

27. *The Catalytic Action of Anionic Catalysts. Part II.¹ The Products of Reaction of Butyl-lithium with 1,1-Diphenylethylene in Benzene.*

By ALWYN G. EVANS and DAVID B. GEORGE.

The products of reaction of 1,1-diphenylethylene with butyllithium have been investigated by using much higher concentrations than were used in previous work. Dilatometric measurements show the same mechanism of addition as was disclosed in the earlier, spectroscopic experiments but also addition of 1,1-diphenylhexyl-lithium, which is first formed, to another molecule of 1,1-diphenylethylene. The latter addition is reversible and occurs to an appreciable extent only in the presence of a large excess of the olefin.

WE have studied the interaction of butyl-lithium and 1,1-diphenylethylene in benzene.² In Part I¹ we reported experiments in which low concentrations of reagents and an excess of butyl-lithium were used, the reaction being followed spectroscopically. In this paper we describe experiments in which higher concentrations were used to enable us to examine the products of the reaction.

EXPERIMENTAL

Materials.—Benzene, 1,1-diphenylethylene, and butyl-lithium in benzene were prepared and purified as described earlier.¹ "AnalaR" sulphuric acid was used without further purification.

Procedure.—Calibrated vessels, fitted with magnetically operated breakers, were filled with benzene, 1,1-diphenylethylene, and a benzene solution of butyl-lithium of known concentration under rigorous high-vacuum conditions. The dilatometers were then filled with these liquids on a high-vacuum system, sealed, and placed in thermostat baths ($\pm 0.01^\circ$). The volume contraction with time was followed.

Analysis of Product.—After reaction the dilatometer contents were hydrolysed with distilled water, the aqueous and non-aqueous layers were separated, and the lithium hydroxide content of the former was estimated by titration with standard hydrochloric acid. The benzene was removed from the non-aqueous layer in a high vacuum, and the weight of product was found.

The amount of unchanged 1,1-diphenylethylene in the yellowish liquid isolated in this manner was estimated by measuring the optical density at $430 \text{ m}\mu$ of a solution of a known weight of the product in a known volume of "AnalaR" sulphuric acid. The spectrum of this solution was identical with that of pure 1,1-diphenylethylene in sulphuric acid, indicating that the other materials present in the product did not affect the spectrum.

The molecular weight of the total product was estimated cryoscopically in benzene.

This total product was separated into its components by distillation under reduced pressure. The material which could not be distilled under the vacuum from a water pump was distilled under a high vacuum from 200° to a liquid-air cooled "cold finger." Molecular weight determinations were performed on the various fractions.

RESULTS

Volume Change.—When butyl-lithium is mixed with 1,1-diphenylethylene in benzene a red colour develops and the volume of the mixture gradually decreases to constancy. An example of the plots obtained is shown in Fig. 1, and in the Table, column 5, are given the values of the overall contraction, ΔV .

Orders in 1,1-Diphenylethylene and Butyl-lithium.—A plot of \log_{10} (initial rate of reaction) against \log_{10} (initial olefin concentration) for constant butyl-lithium concentration indicates that the order of reaction in olefin is 0.9 ± 0.1 (see Fig. 2). The order of reaction in butyl-lithium, found from a log plot as for the olefin, at constant initial olefin concentration was 0.25 ± 0.05 (see Fig. 2).

¹ Part I, Evans and George, *J.*, 1961, 4653.

² Evans and George, *Proc. Chem. Soc.*, 1960, 144.

$[\text{CH}_2:\text{CPh}_2]_i$ (mole l. ⁻¹)	$[\text{BuLi}]_i$ (mole l. ⁻¹)	$[\text{CH}_2:\text{CPh}_2]_i/[\text{BuLi}]_i$	Temp.	Total vol. contraction, ΔV (ml. l. ⁻¹)	$\Delta V/[\text{BuLi}]_i$ (ml. mole ⁻¹)	$\Delta V/[\text{CH}_2:\text{CPh}_2]_i$ (ml. mole ⁻¹)
0.178	0.178	1.0	30°	3.59	20.17	20.17
0.176	0.176	1.0	40	3.59	20.43	20.43
0.172	0.172	1.0	55	3.52	20.46	20.46
0.300	0.300	1.0	20	5.95	19.83	19.83
0.293	0.293	1.0	40	6.12	20.89	20.89
0.287	0.287	1.0	55	6.12	21.32	21.32
0.593	0.593	1.0	30	12.09	20.39	20.39
0.203	0.997	0.2	30	4.19		20.59
0.593	0.910	0.65	30	12.27		20.7
0.692	0.395	1.75	30	9.10	23.03	
0.593	0.296	2.0	30	7.27	24.56	
0.586	0.293	2.0	40	7.55	25.76	
0.575	0.287	2.0	55	7.24	25.20	
0.890	0.296	3.0	30	7.81	26.38	
0.593	0.148	4.0	30	4.20	28.37	
1.16	0.183	6.3	30	5.51	30.1	

Subscript i denotes initial concentration.

Analysis of Products.—(a) *General.* When there was no further change in volume with time the lithium content of the reaction mixtures, as indicated by titration of the aqueous extract with standard hydrochloric acid, was always that expected from the amount of butyl-lithium used initially. The weight of material left after removal of the benzene from the non-aqueous layer was in good agreement with that expected from the quantities of 1,1-diphenylethylene and butyl-lithium used initially.

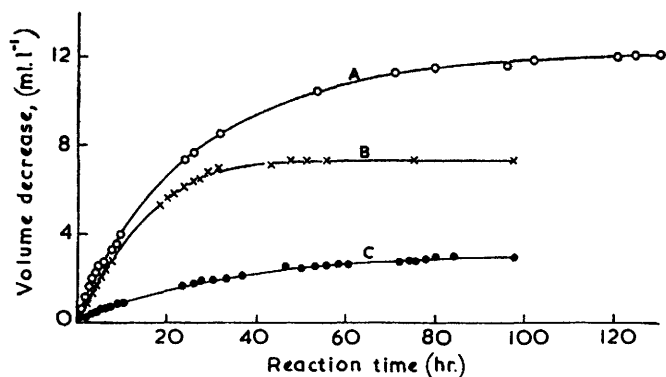


FIG. 1. Typical reaction curves at 30°

Curve	A	B	C
$[\text{CH}_2:\text{CPh}_2]_i$ (mole l. ⁻¹)	0.593	0.593	0.16
$[\text{BuLi}]_i$ (mole l. ⁻¹)	0.593	0.296	0.296

(b) *When* $[\text{CH}_2:\text{CPh}_2]_i \leq [\text{BuLi}]_i$. In the experiments where either an initial excess of butyl-lithium over 1,1-diphenylethylene or equimolar quantities of the reagents were used the material isolated from the non-aqueous layer gave a very faint colour with 98% sulphuric acid. Measurement of the optical density of these solutions at 430 μ indicated that only a trace of 1,1-diphenylethylene remained. When the product was distilled under reduced pressure only one fraction was obtained, the molecular weight of which was always within 5% that of 1,1-diphenylhexane (239), the hydrocarbon which would be formed on hydrolysis of the adduct between butyl-lithium and 1,1-diphenylethylene.

(c) *When* $[\text{CH}_2:\text{CPh}_2]_i > [\text{BuLi}]_i$. When an initial excess of 1,1-diphenylethylene was used, the material isolated from the non-aqueous layer contained slightly less unchanged olefin

than would be present if the only reaction occurring was the irreversible addition of butyllithium to 1,1-diphenylethylene. For example, when the initial concentrations of 1,1-diphenylethylene and butyllithium were 1.18 and 0.185 mole l.⁻¹, respectively, at 20°, 70–74% by weight of the material isolated at the end of the reaction was 1,1-diphenylethylene. This value would have been 80% if the only reaction had been the addition of a butyllithium molecule to a 1,1-diphenylethylene molecule. This shows that when $[\text{CH}_2:\text{CPh}_2]_i > [\text{BuLi}]_i$ there is a further reaction of the excess of olefin with the $\text{Li}^+\text{CPh}_2\cdot\text{CH}_2\text{Bu}$ first formed.

The product was subjected to fractional distillation as follows. It was first distilled under the vacuum from a water pump. Two fractions were obtained and a small amount of a very viscous yellowish material remained. This was further distilled under a high-vacuum. A typical distillation is described below for the product of the reaction between 1.16 moles l.⁻¹ of 1,1-diphenylethylene and 0.183 mole l.⁻¹ of butyllithium in benzene at 30°. The product was

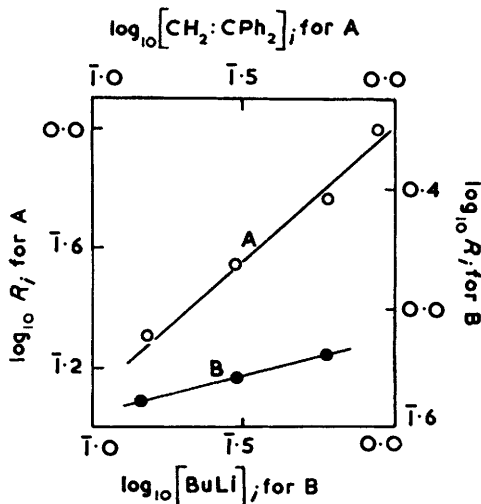


FIG. 2. Logarithmic plots used in determining the orders of reaction (at 30°).

A, $[\text{BuLi}]_i = 0.296$ mole l.⁻¹,
 B, $[\text{CH}_2:\text{CPh}_2]_i = 0.593$ mole l.⁻¹.
 R_i = initial rate of reaction

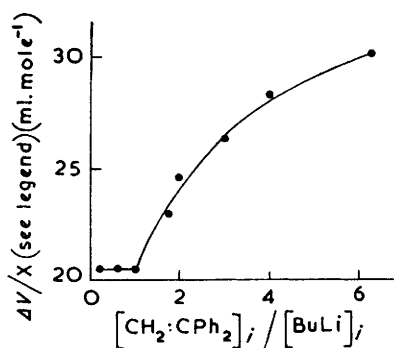


FIG. 3. Plot of $\Delta V/X$, where X is the smaller of $[\text{CH}_2:\text{CPh}_2]_i$ and $[\text{BuLi}]_i$, against $[\text{CH}_2:\text{CPh}_2]_i / [\text{BuLi}]_i$.

yellowish and had a molecular weight of 200. The greater part of it distilled at 141–143°/12 mm. as a clear, colourless liquid which had a molecular weight of 177. The next definite fraction was obtained at 162–166°/12 mm., also a colourless liquid, and had a molecular weight of 227. The remaining material did not distil below 200° and was a very viscous, orange substance. It had a molecular weight of 253. This substance was further distilled under a high vacuum giving a small amount of a colourless liquid which had a molecular weight of 226. The remaining involatile material was very viscous and resinous and had a molecular weight of 435.

DISCUSSION

Dependence of Initial Rate on $[\text{CH}_2:\text{CPh}_2]_i$ and $[\text{BuLi}]_i$.—In Part I¹ we described a spectroscopic technique for measuring the mechanism of this reaction. Our present experiments are concerned with the identification of the products and thus appreciable concentrations of reagents were used. The initial rates of reaction, therefore, are much faster than those of Part I, and their dilatometric determination (the colour is too intense to be measured) is not as accurate as the spectroscopic work. (In our dilatometric studies of cation-catalysed reactions the initial rates can be kept small by the use of low concentrations of catalyst.) In spite of this, the orders in olefin (0.9) and butyllithium

of 435, and is probably 1,1,3,3-tetraphenyloctane (*M* 419). Further, since both 1,1,3,3-tetraphenyloctane and 1,1-diphenylhexane were isolated from the hydrolysed product (even though a six-fold excess of 1,1-diphenylethylene was present) this addition is reversible as shown in equation (3).

Since the amount of 1,1,3,3-tetraphenyloctane isolated in the experiment described above was much less than that of 1,1-diphenylhexane, even though the $[\text{CH}_2\cdot\text{CPh}_2]_i/[\text{BuLi}]_i$ ratio was 6, it follows that the equilibrium position of reaction (3) would lie well to the left for a $[\text{CH}_2\cdot\text{CPh}_2]_i/[\text{BuLi}]_i$ ratio of 2. In an experiment at 20°, where the initial concentrations were 0.7 mole l.⁻¹ of 1,1-diphenylethylene and 0.4 mole l.⁻¹ of butyl-lithium ($[\text{CH}_2\cdot\text{CPh}_2]_i/[\text{BuLi}]_i = 1.8$), no 1,1,3,3-tetraphenyloctane could be found² and the total volume contraction was only slightly greater than 20.5. This fact made us conclude from our early experiments that reaction (3a) was not possible.² We now find that it is possible, although it requires a large excess of 1,1-diphenylethylene to give an appreciable amount of product.

We rule out the possibility that $\text{Bu}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{CPh}_2\text{-Li}^+$ can add on to another molecule of olefin, because we find that polymerisation of the olefin never proceeds beyond the dimer.

Rate Constants.—If we take 20.5 ml. for the volume change due to the addition of 1 mole of one to 1 mole of the other reactant, we can convert our initial rate into rate constants by the equation used in Part I:

$$\text{Initial rate of reaction} = k[\text{BuLi}]_i^{0.18}[\text{CH}_2\cdot\text{CPh}_2]_i$$

We find in this way a value of 2.1×10^{-5} mole^{-0.18} l.^{0.18} sec.⁻¹ for *k* at 30°. This is in quite good agreement with the value of 4.17×10^{-5} mole^{-0.18} l.^{0.18} sec.⁻¹ at 30.5° obtained by the more accurate method described in Part I.¹

Temperature-dependence.—The effect of temperature on the total volume change is given in the Table. When $[\text{CH}_2\cdot\text{CPh}_2]_i/[\text{BuLi}]_i = 1$, the variation of temperature from 30° to 55° has little effect on $\Delta V/[\text{CH}_2\cdot\text{CPh}_2]_i$; this would be the case if equilibrium (1) lay much to the associated side and reaction (2) were irreversible. When $[\text{CH}_2\cdot\text{CPh}_2]_i/[\text{BuLi}]_i = 2.0$ a change of temperature from 30° to 55° has little effect on $\Delta V/[\text{BuLi}]_i$; this would be the case if the enthalpy change for reaction (3a) were small.

Effect of Alkyl-metal Structure on the Ease of its Addition to an Olefin.—The results discussed above show that for diphenylethylene the ease of addition of the alkyl-metal decreases rapidly along the series, Bu, Bu·CH₂·CPh₂, Bu·CH₂·CPh₂·CH₂·CPh₂. For butyl-lithium the addition is irreversible according to equation (2). For Bu·CH₂·CPh₂·Li⁺ the addition is slower and reversible according to equation (3). At low concentrations and with an excess of butyl-lithium (as in our spectrophotometric work¹) this equilibrium lies completely to the left and no addition takes place. To obtain appreciable addition according to equation (3) a large ratio $[\text{CH}_2\cdot\text{CPh}_2]_i/[\text{BuLi}]_i$ is required. With Bu·CH₂·CPh₂·CH₂·CPh₂·Li⁺ no addition takes place.

We attribute this decrease in reactivity to increasing steric hindrance due to the increasing bulkiness of the alkyl group.

With styrene the ease of addition of the alkyl-metal increases from butyl-lithium to Bu·CH₂·CHPh·Li⁺, and so the propagation step in the polymerisation of styrene by butyl-lithium is about 550 times faster than the initiation step.⁶ The fact that the change from butyl to Bu·CH₂·CPh₂ leads to a decreased reactivity in the case of 1,1-diphenylethylene must, therefore, be due to steric hindrance, as we suggest above.

The Effect of Olefin Structure on the Ease of Addition of an Alkyl-metal.—Addition of butyl-lithium is rapid to 1,1-diphenylethylene, much less rapid to triphenylethylene,⁷ and impossible in the case of 1,1,3,3-tetraphenylbut-1-ene¹ and tetraphenylethylene.¹ Thus

⁶ Bywater and Worsfold, *Canad. J. Chem.*, 1960, **38**, 1891.

⁷ Unpublished work.

as we successively replace hydrogen atoms by bulky groups we reduce the ease of addition of butyl-lithium to the double bond. We attribute this decreased reactivity to the increase in steric hindrance.

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CHEMISTRY DEPARTMENT, UNIVERSITY COLLEGE, CARDIFF.

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