylethylene, although both these olefins give coloured carbonium ions when treated with dilute acids.[12] Courtauld's atomic models indicate that the butyl group can be added to the monomer to form $Bu\cdot CH_2\cdot CPh_2^-$, but not to the linear dimer to form $CH_3\cdot CPh_2\cdot CHBu\cdot CPh_2^-$, or to tetraphenylethylene to form $Bu\cdot CPh_2\cdot CPh_2^-$. We attribute the absence of colour in the last two cases to steric hindrance which prohibits the formation of the anion by addition of a butyl group.

Dimerisation.—In our preliminary communication[2] we stated that for a benzene solution containing 0·4 mole l.$^{-1}$ of butyl-lithium and 0·7 mole l.$^{-1}$ of 1,1-diphenylethylene there was no reaction of the ion pair (formed by the addition of the butyl-lithium to the olefin) with the excess of olefin. Further work, with a large excess of 1,1-diphenylethylene, seems to indicate a slow reaction of the ion pair with the excess of olefin. This is being investigated.

The fact that our optical density–time plots are of first order up to at least 96% reaction shows that for the work reported in this paper there is no appreciable dimerisation of the type: $Bu\cdot CH_2\cdot CPh_2^- Li^+ + CH_2\colon CPh_2 \longrightarrow BuCH_2\cdot CPh_2\cdot CH_2CPh_2^- Li^+$, and that this reaction, if it does occur, must be very much slower than the rate of addition of butyl-lithium.

In the case of styrene, on the other hand, the propagation reaction, $\sim CH_2\cdot CHPh^- Li^+ + CH_2\colon CHPh \longrightarrow \sim CH_2\cdot CHPh\cdot CH_2\cdot CHPh^- Li^+$, is much faster than addition of butyl-lithium; Welch[11] suggests a value of 5 and Bywater and Worsfold[11] a value of about 550 for the ratio, k(propagation) : k(initiation).

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[12] Evans, N. Jones, and Thomas, *J.*, 1955, 1824; Evans, P. M. S. Jones, and Thomas, *J.*, 1957, 104.