Stoicheiometry and Synthetic Utility of the Reaction of Alkyl Halides with Lithium Dihydronaphthylide

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Summary Organolithium reagents (RLi) are formed in the reaction of lithium dihydronaphthylide ($Li^+C_{10}H_8{}^{\cdot -}$) with alkyl halides (RX); the stoicheiometry of the reaction ($Li^+C_{10}H_8{}^{\cdot -}$: RX) varied from 2 : 1 (with the highest yield of RLi) to 1 : 1 (no RLi formed).

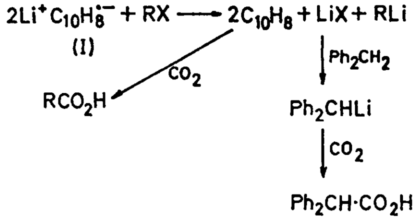
We describe here the conversion of alkyl and aryl halides into organolithium reagents by the action of lithium dihydronaphthylide, in yields ranging from 13 to 90% [*e.g.* reaction (1)]. Alkali metal arylides are known[1] to react

$$PhF + 2C_{10}H_8{}^{\cdot -}Li^+ \xrightarrow{90\%} PhLi + LiF + 2C_{10}H_8 \qquad (1)$$

with alkyl halides according to equation (2), possibly *via*

$$ArH^{\cdot -}M^+ + RX \rightarrow ArH + M^+X^- + R^{\cdot} \qquad (2)$$

radical combinations ($R^{\cdot} + R^{\cdot}$ and $R^{\cdot} + ArH^{\cdot -}$) and hydrogen abstraction from the solvent or parent hydrocarbon,[1a] or *via* reduction of $R^{\cdot}$ to a carbanion by a second electron transfer.[2] An example of the reaction (3) has been known for many years.[3]



$$\mathrm{Ph_3CCl} \xrightarrow{\mathrm{Ph_3B^{\cdot -}\ Na^+}} \mathrm{Ph_3C\cdot} + \mathrm{Ph_3C^-Na^+} \qquad (3)$$

In the present work with lithium dihydronaphthylide or phenanthrenylide the two-electron involvement in the overall process has been established more generally and directly. The production of RLi species was demonstrated by carbonation, followed by characterization of the carboxylic acid RCO_2H. In some cases RLi was 'trapped' by adding excess of diphenylmethane† to the mixture.

A solution of alkyl halide and compound (I) (2 mol. equiv.) in tetrahydrofuran under argon was stirred until reaction was complete (colour change). After carbonation, the carboxylic acid was isolated (see Table).

TABLE 1

RX (5 mmol)	$Li^+ArH^{\cdot -}$ (10 mmol)	Mixing temp.	'Trapping' agent	Yield of RLi (%)	Carbonation product[d]
Bu^nCl[a]	ArH = Phenanthrene	−100 ± 10°	Toluene	18	$PhCH_2{\cdot}CO_2H$
Bu^nCl[a]	»	−100 ± 10°	Diphenylmethane	45	$Ph_2CH{\cdot}CO_2H$
Bu^nCl[b]	»	−50 ± 5°	—	—	Valeric + unidentified acid
Ph_2CHCl	»	−50 ± 5°	—	13	$Ph_2CH{\cdot}CO_2H$
Ph_3CCl	»	25 ± 5°	—	70	$Ph_3C{\cdot}CO_2H$
PhCl	ArH = Naphthalene	−50 ± 5°	—	85	$PhCO_2H$
PhCl	»	5 ± 5°	—	89	$PhCO_2H$
PhF	»	−50 ± 5°	—	91	$PhCO_2H$
cyclo-$C_6H_{11}Cl$[c]	»	−50 ± 5°	—	70	cyclo-$C_6H_{11}CO_2H$

[a] Mixture (containing 25 mmol of 'trapping' agent) was stirred for 2 h at room temperature before carbonation. [b] Mixture was maintained below −10° before carbonation. [c] Mixture was carbonated below −25°, to prevent loss of cyclohexyl-lithium. [d] All products had the correct n.m.r. spectra and/or m.p.s.

The method promises to be synthetically useful, particularly for preparation of cyclohexyl- and phenyl-lithium from the corresponding chlorides. Naphthalene can normally be separated from the products by sublimation or steam distillation.

TABLE 2

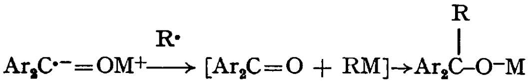
RX	(I):RX	Yield[a,b] of $Ph_2CH{\cdot}CO_2H$ (%)
Bu^nCl	2:1	45
Bu^nBr	1·67:1	37
Bu^nI	1·25:1	16
Allyl chloride	1:1	—
Benzyl chloride	1:1	—

[a] See note a to Table 1. [b] Based on RX.

The stoicheiometry of the reaction was investigated by determining the amount of alkyl halide consumed in discharging the colour of compound (I) at −50°. Ratios of the amount of alkyl halide to the amount of (I) are given in Table 2. The data indicate that there is a correspondence between the yield of organolithium reagent and the stoicheiometry of the reaction. The highest yield of RLi is obtained when the stoicheiometry is 2:1, whereas the yield is zero with 1:1 stoicheiometry. The stoicheiometry of the reaction appears to depend upon the tendency RX to couple with RLi species.[4] The data also suggest that the reported[5] substantial yield of R–R in the reaction of RI with sodium dihydronaphthylide could arise not only from a radical combination (R· + R·) but also through coupling of RI with an intermediate RNa species.

The present results suggest that at least part of the C-alkylation[6] of ketyls by alkyl halides could involve an intermediate of type (IV). The appearance of the characteristic absorption[7] of the anion $DBPA^-$ at *ca.* 600 nm

$$\mathrm{Ar_2C^{\cdot -}{=}OM^+} \xrightarrow{\mathrm{RX}} \mathrm{Ar_2C{=}O} + \mathrm{R\cdot} + \mathrm{M^+X^-}$$



$$\mathrm{Ar_2C^{\cdot -}{=}OM^+} \xrightarrow{\mathrm{R\cdot}} [\mathrm{Ar_2C{=}O} + \mathrm{RM}] \rightarrow \mathrm{Ar_2}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{{-}O^-M}$$

(IV)

when the ketyl, lithium 9-oxofluorenylide, is mixed with Koelsch's radical[8] [1,3-bis(biphenyl-2,2′-diyl)-2-phenylallyl, DBPA] is evidence in support of electron transfer from the ketyl to a radical and conversion of the latter into a carbanion.‡

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† Diphenylmethane was added after complete discharge of the green colour of the radical anion. Thus Ph_2CHLi is actually derived from the metallation of Ph_2CH_2 by RLi and not from the direct action of (I) on Ph_2CH_2 (J. J. Eisch and W. C. Kaska, *J. Org. Chem.*, 1962, **27**, 3745).

‡ $BDPA^-$ is so stable that it does not react with fluorenone, or even with acetone.

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