# Reaction of Butyl-lithium with Stable Free Radicals

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Summary 1,3-Bis(biphenyl-2,2'-diyl)-2-phenylallyl (DBPA) (I) and triphenylmethyl have been converted into their carbanion conjugate species by butyl-lithium; the reaction is Lewis-base catalysed, and a new role is ascribed to the kinetically involved Lewis base.

THE reaction of butyl-lithium with stable free radicals, which is of interest since the presence of radicals in the reaction of alkyl-lithiums with alkyl halides has been demonstrated,[1] has been studied by visible and n.m.r. spectrometry.
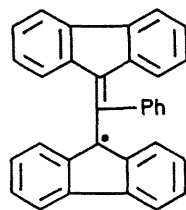
(I)

In preliminary experiments with the stable free radicals* DBPA (known[2] to be completely dissociated) and triphenylmethyl, electron or possibly atom transfer takes place from the organometallic reagent to the free radicals. Thus, the radicals are converted into their corresponding carbanions, namely 1,3-bis(biphenyl-2,2'-diyl)-2-phenylallylide (DBPA[-]) and triphenylmethide. Lewis-bases such as triethylamine and tetrahydrofuran (THF) increase the rate of the reaction markedly.

The 485 nm band[2] of DBPA changed rapidly upon the addition of a large excess of BuLi and a broad† absorption band appeared with two distinct peaks at 510 and 580 nm. The intensity of the 580 nm absorption increased slowly with time, whereas the 510 nm peak eventually disappeared. On the addition of THF the DBPA[-]Li^{+} absorption[2] appeared at a rate which depended on the THF concentration. This can be seen by comparing Figure 1A with 1B. The initial concentration of THF, $[THF]_0$, was 0·059 and 0·176M respectively, whereas $[DBPA]_0 = 1·1 \times 10^{-4}$M and $[BuLi]_0 = 0·050$M in both cases.

In the Table the pseudo-first-order rate constants‡ are given, for constant $[DBPA]_0 = 1·10 \times 10^{-4}$M and $[BuLi]_0 = 0·050$M; $[THF]_0$ varied from 0·059 to 0·235M. Clearly the reaction rate depends on the initial concentration of THF. The ratio of k to $[THF]_0$ becomes nearly constant $(2·0 \pm 0·2)$ at higher $[THF]_0$ values.§
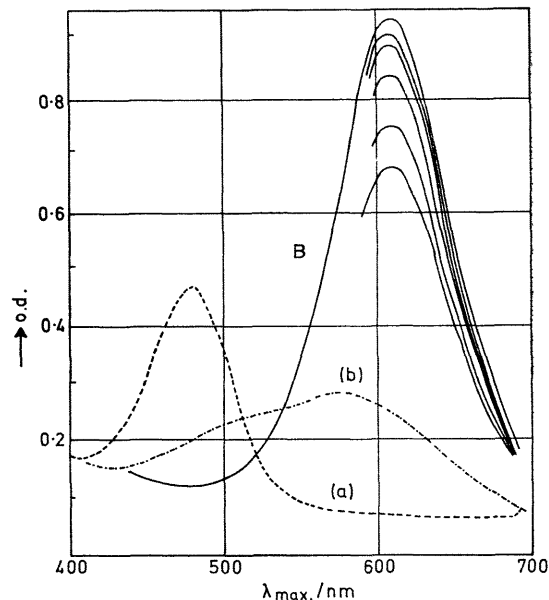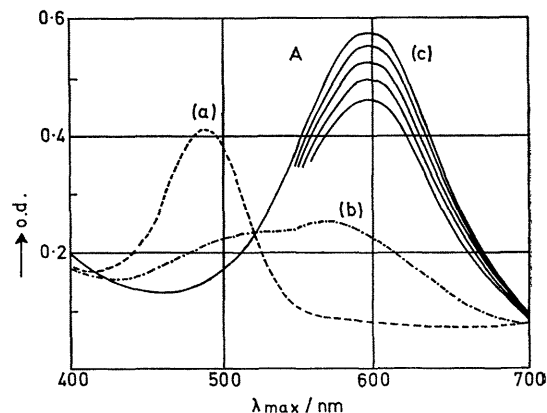
FIGURE 1 A, (a) Visible spectrum of DBPA; (b), after adding excess of BuLi. (c) Visible spectrum of DBPA[-]Li^{+} recorded 2·8, 5·8, 9·1, 12·6, and 16·0 min after addition of THF ($[THF]_0 = 0·059$M). B, (a) Visible spectrum of DBPA; (b), after adding excess of BuLi. (c), Visible spectrum of DBPA[-]Li^{+} recorded 1·7, 2·9, 5·2, 7·3, 8·4, and 10·8 min after addition of THF($[THF]_0 = 0·176$M).

* Prepared by literature procedures, DBPA by the method of Kuhn and Neugebauer[2] and "hexaphenylethane" by the method of G. N. Lewis, D. Lipkin, and T. T. Magel, J. Amer. Chem. Soc.,1944, 66, 1579.

† This absorption is most probably due to a charge-transfer complex with the radical as the acceptor. Waack and Doran (J. Organometallic Chem., 1965, 3, 92, 94) invoked charge-transfer intermediates in the electron transfer from BuLi to the diamagnetic substrate 1,2,3,4-tetraphenylbuta-1,3-diene. The absorption maxmium at 580 nm is attributed to unsolvated DBPA[-]Li^{+} which, in turn, could be "cross-associated" with BuLi just as its structural analogue 1,3-diphenylbut-1-enyl-lithium (J. W. Burley and R. N. Young, Chem. Comm., 1970, 991).

‡ Determined by least-squares.

§ The deviation of $k/[THF]_0$ at low $[THF]_0$ values agrees with the suggestion[5] that the kinetically effective base is that uncomplexed by BuLi. BuLi forms two types of complexes (F. A. Settle, jun., Ph.D. Thesis, University of Tennessee, 1964; H. L. Lewis and T. L. Brown, J. Amer. Chem. Soc., 1970, 92, 4664) with THF, BuLi : THF = 1 or 2.

Figure 2 shows the 60 MHz n.m.r. spectrum of a solution in C_6D_6 of the so-called hexaphenylethane.¶ Addition of an excess of BuLi results in the loss of the fine structure. The triplet of BuLi[3] at τ ca. 10·83 also loses its fine structure.** A few minutes after adding THF the characteristic pattern of triphenylmethyl-lithium[4] appears between τ 2·5 and 4·45.

TABLE

$[THF]_0/M$	k/min^{-1}	$(k/[THF]_0)/(1\ mol^{-1}\ min^{-1})$
0·059	0·0279 ± 0·0004	0·5
0·094	0·086 ± 0·004	0·9
0·118	0·22 ± 0·01	1·9
0·141	0·25 ± 0·01	1·8
0·176	0·35 ± 0·01	2·0
0·188	0·38 ± 0·01	2·0
0·235	0·52 ± 0·01	2·2

A solution of BuLi in hexane was added to a solution of "hexaphenylethane" in benzene. A light red colour developed gradually. Carbonation of the mixture gave valeric acid as the sole acidic product. After reaction for 25 h a brick-coloured precipitate formed which on hydrolysis gave triphenylmethane. Reaction in the presence of THF gave a deep red colour instantly and a brick-coloured precipitate formed when the mixture was set aside for several hours. Carbonation of this mixture afforded triphenylacetic acid and 1,1,1-triphenylpentane (n.m.r. spectra).

The observed products from triphenylmethyl could possibly arise from the direct reaction of BuLi with the dimer rather than with the radical. However, the structure of the dimer makes this possibility less attractive since one would expect addition of BuLi to the methylene double bond to occur rather than carbon–carbon scission by the organolithium reagent.

On the basis of the information given here and elsewhere[5] on the kinetic involvement of Lewis-bases in organolithium reactions, we ascribe a new role to Lewis-bases, namely, one analogous to that of the bridging ligands in "inner sphere" electron-transfer processes.[6] This specific role of the base is to provide substrate orbitals of correct symmetry to receive a delocalized electron from the organometallic species.
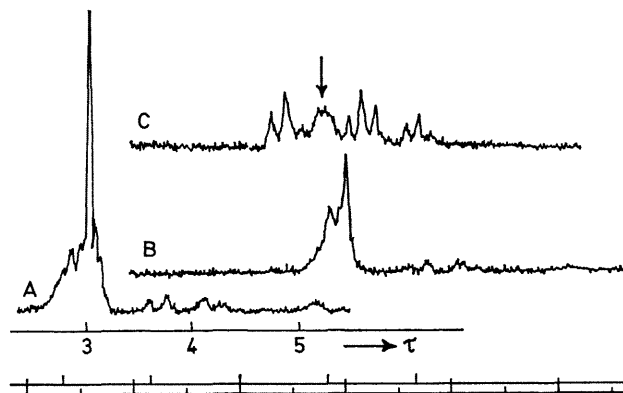

FIGURE 2. N.m.r. spectra; A, of "hexaphenylethane" in C_6D_6; B, after adding BuLi (offset by 180 Hz); C, 3 min after adding THF (offset by 180 Hz). The band shown by the arrow is due to triphenylpentane. The rest of the spectrum is of triphenyl-methyl-lithium.[4]

¶ The dimer of the triphenylmethyl radical has the structure 1-diphenylmethylene-4-triphenylmethylcyclohexa-2,5-diene (H. Lankamp, W. Th. Nanta, and C. Maclean, Tetrahedron Letters, 1968, 249).

** An increase in the paramagnetism of the solution due to preferential complexing of BuLi with the radical rather than with its dimer could explain the observed broadening.

[1] F. S. D'vachkovskii, N. N. Bubnov, and A. E. Shilov, Dokl. Akad. Nauk. S.S.S.R., 1958, 123, 870; G. A. Russell and D. W. Lamson, J. Amer. Chem. Soc., 1969,91, 3967; H. R. Ward and R. G. Lawler, ibid., 1967, 89, 5518; A. R. Lepley and R. L. Landau, ibid., 1969, 91, 748; H. R. Ward, R. G. Lawler, and R. A. Cooper, ibid., p. 746; A. R. Lepley, Chem. Comm., 1969, 64.
[2] R. Kuhn and F. A. Neugebauer, Monatsh., 1964, 95, 3.
[3] Z. K. Cheema, G. W. Gibson, and J. F. Eastham, J. Amer. Chem. Soc., 1963, 85, 3517.
[4] V. S. Sandel and H. H. Freedman, J. Amer. Chem. Soc., 1963, 85, 2328.
[5] C. G. Screttas and J. F. Eastham, J. Amer. Chem. Soc., 1966, 88, 5668.
[6] H. Taube, Chem. Rev., 1952, 69.