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SHORT COMMUNICATION

Colored indicators for simple direct titration of magnesium and lithium reagents

We have been engaged in a general study of the relative ability of a metal alkyl (particularly lithium and magnesium reagents) to react in two rather different ways: (*i*) to react covalently as a carbanionic Lewis base, *e.g.*, to accept a proton from an acid, such as an alcohol; (*ii*) to undergo single electron transfer, *i.e.*, reduce an electron acceptor by charge transfer. Interestingly enough, the latter process involves reaction of the organometallic *with* a base (rather than *as* a base) to form an intermediate charge transfer complex[1]. Quite likely the coordination intermediates so often proposed for organometallic addition reactions can be regarded as charge transfer complexes. Although the general study is far from complete, one preliminary result is reported here because of its practical utility. The complexes formed by some bases with lithium and magnesium reagents are highly colored and sufficiently stable to serve as indicators which allow the organometallic to be directly titrated with acid (an alcohol) to a visible, well defined, stoichiometric end point.

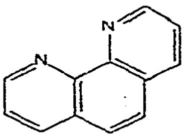
Actually, both lithium and magnesium alkyls are coordinated by virtually any base, including simple ethereal and ammoniacal Lewis bases, but to serve as practical indicators we choose π-type bases, specifically polycyclic aromatic bases which form complexes with intense absorption in the visible spectrum. It is also necessary to choose bases which undergo simple reversible coordination with the organometallic, *i.e.*, which do not react beyond formation of the charge transfer complex; aromatic systems can undergo addition and reduction by metal alkyls[2–7]. Two aromatic bases which we find quite practical are 1,10-phenanthroline (I) and 2,2′-biquinoline (II).

TABLE 1

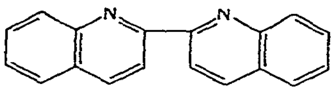
RESULTS FROM DIRECT TITRATIONS OF ORGANOMETALLIC REAGENTS WITH SEC-BUTYL ALCOHOL

Reagent	*Solvent*	*Direct titration molarity*[a]	*Independent analysis molarity*
Di-sec-butylmagnesium	C_6H_{12}	0.78	0.77[b]
Isobutylmethylmagnesium	C_6H_6	0.71	0.72[b]
Phenylmagnesium chloride	$(C_4H_9)_2O$	2.20[c]	2.13[d]
n-Butylmagnesium chloride	$(C_2H_5)_2O$	2.73	2.8[e]
n-Butyllithium	C_6H_{14}	1.62[f]	1.65[g]
sec-Butyllithium	C_6H_{14}	1.31	1.33[g]
tert-Butyllithium	C_5H_{12}	1.54	1.52[h]

[a] Average of two or more titrations. [b] Comparison analysis used for magnesium alkyls in hydrocarbon solutions involved hydrolysis of the reagent and use of the hydrolysate for titrimetric determinations of the total base and the magnesium ion and for VPC analysis of the alkanes corresponding to the alkyl groups; *cf.* ref. 8. [c] Average deviation of four analyses, 0.7%. [d] Comparison analysis involved trimethylsilylation of reagent and VPC of product as described in ref. 11. [e] Value furnished by commercial source of sample analyzed, M and T Chemicals, Inc., Rahway, N. J. [f] Average deviation of five analyses, 0.7%. [g] Comparison analysis involved oscillometry as described in ref. 14. [h] Comparison analysis involved oxidation of reagent with vanadium pentoxide as described in ref. 13.



(I)



(II)

A milligram or so of (I) added to 10–20 ml of a hydrocarbon or ethyl ether solution containing *ca.* 0.1–1.0 *M* dialkylmagnesium reagent produces (instantly) a bright violet solution. Titration of this solution with 1 *M* sec-butyl alcohol in xylene causes no significant diminution in color, until two mole equivalents of the titrant are added and the color fades out sharply. For example, a sample of di-sec-butylmagnesium in cyclohexane[8] which was found by indirect analyses to be 0.77 *M*, was found by our direct titration to be 0.78 *M*. This result and those from titrations of other organometallics are summarized in Table 1.

The sharpness of the end point with ethereal solutions of magnesium alkyls appears to be better than with hydrocarbon solutions. In the hydrocarbon, precipitation of magnesium alkoxide formed during titration may cause turbidity or viscosity problems; the alkoxide precipitates in particulate form and these problems are eliminated by prior addition of a tertiary amine or ethyl ether. Both ethyl and butyl ether have been used as solvents for direct titration of butylmagnesium chloride. Our analysis of a sample of this Grignard reagent, available commercially and indicated to be *ca.* 2.8 *M*, showed it to be 2.73 *M*. Phenylmagnesium chloride was also satisfactorily analyzed by the direct titration. Absolute accuracy is not really established for any independent analyses of organomagnesium reagents[9–11], but the direct titration does show good precision; reproducibility is within ordinary volumetric analysis error.

The real accuracy for this direct titration has been established with organolithium reagents, because the accuracy is known for independent analyses we used on the lithium compounds for comparison[12–14]. Addition of a few milligrams of (II) and about 5 ml of *ca.* 1.5 *M* butyllithium in hexane to 20 ml of benzene produces a yellow-green or chartreuse-colored solution. After titration with 1 *M* sec-butyl alcohol in xylene, the solution is clear and colorless; the disappearance of the green color occurs sharply after addition of one mole equivalent of titrant. For example a sample of butyllithium solution, available commercially and indicated to be 1.6 *M* in lithium reagent, was found to be 1.62 *M* by this direct titration with sec-butyl alcohol. Our independent analyses of the same solution showed it to be 1.65 *M*.

Equally good results in titrating butyllithium were obtained by forming the indicator with (I), which gives a rust-red complex. Hydrocarbon solutions of sec-butyllithium and tert-butyllithium reagents were also satisfactorily analyzed using (I) and direct titration with sec-butyl alcohol. Because they react with the reagents, ethers cannot be added to the titration mixtures with (I) or (II) and lithium reagents*. However, there is no problem here with turbidity and precipitation in the hydrocarbon titration mixture because the lithium sec-butoxide is quite soluble[15]. If the reaction mixture is protected with an atmosphere of nitrogen, it remains bright and clear

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* Ethereal lithium reagents can be directly analyzed by an oscillometric technique[14].

throughout titration. Reaction with n-butyl alcohol as titrant is also stoichiometric[16], but the prim-butoxide formed is insoluble.

Using (I) and butyllithium in benzene, we have examined the reversibility of formation of the colored charge transfer complex which serves as our indicator. After the end point, addition of more lithium reagent to the titration mixture immediately regenerates the red color. The additional reagent still requires just one mole equivalent of alcohol to come back to the end point, loss of the red color. Obviously excess alkoxide, a problem in many organometallic analyses, does not interfere with this direct titration.

It is our impression that our indicator is relatively stable to protonation, that is, the acid (alcohol) used as titrant apparently does not attack the indicator (metal alkyl/base complex) until all of the uncomplexed organometallic reagent is reacted. One reason for this belief is that toward the end of a titration, as indicator and uncomplexed reagent approach equimolarity just before the end point, color does not temporarily disappear and return after each increment of titrant. This premature disappearance (and return) would be expected if the indicator complex were not relatively stable toward chemical reaction involving protonation.

Toward chemical reaction involving charge transfer, however, our indicator complex is not particularly stable. If acetone, instead of alcohol, is used as titrant to consume the butyllithium, the red color of the complex disappears well before a stoichiometric end point. This instability of the charge transfer complex is thought to be a consequence of the particular susceptibility of acetone to reduction. This premature disappearance of our indicator color with acetone as titrant cannot be a consequence of side reactions with the butyllithium, for the true end point is observed with acetone as titrant using oscillometry[14].

In conclusion we suggest that direct titration of other organometallics may prove possible using appropriate charge transfer complexes as indicators*. Although many techniques have been devised for analysis[9-14,16] of Grignard reagents and of lithium reagents particularly, it is our experience that no other technique even approaches this direct titration in expediency and simplicity. Except for the inescapable necessity of protecting such reactive solutions from moisture, air, etc., magnesium and lithium reagents in hydrocarbons may now be titrated as simply as sodium hydroxide in water.

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* We have not made an extensive search for indicators, but we did eliminate several other aromatics (including dimethyl- and diphenylphenanthroline, fluorene and triphenylmethane) as being less suitable before studying bases (I) and (II) with lithium and magnesium alkyls. Hydrocarbon solutions of aluminum and zinc alkyls we find also give good color with base (II), but we have not searched for a titrant to use on these other organometallics; their solvolysis with sec-butyl alcohol is not a rapid stoichiometric reaction.

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