

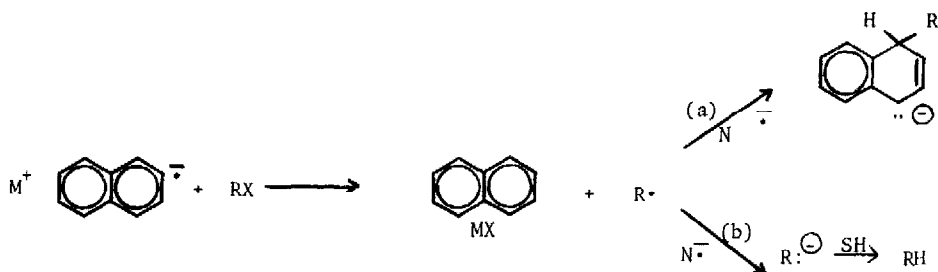
ORGANOLITHIUM REAGENTS FROM ALKYL HALIDES AND LITHIUM DI-tert-BUTYLBIPHENYL

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The reactions of aromatic radical anions with alkyl and aryl halides have received a great amount of attention in recent years.¹ However, the great majority of reports have described the use of sodium naphthalene as the radical anion and only scant attention has been given to other systems. The products of reactions of sodium naphthalene (NaN) and alkyl halides typically partition about equally between hydrocarbon and alkylated dihydro-naphthalene as illustrated in Scheme I below.



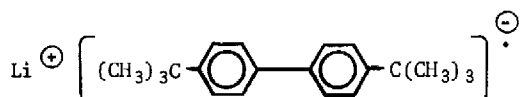
M = Na⁺ or Li⁺

Scheme I.

Thus, with NaN the potentially useful anion is formed in a yield most likely in the range 20-70%, and, as an added difficulty, the anion is immediately destroyed by reaction with the solvent^{1,2} or with parent halide.^{1,3} Recent reports suggest that the alkyl carbanion may be captured in the presence of MgCl₂.⁴

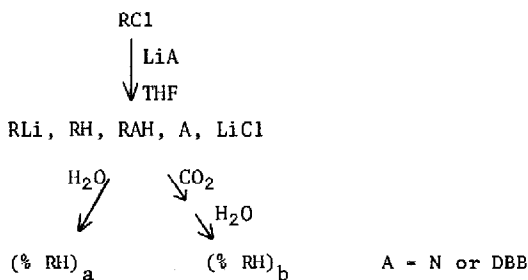
It appeared to us that a dramatic improvement in the synthetic potential for the generation of alkali alkyls might be achieved by (1) substituting Li for Na which should allow

the alkyl carbanion to be trapped in the form of the organolithium reagent⁵ and (2) reducing the ratio of alkylation (route (a)) to electron transfer (route (b)) through a simple modification of the structure of the radical anion. Since electron transfer processes may take place between molecular entities which are separated by as much as 7-9 Å,⁶ whereas the transition state for the alkylation of a radical anion should be at a bond forming distance, increasing the steric requirement of the radical anion might favor route (b) over (a). We chose to consider, therefore, the reactions of lithium di-tert-butylbiphenyl (LiDBB) (I)⁷ and relate these reactions to those of lithium naphthalene (LiN).



I

All experiments were performed by injection of an internal standard (nonane) and the halide into a 0.15 M tetrahydrofuran solution of the radical anion⁸ maintained at -78° . After 5 min an aliquot was removed, quenched with water and the percent hydrocarbon yield determined by VPC, $(\% \text{RH})_a$, (Scheme II).



Scheme II

The remainder of the radical anion solution was saturated with CO_2 , followed by addition of water. The percent reduction in hydrocarbon yield $[(\% \text{RH})_a - (\% \text{RH})_b]$ is taken to be the percent anion trapping. If no dimer formation occurs then this is also the yield of lithium reagent. The extent of alkylation of radical anion can be taken to be the difference between the percent hydrocarbon yield and 100 percent, since dimer formation is negligible for chlorides.¹

An inspection of Table I reveals that for LiN the yields of hydrocarbon and anion

trapping fluctuate over a wide range while the hydrocarbon yield from LiDBB is quantitative within experimental error with consistently 90 percent anion trapping. The yields of lithium reagents obtained from the LiDBB reaction in general are competitive with or exceed those obtained from the conventional reaction of lithium directly with alkyl halide.⁹ In addition the reaction proceeds instantaneously¹⁰ at -78° and probably even at -100° . Due to the homogeneous nature of this method the problem of surface contamination of lithium and consequent difficulty in preparation of lithium reagents does not exist allowing easy preparation of hitherto recalcitrant compounds such as 4-lithio-1,7-octadiene.¹¹ The nonvolatile nature of *p,p'*-di-*tert*-butylbiphenyl makes separation from reaction products easier in most cases than with naphthalene and the *p,p'*-di-*tert*-butylbiphenyl can be recovered in excellent yield.

Thus, improvements may be achieved in several facets of the preparation of lithium alkyls through the use of the new reagent lithium di-*tert*-butylbiphenyl, and, consequently, it seems reasonable to suggest that lithium di-*tert*-butylbiphenyl will turn out to be the reagent of choice in many instances.

Table I. The Reactions of Some Alkyl Chlorides with Lithium Naphthalene and Lithium Di-*tert*-butylbiphenyl

Chloride	LiN		LiDBB	
	%RH ^a	% anion trapping ^a	%RH ^a	% anion trapping ^a
1-chlorooctane	97	60	100	94
2-chlorooctane	64	22	100	87
3-chloro-3-methylheptane	41	76	100	90
7-chloronorcarane (syn: anti = 1.53)	high	63	99	94

^aYields are corrected for the observed loss of octane relative to nonane in a control experiment.

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7. The ESR spectra of potassium di-*t*-butylbiphenyl has been measured by M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, **87**, 2554 (1965).
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