A One-step Alternative to the Grignard Reaction

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The reactions of organic halides with carbonyl compounds in the presence of lithium or sodium and with tetra-hydrofuran as solvent have been studied. When lithium is used alcohols are formed in high yield which in many cases exceed those obtained by the analogous Grignard reaction. The process involves the intermediate formation of organo-lithium species. With sodium, the yield of alcohol is significantly reduced and with carbonyl compounds possessing α-hydrogen atoms, hydrogen abstraction by the intermediate organo-sodium species predominates. The effect of the addition of electron-transfer reagents such as naphthalene or biphenyl to the sodium system has been studied and the yields of alcohols have been shown to increase with the concentration of additive present.

THE Grignard reaction is one of the best known and most widely used reactions in synthetic organic chemistry, particularly in its application to carbonyl-containing compounds. The reaction has been the subject of a number of reviews of which one of the most comprehensive is the text by Kharasch and Reinmuth.[1] It is essentially a two-stage process in which the Grignard species is first prepared and then reacted with the desired reagent. On the other hand, in the Barbier synthesis,[2] which in fact predates the Grignard reaction, the organo-magnesium halide is consumed as it is generated since a mixture of the halide and the carbonyl compound is added to a suspension of magnesium turnings in ether. The yields obtained using this latter process are, however, extremely variable, and the procedure has been completely superseded by the Grignard reaction.

It is known that organo-derivatives of the alkali metals, and particularly those of lithium, behave in a similar way to organo-magnesium halides and react with carbonyl compounds to form the corresponding alcohols.[3] Again in the many instances cited in the literature the reaction involves the prior preparation of the reactive intermediate rather than its generation *in situ* as in the Barbier synthesis. It was reported in an earlier communication,[4] however, that magnesium could be replaced by lithium in the Barbier synthesis with a consequent marked improvement in the yields obtained. This paper presents the results of a more detailed analysis of the scope of this reaction using lithium and an examination of the effect of its replacement by sodium. For clarity, the reactions of the two alkali metals will be considered separately.

Lithium.—The wide applicability of this procedure when lithium metal is used is demonstrated in Tables 1 and 2 where, wherever possible, the yields obtained are compared with those given by the conventional Grignard reaction.

In general the method is equally applicable to aldehydes, ketones, and esters; reaction goes easily with paraformaldehyde (Table 1) to give primary alcohols and with formate esters (Table 2) to give symmetrical secondary alcohols. Organic chlorides, bromides, or iodides may be used, although the efficiency of the

process tends to be lower with iodides almost certainly because of the increased probability of a Wurtz condensation reaction taking place between the organo-lithium species and the iodide. Both alkyl and aryl halides give high yields of alcohols by this process and primary, secondary, and tertiary halides may be employed with similar facility. Interestingly, the efficiency of the reaction seems to be insensitive to the size of the ligands of the halide or the carbonyl compound, and good yields of alcohols with carbon chains up to C_{28} have so far been obtained.

In order to ascertain the sensitivity of the reaction to changes in the experimental parameters, the reaction of n-propyl bromide with n-butyraldehyde in the presence of lithium was studied in some detail. The results of these studies are given in Table 3, although the trends observed should only be generalised with caution.

It is seen that the percentage yield is an inverse function of temperature, although the efficiency is quite high at ambient temperatures. Halide in excess of stoicheiometric requirements is necessary for maximum yield, but 20% excess is sufficient to compensate for halide losses due to side-reactions such as the Wurtz condensation. Similar observations have been made with a number of other systems and it is felt that both these results are a general feature of the reaction. It was also established (Table 3) that the reaction is little affected by concentration and that highly concentrated solutions of the product could therefore be obtained with no diminution in yield. The effect of varying the lithium surface area was examined by carrying out the reaction with a given weight of lithium in wire, slice, and rod form. The results show that the yield falls off slightly as the surface area increases. This could be due to local heating effects at the metal surface increasing the probability of side-reactions although the bulk temperature in each case was kept at 0 °C.

When the reaction is carried out with αβ-unsaturated carbonyl compounds, addition takes place almost exclusively to form 1,2-adducts. Thus high yields of the 1,2-addition products were obtained with acrolein, methacrolein (Table 1), and methyl methacrylate (Table 2). Similarly, the two products obtained with

[1] M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Non-metallic Substances,' Constable, London, 1954.
[2] P. L. Barbier, *Compt. rend.*, 1898, **128**, 110.
[3] G. E. Coates, M. L. H. Green, and K. Wade, 'Organo-metallic Compounds,' Methuen, London, 1967, vol. 1, ch. 1.
[4] P. J. Pearce, D. H. Richards, and N. F. Scilly, (a) *Chem. Comm.*, 1970, **18**, 1160; (b) B.P. Appl. 61957 and 61958/69.

high efficiency in the reaction of bromobenzene with mesityl oxide (Table 2) result from alternative dehydration routes from the 1,2-adduct 4-methyl-2-phenylpent-3-en-2-ol, rather than from any 1,4-adduct present. No attempt has been made as yet to try to prepare significant quantities of 1,4-derivatives by the use of additives such as transition-metal salts, which are known to be active in this way in Grignard reactions.[5]

methoxide and, of course, no condensation reaction can occur. When a mixture of benzyl methyl ether and mesityl oxide was treated with lithium, the expected alcohol was prepared in 65% yield at 0 °C.

The alternative approach was to form a lithium-electron acceptor complex in tetrahydrofuron (THF) before addition of the mixture of reactants; for example, lithium can be dissolved in a naphthalene solution in

TABLE 1

Reactions of aldehydes with organic halides and lithium in THF

Carbonyl compound	Halide	Product	% Yield	% Yield Grignard
Paraformaldehyde	n-Hexyl bromide	Heptan-1-ol	72	
Paraformaldehyde	n-Dodecyl bromide	Tridecan-1-ol	80	
Acetaldehyde	n-Pentyl bromide	Heptan-2-ol	39	
Propionaldehyde	Methyl iodide	Butan-2-ol	51	
Propionaldehyde	Ethyl bromide	Pentan-3-ol	90	47
n-Butyraldehyde	n-Propyl bromide	Heptan-4-ol	89	60—85
n-Butyraldehyde	n-Butyl bromide	Octan-4-ol	73	
n-Butyraldehyde	n-Pentyl bromide	Nonan-4-ol	73	33
n-Butyraldehyde	Isobutyl bromide	2-Methylheptan-4-ol	89	60—85
n-Butyraldehyde	t-Butyl bromide	2,2-Dimethylhexan-3-ol	89	
Isobutyraldehyde	n-Butyl bromide	2-Methylheptan-3-ol	89	
n-Hexaldehyde	Methyl bromide	Heptan-2-ol	70	
n-Decaldehyde	n-Decyl bromide	Eicosan-2-ol	75	
n-Decaldehyde	n-Octadecyl bromide	Octacosan-10-ol	80	
n-Dodecaldehyde	n-Hexadecyl bromide	Octacosan-12-ol	50	
Acrolein	Ethyl bromide	Pent-1-en-3-ol	90	65
Methacrolein	n-Butyl bromide	2-Methylhept-1-en-3-ol	93	
Benzaldehyde	Allyl bromide	1-phenylbut-4-en-1-ol	71	Poor
Benzaldehyde	Cyclohexyl chloride	Cyclohexylphenylmethanol	60	
Benzaldehyde	Cyclohexyl bromide	Cyclohexylphenylmethanol	72	70
Benzaldehyde	Chlorobenzene	Diphenylmethanol	100	
Benzaldehyde	Bromobenzene	Diphenylmethanol	95	55
Benzaldehyde	Iodobenzene	Diphenylmethanol	64	

TABLE 2

Reaction of ketones and esters with organic halides and lithium in THF

Carbonyl compound	Halide	Product	% Yield	% Yield Grignard
Acetone	Bromobenzene	2-Phenylpropan-2-ol	34	
Di-n-butyl ketone	n-Butyl bromide	5-n-Butylnonan-5-ol	91	
Di-isobutyl ketone	n-Butyl bromide	2-Methyl-3-isobutyloctan-4-ol	90	Nil *
Acetophenone	Bromobenzene	1,1-Diphenylethanol	62	58% †
Benzophenone	n-Butyl bromide	1,1-Diphenylpentan-1-ol	95	
Benzophenone	Bromobenzene	Triphenylmethanol	90	90
Mesityl oxide	n-Butyl bromide	{2-Methyl-4-phenylpenta-1,3-diene 4-Methyl-2-phenylpenta-1,3-diene	{32 36}	40
Ethyl formate	n-Butyl bromide	Nonan-5-ol	91	83
Ethyl formate	Cyclopentyl bromide	Dicyclopentylmethanol	85	
Ethyl formate	Cyclohexyl bromide	Dicyclohexylmethanol	80	
Ethyl formate	n-Decyl bromide	Heneicosan-11-ol	62	
Methyl methacrylate	n-Butyl bromide	3-Butyl-2-methyl-hept-1-en-3-ol	89	15—20
Methyl benzoate	Methyl iodide	2-Phenylpropan-2-ol	74	78

* Reduction takes place.   † As olefin.

It has been found that benzyl halide cannot be used efficiently in this reaction. Benzyl-lithium is itself very difficult to prepare by the direct reaction of the halide with lithium metal because of its marked tendency to undergo Wurtz coupling,[3] and large quantities of bibenzyl were found in the reaction product in all cases with little of the required alcohol. This difficulty was overcome in two ways.

In the first method the benzyl halide was replaced with benzyl methyl ether. This reacted directly with the lithium metal to form benzyl-lithium and lithium

THF to form the dark green solution of lithium⁺ naphthalene⁻. When the benzyl halide–carbonyl mixture is added slowly to an excess of this complex an extremely fast electron-transfer reaction occurs to form benzyl-lithium, the speed of reaction minimises the stationary concentration of benzyl halide and hence the probability of undergoing the Wurtz condensation. Thus the reaction of benzaldehyde with benzyl bromide in the presence of an excess of sodium naphthalene gave

5 M. S. Kharasch and P. O. Tawney, J. Amer. Chem. Soc., 1941, 63, 2308.

Effect of reaction parameters on yield for the system n-butyraldehyde, n-propyl bromide, and lithium in THF. Unless otherwise stated, the reaction was carried out at 0 °C with an aldehyde : halide molar ratio of 1 : 1·2

Temp. °C	% Yield heptan-4-ol	Temp. °C	% Yield heptan-4-ol
−70	78	0	72
−40	89	+20	70
−20	78	+40	65

Alkyl halide % Excess		Alkyl halide % Excess	
0	49	50	72
20	72		

Solvent concentration Aldehyde molarity		Solvent concentration Aldehyde molarity	
3·4	72	0·86	68
1·7	72		

Lithium surface area Surface area		Lithium surface area Surface area	
Large	59	Small	74
Medium	72		

a 74% yield of 1,2-diphenylethanol at 0 °C. The reaction of alkyl halides with alkali-metal–electron acceptor complexes will be dealt with more fully in the next section.
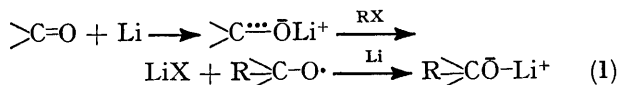
If required, the two methods described above may be combined; thus a mixture of benzyl methyl ether and benzaldehyde was treated with an excess of lithium–naphthalene at 0 °C to give 1,2-diphenylethanol in 50% yield.

A number of competing reactions occur in this system, of which the three most important are Wurtz coupling, pinacol formation, and α-hydrogen abstraction. The Wurtz reaction is minimised by keeping the stationary concentration of halide in the reaction vessel as low as possible. This is effected by reducing the rate of addition of reagents; evidence has been obtained which indicates a direct relationship between the percentage of dimer formed and the rate of addition at constant lithium surface area.

Pinacol formation may also occur under these conditions and it is suspected that this is the main cause of the low yields of alcohol found when acetone is used (Table 2). Lastly, the organometallic intermediate can alternatively react with the carbonyl compound by α-hydrogen abstraction possibly leading further to an aldol condensation. It is known that organo-lithium compounds are the least susceptible of the organometallic derivatives of the alkali metals to this course of reaction [6] and it does not appear to interfere seriously with the efficiency of the desired nucleophilic addition reaction.

Throughout the foregoing discussion it has been assumed that the reaction proceeds by the initial reaction of the halide with lithium to form the organo-

lithium compound and that this intermediate then reacts additively with the carbonyl compound to form the alcoholate. Although the weight of experimental evidence supports this mechanism there remains a possibility that the reaction could proceed via a mechanism analogous to that proposed for dissolving metal reductions such as the Bouveault–Blanc and Birch reductions.[7] This reaction path is shown in equation (1)

$$\text{C=O} + \text{Li} \longrightarrow \text{C}\text{···}\bar{\text{O}}\text{Li}^+ \xrightarrow{\text{RX}}$$
$$\text{LiX} + \text{R}\text{C-O·} \xrightarrow{\text{Li}} \text{R}\text{C}\bar{\text{O}}\text{-Li}^+ \quad (1)$$

and requires that the carbonyl first reacts with the lithium metal to form a radical anion, or ketyl, which then reacts with alkyl halide to give an alkoxide radical. Reaction of this last species with lithium would result in the observed lithium alkoxide.

The following experiment was carried out to test this hypothesis. Benzophenone was allowed to react with an excess of lithium in THF to give blue ketyl. Time was allowed for this species to be quantitatively generated before a stoicheiometric quantity of n-butyl bromide was added to the system. The blue colour characteristic of the ketyl was not discharged by the halide as required by the above mechanism. Thus it appears that intermediate radical-anion formation does not occur in the pseudo-Grignard process and that, as expected, the reaction proceeds via the formation of organo-lithium compounds.

Sodium.—When sodium wire is used instead of lithium and a similar procedure adopted, the reaction stops after ca. 5% conversion. This cessation of reaction is general with sodium and has been observed with a wide variety of reagents. It was assumed the sodium metal was quickly coated with an impervious layer which prevented the reaction from going to completion. Sodium halide, which is generated as the reaction proceeds, is only very sparingly soluble in THF, and it appears probable that deposition of this material on the sodium surface is the reason why passification occurs. The much greater solubility of lithium halide in the solvent prevents rapid deposition and so in this case the reaction is able to go to completion.

This difficulty was overcome by adding a large number of glass spheres to the reaction vessel and vigorously stirring the reaction system. The resulting ' ball mill ' effect on the ductile sodium effectively removed the surface coating and allowed the reaction to proceed more efficiently.

When bromobenzene was treated with benzaldehyde under these conditions a 44% yield of diphenylmethanol was obtained (cf. 95% with lithium). On the other hand the reaction of a mixture of butyraldehyde and butyl bromide gave no detectable amounts of octan-4-ol (cf. 75% with lithium). Again, the reaction between butyl bromide and benzaldehyde gave 36% yield of 1-phenylpentan-1-ol whereas no 1-phenylbutan-1-ol

6 W. I. O'Sullivan, F. W. Swamer, W. J. Humphlett, and C. R. Hauser, J. Org. Chem., 1961, 26, 2306.

7 H. O. House, ' Modern Synthetic Reactions,' Benjamin, New York, 1965, p. 50.

could be detected from the reaction involving bromo-benzene and butyraldehyde.

Two points emerge from these observations. Firstly, significant yields of the desired products are only obtained when the carbonyl compound possesses no abstractable hydrogen in the α-position. This supports the findings of O'Sullivan *et al.*[6] which showed that α-hydrogen abstraction is much more prevalent with organo-sodium species than with organo-lithium species. Secondly, even when α-hydrogen abstraction cannot take place, the yields of alcohols are still inferior to those obtained using lithium metal. It is felt that this is due to an increase in the probability of the competing Wurtz condensation reactions occurring with the more basic organo-sodium derivative than with the corresponding lithium compound.

It therefore appears that sodium is unsuitable for use in these reactions other than in those circumstances where α-hydrogen abstraction cannot occur. When such conditions apply, however, it may be more convenient to use sodium rather than lithium, particularly if the yield can be optimised and so experiments were carried out, using bromobenzene and benzaldehyde as a model system, to examine this possibility.

Two related techniques were developed which can give improved yields; both involve prior reaction of the sodium metal with an electron acceptor (A) such as naphthalene or biphenyl to form the highly coloured charge-transfer complex Na^+A^-. In the first technique sufficient acceptor is added to the sodium in THF to form the complex in excess of the requirements for the subsequent pseudo-Grignard reaction. The mixture of carbonyl compound and halide is then slowly added to this solution. The second method involves adding smaller amounts of electron acceptor such that the amount of complex formed is insufficient to react with all the carbonyl compound and halide. These ingredients are then slowly added until the colour characteristic of the complex Na^+A^- begins to fade, at which point the addition is discontinued to allow the colour to redevelop by further reaction of the regenerated electron acceptor with sodium. Titration is continued in this way until the reagents are consumed. In both these techniques the reaction is made homogeneous so that sodium halide is produced away from the metal surface, and the reaction can be carried through to completion without recourse to the 'ball mill' technique. They both have the disadvantage that the final alcohol has to be separated from the polynuclear hydrocarbon, and in the examples quoted the methods have only been used analytically.

Table 4 shows the effect of changing the proportion of added naphthalene or biphenyl on the yield of diphenyl-methanol formed from bromobenzene and benzaldehyde, whilst Table 5 shows the variation in the yield obtained with this reaction by employing a number of different preparative routes. The yield of 15% given in Table 4

[8] T. C. Cheng, L. Headley, and A. F. Halasa, *J. Amer. Chem. Soc.*, 1971, **93**, 1502.

for diphenylmethanol prepared using sodium without any additives is that obtained from the limited reaction which occurs when the 'ball mill' technique is not used whereas the figure of 44% quoted in Table 5 is that obtained using this technique.

TABLE 4

Reaction of bromobenzene (0·25 M) and benzaldehyde (0·20 M) with sodium (0·75 M) at 0 °C in the presence of varying amounts of (*a*) naphthalene and (*b*) biphenyl. (Molarities are given as if the reactants were dissolved in THF)

| | % Yield of diphenylmethanol | |
Molarity	Naphthalene	Biphenyl
0·0	15	15
0·05	25	17
0·1	33	25
0·20	49	47
excess	66	52

TABLE 5

Yield of diphenylmethanol produced at 0 °C from bromobenzene and benzaldehyde by various techniques

Technique	% Yield
Li metal	95
Na metal	44
Grignard	55
Li^+ naphthalene$^-$ excess	70
Na^+ naphthalene$^-$ excess	66
Na^+ biphenyl$^-$ excess	52

Of the two electron-transfer agents used, naphthalene appears to be marginally the more efficient; more significantly, however, in both cases the yield of diphenylmethanol increases with the proportion of electron-transfer agent to reactants present in the system. Furthermore, the yield in the presence of an excess of sodium naphthalene is less than that obtained with an excess of lithium naphthalene which in turn is considerably below that obtained by direct reaction with lithium metal. These observations may be rationalised as follows.

It has been established that the reduction of organic halides by sodium naphthalene proceeds *via* the formation of an organic radical and halide ion [8-10] [equation (2)]. The radical may then react by dimerisation

$$RX + Na^+N^- \longrightarrow R\cdot + N + NaX \qquad (2)$$
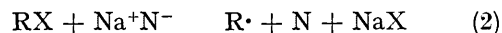
[equation (3a)], react with solvent (3b) or naphthalene (3c), or form the desired organo-sodium species by reaction with a second molecule of sodium naphthalene (3d).

Clearly the efficiency of the pseudo-Grignard reaction will depend on the relative importance of reaction (3d) in this scheme. Because this reaction is the only one which has an overall bimolecular dependence on sodium–naphthalene, it may be enhanced by increasing the concentration of sodium–naphthalene in solution. Thus the observed correlation between the yield of diphenyl-

[9] J. F. Garat, J. T. Barbas, and F. E. Barton, *J. Amer. Chem. Soc.*, 1968, **90**, 7159.

[10] C. D. Sargent and C. A. Lux, *J. Amer. Chem. Soc.*, 1968, **90**, 7160.

methanol and the relative amount of electron-transfer agent present can be explained.

(a) R — R   R — N· (c)

(b) RH + S·   R⁻Na⁺ + N (d)

(3)
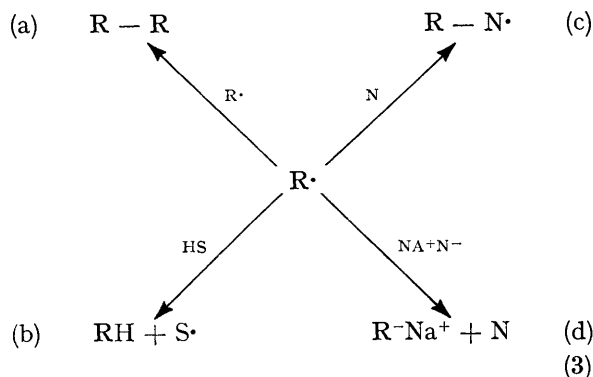
The extremely high yield obtained by direct reaction of the halide with lithium is due to the heterogeneous nature of this process. The reaction takes place on the metal surface thereby ensuring direct conversion into the organo-lithium species probably without generation of the free radical postulated in the homogeneous reaction mechanism. Even with sodium metal the 44% yield obtained when the direct reaction is forced to completion is only matched when an equimolar ratio of electron-transfer agent to aldehyde is used. Thus in this case also the generation of the organo-sodium species is very efficient and the lower yield obtained when compared with lithium is primarily due to the greater reactivity and hence lower selectivity of the organo-sodium species produced.

Conclusions.—It can be seen that the reaction of organic halides with carbonyl compounds in the presence of lithium to give alcohols is one of wide applicability and the yields obtained by this process can be favourably compared, in most cases, with those given in analogous Grignard reactions. It has the further advantages that it is a one-stage process and that the final work up of product is clean and straightforward. The replacement of lithium by sodium results in a significant diminution in the yields of alcohol obtained. This is particularly true of carbonyl compounds which possess α-hydrogen atoms as the desired addition is minimised due to the predominance of the α-hydrogen abstraction reaction.

EXPERIMENTAL

Materials.—The tetrahydrofuran (THF) was dried over molecular sieves before one of the two following procedures was employed: (*a*) the solvent was refluxed over sodium wire, distilled, and stored over fresh sodium wire and under nitrogen before use; (*b*) a previously prepared solution of sodium–naphthalene complex in THF [11] was added to the solvent until it took on the deep green colour of the complex. It was then distilled under nitrogen and stored over fresh sodium wire before use. The latter method gives the cleaner product but experiments have shown that the yield of the reaction is relatively insensitive to traces of impurities.

The reagents used were of the highest purity commercially available and were dried over molecular sieves before being used. Lithium metal was obtained from a number of sources and at various levels of purity. It was washed with light petroleum and sliced into small pieces each *ca.* 0·2 g weight before insertion into the reaction vessel. Sodium metal was similarly washed and then extruded as wire directly into the nitrogen-blanketted reaction vessel.

Apparatus.—The reactions were in general carried out at room temperature or below and the required reaction temperature was controlled to ±1 °C by means of an isopropyl alcohol–solid carbon dioxide bath in association with a Jack-o-matic pneumatic jack and a Thermo-watch control manufactured by Instruments for Research and Industry.

Method of Preparation (Lithium).—Although the method given below is essentially a laboratory-scale preparation, the procedure lends itself easily to scaling up and reactions have been carried out using 50 mol of carbonyl compound and 25 l of THF with no loss in yield due to scaling up.

The reaction vessel was a 1-l flask fitted with a stirrer and a dropping funnel; THF (400 ml) and lithium slices (2·5 mol) were introduced under a slow stream of nitrogen and the temperature was reduced to that desired for the reaction. The carbonyl compound (1·0 mol) was mixed with a slight stoicheiometric excess of the halide (1·2 mol if aldehyde or ketone, 2·4 mol if an ester) and the mixture was transferred to a dropping funnel attached to the reaction vessel and a drying tube was fitted. If either of the reactants was a solid then a concentrated THF solution was made of both components.

A small aliquot portion of the reagent mixture was dripped into the reaction vessel and the solution was stirred for a period before further addition as there was sometimes an induction period of a few min before reaction began. The termination of this period was marked by a change in the appearance of the lithium surface from a dull matt appearance to a golden silvery sheen. When this appeared the addition of reagents was continued at a rate sufficiently slow that the reaction was maintained under isothermal conditions. The rate of reaction was extremely fast and the reaction time was determined almost entirely by the rate of addition of the reagents. Usually the reagents were added over a period of *ca.* 2 h and within min after the addition of the final aliquot portion the reaction had gone to completion. This was evidenced by a return of the lithium surface to a dull colour. The shiny aspect of the lithium surface seemed to be characteristic of the pseudo-Grignard reaction only, as there was evidence that Wurtz condensation of the excess of organic halide continues after the surface had become matt.

After reaction was complete, excess of lithium was filtered off and the THF was removed on a rotary film evaporator. The residue was hydrolysed with dilute acid and the alcohol thus liberated was extracted with ether and dried (MgSO₄). After removal of the solvent, the alcohol was fractionally distilled or recrystallised.

When no separation was required, the following analytical procedure was used: the THF solution after filtration was made up to 500 ml and a 50-ml aliquot portion was taken. The solvent was removed from this portion on a rotary film evaporator and the residue was hydrolysed with dilute acid. The whole was extracted with ether and a suitable standard was then introduced. This extract was then used for g.l.c. analysis.

[11] M. Szwarc, ' Carbanions, Living Polymers and Electron Transfer Processes,' Interscience, London, 1968, ch. IV.

The yields quoted in the tables are those obtained by g.l.c. analysis of the hydrolysed reaction products. When product separation has been carried out the purity of the alcohol has also been determined by g.l.c.

In certain cases the method of preparation given above had to be modified. With some starting materials the induction period was prolonged and occasionally it was difficult to start the reaction at all. It was found that an effective procedure in these circumstances was to add initially a small amount of a mixture which contained about twice the amount of halide required by stoicheiometry. The reaction then started very quickly and, once this had been achieved, the reaction was continued by addition of the normal mixture of reagents.

Because of its low solubility in THF, paraformaldehyde was added initially to the solvent in the reaction vessel as a suspension. The organic halide was then slowly dripped into this suspension in the normal way when a reaction to give the desired product took place smoothly at ambient temperature or above. This was shown by the gradual disappearance of the paraformaldehyde as the reaction proceeded until on completion of the addition a homogeneous liquid remained. At lower temperatures Wurtz condensation of the halide predominated and the paraformaldehyde remained in suspension; apparently the solubility of the material in THF was not high enough at these temperatures to maintain an adequate concentration at the reaction sites.

Method of Preparation (*Sodium*).—The basic method was that described for lithium. When glass balls were used, enough were introduced to fill the flask to within 10 mm of the solvent surface and a strong stirrer such as a glass rod fitted with a PTFE paddle was then used for stirring.

For the reaction involving an excess of sodium–naphthalene (or sodium–biphenyl) it was found desirable to work at a predetermined ratio of electron-transfer agent to halide for comparison purposes; thus an accurate weight of sodium was dissolved in THF containing an excess of naphthalene to give a molar ratio of sodium to halide of 2 : 1. After dissolution, the mixed reagents were added slowly during *ca*. 30 min under isothermal conditions. Excess of sodium–naphthalene was then destroyed by the addition of a little methanol.

When the reagents were treated with sub-stoicheiometric amounts of sodium–naphthalene, an excess of sodium wire was added and an amount of naphthalene was then added which was a known molar fraction of the organic halide. Time was allowed for the complete generation of the complex before titration of the reactants was started. The rate of addition was very dependent on the concentration of naphthalene present. The amount of reagents which could be added before appreciable diminution in colour was, of course, a direct function of the naphthalene concentration. Also, the rate of generation of the complex was strongly dependent on this variable and at low naphthalene concentrations the titration could be very lengthy. In contrast, under the described experimental conditions when the naphthalene to halide ratio was greater than 0·2 : 1, the rate of addition could be adjusted so that the complex could be regenerated as fast as it was discharged and a continuous addition could be achieved.