The Catalytic Action of Anionic Catalysts. Part XIII.[1] The Reaction of n-Butyl-lithium with Triphenylmethane and with Triphenylethylene, and of Triphenylmethyl-lithium with Tetrahydrofuran

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We give results for the reaction of n-butyl-lithium with triphenylmethane in benzene and in tetrahydrofuran, with triphenylethylene in tetrahydrofuran, and for the reaction of triphenylmethyl-lithium with tetrahydrofuran. The order of reaction in n-butyl-lithium is 0·5 in tetrahydrofuran as we have found previously. The results are discussed together with our earlier results, in terms of the effect of (*a*) solvent change, (*b*) change in p*K* of substrate, (*c*) change from carbon to silicon, and (*d*) change in steric hindrance.

We have previously studied the interaction of n-butyl-lithium with various reactants.[1,2] We now give results for the reaction of n-butyl-lithium with triphenylmethane in benzene and in tetrahydrofuran, with triphenylethylene in tetrahydrofuran, and for the reaction of triphenylmethyl-lithium with tetrahydrofuran.

EXPERIMENTAL

Materials.—n-Butyl-lithium and solvents were purified as described earlier.[2] Triphenylmethane (B.D.H.) was recrystallised several times before use from absolute alcohol and had m.p. 93—94 °C (lit.,[3] 94 °C). Triphenylmethyl-lithium was prepared from triphenylmethane and n-butyl-lithium in tetrahydrofuran.[4] Triphenylethylene (B.D.H.) was recrystallised from ethanol and had m.p. 68—70 °C (lit.,[5] 68·5—70 °C).

Procedure.—*Interaction of* Ph_3CH *with n-butyl-lithium in tetrahydrofuran.* This reaction was studied by the stop-flow technique at temperatures below −20 °C so that the reaction of butyl-lithium with tetrahydrofuran could be prevented, and the reaction of butyl-lithium with Ph_3CH slowed to measurable rates. The product of this reaction has previously been established as $Ph_3C^-Li^+$.[4] The development of $Ph_3C^-Li^+$ was followed by measuring the increase with time of the absorption at 500 nm ($\lambda_{max.}$ for $Ph_3C^-Li^+$ in tetrahydrofuran).

Interaction of Ph_3CH *with n-butyl-lithium in benzene.* This reaction was extremely slow, so did not require the stop-flow technique. The development of $Ph_3C^-Li^+$ was followed by measuring the increase with time of the absorption at 430 nm ($\lambda_{max.}$ for $Ph_3C^-Li^+$ in benzene). A value of ε_{430} could not be obtained because of the extreme slowness of the reaction.

Interaction of triphenylmethyl-lithium with tetrahydrofuran. This was followed by measuring the decrease with time of the $Ph_3C^-Li^+$ absorption at 500 nm. This slow reaction does not require the stop-flow technique.

Interaction of n-butyl-lithium with triphenylethylene in tetrahydrofuran. This was followed in the stop-flow apparatus with the experimental procedure for preventing decomposition of butyl-lithium,[1] the increase of absorption with time being measured at 508 nm. The ε_{508} value of the product $BuCHPhCPh_2^-Li^+$ was assumed to be $2\cdot9 \times 10^4$ l mol^{-1} cm^{-1}, the value of ε_{500} for $BuCH_2CPh_2^-Li^+$ in tetrahydrofuran.[1] We had to assume this ε value because (*a*) at room temperature the butyl-lithium decomposition makes it impossible to reach complete reaction, and (*b*) at low temperature, at which the butyl-lithium decomposition does not occur, the reaction with PhCH=CPh$_2$ is too slow to attain completion in a measurable time. The highest value we have obtained for ε_{508} in the room-temperature experiments is $1\cdot7 \times 10^4$ l mol^{-1} cm^{-1}.

RESULTS

Reaction of Ph_3CH *with n-Butyl-lithium in Tetrahydrofuran.*—This reaction proceeds to completion, and an extinction coefficient of $\varepsilon_{500} = 3\cdot35 \times 10^4$ l mol^{-1} cm^{-1} was obtained. The dependence of the initial rate of reaction on the initial concentrations of n-butyl-lithium and Ph_3CH are shown in Table 1.

TABLE 1

Reaction of n-butyl-lithium with Ph_3CH in tetrahydrofuran at −30 °C

(*a*) Dependence of initial rate on [Bu^{n}Li]

$10^2[Ph_3CH]_i$/M	$10^3[Li^+]_i$/M	10^7R_i / l^{-1} mol s^{-1}	10^5k / l$^{0\cdot5}$ mol$^{-0\cdot5}$ s^{-1}
6·33	37·29	5·33	6·35
6·33	20·36	3·92	6·14
6·33	13·55	3·23	6·21
10·06	12·15	4·89	6·24
6·33	5·57	1·99	5·97
(*b*) Dependence of initial rate on $[Ph_3CH]_i$			
10·06	12·2	4·894	6·24
6·33	37·9	5·530	6·35
5·05	40·4	4·560	6·36
2·63	46·4	2·405	6·03
1·10	40·4	0·995	6·38
0·52	40·4	0·465	6·32

$$k = \frac{R_i}{[Ph_3CH]_i\left[\frac{Li^+}{2}\right]_i^{0\cdot5}}$$

R_i = initial rate. $[Li^+]_i$ = total initial concentration of n-butyl-lithium expressed as monomeric butyl-lithium. $[Ph_3CH]_i$ = initial concentration of Ph_3CH.

The orders of reaction found by the least-squares method for butyl-lithium and Ph_3CH are 0·528 and 0·998 respectively, and we have taken these as 0·5 and 1·0 within experimental error, so that the observed rate constant is expressed as (1) where $[Li^+]$ is defined as in Table 1. The dependence

$$\text{Rate of reaction} = k\left[\frac{Li^+}{2}\right]^{0\cdot5}[Ph_3CH] \qquad (1)$$

of velocity constant on temperature is shown in Table 2.

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[1] Part XII, J. G. Carpenter, A. G. Evans, C. R. Gore, and N. H. Rees, *J. Chem. Soc.* (*B*), 1969, 908.

[2] (*a*) A. G. Evans and D. B. George, *J. Chem. Soc.*, 1961, 4653; 1962, 141; (*b*) A. G. Evans and N. H. Rees, *ibid.*, 1963, 6039; (*c*) A. G. Evans, C. R. Gore, and N. H. Rees, *ibid.*, 1965, 5110; (*d*) R. A. H. Casling, A. G. Evans, and N. H. Rees, *J. Chem. Soc.* (*B*), 1966, 519.

[3] J. Schmidlin and A. Garcia-Banus, *Ber.*, 1932, **65**, 1395.

[4] H. Gilman and R. V. Young, *J. Org. Chem.*, 1936, **1**, 315.

[5] W. Tadros, *Nature*, 1941, **148**, 53.

This gives an activation energy of 10·5 kcal mol^{-1}. The thermodynamic constants of activation are in Table 3.

Reaction of n-Butyl-lithium with Ph_3CH *in Benzene.*—This was very slow at room temperature. The colour developed slowly and had a broad peak with $\lambda_{max.} = ca.$ 430 nm. The product separated in the later stages of the reaction; its solubility was estimated as $<4 \times 10^{-5}$ mol l^{-1}. Because of the slowness of the reaction and the low solubility of the product, it was impossible to determine a value of ε_{430}, so the value was assumed to be the same as that for ε_{500} in tetrahydrofuran, *i.e.*, $3{\cdot}35 \times 10^4$ l mol^{-1} cm^{-1}.

TABLE 2

Reaction of n-butyl-lithium with Ph_3CH in tetrahydrofuran

T/K	$10^6 k$ / l$^{0·5}$ mol$^{-0·5}$ s^{-1}
222·8	8·67
227·8	14·6
233·0	24·7
238·0	37·4
243·0	63·5
247·2	88·4

The reaction was so slow that it was impossible to measure orders of reactants, and we have assumed the order for n-butyl-lithium in benzene to be one-sixth, as previously determined.[2] The order in Ph_3CH is taken to be unity as has been found for fluorene in benzene [2b] and for Ph_3CH in tetrahydrofuran (see above). In this way a value for the velocity constant of $1{\cdot}6 \times 10^{-9}$ mol$^{-\frac{1}{6}}$ l$^{\frac{1}{6}}$ s^{-1} was obtained. The change of velocity constant with temperature is given in Table 4, and gives an activation energy of 27·6 kcal mol^{-1} (by least squares). The thermodynamic constants of activation are given in Table 3.

TABLE 3

Thermodynamic constants of activation at +30 °C

RLi	Reactant	Solvent [a]	$\Delta G^‡$ / kcal mol^{-1}	$\Delta H^‡$ / kcal mol^{-1}	$\Delta S^‡$ / cal mol^{-1} K^{-1}
Bu^nLi	Ph_3CH	T.H.F.	20·6	9·9	−32·5
Bu^nLi	Ph_3CH	Benzene	29·9	27·0	−9·7
Bu^nLi	Fluorene	T.H.F.	14·1	4·7	−31·2 [b]
Bu^nLi	Fluorene	Benzene	24·5	15·1	−31·0 [c]
Ph_3CLi	T.H.F.	T.H.F.	27·9	24·3	−11·9
Ph_3SiLi	T.H.F.	T.H.F.	26·7	22·6	−13·6 [d]
Bu^nLi	$Ph_2C{=}CHPh$	T.H.F.	22·6	10·5	−40·1
Bu^nLi	$Ph_2C{=}CHPh$	Benzene	28·7	20·4	−27·5 [e]
Bu^nLi	$Ph_2C{=}CH_2$	T.H.F.	16·1	7·9	−27·2 [f]
Bu^nLi	$Ph_2C{=}CH_2$	Benzene	23·6	15·8	−25·8 [g]

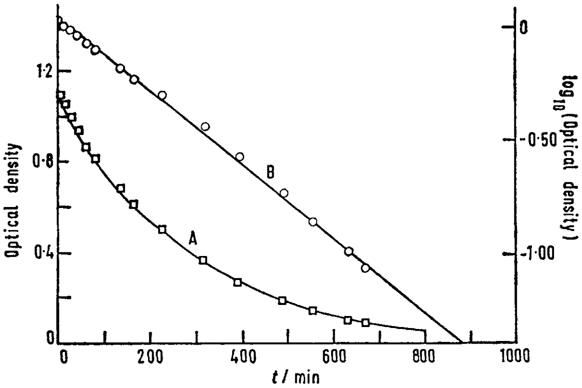
[a] T.H.F. = Tetrahydrofuran. [b] A. G. Evans, N. H. Rees, and A. Walker, *J.C.S. Perkins II*, in the press. [c] Ref. 2*c*. [d] Ref. 6. [e] A. G. Evans and D. B. George, unpublished results. [f] Ref. 1. [g] Refs. 2(*a*), 2(*d*).

TABLE 4

Reaction of n-butyl-lithium with Ph_3CH in benzene

T/K	$10^9 k$ / l$^{\frac{1}{6}}$ mol$^{-\frac{1}{6}}$ s^{-1}
303	1·64
308	3·47
313	6·83
318	14·7
323	30·8
328	50·6
333	102

Reaction of $Ph_3C^-Li^+$ *with Tetrahydrofuran.*—At the end of the reaction between n-butyl-lithium and Ph_3CH in tetrahydrofuran the cherry red colour of $Ph_3C^-Li^+$ slowly disappeared, and finally gave a colourless solution. The rate of decrease with time of the absorption at $\lambda_{max.}$ 500 nm was followed, and it was found that the reaction was of the first order in $Ph_3C^-Li^+$ (Figure), and a value of $6{\cdot}3 \times 10^{-5}$ s^{-1} at +95 °C was obtained for the pseudo-first-order constant (tetrahydrofuran in great excess). The change of this rate constant with temperature is given in Table 5, and gives an activation energy of 24·9 kcal mol^{-1} (least-squares value). The first-order constant calculated at +30 °C by use of this activation energy is $4{\cdot}7 \times 10^{-8}$ s^{-1}. The thermodynamic constants of activation calculated by use of the first-order constants as in our previous paper [6] are given in Table 3.



Reaction of $Ph_3C^-Li^+$ with tetrahydrofuran at 95 °C; first-order analysis of the rate curve. A, Optical density–time curve; B, first-order rate analysis

TABLE 5

Reaction of $Ph_3C^-Li^+$ with tetrahydrofuran

T/K	$10^6 k$/s^{-1}	T/K	$10^6 k$/s^{-1}
333	1·95	353	16·8
338	3·21	358	23·5
343	4·95	363·5	48·8
348	9·22	368	62·5

Reaction of n-Butyl-lithium with Triphenylethylene in Tetrahydrofuran.—This reaction was followed by measuring the rate of development of the 508 nm peak. The value of ε_{508} was assumed to be the same as $\varepsilon_{max.}$ for $BuCH_2CPh_2^-Li^+$ in tetrahydrofuran, *i.e.*, $2{\cdot}9 \times 10^4$ l mol^{-1} cm^{-1}. The

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[6] A. G. Evans, M. Ll. Jones, and N. H. Rees, *J. Chem. Soc.* (*B*), 1969, 894.

dependence of initial rate of reaction on initial concentrations of n-butyl-lithium and of $Ph_2C{=}CHPh$ is shown in Table 6. The order of reaction found by the least-squares method for butyl-lithium and for $Ph_2C{=}CHPh$ at −30 °C are 0·54 and 0·91 respectively, and we have taken these as 0·5 and 1·0 within experimental error, so that the observed rate constant is expressed as (2). The dependence of

$$\text{Rate of reaction} = k\left[\frac{Li^+}{2}\right]^{0.5}[Ph_2{=}CHPh] \qquad (2)$$

velocity constant on temperature is shown in Table 7. This gives an activation energy of 11·1 kcal mol^{-1}. The thermodynamic constants of activation are given in Table 3. The estimated errors for our results are: k, ±7%, $\Delta G^‡$, $\Delta H^‡$ ±5%, and $\Delta S^‡$ ±10%.

TABLE 6

Reaction of n-butyl-lithium with triphenylethylene in tetrahydrofuran at −30 °C

(*a*) Dependence of initial rate of reaction on [Bu^{n}Li]

$10^2[Li^+]_i/M$	$10^2[Ph_2C{=}CHPh]_i/M$	10^8R_i	$\frac{10^6k}{l^{0.5}\ mol^{-0.5}\ s^{-1}}$
5·45	9·91	5·46	3·33
3·36	30·19	12·93	3·30
1·84	30·19	9·03	3·12
1·14	30·19	6·90	3·02

$$k = \frac{R_i}{[Ph_2C{=}CHPh]_i\left[\frac{Li^+}{2}\right]_i^{0.5}}$$

(*b*) Dependence of initial rate of reaction on $[Ph_2C{=}CHPh]_i$

5·45	9·92	5·46	3·33
5·16	4·48	2·61	3·34
5·26	15·26	7·96	3·22
3·36	30·19	12·93	3·30

TABLE 7

Dependence of rate constant on temperature for reactions of n-butyl-lithium with triphenylethylene

T/K	$\frac{10^6k}{l^{0.5}\ mol^{-0.5}\ s^{-1}}$
232·5	1·14
238	1·98
243	3·22
247	5·12
253	7·30

DISCUSSION

For the reaction of n-butyl-lithium with Ph_3CH in tetrahydrofuran, the order of reaction in n-butyl-lithium is 0·5. This is the same as that found previously for n-butyl-lithium in its reaction with 1,1-diphenylethylene in tetrahydrofuran.[1] In the reaction of n-butyl-lithium with Ph_3CH in benzene we have assumed the same order for butyl-lithium, *i.e.*, one-sixth, as we have found previously for its reactions in benzene with 1,1-diphenylethylene [2a] and with fluorene.[2b]

We shall interpret these results as previously [2] in terms of reactions (3) and (4). The rate of reaction is given by equations (5) and (6) where $k = k_2(k_{1a}/k_{1b})$ and the thermodynamic terms by equations (7)—(9). $n = 2$ for tetrahydrofuran and 6 for benzene as solvent.

$$\frac{1}{n}(BuLi)_n \underset{k_{1b}}{\overset{k_{1a}}{\rightleftharpoons}} BuLi \qquad (3)$$

$$BuLi + Ph_3CH \xrightarrow{k_2} Ph_3C^-Li^+ + BuH \qquad (4)$$

$$\text{Rate of reaction} = k_2[BuLi][Ph_3CH] \qquad (5)$$

$$= k_2\frac{k_{1a}}{k_{1b}}[(BuLi)_n]^{1/n}[Ph_3CH] \qquad (6)$$

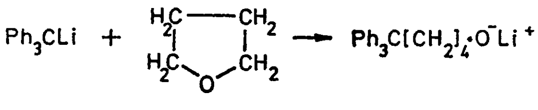
$$\Delta G^‡ = (\Delta G^‡_2 + \Delta G^\circ_{1a}) \qquad (7)$$

$$\Delta H^‡ = (\Delta H^‡_2 + \Delta H^\circ_{1a}) \qquad (8)$$

$$\Delta S^‡ = (\Delta S^‡_2 + \Delta S^\circ_{1a}) \qquad (9)$$

West, *et al.*[7] find that in the reaction between triphenylmethane and RLi, the rate constant decreases markedly as $[Ph_3CH]_i$ increases in excess of $[RLi]_i$. For example, over the range of $[Ph_3CH]_i/[RLi]_i$ from 10·9 to 0·144, a 3·4-fold decrease in rate constant occurs; they attribute this to multi-metallation. We, however, find nothing of this kind; in Table 1 $[Ph_3CH]_i/[Bu^nLi]_i$ varies from 11·4 to 0·13 and over this range our second-order rate constants show no variation within experimental error.

In the reaction of Ph_3CLi with tetrahydrofuran in tetrahydrofuran the order of reaction in Ph_3CLi is 1·0. This is the same as that found previously for the corresponding reaction of Ph_3SiLi.[6] We interpret our results, as in the case of the Ph_3SiLi reaction, as in reaction (10).



(10)

In the case of the reaction of triphenylethylene with n-butyl-lithium in tetrahydrofuran, the reaction will involve equilibrium (3), ($n = 2$), followed by (11) where $k = k_3(k_{1a}/k_{1b})$ and the thermodynamic terms are given by equations (12)—(14).

$$BuLi + PhCH{=}CPh_2 \xrightarrow{k_3} BuCHPhCPh_2^-\ \ Li^+ \qquad (11)$$

$$\Delta G^‡ = (\Delta G^‡_3 + \Delta G^\circ_{1a}) \qquad (12)$$

$$\Delta H^‡ = (\Delta H^‡_3 + \Delta H^\circ_{1a}) \qquad (13)$$

$$\Delta S^‡ = (\Delta S^‡_3 + \Delta S^\circ_{1a}) \qquad (14)$$

Change of Solvent.—In Table 3 we see that the change of solvent from tetrahydrofuran to benzene results in an increase in $\Delta G^‡$ for the reaction of n-butyl-lithium with Ph_3CH, fluorene, triphenylethylene, and 1,1-diphenylethylene by 9·3, 10·4, 6·1, and 7·5 kcal mol^{-1} respectively. In each case this increase in $\Delta G^‡$ involves an increase in $\Delta H^‡$; 17·1, 10·4, 9·9, and 7·9 kcal mol^{-1} respectively. The corresponding changes in $\Delta S^‡$ are +22·8, +0·2, +12·6, and +1·4 cal mol^{-1} K^{-1}.

The change of solvent from tetrahydrofuran to benzene involves an increase in aggregation of n-butyl-lithium from dimer to hexamer, and since it is the monomeric species which is active in the reaction, this increased aggregation will tend to make both $\Delta H^‡$ and $\Delta S^‡$ more positive in the case of benzene as solvent. The change

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[7] P. West, R. Waack, and J. I. Purmort, *J. Amer. Chem. Soc.*, 1970, **92**, 840.

in polar nature from the initial state to the transition state and the steric arrangement of the transition state will also affect these terms in changing from tetrahydrofuran to benzene.

Change of p*K of Substrate*.—For the reaction with n-butyl-lithium the change from Ph_3CH to fluorene results in a $\Delta G^{\ddagger}$ decrease of 5·4 kcal mol^{-1} in benzene and 6·5 kcal mol^{-1} in tetrahydrofuran. The corresponding pK decrease is from pK 33 for Ph_3CH to pK 25 for fluorene.[8] This change in pK corresponds to a ΔG° decrease of 11·1 kcal mol^{-1}. Thus the ratio $\Delta G^{\ddagger} : \Delta G^{\circ}$ for the change from Ph_3CH to fluorene is 0·5 in benzene and 0·6 in tetrahydrofuran. This is the sort of ratio one would expect and agrees with the corresponding ratio of *ca.* 0·5 which we found in the case of the reactions of fluorene and 9-methylfluorene with silyl-lithiums in tetrahydrofuran.[9]

Change from Carbon to Silicon.—Ph_3SiLi reacts more rapidly with tetrahydrofuran than does Ph_3CLi (1·2 kcal mol^{-1} reduction in $\Delta G^{\ddagger}$), owing to a reduction of 1·7 kcal mol^{-1} in $\Delta H^{\ddagger}$ and in spite of a $\Delta S^{\ddagger}$ value which is more negative by 1·7 cal mol^{-1} K^{-1}. Our earlier discussion [10] has shown that the lone pair in $Ph_3Si^-Li^+$ is not delocalised over the phenyl groups as in the case of $Ph_3C^-Li^+$, and for this reason we would expect the reaction with $Ph_3Si^-Li^+$ to be faster. The difference in $\Delta G^{\ddagger}$ of 1·2 kcal mol^{-1} would, by use of the proportionality factor 0·5 (see previous paragraph), give a difference in ΔG° of 2·4 kcal mol^{-1}, and this would correspond to an increase of 1·7 in pK from Ph_3CH to Ph_3SiH. Gilman and Wittenberg [11] have suggested that the pK of Ph_3SiH should be comparable with that of Ph_2CH_2. The increase of pK from Ph_3CH to Ph_2CH_2 has been given as 1·5,[12] 2·0,[8] 1·4,[13] and 1·6.[14] Thus our measurements support Gilman and Wittenberg's suggestion.

Change of Steric Hindrance.—The results for the reaction of n-butyl-lithium with $Ph_2C{=}CHPh$ and with $Ph_2C{=}CH_2$ in tetrahydrofuran and in benzene show that the presence of the third phenyl group slows the reaction very much. $\Delta G^{\ddagger}$ is increased by 6·5 and 5·1 kcal mol^{-1} in tetrahydrofuran and in benzene respectively. This increase in $\Delta G^{\ddagger}$ involves an increase in $\Delta H^{\ddagger}$ of 2·6 and 4·6 kcal mol^{-1} respectively. The corresponding changes in $\Delta S^{\ddagger}$ are —12·9 and —1·7 cal mol^{-1} K^{-1}. The presence of the four phenyl groups in $Ph_2C{=}CPh_2$ completely inhibits its reaction with n-butyl-lithium.[2a]

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[8] W. K. McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124.

[9] A. G. Evans, M. A. Hamid, and N. H. Rees, *J. Chem. Soc.* (*B*), 1971, 2164.

[10] A. G. Evans, M. A. Hamid, and N. H. Rees, *J. Chem. Soc.* (*B*), 1971, 1110.

[11] H. Gilman and D. Wittenberg, *Quart. Rev.*, 1959, **13**, 116.

[12] K. Bowden, *J. Chem. Soc.* (*B*), 1970, 179.

[13] E. C. Steiner and J. D. Starkey, *J. Amer. Chem. Soc.*, 1967, **89**, 2751.

[14] A. Streitwieser, J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Amer. Chem. Soc.*, 1965, **87**, 384.